Development of Green and Environmentally Friendly Alternative Binder to Cement towards Sustainable Construction

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Abstract

Portland Cement (PC) is currently the world most commonly used binder in mortar/concrete applications. PC-based concrete is the world's most consumed man-made material and consequently puts lots of demand on cement as a binder. PC was however discovered to be non-environmental-friendly material due to its green house (carbon dioxide, CO_2) gas emission mainly during production, which contributes greatly to global warming and all its negative impacts worldwide. Concrete production contributes up to 5% of the annual global CO_2 emissions of which the bulk is from the production of cement. Another factor debilitating the use of PC is its high cost which translates to high cost of mortar/concrete-based structures such as buildings, and thereby making housing less affordable for the citizenry. These PC concerns have led to the development of greener and cheaper alternative binders which have so far evolved from the conventional PC to blended and pozzolanic cements. This study is focused on evolving the PC to a fully pozzolanic binder by combining a pozzolan (sourced from NBRRI's Pulverised Calcined Clay {PCC}) with calcium hydroxide ($Ca(OH)_2$ {sourced from Carbide Waste (CW)-- a byproduct of the carbide after being used to generate acetylene used in other industrial processes. This study has shown that these two combinations in the presence of water can produce the C-S-H responsible for strength development as in cement hydration; just that in this case, the CW meant for landfills and pozzolans which could also originate from Agro wastes can be used in the development of an alternative innovative binder to cement. In this study, the strength of the pozzolanic binder was tested in accordance to BS 196-1:2005; the X-Ray Fluorescence (XRF) analysis was also performed. The results show that this binder generated a 28-day curing strength of 11MPa with the potential of generating higher later-day strength. This is about one-third the strength of a 32.5 Cement Grade. The XRF analysis shows that the PCC in this study is a class N pozzolan with strength pozzolanic index of 129% and the CW purity level of 70-80% $Ca(OH)_2$. Commercializing this study outcome can result to the use of cheaper and more sustainable construction material than the most currently used binder, cement.

Keywords: Pozzolan, Carbide-Waste, Cement Alternative, Innovative Binder and Calcined Clay

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1.0 INTRODUCTION

Portland Cement (PC) is currently the world's most commonly used binder in mortar and concrete applications, and the common brands in Nigeria include Dangote, Elephant, Eagle and Ibeto. According to Naik (2008), Portland Cement (PC) based concrete is the world's most consumed man-made material and consequently puts a lot of demand on cement binder. There were other binder being used before the emergence of Portland cements like clays, lime, bitumen and natural pozzolans but the advantage of the Portland Cement was then seen to far outwit these other existing ones. Over the years, some natural (non-synthetic) binders went extinct while the demand for the remaining types of binders like lime was seldom used in mortar and non-structural concrete applications.

Over the years, PC was discovered to be a non-environmentally friendly material due to its green house (carbon dioxide, CO_2) gas emission mainly during production, which contributes greatly to global warming and all its negative impacts worldwide. In fact, Crow (2008) concluded that concrete production contributed 5% of the annual global CO_2 emissions of which the bulk is from the production of cement. Another factor that is debilitating the use of PC is its high cost which further translates to the higher cost of mortar and concrete-based structures like buildings; and making housing less affordable for the citizenry.

These concerns on PC prompted research activities to focus on the development of greener and cheaper alternative binders through the partial replacement of PC to produce blended or pozzolanic cements; thereby evolving the PC to blended and pozzolanic cements. Blended and pozzolanic materials are greener and more affordable additive materials that are mixed with or replaces cement at varying degrees for optimized cement performance in concrete and mortars. Developed countries have started a wider production of these evolved alternative cements and even developed standards like BS EN 197-1:2011 and ASTM C618-2015 for their utilization. Researchers are tending towards the use of binders that are green and more cost-effective.

This binding material developed in this work is intended to produce an alternative to cement from industrial by-products based solely based on pozzolanic process.

1.1 Cement Hydration or Hardening Action of Portland Cements

The main constituents of cements are as shown in Table 1.

