



Production of Cement using Periwinkle Shell Ash and Clay Soil Ash

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Abstract The concept of using periwinkle shell and clay soil ash is a new technology in the production of cement. This study investigates the production of cement using periwinkle shell ash (PSA) and clay soil ash (CSA). Samples of periwinkle shell and clay soil were collected and process through different stages so as to have an end product called formulated cement. Energy disperse x-ray fluorescence spectrometer was used to analyzed the chemical composition of periwinkle shell ash, clay soil ash, bua cement, dangote cement and formulated cement. The formulated cement, bua cement and dangote cement were concreted into the ratios of 1:2:4 and 1:3:6 in both fresh water and salt water in cubes of 150*150*150 millimeters and tested for compressive strength at 7, 14 and 21days. Fineness test was also carried out on the formulated cement. Comparison was made between bua cement, dangote cement and formulated cement to that of British standard. The results revealed that compressive strength increased with an increase in curing age in the cements. A mathematical model which predicts the final concentration of the formulated cement during kilning was developed and it shows that the computed value of activation energy and pre-exponential are $E_a = 17.0653\text{KJ/Mol}$ and $k_o = 1.141 \times 10^{-82} \text{min}^{-1}$. The study concluded that more research should be done on how to improve on the quality of formulated cement so as to improve on the strength of the cement.

Keywords Compressive strength, periwinkle shell ash, clay soil ash, bua cement, dangote cement, formulated cement, mathematical –modeling

Nomenclature: t: time (min.); V_R : volume of the reactor (cm^3); C_A : Final concentration (g/cm^3); C_{AO} : initial concentration (g/cm^3); K_T : rate constant (min^{-1}); E_a : activation energy (KJ/MOL); R: universal gas constant (kJ/molk); T: temperature (K); e: exponential function; N_A : mole concentration

Introduction

Cement production has been in existence since 1796 as reported by James and in his research it was found that cement is a better materials used for construction. The raw materials used in the production of cement by James were calcined nodules of argillaceous limestone known as septarin which produce hydraulic cement. Other research carried out revealed the used of clay and limestone in the production of cement. Joseph (1824) carried out a research on cement production by using the concept of brick layer to produce excellent hydraulic cement by burning clay and limestone at a high temperature. The aim and objectives of cement production is because of its binding characteristics as well as the compressive strength retained when mix with other substance or aggregates such as sharp sand, chippings, etc, as reported by various scientific groups [1-2].

Production of cement using local raw materials such as periwinkle shell ash (PSA) and clay soil ash (CSA) in this study is a new concept and is necessary since there is need to diversified the production of cement from the used of limestone to other raw materials such as periwinkle shell. Periwinkle Shell Ash (PSA) is obtained by burning periwinkle shell which is the by-product of periwinkle which, in zoology is any small greenish marine snail from the class of gastropod, the largest of the seven classes in the phylum mollusc [3-4]. They are



herbivorous and found on rocks, stones or pilings between high and low tide marks; on mud-flats as well as on prop roots of mangrove trees and in fresh and salt water. Dance [5] observed that ten (10) out of the eighty (80) species of periwinkle in the world are found in West Africa. The common periwinkle (*Littorina littorea*) is one of the most abundant marine gastropods in the North Atlantic, but *Tympanotonus fuscatus* is commonly found in the estuaries and mangrove swamp forest of the South - South region of Nigeria [6]. Massive periwinkle harvesting has been reported from some communities in this region of Nigeria [7-9]. Periwinkle shell which is mostly used as aggregates in building has also been researched on as a substance used in blending cement concrete by Kolapo and Akaninyene [10]. Previous research works on the use of PSA in concrete production was reported by Koffi [11]. Dahunsi and Bamisaye, [12] research was centered on the effect of the ash on the concrete compressive strength up to 28-days hydration period. The aim of the study is to investigate the characteristics and the suitability of the formulated cement using local raw materials as a substitute to other cement used locally in Nigeria. Also the objectives of this research work covers the following: to evaluate the chemical composition of periwinkle shell and clay soil ash, to evaluate the chemical composition of Dangote cement and formulated cement, to compare the reliability of formulated cement concrete, Dangote cement concrete to that of British standard, to analyze the concrete strength of Dangote cement to that of Formulated cement and to compare the effect of fresh water and salt water on both cement.

