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# Effects of sulfuric acid attack on hydrated calcined clay-limestone cement mortars

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The paper presents experimental findings on the performance of Limestone Calcined Clay Cement (LC3) in acidic media. LC3 was made by inter-grinding a blend of 50 % clinker with ground 30 % Fired Rejected Clay Bricks (FRCB), 15 % limestone and 5 % gypsum. Compressive strength and water absorptivity of LC3 mortars were investigated vis-à-vis commercial Ordinary Portland Cement (OPC) and Portland Pozzolana Cement (PPC). Microstructural analysis of hydrated LC3 samples was conducted using Scanning Electron Microscope (SEM) before and after immersion in 3% H2SO4. LC3 reported the least water absorptivity than PPC and OPC. Additionally, LC3 exhibited equivalent water absorptivity and resistance to acid attack compared to PPC. Micro-cracks were observed in SEM images from LC3 samples after immersion in acid. In conclusion, strength loss, at w/c = 0.50 and 0.60, LC3 exhibited 12.71 % and 14.06 % respectively, higher resistance to acid attack than OPC.

**Keywords:** acid resistivity; blended cement; fired rejected clay bricks; compressive strength; porosity

#### 1. Introduction

Ordinary Portland cement (OPC) is commonly used in major civil construction activities. However, OPC is an expensive binder due to the fact that during its production, calcareous and argillaceous materials are calcined at temperatures in excess of 1300 °C in rotary kilns [1]. A lot of energy is required to achieve the high temperatures. This makes the cement unaffordable especially in developing countries in the world. Moreover, during the production of OPC, enormous quantities of carbon dioxide (CO<sub>2</sub>) are produced. CO<sub>2</sub> is one of the major greenhouse gases mainly responsible for global warming and climate change [2].

There is an increasing demand for affordable, durable and green cements Limestone-calcined worldwide. clav cement (LC3) has recently emerged as potential low-cost cement with low carbon footprint in cement industries globally. LC3 is an innovative blended cement that is produced by blending of limestone, calcined clay, clinker and gypsum at specified proportions [3]. The cement is potentially affordable in many countries due to the low clinker content required and the relative abundance of raw materials necessary for its products such as clays and limestone. LC3 has also been reported as an eco-friendly material since it can effectively reduce the CO<sub>2</sub> emissions by 30% [4]. Moreover, the production of LC3

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Chemical composition	Clinker	FRCB mix	Limestone	Gypsum
SiO <sub>2</sub>	21.78	58.13	1.85	2.44
$Al_2O_3$	4.55	15.55	0.98	0.87
Fe <sub>2</sub> O <sub>3</sub>	3.97	9.88	1.63	0.79
CaO	62.97	1.66	68.63	34.25
MgO	1.05	0.83	1.86	1.79
SO <sub>3</sub>	2.07	0.04	0.02	40.82
K <sub>2</sub> O	0.6	4.78	2.79	0.05
Na <sub>2</sub> O	0.17	3.18	2.15	0.05
H <sub>2</sub> O	2.33	_	-	_
Sum (SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> )	_	83.34	-	_
Loss on ignition (LOI)	0.96	2.92	10.26	12.99

Table 1. Chemical composition of clinker, limestone, FRCB and gypsum [11].

cement does not require massive capital investments since a modification of existing cement plants can be done. Inclusion of pozzolanic materials such as calcined clays in LC3 has been found to lower the cost of cement, enhance ultimate compressive strength and improve the durability of the resulting hydrated cement-based material [5]. This is mainly due to reduced permeability of aggressive media as a result of the pozzolanic reactions increasing the amount of hydration products such as calcium silicate hydrate (CSH) while diminishing calcium hydroxide (CH) in the hydrated cement matrix. Low CH in hydrated cement increases the durability of cement-based structures. LC3 has been considered as a suitable alternative construction material to OPC and other blended cements [6]. However, very low amount of CH has been found to lead in low pH for protection of rebars, if used and lowering of pH may affect reaction media for more cementitious materials resulting in decreased durability.

