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Effects of biogenic sulfuric acid on simulated concrete septic tanks

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ABSTRACT

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Concrete is the major construction material for infrastructure development. Concrete sewer septic tanks are Constructed using the conventional ordinary portland cement (OPC) and the Portland pozzolana cement (PPC). However, OPC based concrete sewer systems are susceptible to biological, mechanical, and chemical degradation. Degradation of the concrete septic leads to their failure hence imposing tremendous environmental problems. The aftermath is the emergence of sanitation-related diseases. The wastewater from failing septic systems leads to contamination of the groundwater or the surface water resulting in the pollution of drinking water. Therefore, the need to explore other possibilities and potential construction materials to achieve sustainable sanitation is inevitable. The use of Limestone Calcined Clay Cement (LC3) in the construction of degradation-resistant concrete sewer septic systems has not been well explored in Kenya. LC3 concrete is resistant to the deterioration effects of aggressive media such as acids, chlorides, and sulfates. This paper presents experimental performance and findings of LC3 in aggressive media vis a vis OPC. The LC3 was formulated by mixing clinker, Calcined clay, limestone, and gypsum at percentages of 50 %, 30 %, 15 %, and 5 % respectively. Compressive strength, Sorptivity, and weight loss during the wet and dry cycles for both LC3 and OPC were evaluated. Simulated concrete septic tanks made of LC3 and OPC were made by casting cubes at water cement ratio of 0.5 and cured in fresh water at ambient temperature for 28 days. These cubes were passed through a regime of W-D cycles in the 3% concentration of Biogenic sulfuric acid. It was observed that after 28 days of curing OPC cubes had slightly higher compressive strength than LC3. However LC3 concrete cubes are expected to have higher compressive strength than the OPC. Cubes curing time increases due to increased pozzolanic activity. Biogenic sulphuric acid attacks on hydrated cement products cause a decrease in compressive strength. The water absorption profile of LC3 cubes was lower as compared to OPC cubes. In conclusion, LC3 cubes had a high potential of resisting degradation as compared to OPC cubes. LC3 show more impressive performance, hence LC3 It's a potential binder for use in the construction of sewer system.

Introduction and Literature Review

Concrete facilities are designed to serve a long period while maintaining their good mechanical

characteristics. However, the concrete structure may degrade earlier than the speculated design life due to poor maintenance and environmental

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pollution [1]. The degradation happens even when the design of the concrete facilities is sustainable and suitable materials are used in the construction. When the condensing moisture in the concrete facility reacts with hydrogen sulfide gas there is the formation of sulphuric acid, which leads to the degradation of the sewer facilities [2]. This form of corrosion is referred to as microbially induced corrosion, and it poses dire sustainability problems to the concrete septic treatment facilities. Acid degradation of concrete septic treatment facilities leads to structural failures such as collapses and threatening public safety.

It has also been reported that the cost of repair for degraded concrete sewer facilities is high. In the United States of America, the annual cost of rehabilitating degraded concrete sanitary sewer treatment facilities is estimated to be around \$14billion [3]. According to research by IDRISSE *et al.* [4], sulfuric acid has been profiled as the primary causative agent of corrosion in wastewater treatment facilities. Sulfuric acid corrosion is the most aggressive corrosive agent compared to other deleterious materials because of the formation of expansive products, gypsum, and ettringite [5]. Concrete degradation of sewer facilities is initiated through a series of steps [6]. The surface of the concrete is moist and alkaline due to the formation of hydration products. The alkaline pH is lowered to achieve a more neutral pH through dissociation of hydrogen sulfide and carbonation. The neutrophilic sulfide oxidizing bacteria and fungi present in concrete sewer facilities colonize the surface of the moist concrete leading to the oxidation of the sulfur to form dissociated sulfuric acid H_2SO_4 . During this process, the pH of the concrete surface reduces to 2 as the acidophilic microbes take over, and *A. thiooxidans* microorganism becomes the dominating species. The hydration product $Ca(OH)_2$, on the surface of the concrete, reacts with the sulfuric acid leading to the formation of expansive product ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) or gypsum ($CaSO_4 \cdot 2H_2O$). Ettringite is a brittle material formed from the incomplete reaction of H_2SO_4

and cement [7]. The calcium used in the formation of ettringite is provided by CH and the decalcified calcium silicate hydrates (C-S-H). The sulfates causing sulfate attack are supplied by ingressing groundwater containing sulfate. The cracking of the wall is because the ettringite occupies a big volume and exerts pressure on the wall. The decalcification of C-S-H causes further damages to the concrete. In the long run, the concrete is thoroughly degraded and collapses. During the deterioration of concrete, the aggregates do not take part in the reaction; only the sulfates induce the degradation. Usually, a sulfate attack involves a deterioration of the cement paste in the concrete, with the aggregate taking no part in the reaction. However, occasionally, the aggregate can cause a problem if it contains soluble sulfate forms. In the process of sulfate-induced corrosion, thaumasite is also formed. Thaumasite is a rare naturally occurring mineral that occurs as an alteration product of limestone and has the formula ($CaSiO_3 \cdot CaSO_4 \cdot 15H_2O$). The mineral can be formed in both concrete and mortar. Concrete degradation occurs as a result of the decomposition of hydration products by sulfate attack and carbonation. Thaumasite is a weak and brittle material itself, and thus when it replaces C-S-H in the concrete, the concrete is direly weakened.

