Comparative Studies of Physico-chemical Properties of Some Selected Cements in Nigeria

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\textbf{ABSTRACT}: The aim of this study was to evaluate some physico-chemical properties of four major general purpose cement (As, Br, De and Sk) sold in Nigerian market using standard methods; due to the persistent collapse of buildings. The results showed that Br cement recorded the least CaO content (56.17%) while De cement had the highest CaO content being 63.48\%. All the samples have Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2} and Fe\textsubscript{2}O\textsubscript{3} contents within the acceptable limits with the exception of De with SiO\textsubscript{2} content being below the required standard. The MgO and SO\textsubscript{3} compositions were generally below the recommended limit; C\textsubscript{3}S content in De was above the recommended limit while it was below the standard in As. The C\textsubscript{2}A, C\textsubscript{3}AF, LSR, AR and SR of all the brands of cement were within the recommended standards for general purpose cement, with the exception of SR in As. The longest setting time for the cement samples was recorded in Br; LOI and IR were significantly high in all the samples. Sk and Br cements had the highest compressive strength of 50.42 and 50.43 N/mm\textsuperscript{2} respectively after 28 days. The results indicate that the properties of the four brands of cement are comparable and are all of good quality.

\textbf{KEYWORDS}: Cement, properties, good quality, setting time, physic-chemical.

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\section*{I. INTRODUCTION}

Historically cementing materials have played an important role in providing shelter for mankind. The production of cement has played a key role as a construction material throughout the history of civilization. It is very important in the construction of buildings, bridges, tunnels, to mention a few (Faley et al., 2009; Neville, 2000).

One of the most important considerations to make before embarking on the construction of a building is the cement that would be used; the commonest type of cement used across the world is Portland cement. The primary reason for its global use is its composition and essential characteristics in the setting and hardening of the concrete, durability when dry, fire-proof nature, effective protection of iron or timber structures, ability to prevent corrosion, its use in ships, tanks and bunkers (ASTM, 1986). About 90 - 95\% of Portland cement is composed of the four main cement minerals, tricalcium silicate (C\textsubscript{3}S), dicalcium silicate (C\textsubscript{2}S), tricalcium aluminate (C\textsubscript{3}A) and tetracalcium aluminoferrite (C\textsubscript{4}AF) with each of them playing different roles in the hydration process that converts the dry cement into hardened cement paste (Tennis and Bhatti, 2005). About 10.0 – 5.0\% of the remaining compositions are calcium sulphate, alkali sulphones, unreacted calcium oxide, magnesium oxide and other minor constituents left over during the clinkering and grinding steps (Taylor, 1997).

In the study carried out by Sam et al. (2013) on the assessment of the quality of three brands of Portland cement in Ghana, the results indicated that two of the three cement brands conform well to the European (EN 197-1) standard specification. The results of the chemical parameters of two indigenous Portland cement brands sold in Nigeria indicated that the chemical composition conform well to international standards and that majority of the Portland cement sold in Nigeria are better used for structures involved with low loading (Yahaya, 2009). This is an indication that qualities of cement may differ based on the production origin. However, the quality of cement is very important to its application which made the product useful in mortars, plasters, screeds and grouts as a material which can be squeezed into gaps to consolidate the structures. In addition, lime saturation factor (LSF), silica ratio (SR) and aluminum ratio (AR) are important factors for chemical control in cement (Nasir and Elettr, 1996; Ali et al., 2008).

In addition, physical tests on five brands of Portland cement (Dangote, Ibeto, Unicem, Elephant and Atlas) sold in Umuahia, Nigeria revealed that the respective fineness of 2\%, 0.34\%, 0.17\%, 0.3\% and 0.35\% obtained for Dangote, Elephant, Ibeto, Unicem and Atlas cements are in conformity with the standard specification of 10\% maximum. However, the average specific gravity obtained for the samples was below the standard value of 3.1 minimum (Nwankwojike et al., 2014).