Materials and Method

Materials

The following materials was used for this study: Periwinkle shell, clay, furnace, crusher, batch reactor, rotary kiln, grinder, sealed containers, sieve, water, burner, gas cylinder, ball mill, concrete compressing machine, cube crushing machine, mould, weigh balance, sharp sand limestone, additives such as gypsum and energy disperse x-ray fluorescence spectrometer.

Energy Disperse X-ray Fluorescence (GC)

EDX3600B X-ray Fluorescence Spectrometer was used to analyzed the degree of fastness and accurate analysis of complex composition and high resolution on periwinkle shell ash, clay soil ash, formulated cement and Dangote cement was carried as well as the materials used are water, fine powdered samples and Energy Disperse X-ray Fluorescence Spectrometer.

Sample preparation: for non-homogeneous sample, sample was pulverized to fine homogeneous size and the pelletized.

Sample Testing include the following procedures, such as start, initialization (calibration) using pure silver standard as well as the selecting of the working curve according to the sample and then sample tested with an output from excel and programmed ends.

Experimental Procedures

Step 1: Collection of Samples

For the purpose of this study, required quantity of periwinkle shell was bought from a local market in mile 4 market in rivers state. The clay used for this study was collected from a local fresh water swamp in Gokana Local Government Area in Rivers State.

Step 2: Drying

Drying of the periwinkle shell occur in two phases. 1. Pyrolysis phase, so as to collect the pungent gas that is present in it. 2. Using a furnace at a specific temperature so as to reduce the strength of the shell at a specific temperature for easy crushing. Drying of the clay for dehydration before crushing also took place.

Step 3: Crushing

Crushing of the PSA and CSA was done using a crusher to a finely particle size.

Step 4: Sieving

Sieving of the crushed PSA and CSA was done using a 7.5um sieve which is the required finesse for cement



Step 5: Blending of the Raw Mix

The sieved powdered fine particles of PSA and CSA was proportioned in requisite quantity at different ratios through a weigh machine and mixed properly with a mill to a homogeneous stage.

Step 6: Kilning

The blended raw mix was subjected to a rotary kiln at different temperature and time interval.

Step 7: Addition of Additives

Additives such as gypsum, etc were added to the product gotten from the kiln which gave us formulated cement.

Step 8: Production of Cubes

Using the standard mixing ratio of 1:2:4 and 1:3:6 where one (1) is for cement, two (2) and three (3) is for sharp sand and four (4) and six (6) is for chippings. It implies that:

For Cement One (1)

$$A_1+B_1+C_1+D_1$$

$$A_1+B_1+C_1+E_1$$

For Cement Two (2)

$$A_2+B_2+C_2+D_2$$

$$A_2+B_2+C_2+E_2$$

Where $A_1=A_2 =$ Cement

$B_1=B_2 =$ Sharp Sand

$C_1=C_2 =$ Chippings

$D_1=D_2 =$ Fresh Water

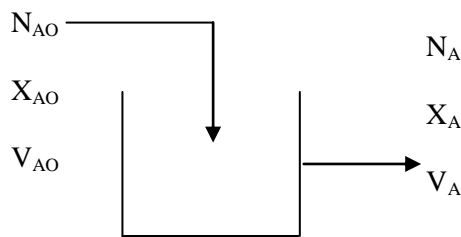
$E_1=E_2 =$ Salt Water

Step 9: Cube Testing

Testing of the cubes was done for seven (7) days, fourteen (14) days and twenty-one (21) days of curing. The cubes were weighed on a weighing machine to determine the weight before testing on the days above. The cubes were placed in an angle of forty-five (45⁰) degree on the cube crushing machine. The concrete compression machine was connected to the cube crushing machine in which the reading for the load (force) of the cube was recorded when there was a failure in the concrete compression machine.

Mathematical Model

Using a furnace which is a batch reactor as an equipment for kilning at a defined temperature. It implies that;