Table 1: Constituents of Portland Cements

Constituent	Short nomenclature	Chemical formulae	Mineral name
Tricalcium Silicate	C_3S	$3CaO{\cdot}SiO_2$	Alite
Dicalcium Silicate	C_2S	$2CaO{\cdot}SiO_2$	Belite
Tricalcium Aluminate	C_3A	$3CaO{\cdot}Al2O_3$	Aluminate
Tetracalcium Aluminoferrate	C_4AF	$4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$	Ferrites

The main constituents responsible for the hardening action of PCs are the C_3S and C_2S. Both react with water to produce an amorphous calcium silicate hydrate gel known as C–S–H which is the main 'glue' that binds the sand and aggregate particles together in concrete; and the excess calcium is precipitated into crystals of Calcium Hydroxide, $Ca(OH)_2$ (Newman and Choo, 2003). The Calcium Hydroxide is symbolized as CH. The chemical equation is as shown below:

$$C_3S + 4.3H \Rightarrow C_{1.7}SH_3 + 1.3CH$$
$$C_2S + 3.3H \Rightarrow C_{1.7}SH_3 + 0.3CH \qquad \text{Eqn 1}$$

Where C is CaO; S is SiO_2; andH is $(OH)^-$

The more the C-S-H gel matrix formed, the harder and stronger the binding property and hence the resulting mortar or concrete.

1.2 Pozzolanic Reaction

According to Mehta (1987), a **pozzolanic material** is a siliceous or siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form and in the presence of water, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties. This added strength is as a result of the development of more gel matrix of C-S-H during the cement hydration in the presence of the pozzolan. In pozzolanic cements or cements blended with pozzolanic materials, the added pozzolan rich in silica oxide (SiO_2) reacts with the calcium hydroxide (CH) as in Equation 1 forming more C-S-H gel matrix that results in the increased strength.

When the whole CH in cement hydration has combined with the SiO_2 from the pozzolan and there still exist excess uncombined SiO_2, the excess interferes with the matrix resulting in overall reduced strength. The greater the uncombined excess SiO_2 from the pozzolan, the greater the strength reduced in the overall concrete or mortar. There is therefore the need to determine experimentally the exact amount of pozzolan needed in the blend with Portland cement for strength optimization. The Pozzolanic reaction is as shown:

$$S + CH \Rightarrow CSH \qquad \text{Eqn (2)}$$

Where S is the silicate from pozzolan and CH is the product of hydration of Portland cement.

1.3 Innovative Alternative Binder: Possible Whole Cement Replacement

It has been shown that when a pozzolan (S) reacts with calcium hydroxide (CH) from the bye product of hydration Equation (1)), a binding gel matrix formation responsible for gain in strength is formed as shown in Equation (2). This study explores the possibility that a pozzolan can react independently with another source of CH *to produce a binding gel matrix of C-S-H* (pozzolanic reaction) as shown in Equation (2). This study sourced the CH in Equation (1) and Equation (2), which is [$Ca(OH)_2$], from the industrial waste generated when Calcium Carbide (CaC_2) reacts with water to produce acetylene (C_2H_2) for industrial applications as shown in Equation (3).

$$CaC_2 + 2H_2O \Rightarrow C_2H_2 + Ca(OH)_2 \qquad \text{Eqn (3)}$$

1.4 Sources of Raw Materials

As can be deduced from above, the primary raw material for the development of pozzolanic binders are pozzolans and calcium hydroxide.

There are a lot of pozzolans currently under research in Nigeria and these include but are not limited to the following:

i. *Palm Kernel Nut Ash* (PKNA): This is a by-product of oil palm nuts after the oil has been extracted (Joshua *et.al,* 2015). Nigeria is currently the third world's largest producer of palm kernel after Malaysia and Indonesia. Nigeria also produces 55% of the palm fruits produced in African (Gourichon, 2013).

ii. *Fly-Ash* (FA): The ash is a by-product obtained from the burning of coal in coal power stations and other applications. They could potentially be sourced from Itobe Power Plant in Kogi State; the Federal Government has even proposed to build three (3) coal power stations in Enugu, Gombe and Kogi States with up to 3000 MegaWatt (MW) capacity. These will generate large capacity for FA production. Nigeria has the cleanest type of natural coal deposits in the world. Sepco III Electric Power Construction Corporation of China and an indigenous company, Pacific Energy, are building Olorunsogo Coal Power Station of 1200MW in Ogun State.

iii. *Other Agro-based Pozzolans*: Ettu *et. al.* (2013) identified eight pozzolanic agricultural by-products in Nigeria, namely Rice Husk Ash (RHA), Saw Dust Ash (SDA), Oil Palm Bunch Ash (OPBA), Cassava Waste Ash (CWA), Coconut Husk Ash (CHA), Corn Cob Ash (CCA), Plantain Leaf Ash (PLA), and Paw-Paw Leaf Ash (PPLA).