Sanitary structures in Kenya and developing nations use ordinary Portland cement (OPC) and Portland pozzolana cement (PPC). However, concrete sanitary facilities built from these binders are susceptible to degradation. The aftermath of degradation is loss of structural integrity, which results in collapsing of the structure. There have been reported cases of structural failures which have led to the loss of lives and property [8]. Many of these structural failures have been attributed to poor workmanship, lack of consistency in the quality of materials such as sand, and mixing water [9]. The structural integrity of buildings made from the OPC and PPC has raised concerns as they have been found vulnerable to degradation by deleterious materials [10]. This has led to agitated research to investigate the potential of

other locally available materials in improving the strength and durability characteristics of OPC. The efficiency of LC3 utilization for the construction of degradation-resistant structures has not been fully explored in Kenya.

Limestone Calcined Clay Cement LC3 is innovative cement that is produced by blending limestone, clinker, calcined clay, and gypsum at specified proportions [11]. According to Haldar *et al.* (2016), the LC3 has shown desirable performance concerning the mechanical performance and durability characteristics. Studies conducted by Antoni *et al.* [13] on cement mortars made from replacing Portland cement with calcined clays and limestone have shown that the blended cement produced a comparable performance as the ordinary Portland cement. This innovative binder can cater to the ever-increasing demand for cementitious materials due to the wide availability of calcined clays [14]. The limestone in the LC3 cement reacts with silica and alumina, leading to the formation of alumina, ferric oxide, mono-sulfate (AFm) phases of monocarboaluminate Hemicarboaluminate. The latter leads to the complementary reaction between the calcined clays and limestone [15]. The amount of limestone reacted is dependent on the amount of the aluminates and their source [16]. The LC3 mechanical and durability performance determinant factor is based on the amount of kaolinitic clay [17]. The presence of the silica and the alumina makes the calcine clays to be highly reactive to pozzolana. This leads to the improvement of the microstructure and refinement of the pore structure of the calcined clay-based binder [18]. Therefore, this work aimed at determining the effects of biogenic sulphuric acid on simulated concrete sewer systems made from OPC and LC3.

Materials and Methods

Materials

The materials that were used in the laboratory experiment are river sand, OPC, LC3, and water. One ton of coarse aggregate was procured from selected stone crushers in Thika, Kenya. The natu-

ral fines were obtained from Makongeni, Thika. The production of biogenic sulfuric acid involves microbial oxidation of sulfide minerals, a process mediated by the enzymatic activities of Acidithiobacillus bacteria. As these bacteria oxidize sulfide compounds, they generate biogenic sulfuric acid as a metabolic byproduct. Therefore, we acquire the correct concentration of biogenic sulfuric acid solution of pH 2 from Kel Chemicals Limited, Nairobi, Kenya. Ordinary Portland Cement (OPC) was produced to standards conforming to ASTM C 150 Type 1 (42.5 N/mm²) and the LC3 was formulated by mixing Limestone 15%, Clinker 50%, Calcined Clay 30%, and gypsum 5%.

Methodology

a) Particle size distribution

The particle size distribution analysis for the coarse and fine aggregates was done per AASHTO T84 (AASHTO-T84, 1996), respectively. Individual sieves were cleaned to remove unwanted materials from them. The sample was weighed. The sieves were arranged with the finest at the bottom of the stack while the sieves with the larger openings were placed on the top in decreasing order as follows 20mm, 10mm, 5mm, 9.5mm, 6.7mm, 4.75mm, 2.36mm, 1.18mm, 0.6mm, 0.425mm, 0.30mm and 0.075mm. The sample particles were poured on the stack and shaken well mechanically.

b) Aggregates Water Absorption

The test was carried out in accordance with the AASHTO T84 (1996) standard for aggregates water absorption, the procedure involves collecting representative samples, measuring their initial dry weight, saturating them through complete immersion, submerging them for a specified duration, measuring the final weight after the soaking period. The sample was washed to remove fines, drained, and then placed in the wire basket and immersed in distilled water of temperature between 22 °C to 32 °C with about 50 mm of the water above it. The entrapped air was removed. The basket with the aggregates was immersed in the



Figure 1: concrete cube in standard curing box



Figure 2: Concrete Compressive Machine



Figure 3: Curing concrete box for wet and dry cycle

water for 24 hours. The basket and the sample were weighed while suspended in the water at the same temperature of immersion. The weight was recorded as W1. The basket and the aggregates were removed from the water and allowed to drain shortly. The aggregates were put in dry absorbent cloth, and the empty basket was returned to the water tank jolted 25 times and weighed as W2. The aggregates were dried with the cloth until no moisture can be removed by the cloth. The aggregates were surface dried using another cloth and weighed as W3. They were oven-dried and weighed as W4.