Recall that:

$$\text{Input} = \text{output} + \text{Rate of disappearance} + \text{Accumulation} \dots \dots \dots (1)$$

$$\text{Input} = \text{output}$$

$$\text{Accumulation} = \text{Rate of disappearance}$$

$$\text{Accumulation} = \frac{d_N}{d_t}$$

$$\text{Rate of disappearance} = (-r_i)V_R$$

Substituting the parameters into equation (1)

$$= \frac{d_N}{d_t} = (-r_i)V_R \dots \dots \dots (2)$$

$$\text{But: } dN_A = V_R dC_A$$



$$\therefore V_R \frac{dC_A}{d_t} = (r_i) V_R$$

$$\frac{dC_A}{d_t} = -r_i$$

Since A → B; $r_i = r_A = K_{(T)} C_A$

$$\frac{dC_A}{d_t} = -K_{(T)} C_A$$

$$\frac{dC_A}{C_A} = -K_{(T)} d_t \dots\dots\dots (3)$$

But Arrhenius equation = $K_{(T)} = k_o \ell^{\frac{-E}{RT}}$

$$\frac{dC_A}{C_A} = \left(k_o \ell^{\frac{-E}{RT}} \right) d_t \dots\dots\dots (4)$$

Integrating both side

$$\int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A} = \left(-k_o \ell^{\frac{-E}{RT}} \right) \int_{t_o}^t dt$$

$$\ln \frac{C_A}{C_{Ao}} = \left(-k_o \ell^{\frac{-E}{RT}} \right) t \dots\dots\dots (5)$$

Results and Discussion

Dangote cement, formulated cement and the ash of periwinkle shell and clay soil were analyzed to check for its chemical properties using Energy disperse x-ray fluorescence spectrometer as materials and method.

Table 1: Chemical Properties of PSA

| Elemental Oxide Concentration (%) | | | | | | | | | | |
|-----------------------------------|--------------------------------|--------------------------------|-------|------|-----------------|------------------|-------------------|--------------------------------|-------------------------------|------------------|
| SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | K ₂ O | Na ₂ O | Mn ₂ O ₃ | P ₂ O ₅ | TiO ₂ |
| 0.30 | 0.37 | 0.16 | 60.59 | 0.00 | 0.46 | 0.00 | 0.00 | 0.007 | 0.27 | 0.00 |

Table 2: Chemical Properties of CSA

| Elemental Oxide Concentration (%) | | | | | | | | | | |
|-----------------------------------|--------------------------------|--------------------------------|------|------|-----------------|------------------|-------------------|--------------------------------|-------------------------------|------------------|
| SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | K ₂ O | Na ₂ O | Mn ₂ O ₃ | P ₂ O ₅ | TiO ₂ |
| 17.98 | 15.55 | 4.31 | 0.36 | 0.00 | 0.42 | 0.20 | 0.00 | 0.02 | 0.11 | 0.20 |

Table 3: Chemical Properties of Dangote Cement

| Elemental Oxide Concentration (%) | | | | | | | | | | |
|-----------------------------------|--------------------------------|--------------------------------|-------|------|-----------------|------------------|-------------------|--------------------------------|-------------------------------|------------------|
| SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | K ₂ O | Na ₂ O | Mn ₂ O ₃ | P ₂ O ₅ | TiO ₂ |
| 5.44 | 2.03 | 1.49 | 66.72 | 0.67 | 4.32 | 0.00 | 0.00 | 0.007 | 0.45 | 0.00 |

Table 4: Chemical Properties of Formulated Cement

| Elemental Oxide Concentration (%) | | | | | | | | | | |
|-----------------------------------|--------------------------------|--------------------------------|-------|------|-----------------|------------------|-------------------|--------------------------------|-------------------------------|------------------|
| SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | K ₂ O | Na ₂ O | M ₂ nO ₃ | P ₂ O ₅ | TiO ₂ |
| 9.86 | 3.64 | 0.43 | 47.51 | 0.00 | 16.58 | 0.00 | 0.00 | 0.0002 | 0.42 | 0.00 |

