Analysis on Chemical Composition of Different Brands of Cement in Nigeria with Their Corresponding Setting Time

Nwokocha Prince U., Ogbodo Munachiso C.

Department of Civil and Environmental Engineering, University of Port Harcourt, P.M.B 5323, Port Harcourt, Rivers State, Nigeria

Abstract: **The quality and standard of cement available in the open market has been a thing of question, which necessitated this research that assessed different Portland cements commonly used in Nigeria within the southern region, in view of understanding the relationship between their chemical compositions and their corresponding setting time. Five brands of cement labelled sample A, B, C, D and E representing Dangote 3x R, Bua, Dangote 3x N, Unicem and Elephant supaset cement respectively were investigated. Chemical composition test was carried out using the atomic absorption spectrophotometer while the vicat apparatus was used for the setting time test. The chemical composition test result showed that the oxides composition of samples A, B and E met the British standard while for samples C and D the CaO, C3S and C2S content did not meet standard. The result further revealed that sample D has the highest percentage of C3S (73.58%) while sample C has the highest percentage of C2S (40.67%). The percentage of C3A is highest in sample E (9.04%) and sample B has the highest percentage of C4AF (10.76%). The setting time result showed that both the initial and final setting time of the cement samples are within the limit values that initial setting should be greater than 60mins and final setting time should be less than 600mins. Sample D has the fastest initial setting time of 70mins which is as a result of the C3S content that indicates that it will develop more early strength while sample E has the fastest final setting time of 405mins as a result of the C3A content which shows that it will generate more heat than other samples during the early stage of hydration. Sample C has the slowest initial and final setting time value of 105mins and 510mins respectively which is as result of the C2S content that shows that it will develop more late strength than any other sample. The correlation between C3A and gypsum indicates that sufficient amount of gypsum was added to delay the hydration of C3A, it was also observed that there was high correlation coefficient value of 0.9802 between chemical composition and setting time showing that there is a relationship between both. This shows that variation in chemical composition will cause a corresponding variation in setting time.**

Key words: **Portland cement, compressive strength, concrete, Ordinary, Brands.**

I. INTRODUCTION

Cement is a very important material in construction today; over time, cementing materials have played an important role in providing shelter for mankind. One of the most important considerations to make before beginning the construction of a building is the cement that will be used; Portland cement is the most common type of cement used around the world. The history of cement in Nigeria can be dated back to 1957; about three cement plants were commissioned by the Northern, Eastern and Mid-western regional governments. Later, other companies such as Ashaka cement, Benue cement company (BCC), West African Portland cement company (WAPCO) and a host of others were established. But this beautiful creation of civilization in Nigeria has been investigated as one of the causes of building collapse due to the substandard production of cement been used in the country. Coalition of civil society groups and professional bodies in Nigeria construction industry accused cement manufacturers and importers of flooding Nigerian markets with substandard products, but the manufacturers under the auspices of Cement Manufacturers Association of Nigeria (CMAN) debunked this allegation claiming that they are complying with conventional practices in cement production (Etim, 2014). The experimental analysis of Muibat (2009), which indicated that chemical and physico-mechanical properties of Dangote, Elephant and Ashaka cements did not conform to international standards, suggests skeletons in the cupboards of both the cement manufacturers, importers and regulatory agency (SON) in the country. These revelations, matching with ceaseless structural failure in the country prompted the recent allegation by coalition groups that government regulatory agencies are turning blind eyes to the scourge of substandard cement in the country, thus, the campaign for standardization of cement production and importation in Nigeria (Nwankwojike et al, 2014).

Cement is a core component of concrete; its properties affect the properties of concrete made using the particular type of cement. The integrity of construction work that involves the use of concrete can therefore be affected if the choice of cement is not suitable for the construction method and the service condition of the resulting structure. It is therefore important to know the characteristics of the materials used in construction. The main properties expected of cement in construction, according to Duggal (2009), are permanency of structure, strength and rate of setting suitable to demand of the work at hand. Due to the significance of this issue, it is necessary to investigate the properties of some of the brands of cement available in the Nigerian market. Some researchers have done some work on some properties of cement; Yahaya (2009) did some classification of Nigerian cement on the basis of their physical and chemical properties. The author reported that some work needs to be done to improve on the properties of the locally manufactured brands of cement to meet some of the international standards.

