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An investigation into the pozzolanic properties of volcanic ash sample obtained from Dutsin Dushowa in Jos Plateau

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Abstract
This study investigates the pozzolanic properties of the volcanic ash (VA) obtained from Dutsin Dushowa in Kerang,Plateau State. Chemical analysis of the VA obtained in the study area was carried out to determine the oxide contents.Tests on some physical properties (specific gravity, fineness, soundness, consistency, water requirement and setting times -initial and final) of the VA and VA-blended cement samples were also carried out.The resultshows a Silicon dioxide (SiO_2)content of 41.13% and a total Silicon dioxide, Iron oxide, and Aluminium oxide (SiO_2 +Fe_2O_3 +Al_2O_3) content of 70.99%. The VA sample has a specific gravity of 2.65 kg/m^{3}and the VA-blended cement was noted to be finer than the control cement. The soundness of the VA-blended cement ranged between 1.5 and 4.5 for replacement levels of 0% to 30%. The consistency increased from 30.0% to 31.5% as VA substitution increase from 0% to 30%. The water required for a standard consistency was noted to increase as the VA content increased. The initial and final setting times increased from 50 to 105 minutes and 135 to 180 minutes respectively for this replacement levels. All the VA-blended cements thereby satisfy the various code requirements up to the 30% replacement levels, hence suitable for use in concrete.

Keywords: volcanic ash (VA),pozzolan, oxide contents, VA-blended cement, setting times.

Introduction

Volcanic ash (VA) utilisation in concrete construction can be linked with the origin of "pozzolanic cement"in Pozzuoli village near Vesuvius in Italy where Roman Builders adopted ground volcanic ash mixed burnt clay tile and sand to form mortar for under water construction (Neville, 2012; Shetty, 2009). The active silica and alumina in the ash and tiles combined with lime produced what is known today as "pozzolanic cement" (Neville, 2012). This concept has led to series of research on possibility of grinding natural materials at normal temperatures while calcination of other materials is also being studied for the assessment of their pozzolanic properties (Matawal, 2005; Raheem, 2006; Alabadan et al., 2006; Elinwa, et al., 2011).VA can therefore be seen as the original pozzolan and attempts should be made for the exploration where possible deposits are located as this will ensure itsproductive use.

Volcanic eruptions and activities can be steam-generated (phyreatic), explosive of high-silica lava (Rhyolite) and effusive of low-silica lava (e.g. Basalt) amongst others (Wikipedia, 2011).Wright (1970) observe that although a significant proportion of Nigeria's volcanic rock are found in the Jurassic younger granite province, the tertiary to quaternary phase of volcanism was most mid spread and voluminous in Nigeria. A summary of the spread is provided in Table 1 as cited in Hassan (2006). Salau (2008) also outlined the spread of Basalt formations in Nigeria. The Basalt formations are said to be found in the South and West of Biu Plateau, Namu, Gindiri, Pankshin and Runka areas and also in Jos Plateau in Plateau State.They also occur in Rabah, Gwaini, Wurno and Sokoto Plateau of Sokoto State. Traces of Basalt can also be found in the Yoruba Plateau (Salau, 2008).The focus of this study is the investigation of the pozzolanic properties of the VA located in Jos Plateau.

Table 1: Summary of volcanic rocks in Nigeria

Approximate Age	Petrographic Affinity	Approximate Distribution
Jurassic (150Ma)	Alkaline to Tholeitic	Basaltic half of Runka (1), also Gazamma (G), Kinberlite of Kafur (K) and clays at Kankara (K)
Cretaceous (100Ma)	Alkaline to Calc Alkaline	Basic to intermediate laxias and proclactic and minor intrusive of Benue trough (2)
Lower Cenozoic (70 - 60Ma)	Rock too altered	Fluvio-volcanic series or laterized older basalts of Jos Plateau region (3)
Upper Cenozoic	Alkaline to per Alkaline	Basalts phlomolites, trachytes of Jos Plateau, Benue valley and Manbilla Plateau (4)

Source: Wright, 1970

Jos Plateau lies precisely within the North Central basement complex of Nigeria. The basement complex rocks of the lower Palaeozoic to Precambrian ages underlie about half of its entire landmass. These rocks are represented by gneiss-migmatites and intrusive into these basement rocks are the Pan-African granites and the predominant Jurassic non-organic alkaline Younger Granites (Turner, 1976).

