Pulverized Calcined Clay and Carbide Waste as Alternative Binder in Concrete and Mortar Applications for Sustainable Construction

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Abstract

Portland cement (PC) based concrete is the world's most consumed man-made material and this consequently puts lots of demand on cement as a binder. The CO_2 gas emission during cement clinker production has placed this important material into non-environmental-friendly classification with quest for greener alternatives being on the rise. A recent study showed combination of Pulverized Calcined Clay (PCC) and Calcium Carbide Waste (CCW) as possible alternative for total PC replacement with resulting appreciable mortar strength but delayed setting times and lower strength than PC mortars. This paper reports on effects of PCC-CCW as alternative binder on strength properties of mortars. The mortar mixes had superplasticizers added to reduce water/binder ratio while the CCW was treated to reduce impurities with a view to improving the strength development and a bid to mitigate the observed setbacks of earlier study. The pozzolanic activity indices of the PCC was determined via X-Ray Fluorescence (XRF) and strength determination (strength activity index). The PCC was combined with Purified CCW to determine the binder's strengths at varying PCC:CCW replacements to determine the prescribed mix combination for optimum strength. Improved optimised mortar strength of 13.11MPa was achieved compared to 11.89MPa in the previous study.

Keywords: Pulverized calcined clay (PCC); Calcium carbide-waste (CCW); Alternative binder; Pozzolanic activity; Cement replacements; Setting times.

1.0 INTRODUCTION.

Over the years, binders in mortar and concrete applications have evolved from clays, limes and natural pozzolans in the past centuries to advanced binder like Portland cements with astronomical strengths compared to the medieval binders used in the production of very high strength concrete. This advanced binder has made possible the development of higher-strength demanding structures like high-rise buildings, complicated bridges and other higher strength demanding applications. The use of cements today is mostly in mortar or concrete production which are used in building structures, dams and other heavy and light weight applications. According to Naik (2008), concrete today is the world most consumed man-made material.

In the 1980s, there was a growing awareness of climate change principally due to global warming. This was attributed to the depletion of a protective layer in the atmosphere, the ozone layer, that shields the earth from dangerous radiations which is being depleted by the greenhouse gasses which are principally by products of our industrial activities and they include carbon dioxide, carbon monoxides and chlorofluorocarbons (United Nations, 1987). One of the major industrial processes that releases these greenhouse gasses is the concrete/cement production. The Portland cement (PC) that was a breakthrough in construction was discovered to be a non-environmentally friendly material as its CO_2 emitions contributes about 5% of the annual anthropogenic global CO_2 emissions of which the bulk is from the production of cement (Crow, 2008). Moreover, the production of one ton of Portland Cement releases as much as about a ton of CO_2 into the atmosphere (Mehta, 2009). The constant excavation and depletion of lime stone (calcium carbonate) from their sources also possess environmental hazards to the source communities and depletes lands meant for farming and other economic activities.

Another factor that is debilitating the use of PC is its high cost which further translates to higher cost of mortar and concrete based structures as buildings and making housing less affordable to the general citizenry.

In the 96th plenary session of the United Nations (UN) resolutions 42/182, the committee recognizes the role of carbon dioxide (CO_2) in climate change and hence, global warming. Member countries were urged to start taking initiatives to reduce the CO_2 emissions in their various countries and especially in the developed countries (United Nations, 1987). These have led to much research to reduce the CO_2 emissions and at a lower production cost. The research has evolved PCs to the discovery and development of pozzolans (from industrial and agro wastes) and other blends that can partially replace PCs to some degree and the utilization of some pozzolans have even been standardized in some standards as in ASTM C618-15 and BS EN 197-1:2011. These methods also have the potential to reduce production costs since they could be partially developed from wastes, saving the environmental hazards of even disposing them since they are being recycled into other forms. Some new studies have developed geopolymer cements with the potential to fully replace PCs (Ul. Haq et. al., 2014; Turner and Collins, 2013). The successes recorded in these efforts possess the potential to drastically reduce the CO_2 emissions associated with Portland Cements and lower cost of production. One of the very few recent efforts is the development of a total Portland Cement replacement by combining a pozzolan mostly from industrial wastes with amorphous slack lime which is another industrial waste from the generation of acetylene (C_2H_2) from calcium carbide, the reaction is as shown in Equation 1.