The main objective of this study is to investigate the chemical composition and setting time of some selected brands of cement available in the Niger Delta region of Nigeria. Experimental test will be conducted to make an effective comparative analysis of the five Portland cement brands that were readily available at the time of this research.

II. MATERIALS AND METHODS

Cement Selection

The five brands of cement selected are Portland composite cement; comprising Portland cement and up to 35% of certain other single constituents. The five brands and their corresponding sample designatory letters are shown in the table below.

Table 1: Sample Classification

Sample	Brand of cement	Classification
A	Dangote 3x (R) cement	CEM II A-L 42.5 R
B	Bua cement	CEM II A-L 42.5 N
C	Dangote 3x (N) cement	CEM II A-L 42.5 N
D	Unicem limestone cement	CEM II B-L 32.5 R
E	Elephant superset cement	CEM II A-L 42.5 N

Determination of Chemical Properties of Selected Samples

Chemical composition was analysed using X-ray flux method in accordance with the EN 196.2. The following apparatus and reagent where used to carry out the experiment such as Beakers and flasks, Solar thermo elemental Atomic Absorption Spectrophotometer (Flame AAS) mode: S4=71096, burner, Hollow cathode lamp, Volumetric flask of suitable precision and accuracy, weighing balance, air, Acetylene Nitrogen dioxide gas, Metal free water, Potassium chloride solution, Aluminium nitrate solution, Hydrogen tetraoxosulphate (vi) acid (H_2SO_4), Trioxonitrate (v) acid (HNO_3) and Perchloric acid ($HClO_4$).

Plate 1: Sample specimen after wet digestion

The percentage chemical composition of the various samples after been acquired was used to calculate the various compound compositions using the Bogue composition formulas.

Tricalcium silicate (C3S) = 4.07C – 7.60S – 6.72A – 1.43F – 2.85Sˆ (1.1)

Di-calcium silicate (C2S) = 2.87S – 0.75 (C3S) (1.2)

Tricalcium Aluminate (C3A) = 2.65A – 1.69F (1.3)

Tetracalcium Aluminoferrite (C4AF) = 3.04F (1.4)

(Only valid when A /F >= 0.64), C= Percentage of calcium oxide (CaO), S = Percentage of Silicon dioxide (SiO_2), A = Aluminum oxide (Al_2O_3), F = percentage of Ferric oxide (Fe_2O_3), Sˆ= Sulphur trioxide (SO_3).

The reaction rate of the cement depends on the ratio C3S/C2S and the fineness of the cement. The burning process of the clinker is steered by modules calculated from the oxide composition of the raw mix which are presented in percent not in mole fractions which includes

Hydraulic (HM) = $CaO/(SiO_2+Al_2O_3+Fe_2O_3)$ (1.5)

Lime saturation factor (LSF) = $100*CaO/(2.8*SiO_2+1.1*Al_2O_3+0.7*Fe_2O_3)$ (1.6)

Aluminate(AM) = Al_2O_3/Fe_2O_3 (1.7)

Silicic(SM) = $SiO_2/(Al_2O_3 + Fe_2O_3)$ (1.8)

Setting Time Test for the Various Samples

The following equipments and apparatus where used to carry out the setting time test on cement; Electronic weighting balance, graduated cylinder, distilled water, stop watch, vicat apparatus, spatula, mixing bowl, towel and mixing rod.

Determination of setting time

The standard consistency values for the various samples were determined with the use of the vicat apparatus and recorded to be used for the setting time test.

Using the weighing balance, 400g of each sample were weighed to an accuracy of ± 1g. The standard batch procedure described in ASTM C187 was followed, consisting of 400g of cement and sufficient water to make a paste of normal consistency. In accordance with ASTM C191, the initial and final setting times of pastes made from each of the samples were determined and investigated.

