Analysis of Chemical Compositions of Portland Cement and Limestone from Four Geopolitical Zones of Nigeria

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Abstract
Cement, a major binding material in concrete making, influences the quality of concrete so produced with it; as such its chemistry dictates the chemistry of the concrete. Poor quality cement has recently been implicated as the main causes of incessant building collapses in Nigeria. The physicochemical analysis of limestone used in the production of various brands of Portland cement in four geopolitical zones of Nigeria (north east NE, north west NW, north central NC, and south west SW) was investigated using standard methods. Each of the limestone and cement samples was randomly collected from their respective sample points at the four different geopolitical zones of Nigeria. Each of the collected samples was ground and sieved to 2 mm mesh size. The limestone was rich in lime content that ranged from 45.91 % ± 0.30% to 49.0% ± 0.19%. Among the cement samples, percent SiO₂ ranged from 19.95 ± 0.25 (NW) to 20.18 ± 1.02 (NC), Al₂O₃ 4.98 ± 0.18 (NW) to 5.82 ± 0.38 (NE), Fe₂O₃ 2.76 ± 1.00 (NE) to 3.82 ± 0.21 (SW), CaO 60.18 ± 0.27 (NE) to 65.10 ± 0.98 (NC), MgO 1.93 ± 0.04 (NC) to 2.50 ± 0.10 (NE), SO₃ 0.93 ± 0.50 (NE) to 2.02 ± 0.13 (NW). The results showed that virtually all the cement samples analyzed conformed well to the BSEN 196-2 standard. However, the loss on ignition (LOI) deviated considerably (7.82% to 8.72%) from 4% maximum by the standard. Also, the lime saturation factor (99.70%) obtained for north central cement was slightly higher than the specified range of 92.0 to 98.0%. It could be deduced from this study that the various cements available in Nigerian market from the four geopolitical zones are of good quality. Nevertheless, other processes that lead to the production of a good concrete such as the mix ratio of cement, gravel, sand and water, use and quality of iron rods, and other building materials need to be professionally checked for
quality assurance. The findings from this study can be a useful guide to the chemist, environmentalist, construction industry, and the general public on the quality of cements available in Nigerian market.

**Keywords**
Geopolitical Zones of Nigeria, Clinker, Limestone, Portland Cement

### 1. Introduction

Ordinary Portland cement or Portland cement is a hydraulic cement (cement that not only hardens by reacting with water but also forms a water-resistant product) produced by pulverizing clinkers which consist essentially of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulphate as an underground addition [1]. Portland cement clinker is a hydraulic material which consists of at least two-thirds by mass of calcium silicates (3CaO·SiO₂ and 2CaO·SiO₂), the remainder consisting of aluminium and iron containing clinker phases and other compounds. Furthermore, Portland cement is caustic, so it can cause chemical burns. The powder can cause irritation on severe exposure, results in lung cancer and can contain some hazardous components such as crystalline silica and hexavalent chromium.

Portland cement is the most common type of cement in general use around the world for the construction of building, roads, concrete, mortar and other local purposes. Some of the raw materials used in the manufacture of ordinary Portland cement include lime which is obtained from limestone or dolomite; silica from clay or laterites; alumina and iron oxide from laterites or clay. All these components interact with one another in the appropriate proportions in the kiln to form series of complex products. Gypsum is normally added during grinding of clinker to control the setting time of the cement [2]. The low cost and widespread availability of the various raw materials used in the production of ordinary Portland cement makes it one of the cheapest materials widely used over the last century throughout the world. Concrete produced from Portland cement is one of the most versatile construction materials available in the world [3].

Limestone is a sedimentary rock composed largely of minerals calcite and aragonite which are different crystal forms of calcium carbonate (CaCO₃). Most limestone is composed of skeletal fragments of marine organisms such as coral, forams and mollusks. Limestone is a general term for rocks that contain 80% or more of calcium or magnesium carbonates, examples are chalk, marble, iolite and marl [4]. About 10% of sedimentary rocks are limestone that often contain a variable amount of silica, alumina etc.