There are several other pozzolans under study such as the Pulverized Calcined Clay (PCC) developed by the Nigerian Building and Road Research Institute (NBRRI), Bagasse ash and naturally occurring volcanic ash. There are enough deposits of pozzolans to justify the different studies and research works.

The second raw material is the calcium hydroxide, which in this study is sourced as an industrial by-product from the hydrolysis of calcium carbide (Equation 3) that hydrolysis generates acetylene for industrial applications especially is in the auto making and repair industry where they are used in the fusing of auto metal parts. **Ihejirika *et.al* (2014) identified the negative impacts of calcium carbide waste on dump sites and the environment; and they include impaired animal and plant life with the possibility of reduced land for agriculture as well as being hazardous to human life. According to** Chukwudebelu (2013), the membership of the Nigerian Automobile Technicians Association (NATA) is about twenty-five thousand (25,000) strong; and each produce an average daily quantity of thirty kilogram (30kg) of carbide waste. This implies that 274,000 tons could be generated annually excluding those generated from other industrial sources. **A sizable quantity of** calcium hydroxide from calcium carbide can be gotten in other countries such as China, Japan, United States of America, Europe, Commonwealth of Independent States (CIS), United Kingdom, and **South Africa** (Davis *et al.*, 2008).

The objectives of this study are to classify the fine aggregates (sand) used in the determination of the mortar strength of the binders; determine the pozzolanic activity/reactivity indices of the pozzolan used; and combine the pozzolan with carbide waste as a binder to check for possible pozzolanic reactions arising therefrom and indicated by strength development.

2.0 MATERIALS AND METHOD

The materials used in this study are borehole water, Dangote cement grade 42.5R, fine aggregate (sand) specially prepared to meet the specification in BS EN 196-1:2005 for the determination of strength of cement, Carbide Waste (CW) collected from road-side auto panel beaters and Pulverized Calcined Clay (PCC) produced from NBRRI Prototype Pilot Pozzolana Plant in NBRRI Laboratory Complex, Ota Ogun State, Nigeria. The CW and PCC were sieved with the 75micron sieve size. The fine aggregate used for determining the mortar strength of the binders was subjected to sieve analysis test and classified using the Unified Soil Classification System (USCS).

The chemical pozzolanic index of the PCC was determined using the X-Ray Fluorescence (XRF) method of analysis to determine its oxide composition, summing up the percentage composition of the silica, aluminum and iron oxides and checking it with ASTM C618 (2015) to determine its reactivity index class. The strength index of the PCC was determined by partially replacing cement with it at varying percentages in steps of 10% from 0%-40% since most pozzolans seldom replaces cement beyond 30%. The mortar strength was determined in a standard manner as specified in BS EN 196-1:2005 at the best workability and observed from the 21st through 28th to the 56th day of curing. The CW and the PCC were mixed at varying percentages and the resulting varying mortar strengths were determined in accordance with BS EN 196-1:2005 at the best workability and observed from the 21st through 28th to the 56th day of curing. The binder mix replacements are as shown in Table 2.

Table 2: Percentage Makeup of the Binder Content in the Determination of Mortar Strength

S/N	Percentage Cement content	Percentage Pozzolan content	Percentage Carbide waste content	Symbol
1	100%	-	-	A
2	90%	10%	-	B
3	80%	20%	-	C
4	70%	30%	-	D
5	60%	40%	-	E
6	-	60%	40	F
7	-	50%	50	G
8	-	40%	60	H
9	-	30%	70	J
10	-	20%	80	K
11	-	100%	-	L
12	-	-	100	M

3.0 RESULTS AND DISCUSSIONS

3.1 Gradation of the Fine Aggregates Used In the Determination of Mortar Strength

From the particle size distribution of the sand in Figure 1, the sand is classified as a poorly graded sand (SP) using the USCS since the Coefficient of Uniformity (C_u) is 2.29 and the Coefficient of Curvature (C_c) is 1.05 as derived from Figure 1. Poorly graded as classed in this case does not connotes that it is close to being a uniformly graded since C_u of 2.29 is closer to 1. The sand satisfies the requirements stipulated in BS EN 196-1:2005 for the determination of mortar strength of cement (binder).