In Kenya, enormous quantities of fired rejected clay bricks (FRCB) are generated 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. The use of FRCB in place of the convectional calcined clays has the potential to further lower the cost of the production of LC3 cement to a greater extent. In addition, the utilization of FRCB in cement production could offer an environmentally friendly method of waste disposal that promotes development. sustainable However, cements are subject to degradation by aggressive media found in various construction environments. Extensive studies have shown that sulfuric acid solutions in sewage, wastewater treatment plants and hot spring places deteriorate cement-based materials by reacting with cement hydrates and free CH in pore solution present in hydrated cement matrix [7-10]. The degradation of cement-based materials results in the reduction of their service life. In addition, sulfuric acid attack increases the cost of repair, serviceability and replacement of the degraded structures [10]. Durability tests are therefore necessary for any cementitious material in a given aggressive envir-There are limited research onment. findings reported on the performance of LC3 binders made from FRCB in acidic environments. The present study therefore aimed at investigating the physicochemical properties of LC3 relation to commercial Portland pozzolana cement (PPC) and OPC in 3% of sulfuric acid at  $23 \pm 1$  °C. The present work reports the experimental findings on the robustness of LC3 in acid media visà-vis commercial PPC and OPC. The 3% of sulfuric acid was chosen to simulate the aggressive environment of some sewer and

Material 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	Portland pozzolana cement (PPC) [32.5 N/mm]
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
FRCB	A mix of fired rejected clay bricks (FRCB) obtained from three landfills
Sand	Standard sand was used in this work conforming to EAS 148-1:2000 specifications

Table 2. Description of various materials used [11].

treatment structures which contain cementitious materials. In addition, the mechanical performance of the LC3 was evaluated in terms of compressive strength at 90 days of curing.

#### 2. Materials and methods

#### 2.1. Materials

Limestone and FRCB were sampled from Ngaaine, Kyuso sub-county in Kitui county in Kenya. The chemical composition of clinker, limestone, FRCB and gypsum is shown in Table 1 whereas Table 2 shows the description of various cements used in the study.

The mineralogical composition of raw clays and FRCB obtained from X-ray diffraction (XRD) analysis is given in Figure 1 [11].

#### 2.2. Methods

#### 2.2.1. Sampling

The FRCB obtained from three landfill sites located in Ngaaine, Kyuso sub-county in Kitui county in Kenya. The sampled FRCB were labeled NS1, NS2 and NS3 with respect to the site where they had been obtained. The FRCB had earlier been calcined at 800 °C for 4 h during clay brick preparation in non-conventional fixed bed kilns. The performance of the non-convectional fixed bed kiln had earlier been tested alongside the convectional kiln and found not to differ significantly.

The sampled FRCB was finely ground in a laboratory ball mill and the FRCB particles with sizes below  $45 \,\mu\text{m}$  were used in pozzolanic assessment and preparation of LC3.

# 2.2.2. Pozzolanic activity

Three samples NS1, NS2 and NS3 were separately subjected to pozzolanic tests in accordance with the procedure outlined by Luxán et al. [12]. In this method, the lime solution was prepared by dissolving 2 g of analytical grade  $Ca(OH)_2$  in a 250 ml conical flask followed by the addition of 200 ml of deionized water. The conical flask was then placed on a magnetic plate maintained at a temperature of 40 °C. The solution was continuously stirred using a magnetic stirrer.

Electrical conductivity of the solution was continuously monitored by a portable pH meter. After lime water reached a constant conductivity, 15 g of ground FRCB material was added to the solution in the conical flask. Conductivity values of solution were determined at 30-min intervals after adding the FRCB sample for 300 min.

The same procedure was repeated for FRCB-water system without lime. Corrected conductivity values for lime-FRCB system were obtained by subtracting the contribution of FRCB-water system from lime-FRCB system.



Figure 1. XRD results for raw clays and FRCB. FRCB samples obtained were originally from kaolin clays. The absence of kaolinite peak mainly indicates that the FRCB was completely amorphous. In this study, the FRCB used "as received" to evaluate its performance and to find a justification for its application if collected as a construction demolition waste.

#### 2.2.3. Compressive strength

Mortar prisms measuring  $40 \text{ mm} \times 40 \text{ mm}$  $\times$  160 mm were cast, cured and their compressive strengths evaluated in accordance with KS EAS 148-1:2000 specifications. Slight modifications to this standard were adopted such that the water/cement (w/c) ratio of 0.50 and 0.60 were used. LC3, PPC and OPC mortar prisms were separately cast with water at w/c of 0.50 and 0.60 using standard sand. After casting, mortars were placed in a temperature-controlled room maintained at a temperature of  $22 \pm 2$  °C and relative humidity above 90% for  $24 h \pm 30 min$ . The mortars were later de-molded after the 24 h  $\pm$  30 min and marked accordingly for identification purposes. The mortars were cured in a humidity-controlled room maintained at  $22 \pm 1$  °C and relative humidity above 95% until the desired testing age of 90 days. On the 90th day, cured mortar prism from each cement category was removed from the curing tank, wiped quickly with a soft piece of cloth and allowed to drain the moisture for 10 min. Each prism was placed in a compressive strength machine and its compressive strength determined.