Type I cement is ordinary cement used for general concrete construction; Type II cement is used for moderate sulphate resistance structures; while Type III cement is used for rapid construction in cold weather concreting that requires high early strength (Portland Cement Association, 1996).

In recent times, Nigeria has witnessed frequent cases of collapsed building. In the year 2006 alone, four cases of such collapses were recorded in Ebute Metta, Lagos claiming over thirty lives in residential buildings (Adegoroye, 2010; Adewole 2014). Oloyede et al. (2014) reported the use of
poor materials as the leading cause of frequent collapse of buildings in Nigeria; and since cement is a major constituent in building construction, focus has been drawn to periodic quality assessment of the product. The aforementioned scenario is further worsened by the porous nature of the boarders into Nigeria, giving avenue for importation of poor quality cements into the country. The need for regular sampling and testing of cement therefore becomes imperative.

Therefore the aim of the present study is to evaluate and compare the qualities of four major brands of cement sold and used in Nigeria. This is important to ascertain whether the cements meet the standard requirements acclaimed

II. MATERIALS AND METHOD

A. Sample Collection

The four major brands of cement sold in Nigeria were used for the study, and were coded as: As, Br, De and Sk cements. The samples were all collected from Sokoto Cement laboratory, Sokoto, Nigeria in March, 2013. The procedures adopted for all the analyses were as described in the laboratory manual available in Sokoto cement quality control laboratory.

B. Determination of Physical Parameters

B1. Determination of Insoluble Residue (IR)

Exactly 1.0 g of each of the cement sample (As, Br, De and Sk) was weighed into 250 ml beakers and dissolved by adding exactly 5 ml of concentrated HCl and diluted to 100 ml with warm distilled water. It was then stirred well with a glass rod before the mixture was heated on a hot plate to boiling. The mixture was then filtered using a Whatman no. 41 filter paper, the filtrate was then washed with hot distilled water about four times in a beaker. The filter paper with the residue was transferred into a 250 ml beaker and 100 ml of 0.10M NaOH solution added, this was followed by 3 - 5 drops of methyl red indicator. The mixture was then boiled on a hot plate again, with drop-wise addition of 4 - 5 drops of concentrated HCl until the colour changed to pink. The mixture was filtered again using a Whatman no. 41 filter paper, after which the filter paper was washed four times with 0.20M NH₄Cl solution. A rubber scrapper was then used to remove all the precipitate adhering during washing (ASTM, 1986).

An empty crucible was ignited for 5 min in a furnace set at 950°C; this was then allowed to cool in a desiccator to ambient room temperature and weighed as W₁. The filter paper with its residue was then transferred into the crucible and ignited in the furnace at temperature 950°C for 30 min, the crucible and its content were then removed and allowed to cool to ambient room temperature inside a desiccator, and then weighed as W₂. The percentage Insoluble Residue (IR) was calculated using eqn (1).

\[
\% \text{ IR} = \frac{(W₂ - W₁) \times 100}{W₁} \tag{1}
\]

B2. Determination of Loss on Ignition (LOI)

Approximately 3.0 g of the cement sample (As, Br, De and Sk) was transferred into a pre-weighed dried platinum crucible; then each of the crucibles with the sample was ignited to above 900°C in a furnace for about 30 min. The crucible was then removed, cooled and weighed (ASTM, 1986).

The percentage loss on ignition (LOI) was calculated using Eqn (2).

\[
\text{LOI} = \left( \frac{W₁ + W₂ + W₃}{W₂} \right) \times 100 \tag{2}
\]

\( W₁ = \text{weight of empty crucible;} \)
\( W₂ = \text{weight of sample + crucible;} \)
\( W₃ = \text{weight of crucible + sample after ignition} \)

B3. Consistency of Standard Cement Paste

Each of the cement sample (400 g) was spread out on a steel plate for about 30 min to cool to the temperature of the mixing room (27 ± 2°C). About 200 ml of water was gradually added into the mixer bowl containing each sample and mixed for 90s; this was allowed to stop at every 15s in order to scrape and transfer any paste adhering to the bowl outside the mixer zone. The top of the mould was smothered off as quickly as possible with the aid of the trowel. The mould and paste were placed on the mortar of the plunger component of the Vicat apparatus. The plunger was then lowered gently to contact the surface of the paste. The material was released quickly and allowed to sink into the paste. The scale reading of the Vicat apparatus was noted after 1 min and recorded. If the plunger penetrates to a point 5 to 7 mm above the bottom of the mould, the water cement ratio is taken as the consistency (BSI, 1978).

