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Sulphuric Acid Resistance of Concrete Blended with Limestone Dust and Locust Bean Pod Ash

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Abstract
This study investigated the effect of sulphuric acid (H_2SO_4) attack on concrete mixtures prepared by partially replacing cement with limestone dust (LSD) and locust bean pod ash (LBPA) at 0% (Control), 5% (0%LSD+5%LBPA), 10% (5%LSD+5%LBPA), 15% (10%LSD+5%LBPA), 20% (15%LSD+5%LBPA), 25% (20%LSD+5%LBPA), 30% (25%LSD+5%LBPA) respectively. Sulphuric acid solution of 5% concentration was used for examining the resistance of concrete specimens for a total exposure period of 28 days. The performance of the degraded specimens was evaluated by measuring the strength loss. The results show that the control mix's compressive strength dropped from 31 N/mm^2 before immersion to 23.15 N/mm^2 after 28 days of immersion in a 5% H_2SO_4 solution. At 10% LSD-LBPA mix, the compressive strength before immersion dropped from 24.33 N/mm^2 to 23.81 N/mm^2 after immersion in a 5% H_2SO_4 solution. The best result with the least amount of strength loss of 2.14 percent was obtained at 10% mix. The control mix suffered the greatest loss of strength of 25.32 percent. Water absorption in the mixes decreased up to 10% mix, and then increased when LSD and LBPA were further added. At a 10% mix, the lowest rate of water absorption of 16.28 percent was obtained. Based on the findings, a 10% LSD-LBPA (5%LSD+5%LBPA) mix with better H_2SO_4 acid resistance than the control mix is recommended for concrete production in acidic environments.

Keywords: Limestone Dust, Locust Bean Pod Ash, Acid Resistance, Water Absorption, Durability.

1.0 Introduction

Concrete structures are subjected to harsh environmental conditions on a regular basis. External and internal influences may cause such interaction, affecting the mechanical and physical properties of concrete (Baradan et al., 2002). Chemical attacks or mechanical damage caused by impact, abrasion, erosion or cavitation are examples of external factors, whereas chemical reactions involving concrete constituents are examples of internal factors (Neville, 2005). The ability of concrete to withstand these factors, as well as any other deterioration process, is used to determine its durability (ACI Committee, 2001). Some concrete structure failures are caused by a lack of durability, which manifests as deterioration caused by external or internal factors within the concrete. Sulphuric acid, which is produced by sewage or sulphur dioxide present in the atmosphere of industrial cities, can attack concrete. This is due to Portland cement concrete's high alkalinity, which can be attacked by other acids as well (Hewayde et al., 2007). The acidic environment is deleterious to concrete durability because acid neutralizes the alkalinity of concrete by reacting with the hydration products of the concrete matrix to form gypsum and ettringite (Yuan et al., 2013). Both gypsum and ettringite possess little structural strength, yet they have larger volumes than the compounds they replace. This results in internal pressures, formation of cracks and eventually, the loss of strength (Monteny et al., 2001). Consequently, the concrete becomes vulnerable to aggressive exposure (Olonade et al., 2014). Sulphuric acid is particularly corrosive due to the sulphate ion participating in sulphate attack, in addition to the dissolution caused by the hydrogen ion (Kulkarni, 2019).

The degree of concrete deterioration increases due to alternate wet-dry cycles of exposure to sulphuric acid and the rate of concrete deterioration along the penetration depth of sulphuric acid could be described by a variation in sulphur concentration with the depth of acid penetration (Hewayde et al., 2007). Various strategies have been used to improve the resistance of concrete in an acidic environment. One of the strategies that have proven to be very effective is the use of various supplementary cementitious materials such as fly ash, slag, micro silica, and calcite laterites (Roy et al., 2001). Aliyu et al. (2020) studied the effect of sulphuric acid on the compressive strength of concrete with quarry dust as partial replacement of fine aggregate at 0 %, 15 %, 25 % and 35 % at 7, 14 and 28 days curing in water and 7, 14 and 28 days curing in 5% solution of sulphuric acid. The study reported that the slump decreased as the percentage addition of quarry dust increased. However, the result of the compressive strength of quarry dust-concrete showed that the compressive strength increased with the curing age and also increased with the addition of quarry dust.

