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Assessment of Quality of the Various Brands of Portland Cement Products Available on the Ghanaian Market

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ABSTRACT

Three brands of Portland cement products (CEM A, CEM B and CEM C) available in Ghana have been studied for their chemical oxide compositions (CaO, SiO_2, Al_2O_3, Fe_2O_3, SO_3 and MgO). The oxide concentrations were determined using energy dispersive X-ray fluorescence (EDXRF) spectrometry. The validity of the EDXRF method was checked by analysis of NIST SRM 1889a (Portland cement). Excellent agreement between measured results and certified values confirms the reliability of the EDXRF method used. The major compounds (C_3S, C_2S, C_3A and C_4AF) and control ratios (LSF, SR and AR) were also assessed for quality of the cement products and the results obtained compared with the European standard (EN 197-1) specification. The results obtained for all the analysis showed that CEM A and CEM B cement conforms well to the European (EN 197-1) standard specification except CEM C cement which did not conform to the standard specification.

Keywords: *Chemical oxides, EDXRF, Ghana, Cement, Quality*.

1. INTRODUCTION

The production of cement has played a key role as a construction material throughout the history of civilization. It is very important in the construction of buildings, bridges, tunnels, to mention a few [5]. Every year a large quantity of Portland cement is produced for general construction purposes. Ghana has two cement producing companies (Ghana Cement Ltd (Ghacem) and Diamond Cement Company) and Dangote Cement Company which only does the bagging of cement imported from Nigeria here in Ghana. Recent development of collapse of building in Ghana has necessitated the study of the quality of cement commercially available in Ghana.

The use of low quality cement in structural and constructional works may cause loss of lives and properties. So, the quality assurance of cement is therefore becoming important and critical factor. Even though a number of tests are performed in the laboratories of cement industries to ensure that the cement is of the desired quality and it conforms to the requirement of the relevant standards [9], independent analysis can be perform to check the quality of cement in the Ghanaian market. Data on the quality of Portland cement brands in Ghana are scarce and almost non-existence. Therefore, the study will provide data on the quality of Portland cement on the Ghanaian market.

Cement manufacturers and their customers realize that, for optimal concrete manufacture, cement must be produced from a consistent clinker which meets prescribed specifications. This, in turn, can only be achieved if the raw mix chemistry is consistent [2]. The major compounds formed in the clinker are tricalcium silicate ($3CaO.SiO_2$), dicalcium silicate ($2CaO.SiO_2$), tri-calcium aluminate ($3CaO.Al_2O_3$) and tetracalcium aluminoferrite ($4CaO.Al_2O_3.Fe_2O_3$). The shorthand notation for these compounds as used in cement industry is C_3S, C_2S, C_3A and C_4AF respectively. C_3S and C_2S are responsible for strength development. C_3A and C_4AF control setting and heat evolution during hydration [9]. The properties of the cement, such as its setting time and strength, are adjusted by the addition of gypsum and by grinding to specific degrees of fineness [14]. There are several brands of Portland cement available in the market but their chemical compositions are the same. Variations in physical properties occur due to the variation in the amount of chemical constituents [4].

The main objective of the study was to determine the chemical oxides (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO and SO_3) compositions using Energy Dispersive X-ray Fluorescence Spectrometer (EDXRF). The result was used to calculate the major compounds (C_3S, C_2S, C_3A and C_4AF) and the control ratios (LSF, SR and AR) of three cement brands (CEM A, CEM B and CEM C). These parameters were used to assessed the quality of the three cement brands based on the European standard EN 197-1 specification for CEM I (Portland cement)

2. MATERIALS AND METHODS

2.1 Instruments

A manually-operated hydraulic press, Carver 3912 (Indiana, USA) was used for the transformation of pulverized cement into pellets. A Compact 3K5 X-ray Generator (GNR Analytical Instruments Group, Italy), equipped with a Digital Pulse Processor, Version 1.0, (KETEK GmbH, München, Germany) and Analytical X-Ray Acquisition System – Digital, Version 2.1 (KETEK GmbH, München, Germany) was used for irradiation and counting. A Mettler Toledo weighing balance AE 163 (Zurich, Switzerland) was used for weighing of cement samples.