The standard cement paste was obtained using eqn (3).

\[
\text{Percentage Consistency} = \frac{\text{Water Consumed} \times 100}{\text{Weight of the cement sample}} \tag{3}
\]

B4. Quality of Cement

The quality of the cement products were calculated from the oxide concentrations of the cement using eqns (4) – (9) (Faleye et al., 2009; Sam et al., 2013). The formulae are described below.

\[
C₃S = \left[ \frac{[4.071 .CuO] - [7.6 .SiO₂] - [6.718 .Al₂O₃]}{[1.4 .Fe₂O₃]} - [2.852 .SO₃] \right] \tag{4}
\]
\[
C₃A = \left[ \frac{[2.650 .Al₂O₃] - [1.682 .Fe₂O₃]}{[3.043 .Fe₂O₃]} \right] \tag{5}
\]
\[
C₄AF = \left[ \frac{[0.403 .Fe₂O₃]}{[2.8 .SiO₂]} + [1.2 .Al₂O₃] + [0.65 .Fe₂O₃] \right] \tag{6}
\]
\[
\text{LSF} = \left[ \frac{[CuO]}{[2.8 .SiO₂]} + [1.2 .Al₂O₃] + [0.65 .Fe₂O₃] \right] \tag{7}
\]

where LSF = Lime saturation factor
\[
\text{AR} = \frac{[Al₂O₃]}{[Fe₂O₃]} \tag{8}
\]
where AR = Aluminum ratio

\[ SR = \frac{(SiO_2)}{(Al_2O_3 + Fe_2O_3)} \]  

(9)

where SR = Silica ratio

B5. Compressive Strength Test

Approximately 450 g of each cement sample (As, Br, De and Sk) was weighed into a bowl; then 225 g of water was added followed by standard sand been transferred into the hopper on the top of the mixer. After 90 s the mixer was stopped for 15 s to allow the mortar on the bowl to move to the bottom of the bowl with a rubber scrapper. The mixing was continued for a further 60 s before the bowl with the mortar was moved to the jolting apparatus (BSI, 1978).

Each layer in the mould was filled with one scope (about 300 g of the mixture). The mould was gently removed from the jolting machine and the hopper removed from the mould. The top of the mould was covered with a plate and the mould marked for identification.

Test specimens for ages greater than 1-day were stored in controlled water container after demoulding; the prisms were then kept apart from each other in the water. The prisms were then removed from the water after 15 min, before the strength test was carried out. The strength test at different ages was carried out within the following limits: 3 day ± 30 min, 7 day ± 2 h and 28 day ± 8 h respectively.

The prism was placed in the compressive strength machine exactly in the middle of the plates. The load was increased at the rate 2.4 ± 0.2 kN/S. The test was repeated with all prism halves; the compressive strength (Re) was calculated using Eqn (10).

\[ Re = \frac{Fc}{1600} \]  

(10)

where Re = compressive strength in N/mm²; Fc = maximum load at fracture in N; 1600 = 40mm if the plates is in mm².

To determine the shaft diameter, Figure 4 is used. (Not found)

B6. Setting Time Determination

About 400 g of each cement brand sample was weighed and added carefully into the mixer bowl within 5 to 10s, in order to avoid loss of water or cement. The mixer was on and the paste obtained was transferred to the mould. The sample was then placed centrally under the vacant plunger, the plunger was then placed against the paste surface and kept still for 1 - 25s, in order to prevent it from falling into the centre of the cement paste.