#### 2.2.4. Water absorptivity

Water absorptivity test was conducted in accordance with the Japanese Industrial Standard (JIS A6203) with slight modifications. In this test, mortar prisms measuring  $40 \,\mathrm{mm} \times 40 \,\mathrm{mm} \times 160 \,\mathrm{mm}$  were separately cast using water at w/c ratio of 0.50 and 0.60. The prepared mortars were ovencured at  $85 \pm 2$  °C for 24 h. Oven-dried mortars were de-molded after 24 h and cured in 95% humidity-controlled room maintained at  $22 \pm 1$  °C for 90 days. The 90-day cured mortar prisms were ovendried at  $85 \pm 2$  °C until a constant weight was achieved. Weighed samples were separately immersed in water for 1, 3, 6, 24, 48 and 72 h. The specimens were taken out and their surfaces wiped quickly with a wet cloth and weighed in the air immediately after each immersion period. The water absorptivity in the mortar specimens was



Figure 2. Pozzolanicity as a function of loss of conductivity with time for FRCB.

calculated using Equation (1).

$$W_{ab} = \frac{W_a - W_d}{W_d} \times 100$$
(1)

where  $W_d$  is the constant dry weight,  $W_a$  is the weight of the samples in air, and  $W_{ab}$ represents the water absorptivity of the samples.

#### 2.2.5. Sulfuric acid resistivity

Acid resistivity test was conducted in accordance with ASTM C 267 (2003) standard based on the study by Mwiti et al. [9] with slight modification adopted. Mortar cubes measuring  $50 \,\mathrm{mm} \times 50 \,\mathrm{mm}$  $\times$  50 mm were prepared and cured in for 90 days. Half of the 90-day cured mortar cubes were completely immersed in 3%  $H_2SO_4$  solution (pH  $\approx 0.6$ ) maintained at  $22 \pm 1$  °C, whereas the rest of the mortar cubes were cured in a temperature and humidity-controlled room maintained at a temperature of  $22 \pm 1$  °C and relative humidity above 90%, respectively. Residual weight and compressive strength of each specimen were taken at every immersion time conducted after 7, 14, 28, 56, 84 and 120 days. At each testing age, the specimens were carefully removed from solutions and gently rinsed with tap water and then air-dried for about 3 h. 3%  $H_2SO_4$  solution was replaced with fresh solution after each immersion time. Subsequently, residual weight and residual compressive strength ware calculated using Equations (2) and (3), respectively.

$$R_{\rm W} = \frac{W_{\rm a} - W_{\rm s}}{W_{\rm a}} \times 100 \tag{2}$$

where  $R_W$  is the residual weight,  $W_a$  and  $W_s$  are the weights of air-cured mortars the weight of mortars after each immersion time, respectively.

$$C_{\rm R} = \frac{C_{\rm a} - C_{\rm s}}{C_{\rm a}} \times 100 \tag{3}$$

where  $C_R$  is the residual compressive strength,  $C_a$  and  $C_s$  are the compressive strengths of air-cured mortar and the compressive strengths of mortars after each immersion time, respectively.

#### 2.2.6. Microstructural examination

The 90-day cured LC3 sample at casted w/c of 0.50 was removed from the curing tank and placed in a temperature-controlled cabinet for 1 day at  $22\pm1$ °C. The dried sample was finely ground and its microstructure examined using the scanning electron microscope (SEM). The procedure was repeated for LC3 sample casted at w/c



Figure 3. 90-day compressive strength results for LC3, PPC and OPC at different w/c ratios.

of 0.50 and immersed in 3% H<sub>2</sub>SO<sub>4</sub> solution for 120 days.

#### 3. Results and discussion

# 3.1. Pozzolanic activity of FRCB

The results for the pozzolanic activity of FRCB are presented in Figure 2. They are presented as percentage loss of conductivity against time. The test gives the progressive consumption of  $Ca^{2+}$  as a result of continued pozzolana reaction. Decrease in the amount of  $Ca^{2+}$  is demonstrated by reduced conductivity in the Ca(OH)<sub>2</sub> solution. Blended cements are known to continuously consume and hence reduce Ca(OH)<sub>2</sub> in hydrated cement or concrete as opposed to OPC. The test, therefore, gives a measure of pozzolanicity.