For Periwinkle Shell Ash

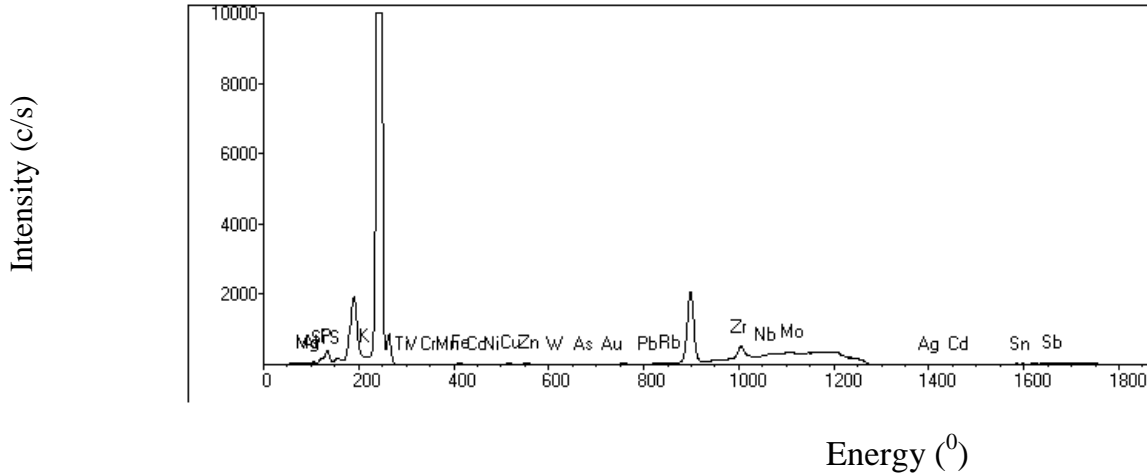


Figure 1: Graph of analysis on the characteristics of Periwinkle shell ash (intensity against energy)
 From Figure1, it is seen that the elemental characteristics of the periwinkle shell ash was obtained using GC which shows concentration of the elements at a given intensity due to its energy.

For Clay Soil Ash

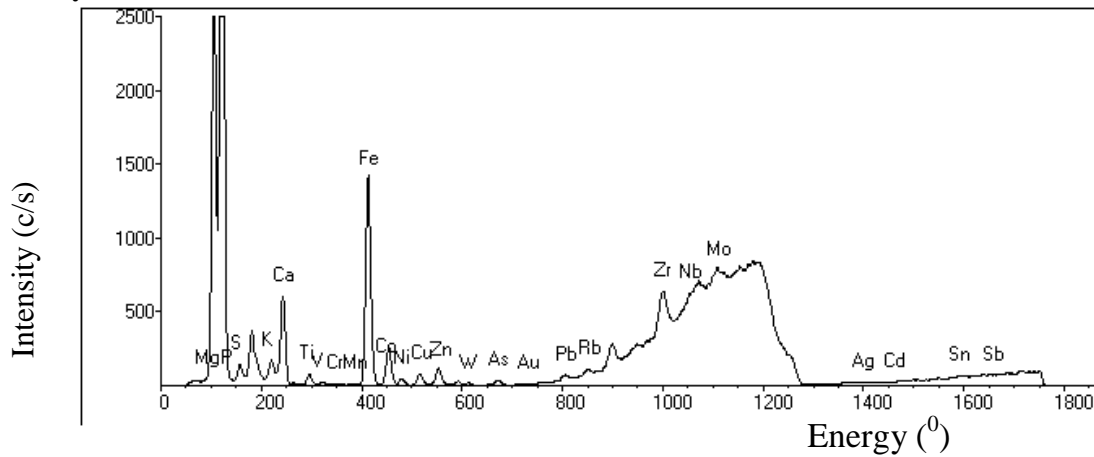


Figure 2: Graph of analysis on the characteristics of clay shell ash (intensity against energy)
 Figure 2 illustrates the characteristics of clay soil ash at a certain degree of energy.

For Dangote Cement

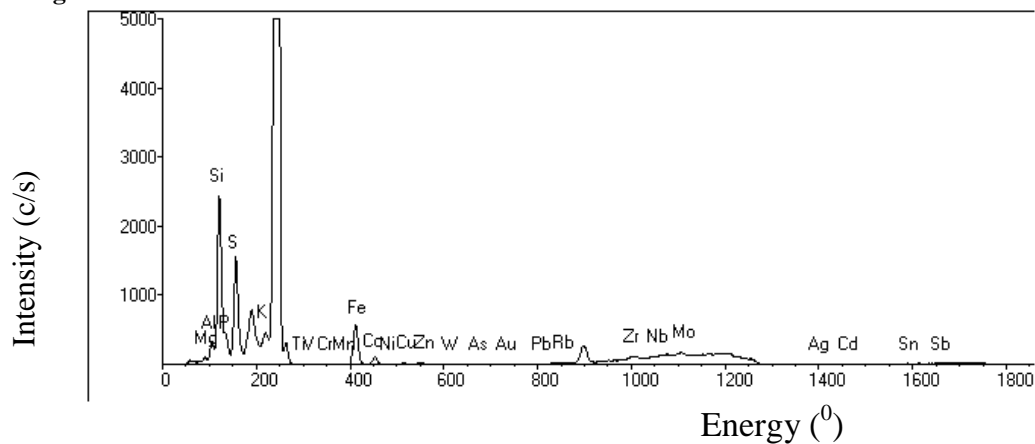


Figure 3: Graph of analysis on the characteristics of Dangote cement (intensity against energy)
 Fig. 3 illustrates above shows the elemental composition of the chemical properties of Dangote cement at every intensity due to its energy.