On the other hand, the resistance of the concrete to acid increases as the percentage addition of quarry dust increased. The weight of concrete decreased with an increase in exposure duration and also decreased with an increase in quarry dust content. But the water absorption of quarry dust-concrete decreased with an increase in quarry dust addition. It was concluded that quarry dust can replace river sand in concrete to improve its resistance to sulphuric acid attack. Kawai et al., (2005) conducted a study to assess the deterioration of concrete caused by sulphuric acid. They reported that the rate of concrete deterioration caused by sulphuric acid attack depends on the acid solutions pH value.

Also, the erosion depth of the concrete is proportional to the exposure time of the concrete to the flow of acid solution. Al-Tamimi and Sonebi (2003) carried a study on resistance of self-compacting concrete (SCC) which contained 47% limestone filler (LF). Cylindrical specimens that were 45 mm in diameter and 90 mm in height were immersed into a 1% acidic solution for a period of 18 weeks. Mass loss and visual inspection were used as indicators of the performance of the different specimens. The results obtained were compared to the results of conventional concrete which contained only Portland cement subjected to the same testing method. The final results showed that conventional concrete had experienced severe degradation and lost 21% of its mass while the SCC mix with limestone powder lost only 9% of its mass at the end of the immersion period. Reddy et al., (2012) investigated the effect of H_2SO_4 on blended cement concrete (BCC).

They reported that the compressive strength of BCC decreases with an increase in the concentration of H_2SO_4 at both 28 and 90 days. The decrease in compressive strengths of BCC was observed to be in the range of 2 to 23 %, with an increase in H_2SO_4 concentration between 28 to 90 days when compared with the control specimens. Senhadji et al., 2014 carried out a study which shows that addition of 10% of lime stone to sulphate resistant cement increases the rate of hydration from 3 up to 90 days curing time. Addition of 5% of both lime stone and silica fume to cement paste gives good mechanical properties at all curing periods. Consistency as well as setting time is observed to decrease slightly with lime stone content due to increase in plasticity of cement paste.

This may be attributed to the effect of lime stone as an active component in the hydration of Portland cement. The rate of hydration increases and the amount of hydrated products enhances. Consumption of calcite, the formation of carboaluminates, and the accelerating effect on the hydration C_3A, C_3S, change in the C–S–H and formation of transition zone between the filler and the cement paste are all facts attributable to the reactivity of lime stone fillers.

Akpenpuun et al., (2019) investigated the effect of replacing cement with LBPA on the setting times and observed that as the LBPA content increased up to 30%, the initial and final setting time experienced retardation by 66.8% and 39.7% respectively. The concrete mix workability diminished as the LBPA content was increased. The enhanced compressive strength of 15% LBPA cement blend agreed with results from SEM, EDS and XRD which indicated a pronounced presence of CSH gel compared to other samples. They suggested that the crystalline or amorphous nature of the LBPA influenced the setting time which was dependent on the process conditions for obtaining the ash. In this study, the effect of sulphuric acid on concrete blended with limestone dust and locust bean pod ash was investigated. The objectives of the study are determination of compressive strength at various percentages of cement replacement with LSD-LBPA in concrete, determination of water absorption in concrete at various percentages of cement replacement with LSD-LBPA and evaluation of sulphuric acid (H_2SO_4) resistance of concrete with varying percentages of LSD-LBPA replacement.

2.0 Materials and Methods

Materials used for this study include; cement (Dangote brand grade 42.5), fine aggregates, coarse aggregates, limestone dust, locust bean pod ash, sulphuric acid and water.

2.1 Cement

The cement used was that of Dangote brand grade 42.5. It was obtained from Samaru market in Zaria, Kaduna state and was safely kept in dry place condition.

2.2 Fine Aggregates

The fine aggregate used in this study was river sand obtained within Samaru, Zaria Kaduna State. The fine aggregate was sieved through a BS 4.75mm sieve to remove larger aggregates.

