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Original Article

Effect of Pretreated Corn Cob Ash on the Mechanical and Durability Characteristics of High-Strength Concrete

Abdoul Karim Ameyric Habib Ouedraogo[1], David Otieno Koteng[2], Nathaniel Ambassah[3]

[1]*Department of Civil Engineering, Pan African University Institute for Basic Sciences, Technology and Innovation hosted at Jomo Kenyatta University of Agriculture and Technology, Kenya.*
[2]*Department of Civil & Construction Engineering, School of Civil & Resource Engineering, Technical University of Kenya, Kenya.*
[3]*Department of Civil, Construction and Environmental Engineering, Jomo Kenyatta University of Agriculture and Technology, Kenya.*

[1]*Corresponding Author : oameyric8@yahoo.com*

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Abstract *- Portland cement, a key binder for concrete, is a significant contributor to non-renewable resource consumption and greenhouse gas emissions. To address these issues, it is often replaced with materials from industrial and agricultural waste. Corn cobs are such agricultural waste. The reactive silica and alumina in corn cob ash can react with free lime in Portland cement, enhancing its strength and durability. However, research has shown that the chemical composition of corn cob ash varies significantly due to agricultural practices. Potassium-rich fertilizers, which promote corn growth, produce corn cob ash with high potassium and phosphorous oxides, which negatively affect concrete strength and durability. The objective of this research was to develop a suitable method for pretreating corn cob to reduce its potassium oxide and phosphorous oxide content and, at the same time, increase the pozzolanicity of the ash. The ash from pretreated corn cob was used to partially replace Portland cement in concrete production, and 28-day strength in excess of 40 MPa was produced, which increased to more than 70 MPa at 90 days. Moreover, the concrete had reduced water absorption, which was an indicator of improved pore density and improved resistance to sulfuric acid attack.*

Keywords *- Water pretreatment, Potassium and phosphorus oxides, Corn cob ash, Mechanical and durability properties, Sustainable concrete.*

1. Introduction

The many desirable qualities of concrete, such as low maintenance, versatility, hardness, and longevity in demanding environments, have contributed to its widespread use as a man-made construction material [1]. Portland Cement (PC) is the primary binder used in concrete. The PC raw meal undergoes heating at a temperature of about 1,450 °C, and the chemical composition of the raw meal is modified to produce four minerals that react with water to form bonds. These are tricalcium silicate, $3Cao.SiO_2$, dicalcium silicate, $2CaO.SiO_2$, tricalcium aluminate, $3CaO.Al_2O_3$, and tetracalcium aluminoferrite, $4CaO.Al_2O_3.Fe_2O_3$. The four major minerals may be represented using pseudo-chemical industrial notations: C_3S for $3CaO.SiO_2$ (Tricalcium Silicate), C_2S for $2CaO.SiO_2$ (Dicalcium Silicate), C_3A for $3CaO.Al_2O_3$ (Tricalcium Aluminate), and C_4AF for $4CaO.Al_2O_3.Fe_2O_3$ (Tetracalcium Aluminoferrite) [2].

To meet the demand of an expanding construction industry, cement production has been increasing rapidly. For instance, from 2005 to 2020, global cement production increased by 2.5% per year, from 2.3 to 3.5 Gt. By 2050, cement production is expected to reach 3.7 to 4.4 Gt [3]. On the other hand, Africa's cement capacity climbed from 262 Mt/a in 2014 to 386 Mt/a in 2020. With 110 kWh of electricity and 1.6 tons of raw materials needed to produce one ton of cement, Portland cement is a high consumer of both energy and raw materials [4].

Furthermore, the breakdown of primary substances such as limestone and chalk, together with the energy needed to calcine and grind these substances, generates around one metric ton of carbon dioxide for each metric ton of cement produced. Human-generated greenhouse gases, such as carbon dioxide, are a significant factor in global warming.

It is estimated that the cement sector is accountable for 6% of the overall carbon dioxide emissions on a worldwide scale. As a result of all these negative effects, Portland Cement is now facing concerns about its long-term sustainability.

In order to mitigate these adverse qualities of Portland cement, its use in the manufacture of concrete is reduced by incorporating a suitable Supplementary Cementitious Material (SCM). Bamboo stem ash, ash from rice husks, ash from elephant grass, fly ash, ash from wood waste, slag from blast furnaces, and silica fumes are common SCMs. Research has shown that the ash from lignocellulosic materials has a reactive silica and alumina content. These can react with the free lime released by the hydration of Portland cement to form pozzolanic compounds, which improve the physical and mechanical qualities of concrete [5, 6].

When PC is combined with a pozzolanic material, the pozzolanic material initially acts as a diluent. However, after sufficient free lime ($Ca(OH)_2$) is produced by the hydration of C_3S and C_2S in the Portland cement, the reactive SiO_2 and Al_2O_3 present in the pozzolanic material begin to react with the free lime to produce more cementitious C-S-H, C-A-H, and C-A-S-H, as shown in Equations 1 to 3.

$$SiO_2 + Ca(OH)_2 + H_2O = C\text{-}S\text{-}H \quad (1)$$

$$Al_2O_3 + Ca(OH)_2 + H_2O = C\text{-}A\text{-}H \quad (2)$$

$$SiO_2 + Al_2O_3 + Ca(OH)_2 + H_2O = C\text{-}A\text{-}S\text{-}H \quad (3)$$

These pozzolanic reactions continue until all the free lime is consumed. Furthermore, the pozzolanic processes enhance the compactness of the pore structure of concrete, resulting in a reduction in its permeability. Pore densification decreases the potential ingress of harmful ions like chlorides and sulfates, thereby reducing the likelihood of rebar corrosion and the overall degradation of hardened concrete.

Corn (or maize) waste products, such as cobs and hulls, are post-harvest residual components with great potential for incineration to produce pozzolanic ash. Africa's production of corn in the years 2020-2021 amounted to 89.3 million metric tons [7]. The total cultivated area for corn (for dry grain) worldwide is 197 million hectares, with significant portions found in sub-Saharan Africa, Asia, and Latin America (FAOStat, 2021) [8].

Several studies have shown that including Corn Cob Ash (CCA) in concrete has beneficial effects on both the fresh and hardened qualities of the concrete. The corn cob, which accounts for 15% of corn grain output, is used as a feedstock for the generation of biofuels because of its abundant cellulose and hemicellulose content [9]. On the African continent, south of the Sahara Desert, corn is an important cereal crop. Tons of corn cobs are produced and are largely used as domestic fuel. CCA is created by burning the corn cob at high temperatures. However, the use of CCA as SCM in concrete is not without setbacks. Plants take minerals from the soil in which they grow in varying amounts [10]. As a result, corn cobs have a unique chemical makeup depending on genetics, environmental conditions, soil composition, and agricultural practices [11]. Table 1 shows the different chemical compositions of CCA from corn cobs from different countries. A material is categorized as a pozzolan suitable for use as an SCM if the fraction of SiO_2 plus Al_2O_3 plus Fe_2O_3 is equal to or higher than 70% (ASTMC618-15, 2015). CCA has been shown to contain as high as 89.23% SiO_2, Al_2O_3, and Fe_2O_3, depending on the farming practices for the corn [12]. This exceeds the ASTM C618-12 requirement of 70% for Class-N pozzolans.

