

Determination of the Pozzolanicity of Cocoa Pod Ash at Different Temperatures

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Abstract

Pozzolans are siliceous or aluminous materials which possess little or no cementing property but chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties. There is paucity of information on the pozzolanicity of Cocoa Pod Ash (CPA). Hence, this study investigated the pozzolanicity of CPA.

Cocoa pods were obtained from selected farms in Egba Odeda, Ogun State Nigeria. The Cocoa pods were washed, sundried and calcinated to ashes in a furnace between 600^o C to 1000^o C at Science Laboratory Technology Department, Federal Polytechnic Ilaro, Ogun State. Chemical analyses and X-ray Crystallography were carried out on the CPA to determine the types of oxides present and their varying percentages. The oxides were Silica (SiO₂), Ferric (Fe₂O₃), combined percentages of Ferric and Aluminum oxides (Fe₂O₃ and Al₂O₃), Calcium (CaO), Magnesium (MgO) and Sulphur (SO₃). The moisture content and the Loss of Ignition (LOI) of the CPA samples were also determined.

The oxides of Silicon, Ferric, Aluminium, Calcium and Magnesium oxide ranged between 6.39-8.00; 0.78 - 0.89; 1.74- 2.29; 7.15-8.42 and 4.38-5.16% respectively. Sulphur trioxide and LOI ranged 3.51- 3.78 and 27.2- 32.0%, respectively. The X-ray crystallography showed that the total percentage composition of SiO₂, Al₂O₃ and Fe₂O₃ in CPA varied from 14.87-24.21%. The study showed that CPA did not satisfy the minimum 70% requirements stipulated by ASTM C618 (2005) for a pozzolan after the analysis of the oxides but it satisfied all the requirements for LOI, hence CPA is a weak pozzolan.

Keywords: Pozzolans, Cocoa Pods Ash (CPA), X-ray crystallography, Oxides, Cementitious

Introduction

Nigeria is the fourth largest producer of cocoa and harvest seasons are often accompanied with tones of residues that constitute environmental menace. Cocoa is produced in fourteen states in Nigeria, but unfortunately average annual growth rates are declining by 8.3%. Cocoa pods can be converted to potassium carbonate (potash) to produce fertilizer, soaps, printing inks; fire extinguisher and dehydrating agent pigments (Asha *et al.*, 2014). Cocoa Pod ash (CPA) is a by-product of cocoa pods obtained after its calcination in a furnace. Calcination is a thermal treatment process that decomposes and cause phase transition or removal of a volatile fraction from the original material like Cocoa pods.

The use of Pozzolans in the production of concrete is not a new development or trend in the construction industry. At the outset, the use of pozzolans for building works was necessitated by the need to find a material that can bind sand and gravel together in the presence of water, and also give the required strength when used for residential and public building construction (Kartini, 2011; Guiherme *et al.*, 2008). A pozzolan is a siliceous or siliceous and aluminous material which possesses little or no cementing property but in a finely divided form and in the presence of water, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties (Dipayan, 2007).

The pozzolanic reaction is the chemical reaction that occurs in Portland cement containing pozzolans. It is a secondary reaction that amplifies the primary cement and water reaction. The characteristic features of pozzolanic reactions are initially slow with the result related to heat of hydration and the strength development will be slow. The reaction involves the consumption of calcium hydroxide (Ca(OH)₂) and not its production. The science behind pozzolanic reaction is that the particle-binding glue of concrete Calcium Silica Hydrate (CSH) results from the combination of hydroxides, which does nothing to contribute to cement and density, but actively works against it (Ghassan and Panagiotics, 2013; Olonade *et al.*, 2011).

Construction of buildings in the 21st century is a day to day activity especially with the increasing demand for safe, durable and economical concrete structures, and this cannot be done without the use of concrete. However, the environmental effects of the release of toxic gases from cement production into the atmosphere and the exorbitant cost of manufacturing cement have all necessitated the use of pozzolans as a partial replacement for cement in the production of concrete (Ernesto *et al.*, 2008; Olonade *et al.*, 2011).

