Physico-Chemical Classification of Nigerian Cement

Muibat Diekola Yahaya

Department of Chemical Engineering, Federal University of Technology
Minna, Niger State, Nigeria
Email: <mdoyejobi@yahoo.com>

Abstract

The characterization and classification of cement is based on the determination of its chemical composition and physico-mechanical properties. The set of standards used for this project included the American Society for Testing and Materials (ASTM) and British Standards Institution (BSI) standards. Titrimetric/gravimetric methods of analysis were used. Four major cement samples using various physico-chemical methods were analyzed; two locally manufactured and two imported. Results of all the analysis showed that the locally produced cements, i.e., Elephant and Ashaka, differ in their physico-mechanical properties from the international ASTM and BSI standards. They are better used for structures involved with low load carrying capacities.

The Burham cement matched well both in its chemical and physico-mechanical properties and thus can be subjected to structures involved with loading. Dangote cement needs to be further investigated upon. The developed assessment technique based on comparative analysis of ASTM and BSI standards with the technical qualities of the local cement brands can be used to control product quality during manufacturing of cement.

Keywords: Chemical composition, titrimetric/gravimetric method, Burham cement, Dangote cement, physico-mechanical structures.

Introduction

Cements may be defined as adhesive substances capable of uniting fragments or masses of solid matter to a compact whole (Ghosh 1983). Cement functions by forming a plastic paste when mixed with water, which develops rigidity (sets) and steadily increases in compressive strength (hardness) by chemical reaction with the water (hydration). When a material increases in strength even when stored under water after setting it, the material is said to be hydraulic (Lea 1970).

This definition includes organic polymer based cements which are used as adhesive, binders for aggregates used as hardening patching materials for damaged roads and bridge decks. However, the use of this organic-based cement is limited due to its expensiveness as compared to the use of inorganic cements among which Portland cement is pre-eminent.

The properties of the final products of Portland cements are dependent on the chemical and morphological composition of clinker, gypsum and other additives introduced during the process of grinding. Changes in cement properties could occur during subsequent storage. Since the cement quality can be overwhelmingly dependent on the quality of clinker, it therefore means that any consideration of its characteristics requires a basic understanding of the factors that control the clinker quality and clinkerization process (Bye 1983).

Objective of Study

Because of the complexity of the factors influencing the rate of hydration and the hydraulics of cement, the assessment of cement classification and quality relies on direct performance tests. It can be seen from the literature that the values obtained for the basic composition, physical properties, etc., are

particularly method dependent, so that a prescribed procedure must be followed and named when referring to the results obtained. This is presently not the case in the assessment of the various brands of cement in the country.

The major objectives of study therefore are:

1. Develop a standard specification method based on the chemical composition and physical characteristics of the Nigerian cement.

2. Develop a classification guideline for purchaser and users by specifying requirements on primary properties of the Nigerian cement influencing its quality and areas of application.

Method and Scope

A preliminary survey on the different types of cement available in Nigeria was done and their relative availabilities considered.

Sampling points include all the six geographical zones in Nigeria. These are as follows:

(i) Sokoto cement of the North-Western zone;

(ii) Ashaka cement of the North-Eastern zone;

(iii) Benue cement of the Middle-Belt;

(iv) The West African Portland cement of South West;

(v) The Nigerian cement, Nkalagu, of South-East;

(vi) The Calabar cement company, Calcemco of South-South.

The imported cements were also considered, namely, Dangote cement and Burham cement.

Due to the skeletal operation and in some cases complete shut down of some indigenous cement companies, only 2 locally produced cements were available at the time of study.

Parameters measured include:

1. The bulk chemical composition of the cement. The cement was analyzed to determine the percentage composition of SiO_2, CaO, Fe_2O_3, Al_2O_3, MgO, SO_3, etc.;

2. Particle size composition of the cement;

3. Setting time of the cement;

4. Compressive strength of the cement;

5. Soundness of the cement;

6. Consistency of the cement.

Relevance of Study

BSI (1978) protects the purchaser of cement by specifying requirements for those properties primarily influencing its quality. It is important that the Nigerian cement conforms to the set of internationally required standards.