At younger ages, CCA-blended cement concrete has a lower compressive strength than plain concrete (control), but the strength improves with time. Hence, research on methods for fostering early-life strength development is essential [17]. The optimal temperature to calcine the corn cob has been established to be from 600 to 650°C. Up to 10% of Portland cement can be replaced by CCA, according to several studies [17]. When used as a partial replacement for Portland cement in concrete, it can increase concrete strength and durability. In the presence of water, pozzolanic reactions take place, as shown in Equations 1 to 3. Suraneni and Weiss [18] classified SCMs into four categories based on their relationship with calcium hydroxide consumption and the release of heat from hydration, as shown in Figure 1. CCA fell near the inert zone, suggesting that it has limited pozzolanic activity [18, 19]. The study showed that untreated CCA accelerates cement hydration due to its high potassium oxide content. However, reactivity testing showed that it exhibits lower reactivity compared to fly ash and is more similar to an inert substance. Untreated Corn Cob Ash (UCCA) in concrete results in reduced compressive strengths, bulk resistivity, formation factor, and increased electrical charge compared to regular concrete.

Table 1. Chemical composition of CCA for different countries

	Countries				
Reference Oxide	**USA** [11]	**Kenya** [13]	**Nigeria** [14]	**Thailand** [15]	**Nigeria** [16]
SiO_2	20.10	38.8	62.2	63.91	64.9
Al_2O_3	0.95	7.9	17.9	4.01	10.79
Fe_2O_3	0.75	7.4	9.13	3.95	4.75
CaO	2.95	1.8	2.96	4.13	10.24
MgO	2.42	2.1	-	2.91	2.08
SO_3	0.56	0.6	-	-	2.53
Na_2O	0.27	0.9	-	-	0.43
K_2O	38.1	23.5	2.13	12.12	4.23
P_2O_5	5.49	-	-	6.49	-
LOI	23.6	10.8	-	-	-
$SiO_2+Al_2O_3+Fe_2O_3$	21.8	54.1	89.23	71.87	80.44

The compressive strength test results of the study carried out by Shakouri et al. [11] showed that the partial replacement of OPC in concrete with UCCA significantly reduced its compressive strength. The disparity between UCCA-blended specimens and the control group becomes more evident as the specimens age. For instance, at 7 days, the strength of specimens containing 3% and 20% CCA was 2% and 42% less than the control group, respectively. However, at 112 days, the strength was 14% and 60% less than the control group. The objective of the study was to investigate the impact of UCCA on the hydration kinetics of cement, the durability of the concrete, and its resistance to chloride intrusion.

The study revealed that the selected strain of maize, specifically irrigated corn, had a significant amount of potassium oxide. Despite the ash being essentially inert, its high content of potassium oxide had a negative effect on the process of cement hydration, resulting in insufficient development of compressive strength in the concrete [11].

Figure 2 shows that the 112-day compressive strength of the UCCA mix of 20% is significantly less than the 28-day compressive strength, which is somewhat aberrant and may be caused by the high potassium content at the 20% replacement level of UCCA [20]. Nevertheless, the observed decrease in strength in this case is far more pronounced, aligning with the idea that the UCCA adversely affects the hydration of cement owing to its elevated potassium concentration [11]. Other researchers have also found that the compressive strength of concrete decreased when the potassium percentage increased [21-23].

On the other hand, Adesanya [24] found that concrete containing CCA had reduced water absorption and increased resistance to sulfate attack in comparison to concrete produced with OPC alone.

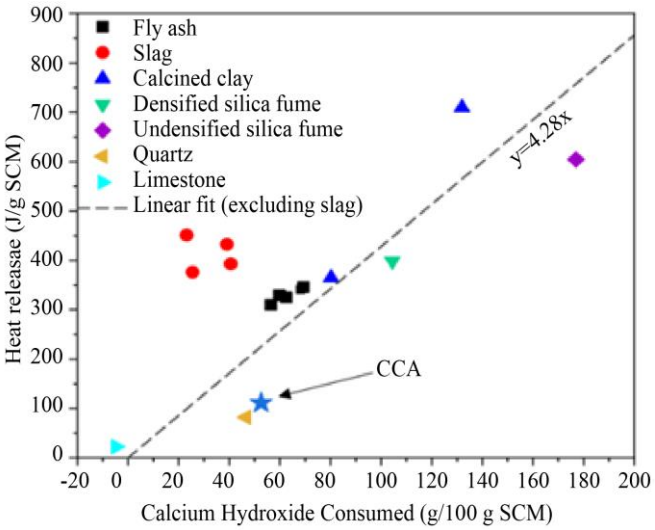


Fig. 1 Reactivity test of cementious materials [11]

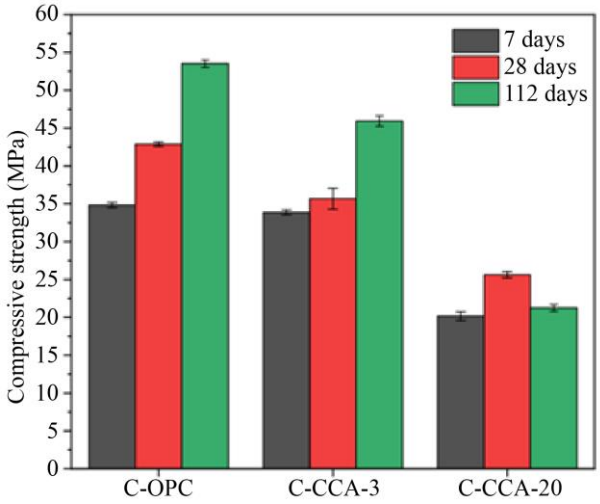


Fig. 2 Effect of an untreated corn cob on concrete compressive strength [11]

In addition, Adesanya and Raheem [25] and Mujedu et al. [26] found that adding CCA to the concrete made it less slumpy. Other researchers reported a significant reduction in compressive strength as a result of replacing OPC with CCA [24, 25, 27].

In separate research, Kamau et al. [13] examined the pozzolanic properties and performance of CCA in sulfate environments as an SCM. Mixtures of concrete were tested for durability using the sulfate elongation test after adding CCA by weight at 5, 7.5, 10, 15, 20, 25, and 30%. In terms of structural integrity, the compressive strengths met or exceeded expectations. The CCA-supplemented concrete performed better in the sulfate elongation test when exposed to extreme conditions. Their conclusion was that CCA could be used as an additive to cement, which would make cement more sustainable by lowering its price and its impact on the environment.