Methodology

The study area

The study was carried out in the town of Odeda, Ogun State, Nigeria, which is located in the South Western part of Nigeria between Latitude 8°06'70" and 8°06'98.7 North and Longitude 4°14'28.2" and 4°14'56.9" East. The study was done in October, 2016 which was the harvesting season so as to have enough quantity needed for this research. Cocoa pods were randomly picked, gathered and washed of dirt. Pods were dried and calcinated in a furnace at a temperature ranging from 600°C to 1000°C at an interval of 100°C. The chemical composition of CPA was determined using chemical analysis and X-ray Crystallography at the Science Laboratory Technology Department, Federal Polytechnic Ilaro, Ogun State with the aid of Bruker's X-ray Diffractometer.

Determination of chemical composition of cpa using chemical analysis

Determination of silica (SiO₂) percentage: CPA of 0.5 g was weighed, mixed thoroughly with 0.5 g of Ammonium Chloride (NH₄Cl) in a 50 ml beaker and covered with a watch glass. 6 ml of Hydrogen Chloride (HCl) was added by allowing the acid to run down the lip of the covered beaker followed by addition of 1-2 drops of Hydrogen Nitrate (HNO₃). The chemical reaction was allowed to subside and stirred with a glass rod. The covered beaker was set on a steam bath for digestion for 30 minutes with occasional stirring and breaking up of any lumps to facilitate complete decomposition of the CPA.

A medium textured filter paper was fitted to funnel, and the jelly-like mass of silica acid was filtered completely without dilution. The solution was allowed to drain through the beaker and was rinsed with hot HCl, and then with 10ml portions of hot water. The filter paper and residue were transferred into weighted platinum crucible and weighed as W₁. The material was dried and ignited slowly without inflaming until the filter paper has charred at 1100 - 1200°C for 1 hour in a muffle furnace. This material was cooled in desiccators and weighed as W₂.

The SiO₂ obtained contained small impurities which were treated in the crucible with 2ml of water, 2 drops of sulfuric acid (H₂SO₄) 1:1, and 20 ml of Hydrogen Fluoride (HF), and cautiously evaporated to dryness. The residue was then heated at 1050 - 1100°C for 5 minutes, and cooled, and weighed as W₃. The difference between this weight and the weight previously obtained represents the weight of SiO₂ using equation (1)

$$\text{Silica \%} = \frac{W_1 - W_2 + W_3}{W} * 100 \quad (1)$$

Where: W₁ = weight of insoluble impurities (g), W₂ = weight of impurities (g); W₃ = weight of silica recovered from iron and aluminium oxide (g); W = weight of sample taken (g)

Determination of ferric oxide (Fe₂O₃) percentage: The solution (100 ml) from silica filtrate (made up to 250 ml) was cooled to 10°C; while a freshly prepared and filtered 5% aqueous cupferron solution was added slowly. These were rigorously stirred until there was no further formation of brown precipitate. After thorough stirring, the solution was filtered through Whatman filter paper No. 41 and was precipitated several times with 10% by volume of HCl containing 1.5 g of cupferron per liter, and twice with 5 ml of ammonia solution to remove excess cupferron, and finally washed once with water. The precipitate was charred in a weighed platinum crucible; ignited to constant weight at 1000°C.

Determination of combined percentage of ferric oxide and aluminium oxide: 5ml of HCl was added to the filtrate reserve after separating silica. Few drops of methyl red indicator was added and treated with Ammonium Hydroxide, NH₄OH₂(1:1) until the colour of the solution became distinctly yellow. The solution containing the precipitate was heated to boiling point for about 50 seconds and allowed to settle for 5 minutes. This material was filtered using medium textured filter paper and hot solution of Ammonium Nitrate (20 g/l) was used in washing the precipitation for at least 3 times.