The newer basalts occupy nearly 150 km^2 in the western and southern Jos Plateau. They also extend towards the Kafanchan area and Southwards down to the Shemankar valley. They occur as cones and lava flow characterised sleep-sided central craters rising a few meters above their surroundings.

VA referred to as "original Pozzolan"is a finely fragmented magma or pulverised volcanic rock, measuring less than 2mm in diameter, which is emptied from the vent of a volcano in either a molten or solid state. The most common state of ash is vitric (glass like), which contains glassy particles formed by gas bubble busting through liquid magma (Encarta, 2009). It comprises small jagged piece of rock minerals and volcanic glass that was erupted by a volcano (Shoji et al., 1993).

VA is hard, does not dissolve in water, extremely abrasive, mildly corrosive and conducts electricity when wet. According to Shoji et al. (1993), the average grain size of rock fragment and VA erupted from an exploding volcanic vent varies greatly among different eruption.

Research on pozzolan or cement supplementary materials has been on the increase in the recent times with attention beingfocussed on ashes of natural materials.In Nigeria, volcanic ash deposit in the study area is also being investigated for pozzolanic properties. Lar and Tsalha (2005) investigated the geochemical characteristics of the Jos Plateau Basalts while Hassan (2006) worked on volcanic ash deposits of Jos Plateau area,examining its suitability for use in concrete. They both reported differing values for chemical analysis of VA in this region with Lar and Tsalha (2005) having a total SiO_2+Al_2O_3+Fe_2O_3 in the range of 53.13 to 71.07% by weight for this zone and specifically 63.74% for Kerang town. Hassan (2006) on the other hand, reported value for Kerang is 67.14%. Both values fall short of the requirements of the codes (ASTM C618: 2008 and BS EN 196 2:1995) of 70.0 %. The work of Lar and Tsalha (2005) however indicates a possibility of source effect on the oxide composition of VA samples. This thereby poses the need for specific assessment of individual samples of VA before it is incorporated in concrete.This paper report a further study of the VAdepositsin Dutsin Dushowa hill of Kerang town, Mangu Local Government of Jos Plateau, assessing its conformity to the recent standards of practice for Class N pozzolan as part of a research work targeted at its utilisation in laterized concrete (Olawuyi, 2011).

Materials and methods

Materials collection

The VA used was obtained from the foot of Dutshin Dushowa (a hill) at Kerang in Mangu local government area (LGA) of Plateau State. This was dug from the foot of the volcanic deposit as solid mass using a shovel and poured directly into empty bags with no other special process. It was then transported to Minna, pounded and groundedto very fine particles and sieved with 75μm sieve before use. The cement used was obtained from abuilding materials'market in Minna and was that produced by the Obajana factory of Dangote cement whose properties should conform to the requirements of BS EN 197-1:2000 for ordinary Portland cement.

Instrumentation

The chemical analysis of VA was carried out at the Sagamu works department of Lafarge cement (West African Portland Cement Company -WAPCO) via an X-ray fluorescent analysis using a Total Cement Analyser model ARL 9900 XP. The pounding and grinding of the volcanic ash was carried out in the Department of Building Laboratory, Federal University of Technology Nigeria (FUT), Minna and at a local shop in Minna respectively.Physical properties tests were also carried out on the VA sample and the VA-blended cements. Furthermore, all mass measurements were taken on weighing balances.

Determination of chemical composition of volcanic ash

The VA sample was prepared in FUT, Minna and then taken to WAPCO, Sagamu for analysis. About 150 g of the prepared sample was involved.It was pounded, grounded and sieved using a 75μm sieve before the 150 g was packaged in small nylon bag.

The determination of the chemical composition at WAPCO involved drying, grinding, pressing and analysing. The materials were dried in an oven at 100 ± 5^0C for about two hours until a constant weight (±0.01 g) was obtained after which the sample was placed in a desiccator to cool for about 30 minutes before grinding commences. In order to aid grinding and to prevent sticking of the sample to dish, 0.8 g of stearic acid was weighed into sample dish before adding 20.0 g of the material (VA sample) into it. Grinding was done on a gyro-mill grinding machine (Model HSM 100H, Serial Number MA 11566-5-1, 2004), which stops automatically after grinding for a pre-set time of 3 minutes. The sample is then ready for pressing.