2.3 Coarse Aggregates

Crushed coarse aggregates were obtained from a local quarry along Sokoto Road, Zaria, Kaduna State, Nigeria. The aggregates consisted of 20 mm as its maximum size and 4.75 mm as its minimum size. Coarse aggregate is a major constituent of concrete, which constitute about 60% to 75% by volume of concrete.

2.4 Limestone Dust

The limestone dust used in this study was obtained from freshly deposited heaps of the waste at Dangote cement factory located at Obajana, Kogi State, Nigeria. It was sieved in a 75µm sieve and its chemical composition was examined using X-ray fluorescence, which was done at chemical engineering, Ahmadu Bello University, Zaria.

2.5 Locust Bean Pod Ash

The locust bean pod used in this was obtained from Mbawer village in Kwande L.G.A, Benue State. Locust bean pod samples collected were burnt in open air, afterwards calcined in an oven at a temperature of 600°C for 2 hours to produce ash at the chemical engineering, Ahmadu Bello University Zaria. The ash was allowed to cool before grinding to a very fine texture and then allowed to pass through No. 200 (75µm) sieve.

2.6 Sulphuric Acid

The sulphuric acid used in this study was obtained in Samaru market Zaria, Kaduna State, Nigeria.

2.7 Water

Portable water from civil engineering laboratory, Ahmadu Bello University, Zaria was used and it was in conformity with recommendation of BS EN 1008:-2002.

3.0 Methods

3.1 Concrete Mix Proportion

The batching was carried out by partially substituting cement with limestone dust (LSD) and locust bean pod ash (LBPA) in a proportion of 0% (control), 5% (0%LSD+5%LBPA), 10% (5%LSD+5%LBPA), 15% (10%LSD+5%LBPA), 20% (15%LSD+5%LBPA), 25% (20%LSD+5%LBPA) and 30% (25%LSD+5%LBPA) respectively. A total of seven (7) batches were made with Dangote cement grade 42.5, with an average of three cube samples for each mix level cured at 3, 7, 14, and 28 days, a 1:2:4 mix ratio, and a 0.50 water cement ratio, with a target strength of 25 N/mm^2 at 28 days. The tests carried out on the specimens were compressive strength test, acid resistance test and water absorption test.

3.2 Compressive Strength Test on Limestone Dust-Locust Bean Pod Ash Concrete

The compressive strength test of the hardened concrete was determined in accordance to BS 1881, part 116 (1983) specifications. A total of eighty four (84) cubes were cast using 100 mm x 100 mm x 100 mm steel moulds and cured in water. The cubes were tested for compressive strength after 3, 7, 14 and 28 days curing. The samples were crushed using the compressive testing machine of 2000 kN load capacity at a constant rate of 15 kN/s at the Civil Engineering Concrete Laboratory of Ahmadu Bello University Zaria.

3.3 Acid Resistance Test

The acid resistance test was done according to ASTM C 267-01. A total of twenty one (21) concrete cubes of size 100 mm x 100 mm x 100 mm were cast and cured in clean water for 28 days. After 28 days of curing in water, the specimens were air-dried for 72 days and immersed completely in twenty-five (25) litres of water containing 5% solution of sulphuric acid (H_2SO_4) with a molar concentration of 0.937 M. These specimens were then tested after 28 days of curing in acidic solution using the compressive testing machine of 2000 kN load capacity at a constant rate of 15 kN/s at the civil engineering concrete laboratory of Ahmadu Bello University Zaria.

The percentage loss in compressive strength was calculated using Equation 1.

Loss in compressive strength,

$$f_{lc} = \frac{f_{cb} - f_{ca}}{f_{cb}} \times \frac{100}{1} \qquad (1)$$

Where f_{lc} = Loss in compressive strength, f_{cb} = compressive strength before acid immersion

f_{ca} = compressive strength after acid immersion

3.4 Water Absorption Test

The water absorption test was conducted in accordance to ASTM C642 (2006). The oven-dry mass of each specimen was obtained by placing them in an oven at a temperature of 100 to 110 ℃ not less than 24 hours. Later, the saturated mass of samples was determined by immersing them in water at approximately 21 ℃ for not less than 48 hours and until two successive measurements of mass of the surface-dried samples at intervals of 24 hours indicated constant mass. The water absorption was then calculated using Equation 2.