The precipitate was dissolved using hot HCl (1:2) and stirred thoroughly by macerating the paper. The solution was diluted to about 100 ml and re-precipitation carried out as done previously. The solution was filtered and the precipitates washed with 10 ml portion of hot NH₄NO₃ solution (20 g/l). These filtrates were combined, set aside and reserved for the determination of calcium oxide (CaO). The precipitate was placed in a weighed crucible and the papers were heated slowly until charred. This material was finely ignited to constant weight at temperature of 1050°C - 1100°C. Equations 2 and 3 were used to determine Iron and Aluminium Oxides present in CPA.

$$FeO_3(\%) = \frac{\text{Weight of Precipitate}}{\text{Weight of Sample}} * 100 \quad (2)$$

$$Al_2O_3 + FeO_3 \% = \frac{Si}{W} * 100 \quad (3)$$

Where: Si = weight of Silica (g)

Determination of calcium oxide (CaO) percentage: Approximately 1.0 g of finely grounded CPA was weighed into an Erlenmeyer flask and 50 ml already heated ethylene glycol (100-120°C) was added. The flask was closed with a stopper and heated on a magnetic stirrer hot plate for about half an hour to bring the free calcium oxide into solution. The temperature of the hot plate was maintained between 70-80°C for 20 minutes. The resultant solution was filtered through a Butcher-funnel containing double filter paper, 10 ml portion of glycol was used to wash the precipitate, and about 15 ml of water was added to the filtrate. The filtrate was titrated against 0.1 ml HCl using 2 drops of 1% bromocresol blue/green indicator. A change in colour from blue to yellow marked the end point. Equation 4 is used to compute CaO%.

$$CaO\% = \frac{0.02804N}{W} * 100 \quad (4)$$

Where: N= normality of HCl, W = weight of CPA (g)

Determination of magnesium oxide (MgO) percentage: The filtrate was acidified with HCl after the removal of CaO, and concentrated to about 50 ml. Approximately 10 ml of Ammonia Hydrogen Phosphate (25% w/r) was added to the solution and cooled to 10°C by placing in iced water. NH₄OH was added in drops to the solution with constant stirring until it turned yellow. Equation 5 is used to compute MgO%

$$MgO\% = \frac{\text{Weight of Ignited Residue}}{W} * 100 \quad (5)$$

Determination of sulphur trioxide (SO₃) percentage: 5 g of finely grinded CPA was weighed into a conical flask. The acidity of HCl was adjusted to 4.5-5 using a pH meter; 1 ml of HCl was then added to the sample in the conical flask. The solution was heated to boiling while stirring gently. Barium chloride (BaCl₂) solution was added slowly until precipitation appears to be complete. Then 2 ml of Barium Chloride (BaCl₂) was added. The precipitate was digested at 80°C to 90°C for not less than 2 hours. The contents solution was added slowly until precipitation appears to be complete. Then 2 ml of Barium Chloride (BaCl₂) was added. The crucible was kept in furnace and ignited at 800°C for 1 hour after which it was cooled in a desiccator and weighed. The Sulphur Trioxide percentage was determined using equation 6

$$SO_3 = \frac{\text{Weight of BaCl}_2}{\text{Weight of Sample}} * 100 \quad (6)$$

Determination of chemical composition of CPA using x-ray crystallography: A sample of CPA was mounted on a goniometer which was used to position the sample at selected orientations. The sample was bombarded with a finely focused monochromatic beam of X-ray producing a diffraction pattern of regular spaced spots known as reflections. The two dimensional images taken at different rotations were converted into three dimensional model of the density of electrons within the crystal using mathematical method of Fourier transform, combined with chemical data known for the sample. The result was then displayed on the computer.