$$\underset{\text{(Calcium Carbide)}}{CaC_2} + \underset{\text{(water)}}{2H_2O} \longrightarrow \underset{\text{(Calcium Carbide waste)}}{Ca(OH)_2} + \underset{\text{(Acetylene)}}{C_2H_2} \quad \text{------ Equation 1}$$

There are current researches to fully replace cement as a binder by combining pozzolans and CCW with some level of successes and they include Rattanashotinunt et. al. (2013) who combined a pozzolan, baggase ash, with CCW in concrete to obtain a 28day compressive strength of about 22MPa; and Makaratat et. al. (2010) combined fly ash and CCW in concrete to obtain a 90day compressive strength of over 28MPa.

This process is simply generating hydration reaction by a fully pozzolanic process, combining a pozzolan and slack lime in the presence of water. Joshua et.al., (2016) established that there was indeed a hydration reaction and strength development when a pozzolan, Pulverized Calcined Clay (PCC), was combined with slack lime ($Ca(OH)_2$, calcium carbide waste (CCW)), an industrial waste from the generation of acetylene gas from calcium carbide used in the production of Polyvinyl Chloride (PVC) and in welding steels especially in the auto industry. It was concluded that this combination (PCC-CCW), when tested for its binder strength as prescribed in BS EN 196-1:2016, generated a twenty-eight (28) day strengths as much as about 11MPa, when combined with as-received CCW without any form of treatment and sieved with the 75μm sieve size (Joshua, et.al., 2016). This study is principally to research on how this strength could be improved upon by purifying the CCW (eliminate impurities and increase the amorphous slack lime concentration) and the use of super plasticizer to reduce the water binder ratio for possible strength improvement. It is expected that if appreciable success is recorded in further research, the cement type and strength-class would be included and defined in national and international standards. The utilization could then be adapted in the study area as highlighted in Joshua et. al., (2017). Though, CCW in Nigeria is between 70-80% calcium hydroxide ($Ca(OH)_2$) concentration and the impurities in CCW include copper, lead, iron, manganese, nickel and zinc (Chukwudebelu *et al*., 2013).

2.0 RESEARCH SIGNIFICANCE

This study is intended to totally replace the environmentally unfriendly PC with a new type of binder that will be made totally from industrial wastes thereby eliminating the CO_2 emission, decongest our landfill and at a reduced binder cost. This can be a measure of implementing the United Nations resolution (Montreal protocol, 1987) on control of activities and substances that depletes the ozone layer.

3.0 AIM AND OBJECTIVES

The aim of this study is to attempt to develop a green binder based on a fully pozzolanic process for concrete and mortar applications that can replace the use of cement and hence eliminate the negative impact of the use of cement in construction with a competitive strength with cement. The primary objectives in this study are to simply source a pozzolan with known pozzolanic indices and calcium hydroxide ($Ca(OH)_2$) sourced from an industrial waste, and combine them in the presence of water to initiate a pozzolanic reaction that results to the formation of calcium-silicate-hydrate (C-S-H) resulting to gain of binding strength. Pozzolans could be sourced from calcining some selected agricultural and industrial wastes like 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), Paw-Paw Leaf Ash (PPLA) and Palm Kernel Nut Ash (Joshua et. al., 2015; Joshua, et. al., 2017; Ettu et. al., 2013) but the one used in this study is Pulverized Calcined Clay (PCC). The amorphous ($Ca(OH)_2$) in this study was sourced from the industrial waste generated from the production of acetylene (C_2H_2) gas from the hydrolysis of calcium carbide (CaC_2). Acetylene are used in the industrial

production of Polyethylene and polyvinyl-Chloride (PVC) plastics, combined with other fuels to power internal combustion engines and combined with oxygen to generate heat for welding in steel (Sharma et. al., 2012). The other objectives are simply to determine the physical and chemical characteristics of the individual materials used in this study and determine the binder strength of the pozzolan/($Ca(OH)_2$) combination in accordance to BS EN 196-1:2016.
This study is a continuation of the pilot study conducted in Joshua et.al. (2016)

4.0 MATERIALS AND METHODS

The materials used in this study are special fine aggregate (sand) that conform to the requirements of BS EN 196-1:2016 for the determination of the strength of cement (binder); the cement used is the rapid hardening Dangote brand with a 42.5 strength class; the pozzolan, Pulverised Calcined Clay (PCC), is a product developed from the Nigerian Building and Road Research Institute's (NBRRI) Prototype Pilot pozzolana plant in NBRRI laboratory complex in Ota, Ogun State; the Calcium Carbide Waste (CCW) was collected from local auto vehicle maintenance workshop; Conplast SP 432MS superplasticizers; and the water is a bore hole water.