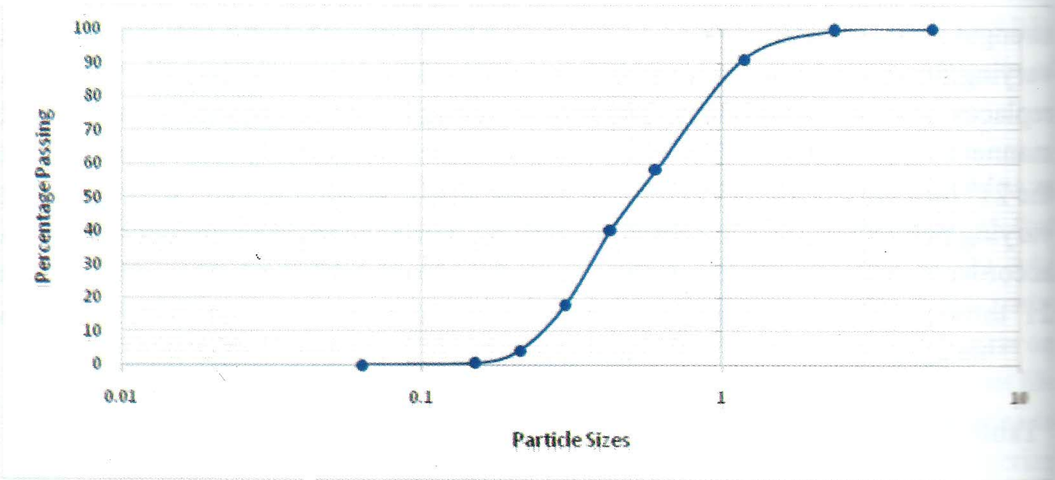

Figure 1: Particle Size Distribution of the Fine Aggregate for All Mortar Strengths

3.2 PCC Pozzolanic Reactivity Index

This was measured by the XRF analysis and the result is a presented in Table 3.

Table 3: NBRRI's Pulverized Calcined Clay (PCC) XRF Analysis

Elemental Oxides	CaO	SiO2	Al_2O_3	Fe2O3	MgO	SO3	Na_2O	K2O	LOI	CaO+ SiO_2+ Al_2O_3
%Composition	2.57	65.45	19.07	6.38	0.6	0.13	0.85	0.19	2.2	87.09

According to ASTM 618 (2015), the NBRRI's PCC is a class N pozzolan since the sum of the percentage compositions of CaO, SiO_2 and Al_2O_3 is more than 70%, Loss On Ignition (LOI) is less than ten (10), SO_3 is less than 4% and its natural source justifies this classification. This class of pozzolan is expected to possess higher pozzolanic activity than other classes.

3.3 PCC Pozzolanic Strength Activity Index

The strength activity index is measured by determining the mortar strengths with the cement content replaced by 20% pozzolan (PCC) and carried out in a standard manner (ASTM C311/C311M, 2013). Though this standard specifies binder to sand ratio of 1:3 and water/cement (w/c) ratio of 0.5, a workable consistence was achieved at w/c ratio of 60%. The mortar strength result is as shown in Figure 2.