In other tests, waste CCA was tested as a cement substitute by Suwanmaneechot et al. [15]. The effect of burning temperature on CCA's chemical composition, physical qualities, and engineering properties was examined. It was found that CCA calcined at 600°C for 4 h had a SiO_2 + Al_2O_3 + Fe_2O_3 content of 72%, making it ASTM C618 Class N calcined natural pozzolan. Amorphous silica increased with calcining temperature, according to X-ray diffraction images. As raw or processed CCA replacement increased, specimen water requirements, initial setting time, and final setting time increased. The cubes with 20% treated CCA had 103% 28-day compressive strength compared to reference samples. The researchers found that CCA treated at 600°C for 4 hours improved concrete splitting tensile and compressive strength somewhat more than untreated CCA. The literature reviews show mixed results when CCA is used as an admixture in concrete. Moreover, there is limited research on the impact of water pretreatment of corn cobs on the quality of CCA, as well

as the effect of CCA from pretreated corn cobs on the mechanical and durability properties of high-strength concrete. The objective of this research is to investigate the effect of presoaking corn cobs in water before calcination on the pozzolanicity of the CCA produced and the reduction of its potassium content. The effect of pre-shredding the corn cobs before soaking and the effect of periodic replacement of the soaking water is also investigated. The research also sets out to verify the optimal calcination temperature for the corn cobs.

2. Materials and Methods

2.1. Materials

The cement used in this study was Portland cement CEM I/42.5N, conforming to EN 197. The corn cobs were obtained from Eldoret in western Kenya. Crushed stone Coarse Aggregate (CA) with a maximum size of 12.5 mm obtained from a quarry in Nairobi was used. The Fine Aggregate (FA) was river sand from Machakos County in central Kenya. Sika Viscoflow 615-KE Superplasticizer (SP) supplied by Sika (K) Ltd. was used for workability enhancement. Tap water from the university mains was used throughout the experiments. Figure 3 shows the raw corn cobs.

2.2. Materials Preparation

2.2.1. Fine Aggregates

FA was washed with running water through sieve #200 to remove clay and dust particles, followed by oven drying at 105°C for 24 hours.

2.2.2. Coarse Aggregates

CA was washed to remove clay and dust particles and oven-dried for 24h at 105°C.

2.2.3. Corn Cobs

Part of the corn cobs was shredded into small pieces using a shredding machine in preparation for pretreatment with water. Figure 4 shows the shredded corn cobs and the shredding machine.

Four samples of corn cob were prepared and pretreated by soaking in water for 12 days, as shown in Table 2. Samples 1 and 2 consisted of unshredded corn cobs. In sample 1, the soaking water remained unchanged for the 12 days of soaking.

Fig. 3 Raw corn cobs

(a) Shredded corn cobs

(b) Shredding machine

Fig. 4 Shredding corn cobs

Table 2. Samples of corn cobs pretreated by soaking in water

Sample No.	Description	Pretreatment Details
1	Unshredded Corn Cobs	Soaked in tap water for 12 days. Water has not changed.
2	Unshredded Corn Cobs	Soaked in tap water for 12 days; water changed every 2 days.
3	Shredded Corn Cobs	Soaked in tap water for 12 days. Water has not changed.
4	Shreaded Corn Cobs	Soaked in tap water for 12 days; water changed every 2 days.

In sample 2, the soaking water was drained off and replaced with fresh water every 2 days. The process was repeated with shredded corn cobs, samples 3 and 4. During the soaking, white foam was observed in the soaking water, as shown in Figure 5(a). This was attributed to chemical reactions taking place in the water from the oxides leaching out of the corn cobs. On the other hand, before completion of the 12 days of pretreatment, upon breaking the unshredded corn cobs, traces of pink coloring were observed in the corn cobs, as shown in Figure 5(b). This was attributed to the presence of Gibberella ear rot caused by the fungus Gibberella zeae.

In order to verify the optimum burning temperature, untreated corn cobs were shredded and then burned at different temperatures for a predetermined period of time. The burning took place in a controlled-temperature furnace, and the burning temperature was varied from 350˚C to 700˚C in increments of 50˚C. At each burning temperature, the sample was kept for 3hr 45 min. The optimal burning temperature was used to burn the pretreated corn cobs. After 12 days of water soaking, the pretreated corn cobs were washed with tap water and then dried in the sun. The unshredded corn cobs were shredded before burning. All four pretreated corn cobs were burned in a controlled-temperature furnace at the predetermined optimal temperature with an exposure of 3 hr and 45 min.

(a) White foam in soaking water during pretreatment

(b) Traces of pink colour in corn cob

Fig. 5 Water pretreatment of corn cobs

(a) CCA before grinding

(b) CCA after grinding

Fig. 6 Corn Cob Ash (CCA) before and after grinding

(a) Controlled temperature furnace

(b) Sample holding pot

Fig. 7 Controlled temperature furnace

The ash was collected, cooled, and then crushed in a ball mill for 1 hr and 30 min to improve its fineness. The ashes were tested for chemical composition, and the sample with the best pozzolanic composition was adopted for use in further tests. Figure 6(a) and Figure 6(b) show the corn cob ash before and after grinding in a ball mill. Figure 7(a) and Figure 7(b) show the temperature-controlled furnace.

2.3. Materials Characterisation

2.3.1. Cement

The properties, including physical and chemical properties, were determined according to BS EN 197-1 (2011). In order to determine its mineral composition, X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) techniques were used for analysis. Furthermore, the samples underwent investigation using the Scanning Electron Microscope (SEM) to visually depict their structure, while Energy-Dispersive x-ray Spectroscopy (EDS) was used to identify the elements present.

2.3.2. Corn Cob Ash

XRD and XRF were used to determine the mineral composition. SEM and EDS were used to display its structure visually and to determine the elements that were present.

2.3.3. Fine Aggregates

FA was sieved through a sieve size of 4.75mm to remove any particles bigger than 4.75 mm. The FA was further run through a series of FA sieve sizes 150µm, 300µm, 600µm, 1.25mm, 2.36mm, and 4.75mm to determine the particle size distribution and the fineness modulus of the FA based on ASTM C136/C136M. Specific gravity and water absorption were determined based on ASTM C128/C128M.

2.3.4. Coarse Aggregates

The CA was sieved through sieve sizes 2.36mm, 5mm, 10mm, and 12.5mm to determine the particle size distribution based on ASTM C136/C136M. Specific gravity and water absorption were determined based on ASTM C128/C128M. Other tests carried out were the Aggregate Impact Value (AIV) and Aggregate Crushing Value (ACV). These tests were carried out on ASTM C535 and ASTM C131/C131M.

2.4. Concrete Mix Design and Concrete Production

The mixes with a water/binder ratio of 0.35 were designed according to the specifications outlined in ACI 211.4R-08. The cubes were designed for a 28-cube crushing strength of 60 MPa. A total of five concrete mixes were made. The control mix did not include any PCCA. The next four mixes had varying amounts of PCCA, namely 5%, 10%, 15%, and 20% of the weight of the cement. A rotating drum mixer was used to mix the concrete. Water was added to the mixer, followed by the cement and PCCA, and mixing was done to produce a uniform paste. Afterwards, the fine aggregate was added to the paste, and the mixing process was continued to create a uniform mortar. Ultimately, coarse particles were added to the mortar and mixed well to produce concrete with a uniform texture. Superplasticizer (SP) was consistently included in the mixture at each stage to provide workable consistency. The dosage of the superplasticizer was calibrated based on the quantity of PCCA to guarantee that the concrete retained its ideal workability.