The methods employed in this study were basically laboratory procedures and they include gradation of the sand used in the determination of the strength of the binder; concentrating the slack lime content of the CCW using the Solubilisation and Evaporation Process Technology (Chukwudebelu, 2013); utilizing the X-Ray Fluorescence (XRF) to determine the oxide compositions of the cement, PCC and the Purified Calcium Carbide Waste (PCCW) as a tool to characterize these materials; X-Ray Diffraction (XRD) to determine the composition of the PCCW and PCC to assess the hydration rate; combine the PCC-PCCW (innovative binder) mix at varying percentages as shown in Table 1; determination of the binder strength in accordance to BS EN 196-1:2016 and comparing the strength values with the standard regulating the use of cement as a binder as recommended in BS EN 197-1:2011; and some other test results from the preceding research work in Joshua et. al., (2016) would be used in this study.

Table 1: Percentage Makeup of the Binder Content in the Determination of Mortar Strength

S/N	*Percentage Cement content*	*Percentage Pozzolan (PCC) content*	*Percentage PCCW content*	*Symbol*
1	-	80	20	PPC82
2	-	70	30	PPC73
3	-	60	40	PPC64
4	-	50	50	PPC55
5	100	-	-	CM100 and A
6	90	10	-	B
7	80	20	-	C
8	70	30	-	D
9	60	40	-	E

4.0 RESULTS AND DISCUSSIONS

4.1 Gradation of the Fine Aggregates Used in the Determination of Mortar Strength

Figure 1 is the gradation curve of the sand used, the sand is classified as a poorly graded sand (SP) using the Unified Soil Classification System (USCS). The Coefficient of Uniformity (Cu) is 2.21 and the Coefficient of Curvature (Cc) is 1.10 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 (Holtz and Kovacs, 1981). This sand satisfies the requirements stipulated in BS EN 196-1:2016 for the determination of mortar strength of cement (binder).

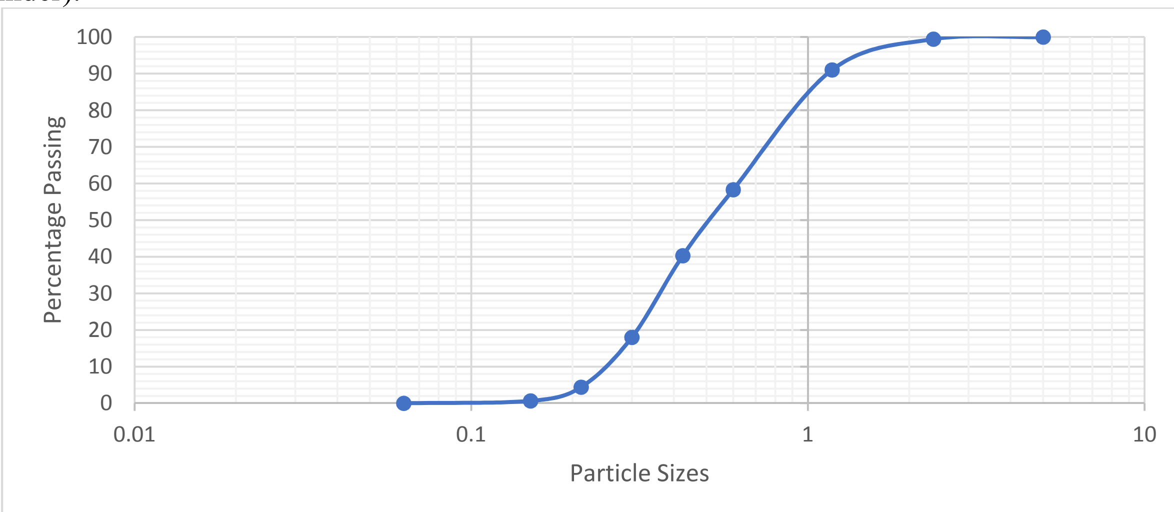

Figure 1: Particle Size Distribution of the Fine Aggregate (Sand) for All Mortar Strengths Setting Times of the Binders

The paste if standard consistent was achieved at a higher water content than the cement as seen in Table 2. Also, the CCW content have a direct relationship with the setting times and water content for their paste of standard consistence. The PCC:PCCW mix binders have delayed setting times than the cement and this is expected because pozzolanic processes are usually a later strength development phenomenon. All test parameters in samples PPC82 and PPC73 are significantly closer than obtained with other PCC:PCCW combinations.