$$\text{Water Absorption} = \frac{M_s - M_o}{M_o} \times \frac{100}{1} \quad (2)$$

Where M_s= Weight of Saturated Sample, M_o= Weight of Dry sample (after oven drying for 24 hours)

4.0 Results and Discussion

4.5 Chemical Oxide Composition of

4.5.1 Cement

X-ray fluorescence (XRF) was used to examine the chemical composition of cement, LSD and LBPA at Chemical Engineering Laboratory, Ahmadu Bello University Zaria, Kaduna State, Nigeria. The results presented in Table 1 show that the chemical composition of the cement used in this study met the BS EN 197-1 (2000) standard. The oxide composition of LSD and LBPA is presented in Table 2.

Table 1: Oxide Composition of Cement

Oxide	Cement (%)	BS EN 197-1 (2000)
CaO	64.57	60 – 67
SiO_2	21.64	17 – 25
Al_2O_3	5.33	3 – 8
Fe_2O_3	3.89	0.5 – 6
MgO	1.76	0.5 - 4
SO_3	1.49	2.0 – 3.5
LOI	1.44	2

Table 2: Oxide Composition of Limestone Dust and Locust Bean Pod Ash

Oxide	Limestone Dust	Locust Bean Pod Ash
CaO	50.16	11.18
SiO_2	7.34	47.36
Al_2O_3	2.33	17.42
Fe_2O_3	1.19	13.01
MgO	0.40	1.50
SO_3	0.09	1.21
LOI	33.42	5.02

4.5.2 Compressive Strength of Limestone Dust-Locust Bean Pod Ash Concrete

The result of the compressive strength of LSD-LBPA concrete is presented in Figure 1. The result shows that compressive strength increased with curing age, but decreased as LSD-LBPA content increased. Apart from the control mix, which had a compressive strength of 31 N/mm^2, the optimum result was obtained at 10% LSD-LBPA mix, with a compressive strength of 24.33 N/mm^2, slightly less than the targeted strength of 25 N/mm^2. The increase in compressive strength with curing age is due to hydration of cement, while the reduction in strength with increase in LSD-LBPA content may be due to the dilution effect of limestone (Irassar et al, 2011). A similar trend was reported by Ghorab et al., 2014. Early strength gain was attained at 3-days curing which may be attributed to the interaction of limestone with alumina in cement to produce calcium carbo-aluminate (Voglis et al., 2005). This result agreed with studies carried out by Matschei and Lothenbach (2007). On the other hand, the optimum result obtained could be attributed to the pozzolanic reaction between the available lime and reactive silica from LBPA.