2.2 Sampling and Sample Preparation

Three brands of cement available on the Ghanaian market and commonly used by Ghanaians for construction purposes were purchased from retail outlets in Accra (the capital city of Ghana). Aliquots of the cement samples were taken with a polyethylene spoon and transferred in clean hermetically-closed polyethylene bags. This was followed by the transformation of the pulverized cement samples into pellets for EDXRF spectrometric analysis. The procedure for the formation of the pellets is as follows:

About ten grams aliquot of the pulverized cement sample was weighed on a calibrated AE 163 Mettler Toledo weighing balance. Manually-operated hydraulic press, Carver 3912 was used to transform the 10 g aliquot pulverized cement sample into a 2.5 cm diameter thick pellets. This was done by transferring the pulverized cement sample into a special cylindrical block attached to the Carver 3912 and applying a maximum press pressure of 10 tons. The pellet was carefully removed from the cylindrical block. This was followed by sample irradiation.

2.3 Sample Irradiation, Counting and Analysis

The elemental concentrations were determined using energy dispersive X-ray fluorescence (EDXRF) spectrometer. EDXRF provides a rapid and non-destructive method for the analysis of trace and major elements in soil samples. All measurements were carried out under atmospheric conditions, using a Compact 3K5 x-ray generator EDXRF spectrometer with Mo as anode target and secondary target arrangement, operated at a current of 10 mA and a voltage of 45 kV. Mo and Ti secondary targets were used to irradiate the cement samples for spectrum collection times of 600s and 300s respectively. Mo secondary target was used to identify Ca and Fe while Ti secondary target was used to identify Si, Al, Mg and S. Silicon Drift Detector (KETEK, Germany) was used for the acquisition of x-ray spectrum. The incident and take-off angles were 45º, with a Be window thickness of 12.5 mm. The distance between the sample (exposed diameter of 22 mm) and the detector was 4.5 cm. The energy resolution was 0.165 keV. In order to maximize the EDXRF sensitivities for the elements of interest, two different combinations of EDXRF parameters (including voltage and current) were used. The applied voltage and current are varied to acquire the required K" or L" energies line. The current was adjusted to maintain similar portions of live detection time. The digital pulse processor software version 2.1 (KETEK, Germany) was used for the qualitative analysis. Linear least squares fitting of the AXIL (**A**nalysis of **X**-ray spectra by **I**terative **L**east-squares) software program was used for spectrum deconvolution (IAEA, 2005) to obtain x-ray intensities of the identified elements.

3. RESULTS AND DISCUSSION

3.1 Validation of EDXRF Method

The validity of the EDXRF method for the determination of the oxides in cement was checked by analysis of standard reference material, NIST SRM 1889a (Portland cement). The reference material was prepared and analyzed under the same conditions as the samples. The concentration of oxides obtained in the reference material is in good agreement with certified values (Table 1). This confirms the reliability of the EDXRF analytical method for the determination of oxides in cement.

3.2 Concentration of Oxides in Cement

The concentration of oxides in the different cements brands available on the Ghanaian market is presented in Table 2. The various percentage oxides compositions (CaO, Fe_2O_3, Al_2O_3, SiO_2, SO_3 and MgO) are presented graphically in Fig. 1, followed by detailed discussion of the results.

Table 1: Validation of EDXRF method for oxide determination with NIST SRM 1889a (Portland cement)

Oxides	Concentration (% weight)		
	Measured value	Certified value	Relative deviation
CaO	65.33±0.41	65.34	0.02
Fe_2O_3	1.94 ±0.01	1.94	0.00
SiO_2	21.02±0.21	20.66	1.74
Al_2O_3	3.59±0.51	3.89	7.71
MgO	0.95±0.01	0.81	17.28
SO_3	3.08±0.45	2.69	14.50

Data are presented as mean ± standard deviation of four replicate measurements

Table 2: Mean chemical oxide concentration in different brands of cement samples

Oxides	Concentration of oxides (% weight)		
	CEM A	CEM B	CEM C
CaO	61.74±0.4	62.19±0.4	57.37±0.3
SiO_2	18.77±0.6	21.90±0.6	21.69±0.2
Al_2O_3	5.41±0.2	2.50±0.9	6.40±0.2
Fe_2O_3	3.01±0.1	2.92±0.3	3.10±0.1
SO_3	3.89±0.6	4.03±0.1	4.05±0.1
MgO	3.13±0.4	2.23±0.1	3.34±0.1

Data for measured values are presented as mean ± average absolute deviation

Mean absolute deviation = $\frac{1}{n}\sum_{i=1}^{n}|x_i - \bar{x}|$ Where: x_i is the mass fraction; $\bar{x}$ is the mean mass fraction; and, n is the number of measurements.

