International Journal of Civil Engineering and Technology (IJCIET)
Volume 9, Issue 2, February 2018, pp. 1–12, Article ID: IJCIET_09_02_001
Available online at http://www.iaeme.com/ijciet/issues.asp?JType=IJCIET&VType=9&IType=2
ISSN Print: 0976-6308 and ISSN Online: 0976-6316

DEVELOPMENT OF A FULLY POZZOLANIC BINDER FOR SUSTAINABLE CONSTRUCTION: WHOLE CEMENT REPLACEMENT IN CONCRETE APPLICATIONS

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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 later 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. Other factor debilitating the use of PC is its high cost which further translates to the cost of mortar/concrete-based structures as buildings, 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 the PC to blended and pozzolanic cements. This study is further developing a binder through by combining a pozzolan, Pulverised Calcined Clay (PCC), and *calcium hydroxide ($Ca(OH)_2$), Carbide Waste (CW), which is the byproduct of carbide after being used to generate acetylene used in other industrial processes. This study has however shown that these two combinations in the presence of water can produce the C-S-H responsible for strength development as in cement hydration. 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. This study tested the pozzolanic binder's strength to British Standard [29] and X-Ray Fluorescence (XRF) analysis and the results shows that this binder generated a 28-day curing strength of about 11MPa with the potential of generating higher later-day strength. This is about one-third the strength of a 32.5N/R cement grade. 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 is about 70%-80% $Ca(OH)_2$. The success of this study could culminate to the use of cheaper and more sustainable construction than the most currently used binder, cement.*

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

Cite this Article: Opeyemi Joshua, Danladi S. Matawal, Tolulope D. Akinwumi, Kolapo O. Olusola, Ayodele S. Ogunro and Razaq B. Lawal, Development of A Fully Pozzolanic Binder for Sustainable Construction: Whole Cement Replacement in Concrete Applications, International Journal of Civil Engineering and Technology, 9(2), 2018, pp. 1–12.
http://www.iaeme.com/IJCIET/issues.asp?JType=IJCIET&VType=9&IType=2

1. INTRODUCTION

Portland Cement (PC) is currently the world most commonly used binder in mortar and concrete applications and the common brands in Nigeria include Dangote, Elephant, Eagle and Ibeto. According to [1], 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 Cements was then seen too far outwit these other existing ones. Over the years, some natural (non-synthetic) binders went extinct while the demands for the remaining types of binders like lime were seldomly 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, [2] concludes that concrete production contributes 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 cost of mortar and concrete based structures as buildings and making housing less affordable for the citizenry. These concerns on cements began to prompt researchers to search for greener and cheaper alternative binders which have so far evolved 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 various 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 [3] and [4] for their utilization but they still have not outweighed the use of PC. Researchers are tending towards the use of binders that are green and more cost-effective.

Although, there have been several attempts by researchers to minimize concrete/mortar-based housing and construction cost such as the use of laterite and gravel in sandcrete block and concrete production [5] [6] [7][8], waste glass as aggregates [9] and as pozzolan [10] [11] and [12]. Some has even used housing financing systems and construction management tools to lower construction cost [13] [14] and [15]. Also, pozzolans improves concrete durability by being more resistant in aggressive environments like in Nitric and Sulphur environments that induce unsoundness in concrete [16]. Researchers are also incorporating indigenous materials and principles to achieve green building [17] [18] [19].

This proposed innovative binding material in this work is intended to produce an alternative to cement from industrial by-products which is intended to be a binder 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 known as C–S–H gel 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, $Ca(OH)_2$ [20]. The Calcium Hydroxide is symbolized as CH. The chemical equation is as shown below:

$C_3S + 4.3H \Rightarrow C_{1.7}SH_3 + 1.3CH$

$C_2S + 3.3H \Rightarrow C_{1.7}SH_3 + 0.3CH$ ------------------------------- Rxn (1)

Where C is CaO; S is SiO_2; and H 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 [21], 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 Rxn (1) above 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 where in there still exist excess uncombined SiO_2, this 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, so there is need to determine experimentally the exact amount of pozzolan needed in the blend with Portland cement for strength optimization. Pozzolanic reaction is as shown:

$S + CH \Rightarrow CSH$ --------------------------------- Rxn (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.

