

Cassava Peel Ash as a Supplementary Cementitious Material: A Review of Physicochemical Characterization and Pozzolanic Activity

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ABSTRACT : The high global demand and a significant carbon footprint of around 8% of anthropogenic CO₂ emissions from the production of Portland cement, intensive research has been conducted on the use of supplementary cementitious materials (SCMs) from agricultural waste has been conducted. Cassava (*Manihot esculenta* Crantz) is a widely farmed staple food in the tropics, with an estimated amount of 20–35% of cassava tubers wasted as peel. In this review, the cassava peel ash (CPA) as a new Supplementary Cementitious Material (SCM) is critically discussed mainly regarding its physicochemical characterization, pozzolanic properties, and performance in cementitious systems. Analysis of available literature shows that the typical CPA would contain 55.93% SiO₂, 19.88% Al₂O₃, and 6.02% Fe₂O₃ which equals a total content of pozzolanic oxides of 81.83%, which is much higher than the minimum of 70% prescribed in ASTM C618. According to the pozzolanic activity index (PAI) of CPA 75.8% is satisfactory pozzolanic reactivity. The optimum calcination temperature is 600–700°C which yields ash with a high amorphous silica content for pozzolanic reactions. Concrete with 5–15% CPA replacement has compressive strengths similar to those in control concrete at 28 days, and additional strength gain is promoted by the creation of secondary calcium-silicate-hydrate (C-S-H) formation in the concrete. This review summarizes the current state of the art for CPA production methodologies, characterization techniques (XRF, XRD, SEM-EDS, FTIR), and how replacement levels affect the properties of fresh and hardened concrete. Moreover, it discusses standardization issues, environmental sustainability consequences and points out key research gaps preventing the commercialization of CPA for construction. The results justify the cassava peel waste valorisation as a realistic and eco-efficient SCM, especially on the African continent where the construction industry is highly developed and there is a wide range of cassava production areas.

Keywords: Cassava peel ash; Supplementary cementitious material; Pozzolanic activity; Physicochemical characterization; XRD; SEM; Concrete.

1. INTRODUCTION

1.1 Background and Context

The construction sector is one of the biggest consumers of natural resources and energy, accounting for around 8% of global anthropogenic CO₂ emissions, in the production of Portland cement alone [1]. About 0.87 tonnes CO₂ are emitted in the production of one tonne of Portland cement, which is mainly due to the calcination of limestone (CaCO₃ → CaO + CO₂) and the combustion of fossil fuels in the rotary kilns at temperatures higher than 1450°C [2]. The push to decarbonize the cement industry is greater now than ever as nations work towards achieving their CO₂ reduction targets in the Paris Agreement and Sustainable Development Goals (SDGs). The use of supplementary cementitious materials (SCMs) is one of the key measures to minimize the clinker factor in cement and concrete. SCMs can partially substitute for Portland cement, which helps to reduce the environmental impacts of the cement, while also providing both durability

and long-term strength characteristics, and reducing concrete permeability. SCMs such as fly ash, ground granulated blast-furnace slag (GGBFS) and silica fume have been widely used in developed areas. However, availability in developing countries, especially sub-Saharan Africa, is limited due to the lack of industrial infrastructure and high import expenses [4]. The agricultural waste ash is also emerged as a potential alternative SCM because of the large amount of biomass residues produced throughout the tropical and subtropical regions. All types of rice husk ashes, sugarcane bagasse ash, corn cob ash and wood waste ash have been found to react in varying degrees as pozzolanic materials and have been applied to concrete systems successfully [5]. Of these, the cassava peel ash (CPA) has been a subject of increasing research interest because of the huge production volume of cassava in Africa and the high amount of waste produced during the processing of cassava.

1.2 The African Cassava Production Landscape.

Cassava, *Mannihot esculenta* Crantz, is the third largest source of carbohydrates in the tropics, after maize and rice and a dietary staple for more than 800 million people worldwide [6]. In 2021, about 204 million tonnes of cassava was produced in Africa, which is the biggest producer of cassava, increasing from 177 million tonnes in 2017 [7]. Nigeria is the largest producer with 63 million tonnes production (20% of global production) followed by the Democratic Republic of Congo (41 million tonnes), Ghana (22 million tonnes), and Tanzania (8.5 million tonnes) [7]. Significant amount of waste is produced when cassava roots are processed, such as peels which make up 20-35% of the total mass of the root [8]. Nigeria, in particular, produces >60 million tonnes of cassava annually, with some 15–20 million tonnes of peel waste produced annually. Historically these peels have been disposed of in open dumps, landfills, or waterways, where they decompose, giving off methane, a powerful greenhouse gas, and polluting surface and groundwater with cyanogenic compounds [10]. This is especially problematic in highly populated cassava processing centres across West Africa where the disposal of cassava waste has an environmental and public health impact. This double benefit approach of mitigating environmental pollution by harnessing the valorization of cassava peel waste in controlled thermal manner to generate value added construction material is considered to be worth considering. In this review, the scientific evidence related to the use of CPA as a supplementary cementitious material is discussed with a particular focus on the physicochemical properties that determine its pozzolanic properties.

1.3 The objectives of the Review

The overall aim of this review is to achieve five main objectives:

1. Synthesize and critically discuss the existing literature regarding physicochemical properties of cassava peel ash such as chemical composition, mineralogical composition, morphology and thermal properties.
2. To analyze the pozzolanic properties of CPA compared to known SCMs and other agricultural wastes ashes based on the standard index and test method.
3. To evaluate the performance of CPA blended cement and concrete in both fresh and hardened state, in order to determine the optimum level of replacement and hydration mechanisms.
- To assess the environmental sustainability aspects of the use of CPA, such as reduction of carbon footprint, waste management and life cycle aspects.
5. To recognise the gaps in research, the challenges of standardisation and future research directions in the commercialisation of CPA in building, specifically in Africa.

2. RELATED WORKS AND LITERATURE REVIEW

2.1 Agricultural Waste Ashes as Supplementary Cementitious Materials

In the last 30 years, the use of agricultural waste ashes as supplementary cementitious material has grown from an exploratory research to practical use. Silica, Alumina and Iron Oxide (Fe_2O_3) content, amorphous (non-crystalline) structure and particle size distribution are basic compositions of biomass ashes, which greatly influence the pozzolanic potential of biomass ashes [11]. ASTM C618 defines a natural pozzolan (Class N) as material in which the total amount of SiO_2 and Al_2O_3 and Fe_2O_3 is equal to or greater than 70%, the sulfur trioxide (SO_3) content is less than 4%, and the moisture content is less than 3% [12].

Rice husk ash (RHA) is the most studied agricultural waste ash, and up to 90% silica has been found when RHA is produced in a controlled combustion condition (500–700°C) [13]. Sugarcane bagasse ash (SCBA) has also shown a good pozzolanic activity especially when obtained from plants that have a controlled burning program [14]. Corn cob ash, wood waste ash and millet husk ash have demonstrated inconsistent performance, depending on conditions of combustion, such as the combustion temperature and combustion time, and the characteristics of the biomass source [15]. These agro-ashes were comprehensively reviewed by [16] to systematically summarize the physical and chemical characteristics, cement replacement ratios, and performance effects on concrete.