2.5. Preparation and Curing of Test Samples

100 x 100 x 100 mm cubes and 100 mm diameter x 200 mm deep steel molds were used to cast concrete cubes for compression strength tests and for splitting tensile strength tests. Similarly, molds of 100 mm x 100 mm cross-section x 350 mm length were used to cast prisms for the flexural strength test. The molds were cleaned, and a thin layer of oil was applied on the inside to prevent concrete from sticking to the surface. Concrete was placed in the molds in two equal

layers, and compaction was done with a poker vibrator. The surface of the concrete was then leveled and smoothed with a steel trowel. The prepared sampled were covered with a moist cloth and left to stand overnight. The samples were then demolded and placed in a water tank to cure until the time of the test.

2.6. Tests on Fresh Concrete

2.6.1. Setting Time

Tests on setting time were carried out in accordance with BS 4554. The initial setting time was determined using a Vicat apparatus with a 1 mm^2 needle, and the final setting time was determined using a needle with an annular attachment.

2.6.2. Workability

Workability was determined by the slump test according to ASTM C143/C143M. This involved filling a metal cone of 100 mm upper diameter, 200 mm lower diameter, and a height of 300 mm with fresh concrete in three equal layers and compacting each layer with 25 tampings of a standard metal rod. The top of the concrete was then levelled and smoothed. The cone was gently lifted, and the slump of concrete against the cone was measured.

2.7. Tests on Hardened Concrete

2.7.1. Compressive Strength

Compression strength tests were carried out at 3, 7, 14, 28, 56, and 90 days. Tests were carried out according to BS EN 12390-03 using a 150 kN load capacity universal testing machine. Three samples were tested, and the average strength was calculated for each record.

2.7.2. Split Tensile Strength

Split-cylinder tensile tests were carried out according to ASTM C496/C496M-04 at 14, 28, and 90 days. Three specimens were tested, and the average strength was taken for each record.

2.7.3. Flexural Strength

Flexural strength tests were carried out at 14, 28, and 90 days according to ASTM C78 – 02. Three prisms were tested, and the average strength was taken for each record.

2.7.4. Water Absorption

Water absorption tests were carried out according to BS 1881-122 (2011) at 28 days. 100 mm diameter x 200 mm high cylinders were used for the test. Three cylinders were tested, and the average result was taken for each record.

2.7.5. Acid Attack Resistance Test

Acid resistance tests were carried out using 100 x 100 x 100 mm cubes. Tests were carried out according to ASTM C-267. The samples were cured in tap water for 90 days and then submerged in a 5% sulfuric acid solution for 90 days. They were then tested for compressive strength loss.

3. Results and Discussions

3.1. Determination of Optimal Burning Temperature

The results of the determination of the optimal burning temperature using untreated corn cobs are shown in Table 3. It was observed that as the burning temperature increased up to 650°C, SiO_2, Al_2O_3, Fe_2O_3, and CaO increased while K_2O, MgO, and P_2O_5 decreased.

There were only marginal changes in these chemical compositions beyond 650°C. Therefore, 650°C was adopted as the optimal burning temperature and was used in further CCA production. This research was not able to explain the chemical changes that took place, and further research on the same is recommended.

3.2. Effect of Water Pretreatment

Table 4 shows the chemical composition of CCA from corn cobs soaked in water for 12 days without changing the soaking water. S1 refers to unshredded corn cobs, while S3 refers to shredded corn cobs. On the other hand, Table 5 shows the chemical composition of CCA from unshredded corn cobs, S2 soaked in water for 12 days with soaking water replaced every 2 days. Similarly, Table 6 shows similar results for shredded corn cobs S4. A number of observations were made from the results:

- Shredding corn cobs before soaking in water improved the pozzolanicity of CCA. This is observed in Table 4 between samples S1 and S3 and in Tables 5 and 6 between samples S2 and S4.

Table 3. Results of the burning temperatures

Chemical Composition	350°C	400°C	450°C	500°C	550°C	600°C	650°C	700°C
SiO_2	10	10.7	12.4	14	15.1	18.3	20.2	20
Al_2O_3	1	1.5	1.7	1.9	1.9	2.7	3.1	2.9
Fe_2O_3	2.3	2.5	2.7	2.8	2.9	3.12	3.7	3.5
CaO	4.2	4.4	5	7	6.9	8	10	11
K_2O	57.5	57	56	52.5	52	47.2	45.4	45.3
MgO	10	10.1	9	9.5	9	10.2	8.4	8.2
P_2O_5	14.9	13.7	13.1	12.2	12.1	10.4	9.1	9

- Changing the soaking water increased the amount of SiO_2, Al_2O_3, and Fe_2O_3 in CCA and decreased the amounts of K_2O, MgO, and P_2O_5. Changing the soaking water reduced the concentration of the leached chemicals in the soaking water, thereby allowing more to leach out of the corn cobs with ease.
- The best results were observed in CCA obtained from sample S4 consisting of corn cobs that were shredded before soaking. Shredding corn cobs allowed leaching to take place more efficiently with the increased surface area.
- In Table 6, it is observed that changes in the chemical composition of CCA took place up to 10 days, with marginal change beyond 10 days.

When K_2O in corn cobs is exposed to water, it reacts violently to produce potassium hydroxide, KOH. On the other hand, P_2O_5 reacts with water to produce phosphoric acid, H_3PO_4. The H_3PO_4 reacts with KOH to produce K_3PO_4, a water-soluble salt. Similarly, MgO reacts with water to produce Mg $(OH)_2$. Thus, all three oxides can be removed from corn cobs by soaking them in water.

3.3. Physical and Chemical Properties

3.3.1. Physical Properties

Fine Aggregates

FA was graded according to ASTM C136/136M. It was observed that the curve of percentage passing was within the upper and lower limits, as presented in Figure 8. Thus, the results satisfied the requirements of the standard. The physical properties are shown in Table 7. The fineness modulus of FA was determined as 2.7.