Table 2: Paste of Standard Consistence and Setting Times of the binders used

Specimen	Weight of Cement (Kg)	Quantity of Water (Kg)	Water Content, Paste of Standard Consistence (%)	Initial Setting Time (Mins)	Initial Setting Time (To the Nearest 5mins)	Final Setting Time (Mins)	Final Setting Time (To the Nearest 15mins)
PPC82	0.500	0.152	30.4	391	390	523	525
PPC73	0.500	0.156	31.2	401	400	548	550
PPC64	0.500	0.184	36.8	427	425	581	580
PPC55	0.500	0.191	38.2	442	440	598	600
CM100	0.500	0.132	26.4	128	130	187	180

4.2 Solubilisation and Evaporation Process of the CCW to Obtain PCCW.

The calcium carbide waste (CCW) was purified by solubilisation and evaporation process. In this method as reported by Chukwudebelu (2013), a gram of the CCW was left in a liter of water to dissolve for a period of 24 hours, filtered and the filtrate vaporized to recover the dissolved solute, Purified Calcium Carbide Waste (PCCW). About 78% recovery was achieved but this study had to elevate the dissolution temperature to 50^oC to achieve a percentage recovery about 75% solute. The anhydrous $Ca(OH)_2$ content in the CCW was 65% and PCCW was 88% from the XRF analysis, see Table 3.

4.3 PCC's Classification Index and chemical analysis of the binders' materials

This was achieved by the XRF analysis and the result is as presented in Table 3

Table 3: Binders XRF Analysis Results

Elemental Oxides	Oxide Percentage Composition by mass													$Fe2O_3$+ SiO_2+ Al_2O_3
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	Mn_2O_3	Cr_2O_3	LOI	
CM100	60.99	15.91	4.51	3.42	2.78	1.67	0.05	0.24	0.23	0.28	0.04	0.02	10.72	
PCC	0.73	66.54	18.6	6.75	0.57	0.03	0.04	0.23	2.25	0.09	0.09	0.03	5.13	91.89
CCW	65.77	3.56	1.59	0.21	0.06	0.02	0.09	0.01	0.05	0.01	0.02	0.01	26.3	
PCCW	88.17	1.32	0.72	0.15	0.1	0.01	0.1	0.02	0.01	-	-	-	14	

According to ASTM 618 (2015) and as shown in Table 3, the NBRRI's PCC is a class N pozzolan since the sum of the percentage compositions of Fe_2O_3, SiO_2 and Al_2O_3, 91.89%, is significantly 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.

From the XRF analysis, there was an improvement in the CaO content from about 66% CCW as-collected to 88% after treatment. Some other elemental percentage composition became negligible. The improvement in the CaO content is an indication of increase in the concentration of the $Ca(OH)_2$ in the purified waste (PCCW). There were slight improvements in the contents of Na_2O and K_2O probably because they are also soluble in water.

4.4 PCC Pozzolanic Strength characteristics

Figure 2 is the mortar strength of the binder determined as specified in BS EN 196-1:2016 with the cement partially replaced by the pozzolan (PCC) at varying degree of replacements.

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 50%, a workable consistence was achieved at w/c ratio of 60%. The mortar strength result is as shown in Figure 2.