The quality of cement may differ from one plant to another due to changes in raw material properties, kiln temperatures as well as fineness upon grinding. These changes can significantly affect the concrete properties especially when different cements are used. For example the tricalcium aluminate (C₃A) and al-
kali content of cement have been found to possess dominant effect on drying shrinkage of concrete [5]. Similarly, [6] studied the effect of fineness of cement on early strength of concrete. They observed that the coarser cement exhibits compressive strengths well below those of the finer ones at all ages tested with less heat of hydration, which results in a substantially lower semi-adiabatic temperature rise.

Cement is one of the most used basic materials which is in demand in virtually all areas of construction [7], and a major binding material in making concrete; it influences the quality of the concrete so produced with it. Therefore, its chemistry dictates the chemistry of concrete [8]. The use of poor quality cement in structural and constructional work has caused a lot of problems, including loss of lives and properties, and has been identified to have negative effects on the overall performance of cement in concrete. As a result, a lot of structures collapse. Poor quality cement has been implicated as one of the major causes of increasing building collapse in Nigeria [9].

The various chemical components of cement have an effect on the physical properties of the cement product. The American Society for Testing Materials designation C150 [10] and the American Association for State Highway Transportation Officials designation [11] have specified physical requirements for each type of cements. These properties include fineness, soundness, consistency, setting time, flexural/compressive strength, heat of hydration, specific gravity and loss on ignition [12]. Each of these properties has an influence on the performance of cement in concrete. The fineness of cement, for example, affects the rate of hydration; greater fineness increases the surface available for hydration causing greater early strength and more rapid generation of heat [13] [14].

In Nigeria the uses of poor quality cement in structural and constructional works may cause a lot of problems to the citizens, which may include cracking and collapse of structures that may lead to loss of lives and properties. As a result, quality assurance of ordinary Portland cement or Portland cement has become a very important and critical factor in cement industries. The assessment and comparative studies of the chemical components of the various cements from different manufacturers available in Nigerian market will ascertain whether they conform to available standards. This information is timely as it’s a critical factor to cement chemists and the findings from this research work will be a guide to chemists, environmentalists, regulatory bodies and general public on the quality of cements in Nigerian market.

2. Materials and Methods

2.1. Sample Collection

Portland cement and limestone used in this study were randomly collected from their respective sample points at four different geopolitical zones of Nigeria (i.e. northeast, NE; northwest, NW; north central, NC, and southwest, SW). The zones were selected based on the cement industries in those locations. Included
in this study are Ashaka cement (in Gombe State), cement of northern Nigeria (in Sokoto State), Obajana cement (in Kogi State) and Ibese cement (in Ogun State), respectively.

2.2. Sample Pre-Treatment
Each of the samples (50 g) collected was ground, sieved through a 2 mm mesh, and stored in different sample sacks until analysis.

2.3. Determination of Physicochemical Parameters
2.3.1. Determination of Moisture Content
Each sample (1 g) was weighed into a previously cleaned and weighed porcelain crucible and placed in an oven set at 1100°C for 1 h, and heated at the rate of 18°C/min. Thereafter, the crucible was removed from the oven until it was completely cool, and was re-weighed. The difference in the final and weights of the sample gave the moisture content. This procedure was repeated for all the samples according to standard methods [15] [16].

2.3.2. Loss on Ignition
Each sample (1 g) was weighed into a cleaned and weighed platinum crucible and placed in a muffle furnace set at 1000°C for 1 h. Thereafter, the crucible was removed from the furnace and kept in a desiccator until it was completely cool, and was re-weighed. The difference in the final and initial weights of the sample gave the loss on ignition. This procedure was repeated for all the other samples [15] [16].