The ground sample plus 1.0 g of stearic acid to ensure adequate binding, was used to fill the pellet cup to the brim. The pellet cup was then centrally placed in an automatic hydraulic operated press (Model TP 40/2D), pressed at 20 tons load and 30 seconds hold time. On completion of pressing, the pressed pellet was carefully removed from the cylindrical pressing die and transferred into the X-ray analyser sample holder ready for analysis.

The analysis was carried out using X-Rayfluorescent analyser called Total Cement Analyser (Model ARL 9900 XP), which is connected directly to a computer system. The pressed pellet was loaded in the sample port of the analyser and the assembly left for about three minutes after which the values of elements concentration were displayed on the monitor. The system in place at the Shagamu works Chemical Laboratory of Lafarge Cement has installed software which automatically generates the result of the analysis.

The loss on ignition (LOI) was however obtained by the simple procedure of subjecting the sample to elevated temperature. A known weight of sieved volcanic ash was first heated at a temperature 100 ± 5 ^{o}C for 24 hrs to remove evaporable water after which it was then heated at a temperature of 800 ± 5 ^{o}C for two hours and weight differences determined to calculate the LOI.

Determination of physical characteristics of VA-blended cements

The following physical characteristics of the VA-blended cement were considered:

i. Fineness (Sieving Method)
ii. Consistency
iii. Soundness and
iv. Initial and final setting times.

a) Fineness (sieving method)

The fineness of cement is measured by sieving it on standard sieves. The proportion of cement grain sizes larger than the specified sieve (i.e. mesh) size is thus determined (BS EN 196 6:1992).

This test was carried out to determine cement residue as specified in BS EN 196 6:1992 using a 53μm and 75μm sieve since the volcanic ash sample being used are those passing 75μm sieve. The sample to be tested was agitated by shaking for 2 min in a stoppered jar to disperse the agglomerates. After waiting for 2 min the resulting powder was stirred gently using a clean dry rod in order to distribute the fines throughout the cement,hence the tray was fitted under the sieve and approximately 10 g of cement to the nearest 0.01 g was weighed and placed in the sieve.Adequate care was taken to avoid loss. Agglomerates were then dispersed and the lid fitted back over the sieve. The sieve was agitated using a sieving machine at a pre-set time to 5 minutes. The residue was then removed and weighed and this mass expressed as a percentage, $R1$, of the quantity first placed in the sieve to the nearest 0.1 %. Brushing all the fine material off the base of the sieve into the tray, the whole procedure was repeated using a fresh 10 g sample to obtain *R2*. The residue of the cement *R was then calculated* as the mean of *R*1 and *R*2 as a percentage, expressed to the nearest 0.1 %.

b) Consistency Test

The consistency of standard cement paste was determined using Vicat apparatus with a 10 mm diameter plunger as specified in BS EN 196 3:2005 +A1:2008. 500 g of cement sample (also the blended cement) was weighed and spread out on steel plate; in case of the VA-blended cement the appropriate percentage of replacements was noted and weighed as required with everything thoroughly mixed together. Using the measuring cylinder, 125 g of clean tap water was added and mixing with trowel was done for 4 ± 0.25 minutes to give a paste (as allowed for in the BS EN 196 3: Clause 5.2.1 Note 2). The paste was then transferred into the Vicat mould which had earlier been cleaned and lightly oiled. The top of the mould was levelled and the mould with the paste placed under the Vicat apparatus with the plunger gently lowered to contact surface of the paste and quickly released to allow it sink into the paste. Under the action of its weight the plunger will penetrate the paste, the depth of the penetration depending on the consistency. When the plunger penetrates the paste to a point 6 ± 2 mm from the bottom of the mould, the water content of the standard paste is expressed as a percentage (to the nearest 0.5 %) by mass of the dry cement, the usual range of values between 26 and 33 (as provided by the earlier version of the standard).

c) Initial and Final Setting Times

The setting times tests were carried out using the Vicat apparatus. The temperature of the test room was kept at 20 ± 1°C. Cement paste of standard consistency as described above and the two types of setting time tests (Initial and Final) were carried out on the cement pastes of the four different levels of percentage replacement of cement by volcanic ash (0%, 10%, 20% and 30% respectively) in accordance to BS EN 196 3:1995 and Neville, 2012 as discussed below:

- Initial setting time: For the determination of the initial set, a round needle with a diameter of 1.13± 0.05 mm was used. The needle, acting under a prescribed weight, was used to penetrate the paste of standard consistency placed in the Vicat mould. When the paste stiffens sufficiently for the needle to penetrate no deeper than to a point 5± 1 mm from the bottom, initial set was recorded. Initial set is expressed as the time elapsed since the mixing was added to the cement.
- Final setting time: Final set was determined by a similar needle fitted with a metal attachment hollowed out so as to leave a circular cutting edge 5 mm in diameter and set 0.5 mm behind the tip of the needle. Final set is said to have taken place when the needle gently lowered to the surface of the paste, penetrates it to a depth of 0.5 mm but the circular cutting edge fails to make an impression on the surface of the paste (Neville, 2011). The final setting is reckoned from the moment when mixing water was added to the cement.

d) Soundness Test

The soundness or cement expansion test was performed using the Le-Chatelier apparatus. A cement paste of standard consistency was prepared and used to fill the expansion mould on a glass plate, keeping the split of the mould gently closed. The top of the mould was smoothened and levelled and a glass top end applied. The assembly was then placed in water at 20 ± 3°C with a small weight placed on the top end plate. The mould was removed after 24hours and the distance between the two points (i.e. the split opening) was measured to the nearest 0.5 mm (say A mm)

The mould was then placed in a heating bath and the temperature rose to boiling point within 15 minutes and then allowed to boil for 1 hour. The mould was thereafter removed from the bath and allowed to cool for 1 hour after which the distance between the two pointers was measured again to the nearest 0.5 mm (say B mm). The difference between the two measurements (B A) was recorded as the expansion of the cement.

Results and discussion

Chemical analysis of the VA sample

The result of chemical analysis of the VA sample is as shown in Table 2.

This reflects a Silicon dioxide (SiO_2) content of 41.13% which is greater than BS EN 197-1(2000) minimum requirement of 25.0% and a total Silicon dioxide, Iron oxide, and Aluminium oxide

(SiO_2+Fe_2O_3+Al_2O_3) content of 70.99% which is slightly higher than the values reported in earlier studies; 63.74% by Lar and Tsalha (2005) and 67.14% by Hassan (2006).

This new value is noted to be slightly above the code (ASTM C618 2008) requirement of 70% minimum for a pozzolan. The SO_3 content is -0.13 which is below the maximum value of 4.0% as specified for Class N pozzolan to which it belongs, in ASTM C618-2008. The loss on ignition (8.60) though higher than the value (2.71) got in earlier study by Hassan (2006), is also below the maximum allowable (10.0) specified.

Table 1: Result of chemical analysis of the volcanic ash sample

Elements	% Composition by weight
SiO_2	41.13
Al_2O_3	18.36
Fe_2O_3	11.5
CaO	6.57
MgO	4.24
SO_3	-0.13
K_2O	1.12
Na_2O	1.29
Mn_2O_3	0.29
P_2O_5	1
TiO_2	3.56
Cl-	0
SUM	88.92
LSF*	4.64
SR**	1.38
AR***	1.6
L.O.I	8.30
SiO_2+Al_2O_3+Fe_2O_3	70.99

*LSF Lime Saturation Factor; **SR Silica Ratio; ***AR Alumina Ratio.

The VA sample from Dutsin Dushowa hill in Kerang, Mangu LGA of Plateau State, Nigeria which was used for the research work can then be said to be a pozzolan on basis of chemical composition.

Physical properties of the VA-blended cement
The physical properties of the VA-blended cement are presented in Table 3.

The fineness test (residue on 75μm and 53μm sieve) shows that the blended cements were finer than the control (Dangote - Obajana) cement. Both 75μm and 53μm sieves were used since the VA sample has passed a 75μm mesh, hence using a 90μm mesh as specified by BS EN 196 6:2005+A1:2008 will be in-appropriate and a 45μm was not available in the Laboratory in FUTMinna.