c) Workability & Slump Test

The Slump test was done according to ASTM C143 (2020) standard. The container was filled with concrete in three layers, whose workability was checked, and the foundation was mounted on a smooth surface. A regular 16 mm (5/8 inch) diameter steel rod, rounded at the end, was used to tamp each layer 25 times. The top surface of the mold was struck off using screening and a rolling motion of the tamping rod until filled with concrete. The mold was fixed tightly against its base during the process so that it does not move due to the pouring of concrete, and this was accomplished with the help of handles or footrests brazed to the mold. See figure 1.



Figure 4: *Water Absorption Test*

d) Casting of Concrete Cubes and Testing

Concrete cubes of Ordinary Portland Cement (OPC) and Limestone Calcined Clay Cement (LC3), each measuring $150 \times 150 \times 150 \text{ mm}^3$, were cast and water-cured for a duration of 28 days to allow them to harden and achieve their maximum strength. The casting was carried out in two sets, with each set consisting of 60 cubes. One set of cubes was then subjected to biogenic sulfuric acid solution of pH 2 for 30 days in repeated wet and dry (W-D) cycles at interval of 12 hours per cycle. The second set acting as a positive control, was placed in pure water for 30 days. After 30 days of soaking in biogenic sulfuric solution and pure water, the cubes were subjected to different tests, The tests conducted, including compressive strength, sorptivity, and porosity, aimed to determine the impact of wet and dry cycles on septic tanks under varying environmental conditions, specifically in relation to ash conditions induced by biogenic sulfuric acid

e) Concrete Mix Design for LC3 Cement

The LC3 was prepared to maintain the standard proportion of Limestone 15%, Clinker 50%, Calcined Clay 30%, and gypsum 5%, according to Marangu [10]. The concrete mix was batched and manually mixed at a ratio of 1:1:2 for grade M25 mix proportions. The concrete molds measuring

$150 \text{ mm} \times 150 \text{ mm} \times 150 \text{ mm}$ were used to cast the concrete cubes.

f) Compressive Strength

The compressive strength of the cubes was determined as prescribed in the KS EAS_148-1(2017). Another set of cured cubes, taken in triplets, were subjected to biogenic sulfuric acid for a span of 30 days. This experimental setup aimed to replicate the conditions under which deleterious materials could potentially affect concrete septic systems. After the 30-day exposure period, the cubes were carefully removed from the biogenic sulfuric acid solution. To assess any structural changes, particularly in terms of compressive strength, the cubes were tested using a precise Concrete Compression Strength Testing Machine. This comprehensive approach allowed for a detailed analysis of the impact of biogenic sulfuric acid on the mechanical properties of the concrete cubes in the context of septic system durability. See figure 2.

g) Dry-Wet Cycles Test

This study was carried out to study the microbial degradation of concrete under wet-dry cycles. The design of the wet-dry cycles was done per (ASTM C1012, 2010). The biogenic sulfuric acid solution of concentration 2 pH was used as the biodegradation media to simulate the concentration of the

concrete sewer effluents. Three samples from each cement type were submerged in a curing tank containing the 0.8 m³ biogenic sulfuric acid solution for 12 hours. The weight of the cubes was taken and recorded. The cubes were later oven-dried in an oven for 12 hours at a temperature of 50 °C to make a complete wet-dry cycle. The dry weights of the cubes were measured and recorded. This process was repeated for 30 days, with each day consisting of 12 hours of wet cycles followed by 12 hours of dry cycles, making one complete cycle each day. Upon the completion of each cycle, the average weights of the three concrete cubes from each series were determined. The concentration of the biogenic sulfuric acid solution was refreshed after 10 days to maintain the concentration constant of 2 pH and to keep the cubes submerged in the solution as a result of absorption. A total of 30 wet-dry cycles were carried out.

h) Sorptivity

By definition, sorptivity is a function of the increase in mass of the test specimens due to water absorption relative to the time that one surface is exposed to the water [23]. The test was done as per ASTM C1585-04 [24]. This test aimed to investigate the rate of water absorption by both microbial and control concrete cubes. The damaged concrete cubes were oven-dried at a temperature of 100 °C for 24 hours to stop hydration and achieve a constant dry weight (dw). The cubes were allowed to cool completely for one day to avoid the thermal shock upon suspending them in water. For each of the types of cement, four cubes were used. Before the test, the dry weights of each cube were taken and recorded at a time of $t = 0$ minutes, and subsequently, the cubes were placed in the containers partially filled with water. The specimens were placed on spacers so that the cubes can absorb the water unidirectionally through capillary action. The water level in the containers was maintained at approximately 4±1mm above the notch at regular time intervals: 0 min, 25 min, 49 min, 100 min, and 400 min. The

concrete samples were subsequently taken out of the water, wiped with a wet cloth, and their weights were immediately recorded as S_1W for each time interval. The water absorption was then determined according to the below equation 2.1.

$$S = \frac{S_1W - DW}{DW} \times 100 \dots\dots\dots \text{Ept 2.1}$$

Where S_1W is the weight of the cube after capillary suction and DW is the dry weight of the cube in grams.