Determination of CPA moisture content: Samples of CPA were weighed and recorded as wet weight of sample (A). The wet sample was dried to a constant weight at a temperature not exceeding 115°C using an oven. The sample was allowed to cool and weighed again as the dry weight of sample (B). The relationship for the computation of moisture content is described in equation 7

$$\text{Moisture Content \%} = \frac{A-B}{B} * 100 \quad (7)$$

Determination of loss of ignition of CPA: A ceramic crucible was weighed empty and the CPA sample was added to the ceramic crucible. The crucible was placed in the oven and burnt at 600, 700, 800, 900, and 1000°C for one hour. The crucible was then brought out of the oven and placed on a fiber ceramics plate and allowed to cool and weighed. The LOI was computed using equation 8

$$LOI = \frac{n_2 - n_3}{n_2 - n_1} * 100 \quad (8)$$

Where: n₁ = weight of crucible (g), n₂ = weight of crucible and sample (g), n₃ = weight of crucible and sample after burning (g).

Results and Discussion

At 800°C, silicon dioxide had the highest percentage of 8.05 while the lowest percentage of silicon dioxide was 6.39% at 1000°C. The result showed that at 600°C to 800°C, Silicon dioxide increased from percentage of 6.86 to 8.05 before finally diminishing at a temperature of 900°C from percentage of 7.24 to 6.39 at 1000°C. The required

parameters for the determination of SiO_2 and Fe_2O_3 are presented in Tables 1 and 2.

Weight (Kg)	Temperature ($^{\circ}\text{C}$)				
	600	700	800	900	1000
W_1	1.284	1.746	2.491	1.651	1.343
W_2	1.262	1.737	2.463	1.632	1.314
W_3	0.0123	0.0231	0.0123	0.0172	0.003
W	0.5	0.5	0.5	0.5	0.5

Ferric oxide had the highest percentage of 0.89 at temperature of 800°C while the lowest percentage was 0.72 at 900°C and 1000°C . Percentage of Al_2O_3 was the lowest at 1000°C with value of 1.81 while the highest value of 2.29 was recorded at 800°C .

Temperature ($^{\circ}\text{C}$)	Weight of Precipitate (g)	Weight of Samples (g)	Ferric oxide (FeO_3) (%)
600	0.0797	10.223	0.78
700	0.0824	10.173	0.81
800	0.091	10.223	0.89
900	0.0732	10.167	0.72
1000	0.0731	10.153	0.72

In comparison with ASTM C618 (2005) specification, the total percentage of SiO_2 , Al_2O_3 , and FeO_3 in CPA must not be less than 70% before it can be considered as a pozzolan. None of the ashes produced met the minimum requirements for pozzolans. Moreover, the highest value of total percentage SiO_2 , Al_2O_3 , and FeO_3 was 11.22 at temperature of 800°C while the least value was 8.92 at temperature of 1000°C .

The highest percentage of CaO was 8.42% at 800°C and lowest value was 6.71% at 1000°C . The percentage composition of magnesium oxide (MgO) in CPA for each of the temperature ranged from 4.11-5.16%. The lowest and highest percentage occurred at 800°C and 1000°C , respectively. The required parameters used for estimating CaO content of CPA in this study is presented in Table 3.

Table 3: Required Parameters for Calculating CaO Content

Temperature ($^{\circ}\text{C}$)	Normality of HCl	Weight of sample (g)	Calcium oxide (%)
600	0.1	0.0392	7.15
700	0.1	0.0363	7.75
800	0.1	0.0333	8.42
900	0.1	0.0381	7.36
1000	0.1	0.0418	6.71

The percentage of SO_3 which was determined at different temperatures fell below the 4% limit as specified by the ASTM C618 (2005) for pozzolans. The percentages of SO_3 at different temperatures were presented in Table 4. The highest value for loss of ignition (LOI) was 3.78% and the lowest value of 2.09% was observed and recorded at temperature of 600°C and 800°C , respectively. The highest value of 32% was observed and recorded at 800°C while the least value of 25.5% was at 1000°C . All the values obtained for LOI at different temperatures exceeded the stipulated value by ASTM C618.