Table 1. Chemical Composition of Selected Agricultural Waste Ashes Compared with ASTM C618 Requirements

Material	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	Σ(S+A+F) (%)	PAI (%)
Cassava Peel Ash (CPA)	55.93	19.88	6.02	81.83	75.8
Rice Husk Ash (RHA)	91.20	0.45	0.35	92.00	85.0
Sugarcane Bagasse Ash	62.50	8.20	5.80	76.50	78.5
Corn Cob Ash	58.00	12.50	3.50	74.00	72.0
Wood Waste Ash	52.00	10.00	8.50	70.50	70.5
Millet Husk Ash	48.00	15.00	5.00	68.00	68.0
ASTM C618 (Class N) Min.	—	—	—	70.00	75.0

It is found that the data in Table 1 show that the cassava peel ash has a favorable position among the agricultural waste ashes as it has a content of pozzolanic oxide that is quite high, which is 81.83% compared to the minimum content of pozzolanic oxide required by ASTM C618 is 70% [17]. RHA has a higher silica purity, whereas CPA has a balanced alumina content (19.88%) which could offer benefits in terms of early strength development and setting time control. The results of the pozzolanic activity index of CPA (75.8%) are close to the ASTM C618 requirement (75%), and it is a good pozzolan but not a great one [18].

2.2 A chronological overview of Cassava Peel Ash research is presented below.

Since 2015, the research on cassava peel ash (CPA) as a cementitious material has gained momentum with most of the studies done in the Nigerian institutions, which are the major cassava producers in Africa. The chemical composition analysis and strength activity index testing conducted by early investigations by [19] and [20] confirmed the basic pozzolanic potential of CPA. These basic studies showed that the compressive strength of the resulting mortars would only be slightly reduced when CPA was used in place of Portland cement up to 10%.

Further work involved the durability properties, microstructural characterization, and optimization of production parameters. Central composite design (CCD) methodology was used in [21] to optimize the CPA-concrete

mixture and to obtain maximum compressive strength of 29.83 MPa and flexural strength of 10.95 MPa were obtained at optimal ratio. Sulfate resistance of fiber-reinforced mortar containing CPA was studied by [22] and it was concluded that the 10% CPA replacement rate increased the resistance to magnesium sulfate attack of fiber-reinforced mortar in comparison to the control specimens.

Research in the field of advanced applications has been carried out recently, such as the development of alkali-activated CPA-based geopolymers [23], CPA-stabilized marine clay soils [24] and the use of CPA in combination with other SCMs, e.g., metakaolin [25]. The versatility of the applications extends beyond concrete, as CPA can be used in soil stabilization, pavement construction and sustainable building materials.

2.3 The performance of pozzolanic materials under different conditions.

A comparative analysis of the pozzolanic activity indices for the main agricultural wastes ashes is shown (fig. 3). The CPA is competitively positioned within agro-ash spectrum with PAI of 75.8% when compared to RHA (85%) and sugarcane bagasse ash (78.5%). The difference in PAI values is due to the difference in silica content, amorphous phase proportion and fineness of particles. Interestingly, CPA's PAI only meets the ASTM C618 specification of 75%, while corn cob ash (72%) and millet husk ash (68%) do not meet this requirement [18].

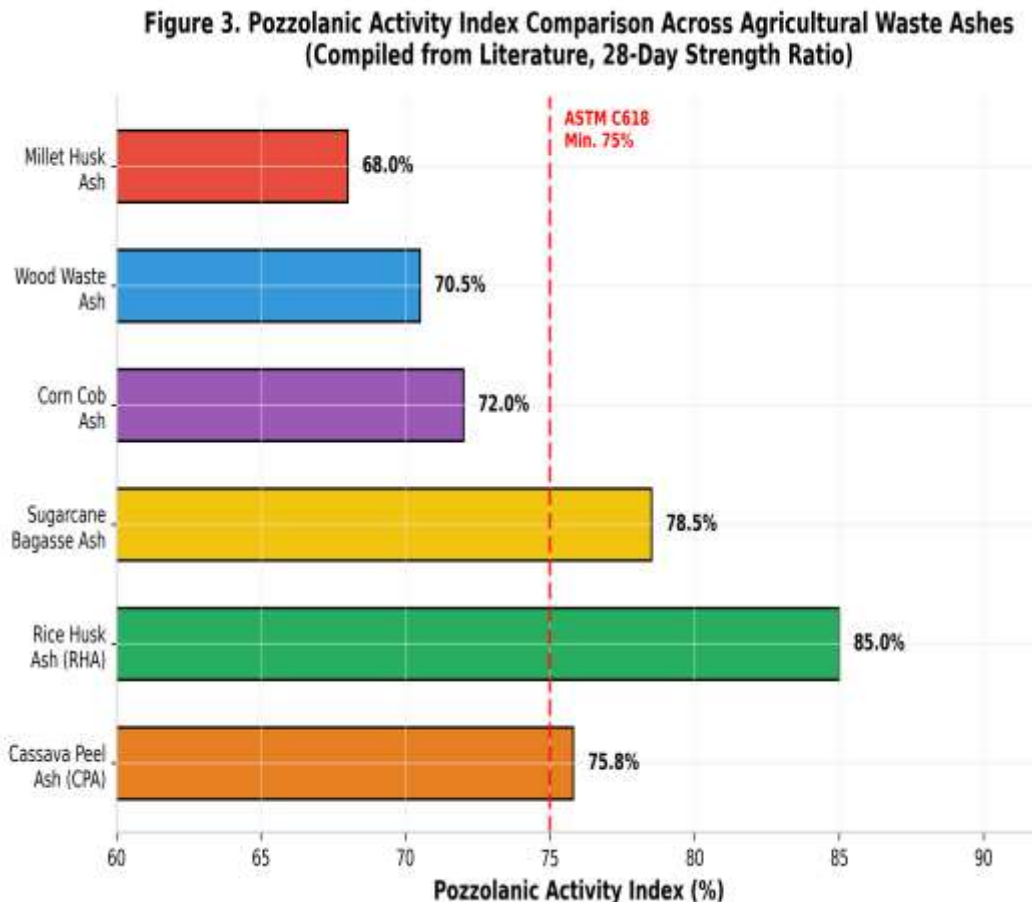


Figure 3. Pozzolanic Activity Index comparison across agricultural waste ashes (compiled from literature, 28-day strength ratio). The red dashed line indicates the ASTM C618 minimum requirement of 75%.

3. PRODUCTION AND PREPARATION OF CASSAVA PEEL ASH

3.1 Raw Material Sourcing and Pre-treatment

The Cassava peels are produced during the processing of cassava root to produce food (garri, fufu, starch, flour) and for industrial use (bio-ethanol and adhesives). The peels account for 20–35% of the tuber weight, and tend to be thicker in the industrial mechanical peeling process and thinner in the manual peeling process [8]. Fresh cassava peels have high moisture content (60-75%), organic matter and cyanogenic glucosides (linamarin and lotaustralin) that need to be tackled before undergoing thermal processing.

The pre-treatment protocols used in different studies also differ but generally consist of the following steps: (1) soil and debris are removed from the plants; (2) sun drying or oven drying at 105°C to reduce moisture content to below 10%; (3) size reduction as a result of grinding or shredding operations; and (4) sieving for uniform particle size (e.g. 75 µm or 150 µm) [26]. The removal of cyanide is recommended by some researchers to be washed in distilled water before peels [27]

but the high temperature that is required in the calcination (>500°C) is enough to decompose cyanogenic compounds.