2.3.3. Insoluble Residue
Each sample (1 g) was weighed into a preciously cleaned platinum crucible. 3 g of Na₂CO₃ (Riedel-Dottaen) was added to the crucible and stirred thoroughly with the aid of the flattened end of a glass rod. The crucible was placed in a muffle furnace set at 1000°C for 1 h for fusion. After fusion, 5 cm³ concentrated HCl (BDH, 37%) was added to dissolve the sample, to which 10 cm³ distilled water was added and warmed, and the solution was filtered through Whatman No. 40 filter paper and the residue was washed with distilled water. The filtrate was set aside for SO₃ determination. The filter paper containing the residue was placed into weighed platinum crucible and ignited in a muffle furnace at 1000°C for 30 mins. Then, the crucible was removed and kept in a desiccator until it was completely cool, and re-weighed. The insoluble residue was obtained by difference expressed as a percentage of the initial weight of the sample taken. For cement sample, fusing is not required. 1 g of cement sample was weight into a dried beaker. 25 cm³ of distilled water was added followed by the addition of 5 cm³ of concentrated HCl and stirred thoroughly, warmed, and to which 25 cm³ of distilled water was added. To this was added 5 cm³ of HCl and the solution later digested at 60°C for 15 mins. This solution was filtered using Whatman No. 40 and washed thoroughly with distilled water. The filtrate was also kept aside for
SO$_3$ determination according to standard methods [15] [16]. This procedure was repeated for all the samples.

2.3.4. Determination of SO$_3$

The filtrate set aside during the determination of insoluble reside was diluted to 250 cm$^3$ with distilled water and boiled to reduce the filtrate to 150 cm$^3$. 10 cm$^3$ of hot 10% barium chloride solution was added drop wisely to the filtrate with continuous stirring for 30 mins, until all the precipitate was formed. The liquor containing the precipitate was digested on water bath for 4 h. Precipitate was filtered using Whatman filter paper No.42. The residue was washed with hot distilled water. The filter paper along with the residue was re-weighed in a crucible and ignited for 1 h. The SO$_3$ content was obtained by difference expressed as a percentage of initial weight of sample taken during insoluble residue determination [15]. This procedure was repeated for all the samples.

2.3.5. Determination of Silica (SiO$_2$)

Each sample (0.5 g) was weighed into a clean dry platinum crucible. 1.5 g of Na$_2$CO$_3$ was added to the sample and mixed thoroughly and the crucible put in a muffle furnace at 1000˚C for 1 h to fuse. After fusion was completed, 10 cm$^3$ concentrated HCl was added to dissolve the fused sample. The solution was digested at low temperature to almost dryness.

For the cement sample, 0.5 g was weighted into a tarred clean dry beaker to which 1.5 g of ammonium chloride was added and mixed thoroughly by using the tip of a glass rod to avoid lumps, followed by the addition of 5 cm$^3$ of concentrated HCl with thorough stirring. The solution was digested at low temperature to almost dryness. 20 cm$^3$ of distilled water was be added with stirring, followed by the addition of 3 cm$^3$ concentrated HCl in which a yellow color was observed. The solution was filtered through Whatman No 40 filter paper. The precipitate was washed with hot distilled water and the filtrate kept aside for combined oxide determination. The filter paper along with the residue was placed into a weighed platinum crucible and ignited for 1 h. The silica content was obtained by difference expressed as a percentage of the initial weight of the sample taken [15] [16]. This procedure was repeated for all the samples.

2.3.6. Determination of Combined Oxide (R$_2$O$_3$)

Ammonium chloride (BDH, 2.3 g) was added to the filtrate set aside during silica determination and boiled for 10 mins. 3 drops of conc. HNO$_3$ (BDH, 69%) was added and the solution was allowed to boil for some minutes. On boiling, 20 cm$^3$ of concentrated ammonia was added until precipitate formed. To the precipitate was added little and then excess concentrated NH$_3$ until no color change was observed. The solution was filtered through Whatman No. 41 filter paper. The precipitate was washed with hot distilled water and the filtrate set aside for CaO determination. The residue was washed with 2% ammonium nitrate solution then with hot distilled water till the residue was free from chloride. The filter paper along with the residue was placed into a weighed crucible and ignited.
The percentage of iron oxide was obtained by the formula:

\[
\frac{0.4 \times \text{Volume of } K_2Cr_2O_7 \ \text{Consumed}}{\text{Weight of sample}} \times 100\% 
\]

(1)

2.3.8. Determination of Alumina (Al₂O₃)

This was obtained by difference. The combined oxide (R₂O₃) is the combination of both iron oxide and aluminum oxide,

\[
R_2O_3 = Fe_2O_3 + Al_2O_3 
\]

(2)

\[
Al_2O_3 = R_2O_3 - Fe_2O_3 
\]

(3)

2.3.9. Determination of Lime (CaO)

The filtrate set aside during determination of combined oxide was boiled to reduce the volume to 150 cm³ after which 30 cm³ of 5% ammonium oxalate (May & Baker) solution was added until a white precipitate formed. The liquor containing the precipitate was digested on a water bath for 4 h, filtered through Whatman No. 42 filter paper and filtrate set aside for magnesium oxide determination. The filter paper along with the residue was placed into a weighed platinum crucible and ignited for 1 h. The percentage lime content was obtained by difference, expressed as a percentage of the initial weight taken for determination of silica. This procedure was repeated for all the samples [15] [16].