It was observed that the presence of FRCB on lime water resulted in decreased conductivity of the water–lime mixture. The loss in electrical conductivity could be attributed to the lime fixation as a result of pozzolanic reactivity. Luxan et al. [12] studying the pozzolanic activity of rice husk ash made similar observations and attributed this to decrease in the amount of  $Ca^{2+}$  and  $OH^-$  ions in the water–lime suspension. The silica and aluminate phases in pozzolana consume  $Ca(OH)_2$  (CH) as given by Equations (4) and (5) [9].

$$3CH + 2S + 3H \rightarrow C_3S_2H_3 \qquad (4)$$

$$A + H + CH \to CAH \tag{5}$$

The three samples, NS1, NS2 and NS3, resulted in the loss of electrical conductivity of water-lime mixture. This shows that they all exhibited pozzolanic properties. The conductivity of the three samples was found to be nearly equivalent and hence they were mixed in equal proportions to form the FRCB mix which was therefore used in the preparation of LC3. KS 02 1260 [13] and ASTM C618 [14] prescribes that the sum of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> should be above 70% for pozzolanic materials. In this study, the sum SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> in FRCB surpassed the aforementioned specifications as noted in Table 1. As expected, FRCB were found to be pozzolanic. This is because FRCB are largely calcined clays exhibiting pozzolanic properties [11].

#### 3.2. Compressive strength

The 90-day compressive strength results for LC3, PPC and OPC at different w/c ratios are presented in Figure 3.

From the results, the compressive strengths of LC3 and PPC were higher than that of OPC at 90 days of curing at each w/ c ratio. Hardened LC3, PPC and OPC contain CSH due to the hydration of tricalcium



Figure 4. Water absorption profiles of LC3, PPC and OPC mortars at w/c 0.50.

silicate (C<sub>3</sub>S) and dicalcium silicate (C<sub>2</sub>S) as shown in Equations (6) and (7) [9].

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH$$
 (6)

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH \tag{7}$$

 $C_3S_2H_3$  or simply CSH is a cementitious material primarily responsible for the strength of hydrated cement-based materials. CSH is responsible for strength in both OPC and blended cements. In blended cements, the pozzolanic reaction takes place when CH is released during the hydration of clinker phases in cement. The released CH reacts with pozzolanic materials in the presence of water to form CSH and calcium aluminate hydrate (CAH) as shown in Equations (4) and (5) [9].

CSH and CAH are the secondary cementitious materials. The pozzolanic reaction can be compared to the hydration of Portland cement since both reactions lead to the formation of CSH [9]. Both CSH and CAH from pozzolanic reaction contribute to the ultimate compressive strength of the blended cement mortars. This explains why blended cements were observed to exhibit higher compressive strength at 90 days of curing which leads to greater pore refinement and densification hence improving the ultimate compressive strength of blended cements.

It was observed that w/c ratio greatly influenced the strength of all test cement mortars at all the testing ages. The strength decreased in the order w/c = 0.50 > w/c = 0.60. w/c ratio is considered as the most important factor affecting mortars/ concrete strength. This is because it affects the quantity of water used affects the flow or rheology of the mixture as well as cohesion between paste and aggregate [11]. As a result, it influences the overall strength of mortars. Related observations have been reported in similar studies [15].

#### 3.3. Water absorptivity

Figures 4 and 5 show the water absorption profiles of LC3, PPC and OPC mortars at 90 days of curing age.

It was observed that OPC exhibited higher water absorptivity than PPC and LC3 cements. This could be attributed to the higher permeability of hydrated OPC than blended cement mortar matrix. This is mainly because blended cements contain pozzolana materials which react with CH produced from the hydration of OPC

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Figure 5. Water absorption profiles of LC3, PPC and OPC mortars at w/c 0.60.

forming secondary cementitious materials (CSH and CAH) [9, 12, 16, 17]. In addition, the incorporated pozzolanic materials act as a filler material in the hydrated cement matrix. The presence of additional cementitious material and the filler effectively reduces the pore volume in mortar hence reducing the permeability of water. This lowers the water absorption ability in blended cements. In case of OPC, the CH produced during the hydration process makes the hydrated cement structure porous. This creates voids that act as pathways to allow greater permeability of water thus increase water absorptivity.