Data Analysis

Triplicate measurements, including data on temperature and pH effects, were obtained for each parameter. The collected data, incorporating the comprehensive use of a Concrete Compression Strength Testing Machine and a specialized concrete curing box, were meticulously analyzed using Excel 2013. The concrete curing box was specifically employed to simulate wet and dry cycles, with each cycle lasting 12 hours of wet conditions followed by 12 hours of dry conditions, and this process was repeated over 30 days. This controlled environmental setup allowed for a detailed examination of LC3 and OPC performance.

In addition, the water absorption test was conducted to evaluate how much water the concrete samples could absorb. This test was essential in understanding the materials' response to acidic conditions. The Concrete Compression Strength Testing Machine played a crucial role in assessing compressive strength, while the water absorption test provided insights into the materials' porosity and durability. Temperature and pH levels were closely monitored and recorded during the experiment to account for their potential influence on the outcomes. The data collection process involved precise measurements and observations to ensure result reliability.

The subsequent analysis in Excel 2013 facilitated a thorough interpretation of the data, support-

Chemical Composition	OPC	LC3		
		Clinker	Calcined Clay	Limestone
Lime (CaO)	64.59	63.81	0.09	48.54
Silica (SiO ₂)	19.01	21.12	58.43	10.07
Alumina (Al ₂ O ₃)	4.17	5.24	24.95	1.74
Fe ₂ O ₃	3.89	3.41	5.08	1.62
MgO	0.88	3.06	0.19	0.647
Mn ₂ O ₃	0	0.06	0	0.035
Na ₂ O	0.16	0.32	0.05	0
K ₂ O	0.59	0.19	0.21	0.13
TiO ₂	0.23	0.1	1.41	0.206
SO ₃	1.7	0.63		0.01
Loss On Ignition (LOI)	1.4	0.98	9.58	37.09
Specific gravity	3.16		2.67	2.63
Blaine specific surface area	340		520	
Medium grain size	18		11	

Table 1: Chemical properties of OPC and LC3 Cement.

ing the observation of significant differences in the performance of LC3 and OPC. Specifically, the effect of biogenic sulfuric acid on the compressive strength and water absorption of OPC was notably more pronounced than in LC3. This comprehensive approach, integrating both machinery and controlled conditions, enhanced the validity and significance of the experiment's findings across multiple parameters.

Results and Discussion

Chemical composition of OPC and LC3

The Ordinary Portland ASTM C 150 Type 1 (42.5 N/mm²) and the LC3 were adopted in this study. The use of LC3 cement has been reported to resist degradation caused by deleterious materials such as chlorides and sulfates [10].

The chemical properties of the OPC and LC3 are presented in Table 1. From the provided table, several significant results can be identified, contributing to the understanding of the research on Ordinary Portland Cement (OPC) and Limestone Calcined Clay Cement (LC3) under specific experimental conditions. The chemical composition and

physical properties comparison between Ordinary Portland Cement (OPC) and Limestone Calcined Clay Cement (LC3) reveal notable differences. OPC exhibits higher lime content, specific gravity, and medium grain size, while LC3 has higher levels of silica, alumina, MgO, and a smaller grain size. The presence of sulfur (SO₃) in OPC and its absence in LC3, along with variations in Loss On Ignition (LOI), suggest potential differences in their performance under specific conditions. LC3's finer particle size, higher Blaine specific surface area, and distinct chemical composition may contribute to its enhanced durability and strength, showcasing the significance of these factors in understanding the observed variations in performance under experimental conditions.

Particle Size Distribution of the fine and coarse aggregates.

Figures 5 and 6 present the particle size distribution of the river and the coarse aggregates which were conducted as per AASHTO-T84 (AASHTO-T84, 1996),

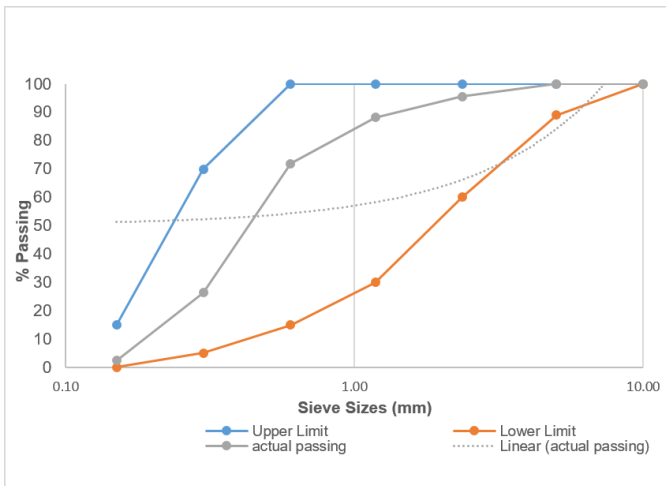


Figure 5: Chemical properties of OPC and LC3 Cement.