For Formulated Cement

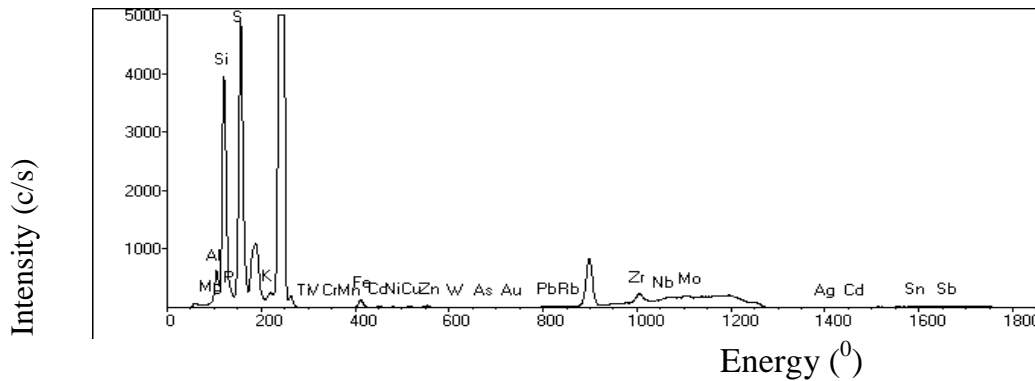


Figure 4: Graph of analysis on the characteristics of Formulated cement (intensity against energy)

The illustration of figure 4 shows the elemental properties present in Formulated cement at their degree of energy.

Functions of each Constituent

Every chemical constituent listed below has its unique characteristics which contribute immensely in the strength and reliability of cement products.

Alumina (AL₂O₃): This is responsible for the setting time of cement.

Silica (SiO₂): It is responsible for strength impart to cement when it reacts with calcium to form hard silicate.

Lime (CaO): This is the most important ingredient for cement production. It is responsible for the strength characteristics in cement.

Iron Oxide (Fe₂O₃): Its responsibility is to impart colour to cement. Chemically, it combines with other constituents to increase strength and hardness of cement.

Magnesium Oxide (MgO): It is always present in small quantities. It imparts strength and hardness to cement.

Sulphur Trioxide (SO₃): It is responsible for soundness in cement.

Alkalis: It is always present in raw materials but disappear during kilning by flue gases. Though, small amount of alkalis is allowed to be present in cement since its excess caused efflorescence in the cement and thus act as impurity.

The result obtained from this research work is presented in tables and figures as shown in this paper.

Table 5: Comparison of BS 12, Bua cement concrete, Dangote Cement Concrete and Formulated Cement Concrete at Ratio of 1:2:4 using Fresh Water

| Period (days) | Bua Cement | Dangote Cement | Formulated Cement | Minimum values for British Standard (BS12) |
|---------------|------------|----------------|-------------------|--|
| 7 | 24.0 | 18.67 | 16.87 | 16 |
| 14 | 25.78 | 24.89 | 18.58 | 19 |
| 21 | 26.67 | 28.44 | 23.64 | 21 |

Strength of BS 12, Bua cement concrete, Dangote cement concrete and formulated cement concrete versus period of curing for 1:2:4 in fresh water.

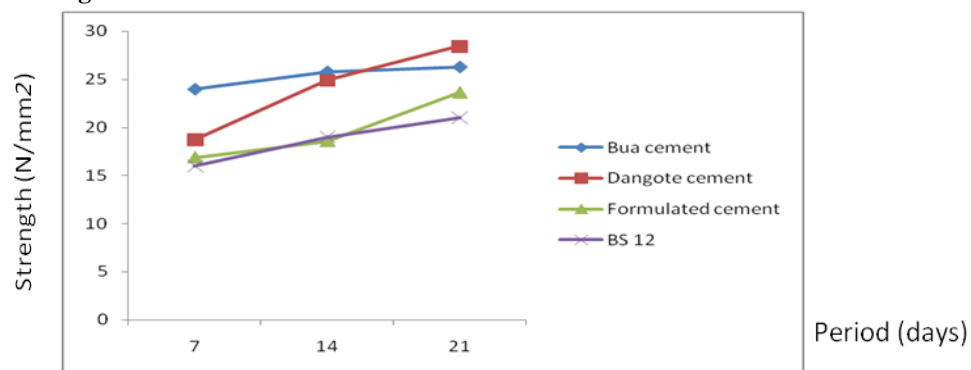


Figure 5: Graph of comparison of Bua cement concrete, Dangote cement concrete, formulated cement concrete and British standard concrete strength against curing period at ratio of 1:2:4 in fresh water.