LC3 exhibited lower water absorptivity than commercial PPC. This could be attributed to the fact that LC3 is a ternary system containing calcined clay and limestone, whereas PPC contains volcanic ash as pozzolana. More hydration products are usually formed in LC3 hence resulting in greater pore refinement and densification of the hardened mortars [15]. This reduces the permeability of water into the hydrated cement matrix. 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 [7, 18]. The increased pore refinement effectively decreases the water absorptivity of hardened cement more in LC3 cements than ordinary PPC. This could lead to a retarded moisture migration through the hydrated LC3 cement matrix. In a related study [19], the authors investigated the microstructure-related characteristics to elucidate the performance of composite cement with limestone-calcined clay combination. The authors [19] also attributed the pore refinement and densification of hydrated LC3 matrix to the presence of limestone and calcined clay.

Water absorptivity was observed to increase with increase in w/c ratio. The water absorptivity increased in the order w/c = 0.50 < w/c = 0.60. This is could be attributed to the presence of more mixing water with increased w/c ratio. The increased w/c ratio results lead to a more non-homogeneous pore distribution. This results in reduced pore refinement hence increasing the permeability of water thus higher water absorptivity.

Water absorption is lower at the initial stages of the immersion period (<3 h) for all the cement categories and all w/c ratio.



Figure 6. Percentage loss in weight of mortars at w/c 0.50.

This can be attributed to the fact that initially, the samples were somewhat dry due to the fact that all the pore water was consumed during hydration of the cement phases. However, on exposure to water, moisture migration through the cement matrix occurs due to the differences in moisture content inside the hydrated cement pores and voids. At the later stages (>3 h), the water absorption becomes constant indicating that the pores in hydrated cement matrix are fully saturated with water.

#### 3.4. Acid resistivity

Figures 6 and 7 present the percentage loss in weight for different mortars casted at w/ c = 0.50 and w/c = 0.60 after being subjected to 3% sulfuric acid at varying immersion durations.

Figures 8 and 9 present the percentage loss in compressive strength of different mortars casted at w/c = 0.50 and w/c = 0.60 after being subjected to 3% sulfuric acid at varying immersion durations.

In this study, all the mortars showed loss in weight and strength in all the w/c considered when immersed in sulfuric acid. The loss in weight and strength can be attributed to the sulfuric acid attack on CSH and CH phases present in LC3, PPC and OPC [9, 10, 19-21]. This is because sulfuric acid introduces SO<sub>4</sub><sup>2-</sup> and H<sup>+</sup> into the pore water which contributes to sulfate attack. The  $SO_4^{2-}$  and H<sup>+</sup> ions are deleterious to cementitious materials. SO4<sup>2-</sup> ions result in the formation of ettringite which is expansive, whereas H<sup>+</sup> ions can directly attack the CH and CSH phases or indirectly cause reduction in pH of pore water since the exposure of mortar specimens to acidic media generally leads to a neutralization reaction between hydrogen ion and Ca(OH)<sub>2</sub> in the cementitious materials to occur. This decreases the alkalinity of mortar and causes dissolutions of the hydration products (mainly CSH and CH) leading to the deterioration of mortar reflected in loss of weight and compressive strength. Sulfate ion reacts with



Figure 7. Percentage loss in weight of mortars at w/c 0.60.



Figure 8. Percentage loss of compressive strength in mortars at w/c 0.50.

free lime to form gypsum by the following equation (Equation (8)) [22–24].

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O$$
 (8)

Then, gypsum reacts with CAH to form ettringite as shown in Equation (9) [23, 24].

$$3\text{CaSO}_4 + 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} + 25\text{H}_2\text{O}$$
$$\rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$$
(9)

The ettringite formed as shown in Equation (9) is very expansive. It produces high internal stresses in hydrated cement



Figure 9. Percentage loss of compressive strength in mortars at w/c 0.60.

materials resulting in spalling, cracking and general strength loss of mortar/concrete. This explains why there was loss in weight and strength when mortars were immersed in 3% sulfuric acid.