Since it is proven that when a pozzolan (S) reacts with calcium hydroxide (CH) from the bye product of hydration (Rxn (1)), it results in a binding gel matrix formation that is responsible for gain in strength as shown in Rxn (2). Then there exists a possibility which this study intends to explore, that a pozzolan can react independently with another source of CH to produce a binding gel matrix of C-S-H (pozzolanic reaction) in Rxn (2).

This study wants to source the CH in Rnx (1) and Rnx (2) which is [$Ca(OH)_2$], from the industrial waste when acetylene (C_2H_2) is generated from Calcium Carbide (CaC_2) in the presence of water as shown in Rxn (3).

$CaC_2 + 2H_2O \Rightarrow C_2H_2 + Ca(OH)_2$ --------------------------------- Rxn (3).

1.4. Sources of Raw Materials

The major raw materials for the innovative binder are pozzolans and calcium hydroxide. There are a lot of pozzolans currently under research in Nigeria which include:

1. Palm Kernel Nut Ash (PKNA) which is bye products of oil palm nuts after the oil is being extracted [22], Nigeria is currently the third world producer of palm kernel after Malaysia and Indonesia and also produce 55% of the African produce [23].
2. Fly-Ash (FA) which are ash bye products from burning of coal in coal power stations and other applications. They could potentially be sourced from Itobe Power Plant in Kogi state and the federal government has proposed to build three (3) coal power stations in Enugu, Gombe and Kogi States with up to 3000 MegaWatt (MW) capacity. These well 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.
3. [24] identified eight pozzolanic agricultural bye-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 more pozzolans under study like Pulverized Calcined Clay (PCC) currently being developed by the Nigeria Building and Road Research Institute (NBRRI), Bagasse ash and naturally occurring volcanic ash. There are enough deposits of pozzolans to justify this study.

The second raw material is the calcium hydroxide which is intended to be sourced from the by-product of acetylene generation from the hydrolysis of Calcium Carbide, see Rxn (3). The most common and widely used application in Nigeria is in the auto making and repair industry where they are used in the fusing together of auto metal part. [25] identified the negative impacts of calcium carbide waste on dump sites and it's environ, and they include impaired animal and plant life with the possibility of reduced land for agriculture and hazardous to human life. According to [26], the membership of the Nigerian Automobile Technicians Association (NATA) is about twenty-five thousand (25,000) and each produce an average daily quantity of thirty kilogram (30kg) of carbide waste. This implies that about

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 [27].

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

2. MATERIALS AND METHOD

The materials used in this study are borehole water, Dangote cement grade 42.5R, specially prepared fine aggregate (sand) to meet the specification in [28] for the determination of strength of cement, Carbide Waste (CW) collected from road-side auto panel beaters and Pulverized Calcined Clay (PCC) developed in NBRRI. All CW and PCC used in this study was sieved with the 75micron sieve size.

The fine aggregate used in this study for determining the mortar strength of the binders tested was classified using the Unified Soil Classification System (USCS) and the classification tool used was the gradation test via sieve analysis.

The chemical pozzolanic index of the PCC was determined by using the X-Ray Fluorescence (XRF) method of analysis to determine its oxides composition, summing up the percentage composition of the silica, aluminum and iron oxides and checking it with [4] to determine the reactivity index class it belongs. 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 then determined in a standard manner as specified in [28] at the best workability and observed from the 21st through 28th to the 56th curing days. The CW and the PCC were mixed (as a binder) at varying percentages with themselves and the various mortar strengths determined to [28] at the best workability and observed from the 21st through 28th to the 56th curing days. 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. 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 (Cu) is 2.29 and the Coefficient of Curvature (Cc) is 1.05 as derived from Figure 1. Poorly graded as classed in this case does not connote its bad but that it is close to being a uniformly graded since Cu of 2.29 is closer to 1. This sand satisfies the requirements stipulated in [28] for the determination of mortar strength of cement (binder).