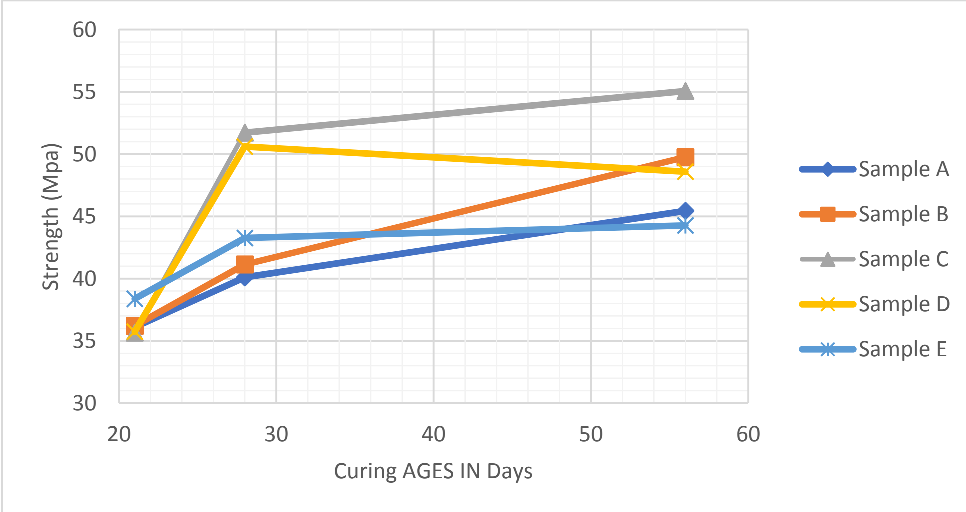

Figure 2: Mortar Compressive Strengths of Cement/Pozzolan Binder at Different Curing Days

The curing ages for all the PCC replacements were generally more than the control (sample A, 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 very high and it complements the findings in the pozzolanic reactivity index by the oxides classifying it as a class N pozzolan.

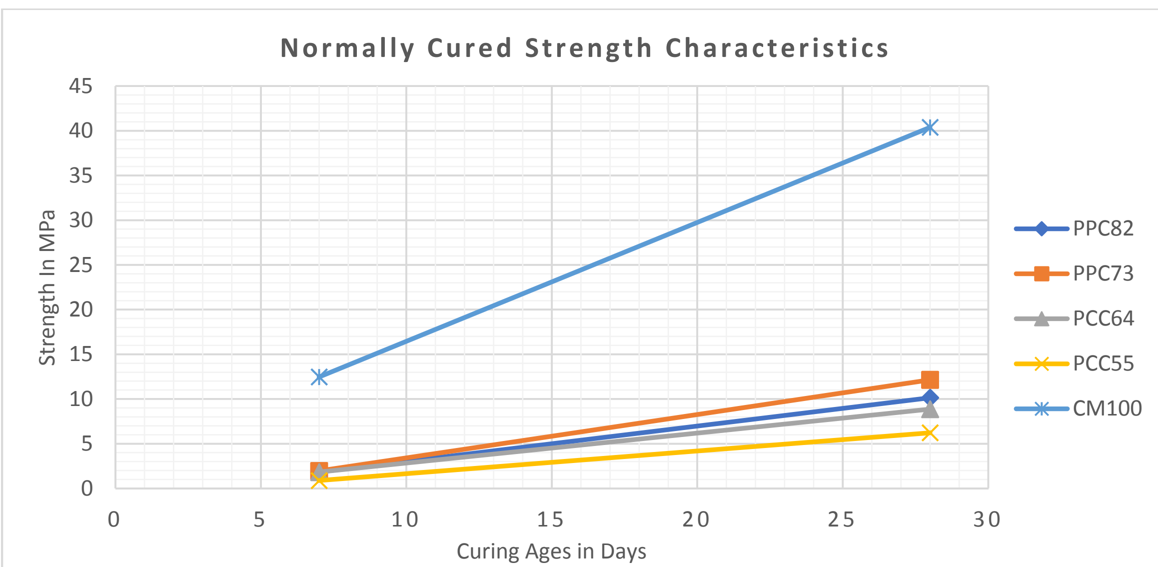

Figure 3: Mortar Strength of the PCC/PCCW Binder at 7 and 28 Curing Ages at Normal Temperatures

Figure 3 shows the strength of the different combination ratios of the PCC/PCCW binder at 7 and 28 curing ages at natural ambient temperatures of between 20^{o}C-27^{o}C. The optimum 28-day strength of 12.14MPa was obtained at a PCC:PCCW combination at 7:3 ratios respectively.
When the same process that obtained the results in Figure 3 was repeated but cured at 50^{o}C for the first-seven days, there was a slightly significant increase in the strength values at the different

curing ages. The optimum 28-day strength was 13.11MPa at PCC:PCCW combination ratio of 7:3 respectively as shown in Figure 4.
The optimum 28-day strength in the previous study was 10.89MPa at a PCC:CCW ratio of 6:4 respectively. The slight strength increase could be attributed to the lower water demand due to the use of superplasticizers, and increased concentration of the $Ca(OH)_2$ by treating the CCW to obtain the PCCW. There was also reduction in the level of impurities as the colour of the CCW was a slightly greyish-white while that of the PCCW was a brighter and purer white colouration.