The penetration depth was determined after 30 s; at the time when the water content was near 0.5%. The right consistence was achieved when the distance between the plunger and the plate was 6 ± 1 mm, (BS: 12, 1978; Jackson, 1981).

The final setting time was determined from the time the mixture started setting to when no mark was shown on the outer ring on the Vicat rod (BSI, 1978; Jackson, 1981).

C. Determination of Chemical Parameters

The methods used for the analysis are as specified in ASTM (1986) and BSI (1978).

C1. Determination of SiO₂

Each cement sample (As, Br, De and Sk cement) of mass 100 g in 100 ml beaker containing 1 g of NH4Cl was mixed thoroughly, before adding 10 ml of concentrated HCl. After heating each mixture to 60°C for 30 min, 5 ml of hot distilled water was added and heated again for 15 min. It was then filtered through a munktell filter paper OOM and diluted to the mark with distilled water. The mixture was then allowed to cool to ambient temperature. The filter paper with its residue were then placed on a dried pre-weighted platinum crucible and ignited in the furnace for 30 min at temperatures above 900°C before it was removed, cooled and weighed (ASTM, 1986). The percentage SiO₂ was calculated using Eqn (11).

\[ %SiO₂ = \left( \frac{W₂ - W₁}{W₁} \right) \times 100 \]  

(11)

where: W₁ = weight of sample before ignition, W₂ = weight of sample after ignition.

C2. Determination of calcium oxide (CaO)

About 50 ml of the filtrate from the SiO₂ determination above was transferred into a 300 ml beaker containing each of the cement sample (As, Br, De and Sk); and then diluted with distilled water to 200 ml. The mixtures were then heated and stirred. The pH of the solution was adjusted to 5 by using drops of 25% KOH. Then 10 ml triethanolamine and 20 ml of KOH (25%) were added, followed by 5 g of calcone indicator which changed the solution to red violet. The solution was then titrated with 2M EDTA until it turned to clear blue (ASTM, 1986). The percentage calcium oxide was calculated using eqn (12).

\[ %CaO = V \times F \]  

(12)

where V = volume of EDTA in (ml) and F = factor of EDTA = 2.3016

C3. Determination of iron oxide (Fe₂O₃)

To about 100 ml of the filtrate obtained from the SiO₂ determination of each cement sample, 3 - 5 drops of bromophenol was added, followed by another 3 - 5 drops of NH3 solution until the colour changed to pale blue. Then 20 ml of 0.10M HCl was added followed by 15 ml of buffer solution and 3 - 5 drops of salicylic acid. The solution was then warmed to 40 – 60°C before it was titrated against 0.5M EDTA. The endpoint was signalled with a pink to clear yellow colour (BSI, 1978). The percentage of Fe₂O₃ was calculated using Eqn (13).

\[ %Fe₂O₃ = V \times F \]  

(13)

where: V = Volume (ml) of 0.5M EDTA used; F = factor of dilute EDTA = 0.3671

C4. Determination of Al₂O₃

To approximately 100 ml of each of the filtrate from the SiO₂ determination, three drops of ammonium hydroxide was added until the colour changed to pale blue. Then 3 drops of concentrated acetic acid, 3 - 5 drops of complexion indicator and 3 drops of PAN indicator were added. Each of the solutions was heated to boiling point and titrated against 0.5M EDTA solution until end point (pink to clear yellow
colour) \cite{ASTM, 1986}. The percentage of Al\(_2\)O\(_3\) was calculated using Eqn (14).

\[
\% \text{Al}_2\text{O}_3 = \frac{V \times F}{W} \tag{14}
\]

where \(F = 0.2344\).