2.3.10. Gravimetric Determination of MgO

To about 250 cm³ of the filtrate set aside during lime determination, 10 cm³ concentrated HCl was added and then reduced to 150 cm³ by boiling. The solution was allowed to cool to room temperature after which 40 cm³ of concen-
trated ammonia was added. 10 cm$^3$ of ammonium dihydrogenorthophosphate solution was added and stirred thoroughly until a cloudy precipitate. The liquor containing the precipitate was kept in a dark place overnight after which it was filtered through Whatman No. 40 filter paper and washed with hot distilled water. The filter paper containing the precipitate was placed inside a weighed crucible and ignited for 1 h. The MgO content was obtained by difference, expressed as a percentage to the initial weight of sample taken for determination of silica [15] [16].

2.4. Determination of K$_2$O by Flame Atomic Absorption Spectrophotometer (AA32 Model)

Digestion of Samples
Each sample (0.5 g) was weighed into 50 cm$^3$ beaker then 10 cm$^3$ of distilled water was added to form slurry. 10 cm$^3$ of 2 M HCl (1:19) was added and the mixture was warmed until the sample dissolved. Glass rod was used to break any lumps formed and the solution was filtered through filter paper into 100 cm$^3$ volumetric flask. The residue was washed with boiling water until the filtrate was about 80 cm$^3$ in the 100 cm$^3$ volumetric flask. The filtrate was allowed to cool to room temperature after which 10 cm$^3$ of 2M phosphoric acid (1:19) was added to the solution and made to the mark with distilled water. The solution was aspirated into the flame photometer and the absorbance of potassium was measured at 768 nm [15].

2.5. X-Ray Fluorescence (XRF) Determinations

Preparation of the Sample
Each sample (10 g) was weighed into a weighted boat. Four tablets of ethylene glycol were added to the weighed sample and ground together with the aid of an automated milling machine. The ground mixture was pelletized with the aid of a pelletizing machine inside a ring after which the ring put into the XRF (Thermo scientific; model ARL-990) for analysis [17].

The cement control parameters such as lime saturation factor (LSF), silica ratio (SR) and alumina/iron ratio (AR) influences the performance of cement and it is most often used for control purposes (Taylor, 1990). These values are obtained from the formulae shown in Equations (4) to (6):

$$\text{LSF} = \frac{\text{CaO}}{2.8\text{SiO}_2 + 1.2\text{Al}_2\text{O}_3 + 0.65\text{Fe}_2\text{O}_3} \times 100$$  \hspace{1cm} (4)

$$\text{SR} = \frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$$  \hspace{1cm} (5)

$$\text{AR} = \frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3}$$  \hspace{1cm} (6)

3. Statistical Analysis

The data obtained were analyzed using mean, standard deviation, and ANOVA
4. Results and Discussion

The XRF composition of cements from the four geopolitical regions of Nigeria is presented in Table 1.

A comparison of the XRF and gravimetric compositions (Table 2) of cement from the four geopolitical zones showed that most of the parameters were higher in the XRF than the gravimetric values, except for MgO, SiO2, Al2O3, and SO3. This difference may have been due to losses usually associated with gravimetric method.

The composition of the oxides in various brands of cement as determined indicated that they are within the stipulated limits given by [18]. The values of loss on ignition (LOI) obtained from this analysis were found to be higher when compared with the result obtained by [19] whose result included the analysis of imported cement samples. LOI is a measure of the amount of CO2 and water present in the cement which are emitted when cement is incinerated up to 950˚C. This indicated that the samples of this research work are likely to possess

Table 1. XRF composition of cement from the four geopolitical regions of Nigeria.