Table 4. Chemical composition of CCA from corn cobs sample 1 (unshredded) and 3 (shredded), soaked in water for 12 days without changing the water, then burned at 650°C

Chemical Composition	S1	S3
SiO_2	40.5	48
Al_2O_3	4.2	4.7
Fe_2O_3	2.32	3.5
CaO	12.9	12.8
K_2O	19	16
MgO	12.7	10.5
P_2O_5	7.4	4.2

Table 5. Chemical composition of CCA from corn cobs sample 2 (S2), which was unshredded and soaked in water for 12 days with water replacement every 2 days, then burned at 650°C

Chemical Composition	Period of Water Replacement (days)					
	2	4	6	8	10	12
SiO_2	20.9	27.3	35.4	42	52.5	54
Al_2O_3	3.2	3.4	3.6	4	5.5	6.2
Fe_2O_3	3.7	3.9	3.9	4.2	5	5.5
CaO	10.2	10.7	10.4	10.5	9.5	9
K_2O	45	40.1	33.2	29	20.2	19.2
MgO	8.3	7.5	6.5	6.1	4.7	4.3
P_2O_5	8.6	7	6.9	4.1	2.5	1.7

Table 6. Chemical composition of CCA from corn cobs sample 4 (S4), shredded and soaked in water for 12 days with water replacement every 2 days, then burned at 650°C

Chemical Composition	Period of Water Replacement (Days)					
	2	4	6	8	10	12
SiO_2	28.1	34.3	40	51	58	58
Al_2O_3	3.3	3.4	3.9	5.2	6.7	6.7
Fe_2O_3	3.9	4.1	4.3	4.9	5.7	5.8
CaO	10.5	10.1	10.9	10.8	11.2	11.2
K_2O	39.1	34.1	27.9	19.5	12.5	12.4
MgO	7.9	7.2	6.7	5.4	4.2	4.3
P_2O_5	7.1	6.7	6.2	3.1	1.6	1.5

Table 7. Physical properties of FA

Tests	FA
Specific Gravity	2.62
Water Absorption (%)	2.4
Moisture Content (%)	1.3
Fineness Modulus	2.7
Bulk Density (kg/m3)	1649
Voids (%)	27

Coarse Aggregates

CA were graded according to ASTM C136/C136M. It was observed that the curve of percentage passing was within the upper and lower limits, as presented in Figure 9. Thus, the results satisfied the requirements of the standard. The physical properties are shown in Table 8.

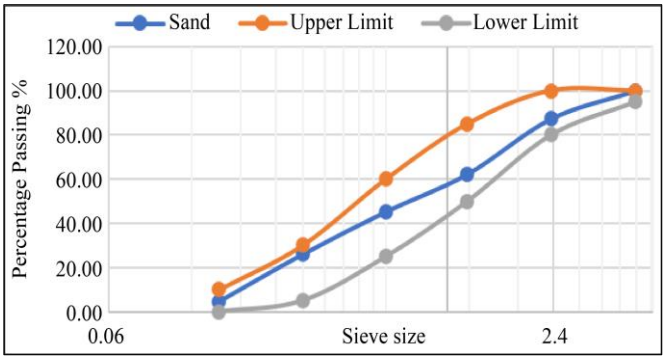


Fig. 8 Sieve analysis of fine aggregates

Table 8. Physical properties of coarse aggregates

Tests	CA
Specific Gravity	2.67
Water Absorption (%)	3.4
Aggregate Impact Value	6.1
Aggregate Crushing Value	16.74
Bulk Density (kg/m^3)	1478
Voids%	40

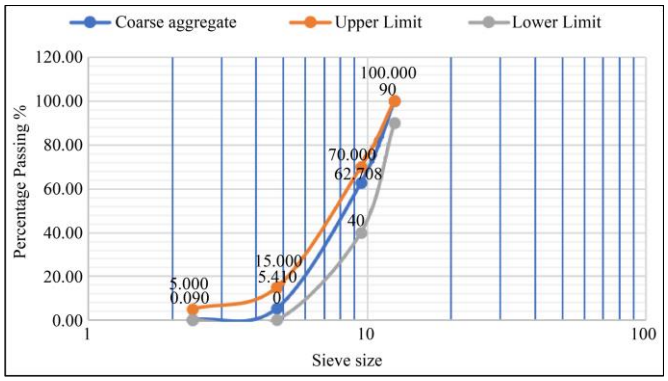


Fig. 9 Sieve analysis of coarse aggregates

Corn Cob Ash

Table 9 gives the physical properties of corn cob ash, and Figure 10 shows SEM images of the same. It was observed that pretreating and grinding CCA improved its densification. In Figure, the SEM images show close similarity in the morphology of unground and ground CCA with spherical shapes with holes.

Table 9. Physical properties of corn cob ash

Tests	Untreated and Unground CCA	Treated and Ground CCA
Specific Gravity	**2.07**	**2.28**

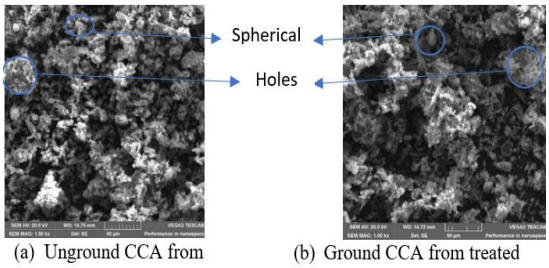


Fig. 10 SEM images of unground CCA from untreated corn cobs and ground CCA from pretreated corn cobs

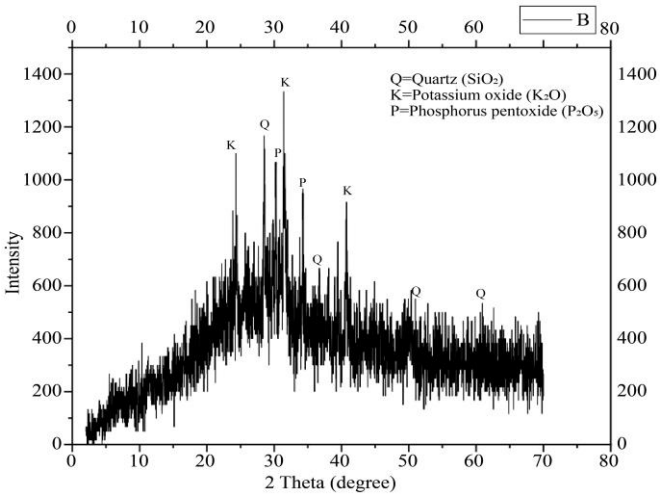
3.3.2. Chemical Properties of Corn Cob Ash and Cement

Table 10 shows the chemical composition of cement and CCA from untreated and pretreated corn cobs determined by the X-Ray Fluorescence (XRF) method. On the other hand, Figure 11 shows x-ray diffraction images of the same. In addition, Figure 12 shows SEM/EDS images. From Table 10, it is observed that pretreating corn cobs increased the total SiO_2+ Al_2O_3 + Fe_2O_3 content of CCA, while the total amount of K_2O + P_2O_5 was drastically reduced.

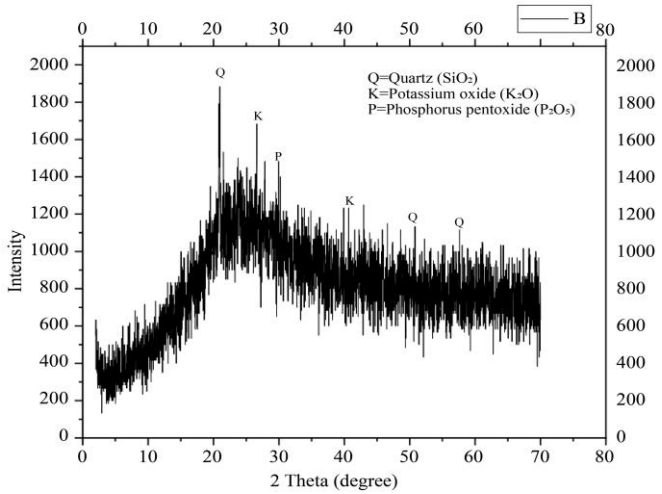
This observation was supported by XRD images in Figure 11, which show the predominant chemical in CCA from untreated corn cobs to be K_2O, while in CCA from pretreated corn cobs, the predominant chemical is SiO_2. This observation was also supported by EDS images in Figure 12. The increase in total SiO_2+ Al_2O_3 + Fe_2O_3 and the decrease in total K_2O + P_2O_5 was due to the leaching out of soluble potassium and phosphorous compounds, leaving a concentration of less leachable silicon, aluminum, and iron compounds.