3.2 Calcination parameters and their effects.

Cassava peels are burned in a controlled manner (calcined) and the most critical process in the production of CPA determines the quality of ash, amorphous silica content and pozzolanic reactivity is the temperature and duration of the burning. As shown in Figure 5, the correspondence between the temperature of the calcination and the amorphous silica content and the pozzolanic activity index is drawn.

An optimum calcination temperature range has been found to be 600-700 °C and a holding time of 90 minutes to 3 hours [28, 29]. If the temperature is below 500°C, the organic matter is not fully burned and the loss on ignition (LOI) is high and the pozzolanic activity is less. XRD analysis of the CPA calcined at 450°C showed the presence of high peaks of quartz (crystalline silica) and small peaks of amorphous silica, which resulted in the lower values of PAI [30].

Decomposition of cellulose and lignin is complete at 600–700°C and at this stage, the silica will be converted from the crystalline to amorphous form, which is essential for pozzolanic reactivity [28]. The XRD pattern of CPA

calcinated at 600°C shows the presence of both crystalline peaks (quartz and sodalite) and a broad amorphous hump peaking at 20-30° 2θ, which is indicative of the presence of reactive silica [29]. SEM image shows that the particles have irregular shape with deep crevices and microporosity which produces a large surface area available for pozzolanic reactions [29].

Sintering and recrystallization of silica will begin at temperatures above 800°C, which will decrease the

amorphous content and therefore the pozzolanic activity [28]. This thermal degradation phenomenon is common for all the agricultural waste ashes and further demonstrates the need to precisely control the temperature during the CPA production.

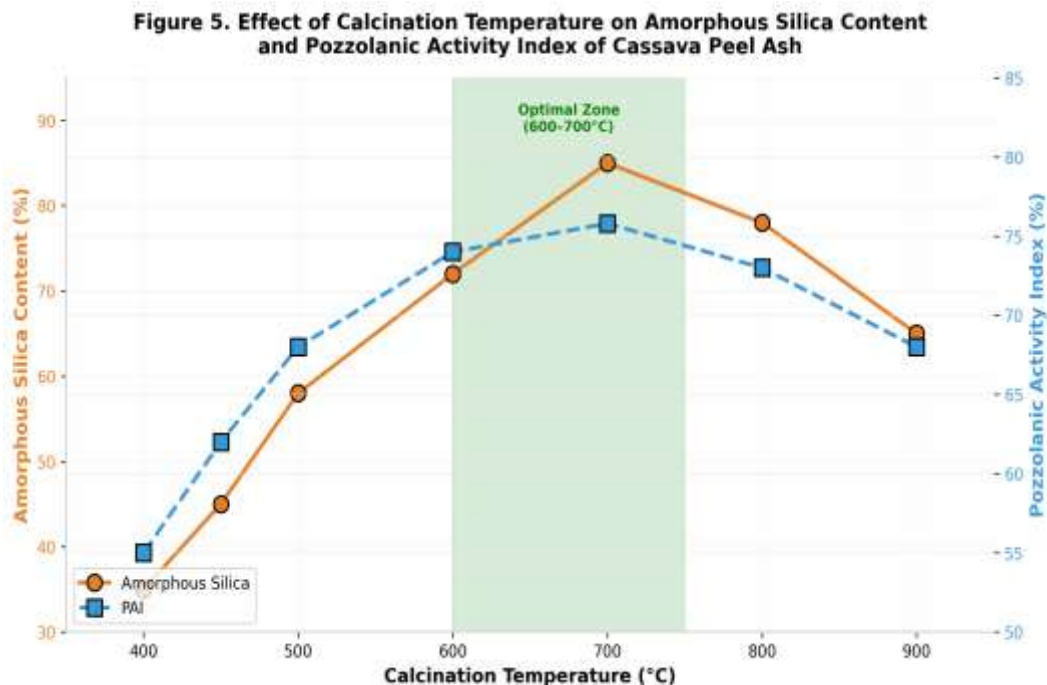


Figure 5. Effect of calcination temperature on amorphous silica content and pozzolanic activity index of cassava peel ash. The green shaded region indicates the optimal calcination zone (600–700°C).

3.3 Grinding and Particle Size Optimization

CPA's reactivity and performance in the cementitious systems are considerably affected by the fineness of CPA. The finer the particles, the more surface area they offer for pozzolanic reactions and the more densely they can be packed in the cement matrix. Most studies have found that calcined CPA is ground via ball mill or mortar/pestle, then sieved through 75 µm (No. 200) or 150 µm sieves [31].

The specific surface area (Blaine fineness) of CPA usually lies between 250 – 450 m²/kg which is lower than Portland cement (300 – 500 m²/kg), but is of the same order of magnitude as Class F fly ash [32]. According to the particle size distribution analysis, the particle size of CPA is generally larger than that of cement and the particle size distribution range is wider, and the amount of 10–45 µm is relatively high [33]. The mechanical activation has been studied by others

using extended grinding to achieve even smaller particles and higher reactivities, but the benefit of this needs to be weighed against cost of the energy required for the process [34].

4. PHYSICOCHEMICAL CHARACTERIZATION OF CASSAVA PEEL ASH

4.1 Chemical Composition (XRF Analysis)

The pozzolanic potential of cassava peel ash is mainly determined by its chemical composition which was determined by X-ray fluorescence (XRF) spectroscopy. The consolidated summary of chemical compositions of CPA from various studies is provided in Table 2 and compared with ASTM C618 specifications and typical Portland cement values.

Table 2. Consolidated Chemical Composition of Cassava Peel Ash from Literature

Oxide	CPA Range (%)	CPA Average (%)	OPC Typical (%)	ASTM C618 Requirement
SiO ₂	48.0–62.5	55.93	20.0–22.0	—
Al ₂ O ₃	15.0–22.5	19.88	4.5–6.5	—
Fe ₂ O ₃	4.5–7.0	6.02	2.0–4.0	—
Σ(S+A+F)	75.0–85.0	81.83	26.5–32.5	≥70%
CaO	7.5–12.0	9.85	62.0–67.0	—
MgO	2.0–4.5	3.20	1.0–3.0	≤6%
SO ₃	0.5–2.0	1.15	2.0–4.0	≤4%
Na ₂ O	0.5–1.5	0.98	0.2–0.5	—
K ₂ O	0.0–0.5	0.00	0.5–1.0	—
LOI	8.0–15.0	12.50	1.5–3.0	≤10%
SiO ₂ /Al ₂ O ₃ Ratio	2.5–3.5	2.82	3.5–4.5	—

The combined pozzolanic oxide content (SiO₂ + Al₂O₃ + Fe₂O₃) for CPA is 81.83% which is well above the ASTM C618 requirement of 70% for natural pozzolans [12]. This high oxide content has been mainly attributed to the characteristics of the cell wall of cassava peel which is made up of silica and aluminous substances which are deposited as phytolith during the growth of the plant [35]. The silica to alumina ratio (SiO₂/Al₂O₃ ~ 2.82) in the CPA can be classified as silica rich but with significant alumina content unlike highly siliceous RHA (SiO₂/Al₂O₃ > 100) and closer to metakaolin in terms of chemical character [36].