\section*{C5. Determination of free-lime (CaO)}

Approximately 100 g of each cement sample was poured into a 500 ml flask followed by the addition of 2 g of dry sand and 40 ml of glycol, the mixture was then corked with the stopper. The mixture was shaken vigorously and the flask placed in an oven set at 70 °C for 30 min, and further shaken every 5 min. The solution was then filtered by suction through a dry filter paper. Then 3 drops of bromophenol blue indicator was added to the filtrate and titrated with 0.10M HCl until colour change \cite{BSI, 1978}. The Free-lime was calculated using the relationship in Eqn (15).

\[
\% \text{FL} = \text{Factor} \times \text{Vol(HCl)} \tag{15}
\]

where \(\% \text{FL} = \text{Percentage free lime}\)

The factor is given as 0.35

\section*{C6. Determination of sulphur trioxide (SO\(_3\))}

To 100 g of As, Br, De and Sk cement each weighed into a 100 ml beaker, 10 ml of warm distilled water was added followed by 5 ml of concentrated HCl, the mixture was then stirred thoroughly. After the mixture was heated on a hot plate to boiling point, it was allowed to cool and then filtered using munktell filter paper OOM into a 25 ml beaker. Then 20 ml of (10%) BaCl\(_2\) solution was added and boiled again. The solution was allowed to cool and precipitate for about 2 h, before filtering the mixture through a munktell filter paper OOM again. An empty crucible was ignited for 5 min in the furnace set at 900°C and then allowed to cool in a desiccator to ambient temperature and weighed as \(W_1\). The filter paper was then transferred from the funnel into the crucible and ignited in the furnace at 900°C for complete ignition before cooling the sample to ambient temperature in the desiccator and weighed as \(W_2\) \cite{BSI, 1978}.

The percentage sulphur trioxide was calculated using Eqn (16).

\[
\% \text{SO}_3 = 0.343(W_2 - W_1) \times 100 \tag{16}
\]

\section*{III. RESULTS AND DISCUSSION}

Evaluation of the characteristics of the available brands of Portland cements is necessary in order to ascertain the product quality of the brands. The experimental results of the parameters are presented in Tables 1 – 4.

\subsection*{A. Determination of the Composition of Calcium Oxide}

The percentage compositions of calcium oxide in the cement samples: As, Br, De and Sk are 58.92, 56.17, 63.48 and 62.14% respectively as shown in Table 1. This indicates that De and Sk cement have their calcium oxide content within 61 - 67% specifications of ASTM C 150 and BSI (1978). The result compares well with the mean level of 65.33 ± 0.41% and 57.54 ± 1.48% obtained for cement brands in Ghana and Nigeria respectively as reported by Sam et al., 2013 and Yahaya, 2009.

\subsection*{B. Determination of the Composition of Silicon Oxide}

The percentage of silicon oxide in the cement samples As, Br, De and Sk are 20.47, 19.68, 16.56 and 19.08 respectively following from Table 1. All the samples with exception of De cement are within the ASTM C 150 range of 19.00 - 23.00% for general purpose cement. The range obtained in this study conforms closely to the results obtained for Nigerian cement as reported by Akanni et al., 2014.

\subsection*{C. Determination of the Composition of Aluminum Oxide}

From the results the percentage of aluminum oxide in the cement samples As, Br, De and Sk are 3.83, 5.30, 4.78 and 4.69% respectively (Table 1). All the values fall within the ASTM C 150 specification of 2.5 - 6.0% aluminum oxide for general purpose cement \cite{BSI 1978}. The results compare well with the report of Yahaya, 2009 for Nigerian cement, with the exception of one brand with mean value of 1.25 ± 0.25%.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Cement sample code & Percentage composition & & & \\
\hline
 & CaO (%) & SiO\(_2\) (%) & Al\(_2\)O\(_3\) (%) & Fe\(_2\)O\(_3\) (%) \\
\hline
As & 58.92 & 20.47 & 3.83 & 2.31 \\
Br & 56.17 & 19.68 & 5.30 & 2.13 \\
De & 63.48 & 16.56 & 4.78 & 2.86 \\
Sk & 62.14 & 19.08 & 4.69 & 2.39 \\
ASTM C150-07 & 61-67 & 19-23 & 2.5-6.0 & 0-6.0 \\
\hline
\end{tabular}
\caption{Percentage composition of the major chemical constituents of some Nigerian cement}
\end{table}