Table 10. Chemical composition of untreated and treated corn cob ash

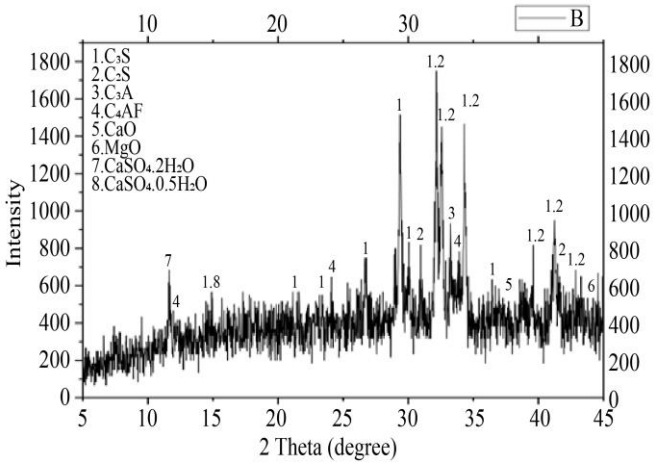
Chemical Composition	OPC	Untreated CCA	Treated CCA (S4)
SiO_2	24.619	20.2	58.1
Al_2O_3	5.454	3.1	6.7
Fe_2O_3	2.741	3.7	5.85
CaO	62.741	10	10.2
K_2O	0.607	45.4	12.4
MgO	0.000	8.4	4.3
P2O5	0.439	9.1	1.5
SiO_2+Al_2O_3+ Fe_2O_3		27	70.65
K_2O + MgO + P_2O_5		62.9	18.2



(a) XRD images of CCA from untreated corn cobs

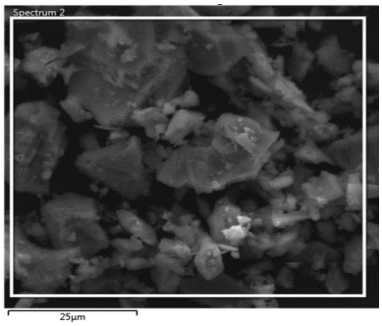


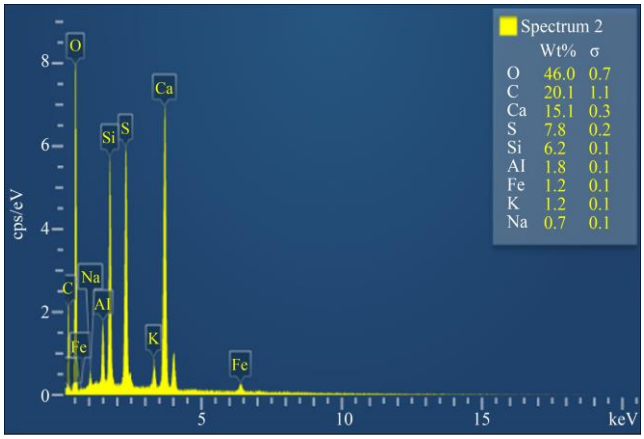
(b) XRD image of CCA from treated corn cobs



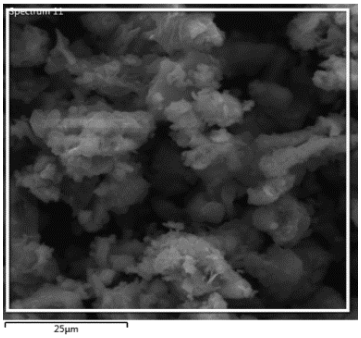
(c) XRD image of cement

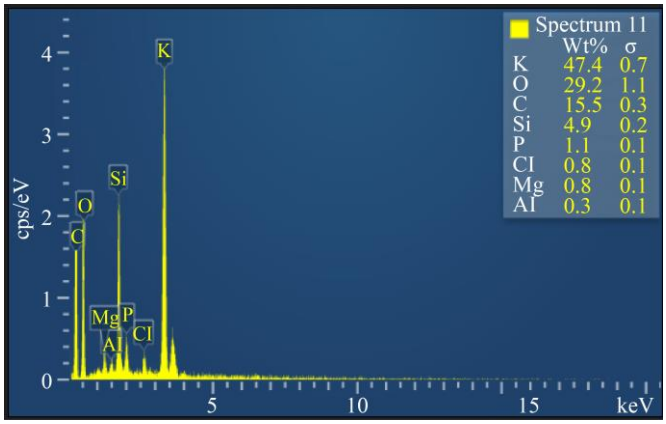
Fig. 11 XRD images of CCA and cement



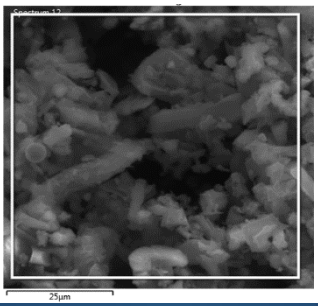


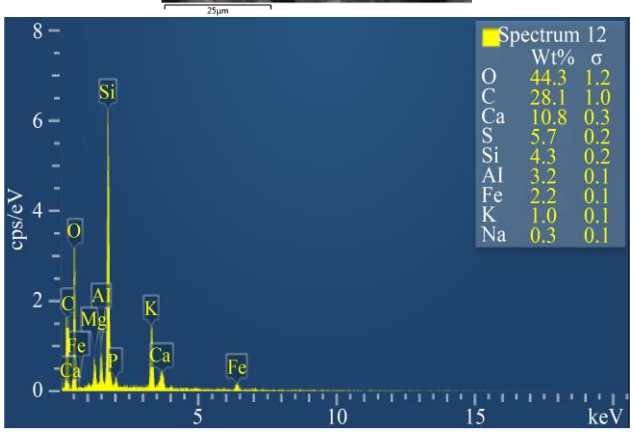
(a) SEM/EDS images of cement





(b) SEM/EDS images of CCA from untreated corn cobs





(c) SEM/EDS images of CCA from pretreated corn cobs

Fig. 12 SEM/EDS images of cement and CCA from untreated and treated corn cobs

3.4. Concrete Mix design

The results of the mix design to ACI 211-4R are shown in Table 11.