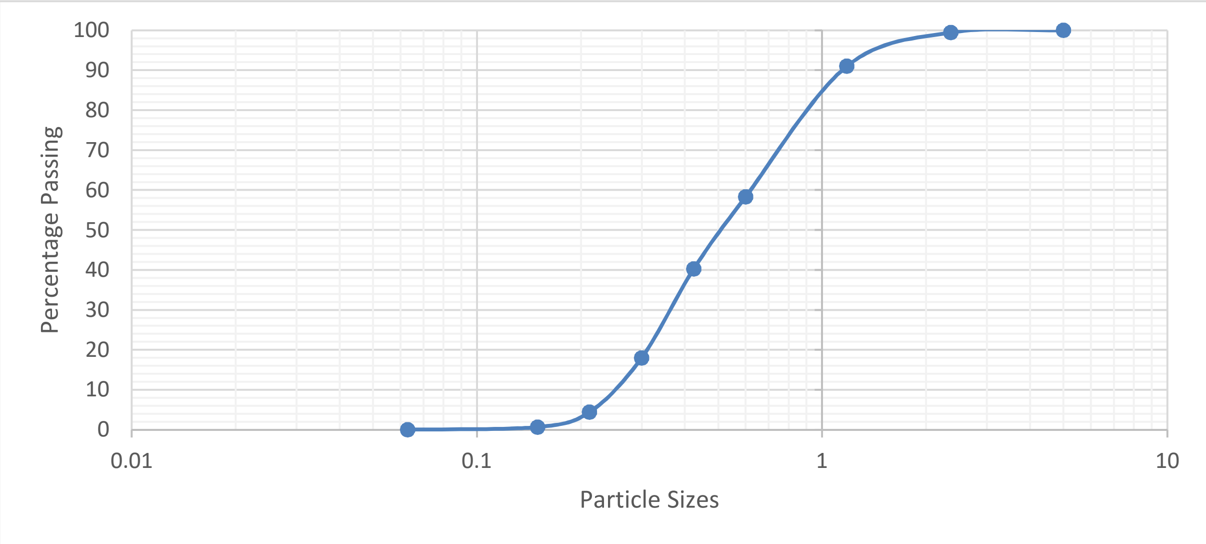

Figure 1 Particle Size Distribution of the Fine Aggregate for All Mortar Strengths

3.2. PCC's 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	TiO_2	P_2O_5	Mn_2O_3	Cr2 O3	LOI	SiO_2+ Fe2O3+ Al_2O_3
% Composition	0.73	66.54	18.60	6.75	0.57	0.03	0.04	0.23	2.25	0.09	0.09	0.03	5.13	91.98

According to [4], 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 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 [29]. Though this standard specifies binder to sand ratio of 1:3 and water/cement (w/c) ratio of 50%, a workable consistence was achieved at w/c ratio of 60%. The mortar strength result is as shown in Figure 2.

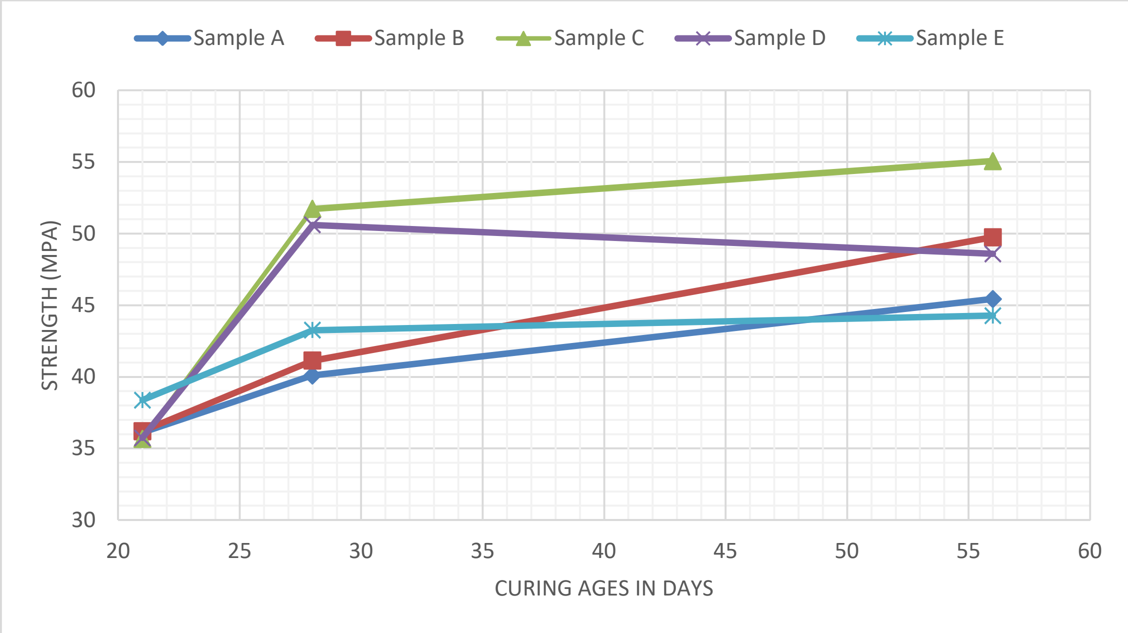

Figure 2 Mortar Compressive Strengths of Cement/Pozzolan at Different Curing Days