In practice, cement structure durability, i.e., resistance to aggressive agents, is determined largely by concrete permeability and it is influenced by the efficiency with which cement hydration products fill the void between the grains of aggregates. Poor conformity of structures to established guidelines leads to the development of their degradation. This has necessitated investigations into the basic raw materials compositions, the finished products and other factors that could ensure longer service life for cement-based structures.

Therefore, with the present socio-economic development and the envisaged technological advancement, the increased demand for cement cannot be overemphasized. It has become necessary, therefore, to characterize the available cement and effectively determine the area of optimal application.

Methodology

All the experimental methods carried out in this project are aimed at analyzing and determining the percentage chemical composition of the various oxides in cements, the mechanical and physical properties and the calculated mineral content of the cement. The methods used are as specified in ASTM (1986) and BSI (1978).

Chemical Analysis by Conventional Method

Analysis of major components of various cement slurries was performed. The said components are SiO_2, CaO, Fe_2O_3, Al_2O_3, MgO, SO_3 as well as compounds such as K_2O, Na_2O, Ca_2O_2, MnO_2, and other impurities that make up the remaining balance.

Loss on Ignition, Procedure: Approximately 1.0g of sample was weighed in

a platinum crucible at a temperature of 25°C, capacity of 25-30 ml. This material was heated in a muffle furnace at a temperature between 900-1,000°C, cooled and weighed, W_1. The loss in weight was checked by a second heating at same temperature for 5 min and the content reweighed. This process was repeated until a constant weight was attained, W_2. The loss in weight was recorded as the loss in ignition. Percentage loss on ignition was calculated as follows:

$$W = W_1 - W_2,$$
$$\% \text{ loss of ignition} = (W \text{ x } 100)/W_1,$$
where: W = weight of sample taken.

Determination of Oxide in Cement Silica, Procedure: As stated in the Annual Book of the ASTM Standard (ASTM 1986), the procedure is as follows:

0.5g of the cement sample was mixed thoroughly with 0.5g of NH_4Cl in a 50-ml beaker. The beaker was covered with a watch glass and 5ml of HCl was cautiously added by allowing the acid to run down the lip of the covered beaker. Then 1-2 drops of HNO_3 was added to the mixture after the chemical reaction has subsided and stirred with a glass rod. The covered beaker was set on a steam bath for digestion for 30 minutes with occasionally stirring and breaking up of any lumps to facilitate complete decomposition of the cement.

A medium-textured filter paper is fitted to the funnel and the jelly-like mass of silicic acid is filtered as completely as possible without dilution and the solution is allowed to drain through. The beaker was rinsed with hot HCl (1:99) 2 to 3 times and then with 10-12 small portions of hot water. Each portion is allowed to drain through completely before adding another. The filtrate was reserved for determination of ammonium hydroxide group.

The filter paper and residue was transferred into weighed platinum crucible, W_1. This material was dried and ignited first slowly without inflaming until the filter paper was charred and finally at 1,100-1,200°C for 1 hr in a muffle furnace. This material was cooled in desiccators and weighed, W_2.

The SiO_2 obtained contains small impurities which were treated in the crucible with 1 or 2 ml of water, 2 drops of H_2SO_4 (1:1) and 20 ml of HF and cautiously evaporated to dryness. The residue was heated at 1,050-1,100°C for 5 minutes, and cooled and weighed, W_3.

The difference between this weight and the weight previously obtained represents the weight of SiO_2.

Calculations:
Silica (%) = $(((W_1 - W_2) + W_3)/W)$ x 100,
where:
W_1 = weight of silica and insoluble impurities;
W_2 = weight of impurities;
W_3 = weight of silica recovered from iron and aluminium oxide;
W = weight of sample taken.

Combined Ferric Oxide and Alumina, Procedure: As carried out in the Annual Book of the ASTM Standard (ASTM 1986), the procedure used was as follows. 5ml of HCl was added to the filtrate reserve after separating silica. Few drops of methyl red indicator was added and treated with NH_4OH (1:1) dropwise until the colour of the solution becomes distinctly yellow, a drop is added in excess for confirmation.

The solution containing the precipitate was heated to boiling for about 50 to 60 seconds and was allowed to settle down 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 precipitate for at least 2-3 times.