Table 11. Concrete mix proportions (kg/m^3)

Mix	Cement	PCCA%	Water	SP	FA	CA	W/C Ratio
Mix1	500	0	174	3	725	1020	0.35
Mix2	495	5	174	4.5	725	1020	0.35
Mix3	490	10	174	6	725	1020	0.35
Mix4	485	15	174	7.5	725	1020	0.35
Mix5	480	20	174	9	725	1020	0.35

Legend: PCCA=Pretreated Corn Cob Ash, SP=Superplasticizer, FA=Fine Aggregates, CA=Coarse Aggregates

3.5. Tests on Fresh Concrete

3.5.1. Setting Time

Setting time refers to how long it takes for cement paste to dry to a certain consistency. Figure 13 shows the results of the concrete setting time with different amounts of PCCA. This difference was caused by the inactivity of PCCA, which reacts only after free $Ca(OH)_2$ is produced by cement hydration. Thus, at early ages, PCCA is a dilutant to cement. The time needed for solidification was lengthened due to the reduction of reactive cement and the interference with its access to moisture.

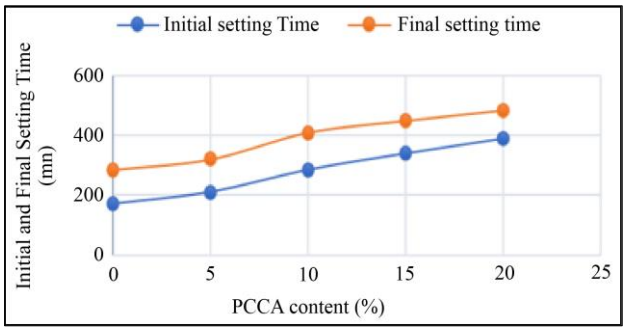


Fig. 13 Effect of PCCA on the concrete setting time

3.5.2. Workability

Figure 14 shows the effect of PCCA on the workability of fresh concrete. It was observed that the workability, as measured by the slump test, decreased with increasing amounts of PCCA. Prior research by Adesanya & Raheem [25], Mujedu et al. [26] and Suwanmaneechot et al. [15] have also shown that the water requirement in concrete rises proportionally with the increase in CCA replacement ratio, resulting in a deterioration in workability. The reduction in workability is ascribed to the presence of spherical capillary voids on the surface of PCCA, as seen by SEM pictures, which lead to water absorption by PCCA grains, leaving less water to lubricate the fresh concrete.

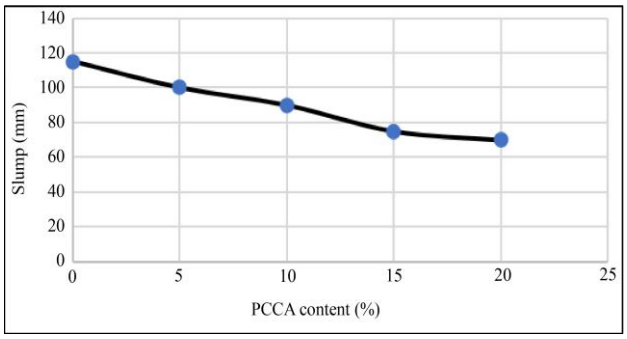


Fig. 14 Effect of PCCA on concrete workability

3.6. Tests on Hardened Concrete

3.6.1. Compressive Strength

Figure 15 shows the effect of PCCA on the compressive strength of concrete with increasing age up to 90 days. The strength of the control concrete without PCCA was higher than that of the concrete with PCCA but leveled off after 28 days, indicating near complete hydration of the cement. On the other hand, concrete mixes with PCCA showed a rising trajectory with increasing age of concrete, and at 90 days, the mix with 15% PCCA surpassed that of the control concrete. The continuous rise in the strength of PCCA concrete is attributed to a slow but steady pozzolanic reactions of PCCA with free lime in the concrete released by the hydration of Portland cement. At early ages, PCCA results in the dilution of Portland cement, leading to reduced strength.

On the other hand, at later ages, the additional cementitious products from pozzolanic reactions lead to increased strength. However, when the amount of PCCA is too high, part of the PCCA does not have free lime to react with, leading to an overall reduction in strength compared to the control concrete. Similar results were obtained by Olafusi & Olutoge [28], price et al. [29], and Adesanya [24].

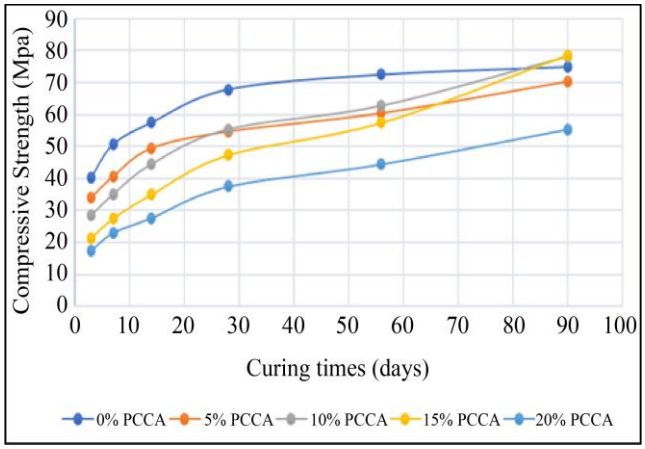


Fig. 15 Effect of PCCA on concrete compressive strength

3.6.2. Splitting Tensile Strength

Figure 16 shows the effect of PCCA on the splitting tensile strength of concrete at the early ages of 14 and 28 days and 90 days of curing. It was observed that at the early ages, the splitting tensile strength decreased steadily with increasing amounts of PCCA, as was also observed for compressive strength, which was attributed to low pozzolanic activity and the dilution effect of PCCA. However, at 90 days, there was a dramatic increase in strength for PCCA concrete with 10 and 15% PCCA, which was attributed to increased pozzolanic reactions. With a PCCA content of 20%, there was a loss of strength attributed to unreacted PCCA due to oversupply, leading to a dilution effect.

3.6.3. Flexural Strength

The test results for Flexural Strength (FS) are shown in Figure 17. Similar results are observed with splitting tensile strength, with the highest 90-day strength being obtained with a PCCA dosage of 15%.

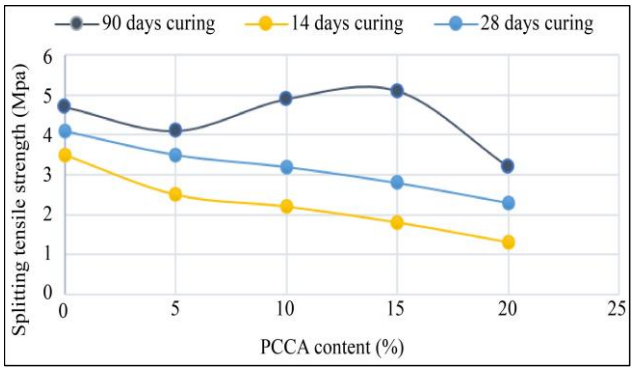


Fig. 16 Effect of PCCA on the concrete splitting tensile strength

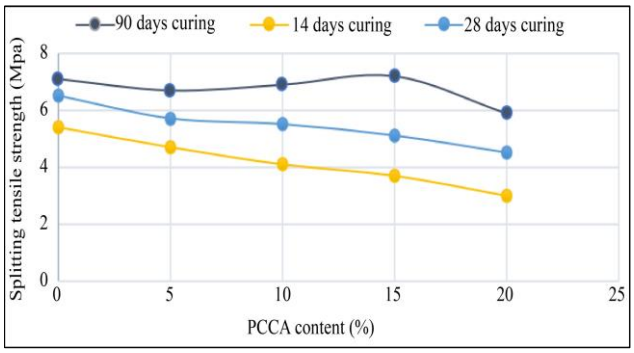


Fig. 17 Effect of PCCA on concrete flexural strength

3.6.4. Water Absorption

The results of the water absorption test carried out after 28 days of water curing are given in Figure 18. As the amount of PCCA in concrete increased, the water absorption decreased. The formation from the compounds of the pozzolanic reaction of PCCA with free lime in concrete led to increased pore densification and reduced water absorption. In addition, even unreacted PCCA filled the pores of concrete and prevented moisture ingress. Similar observations were made by Dineshkumar and Balamurugan [30] as well as by Amin et al. [31].