CPA contains high amounts of loss on ignition (LOI, 8% - 15%) which is attributed to the presence of residual organic

carbon and structural water in CPA even after calcination. Although ASTM C618 stipulates a limit of 10% for the LOI of Class N pozzolans, certain samples of CPA have LOI values greater than this limit, which may lead to changes in the air content of concrete and necessitate changes in the dosage of admixtures [37]. The CaO content of CPA (7.5–12 %) is in between that of typical pozzolans (<10 %) and Portland cement (>60 %), which means that CPA can display weak hydraulic properties besides the pozzolanic reactivity.

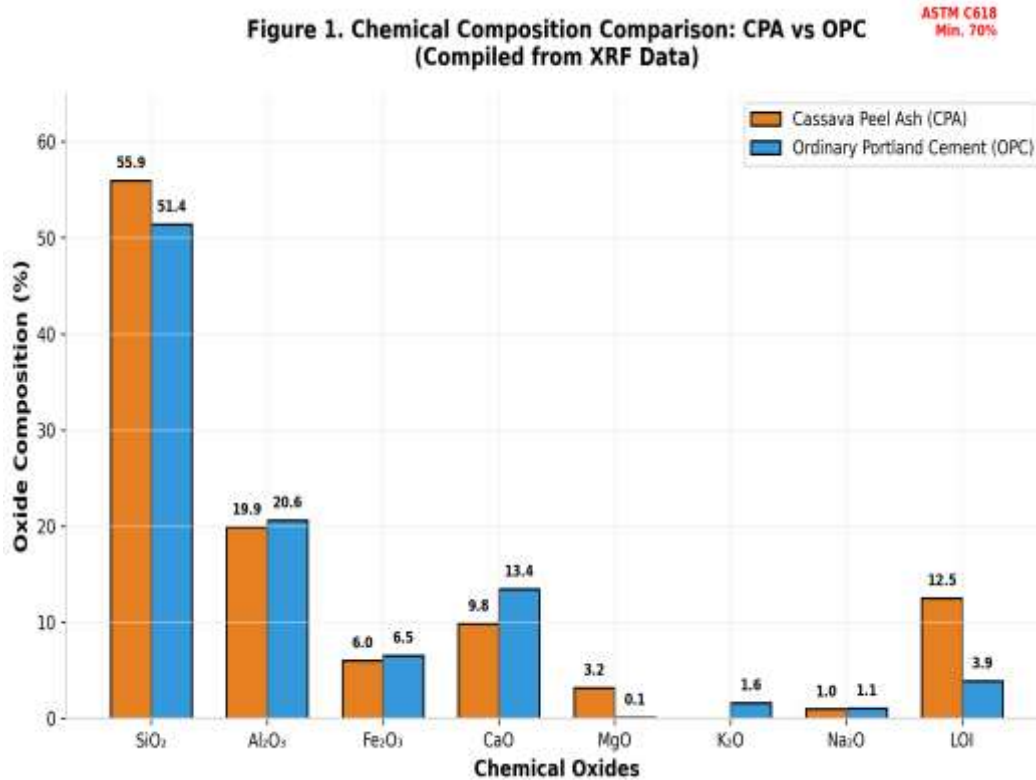


Figure 1. Chemical composition comparison between cassava peel ash (CPA) and ordinary Portland cement (OPC) based on consolidated XRF data. The red dashed line indicates the ASTM C618 minimum combined oxide requirement of 70%.

4.2 Mineralogical Characterization (XRD Analysis)

The analysis of the crystalline and amorphous phases in CPA by X-ray diffraction (XRD) helps to give key insights related to the pozzolanic reactivity of the material. The XRD pattern of CPA calcined at 600°C shows the presence of a complex mineralogy, containing both crystalline and amorphous constituents [29].

Crystalline Phases:

- Quartz (SiO₂): Dominant crystalline phase, exhibiting sharp diffraction peaks at 20.9°, 26.6°, 36.5°, 39.5°, 42.5°, 45.8°, 50.1°, 54.9°, 59.9°, and 68.1° 2θ [29].
- Sodalite (Na₈Al₆Si₆O₂₄Cl₂): Minor phase, occurs as a result of the presence of sodium and chloride in the biomass [29].
- Hematite (Fe₂O₃): Trace iron oxide phase that accounts for the reddish-brown coloration of some CPA samples [39].

Amorphous Phase: A wide and diffuse peak centered at 20° – 30° 2θ typical for non-crystalline silica (SiO₂•nH₂O). The amorphous component is the most pozzolanic, and easily soluble in the alkaline pore solution of the hydrating cement to form the calcium-silicate-hydrate (C-S-H) gel [40].

The amorphous/crystalline silica ratio is temperature dependent. Crystalline quartz is predominant and the content of amorphous silica is minimal at 450°C, while the amorphous hump becomes stronger with increasing temperature, as organic structures are broken down and silica

becomes more reactive in the glassy state at 600–700°C [28]. Sintering will facilitate the recrystallization above 800°C, thereby lowering amorphous amount and the pozzolanic potential of them [28].

4.3 Morphological Characterization (SEM-EDS)

The microstructural features and the distribution of the elements of the CPA particles are obtained by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). Particles produced by CPA calcined at 600°C have an irregular and angular shape with flake-like morphology, deep surface crevices and high microporosity [29, 41]. Such irregularities give the cement a greater surface area for pozzolanic reactions and gives mechanical interlocking between the cement matrix [42].

The spot analysis data from EDS confirms the predominance of silicon and oxygen, with minor amounts of aluminum, iron, calcium and magnesium spread over the surface of the particles [29]. Elemental heterogeneity is due to their complex cellular structure, where epidermal cells have high silica content, while the vascular tissues have deposits of calcium and potassium [43].

The fine particle size distribution analysis shows that the particles of CPA are generally larger than the Portland cement, and the median particle size (d_{50}) is 15–25 μm , which is larger than that of OPC (10–15 μm) [33]. This finer distribution may impact workability and early age strength development, and lead to increased water requirement or need for superplasticizers in H-CPA concrete mixtures [44].

5. POZZOLANIC ACTIVITY OF CASSAVA PEEL ASH

5.1 Theoretical Framework of Pozzolan Reactions

Pozzolan reactions are between reactive silica (SiO_2) &/or alumina (Al_2O_3) found in the pozzolan and portlandite, calcium hydroxide (Ca(OH)_2), produced during the hydration of Portland cement. Calcium-silicate-hydrate (C-S-H) gel is the main product of the primary reaction, which is the major binding component in hardened cement paste, and calcium-aluminate-hydrates (C-A-H) and calcium-alumino-silicate-hydrates (C-A-S-H) depending on the alumina content [49]. These secondary hydration reactions remove the Ca(OH)_2 which is available as crystals of portlandite in the cement paste, and improve the overall structure of the cement paste, make it more compact, less porous, and more durable and strong in the long term [50]. There are a number of factors which will influence the rate and extent of pozzolan reaction: the reactive silica and alumina content; the specific surface area of the pozzolan; the alkalinity of the pore solution, due to the pH of the pore solution, which is typically >12; temperature; and water-to-binder ratio [51].