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 very high which complements the findings in the pozzolanic reactivity index by the oxides classifying it as a class N pozzolan.

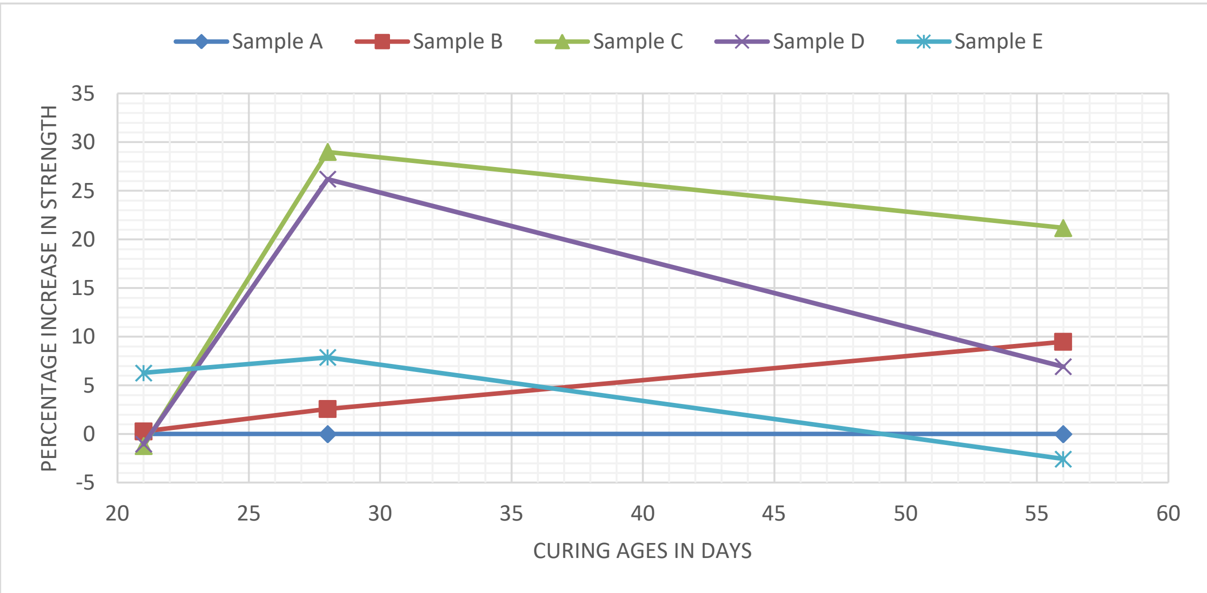

Figure 3 Percentage Increase in Mortar Strengths from the Control of 100% Cement Content

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 attributes generally to the decrease in percentage increase in strength at 56-day curing age compared to the 28-day.

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

This mortar was made with binder wholly void of cement and the strength gain is due to a pozzolanic process alone where C-S-H matrix is formed. The highest strength obtained in this innovative binder is about 11MPa at 28 curing days. This is up to a third of the estimated mortar strength of a grade 32.5N/R cement. This is very remarkable as it indicates that cement which is a universally utilized material can be wholly replaced. A strength gain from 28 to 56 curing-day 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 which include the presence of impurities in the carbide waste that could be deleterious to the expected later strength gain.