<table>
<thead>
<tr>
<th>Parameter (%)</th>
<th>N.E</th>
<th>N.W</th>
<th>N.C</th>
<th>S.W</th>
<th>p-Value</th>
<th>BSEN 196-2 [18]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>20.00 ± 1.60a</td>
<td>19.95 ± 0.25a</td>
<td>20.18 ± 1.02a</td>
<td>20.16 ± 0.26a</td>
<td>0.988</td>
<td>18.0 - 24.0</td>
</tr>
<tr>
<td>Al2O3</td>
<td>5.82 ± 0.38a</td>
<td>4.98 ± 0.18a</td>
<td>5.34 ± 0.09a</td>
<td>5.04 ± 0.12a</td>
<td>0.117</td>
<td>2.6 - 8.0</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>2.76 ± 1.00a</td>
<td>3.20 ± 0.18a</td>
<td>3.67 ± 0.08a</td>
<td>3.82 ± 0.21a</td>
<td>0.206</td>
<td>1.5 - 7.0</td>
</tr>
<tr>
<td>CaO</td>
<td>60.18 ± 0.27a</td>
<td>61.40 ± 2.65bc</td>
<td>65.10 ± 0.98bc</td>
<td>62.75 ± 1.15bc</td>
<td>0.0126</td>
<td>1.0 - 69.0</td>
</tr>
<tr>
<td>MgO</td>
<td>2.50 ± 0.10a</td>
<td>2.20 ± 0.22bc</td>
<td>1.93 ± 0.04bc</td>
<td>2.00 ± 0.20bc</td>
<td>0.009</td>
<td>0.5 - 4.0</td>
</tr>
<tr>
<td>SO3</td>
<td>0.93 ± 0.05a</td>
<td>2.02 ± 0.13bc</td>
<td>1.86 ± 0.14bc</td>
<td>1.68 ± 0.04bc</td>
<td>0.000</td>
<td>0.2 - 4.0</td>
</tr>
</tbody>
</table>

BSEN196-2 = British Standard Specification; Means with different superscripts across the row are significant (P ≤ 0.05). Means with the same superscript across the rows are not significant (P ≥ 0.05).

Table 2. Gravimetric compositions of cement from the four geopolitical regions of Nigeria.

<table>
<thead>
<tr>
<th>Parameter (%)</th>
<th>N.E</th>
<th>N.W</th>
<th>N.C</th>
<th>S.W</th>
<th>p-Value</th>
<th>BSEN 196-2 [18]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>19.0 ± 0.25a</td>
<td>22.10 ± 0.76b</td>
<td>19.50 ± 0.07b</td>
<td>21.90 ± 0.58c</td>
<td>0.00</td>
<td>18.0 - 24.0</td>
</tr>
<tr>
<td>Al2O3</td>
<td>5.18 ± 0.18a</td>
<td>5.85 ± 0.01b</td>
<td>5.01 ± 0.03a</td>
<td>6.25 ± 0.14bc</td>
<td>0.00</td>
<td>2.6 - 8.0</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>2.50 ± 0.17a</td>
<td>5.00 ± 0.08b</td>
<td>3.23 ± 0.40c</td>
<td>4.85 ± 0.05b</td>
<td>0.00</td>
<td>1.5 - 7.0</td>
</tr>
<tr>
<td>CaO</td>
<td>58.60 ± 0.40a</td>
<td>64.25 ± 0.23b</td>
<td>60.50 ± 0.67c</td>
<td>61.58 ± 0.64b</td>
<td>0.00</td>
<td>61.0 - 69.0</td>
</tr>
<tr>
<td>MgO</td>
<td>1.20 ± 0.10a</td>
<td>3.50 ± 0.06b</td>
<td>1.80 ± 0.14c</td>
<td>3.52 ± 0.05b</td>
<td>0.00</td>
<td>0.5 - 4.0</td>
</tr>
<tr>
<td>SO3</td>
<td>2.01 ± 0.15a</td>
<td>3.50 ± 0.08b</td>
<td>1.57 ± 0.21a</td>
<td>2.85 ± 0.09bc</td>
<td>0.00</td>
<td>0.2 - 4.0</td>
</tr>
<tr>
<td>IR</td>
<td>1.70 ± 0.02a</td>
<td>2.20 ± 0.04b</td>
<td>1.50 ± 0.16a</td>
<td>1.80 ± 0.16a</td>
<td>0.00</td>
<td>≤1.5</td>
</tr>
<tr>
<td>LOI</td>
<td>8.10 ± 0.03a</td>
<td>7.82 ± 0.10b</td>
<td>8.72 ± 0.06b</td>
<td>8.50 ± 0.24bc</td>
<td>0.003</td>
<td>≤4.0</td>
</tr>
<tr>
<td>MC</td>
<td>0.25 ± 0.08a</td>
<td>0.50 ± 0.09b</td>
<td>0.20 ± 0.03c</td>
<td>0.35 ± 0.08bc</td>
<td>0.006</td>
<td>-</td>
</tr>
<tr>
<td>Free Lime</td>
<td>1.04 ± 0.05a</td>
<td>1.20 ± 0.12b</td>
<td>0.88 ± 0.04b</td>
<td>0.98 ± 0.04bc</td>
<td>0.002</td>
<td>≤2.0</td>
</tr>
</tbody>
</table>
more water and CO₂ that are readily available to evaporate during burning. This may be partly attributed to improper and prolonged stage or adulteration of cement during transportation [20]. The percentage of sulphite (SO₃) present in all the samples were found to be less than 3.5% which is the upper limit for sulphite (SO₃) content in cement, hence there may be no risk of failure due to heat curing of concrete [21].