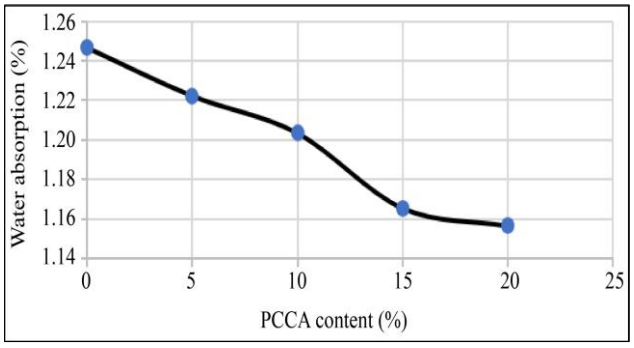


Fig. 18 Water absorption

3.6.5. Acid Attack Resistance Test

Figure 19 shows the physical appearance of concrete samples immersed in sulfuric acid for 90 days. Similarly, Figure 20 shows the effect of the acid treatment on the cube-crushing strength of the concrete. It was observed that concrete with PCCA had less surface erosion than the control concrete. Similarly, concrete with 5 to 15% PCCA had higher residual strength than the control, with the concrete with 15% PCCA showing the best results with the highest residual strength and the least loss of strength.

Concrete with 20% PCCA had the least residual strength. The compressive strength of mixes containing 0%, 5%, 10%, 15%, and 20% of PCCA exhibited a reduction in strength of 38.8%, 32.7%, 27.2%, 21.4%, and 46.4%.

Sulfuric acid reacts with $Ca(OH)_2$ in cement paste to form $CaSO_4.2H_2O$, as shown in Equation 4. The latter is moderately soluble in water and can be leached out of the cement paste. On the other hand, $CaSO_4.2H_2O$ can react with hydrated C_3A in the cement paste to form ettringite, which is a large compound that exerts expansive pressure, leading to the microcracking of concrete. The reaction is shown in equation 5. The combined effect of leaching out of $CaSO_4.2H_2O$ and the disruptive effect of ettringite leads to the loss of strength in concrete.

$$H_2SO_4 + Ca(OH)_2 = CaSO_4.2H_2O \quad (4)$$

$$CaSO_4.2H_2O + 3CaO{\bullet}Al_2O_3 + 30H_2O = 3CaO{\bullet}Al_2O_3{\bullet}3CaSO_4{\bullet}32H_2O \text{ (ettringite)} \quad (5)$$

There is still a lot of unreacted $Ca(OH)_2$ due to the slow rate of pozzolanic reactions. There is more unreacted $Ca(OH)_2$ in the control concrete and a decreasing amount in concrete with increasing amounts of PCCA. However, in PCCA concrete, the negative effect of acid takes place amid pozzolanic reactions, which add to the strength.

This increases residual strength over the control. In PCCA with 20% PCCA, the dilution of the Portland cement is very high, leading to a reduced amount of $Ca(OH)_2$, which can generate pozzolanic strength. There is thus less pozzolanic reaction, which can counter the destructive effect of the acid effectively. This explains the high loss of strength.

(a) Plain concrete after immersion in sulfuric acid for 90 days

(b) Concrete mixed with PCCA after immersion in sulfuric acid for 90 days

Fig. 19 Physical images of plain concrete and concrete mixed with CCA immersed in sulfuric acid for 90 days

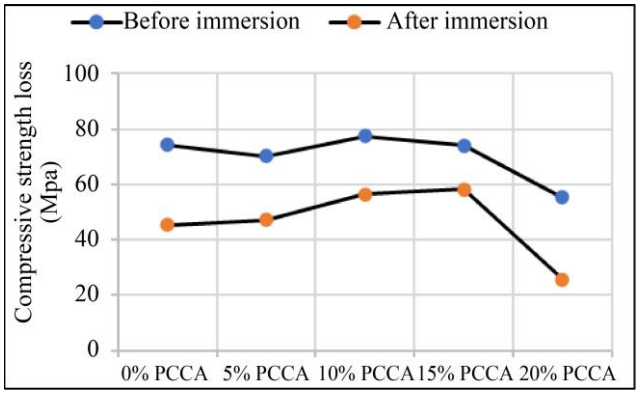


Fig. 20 Acid attack resistance test results

4. Conclusion and Recommendations

4.1. Conclusion

From the findings of this research, the following conclusions are drawn:

- Soaking corn cobs in water for at least 10 days leaches out potassium and phosphorous oxides and therefore concentrates the silicon, aluminum, and iron oxides in the corn cobs.
- Shredding the corn cobs before soaking in water increases the surface area and increases the ease with which leaching takes place.
- Changing the soaking water periodically reduces the concentration of leachate in the soaking water and increases the removal of leachable oxides.
- The ideal burning temperature for corn cobs is 650°C.
- Shredding corn cobs and soaking them in water for at least 10 days with periodic replacement of the soaking water, and then burning the corn cobs at 650°C leads to the production of Class N calcined natural pozzolana that satisfies ASTM C618.
- SEM images show that ground UCCA and PCCA consist of spherical shapes with holes.
- The best strength was obtained with 15% PCCA.
- In addition, the results demonstrate that structural-grade concrete can be made by substituting up to 20% of the cement by weight with PCCA. This option has many benefits, such as preserving raw materials, reducing pollution from CO_2 emissions, decreasing energy consumption during cement production, and adding value to PCCA, which currently has few other uses.

4.2. Recommendations

This research was not able to explain the reduction of K_2O, MgO, and P_2O_5 when subjected to heat up to 700°C since all these oxides vaporise at higher temperatures. The mechanism by which they are reduced with increasing burning temperatures requires further investigation.

Credit Authorship Contribution Statement

Abdoul Karim Ameyric Habib Ouedraogo: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – Review and Editing, Visualization. David Otieno Koteng: Conceptualization, Methodology, Writing – original draft, Writing – Review and Editing, Supervision. Nathaniel Ambassah: Conceptualization, Methodology, Writing – original draft, Writing – Review and Editing, Supervision.

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