Table 4: Percentages of SO_3 at Different Temperatures

Temperature ($^{\circ}\text{C}$)	600	700	800	900	1000
SO_3 (%)	3.78	2.91	2.09	2.72	3.51

Percentages of various oxides obtained from chemical analysis of CPA with LOI and moisture content were compared with the ASTM C618 standard for pozzolans. From the results obtained, only sulfur trioxide (SO_3)

satisfied ASTM C618 standards while LOI, moisture content and the total percentage composition of silicon dioxide, aluminum oxide and ferric oxide fell below ASTM C618 specification. Optimum temperature was found at 800°C which gave a total percentage composition of silicon dioxide, aluminum oxide and ferric oxide of 11.23%.

The result obtained from X-ray crystallography is presented in Table 5 and did not satisfy the requirements stipulated by ASTM C618. Addition of percentage composition of SiO₂, Al₂O₃, and Fe₂O₃ ranged from 14.86-24.21% for 600°C and 800°C. This does not satisfy the minimum percentage of 70% as stipulated by ASTM C618 for a pozzolan. Moisture content of CPA was 74.3% and exceeded 3% maximum content as specified by ASTM specification.

The results from this study indicate that CPA is a very weak pozzolan as it does not satisfy the minimum requirements specified after all the required tests were carried out, especially the chemical analysis of all the oxides present in CPA.

Table 5: Summary of Chemical Analysis and X-Ray Crystallography Results

Chemical Composition of CCPA	ASTM C618 (%)	Control Cement (%)	Composition of CPA using Chemical Analysis at Different Temperature (%)					Composition of CPA using X-ray Crystallography at Different Temperature (%)		
			600°C	700°C	800°C	900°C	1000°C	600°C	800°C	1000°C
SiO ₂	-	19-23	6.89	7.62	8.05	7.24	6.39	8.16	16.26	15.99
Al ₂ O ₃	70	2.5-6	1.94	2.15	2.29	2.05	1.81	3.88	4.35	4.38
Fe ₂ O ₃	-	0-6	0.78	0.81	0.89	0.72	0.72	2.83	3.6	3.47
CaO	-	61-67	7.15	7.75	8.42	7.36	6.71	4.34	5.87	6.61
MgO	4	5	4.38	4.65	5.16	4.54	4.11	4.99	6.61	7.18
SO ₃ (max.)	10	1.5-4.5	3.78	2.91	2.09	2.72	3.51	1.29	1.05	1.18
LOI (max.)	-	-	27.2	29.2	32	27.4	25.5	-	-	-
C ₃ S	-	45-75	-47.93	-50.24	-49.5	-47.67	-44.43	-78.11	-137.01	-132.33
C ₂ S	-	7-32.0	55.83	59.75	60.43	56.72	51.84	82.31	149.97	145.67
C ₃ A	-	0-13	3.82	4.33	4.56	4.24	3.58	5.49	5.45	5.74
C ₄ AF	-	0-18	2.37	2.46	2.71	2.19	2.19	8.61	10.95	10.56
SR	-	1.7-3.5	2.52	2.57	2.53	2.61	2.53	1.22	2.05	2.04
AR	-	2.4	2.49	2.65	2.57	2.85	2.51	1.37	1.21	1.26
CaO:SiO ₂	-	2	1.04	1.02	1.05	1.02	1.05	0.53	0.36	0.41

$$AR = \frac{Al_2O_3}{Fe_2O_3} \quad (9)$$

$$SR = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} \quad (10)$$

Conclusions

From the present investigation, the following conclusions were drawn:

- The total percentage composition of SiO₂, Al₂O₃, and Fe₂O₃ in CPA for each temperature using chemical analysis method and X-ray Crystallography does not measure up to the minimum 70% required for pozzolans by ASTM-C618 (2005).
- The optimum Calcinating temperature was found to be 800°C with a total oxide composition of 11.23% after chemical analysis and 24.21% for X-ray Crystallography.
- Only the moisture content value of 74.3% and loss of ignition values fell within the prescribed 3% and 10% by ASTM-C618 (2005).
- CPA therefore is a weak pozzolanic material since its optimum pozzolanic property was at 800°C.

Recommendation

It is therefore recommended that CPA may be further analysed for use as a partial replacement for cement because of its chemical composition, since it is a weak pozzolanic material.

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