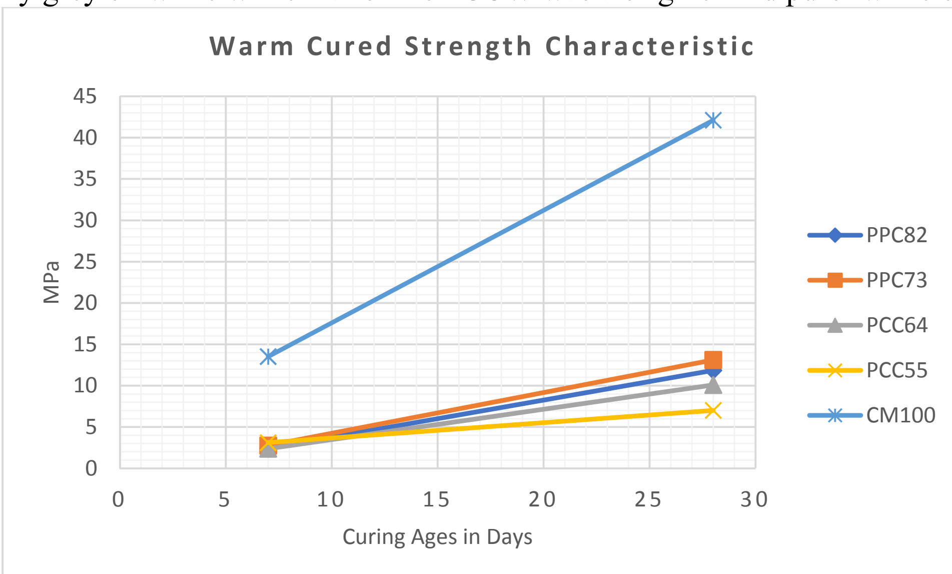

Figure 4: Mortar Strength of the PCC/PCCW Binder at 7 and 28 Curing Ages at 50°C in the first-seven days

5.0 Conclusion and recommendation

Results from the study show the alternative binder to cement shows that the PCC:PCCW with superplasticisers and PCC:CCW binder possess moderate binding property based on a fully pozzolanic process, though the PCC:PCCW combination with superplasticizers shows improved strength characteristics than the PCC:CCW combination as shown in Figures 2, 3 and 4.

From Table 3 and Figure 2, the NBRRI developed PCC is a pozzolan of a very high strength activity index of 129% and belongs to the class N pozzolan as specified in ASTM C311/C311M (2013) and ASTM 618 (2015). The of the sum of oxides Fe_2O_3, SiO_2 and Al_2O_3 is 91.89% which is significantly higher than the 70% recommended by the code. This indicates a possible higher pozzolanic activity and justifies the natural (N) classification since it was sourced from a natural source, clay deposit.
The warm curing at 50°C shows faster hydration and slightly better strength property as shown in Figures 3 and 4. This is evident by higher strengths in the warm cured mortars than the ones normally cured. And the optimized strength of 13.11MPa was obtained at PCC:PCCW ratio of 7:3 respectively. The greater the PCCW content than the optimum, the greater the decline in strength.
It is no doubt that the direction of this study will drastically address the ill environmental impact and global warming effects due to cement and lead to the development of a cleaner binder since its beign generated from wastes.
Based on these conclusions, the following are hereby recommended:

i. Examining the microstructure of the hydrated phase of the PCC:PCCW combinations 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.
ii. This study could be repeated with the use of other pozzolans to study the effect of different pozzolanic indices on the strength characteristics when combined with PCCW.
iii. Further tests should investigate the effects of admixtures like accelerators and other possible ones like water reducers in an attempt to reduce setting times and water binder ratio to enhance the strength characteristics in the PCC/PCCW mortars.
iv. To study the effect of carbide-waste/pozzolan mortars on the health of humans since CCW dump sites have been shown by Ihejirika *et.al*. (2014) to impair plant and animal life.
v. The optimised binder of PCC:PCCW could be recommended in low strength demand concrete and mortar applications.

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