The filtrate was set aside and the precipitate was transferred alongside the filter with the same beaker where the first precipitation was effected. The precipitate was dissolved by using hot HCl (1:2) and stirred by thoroughly macerating the paper. The solution was diluted to about 100ml and re-precipitation was carried out as done previously The solution was filtered and the precipitate was washed with about four 10ml portion of hot NH_4NO_3 solution (20g/l). The filtrates were combined, set aside and reserved for the determination of CaO.

The precipitate was placed in a weighed platinum crucible and the papers were slowly heated until they charred. This material was finely ignited to constant weight at 1,050-

1,100°C.

Calculations:

Combined $Al_2O_3 + Fe_2O_3$ (%) = (Si x 100)/W,

where:

Si = weight of crucible;

W = weight of the sample taken.

Ferric Oxide, Procedure: From the chemical analysis of cement by conventional and instrumental techniques as operated under BSI (1978) alternate method, iron can be determined gravimetrically by nitrosopherryl hydroxylamine (cupferron) as ferric oxide. The procedure employed was as follows. The solution (100ml) from silica filtrate (made up to 250ml) was cooled to 10°C. A freshly prepared and filtered 5% aqueous cupferron solution was slowly added. These were rigorously stirred until no further formation of brown precipitate. After thoroughly stirring it, this material was filtered through Whatmann filter paper No.41 and the precipitate was washed several times with 10% by volume of HCl containing 1.5g of cupferron per litre and twice with 5M of ammonia solution to remove excess cupferron and finally washed once with water.

The precipitate in a weighed platinum crucible was slowly charred and finally ignited to constant weight at 1,000°C.

Calculation:

Fe (%) = (Weight of precipitate x 100)/(Weight of samples).

Magnesium Oxide, Procedure: The filtrate after removal of CaO was acidified with HCl and concentrated to about 150ml. Approximately 10ml of ammonium hydrogen phosphate (25% w/v) was added to the solution and cooled to 10°C by placing it in ice cold water. NH_4OH was added dropwise with constant stirring until becoming yellow and 1-2 ml in excess.

The solution was kept in a cool atmosphere, overnight and filtered through Whatman filter paper No.42. The precipitate was washed with 10g NH_4NO_3 + 20ml NH_4OH and diluted to 100ml. In a weighed platinum crucible, the precipitate with filter paper was placed and slowly heated to char the paper without inflaming it and finally ignited until

obtaining constant weight at a temperature of 1,100-1,200°C.

Calculations:

MgO(%) = Weight of Ignited Residue x 0.362 x 100)/W,

where:

W = Weight of sample;

conversion factor of $Mg_2P_2O_7$ to MgO = 0.362.

Sulphate (as SO₃), Procedure: Approximately as stated in BSI (1978) of testing and quality control in cement industry, 1.0g of cement sample accurately weighed to four decimal places was taken and 25ml of cold water and 5ml of HCl was added while stirring the mixture vigorously. The solution was heated for complete decomposition of sample and diluted to 50ml. Solution was digested for 15 minutes at a temperature just below boiling. This material was filtered through a medium-textured paper and washed thoroughly with hot water. The filtrate was diluted to 250ml and heated to boiling, 10ml of hot $BaCl_2$ (100g/l) was added and boiling was continued until the precipitate was well formed. The solution was digested for 8 hrs at temperature just below boiling and the volume of solution was maintained between 225-260ml by adding water when necessary.

The solution was filtered through a retentive paper and washed thoroughly with hot water. The filter paper with precipitate in a weighed platinum crucible was charred without inflaming and finally ignited at a temperature of 800-900°C until constant weight was attended, then it was cooled in a dessicator and weighed at SO_3.

Calculations:

SO_3(%) = (Weight of Ignited Residue x 0.343 x 100)/W,

where:

W = Weight of the sample;

conversion factor for $BaSO_4$ to sulphate (SO_3) = 0.343, i.e., the molecular ratio of SO_3 to $BaSO_4$.

Calcium Oxide (CaO), Procedure: From the Annual Book of ASTM Standard (ASTM 1986) alternate method, the procedures used were as follows.