Plate 2: Scale reading with vicat apparatus

III. CHEMICAL TEST RESULT

The following data/results shown in the table below shows the percentage chemical composition of the various samples which are Portland composite cement.

Table 2: Chemical Composition of samples

Sample	A	B	C	D	E
SiO_2 %	18.64	20.05	20.26	19.43	18.92
Al_2O_3 %	4.89	5.27	4.96	4.80	5.63
Fe_2O_3 %	3.21	3.54	3.08	3.36	3.48
CaO %	58.90	61.18	53.69	64.51	60.74
MgO %	1.81	0.93	1.06	1.33	1.12
K_2O %	0.14	0.07	0.52	0.19	0.02
SO_3 %	1.35	1.24	1.53	1.49	0.98
Na_2O %	0.38	1.01	0.27	0.15	0.08

Table 2 shows the compound composition and modules ratio of the various samples calculated with the Bogues formulas given in Equation (1.1) to (1.8).

Table 3: Compounds composition and modules ratio of samples

Sample	A	B	C	D	E
C_3S %	56.76	52.61	23.30	73.58	57.82
C_2S %	10.93	18.08	40.67	0.58	10.94
C_3A %	7.53	7.98	7.94	7.04	9.04
C_4AF %	9.76	10.76	9.36	10.21	10.58
HM	2.2	2.12	1.90	2.34	2.17
LSF	98.47	94.98	83.45	103.99	98.60
AM	1.52	1.49	1.61	1.43	1.62
SM	2.30	2.28	2.52	2.38	2.07

Table 3 shows the comparative chemical composition with the specified code standard to check for adequacy of the samples in accordance to BS EN 197-1:2000 and BS 12-78 for CEM II Portland-composite cement.

Table 4: Adequacy check on sample chemical composition in accordance to specified code

	A	B	C	D	E	BS LIMITS
SiO_3 %	18.64	20.05	20.26	19.43	18.92	17.46-21.59%
Al_2O_3 %	4.89	5.27	4.96	4.8	5.63	3.29-6.14%
Fe_2O_3 %	3.21	3.54	3.08	3.36	3.48	1.21-3.76%
CaO %	58.9	61.18	53.69	64.51	60.74	58.67-63.90%
MgO %	1.81	0.93	1.06	1.33	1.12	0.61-3.30%
SO_3 %	1.35	1.24	1.53	1.49	0.98	<3.5
K_2O %	0.14	0.07	0.52	0.19	0.02	
Na_2O %	0.38	1.01	0.27	0.15	0.08	
K_2O+Na_2O %	0.52	1.08	0.79	0.34	0.1	<2.0
C_3S %	56.76	52.61	23.3	73.58	57.82	50-70%
C_2S %	10.93	18.08	40.67	0.58	10.94	15-30%
C_3A %	7.53	7.98	7.94	7.04	9.04	5-10%
C_4AF %	9.76	10.76	9.36	10.21	10.58	5-15%
HM	2.2	2.12	1.9	2.34	2.17	1.7-2.3
LSF	98.47	94.98	83.45	103.99	98.6	66-102
AM	1.52	1.49	1.61	1.43	1.62	1.5-2.5
KM	2.3	2.28	2.52	2.38	2.07	1.9-3.2

Result For Setting Time of Cement Samples

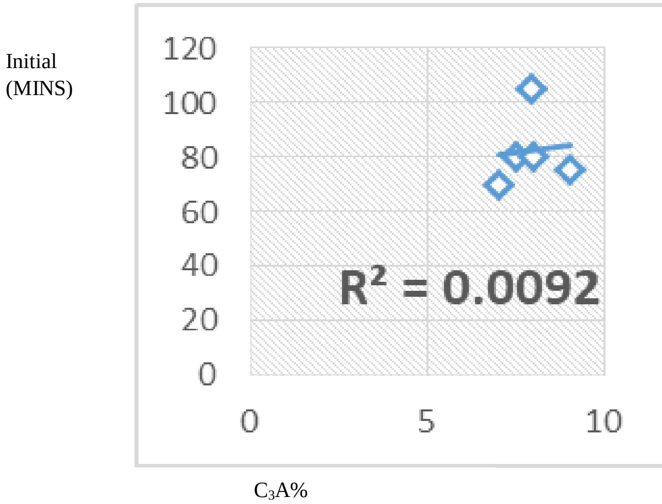
Tables 5 shows the results for standard consistency values which include the initial and final setting time of the cement pastes with were read at 5 minutes interval.