The British standards specified that the lime (CaO) content should be within the range 63% to 67%. It was observed that all the brands of cement analyzed fall within this specified range as shown in Table 1 and Table 2. The proper lime content is limited due to the lower early strength produced when the lime content of ordinary Portland cement is too low and unsoundness when the lime content is too high [22] [23]. High lime content is associated with early strength which favors ultimate strength that develops gradually over a long period of time [23]. In order to increase the strength, it is necessary to raise the lime content, or grand finer or combining both, but this may be with an adverse effect since high temperature will be required to burn the high lime mixture [24]. It was observed that the entire sample analyzed did not exceed the maximum MgO limit of 4.0%, as specified by [18]. [24] stated that higher magnesia content may be detrimental to the soundness of the cement resulting in expansion crack commonly known as magnesia expansion. This occurs when the magnesia content is beyond the upper limit as specified by [18]. The magnesia appears in clinker as free MgO (Periclase), this reacts with water to form Mg(OH)₂ which is the slowest reaction among all other hardening reactions [25]. Since Mg(OH)₂ occupies a larger volume than MgO and it is formed on the same spot where the periclase particle is located, it can split apart the binding of the hardened cement paste thereby causing cracking [23] [26]. The free lime was found to be within the specified limit of the British standard for all the samples analyzed. There is no advantage in adding extra lime unless it is brought into combination with other constituents. If appreciable lime is left uncombined, it may cause expansion which may possibly result into cracking of the mortar [23] [27].

The statistical analysis (ANOVA) of the cement samples indicated that for SiO₂, Al₂O₃, Fe₂O₃ there is no significant difference across the geopolitical zones as the p-value of the parameters were greater than 0.05; but for CaO, MgO and SO₃ in N.E and N.W samples there is significant difference, the p-value is less than 0.05.

Limestone and dolomite constitute a group of raw-materials commonly referred to as carbonate rocks [28], that affect the composition and properties of cement. The XRF composition of limestone from the four geopolitical regions of Nigeria is presented in Table 3.

[29] reported that strength at 2 days was increased by K₂O additions of up to 1.5%, and Na₂O additions of up to 1.5% when the degree of sulfatisation was 100%; Strengths after 2 and 7 days were increased by K₂O and Na₂O contents up to about 1.5%. Higher alkali contents and supersulfatisation reduced strengths.
Table 3. XRF composition of limestone from the four geopolitical regions of Nigeria.