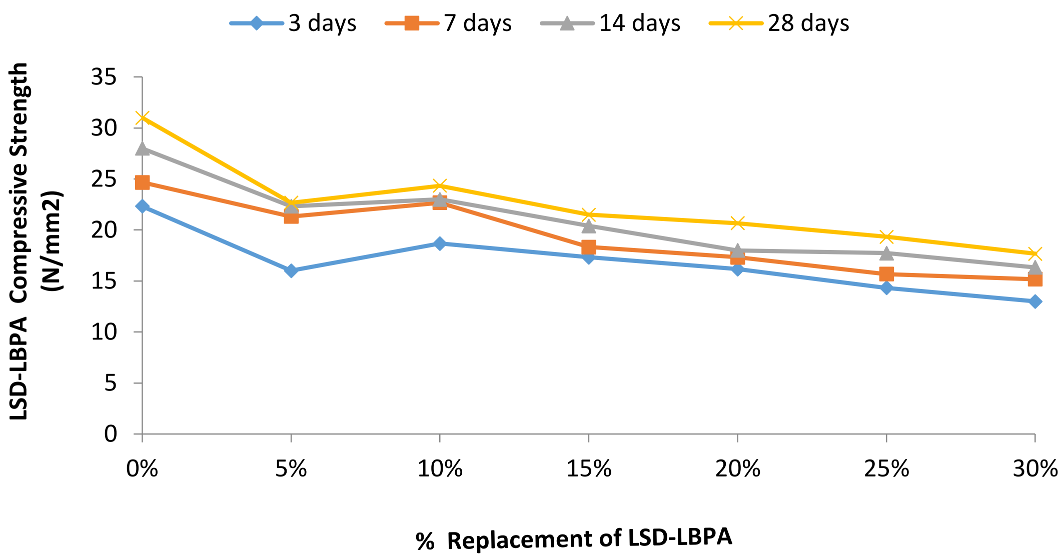

Figure 1: Compressive strength variation with percentage replacement

4.5.3 Effect of Sulphuric Acid on Limestone Dust-Locust Bean Pod Ash Concrete

Figure 2 shows the variation in compressive strength before and after immersion in a 5% sulphuric acid (H_2SO4) solution for 28 days, while Figure 3 illustrates the strength loss of concrete containing various percentages of LSD and LBPA after immersion in a 5% sulphuric acid (H_2SO_4) solution for 28 days. The best result with the least amount of strength loss was achieved with 10% LSD-LBPA concrete. The control concrete with no LSD-LBPA content lost the most strength. After 28 days of immersion in a 5% H_2SO_4 solution, the control mix's strength dropped from 31 N/mm^2 before immersion to 23.15 N/mm^2 after immersion in 5% sulphuric acid solution, a 25.32 percent reduction. At 10% LSD-LBPA, the compressive strength before immersion was 24.33 N/mm^2 which dropped to 23.81 N/mm^2 after immersion in 5% sulphuric acid solution, a minimum strength loss of 2.14 percent was achieved. When compared to the control sample, the sample containing LSD-LBPA showed less reduction in strength. This could be due to the formation of a silicate gel by LBPA during the hydration process, which coats and binds the matrix while also blocking acid action in the concrete structure, preventing acid damage. LSD's provision of more nucleation sites, which results in an acceleration of cement hydration rate, can also be attributed to the better performance of the concrete resistance to acid attack. The amount of hydrated products increases as the rate of hydration increases. The reactivity of limestone dust is responsible for the consumption of calcite, the formation of carboaluminates, the acceleration of hydration C_3A, C_3S, the change in the C–S–H, and the formation of a transition zone between the filler and the cement paste (Heikal *et al.*, 2000)

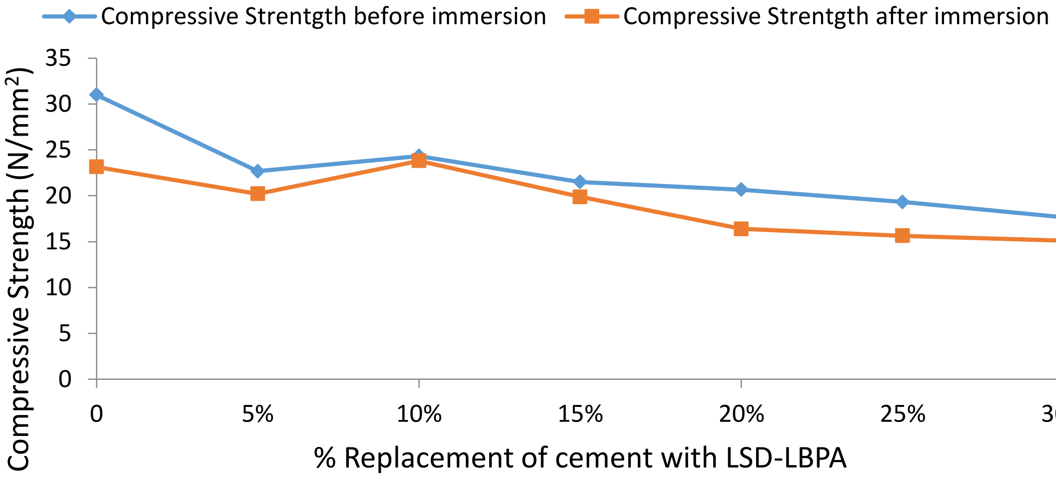

Figure 2: Variation of compressive strength before and after sulphuric acid immersion