Table 5: Standard consistency, initial and final setting time result

Samples	Standard consistency %	Initial setting time (mins)	Final setting time (mins)
A	28.5	80	420
B	29	80	495
C	28.5	105	510
D	27.5	70	435
E	27.5	75	405

Data Analysis

The correlation and regression values of the chemical compound composition with both the initial and final setting time were determined and are shown below.



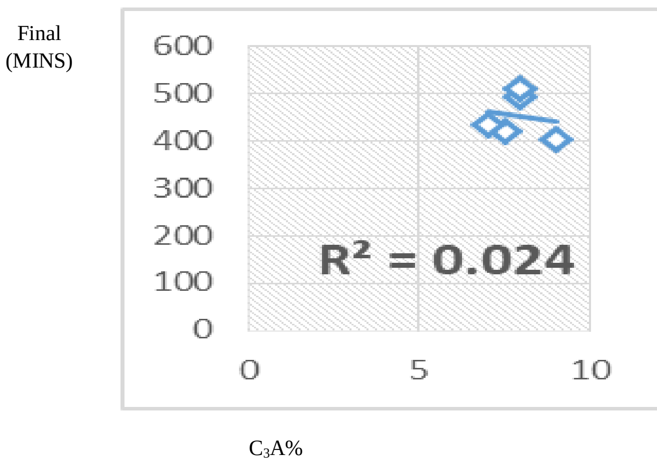
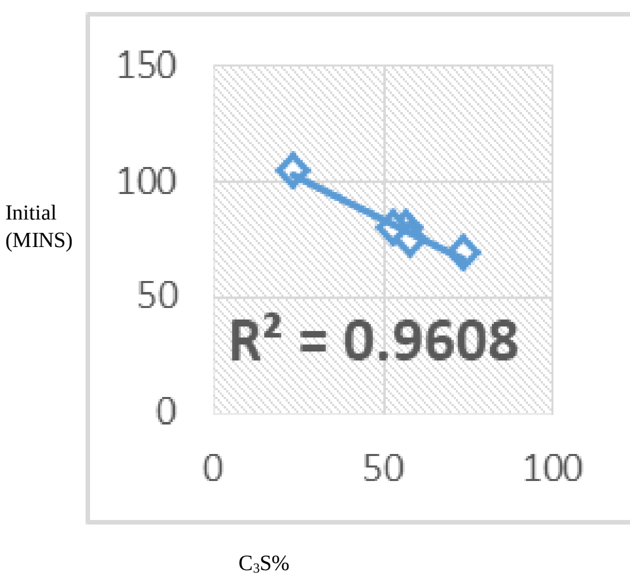


Figure 1: Initial (i.s.t.) and final setting time (f.s.t.) as a function of tricalcium aluminate (C3A)



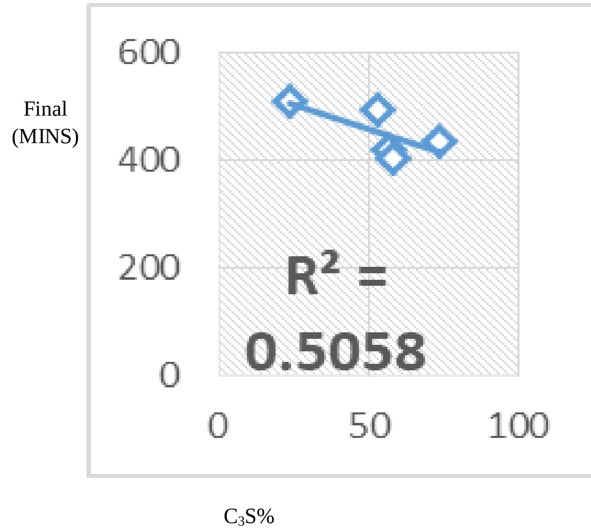


Figure 2: Figure 2: Initial (i.s.t) and final setting time (f.s.t) as a function of tricalcium silicate (C3S)