<table>
<thead>
<tr>
<th>Parameter (%)</th>
<th>N.E</th>
<th>N.W</th>
<th>N.C</th>
<th>S.W</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>11.63 ± 0.12&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.58 ± 0.12&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.50 ± 0.09&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4.08 ± 0.08&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.000</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.94 ± 0.08&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.90 ± 0.09&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.66 ± 0.24&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.22 ± 0.03&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.000</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.59 ± 0.14&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.35 ± 0.06&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.94 ± 0.02&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.88 ± 0.22&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.000</td>
</tr>
<tr>
<td>CaO</td>
<td>45.91 ± 0.30&lt;sup&gt;a&lt;/sup&gt;</td>
<td>46.42 ± 0.16&lt;sup&gt;b&lt;/sup&gt;</td>
<td>48.90 ± 0.12&lt;sup&gt;c&lt;/sup&gt;</td>
<td>49.0 ± 0.19&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.000</td>
</tr>
<tr>
<td>MgO</td>
<td>0.44 ± 0.04&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.94 ± 0.03&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.71 ± 0.03&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.01 ± 0.04&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.000</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.73 ± 0.03&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.58 ± 0.02&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.19 ± 0.03&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.25 ± 0.02&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.000</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.57 ± 0.03&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.20 ± 0.02&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.06 ± 0.03&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.07 ± 0.03&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.000</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.08 ± 0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.0 ± 0.00&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.0 ± 0.00&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.0 ± 0.00&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Means with different superscripts across the row are significant (P ≤ 0.05). Means with the same superscript across the rows are not significant (P ≥ 0.05).

The strengths at 28 and 90 days were reduced by additions of Na₂O and K₂O; for equal additions, Na₂O had a greater influence than K₂O. For K₂O, the optimum degree of sulfatisation was 60% - 70% and for Na₂O it was 90% - 100%. The reduction in strength at 28 and 90 days in cements containing K₂O can be offset by increasing the silica ratio, regardless of whether there was an optimum degree of sulfatisation. This action is only successful in cements containing Na₂O. The strengths after 28 and 90 days were increasingly reduced by increasing K₂O and Na₂O contents. For equally high contents of alkali oxides, the strengths after 28 and 90 days were reduced to a greater extent by Na₂O than by K₂O. Equal molar proportions of the two alkali oxides lowered the strengths by equal amounts where the degree of sulfatisation was below 100%. For alumina ratios between 1.3 and 2.7, the optimum degree of sulfatisation was about 60% for K₂O and about 100% for Na₂O. The reduction in strength after 28 and 90 days by K₂O contents up to ~1.5% can be offset by lowering the alumina ratio where there is an optimum degree of sulfatisation, but the reduction in strength caused by Na₂O contents up to 1.5% is only partly compensated.

Table 4 shows the cement control parameters such as lime saturation factor (LSF), silica ratio (SR) and alumina to iron ratio (AR), that influence the performance of cement and it is most often used for control purposes [30]. The LSF controls the C₃S and C₂S ratio in the clinker. A clinker with a higher LSF value will pose a high proportion of C₃S to C₂S ratio than that with a low LSF value [19].

Table 4 indicated that the N.C cement sample had higher LSF value of 99.70% when compared with the value obtained for N.E cement sample (92.62%), so the corresponding proportion of C₃S to C₂S in N.C cement is 65.16% to 8.79%, while that of N.E cement is 43.46% to 24.63%. The silica ratio (SR) and Alumina ratio (AR) of the cement samples considered in this study did not significantly deviate from each other, hence the calcium silicate and aluminate in the cement as considered in this study are within the acceptable limits. A high silica ratio indicated...
Table 4. Silica ratio, alumina ratio, and lime saturation factor of cement from four geopolitical regions of Nigeria.