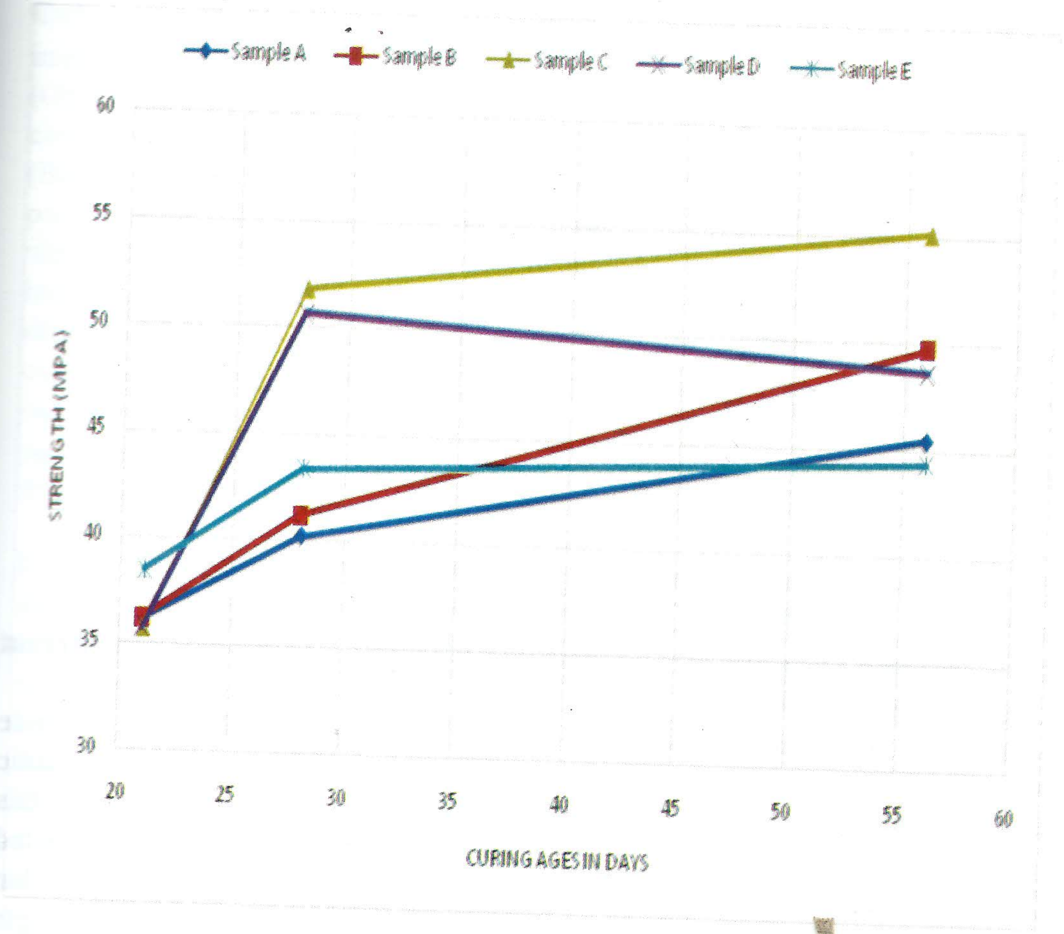

Figure 2: Mortar Compressive Strengths of Cement/Pozzolan at Different Curing Days

The mortar strengths of all PCC (pozzolanic) replacements at all curing ages were generally more than the control (100% cement) indicating evidence of pozzolanic activity and maximum at 20% replacement. The percentage strength at 20% replacement is 129% of the control. Therefore the strength activity index of PCC is 129% which is quite high and complements the classification as highly reactive Class N pozzolan based on the oxide composition.

In Figure 2 at 21-day curing age, it is only sample D that possess strength below the control and it significantly gained strength beyond the control at higher curing ages. The 28-day curing strength was significantly higher than the control with sample C and D being almost 30% higher than the control (see Figure 3). There was little strength gain between the 28 to 56-day strength as observed in Figure 2 and Figure 3; this probably is attributable generally to the decrease in percentage increase in strength at 56-day curing age compared to the 28-day.