The filtrate (200 ml) obtained in the

determination of the ammonium hydroxide group was acidified by using 5ml of HCl. A few drops of methyl red indicator were added to the solution and 30ml of warm ammonium oxalate (50g/l) was also added. The solution was heated to a temperature of 70-80°C. NH_4OH (1:1) was added dropwise with constant stirring until changing the colour from red to yellow. The solution was allowed to stand for 1 hour with occasionally stirring during the first 30 minutes. The solution was filtered using a retentive paper and was washed moderately with cold ammonium oxalate (1g/l). The filtrate was reserved for the determination of MgO.

The precipitation and filter paper were transferred to the same beaker in which precipitation was first made. The oxalate was dissolved in 50ml of hot HCl (1:4) and the filter paper was macerated. The mixture was diluted to 200ml with water and few drops of methyl red indicator were added together with 20ml of ammonium oxalate. The solution was heated nearly to boiling and calcium oxalate was precipitated again by neutralizing the acid solution with NH_4OH (1:1) dropwise until distinctly changing the colour to yellow. The solution was combined with that already obtained for the determination of MgO.

The precipitate was dried in a weighed covered platinum crucible and the paper was charred without inflaming. Finally, the tightly covered crucible was heated in a muffle furnace at a temperature of 1,100 to 1,200°C, cooled in a desiccator and weighed as CaO. The ignition was repeated until a constant weight was obtained.

Calculation:
CaO (%) = Weight of Precipitate x 100)/W,
where: W = Weight of the sample taken.

Insoluble Residue, Procedure: From the chemical analysis of cement by conventional and instrumentation techniques according to the ASTM reference method (ASTM 1986), the procedures used were as follows.

1 g of the sample was weighed and 25ml cold water was added to the dispersed cement while swirling was quickly added to 5ml of HCl. The solution was warmed and the material was well grinded with the flattened end of a glass until the cement was well decomposed. The solution was diluted to 50ml in hot water and heated to near boiling by means of a high-temperature hot plate. The covered mixture was further digested for 15 minutes at a temperature just below boiling. The solution was then filtered through a medium-textured paper into a 400ml beaker and the precipitate was thoroughly washed with hot water. The filter paper was transferred into the original beaker and 100ml of hot (near boiling) NaOH solution (10g/l) was added. This material was digested at a temperature below boiling for 15 minutes. During digestion, the mixture was occasionally stirred and the filter paper was well macerated. The solution was acidified with HCl and methyl red indicator was added.

The solution was filtered through medium-textured paper and washed with hot NH_4NO_3 solution (20g/l) at about 14 times. The residue was ignited in a weighed platinum crucible at 900-1,000°C and cooled in a dessicator. The cooled product was weighed as percentage of insoluble residue.

Calculations:
Insoluble Residue (%) =
(Weight of ignited residue x 100)/W,
where: W = Weight of sample.

Free Lime, Procedure: As related to the chemical analysis of cement by conventional and instrumental techniques by BSI (1978), the procedure used was as follows.

Approximately 1.0g of finely grounded cement sample was weighed in a long-necked Erlenmeyer flask and 50ml 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 15-20 min. The resultant solution was filtered through Bucher-funnel containing double filter paper. The precipitate was washed with 10ml portion of glycol and about 10-15ml of water was added to the filtrate. This material was titrated against 0.1N HCl using 2-3 drops of 1% bromocresol blue/green indicator. The end-point was noted when there was a change in

colour from blue to yellow.

Calculations:

Free lime (%) = (0.02804 x N x 100)/W,

where:

W = weight of sample in g; and

N = normality of HCl.

Determination of Physical Properties of various Portland Cements

Consistency of Standard Cement Paste: As given in BSI (1978), the procedure employed was as follows.

400g of cement sample was weighed and spread out on a steel plate for about 30 minutes to cool to the temperature of the mixing room (27±50°C). 30% water content of the mass of dry cement was added as a start. The mixture was mixed for 4±0.25 minutes by using a trowel to give a paste and was immediately transferred into the mould laying on the steel plate. The top of the mould was smoothened off as quickly as possible with the aid of the trowel. The mould and paste were placed under the plunger in the vicat apparatus and the plunger lowered gently to contact the surface of the paste. This material was released quickly and allowed to sink into the paste.

The scale reading of the vicat apparatus was noted after 1 minute 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, if not, a new water-cement ratio is taken and the procedure repeated.

Compressive Strength Test: From the procedure of British Standard Specification for Portland cement BS 12:1958 (BSI 1978) the compressive strength was carried out as follows.