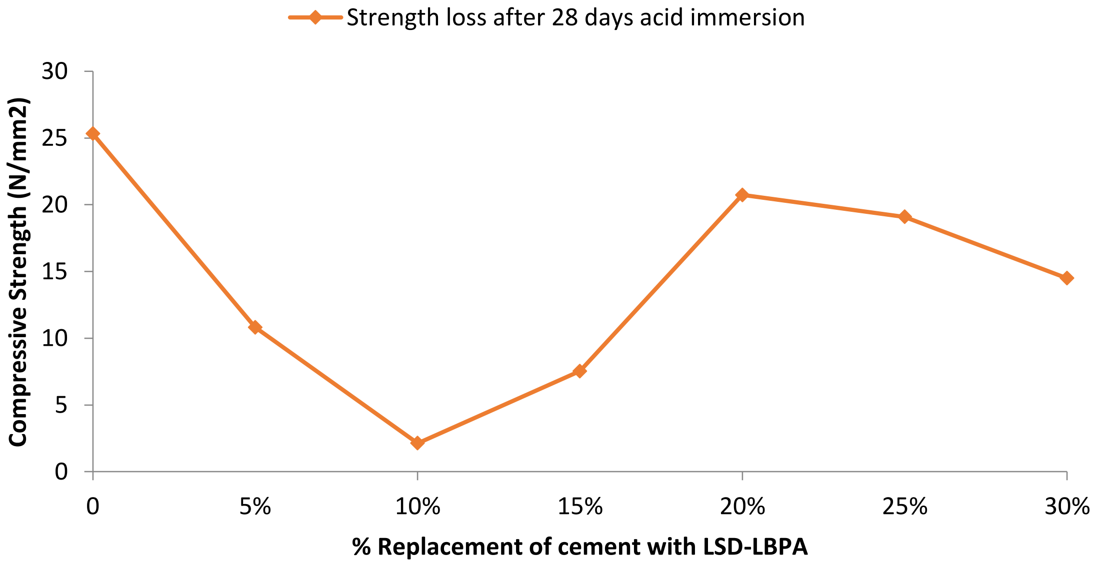

Figure 3: Variation of strength loss with addition of LSD-LBPA content

4.5.4 Water Absorption Test

Figure 4 depicts the result of variation in the oven dry and saturated samples, while Figure 5 depicts the rate of water absorption. Water absorption in the mixes reduced up to 10% and then increased when limestone dust and locust bean pod ash were further added. At a 10% (5% LSD, 5% LBPA) mix, the lowest rate of water absorption of 16.28 percent was obtained. The decrease in water absorption could be due to the concrete's porosity being reduced. The presence of LBPA makes the sample less porous and impermeable than the control sample, by filling voids and reducing water ingress pathways. More so, limestone dust generates a large number of hydration product nucleation sites, resulting in a more homogeneous C-S-H gel distribution and thus less pore structure. The findings are in line with a study conducted by Li *et al.* (2020).