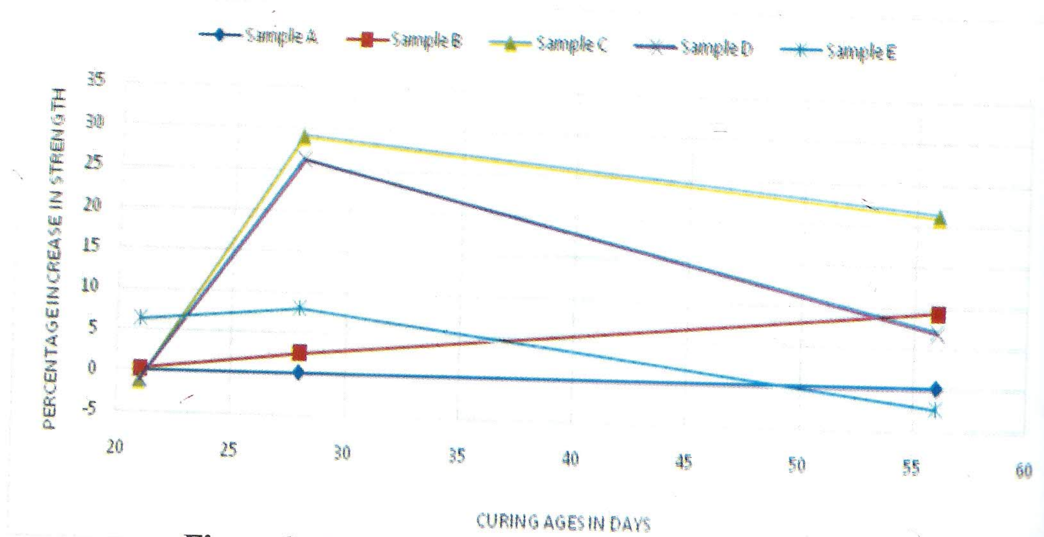

Figure 3: Percentage Increase in Mortar Strengths from the Control of 100% Cement Content

3.4 Mortar Strength of Carbide Waste/Pozzolan (As Binder) at Different Curing Ages

Mortar was produced with binder wholly void of cement by combining Carbide Waste and the Clay Pozzoln. The observed strength gain was due to pozzolanic process in which the C-S-H matrix is formed. The highest strength obtained in this innovative binder is 11MPa at 28-day curing. This is up to a third of the estimated mortar strength of Grade 32.5N/R cement. This is remarkable as it indicates that cement which is a universally utilized material could be wholly replaced. A strength gain from 28 to 56-day curing was expected as it is typical of a pozzolanic process, but this study shows reduced strength at 56 days compared to the 28-day strength. Several reasons could be attributed to this and include the presence of impurities in the carbide waste that could be deleterious to the expected later-day strength gain.

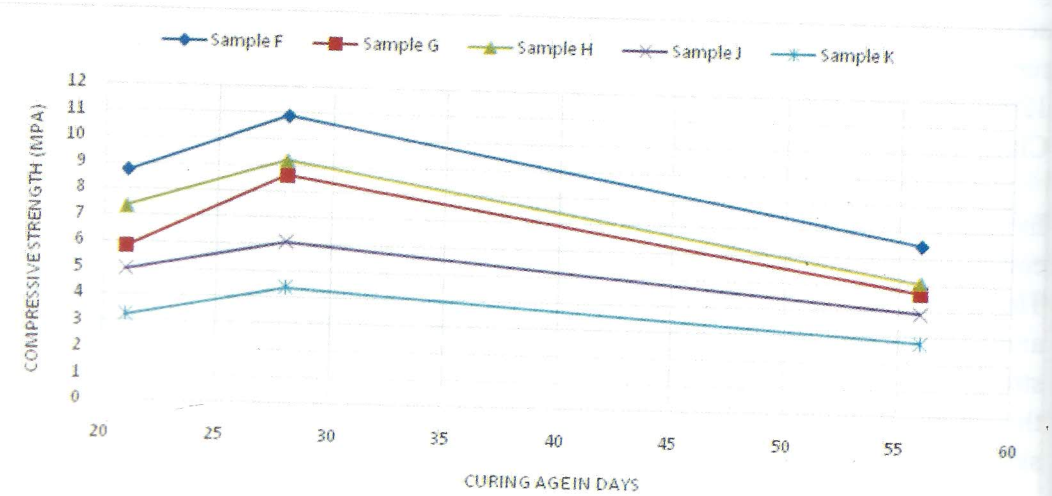

Figure 4: Mortar Strength of Carbide Waste/Pozzolan (Innovative Binder) At Different Ages

Carbide waste in Nigeria is between 70-80% calcium hydroxide $\{Ca(OH)_2\}$ and the impurities in carbide wastes include copper, lead, iron, manganese, nikel and zink (Chukwudebelu *et al.*, 2013); and the effects of some of these elements on concrete/mortar strengths are yet unknown, though it possess a PH of about 12.2 (Bogner *et al.*, 2002) that favours the performance of steel in reinforced concrete by providing the basic environment for its optimized performance. Sample L and M were not curable in water because they disintegrated when put in water after being hard enough to demold. Sample L disintegrated immediately while sample M disintegrated over a period of about seven (7) days by swelling and chipping in the curing water tank. Though this was expected, but the experimentation was carried out to ensure that whatever bonding that might exist between the carbide waste and pozzolan (PCC) will not be attributed to the PCC alone, since it is from a clay-based material that might have a natural binding property or the carbide waste alone.