\subsection*{D. Determination of the Composition of Iron Oxide}

The percentage iron oxide in the cement samples: As, Br, De and Sk are 2.31, 2.13, 2.86 and 2.39% respectively (Table 1). Generally, the values obtained in the studies were below the maximum requirement of 6.0% iron oxide content in common cement as recommended by ASTM C 150. Similarly, Akanni et al. 2014 reported mean Fe\(_2\)O\(_3\) of 3.0 to 5.2% for cement brands sold in South- Western states in Nigeria.

\subsection*{E. Determination of the Loss on Ignition}

The percentage loss on ignition in the cement samples studied, As, Br, De and Sk are 7.60, 6.16, 11.32 and 6.29% respectively as shown in Table 2. The values are generally above the ASTM C 150 maximum limit of 6.00% for Type I cement, implying that the cement products are poor in mineral content and high in combustible materials \cite{AOAC, 1990}.

\subsection*{F. Determination of Insoluble Residue}

As presented in Table 2, the percentage insoluble residue content of the cement samples As, Br, De and Sk studied are 2.73, 3.86, 2.24 and 2.24% respectively. The values are generally above the 0.75% maximum limit.
specified by ASTM C 150 for general purpose cement. Though the result of this study is lower than the range 4.7 – 32.5% reported for Nigerian cement by Faleye et al., 2009.

Table 2: Physico-chemical properties and some minor constituents in some Nigerian cement

| Cement sample | LOI (%) | IR (%) | Free CaO (%) | SO₃ (%) | MgO (%) |
|---------------|---------|--------|--------------|---------|---------|
| As            | 7.60    | 2.73   | 2.10         | 2.05    | 2.75    |
| Br            | 6.16    | 3.86   | 1.86         | 2.14    | 2.30    |
| De            | 11.22   | 2.24   | 2.03         | 2.15    | 1.45    |
| Sk            | 6.29    | 2.22   | 1.75         | 2.04    | 2.40    |
| ASTM C150     | 3.00    | 0.75   | 1.00         | 2.90    | 6.00    |

LOI = Loss on ignition; IR = Insoluble residue (%) and Free CaO = Free lime

G. Determination of Free CaO

As presented in Table 2, the percentage free lime composition in the cement sample As, Br, De and Sk are 2.10, 1.86, 2.03 and 1.75% respectively. The values are generally above the 1.00% ASTM C150 limit for type I cement and the 1.30% for type III. On the other hand, the study conducted by Sam et al., 2013 using EDXRF for cements in Ghana, and that by Akanni et al., 2014 for cements in Nigeria indicated higher free CaO of mean value 65%.

H. Determination of the Composition of Sulphur Trioxide

From the study, the percentage sulphur trioxide in the cement samples As, Br, De and Sk are 2.05, 2.14, 2.15 and 2.04% respectively (Table 2). The values are slightly below the 2.09% recommended limit by ASTM C 150 specification. However, the percentage content of SO₃ is in agreement with Type I and II, though slightly high in comparison to the other cement types.

I. Determination of the Composition of Magnesium Oxide

As presented in Table 2, the percentage magnesium oxide in As, Br, De and Sk cement are 2.75, 2.30, 1.45 and 2.40% respectively. These values are generally below the 6.00% maximum limit specified by the American standard (ASTM, 1986). However, the MgO contents conform with the British standard for Ordinary Cement (BSI, 1978). The result is similar to those reported by Yahaya (2009) and Faleye et al., 2009.

J. Quality Assessment of the Different Brands of Cement

According to Lea 1970 and Sam et al., 2013 the quality of Portland cement is assessed by four major constituents namely: tricalcium silicate [3CaO•SiO₂], dicalcium silicate [2CaO•SiO₂], tricalcium aluminate [3CaO•Al₂O₃] and tetracalciumaluminoferrate [4CaO•Al₂O₃•Fe₂O₃] coded as C₃S, C₂S, C₃A and C₄AF respectively. The results obtained for the samples are presented in Table 3.