5.2 Pozzolan Activity Index (PAI).

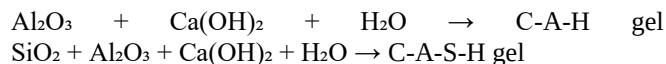
The pozzolan activity index is calculated by multiplying the compressive strength of the mortar cubes made with 20% pozzolan replacement with 75% of the water content of the control water by the number of days, and then comparing the result with the strength of cubes



4.4 The thermal and spectroscopic characteristics.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) give quantitative information about the thermal stability, organic matter content and phase changes of CPA. The TGA curves of raw cassava peels contained three main mass loss regions: moisture evaporation (50–150°C, ~8% mass loss); hemicellulose and cellulose decomposition (200–400°C, ~45% mass loss); and lignin decomposition and oxidation of organic carbon (400–600°C, ~25% mass loss) [45]. The inorganic ash remaining at 700°C is the residual mass which is usually in the 8–12% range of the original peel mass [46].

The Fourier-transform infrared (FTIR) spectroscopy is used to detect the functional groups of CPA and to observe the changes in their composition during the calcination process. The most important absorption bands are: 3,430 cm^{-1} (O–H stretching from silanol and adsorbed moisture), 1,630 cm^{-1} (H–O–H bending from adsorbed water), 1,100 cm^{-1} (Si–O–Si asymmetric stretching, predominant in amorphous silica), 800 cm^{-1} (Si–O symmetric stretching), 470 cm^{-1} (Si–O bending) [47]. The Si–O–Si band has a correlation with amorphous silica content, and can be used as a qualitative indicator of pozzolanic activity [48].



made of Portland cement mortar with 100% water content. It is calculated by multiplying the compressive strength of the mortar cubes made with 20% pozzolan replacement with 75% of the water content of the control water by the number of days, and then comparing the result with the mortar cubes made of Portland cement mortar with 100% water content. Material is considered a pozzolan if it has a PAI $\geq 75\%$ at 28 days as specified by ASTM C618. Other indices are the Frattini test (EN 196-5) which measures the consumption of Ca(OH)_2 in a saturated lime solution, or the Chapelle test which measures the consumption of Ca(OH)_2 per gram of pozzolan [52].

The PAI of cassava peel ash varies from 68% to 78%, and most studies found values slightly below or above 75% [18, 53]. This variation is due to the differences in the condition of calcination, fineness of particles and type of cement used for the test. Ground to pass a 75 μm sieve, a typical value for CPA is 74-76% PAI, and finer grinding ($<45 \mu\text{m}$) and optimized calcination (650°C, 2 hours) can increase the PAI to about 78% [54].

The strength activity index of CPA at 7 days is usually less than that at 28 days due to slower kinetics of pozzolanic reactions than cement hydration. This loss of strength at an early age is a common characteristic property of pozzolanic materials and should be taken into account when designing construction schedules and formwork designs [55].

5.3. Frattini Test and Lime Reactivity.

The Frattini test is a direct test for pozzolanic reactivity which can be conducted by measuring the decrease in calcium ion and hydroxyl ion concentrations in a saturated lime solution ($\text{pH} \sim 12.4$) following the interaction with the pozzolan. From EN 196-5, any material whose $[\text{Ca}^{2+}]$ and $[\text{OH}^-]$ concentrations are less than the saturation curve for portlandite at test temperature [56] can be regarded as pozzolanic material.

Research with CPA has shown that calcium ion concentration has decreased from 1,200 mg/L to 600–800 mg/L after 8 days of interaction with the CPA at 40°C [57]. The hydroxyl ion concentration also decreases, indicating that Ca(OH)_2 has also reacted with the pozzolanic reaction. The consumption rate for Ca(OH)_2 in CPA is, however, lower than CPA's consumption rate in metakaolin or silica fume as expected, since the specific surface area and amorphous silica content of CPA are lower than that of both materials [58].

In lime reactivity test (IS 1727), the mortar cubes of size 50 mm are prepared by mixing 1 part of lime, 2 parts of pozzolanic cement and 9 parts of sand, and are tested after 10 days for compressive strength. CPA has shown lime reactivity values ranging from 3.5MPa to 4.2MPa which meet the minimum criteria of 3.0MPa for Class F fly ash, but do not meet the criteria of 5.0MPa for high reactivity pozzolans [59]. The following factors affect the pozzolanic activity.

As seen in Figure 5, the calcination temperature has an indirect effect on the pozzolanic activity of CPA, with maximum amorphous silica content at 600-700°C, which is the temperature with maximum PAI. Below this range, unburned organic material leads to decreased reactivity, and above this range, the silica recrystallization decreases the amorphous material. [28]

The specific surface areas of the finer CPA particles ($<45\ \mu\text{m}$) are higher and the diffusion path of the ions are shorter, which leads to an increase in the rate of the pozzolanic reactions. But if too fine, there is an increased requirement for water and sometimes chemical admixtures to achieve the desired workability [60].

Chemical composition: High SiO_2 and Al_2O_3 contents are related with high pozzolanic potential. The presence of alkalis (Na_2O , K_2O) can increase early age reactivity via alkali silica reaction mechanisms however, excessive alkalis can carry out undesirable alkali silica reaction in concrete with reactive aggregates [61].

Alkali content and the ratio of $\text{C}_3\text{S}/\text{C}_2\text{S}$ of Portland cement will affect the driving force for pozzolanic reaction by affecting the rate of liberation of $\text{Ca}(\text{OH})_2$. Most pozzolanic reactions occur more rapidly with cements of high alkali content ($>0.6\% \text{Na}_2\text{Oeq}$) [62].

Curing Conditions: Elevated temperature curing (35-50°C) increases the rate of pozzolanic reaction in the cement, while moist curing is required to ensure sufficient water is available for the secondary pozzolanic reactions. The steam curing has been proved to greatly improve the reactivity of CPA [63].

6. PERFORMANCE IN CEMENTITIOUS SYSTEMS

6.1 Fresh Concrete Properties

Cassava Peel Ash (CPA) has several mechanisms which affect the properties of workability, setting time and water

demand in concrete mixture. CPA particles are coarser and more porous than Portland cement, which causes an increase in the amount of water required for concrete mixtures. The absorbent property of the CPA particles and their irregular surface morphology were cited as the reason for the need of 5–10% extra water to produce the same slump as for the control mixes, as reported by studies [64].

Typically, the setting times of the CPA-blended cement paste are long. The initial setting time increases by about 15–30 minutes and the final setting time increases by about 30–60 minutes for 10% replacement of CPA [65]. This retardation is advantageous in hot climates where the fast setting is not desirable in placing and finishing operations but not desirable in cold weather concreting where delayed strength development is not desirable [66]. The setting time extension is due to the adsorption of calcium ions to the surface of CPA particles and the dilution effect (lower cement quantity) in the pore solution [67].

Specific gravity (2.20-2.35) of CPA is lower than that of Portland cement (3.15) which leads to lesser density of CPA-blended concrete. In this case, the density of the concrete will also decrease by 3-5% for 20% CPA replacement, which can be beneficial for lightweight structures but must be taken into account when calculating concrete mixture properties [68].