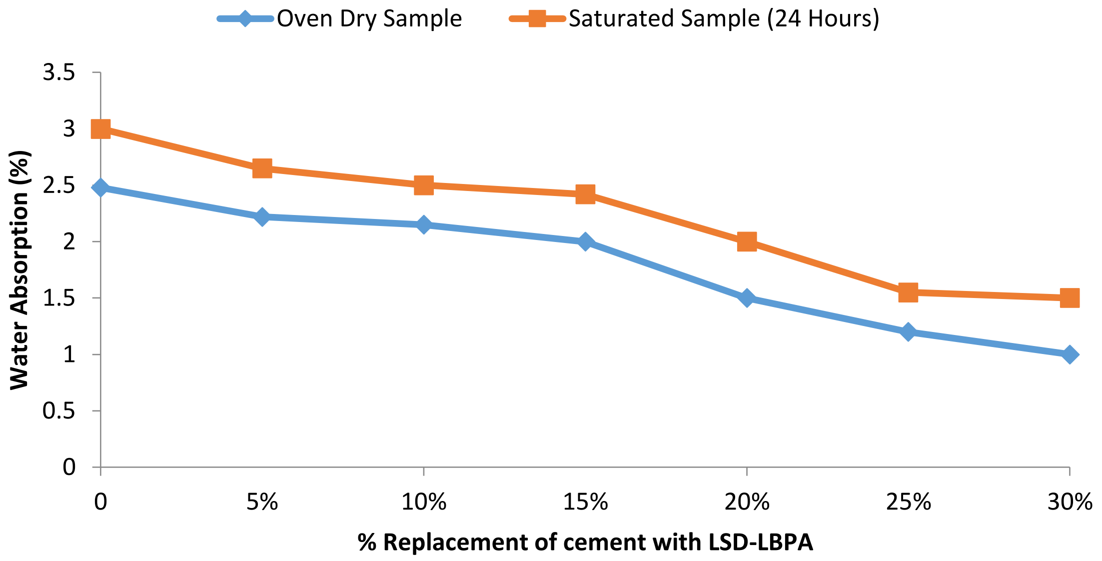

Figure 4: Variation of oven dried and saturated samples with addition of LSD-LBPA

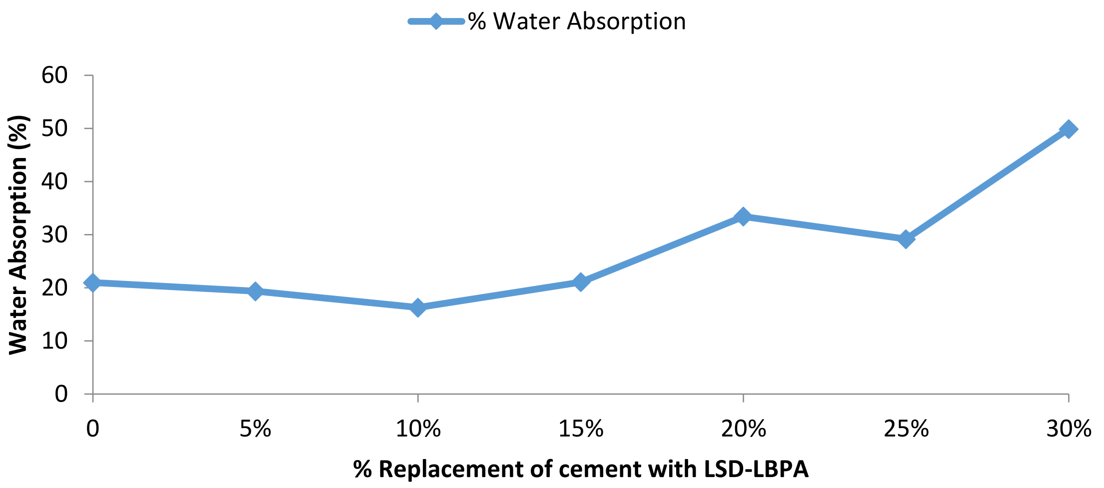

Figure 5: Variation of water absorption with addition of LSD-LBPA content

5.0 Conclusion

The results show that the control mix's compressive strength dropped from 31 N/mm^2 before immersion to 23.15 N/mm^2 after 28 days of immersion in a 5% H_2SO_4 solution. At 10% LSD-LBPA mix, the compressive strength before immersion dropped from 24.33 N/mm^2 to 23.81 N/mm^2 after immersion in a 5% H_2SO_4 solution. *The best result with the least amount of strength loss of 2.14 percent* was obtained at 10% mix. The control mix suffered the greatest loss of strength of* 25.32 percent*. Water absorption in the mixes decreased up to 10% mix, and then increased when LSD and LBPA were further added. At a 10% mix, the lowest rate of water absorption of 16.28 percent was obtained. Apart from the control mix, the optimum compressive strength of the LSD-LBPA cement blend at 10% correspond to the optimum results of acid resistance and water absorption tests respectively obtained at the same mix level, indicating that this mix level performed better in compressive strength, acid resistance, and rate of water absorption than the other mixes. Based on the findings, a 10% LSD-LBPA (5%LSD+5%LBPA) mix with better H_2SO_4 acid resistance than the control mix is recommended for concrete production in acidic environments.

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