In addition, sulfuric acid introduces  $H^+$ into the pore water in hydrated cement matrix.  $H^+$  reacts with CSH which is the main hydration product responsible for the cementitious property of cement-based materials as shown in Equation (10).

$$3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + \text{H}_2\text{SO}_4$$
$$\rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{Si}(\text{OH})_4 \qquad (10)$$

OPC mortars exhibited greater loss in both weight and strength than blended cement (LC3 and PPC) mortars. This is perhaps due to the fact that OPC contains more CH than in blended cements. CH is the phase most prone to attack from acid attack. The attack on CH results in the formation of ettringite (3CaO Al<sub>2</sub> O<sub>3</sub> 3CaSO<sub>4</sub> 31H<sub>2</sub>O) as shown in Equation (8) since it is expansive and leads to the formation of micro-cracks and spalling resulting to ultimate loss of weight and strength.

More loss in weight and strength was observed with longer immersion period. This can be attributed to prolonged exposure of hydrated cement mortars to sulfuric acid solution. Increased exposure duration results in enhanced reaction of H<sup>+</sup> ions with CH resulting in the formation of more ettringite (3CaO Al<sub>2</sub> O<sub>3</sub> 3CaSO<sub>4</sub> 31H<sub>2</sub>O) resulting in its leaching and re-crystallization in void spaces in the hydrated cement matrix. This is often detrimental to the durability performance of cement-based materials since it leads to the formation of micro-cracks. Micro-cracks in hardened cement-based materials result in significant loss of strength due to the destruction of the dense pore connectivity in hydrated cement matrix leading to a very porous cementitious material. Furthermore, micro-cracks act as active pathways that enhance the ingress of potentially aggressive ions that are deleterious in hydrated cementitious materials. Similar observations were made by Rashwan et al. [25] although studying the effect of local metakaolin on properties of concrete and its sulfuric acid resistance.

LC3 exhibited lower weight and strength loss than commercial PPC. This



Figure 10. SEM Image for LC3 Samples without and with Immersion in Acid.

can be attributed to their differences in permeabilities as observed in water absorptivity tests. LC3 showed lower water absorptivity [7] than PPC. Therefore, LC3 was less permeable than PPC. In this case, the lower permeability of LC3 implied that it offered greater resistance to the ingress of sulfuric acid solution than PPC. However, the difference in weight and strength loss between LC3 and PPC was not statistically significant. Reduced permeability/porosity of hardened cementitious materials has been found to decrease their acid resistivity [9, 21, 26-33]. In a related study, Lee et al. [34] studying the effect of limestone filler on the deterioration of mortars and pastes exposed to sulfate solutions at ambient temperature reported that the presence of limestone in hydrated cement matrix reduces the degradation of the cementitious materials caused by acid attack.

Higher loss in weight and compressive strength was observed with increase in w/c ratio at all the cement categories. This could be attributed to the increased porosity with increase in w/c ratio as observed in the water absorption tests.

# 3.5. Microstructural examination

Figure 10(a) shows the SEM image for LC3 observed at 90 days without immersion in 3% sulfuric acid whereas Figure 10(b) shows the SEM image for LC3 observed at 90 days after immersion in 3% sulfuric acid.

It was observed that the LC3 mortars previously immersed in sulfuric acid were degraded resulting in the presence of micro-cracks as shown in Figure 10(b). The formation of cracks can be attributed to the presence of expansive products such as gypsum and ettringite. The pH of 3% sulfuric acid used was found to increase with continued immersion. This could be attributed to the erosion of hydration products majorly CH in the microstructure [35]. Subsequently, the eroded CH might have reacted with sulfuric acid resulting in the formation of calcium sulfate and later ettringite which is evidently indicated by the presence of visible cracks. The decrease in CH has been reported to result in decreased strength of hardened cement. The presence of cracks also deteriorates the strength of mortars.

# 4. Conclusion

The following conclusions were made based on the study:

- i. LC3 mortars exhibited higher compressive strength than OPC at 90 days of curing. This shows that the compressive strength of LC3 mortars increased with curing as a result of increased pozzolanic activity of FRCB.
- ii. Water absorptivity was found to increase with increase w/c. This implied that additional water increases the permeability of the mortars.
- iii. LC3 and PPC exhibited lower water absorptivity than OPC. This indicated that blended cements are less porous compared to OPC. They are hence less prone to degradation due to the penetration of aggressive media.
- iv. LC3 and PPC exhibited the higher resistance to sulfuric acid attack than OPC. This demonstrated that they are potential materials for more durable structures.
- v. In terms of strength loss, at w/c = 0.50 and w/c = 0.60, LC3 exhibited 12.71% and 14.06%, respectively, higher resistance to sulfuric acid attack than neat OPC.
- vi. Decrease in compressive strength as a result of sulfuric acid attack on the cement hydration products.

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