Figure 5 illustrates the relationship between the curing period and the concrete strength for Bua cement concrete, Dangote cement concrete and formulated cement concrete. The result obtained was compared with minimum British standard (BS 12) strength values for concrete mix. The result shows a good match for Bua cement, Dangote cement and formulated cement.

Table 6: Comparison of BS 12, Bua cement Dangote Cement and Formulated Cement at Ratio of 1:3:6 using Fresh Water

| Period (days) | Bua Cement | Dangote Cement | Formulated Cement | Minimum values for British Standard (BS12) |
|---------------|------------|----------------|-------------------|--|
| 7 | 14.89 | 15.33 | 13.52 | 16 |
| 14 | 17.78 | 18.22 | 16.87 | 19 |
| 21 | 18.56 | 19.67 | 18.58 | 21 |

Strength of BS 12, Bua cement concrete, Dangote cement concrete and Formulated cement concrete versus period of curing for 1:3:6

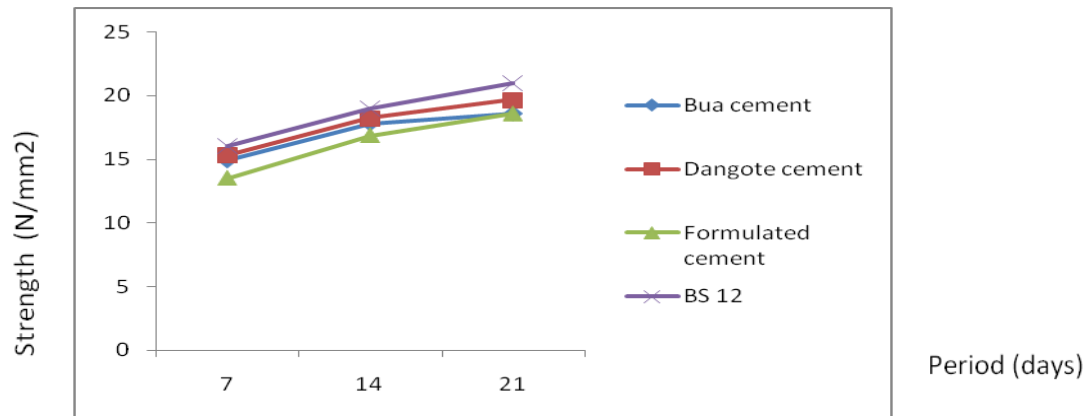


Figure 6: Graph of comparison of Bua cement concrete, Dangote cement concrete, formulated cement concrete and British standard concrete strength against curing period at ratio of 1:3:6 in fresh water

The illustration of figure 6 above, shows that the strength of Bua cement, Dangote cement and formulated cement at ratio of 1:3:6 in fresh water did not match with the British standard (BS 12) of concrete strength.

Table 7: Comparison of BS 12, Bua Cement Dangote Cement and Formulated Cement at Ratio of 1:2:4 using Salt Water

| Period (days) | Bua Cement | Dangote Cement | Formulated Cement | Minimum values for British Standard (BS12) |
|---------------|------------|----------------|-------------------|--|
| 7 | 16.89 | 16.89 | 15.53 | 16 |
| 14 | 19.56 | 20.44 | 19.10 | 19 |
| 21 | 23.11 | 25.78 | 21.87 | 21 |

Strength of, BS 12, Bua cement concrete, Dangote cement concrete and Formulated cement concrete versus period of curing for 1:2:4 in salt water.