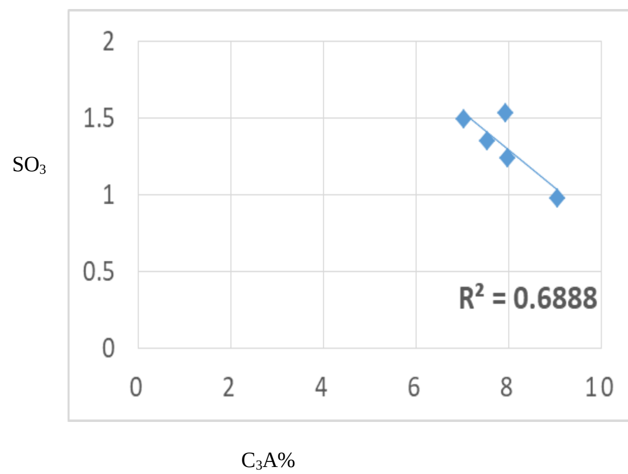


Figure 3: Relationship between tricalcium aluminate (C3A) and sulphur trioxide (SO3)

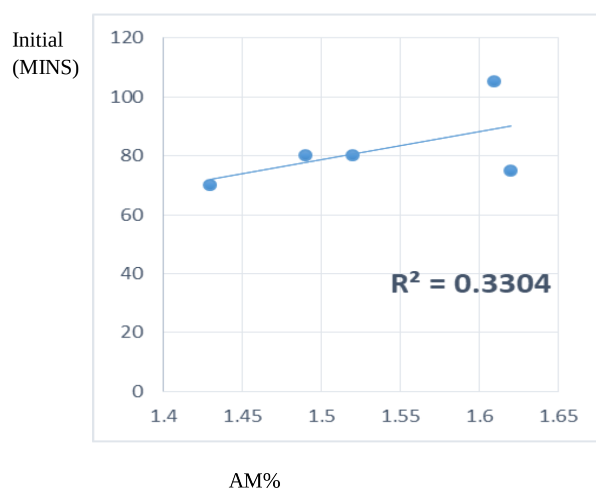


Figure 4: Initial setting time (i.s.t) as a function of alumina ratio

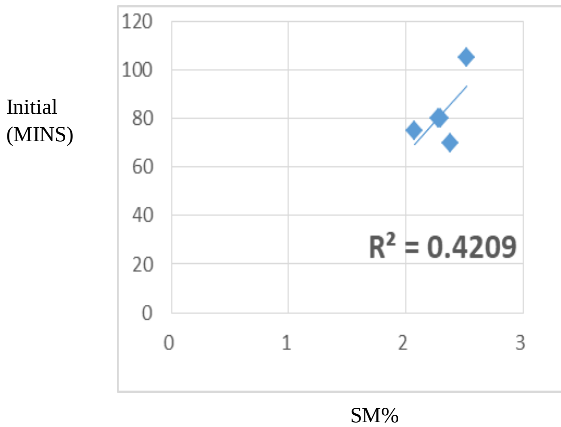


Figure 5: Initial Setting Time (i.s.t) as a function of silica ratio

IV. DISCUSSION

From Table 3, all samples apart from sample C have high Tricalcium Silicate (C_3S) content which causes cement to harden rapidly and is largely responsible for initial set and early strength. Figure 1 shows a correlation coefficient value of positive 0.9802 which means that there is a perfect relationship between C_3S and initial setting for the various cement samples. In general, the early strength and initial set of Portland cement concrete is higher with increased percentages of C_3S (low Dicalcium Silicate (C_2S) content) which lead to much faster hydration rate, contributes to higher early strength gain. Thus, cement with a higher proportion of C_3S, as is the case with most of today's cement, will tend to have a higher early strength, and allow for early formwork removal or post tensioning. On the other hand, cement with higher C_3S will cause issues due to heat of hydration specially in mass pouring. Tricalcium Aluminate (C_3A) liberate a large amount of heat during the first few days of hardening, and together with C_3S and C_2S may somewhat increase the early strength of hardening cement. It has been researched that C_3A causes quick setting or "flash set" without addition of gypsum to slow the process, but correlation analysis shown in Figure 2 shows a correlation coefficient of 0.096 which means that there is no relationship between C_3A and setting time. Low percentage of C_3A cement is more resistant to sulphates. All cement shows desirable C_3A content of 6-10%. Tetracalcium Aluminoferrite (C_4AF) contributes very slightly to strength gain and contribute to the color effects that makes cement gray.