The particle size distribution of the aggregates has more influence on the performance of the hardened concrete, asphalt, and base material than any other aggregates characteristics. The size and the distribution of the particles directly influence the concrete properties such as strength, stiffness, workability, skid resistance, permeability, and stability. Both the coarse and the fine aggregates were classified as 5/20 and 0.5 according to the C09 Committee, 2018

Figure 5 the examination of fine aggregates is integral, with particular attention to the percentage of particles falling within the 5/20 classification (0.074 mm to 4.75 mm) according to the C09 Committee, 2018 . The importance of these fine aggregates in influencing concrete workability, strength, and durability is well-established. This analysis becomes particularly relevant in the context of our study on Ordinary Portland Cement (OPC) and Limestone Calcined Clay Cement (LC3), where understanding how their respective particle size distributions align with this classification provides insights into their potential divergent behaviors under varying environmental conditions.

Similarly, Figure 6, depiction of coarse aggregates becomes crucial in the discussion. The emphasis on identifying the percentage of particles within the 5/20 classification (5 mm to 20 mm) is vital

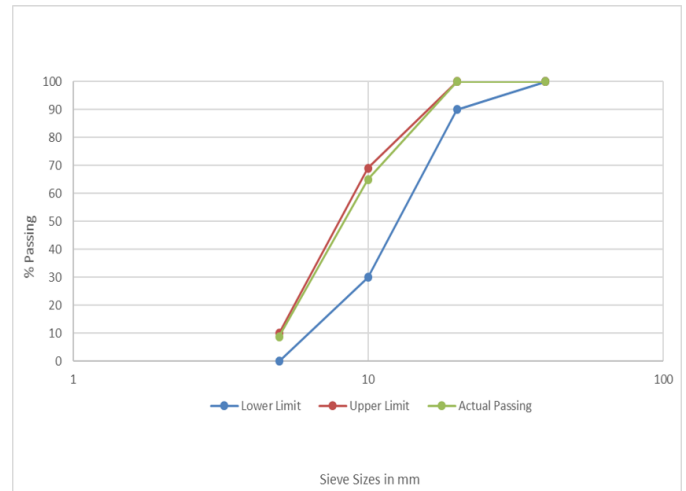


Figure 6: Particle Size Distribution Curve for Coarse Aggregates

according to the. Considering the significant contribution of coarse aggregates to concrete's structural strength, stability, and resistance to wear. This aspect is particularly relevant for our research on OPC and LC3, as differences in their coarse aggregate characteristics can contribute to disparities in mechanical properties and durability. Integrating the particle size distribution analysis with other data, such as chemical composition and physical properties, enriches our understanding of the observed variations in performance between OPC and LC3. The comprehensive interpretation aids in drawing meaningful correlations between aggregate characteristics and the response of these cementitious materials to factors like biogenic sulfuric acid and diverse environmental conditions.

Visual Inspection of the Damaged Cubes

A visual inspection of the cubes was conducted before and after subjecting them to biogenic sulfuric acid for the entire 90-day experimental duration while exposing it to wet and dry cycle for 12 hours each day respectively. The extent of surface deterioration became evident after exposure to varying wet-dry cycles in the concentrated biogenic sulfuric acid of pH 2 , as illustrated in the results. Figure 7



Figure 7: The extent of surface deterioration became evident after exposure to varying wet-dry cycles in the concentrated biogenic sulfuric acid



Figure 9: Damaged Concrete Cubes After Compressive Strength Test.

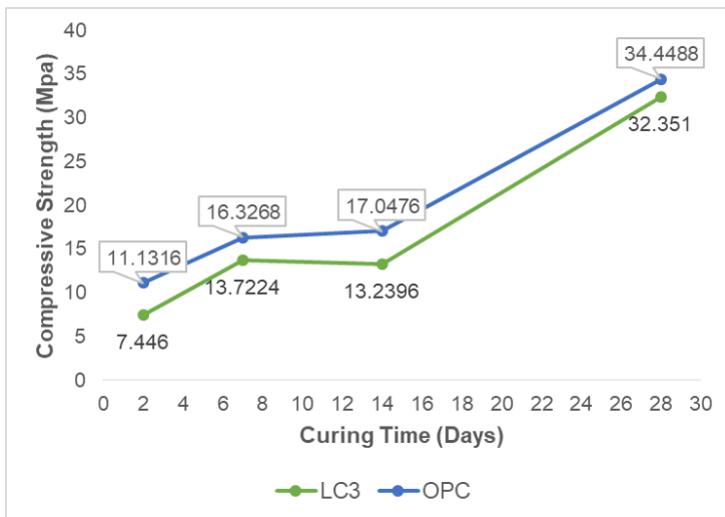


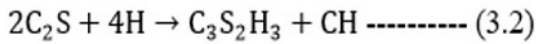
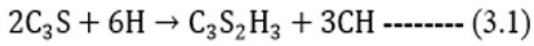
Figure 8: Compressive strength development of OPC and LC3 after 28 days curing