J1. Composition of Tricalcium Sodium Oxide (C₃S)

The percentage composition of tricalcium sodium oxide in the cement samples As, Br, De and Sk studied are 42.65, 64.13, 99.04 and 56.52% respectively. As, Br and Sk cement have their C₃S values within the 45.0 – 65.0% limit as specified by ASTM C 150 for general purpose cement. Though, the percentage of C₃S reported by Yahaya (2009) for Nigerian cement was 20.58 - 33.33%. The hydration of C₃S gives cement pastes most of its strength, particularly at early times (Taylor, 1997).

J2. Composition of Dicalcium Silicate (C₂S)

The study indicated that the percentage dicalcium silicate (C₂S) in the cement samples As, Br, De and Sk are 24.40, 5.96, 26.45 and 11.99 % respectively. As, De and Sk cement have their C₂S values within the 7.0 – 32.0% limit as specified by ASTM C 150 for general purpose cement. Yahaya (2009) reported the range 26.47 – 46.41% C₂S for the Nigerian cement studied. C₂S has a very stable crystal structure that is completely unreactive in water, and an excess of it introduces impurities in cement compared to C₃S (Taylor, 1997).

J3. Composition of Tricalcium Aluminate (C₃A)

The cement brand As, Br, De and Sk has percentage tricalcium aluminate being 12.42, 7.98, 7.98 and 8.77% respectively. All the cement samples have C₃A within the 8.0 – 12.0% limit specified by ASTM C 150 for Type I general purpose cement as well as Type III. The result agrees with those conducted by Yahaya (2009) and Sam et al., 2013 for Nigerian and Ghanaian cements respectively. In the presence of sulphate ions, C₃A and its products can actually harm concrete, by participating in expansive reactions that can lead to stress and cracking (Taylor 1997).

J4. Composition of Tetracalcium Aluminoferrite (C₄AF)

The percentage aluminum oxide in the cement samples As, Br, De and Sk are 9.41, 12.16, 9.17 and 9.17 % respectively. The content of C₄AF in Br cement is slightly above the 8.0 - 12.0% limit specified by ASTM C 150 for general purpose cement, and is also in conformity with the 12.0% specification for Type IV cement (Type IV cement has low heat of hydration, low content of C₃S (<50%) and C₂S and is used for massive structures). De and Sk cement brands on the other hand have C₄AF being in agreement with the 9.0% specification for Type V cement (Type V cement has high sulphate resistance) (Bensted, 1979).

K. Lime Saturation Factor (LSF), Silica Ratio (SR) and Aluminum Ratio (AR)

The results for LSF, SR and AR in the cement brands are shown in Figure 1. The range 5.62 – 7.38 for LSF in the four cement brands is higher than 0.9 – 1.1 reported by Sam
et al. (2013) in some Portland cement sold in the Ghanaian market. But LSF value above 1.0 indicates that free lime is likely to be present in the clinker. In principle, at LSF = 1.0, all the free lime would have combined with belite to form alite. Conversely, if the LSF value is higher than 1.0, the surplus free lime has nothing to combine with and will remain as free lime (Nicolas, 2005). The brands of cement studied have LSF far greater than 1.

Figure 1: Cement ratio in different brands of cement.

L. Physical Properties of the Cement Samples

LI. As Cement Brand

The physical properties presented in Tables 4 and 5 indicated that the initial setting time for As cement brand was the least when compared to the others, but it has the fastest final setting time like Elephant cement as reported by Sosman and Merwin (1916) and corroborated by Faleye et al., (2009). This implies that the product would exhibit good workability. Increasing compressive strength was consistent over time, with the mix attaining over 60% of its 28-day strength in 7 day. When this is considered against the background that concrete is expected to attain about 60% of its 28 day strength at 7 day (Nevillle, 1981), its workability is considered good.