<table>
<thead>
<tr>
<th>Parameters (%)</th>
<th>N.E</th>
<th>N.W</th>
<th>N.C</th>
<th>S.W</th>
<th>p-value</th>
<th>BSEN 196-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lime Sat. Factor (LSF)</td>
<td>92.62 ± 0.13a</td>
<td>96.06 ± 0.09b</td>
<td>99.70 ± 0.65c</td>
<td>96.57 ± 0.34b</td>
<td>0.000</td>
<td>92.0 - 98.0</td>
</tr>
<tr>
<td>Silica Ratio (SR)</td>
<td>2.33 ± 0.09a</td>
<td>2.44 ± 0.10a</td>
<td>2.24 ± 0.08a</td>
<td>2.28 ± 0.04a</td>
<td>0.074</td>
<td>2.0 - 3.0</td>
</tr>
<tr>
<td>Alumina Ratio (AR)</td>
<td>2.11 ± 0.11a</td>
<td>1.55 ± 0.07b</td>
<td>1.46 ± 0.04bc</td>
<td>1.32 ± 0.13c</td>
<td>0.000</td>
<td>1.0 - 4.0</td>
</tr>
</tbody>
</table>

Means with different superscripts across the row are significant (P ≤ 0.05); means with the same superscript across the rows are not significant (P ≥ 0.05).

that more calcium silicate is present in the clinker and less aluminate and ferrite. The conventional silica ratio (SR) is between 2.0 and 3.0. A high AR value means that there will be proportionally more aluminate than ferrite in the clinker. In Ordinary Portland Cement (OPC) clinker, the alumina (AR) ratio is within the range of 1 to 4 [30].

Table 4 showed that silica ratio (SR) varied slightly among the cement samples from the four different geopolitical zones being highest in N.W (2.44%) and lowest in N.C (2.44%). The alumina ratio (AR) was highest in N.E (2.11%) but lowest in S.W (1.32%). The LSF is the molar ratio of CaO to the other three main oxides. The lime saturation factor (LSF) ranged from 99.70% in N.C to 92.62% in cement samples from north eastern Nigeria. There will be a condition where the amount of CaO present will be sufficient to produce only C₃S, C₃A and C₄AF and under these circumstances the LSF is 1.0. If the LSF is increased in a clinker raw feed while maintaining the SR and AR, effects are observed in the clinker such as quantity of alite increases showing potential strength improvement; quantity of belite decreases, indication of more heat evolution on hydration; and higher burning temperatures are indicative that burnability decreases. The variation of parameters SR, AR, or LSF significantly affects the quality of the cement clinker. [31] investigated on laboratory clinker made from cement raw meals with a lime saturation factor of 93%, and an alumina ratio of 2.0. The silica ratio (1.6 - 3.2), the alkali contents and the degree of sulfatisation were varied. Strength tests showed that: increasing silica ratio strength was generally increased, and reduced with increasing SO₃ content. Further investigations on laboratory clinker made from cement raw meals with a uniform lime saturation factor of 93% and a silica ratio of 2.4. The alumina ratio (1.3 - 2.7), alkali contents (Na₂O and K₂O each ~0% - 2%) and the degree of sulfatisation were varied. Strength tests showed that the strengths always increased with falling alumina ratio. [29] reported that when the investigations were with a silica ratio of 2.4 and an alumina ratio of 2.0, the lime saturation factor, the alkali contents and the degree of sulfatisation were varied. Strength tests showed that the strengths were increased with increasing lime saturation factor. Cements rich in tricalcium silicate showed high strength at early ages, while those which were low in this compound showed much lower strengths at early ages, but a progressive increase with age, so that at 6 months the differences in the strengths were relatively small. At 12 months the strengths of the two groups of cements were about equal.
The cement control parameters LSF and AR, showed significant difference across the zones 0.05 (p ≤ 0.05), unlike the SR parameter, that showed no significant difference across the zones (p ≥ 0.05).

5. Conclusion

The physicochemical analysis of limestone used in the production of Portland cement in four geopolitical zones of Nigeria (north east, north west, north central, and north east) was investigated. The results obtained from this research work show that virtually all the cement samples analyzed conformed well to the BSEN 196-2 standard. However, the loss on ignition (LOI) deviated considerably (7.82% to 8.72%) from 4% maximum by the standard. Also, the lime saturation factor (99.70%) obtained for north central cement was slightly higher than the specified range of 92.0% to 98.0%. Although poor quality cement has recently been implicated as the main cause of incessant building collapses in Nigeria, it could be deduced from this study that the various cements available in Nigerian market from the four geopolitical zones are of good quality. Nevertheless, other processes that lead to the production of a good concrete such as the mix ratio of cement, gravel, sand and water, use and quality of iron rods, and other building materials need to be professionally checked for quality assurance.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References