The severity of concrete surface degradation increases as the dry–wet time increases. Sulfate moved into the specimen during the wetting process, and enlarged sulfate crystals appeared in the specimen's pores during the drying process, resulting in physical weathering of the exposed surface particles, which disintegrated or dropped off. As a result, the surface of the specimen gradually chalked off as the number of cycles rose, as seen in Figure 9. This is the most common salt-weathering effect in nature [25]. In the wetting condition, no crystals form, as observed in Figure 9. The evaporation of water in the drying condition

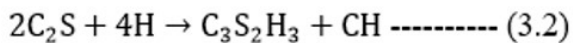
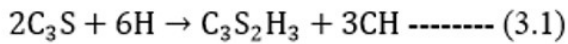
resulted in a continual concentration of a salt solution from the surface to the inside of the concrete. The white salt crystals precipitate and develop fast after the supersaturated solution is produced. A supersaturated film layer forms between the crystal and the pore wall, and there is an energy differential between the crystal and the pore wall, allowing the crystal to continue to develop toward the pore wall, creating crystallization pressure, and causing concrete cracking degradation. This in line with earlier studies [24-26].

Compressive Strength after 28 Days Curing

Figure 8 shows the 28th day compressive strength findings for LC3 and OPC at a 0.5 w/c ratio. According to the findings, the compressive strength of OPC was higher than the compressive strength for LC3 at 28 days of curing at a 0.5 w/c ratio. OPC recorded a compressive strength of 34.4488 MPa, while LC3 recorded a compressive strength of 32.352 MPa. The hydration of tricalcium silicates (C3S) and dicalcium silicates (C2S) leads to the production of calcium silicate hydrates (CSH) in the hardened concrete is responsible for early strength, as shown the following equations [28].



$C_3S_2H_3$ or simply CSH is a cementitious substance that gives hydrated cement-based materials their strength. In both OPC and LC3 cement blend, CSH is responsible for strength. When CH is released during the hydration of clinker stages in blended cement, the pozzolanic reaction occurs. As indicated in Equations (3.3) and (3.4) [28], the released CH combines with pozzolanic materials, silicates, and aluminates in the presence of water to create CSH and calcium aluminate hydrate (CAH) responsible for hardening.



Water Absorption

The water absorption profiles of LC3 and OPC mortars at 30 days after curing are shown in Figures 3.5 to 3.8

The water absorptivity of OPC was found to be higher than that of LC3 cement. This could be because hydrated OPC has a higher permeability than blended cement mortar matrix. This is due to the presence of pozzolana elements in blended cement, which react with CH produced by the hydration of OPC to form secondary cementitious materials (CSH and CAH) [28, 27]. Moreover, the pozzolanic elements that have been integrated into the hydrated cement matrix serve as a filler ingredient. The presence of more cementitious material introduces the filler effect in the concrete causing densification of the matrix, hence water permeability is reduced significantly.

The CH formed during the process of hydration leads to a more porous and permeable OPC concrete structure. This creates spaces that act as

channels, allowing for increased water permeability and absorption. On the other hand, water absorption was observed to be in LC3 concrete because of the presence of calcined clay and limestone in the ternary binder. According to Dhandapani *et al.* [30], there are more products of hydration formed in the LC3 ternary system. This leads to more refined pores and denser structures [31]. Water permeability into the hydrated cement matrix is reduced as a result. The pore refinement is due to LC3 hydration products has been attributed to their occupation of large volume, which is twice the volume of anhydrous cement [32]. In LC3 cement, the higher pore refinement significantly lowers the water absorptivity of hardened cement more than in conventional OPC cement. As a result, the moisture migration through the LC3 matrix is significantly retarded. The authors of a related study Dhandapani *et al.* [33], looked into microstructure-related aspects to better understand the performance of limestone-calcined clay cement composite. The inclusion of limestone and calcined clay was also credited by the authors Dhandapani *et al.* [33] for pore refinement and densification of hydrated LC3 matrix.