Table 4: Compressive strength (N/mm²) of As, Br, De and Sk cement

| Cement sample | 3 Days | 7 Days | 28 Days |
|---------------|--------|--------|---------|
| As            | 16.03  | 26.22  | 33.50   |
| Br            | 20.71  | 38.51  | 50.43   |
| De            | 16.53  | 31.13  | 44.93   |
| Sk            | 20.70  | 38.50  | 50.42   |
| B.S 12: 1971  | 15.20  | 23.40  | 47 – 67 |

Table 5: Setting time in minute and expansion (mm) for As, Br, De and Sk cement

| Cement sample | Initial setting time (Min.) | Final setting time (Min.) | Expansion (Soundness in mm) |
|---------------|----------------------------|---------------------------|-----------------------------|
| As            | 191                        | 236                       | 3.43                        |
| Br            | 187                        | 284                       | 1.00                        |
| De            | 198                        | 253                       | 3.00                        |
| Sk            | 178                        | 238                       | 1.00                        |
| ASTM C150-07 | 60 and above               | Not more                  | -                           |
| SPECIFICATION| below 600                  |                            |                             |

Nevertheless the low compressive strength and poor soundness of the cement when compared to others may be due to low CaO content (Ghosh, 1983), though the variations in the physical properties of As cement are within the acceptable limit (BSI 1978; and ASTM 1986) for type I (ordinary cement used for general concrete construction).

L2. Br cement Brand

The initial setting time for Br cement was 187 min and 233 min for the final setting which could be attributed to the relatively low gypsum content compared to the high C₃A (ASTM 1986). The highest compressive strength of 50.43 N/mm² and low expansion value of 1.00 mm implies a better workability compared to others (Ghosh, 1983). Higher compressive strength may be due to its relatively high C₃A content which is said to enhance initial strength gain. Compressive strength of 50.43 N/mm² recorded is within the acceptable limit for general purpose cement (BSI, 1978).

L3. De cement Brand

De cement recorded an initial setting time of 198 min and final setting time of 253 min, which was longer when compared to others as well as its high expansion of 3.00 mm implies a poor workability of the product when compared to the others; this may be responsible for its lower compressive strength of 44.93 N/mm². Nevertheless, the consistently increasing compressive strength of the product from day 3 to 28, with the mix attaining over 60% of its 28-day strength in 7 day implies good workability (Nevillle, 1981; Faleye et al., 2009). All the stated physical parameters were within the British standard limit for ordinary cement (British Standards Institution (B.S12), 1971).

L4. Sk Cement Brand

Sk cement has an initial setting time of 178 min and final setting time of 232 min, this agrees with (British Standards Institution (B.S12), 1971). The setting time obtained compared to the other brands, could be attributed to its relatively low sulphur trioxide content and relatively high C₃A content (ASTM, 1986). Sk brand recorded high compressive strength with the mix attaining over 60% of its 28-day strength in 7 days; implying a good workability of the product (Nevillle, 1981). The high compressive strength may be due to its high silica, CaO contents and relatively high C₃A content, which enhance the initial setting as well as low expansion of 1.00 mm. All the stated physical properties are within the British specifications (British Standards Institution (B.S12), 1971).

IV. Conclusion

The major general purpose cement brands studied have Al₂O₃, SiO₂ and Fe₂O₃ contents within the acceptable limits, though De brand has SiO₂ below the required limit. The cement brands also have MgO and SO₃ being generally below the recommended limit. Also C₃A, C₃AF, LSR, AR and SR in all the brands were within the recommended levels. Br brand has the longest setting time. The highest compressive strength of 50.42 and 50.43 N/mm² was recorded in Sk and Br brands respectively after 28 days. The results indicated that the
brands of cement analysed in this study showed some variation in physico-chemical properties, though they all conform to both the American and British standard specifications adopted in Nigeria for general purpose cement.

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