According to BS standard limits shown in Table 4, it was observed that for the major oxides, SiO_3, Al_2O_3 and Fe_2O_3 content (%) for the various samples are within the limit while for CaO, samples A, B and E are within the limit but sample C is less than the lower limit and sample D is higher than the upper limit. For the minor oxides, SO_3, the alkaline (k_2O and Na_2O) are within the limit. For the compounds C_3A and C_4AF content (%) for the various samples are within the limits. For C_3S samples A, B and E are within the limit but sample C is less than the lower limit and sample D is higher than the upper limit and for C_2S samples A, B and E are within the limit but sample D is less than the lower limit and sample C is higher than the upper limit.

According to BS EN 197.1, the various samples shown in Table 5 met the specification which states that initial setting time should be greater than 60 mins for both 42.5R and 42.5N and the final setting time should be less than 600 mins, it was observed that sample D has the fastest initial setting time of 70 mins, while sample E has the fastest final setting time of 405 min.

Sulphur Trioxide (SO_3) is an indirect measure of the amount of gypsum or calcium sulphate ($CaSO_4$) in the cement. Gypsum is added to cement for the purpose of regulating setting time. Too much gypsum can cause expansion and, therefore, Gypsum predominantly affects concrete set times by delaying the hydration of C_3A which typically "flash sets" on contact with water. Figure 3 shows that there is a perfect relationship between the C_3A and SO_3 content of the various samples with a 0.8295 value of correlation coefficient. A high alumina ratio together with a low silica ratio results among other things, in a fast setting of the cement; this requires the addition of a higher gypsum rate to control the setting time which is shown in Figure 4 and Figure 5, that there is a partial relationship between alumina and silica ratio with setting time.

V. CONCLUSION

Based on the investigation, the experimental results obtained from the chemical composition and setting time tests revealed variations among the different cement brands, which led to the following conclusions being drawn:

1. Sample A met the specification by the British standard for its chemical composition and also setting time, having an initial setting time of 80mins and final setting time of 420mins of which the cement gains its strength.
2. Sample B also met the specification by the British standard for its chemical composition and also setting time, having an initial setting time of 80mins and final setting time of 495mins of which it gains its strength. It was also observed that sample B has the highest percentage of C_4AF (10.76 %) which governs the colour of the cement; which state that the higher the C_4AF, the darker the cement, therefore sample B will be darker followed by sample E, D, A and C.
3. Sample C also met most of the specification by the British standard for its chemical composition of all the major oxides expect CaO which is below the lower limit shown in Table 4. Sample C also has the highest percentage of C_2S (40.67%) and the lowest value of C_3S (23.3%) which is responsible for late strength in Portland cements but does not meet the British code specification. Therefore, sample C will develop more strength at late age, followed by

sample B, E, A and D. Sample D will develop the least late strength among the cement samples. Sample C also met the setting time requirement, having an initial setting time of 105mins which is the slowest among the samples to start gaining strength and a final setting time of 510mins which means that the samples sets late. This means that it will develop the least early strength among the cement samples.