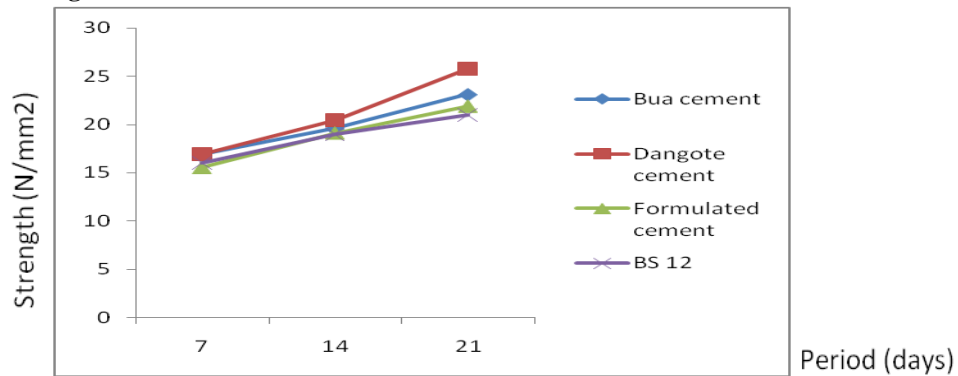


Figure 7: Graph of comparison of Bua cement concrete, Dangote cement concrete, formulated cement concrete and British standard concrete strength against curing period at ratio of 1:2:4 in salt water

Figure 7 illustrate the relationship between the curing period and the concrete strength for the three types of cement. The result obtained was compared with minimum British standard (BS 12) strength values for concrete mix. The result shows a good match for the three types of cements.

Table 8: Comparison of BS 12, Dangote Cement and Formulated Cement at Ratio of 1:3:6 using Salt Water

| Period (days) | Bua Cement | Dangote Cement | Formulated Cement | Minimum values for British Standard (BS12) |
|---------------|------------|----------------|-------------------|--|
| 7 | 13.78 | 13.78 | 11.82 | 16 |
| 14 | 14.78 | 15.33 | 13.53 | 19 |
| 21 | 17.67 | 19.0 | 16.87 | 21 |

Strength of, BS 12, Bua Cement concrete, Dangote cement concrete and Formulated cement concrete versus period of curing for 1:3:6 in salt water.

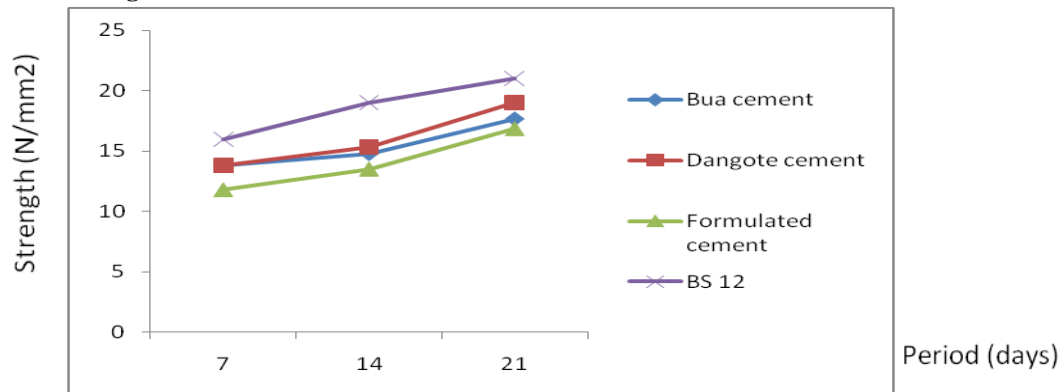


Figure 8: Graph of comparison of Bua cement concrete, Dangote cement concrete and formulated cement concrete and British concrete strength against curing period at ratio of 1:3:6 in salt water.

The illustration of figure 8 above shows that the strength of the three types of cement at ratio of 1:3:6 in fresh water did not match with the British standard (BS 12) of concrete strength.

Conclusion

The following conclusions were drawn from the research work, such as:

- The strength of the formulated cement matches with that of Bua cement and Dangote cement.
- The best ratio for the mixture of cement for construction is 1:2:4, for at this ratio, the strength of the formulated cement Bua cement and Dangote cement is higher than the British Standard value for concrete strength.
- The compressive strengths of formulated cement Bua cement and Dangote cement were significantly affected by curing age.
- Periwinkle shell can best be used as a material for the production of cement because of its high percentage of calcium.
- From the study it is also shown that fresh water should best be used always for the production of concretes because of the high percentage of sodium chloride that is found in salt water.
- The finesse of the formulated cement is the same to that of other types of cement.

Recommendation

From the study, more research should be carried out in order to improve on the quality of the formulated cement.

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