This could be because LC3 is a ternary system with calcined clay and limestone. In LC3, more hydration products are produced, resulting in more pore refinement and densification of the hardened mortar [31]. Water permeability into the hydrated cement matrix is reduced as a result. Hydration products in ternary cement mixes like LC3 have been observed to take up more than twice the volume of anhydrous cement, resulting in improved pore refinement. In LC3 cement, the higher pore refinement significantly lowers the water absorptivity of hardened cement more than in typical OPC cement. This could cause moisture migration through the hydrated LC3 cement matrix to be slowed. The authors of a related study Dhandapani [33] looked into microstructure-related aspects to better understand the performance of composite cement with limestone-calcined clay combination. The inclusion of lime-

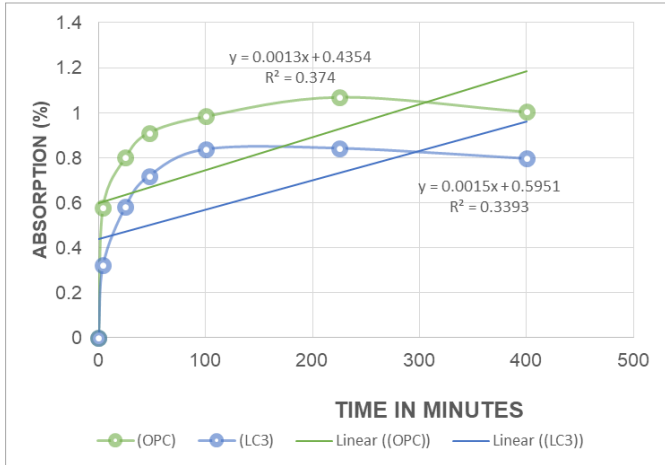


Figure 10: Sorptivity profile for LC3 and OPC at water cement ratio of 0.5.

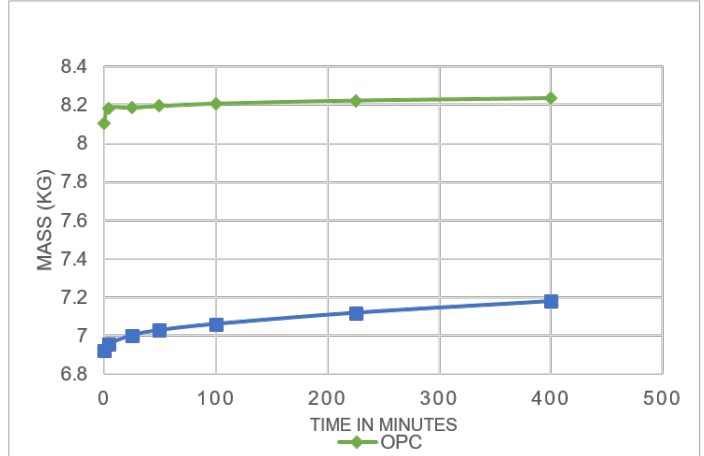


Figure 12: Water absorption after damage by H₂SO₄

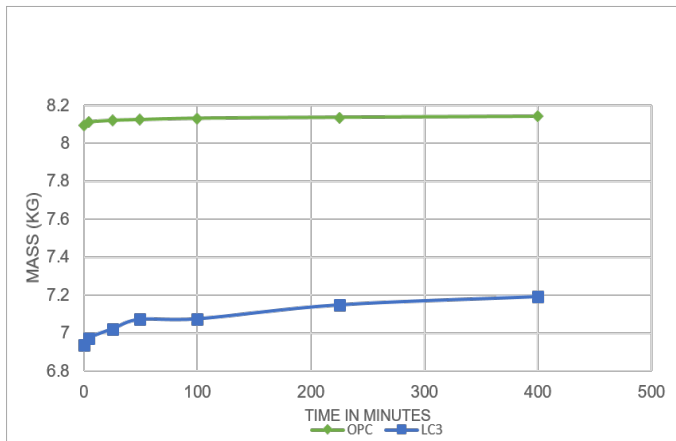


Figure 11: Water absorption before degradation by biogenic sulfuric acid.

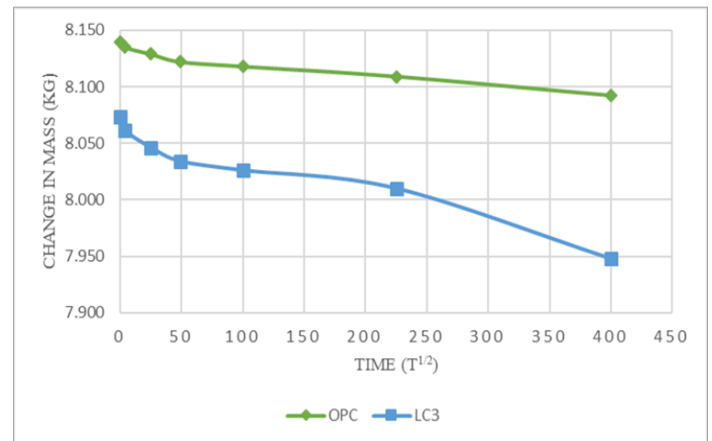
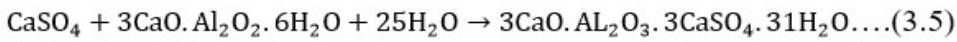


Figure 13: Weight loss of the concrete cubes immersed in 3 % H₂SO₄

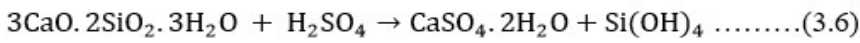
stone and calcined clay was also credited by the authors Dhandapani [31] for pore refinement and densification of the hydrated LC3 matrix. Water absorption is lower at the beginning of the immersion time (three hours) for all cement types and w/c ratios. This is because the samples were initially rather dry because all of the pore water was consumed during the hydration of the cement stages. Moisture migration through the cement matrix happens when exposed to water due to changes in moisture content inside the hydrated cement pores and voids.