4. For sample D, all the oxides expect CaO met the specification by the British standard. CaO content is higher than the permissible limit as shown in Table 4. Sample D has the highest percentage of C_3S (73.58%), which is the most important constituent for strength development and high heat generation in Portland cements. Therefore, sample D will develop more strength, especially at early age and is in uniformity with the initial setting time which shows that sample D has the quickest initial setting time (70mins), followed by sample E, A, B and C.
5. Sample E met the specification by the British standard for its chemical composition and setting time. Sample E has an initial setting time of 75mins, while its final setting time was 405mins which was the quickest final setting time followed by sample A, D, B and C.
6. Due to researches made, it has been discovered that four major factors affect the setting time of cement which includes that the setting time of cement increases with the increase of w/c ratio, the setting time of cement decreases with a rise in temperature and decrease of relative humidity and that the setting time of cement decreases with a rise in fineness of cement. The final factor is the cement's chemical composition which covers the major scope of this research, shows that there is a high correlation coefficient value between chemical composition of the various samples and its corresponding setting time which was observed that variation in chemical composition causes variation in setting time and its strength gain.

VI. RECOMMENDATION

Based on the results obtained from the chemical analysis and setting time of the various cement brands, the following recommendations are made.

1) Sample A is said to be type III cement, known for its early strength. Therefore, should be used for concrete works that will require quick removal of form work or rapid turn-around of precast concrete units in a mould and also due to its fast setting can be used for road construction and structural projects to reduce and save project duration time. It is also advised to be used particularly for structures with low loading capacity.
2) Sample B can be referred to as type I cement, therefore should be admirably suitable for use for general concrete construction when there is no exposure to sulphate in the soil or groundwater due to its high C_3A content (%).
3) Sample C is said to be type IV cement, known for its low heat of hydration, late strength gains and slow setting time. Therefore, should be used for mass structures with high loading capacity and will produce concrete with good workability attribute.
4) Sample D does not conform to any of the cement types due to its mineral composition, but for its high percentage of C_3S which will cause early strength and its fast initial setting; it can be used for concrete works that requires quick removal of formworks. Although, this cement can be further investigated on for more findings.
5) Sample E is also type III cement from its chemical compositions, which is also known as rapid hardening and also has the fastest final setting time and therefore should be used for concrete works that will require quick removal of form work or rapid turn-around of precast concrete units in a mould. It can be used for road construction and structural projects to reduce and save project duration time. It is also advised to be used particularly for structures with low loading capacity.

REFERENCES

[1] ASTM. 1986. Annual Book of ASTM Standards. Volume 04.01. Cement; Lime; Gypsum. American Society for Testing and Materials (ASTM), West Conshohocken, PA, USA.
[2] ASTM C191 (1992). Test for Time of Setting Hydraulic Cement by Vicat Needle. ASTM International, West Conshohocken, PA, USA.
[3] BS 4550: Part 0: 1978. Method of testing cement. General Introduction on Cement. BSI, London.
[4] BS 4550: Part 3: 1979. Method of testing cement BSI, London.
[5] BSI. 1978. BS 4550-3.4:1978 Methods of testing cement. Physical tests. Strength tests. British Standards Institution (BSI), London, UK.
[6] Duggal, S.K. (2009). Building Materials. New Delhi, India. New Age International
[7] Etim, I. (2014). The Cement War: An Alternative View. Vanguard, February 20, 2014. http://www. Vanguard News.com. Assessed on 5/10/2014.
[8] EN 196-1 2005, Methods of testing Cement – Part 1: Determination of strength, European Standard, pp. 1-36.
[9] EN 196-3 2005, Methods of testing Cement – Part 3: Determination of setting times and soundness, European Standard, pp. 1-18.
[10] EN 196-6 2005, Methods of testing Cement – Part 6: Determination of fineness, European Standard, pp. 1-24
[11] EN 197-1 2000, Cement – Part 1: Composition, specifications and conformity criteria for common cements, pp. 1-20
[12] Muibat, D. Y. (2009). Physico-Chemical Classification of Nigerian Cement. AU J.T. 12(3). pp. 164-174.
[13] Nwankwojike, B. N. Onwuka, O. S. and Ndukwe, E. C. (2014). An appraisal of different brands of Portland cement in Umuahia industrial market, Nigeria. Journal of Research Information in Civil Engineering, Vol 10, PP.39-44
[14] Yahaya, M.D. (2009). Physico-Chemical Classification of Nigerian Cement.Au J.T. 12(3) pp. 164-174.