Table 1: Summary of physical properties of VA-blended cement

Parameters	Percentage Replacement by VA			
	0	10	20	30
Fineness (% Residue on 75 .m Sieve)	12.5	11.0	8.5	7.0
Fineness (% Residue on 53. M Sieve)	52.0	39.0	34.5	33.5
Soundness (mm)	1.5	2.5	3.5	4.5
Consistency (%)	30.0	30.0	31.0	31.5
Water Requirement (% of control)	100.00	100.2	104.2	104.8
Initial Setting Time (min)	50	75	85	105
Final Setting Time (min)	135	165	180	180

The higher the VA content in the blended cement the lower the residue observed in both cases. Table 3 reveals that the soundness of the cement ranges between 1.5 and 4.5 for replacement levels of 0% to 30%. These values are far lesser than the 10 mm limiting value recommended by both NIS 439:2000 and BS EN 197 1:2000, hence the blended cement does not show any appreciable change in volume after setting.

The consistency increases from 30.0% to 31.5% as VA substitution increases from 0% to 30%. The water required for a standard consistency was noted to increase as the VA content increases, although this was noted to be within the limit of 115% as specified for Class N pozzolan in ASTM C618:2008.

The initial and final setting times increased from 50 to 105 minutes and 135 to 180 minutes respectively when percentage VA replacement increased from 0% to 30%. All the cement satisfy the NIS 439:2000 and BS EN 197 1:2000 requirements of 45minutes minimum initial setting time and maximum of 10 hours final setting time as spelt out by NIS 439:2000 and the 375 minutes maximum specified for final setting time by ASTM C150. BS EN 197 -1:2000 was however silent on the maximum final setting time. The variation of setting times with percentage VA replacements shows that both initial and final setting times increased as the percentage VA increased. As a result, the hydration process is slowed down in consonance with the views of Hossain (2003). The slow hydration means low rate of heat development which is one of the notable characteristics for which pozzolanic cements are known. This is of great importance in mass concrete construction where low rate of heat development is very essential as it reduces thermal stress.

A plot of the initial setting time against the final setting time as shown in Figure 1, indicates a very strong linear relationship between the parameters as the coefficient of correlation was calculated to be 0.944 (square root of R^2). As stated by Johnson (1994), a strong relationship exists between two variables when $0.5 < /r/ < 1$. Thus an estimate of the final setting time can be calculated from Equation 1 when an initial time has been obtained.

$$y = 0.838x + 98.71 \quad (1)$$

Where: y = final setting time
X = initial setting time

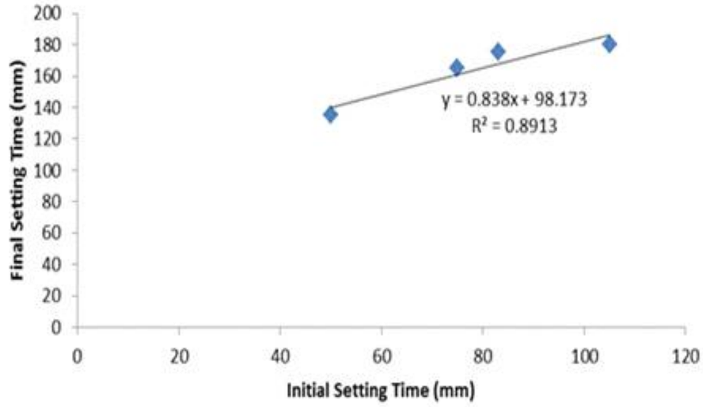

Figure 1: Relationship between Initial and Final Setting Times of VA-Blended Cement

Conclusion

The VA sample obtained from Dutshin Dushowa (a hill) in Kerang, Mangu LGA of Jos, Plateau State, Nigeria is a suitable material for use as a pozzolan, since it satisfied the requirements for such a material as spelt out in ASTM C618-2008 by having a combined SiO_2, Al_2O_3 and Fe_2O_3 of 70.99% which is more than the required 70%.

The VA-blended cement satisfies the NIS 439:2000; BS EN 196 6:2005 and ASTM C618:2008 requirements (for Class N pozzolanas) even up to 30% substitution on the basis of fineness (residue on 53 µm sieve), soundness, consistency, and ASTM C150 :2008 for setting times.

The VA-blended cements have higher setting times than the control; hence, they are most applicable where low rate of heat development is required such as in mass concreting. This shows that VA-blended cement is good as low heat cement.

Efforts should be made at exploring the utilisation of the abundant deposit of volcanic ash spread over wide areas around Jos plateau with a view to its adoption as a supplementary cementitious material. This will go a long way in averting the impending danger to which a volcanic explosion poses to a nation and the world at large. The excavation and utilisation have to be controlled to avoid environmental degradation trends.

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