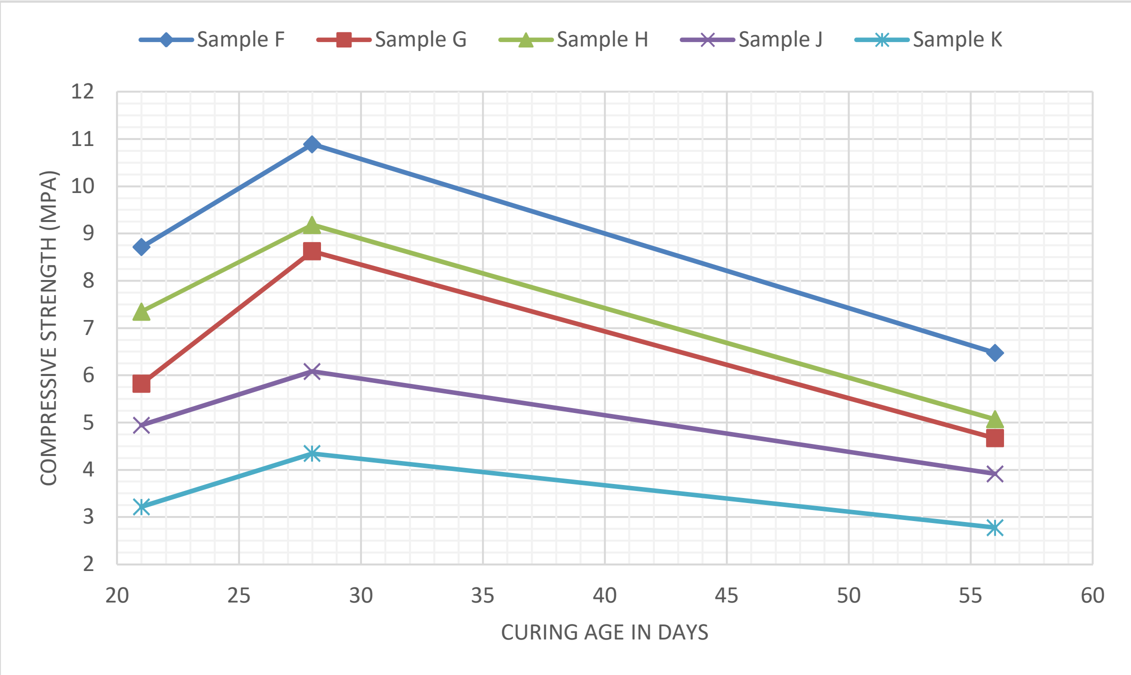

Figure 4 Mortar Strength of Carbide Waste/Pozzolan (Innovative Binder) At Different Ages

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 [26] and the effects of some of these elements on concrete/mortar strengths are yet to be known though it possess a PH of about 12.2 [30] which favours the performance of steel in reinforced concrete by providing 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 was still done to ensure that whatever bind 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 possess 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 about a week before demolding. There exists 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 made demolding 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. CONCLUSION AND RECOMMENDATIONS

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

- From section 3.1 and Figure 1, the sand used in the mortar mix satisfies the requirements stipulated in [28] 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 NBRRI's PCC used in this study belongs to class N pozzolan which is expected to be a natural pozzolan with high pozzolanic reactivity index as classed by [4]. This is actually true of PCC since it is a calcined natural clay deposit.
- From section 3.3, Figure 2 and Figure 3, the NBRRI's PCC is a pozzolan of a very high strength activity index of 129% as specified in [29]
- From section 3.4 and Figure 4, there exists a strength development based solely on a pozzolanic process on the interaction between the PCC (pozzolan) and carbide waste in the complete absence of cement. The optimum strength of about 11MPa at 28 curing days from a binder combination ratio of 60%:40% of PCC (pozzolan) and carbide waste respectively (sample F) which is about a third of the mortar strength from cement grade 32.5N/R. This is quite remarkable as the development of this study have a potential to eliminate the use of cement in construction and in consequence introduce more economically affordable binder that is also environmental friendly than cement. This has a potential to the provision of more affordable housing to the citizenry.
- It was observed that there was no strength when each 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.

This study hereby recommends the following:

1. More research to rid the carbide wastes of impurities to concentrate the calcium hydroxide ($Ca(OH)_2$) content to check for the possibility of improved strength.
2. Examining the microstructure with the aid of 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.
3. Do this same study with other pozzolan to study the inter pozzolanic strength variation and development with carbide waste.

4. In this line of research, this is a new evolution of binder from the previous pozzolanic and blended cements in strength optimization and greener binder development.
5. 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.
6. 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.
7. To study the effect of carbide-waste/pozzolan mortars on the health of humans.

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