2 Compressive Strength Development

The most widely studied performance parameter of CPA concrete is its compressive strength, which has reported wide ranges depending on the level of replacement, the w/b ratio of concrete, the curing regime, and testing age. The trends of compressive strength from various studies are consolidated in Figure 2.

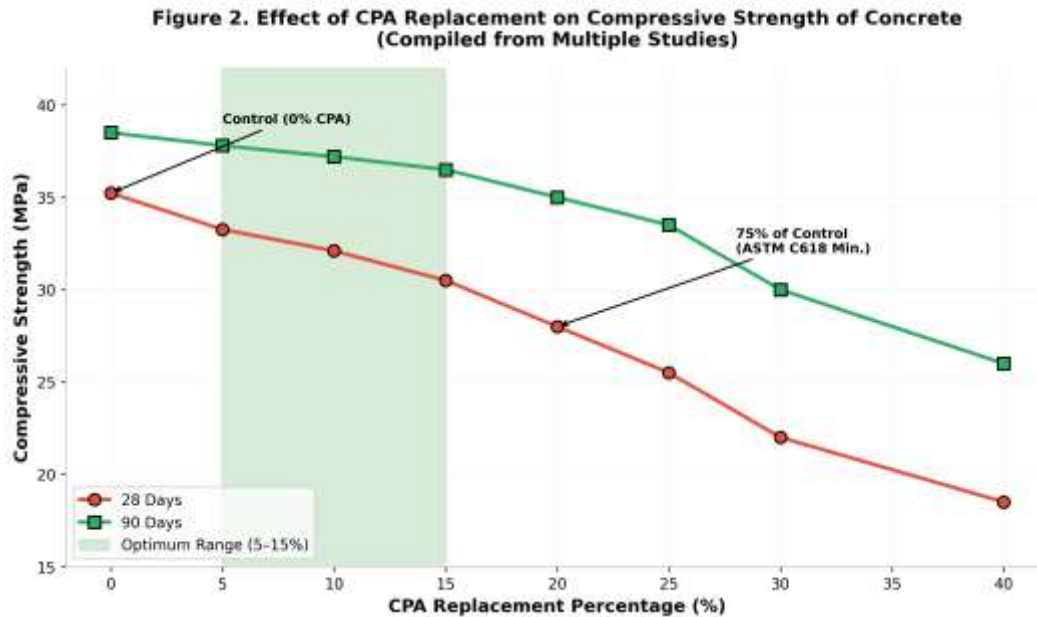


Figure 2. Effect of CPA replacement percentage on compressive strength of concrete at 28 and 90 days. The green shaded region indicates the optimum replacement range (5–15%). Data compiled from multiple studies [18, 21, 53, 64].

The replacement levels of 5–10% CPA at 28 days result in compressive strength values similar to or slightly below the control mixes (90–100% of the control strength) [18, 53]. Typically, 28-day strength drops to 85–90% of control at 15% replacement, and to 15–25% at 20% replacement [64]. When more than 25% of the CPA is replaced, the strength decreases more dramatically: 30% CPA mixes attain only 60–70% of the strength of the control mix after 28 days [21].

The long term development of the strength of CPA concrete is more favorable. In the case of mixes containing 10–15% replacement at 90 days, the strengths are commonly similar to or sometimes superior to strength of control specimens, which is due to secondary C-S-H formation from pozzolanic reactions to fill the microcapillary pores [69]. This is a characteristic feature of pozzolanic materials, and highlights the need for long curing periods for CPA concrete [70].

Similar to the compressive strength, the flexural and split-tensile strength of CPA concrete showed comparable trend with 10% CPA replacement yielding flexural strength of 3.8–4.2MPa against 4.0–4.5MPa for the control mixes at 28 days [71]. The reduction in the modulus of elasticity with increasing CPA content is indicative of less stiffness of CPA particles and higher porosity of the hardened paste [72].

6.3 Durability Properties

Concrete made with CPA has been investigated in various degradation mechanisms, and it has been found that the general results are good for moderate replacement levels:

Water Absorption and Permeability: With replacement rates ranging from 10% to 15%, the water absorption of CPA concrete is lower than that of the control concrete, due to the pore filling effect of the secondary C-S-H gel [73]. The water absorption coefficient of the 10% CPA mixes is reduced by

only 10–20% at 28 days, and even greater replacements (>20%) could lead to higher water absorption properties because of the higher capillary porosity resulting from the incomplete pozzolanic reaction [74].

Sulfate Resistance: Use of $\text{Ca}(\text{OH})_2$ due to pozzolanic reactions decreases the quantity of reactive Ca available to the formation of ettringite, which leads to improved sulfate resistance [75]. The study of CPA mortar by exposure to the magnesium sulfate solution (5% concentration) showed that the specimens with 10 % CPA replacement exhibited the least loss in mass and strength degradation among all other specimens compared to the control specimens [22].

Chloride Ingression: The ability of the CPA concrete to resist the penetration of chloride ions into the structure was confirmed by rapid chloride permeability test (RCPT) and chloride diffusion coefficients [76]. The fine pore structure and low interconnectedness of the capillary pores restrict the mobility of chloride ions, making CPA concrete a good choice for marine and coastal applications [77].

Carbonation Resistance: Less alkaline reserve will be available to neutralize atmospheric CO_2 , which may result in deeper carbonation due to the reduction in $\text{Ca}(\text{OH})_2$ content as a result of pozzolanic reaction [78]. In reinforced concrete applications where carbonation-induced corrosion is an issue, typical carbonation depths of 10–20% greater than control concrete at 28 days have to be considered for 10% CPA concrete [79].

Low alkali content of CPA ($\text{Na}_2\text{O}_{\text{eq}} < 1.5\%$) decreases potential for deleterious alkali silica reaction (ASR) expansion with reactive aggregates [80]. Despite the high-alkali cement, however, the high replacement rate ($>20\%$) of CPA can still cause ASR, requiring the use of preventative measures such as lithium admixtures or by using low-alkali

6.4 Microstructural Evolution

Microstructural properties of CPA-blended cement paste show that the formation of hydration products and refinement of pore structure increase with time. After 7 days, SEM images reveal discrete CPA particles covered by hydration product shells and some pozzolanic reaction activity at particle boundaries [82]. At 28 days, the CPA particles at the interface with the cement paste are no longer clearly visible, as the pozzolanic C-S-H gel forms and eats away at the particles, thus densifying the interfacial transition zone (ITZ) [83].

The microstructure at 90 days is more homogenous with fewer large capillary pores and lower porosity as seen through backscattered electron (BSE) imaging [84]. The energy-dispersive X-ray (EDS) mapping confirms that calcium-silicate-hydrate (C-S-H) gel, containing a higher amount of Al, is formed around partially reacted CPA particles, which agreement with the alumina content of CPA [85]. The pore size distribution data from the mercury intrusion porosimeter showed that the critical pore diameter decreased from 50 nm (control) to 35 nm (10% CPA) after 90 days [86].

Typical CPA replacement levels are 10% for 40–60% degree of CPA reaction, whereas, the same level of replacement with metakaolin or silica fume results in 70–80% and 90–100% degrees of reaction respectively [87]. This lower reactivity is similar to that of CPA due to its larger particle size and lower amorphous silica content than these high-reactivity pozzolans.