It was generally observed that the cement–pozzolan mortar possesses higher fresh shrinkage than the carbide waste-pozzolan mortars as the same batch by weight of cement-pozzolan mortars produced less volume of fresh mortars than the carbide waste-pozzolan mortars.

3.5 Limitation and Challenges

The major challenge encountered from the process of mortar preparation to the compression strength test was delayed mortar-hardening time which resulted to waiting for a week before demolding. There is a possibility that there was actually no setting time for the pozzolan/carbide-waste mix because the stiffening or hardening process began as the mortar mix began to dry. It was at this point that demolding was possible after several failed attempts to demold before seven (7) days after casting. This was somewhat expected because pozzolanic processes is mostly a later-strength development phenomenon.

4.0 CONCLUSION AND RECOMMENDATIONS

From the results and discussions, the following were the conclusions made:

- The sand used in the mortar mix as presented in section 3.1 and Figure 1 satisfies the requirements stipulated in BS EN 196-1:2005 for the determination of mortar strength of cement (binder). This justifies the mortar strength and makes the values comparable to standards in BS EN 197-1:2011.
- From section 3.2 and the XRF analysis result in Table 3, the PCC obtained from NBRRI Pilot Pozzolana Plant and used in this study belongs to Class N pozzolan which is a natural pozzolan with high pozzolanic reactivity index as classeified by ASTM 618 (2015). This is not unexpected as the PCC is a calcined natural clay.
- The NBRRI PCC as presented in section 3.3, Figure 2 and Figure 3, is a pozzolan of a very high strength activity index of 129% as specified in ASTM C311/C311M (2013)

- From section 3.4 and Figure 4, the observed strength development was based solely on pozzolanic processes arising from the interaction between the PCC (pozzolan) and carbide waste in the complete absence of cement. The observed optimum strength of 11MPa at 28-day curing for a PCC (pozzolan):carbide waste binder combination ratio of 60%:40% (sample F) which is about a third of the mortar strength from cement Grade 32.5N R. This is quite remarkable as this study has demonstrated the potential for complete elimination of cement in the production of Binder; the elimination of the use of cement in construction; and in consequence the introduction of more economical and affordable binder that is more environmental-friendly than cement. Further work on this has great potential for the provision of more affordable housing to the citizenry.
- No strength gain was observed when either the PCC or the carbide waste was used as a binder alone; but when combined, a cementitious property between the two (PCC and carbide waste) was observed by strength gain. The cement–pozzolan mortar possess higher fresh shrinkage than the carbide waste-pozzolan mortars
- There is a potential of generating higher strength with lesser carbide waste and more PCC since the sample F composition produced the highest strength. More research needs to be done to address the reduced strength from 28days to 56 days of curing.
- This study has demonstrated the evolution of a binder devoid of the use of cement, thereby effectively contributing to greener binder development.

This study recommends the following:

i. More research is desirable to rid the carbide wastes of impurities and concentrate the calcium hydroxide ($Ca(OH)_2$) content in order to achieve higher, improved strength as the binder is cured.

ii. There is a need for examining the microstructure using the Scanning Electron Microscopy (SEM) to see the interactions amongst its constituent's materials; and to have a better understanding of the morphology of the C-S-H formed, the reacted and unreacted constituents.

iii. There is a need to conduct similar studies on other types of pozzolan with carbide wastes; and observe among other things, the inter-pozzolanic strength development and variartion.

iv. The capacity of the carbide waste generation in Nigeria can be enhanced by establishing polyvinyl chloride (PVC) making industry and thermal power plants using acetylene as fuel.

v. Further tests should investigate the effects of admixtures like accelerators and plasticizers in an attempt to reduce setting times and optimize strength in the CW/PCC mortar mix.

vi. Study the effect of carbide-waste/pozzolan mortars on the health of humans.

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