The ELE mixing bowl and paddles were wiped clean with a damp cloth and different grades of cement, sand and aggregates in the ratio of 1:2:4 were weighed into the mixing bowl. 10% weight calculated as tap water was added and mixing was carried out until a cement mortar of homogenous consistency was obtained. The concrete was turned in the bowl over 3-4 times by using the scoop and trowel. 12 pieces of clean 150 x 150 x 150mm cube

mould were set on the working bench and all bolts were tightened using the spanners. The base of the mould was greased with a thin film of petroleum jelly and also the joints of the two halves. As quick as possible, the concrete mixture was scooped into each mould (to half the depth) in a single layer. The concrete mixture was tamped in each mould with 25 strokes of the tamping bar spread uniformly over the cross-section of the mould and exerting the same force in each case by raising the bar about 30mm above the surface of the concrete and guiding it as it is then allowed to fall under its own weight.

More mixture was scooped into each cube being completely filled to the brim. This material was tamped again 35 times for each mould. The assembled mould was placed on a vibrating machine and well secured in place, a suitable hopper was used to facilitate filling. The mould was vibrated on a jolting machine for 2 minutes. Afterwards, the cubes were covered with an impervious sheet to avoid evaporation and were allowed to cure at room temperature for 24 hours. The cubes were removed from their mould after 24 hours and were marked for identification. This material was then immersed in clean water to be removed for crushing after a required number of days.

The cubes were brought out of the water in due time and their surface was carefully wiped clean of water and adhering loose sand. The DM0 Samuel Denison Compression machine was switched on 15 minutes before use. The weights of the cubes in air were determined by using a spring balance. Each cube was then placed inside the crushing machine centralizing it by using the scribe lines of the four locating pins on the bottom plates and with the marked face of the cube to the front of machine. The Perspex guard was closed and the 'Enter' sign pressed on the machine.

Slump Test on Cement: As stated in the laboratory work instruction of WAPCO (1986), the procedures used are as follows.

The same mix for concrete cubes in compressive strength test shall be used for the slump test. The time clock was immediately

switched on. The mould was placed on a smooth horizontal rigid non-absorbent surface and while being firmly held in place was filled in 3 layers, each approximately one third of the height of the mould. Each layer was tamped with the round end of the tamping rod for about 25 times. The strokes were well distributed in a uniform manner over the cross-section of the mould. For the second and subsequent layers, the tapping rod was able to penetrate the underlying layer. After the top layer has been well tamped, the surplus concrete from the top of the cone was stricken off with a sawing/rolling motion of the rod.

The mould was removed from the concrete slowly and carefully in a vertical direction. The time elapsed was six minutes and thus allowed for the concrete to slump.

The cone was turned upside down and placed on the base plate next to the slumped concrete. The tamping rod was placed on top of the cone, projecting over the highest point of the concrete. The distance from the top of the slumped concrete was measured to the underside of the rod and recorded.

Setting Time Determination on Cement: As stated in BSI (1978), a sample of cement paste of standard consistency was prepared and the time of first mixing the water with cement was noted down. A slight excess of paste was immediately transferred into the mould in one layer by using hand trowel. The top of the mould was smoothened and levelled. The mould was placed under the initial set needle of cross-sectional area of 1mm and the needle was covered gently onto the surface of the paste and was quickly released by allowing it to sink to the bottom. These tasks were repeated several times at regular intervals of 10 minutes in different positions of mould until the paste has stiffened sufficiently for the needle not to penetrate deeper than 5mm above the bottom of the mould.

The time interval between the addition of water and the initial setting time was recorded. Finally, the needle was replaced with a 1mm square needle fitted with a metal annular attachment and this probe was allowed to come gently with contact with the surface of the cement paste at an interval of 15 minutes. The

final set was reached when the needle makes an impression on the surface but annular cutting edges fail to do so.

Soundness Test (Expansion Determination on Cement): One of the accelerated tests used in BSI (1978) and laboratory work instruction of (WAPCO 1986) was created by Le Chatelier (1904). This test was carried out as follows.