7. ENVIRONMENTAL SUSTAINABILITY AND LIFE-CYCLE IMPLICATIONS

7.1 Carbon Footprint Reduction

Use of Portland cement in concrete production can be reduced with cassava peel ash (CPA), which has a significant potential for carbon footprint reduction in concrete production. The carbon intensity of Portland cement production is around 0.87 kg CO₂ per kg of cement, made up of 0.55 kg CO₂ from limestone calcination and 0.32 kg CO₂ from fuel combustion [88]. On the other hand, CPA production has minimal direct CO₂ emission because the carbon released in the combustion of peels comes from atmospheric CO₂ absorbed during the growing of cassava which is considered as carbon neutral according to IPCC accounting [89].

About 0.87 tonnes of CO₂ is avoided for every tonne of CPA that is being used instead of Portland cement. If the cement is replaced by CPA at a rate of 10% in concrete with 350 kg of cement per cubic metre, then 30.5 kg of CO₂ per cubic metre of concrete can be avoided [90]. If extrapolated to the national level, the potential CO₂ mitigation is quite large: Nigeria's annual cassava peel waste (15–20 MT/yr) can theoretically produce 1.2–1.6 MT of CPA which can replace 12–16 MT of cement and prevent 10.4–13.9 MT CO₂ per year [91].

The net carbon benefit needs to include the carbon used in the production of CPA (drying, grinding, calcination), as well as its transportation costs. CPA calcination energy consumption

in the controlled kiln or the muffle furnaces is estimated to be 0.5–1.0 MJ kg⁻¹ of the ash, much lower than the 3.5–5.0 MJ kg⁻¹ for Portland cement clinker production [92]. The energy requirements for the production of CPA can be further reduced, when the energy for the production is generated from waste heat of cassava processing industry or from the combustion of biomass [93].

7.2 Waste management and circular economy

The valorisation of cassava peel waste is an effective solution for the problem of cassava waste in cassava producing areas. In Nigeria, Ghana and other West African countries, cassava peels are usually disposed into open dumps, roadside heaps and water bodies where they decay anaerobically, producing methane (CH₄, 28× CO₂) and leaching cyanogenic compounds into groundwater [94]. Peels are routinely burned in open piles which can lead to the production of particulate matter, carbon monoxide and polycyclic aromatic hydrocarbons that affect air quality and respiratory health of nearby communities [95].

By using the waste stream of cassava peels for value-added construction materials through controlled calcination, the circular economy concepts and the waste hierarchy (reduce, reuse, recycle, recover) [96] are followed. The economic advantages do not only include material substitution, but also employment opportunities in rural areas, cost reduction for waste management companies in waste treatment facilities and reduction of waste to be disposed in landfills [97].

Besides, the ash produced from cassava peel combustion has a relatively small volume (8–12% of original peel volume) and mass (10–15% of the original peel volume), which results in a significantly reduced area of land needed for disposal and also lowers transportation costs. Unlike raw peels containing cyanogenic glucosides (which can be hydrolysed to release hydrogen cyanide (HCN)) inorganic ash is chemically stable and non-toxic [99].

Figure 4. Cassava Production Landscape in Africa

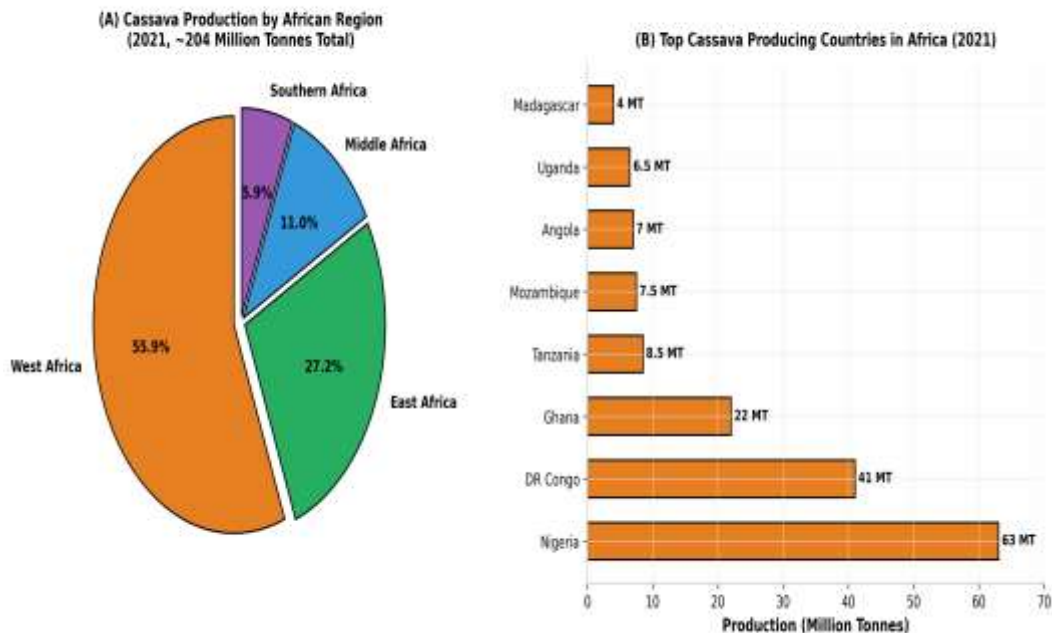


Figure 4. Cassava production landscape in Africa. (A) Production distribution by region (2021, ~204 million tonnes total). (B) Top cassava producing countries. Data from FAOSTAT [7].

7.3 Life-Cycle Assessment Considerations

Life-cycle assessment (LCA) is used to give a comprehensive picture of the environmental impacts of CPA concrete from the point of extraction to disposal at the end of its life. Although LCA studies of CPA are limited, preliminary studies with attributional LCA methodology indicate that CPA concrete has a lower global warming potential (GWP) than conventional concrete, as well as lower acidification potential and abiotic depletion potential (ADP) [100].

For the CPA LCA, the system boundary should include

- (1) cultivation and harvesting of cassava;
- (2) collection and preliminary treatment (washing, drying, grinding) of cassava peels;
- (3) preliminary treatment (washing, drying, grinding) and control of emissions during calcination (fuel burning);
- (4) grinding and classification of the cassava peel waste;
- (5) transportation of the cassava peel waste to concrete batching plants;
- (6) concrete production and placing; and
- (7) end-of-life management (recycling, land-fill) [101].

For the CPA (concrete) material, important categories of impact in the LCA are: Global Warming Potential (GWP): 10-15% less than control concrete (10% CPA replacement) mostly because of the emissions avoided from cement production [102].

Avoiding cement production emissions leads to reductions in SO_2 and NO_x emissions, which contribute to Acidification Potential (AP); if fossil fuel is used, CPA calcination may contribute to AP.

Eutrophication Potential (EP): Avoided nutrient runoff from landfills, since CPA is inert and does not leach nutrients [104]. Abiotic Depletion Potential (ADP): Lower use of limestone and clay resources (energy resources needed for calcination need to be considered).

According to the sensitivity analysis, the environmental performance of CPA concrete is highly dependent on the type of calcination fuel (biomass or fossil fuel) and transportation distances as well as replacement level [106]. The best environmental performance occurs when CPA is manufactured based on renewable energy at plants within 50 km of concrete batching plants [107].