The biogenic sulfuric acid attack on the CSH

and CH phases and OPC is responsible for the weight and strength loss [33, 34]. Since biogenic sulfuric acid introduces SO₄²⁻ and H⁺ into the pore water, sulfate attack is facilitated. The ions SO₄²⁻ and H⁺ are harmful to cementitious materials. H⁺ can directly attack the CH and CSH phases or indirectly cause a reduction in the pH of pore water by causing a neutralization reaction between hydrogen ions and Ca(OH)₂ in the cementitious materials, whereas SO₄²⁻ ions cause the formation of ettringite, which is expansive, occupies large volume and causes cracks. This lowers the alkalinity of the mortar and causes the hydration products



Equation 3.5: gypsum reaction with calcium aluminate hydrate



Equation 3.6: gypsum reaction with calcium aluminate hydrate

(mostly CSH and CH) to dissolve. Consequently, the mortars deteriorate, resulting in weight and compressive strength loss

According to Mwititi *et al.* [28], the sulfate ion reacts with lime leading to the formation of gypsum as shown in equation 3.4 [36]. The formed gypsum reacts with the calcium aluminate hydrate phase to form the expansive ettringite, as shown in the equation 3.5 above.

The ettringite formed causes high internal stresses in hydrated cement materials, resulting in mortar/concrete spalling, cracking, and general strength loss.

This is linked to the loss of weight and strength of the cubes when soaked in the biogenic sulfuric acid solution of pH 2 in the repeated wet-dry cycles. Additionally, the induced hydrogen ions into the pore water in the matrix of the hydrated cement. The hydrogen ions react with CSH which is the primary product of cement hydration, responsible for the binding property of the concrete as shown in Equation 3.6 given above

In comparison to blended cement (LC3) concrete, OPC concrete lost more weight and strength. This could be because OPC has a higher CH content than mixed cements. Calcium hydroxide (CH) is the phase that is most vulnerable to acid assault. Since the attack is expansive, it results in the development of ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$) as stated in Equation (3.5), which leads to the formation of micro-cracks and spalling, ultimately leading in weight and strength loss.

Longer immersion periods resulted in greater weight and strength loss. This can be due to hydrated cement mortars being exposed to the biogenic sulfuric acid solution for an extended peri-

od. Increased exposure time causes more H ions to react with CH, resulting in the creation of additional ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$), which is then leached and re-crystallized in the wet cement matrix's void spaces. This harms the durability of cement-based materials because it causes micro-cracks to form. Microcracks in hardened cement-based materials cause a considerable loss of strength because the dense pore connectivity in the hydrated cement matrix is destroyed, resulting in a porous cementitious material. Micro-cracks also operate as active channels for the entrance of potentially hostile ions that are harmful to hydrated cementitious materials. Rashwan *et al.* [37], made similar discoveries while researching on the effect of local metakaolin on concrete characteristics and biogenic sulfuric acid resistance.

Conclusions

Based on the findings, the following conclusions were reached:

- i) After 28 days of curing, the compressive strength of OPC cubes was slightly higher than that of LC3 mortars. However, due to the increased pozzolanic activity of the clay pozzolana, it is anticipated that the compressive strength of LC3 mortars will experience significant improvement compared to OPC when subjected to curing in biogenic sulfuric acid. This is evident from visual inspections, sorptivity tests, and the effects of wet and dry cycles, all of which indicate that OPC cubes were adversely affected by biogenic sulfuric acid, while LC3 cubes exhibited resistance to its impact. The susceptibility of OPC to biogenic sulfuric solution

is notably higher than that of LC3, emphasizing the latter's resistance to sulfate attack and its consequent ability to achieve higher compressive strength..

- ii) Water absorption was lower in LC3 than in OPC. Blended cement is less porous than OPC, according to this research. As a result, they are less susceptible to degradation as a result of strong media penetration. Therefore, LC3 offers great shielding capability to sulphate attack compared to OPC.
- iii) The resistance to biogenic sulfuric acid attack was stronger in LC3 than in OPC. This revealed that they might be used to make more durable constructions.
- iv) Biogenic Sulfuric acid attack on cement hydration products causes a decrease in compressive strength which was witness in OPC cement.

Recommendations

From this work, it can be concluded that LC3 has a good performance profile in resisting deleterious materials. Therefore, further research is recommended to ascertain its use in the construction of resilient and durable sanitary facilities such as septic tanks for a long design period. It is also recommended that more tests be carried out after longer periods of curing the cubes including after 60 and 90 days of curing.

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