The cement paste was prepared as of a standard consistency and filled in to the expansion mould, or Le Chatelier mould (Le Chatelier 1904), placed on a glass plate. The split end of the mould was gently closed by tying it with a piece of cotton as the operation was being carried out. The surface of the paste was well smoothened and levelled with the blade of a gauging trowel and was covered with another piece of glass and was immediately immersed in clean water. A 50g weight was placed on top of the plate for compaction.

After 24 hours, the mould was removed from the water and the distance between the pointers measured by using a meter rule. The mould was re-immersed in water again and was brought to boiling point within 30 minutes and afterwards allowed to boil for one hour. This material was then kept in the water and allowed to cool. The distance between the pointers was again measured. The difference between the two measurements represents the value for soundness.

Discussion of Results

The characterization and evaluation of the available brands of Portland cements have become necessary in order to correctly evaluate the product quality and, hence, the area of application. From the experimental results presented in Tables 1-3, the percentage composition of the various cements analyzed varied from one cement brand to the other.

There were significant differences in the values of their chemical composition when subjected to variance test and also a high correlation was obtained when the physical parameters (dependent variables) were varied with the chemical composition (independent variable).

Table 1a. The composition of major constituents of some indigenous and imported Portland cement (ANOVA).

Test Samples	CaO (%)	SiO$_2$ (%)	Al$_2$O$_3$ (%)	Fe$_2$O$_3$ (%)
Ashaka	60.00±0.58^a	20.65+1.33^a	3.83±1.17^a	2.20±0.12^a
Elephant	58.83±2.09^b	17.33±l.76^a	5.07±1.48^a	2.50±0.29^a
Burham	56.17±1.0l^a	19.07±0.88^a	5.30±0.45^a	3.15±0.60^a
Dangote	51.67±3.84^a	18.02±0.66^a	1.25±0.25^b	10.5±0.76^d
Sem	±2.26	±1.23	±0.54	±0.25

Figures in the same column having the same superscript are not significantly different ($P > 0.05$).
Figures in the same column having different superscript are significantly different.

Table 1b. The composition of some minor constituents of some indigenous and imported Portland cement (ANOVA)

Test Samples	LOI (%)	IR (%)	Free CaO (%)	SO$_3$ (%)	MgO (%)
Ashaka	2.27±0.11^{ab}	2.76±0.02^{ab}	1.50±o.12^a	1.70±0.04^d	0.75±0.10^a
Elephant	1.50±0.0l^a	3.02±0.04^b	2.60+0.47^a	0.32±0.04^a	2.30±0.72^c
Burham	3.16+0.02^{bc}	3.91±0.38^c	1.83±0.04^a	l.14±0.06^b	0.74±0.12^a
Dangote	3.27±0.38^c	2.03±0.l5^a	2.15±0.03^a	l.40±0.02^c	l.45±0.03^d
Sem	±0.20	±0.19	0.24	±0.04	±0.04

Figures in the same column having the same superscript are not significantly different ($P > 0.05$).
Figures in the same column having different superscript are significantly different.

Table 2. Calculated mineral percentage composition of Portland cement.

Samples	C$_3$S	C$_2$S	C$_3$A	C$_4$AF	Total Sum (Σ)
ashaka	22.55	46.41	12.51	6.08	87.55
elephant	20.58	41.83	6.36	762	76.36
burham	22.91	42.94	12.51	6.08	84.44
dangote	33.33	26.47	14.33	4.77	78.9

Table 3. Analysis on variance (Anova) on physical and mechanical properties of Portland cement.

Test samples	Consistency %	Setting time (mins)	Soundness (mm)	Compressive strength (N/mm^2)
Ashaka	31.00±0.58^b	20.50±0.29^b	3.43±0.35^b	21.96±0.15^a
Elephant	28.73±0.33^b	25.00±0.58^b	3.00±0.01^b	17.04±0.65^a
Burham	31.07±0.58^b	31.00±0.58^c	1.01±0.07^b	23.92±0.15^c
Dangote	31.15±0.08^b	11.34±0.60^a	1.17±0.16^b	22.00±0.40^{bc}
Sem	±0.35	±1.03	±0.19	±0.39

The cement samples shall be individually discussed and overall deduction would be given in the conclusion.