8. RESEARCH GAPS AND FUTURE DIRECTIONS

8.1 Critical Research Priorities

Although cassava peel ash has been extensively characterized as supplementary cementitious material, there are still many gaps of knowledge that hinder its commercialization and standardization:

There are no standard production protocols for the production of CPA. The range of temperatures used in studies is very

wide (450 – 800 °C), as well as heating rates and cooling conditions, and the duration of studies varies from one to four hours, which makes it difficult to compare the results of studies and hinders the development of quality benchmarks. There is an urgent need for a standardized protocol, specifying optimal temperature ($650 \pm 50^\circ\text{C}$), duration (2 hours) and particle size ($d_{50} < 20 \mu\text{m}$).

Most CPA studies have 28 and 90 day results, and limited CPA durability data exists for more than 1 year of exposure in the field. CPA concrete's carbonation resistance, chloride ingress and sulfate resistance in tropical climatic conditions (high temperature, high humidity and cyclic wetting-drying) must be systematically studied [109].

Rheological characteristics of CPA concrete such as yield stress, plastic viscosity and thixotropy have been scarcely studied. These properties are important characteristics of pumpable concrete, self-compacting concrete and 3D-printing applications where the flow properties are important [110].

The potential of CPA as a precursor for alkali activated materials (geopolymers) has so far not been fully exploited. Initial research indicate that the alumina content of CPA (19.88%) is suitable for geopolymer synthesis using sodium hydroxide or sodium silicate activators, however, the mix designs, curing regimes and mechanical properties must be optimized systematically [23].

Synergistic effects of using hybrid systems of CPA and other SCM (fly ash, slag, metakaolin, silica fume) have not been systematically studied. Optimizing performance whilst maximizing waste utilization and cost-effectiveness could be achieved by using binary, ternary or quaternary blends [111]. Most CPA research is conducted in the laboratory with small size specimens under controlled conditions. To confirm laboratory test results and to uncover real-world issues with batching, placing, curing, and quality control in the field, large-scale field tests of structural components, pavements, and masonry units are required [112].

Techno-economic studies of CPA concrete would be beneficial, as it would allow for the comparison of concrete costs, labour, equipment, transport, and external cost to the environment in comparison with conventional concrete, which can be used to inform commercial viability and policy incentives [113].

8.2 Standardisation and Regulatory Issues.

The use of CPA as a supplementary cementing material in commerce will still depend on the acceptance of CPA in national and international standards. There are currently no national standards bodies in Africa or in the world that have CPA on their list of approved SCMs.

The process of standardisation has several steps:

The development of ranges and quality grades for CPA on the basis of comprehensive characterization of CPA from various geographical origins [114].

1. Development of national standards for production, testing and quality control of CPA, based on ASTM C618, EN 197-1 or BS 3892 [115].

2. Certification of CPA producers based on third party testing and quality assurance [116].
3. National building codes and concrete design standards are currently being integrated with CPA, and limits and performance requirements are being described [117].
4. Capacity building for construction professionals such as engineers, architects and contractors with regards to the use of CPA in concrete [118].

The African Organisation for Standardisation (ARSO), and the national standards bodies (SON in Nigeria and GSA in Ghana) are ideally suited to drive this process of standardization on pozzolanic materials [119]. The possibility of mutual recognition and export possibilities for construction materials based on CPA through international cooperation with ASTM International and the European Committee for Standardization (CEN) [120] should be explored.

8.3 Emerging Applications and Innovations

In addition to the traditional use of concrete, there are multiple innovative applications being investigated with CPA:

Geopolymer Concrete: Alkali-activation of CPA with NaOH/Na₂SiO₃ solutions results in the formation of geopolymer binders that can achieve compressive strengths of 25-40MPa at 28 days, and can provide a cement-free solution with near zero carbon footprints [23].

Soil Stabilization: CPA has been proven to be effective for soil stabilization, for expansive clay soils and marine clays, reducing the plasticity index and increasing the California Bearing Ratio (CBR) for road subgrade applications [24].

Low Weight Aggregate: CPA pellets can be used as lightweight aggregate for the structural and non-structural concrete; thereby it reduces the dead load and enhances the thermal insulating property [121].

Heavy metals (Pb²⁺, Cd²⁺, Cr6+) and organic pollutants of wastewater can be adsorbed onto the high surface area and porous structure of CPA, and thus can be used in wastewater treatment.

3D-Printed Construction: 3D concrete printing using Extrusion method requires special rheological properties of cement pastes, which are studied by modifying cement pastes (CPA) [123].

9. CONCLUSION

Cassava peel ash is a potential new supplementary cementitious material which tackles two of the major challenges facing the construction sector in Africa: the environmental impact of the production of Portland cement and the need to manage large volumes of agricultural waste. This review has systematically analysed the physicochemical characteristics, pozzolanic activity and performance of CPA in cementitious systems based on the growing amount of CPA

research from the developing countries of Nigeria and other cassava-producing countries.

The evidence is used to draw the following major conclusions:

First, the chemical properties of cassava peel ash meet the standard requirement for natural pozzolans in ASTM C618, whose $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ average value is 81.83% which is greater than the minimum value of 70%. The silica-rich, alumina-significant composition of CPA is different from other highly siliceous agricultural ashes like rice husk ash and makes it a pozzolanic material with medium reactivity which is similar to sugarcane bagasse ash.

Second, the pozzolanic activity index of CPA (75.8%) is marginally acceptable as per ASTM C618 (pozzolanic activity in 75%) criteria and considered good but not excellent reactivity. In order to optimize the amorphous silica content and pozzolanic performance, the optimum calcination temperature is decided as 600-700°C, whereabove 800°C the temperature causes the formation of undesirable recrystallization.

Third, concrete with a 5–15% replacement of CPA has comparable 28-day strengths to the control, and offers superior strength gain at later ages because of secondary C-S-H formation. The durability properties, such as water absorption, sulfate resistance, and chloride ingress, tend to be enhanced at moderate replacement levels, but carbonation resistance should be taken into account when using reinforced concrete.

Fourth, the environmental advantages gained from the utilisation of CPA are enormous. The use of 1 tonne of CPA in place of 1 tonne of Portland cement results in emissions of around 0.87 tonne of CO_2 . Further, cassava peels are causing a waste management problem for which an effective solution is needed. The annual peel waste in Nigeria can adequately produce enough CPA equivalent to the replacement of 10 to 14 million tonnes of CO_2 from the use of 12 to 16 million tonnes of cement.

But there are still major hurdles to commercialization. Lack of standardized production protocols, limited long-term durability data, lack of regulatory recognition and lack of field scale validation limit the transition from lab research to industrial use. To bridge these gaps, it is necessary to move towards a coordinated effort between interested researchers, standards organizations, industry and policy makers.

The way forward requires: (1) establishment of standardized CPA production and testing procedures; (2) long-term durability tests in the tropics; (3) national standards for CPA quality and concrete mix design; (4) demonstration projects at field level; and (5) economic incentives for CPA use in public buildings.

The potential for valorizing cassava peel waste to become an alternative material with a performance level similar to conventional SCMs is not just a concept—it is a practical solution that could transform the built environment in Africa, a place where climate change and urbanization are increasingly urgent challenges. The science has been done and the need now is to apply it to practice.

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