Ashaka Cement

From Table 1a, the CaO of Ashaka cement merges well with Type IV of ASTM Portland cement (ASTM 1986) and was slightly in conformity with Type I. This corresponded to the Low Heat Portland Cement of BSI (1978) and Ordinary Portland cement, respectively. The percentage content of SiO_2, Al_2O_3, Fe_2O_3 and MgO were all in conformity with Type I. Although MgO was quite low, the value corresponded well with Ordinary Cement of BSI (1978). The percentage content of SO_3 is of the same magnitude with Type I and Type II though slightly high in comparison to other cement.

The free-lime (CaO_f) is in conformity with type I, so also is the mineralogical content. However, the CaO differ totally from Type I but corresponded with Type IV Low Heat of BSI (1978).

The physical properties (Table 3) showed that the initial setting time was the least in comparison to other analyzed cement. Ashaka brand also had the fastest final setting time. Along with the Elephant brand, they showed poor soundness value. This may be associated with high CaO free content (Sosman and Merwin 1916).

These variations are all within the acceptable limit (BSI 1978; and ASTM 1986). It can be deduced that Ashaka is more of type I ordinary cement used for general concrete construction. However, the poor soundness and early final setting times seriously limit its area to structures not subjected to loading (Ghosh 1983).

Elephant Cement

From Table 1a-b presented, Elephant cement has some of its composition, i.e., SiO_2 Al_2O_3, Fe_2O_3 and MgO in conformity with Type I Ordinary Portland Cement of BSI (1978).

The SO_3 percentage though low can still be approximated as ordinary Portland cement,

in fact, this is the least value when compared to the other analyzed cements.

The CaO percentage composition was quite low in comparison with its indigenous counterpart as a result of the higher uncombined lime in the clinker. This high CaO-free content could be attributed to improper sintering condition or long storage of the clinker before grinding. This may enhance polymerization of the unstable alite and belite forms into the subsequent release of free CaO (Bensted 1979).

The C_3S and C_2S phases are in the region of type IV whereas the C_3A and C_4AF are of type I (Table 2). The value of C_3A was quite low (the least), 6.36%, and thus affected the setting time, initial setting was after 120 minutes and final setting was 145 minutes. The presence of C_3A enhances the rate of hydration and thus initial strength development (Le Chatelier 1904). The physico-mechanical analysis showed that the Elephant brand has the lowest compressive strength of 17N/mm which is consistent with the observed poor consistency and soundness test value (Ghosh 1983).

Based on this analysis, it is evident enough to say that Elephant cement lies in the region of type I Portland cement and can be used for general concrete construction. However, structures must not be subjected to loading.

Burham Cement

In Table 1a-b, the percentage values of SiO_2, Al_2O_3 and Fe_2O_3 fell within the range of type I Portland cement. The MgO, though out of range of ASTM (1986), still merges well with BSI (1978) of Ordinary Cement.

On the other hand, the percentage values recommended for CaO, SO_3 and CaO all fell within type IV of Portland cement. The high percentage recorded for free lime is as a result of inefficiency in burning and may be explained as in the case with Elephant cement (BSI 1978).

The C_3S and C_2S contents tally well with type IV low heat Portland cement, but the C_3A and C_4AF corresponded to type I (Table 2). Based on the high silica content, Burham

cement has a higher compressive strength and also the relatively high C_3A content will enhance initial strength gain. A compressive strength of 23.92 N/mm^2 was recorded which is according to the acceptable limit (BSI 1978).

The setting time for Burham cement was having initial setting of 125 minutes and final setting of 162 minutes. This could be attributed to the relatively low gypsum content compared to the high C_3A (ASTM 1986).

Sequel to this, it can be said that Burham cement lies within the region of type I Portland cement. It can be used for general concrete structures considering the obtained soundness value, such structures could be subjected to loading.

Dangote Cement

Dangote cement has so many varying properties that are comparable with all the cement types. It recorded the lowest percentage of composition of CaO and also the highest percentage of Fe_2O_3. The SiO_2 percentage value was in accordance with the Ordinary Cement of BSI (1978) and thus recorded an average Compressive Strength of 22.0N/mm. The Al_2O_3 of about one percent composition corresponded slightly with type IV of ASTM (1986). The MgO and SiO_2 values are of type I and its CaO and SO_3 percentage composition are of type IV. It has the highest uncombined lime, thus resulting in its low CaO.

According to its mineralogical composition (Table 2), its C_3S and C_3A corresponded to type I, while its C_2S and C_4AF are type IV and type V, respectively. The low value of C_4AF was observed as a result of the substitution of ferric oxide for Alumina and thus following to an increase in C_3A and a reduction of C_4AF. This observation was ascertained as given in analytical form (Volzenski 1986).

The high C_3A value is reflected in the interval between the setting times of 11.38 minutes. This is an indication of poor workability (Jackson and Dhir 1996). It is difficult to ascertain the grade of Dangote cement. It is most likely to be a slag Portland cement. This can only be verified with further investigation.

From the performed analyses, it was observed that the two brands, Ashaka and Elephant Portland cement, produced in the country are defective, especially if judging by the physico-mechanical properties. The Fe_2O_3 content in both cement brands is less than 3% and MnO is practically absent in the raw material used. This eliminates their influence on the clinker formation mechanism of alite, belite and calcium-alumino-ferrite solid solutions (Odigure 1997).

Consequently, the poor performance of these cement brands is connected with poor sintering conditions, especially inability to obtain the required sintering temperature and cooling regime (Volzenski 1986). This has allowed the formation of predominantly poor hydrating belite solid solutions. It is recommended that the locally produced cement be used particularly for structures with low loading capacity.

The imported cement brands were not uniform in their physico-mechanical and chemical properties. The Dangote Portland cement has relatively high Fe_2O_3 content. It is impossible to sinter such cement in a normal rotary kiln. Consequently, microscopic analysis needs to be performed to ascertain the class of cement. This brand belongs to a slag Portland cement.

The Burham brand has a chemical composition and physio-mechanical properties of a normal Portland cement. Both cements can be used for structures with high loading capacity.

Conclusion

Based on the investigation and experimental results, the following conclusions can be deduced:

1. The indigenous Portland cement brands, Ashaka and Elephant, conform in their chemical composition with the set of standards. However, their physico-mechanical analysis assessments show considerable deviation from ASTM (1986) and BSI (1978). They are better used for structures involved with low loading.

2. The Burham cement conforms well both in its chemical and physico-mechanical composition with the international standards

except in the free-lime percent value. Based on its soundness, it can be subjected to structures involved with loading.

3. The chemical and physico-mechanical properties of Dangote cement did not conform to any of the international standards. It needs to be further investigated upon.

A classification guideline based on ASTM (1986) and BSI (1978) was developed to enhance easy assessment of the Nigerian cement. This developed assessment technique can be used to control product quality during manufacturing of cement.

References

ASTM. 1986. Annual Book of ASTM Standards. Volume 04.01. Cement; Lime; Gypsum. American Society for Testing and Materials (ASTM), West Conshohocken, PA, USA.

Bensted, J. 1979. Early hydration behaviour of Portland cement containing chemical by-product gypsum. World Cement Technology 10: 404-10.

BSI. 1978. BS 4550-3.4:1978 Methods of testing cement. Physical tests. Strength tests. British Standards Institution (BSI), London, UK.

Bye, G.C. 1983. Portland cement: composition, products and properties. Pergamon Press, Elmsford, NY, USA.

Ghosh, S.N. (Ed.). 1983. Advances in Cement Technology: critical reviews and case studies on manufacturing, quality control, optimization and use. Pergamon Press, Oxford, UK.

Jackson, N.; and Dhir R.K. (Eds.). 1996. Civil engineering materials. 5th ed. McMillan, London, UK.

Le Chatelier, H.L. 1904. Recherches expérimentales sur la constitution des mortiers hydrauliques. 2nd ed., Dunod, Paris, France (in French).

Lea, F.M. 1970. The chemistry of cement and concrete. 3rd ed. Edward Arnold, London, UK.

Odigure, J.O. 1997. Preparation of cement raw mix containing metallic particles. Cement and Concrete Research 27(11): 1641-8.

Sosman, R.B.; and Merwin, H.E. 1916. Preliminary report on the system lime-ferric oxide. Journal of the Washington Academy of Sciences 6: 532-7.

Volzenski, A.V. 1986. Mineral binding materials. 4th edition. Stroyizdat, Moscow, Russia (in Russian).

WAPCO. 1986. Laboratory work instruction of West African Portland Cement PLC (WAPCO). Lagos, Nigeria.