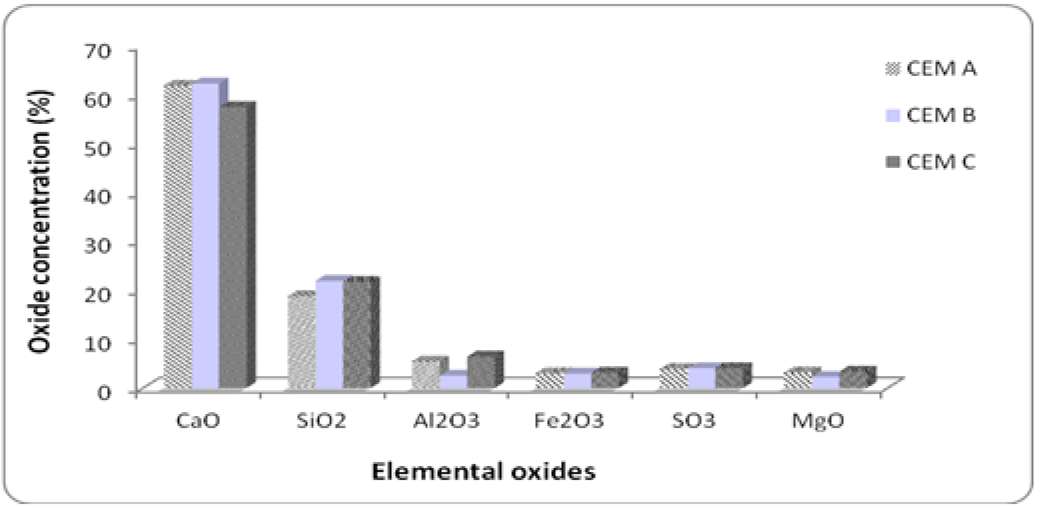

Fig. 1: Variation of chemical oxides composition in different cement brands

Fig. 1 shows the variation of chemical oxides composition in different cement brands available in Ghana compared to European standards specification. The amounts of CaO according to European standard specification in ordinary Portland cement is in the range of 61-67 % [12]. CEM A and CEM B cement are within the range however, CEM C fell below the range. The European standard specified amount of SiO_2 in Portland cement should be within the range 19-23 % [12]. It was observed that all the three brands of cement are within the specified limit (Fig. 1). According to the European standard (EN 196-2), the sum of the proportions of CaO and SiO_2 in cement should not be less than 50 % by mass. Similarly, the ratio by mass of CaO to SiO_2 should not be less than 2.0. From the results obtained, the sum of CaO and SiO_2 in the cement samples analyzed exceeded 50 % by mass and have ratios above 2.0 [3].

The amounts of Al_2O_3 in the various brands (Fig. 4) are within the range of 2-6 % specified by the European standard [12]. The amount of Fe_2O_3 according to the European standard should be within the range, 0-6 %. The levels of Al_2O_3 and Fe_2O_3 in all three brands of cement used for this study are within their respective ranges specified by the European standard. Also, the contents of MgO were below the 5.0 % by mass recommended by the European standard. The levels of SO_3 in the cement brands were above the 1.5 %-2.5 % European standard recommended range in Portland cement (Fig 1).

3.3 Quality of Cement

The major constituents of Portland cement are tricalcium silicate [$3CaO \cdot SiO_2$], dicalcium silicate [$2CaO \cdot SiO_2$], tricalcium aluminate [$3CaO \cdot Al_2O_3$] and tetracalcium aluminoferrate [$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$] (Natalya, 2003). The shorthand notation for these compounds in the global cement industry is C_3S, C_2S, C_3A and C_4AF respectively [9]. The compositions of the constituents are used to determine the quality of the Portland cement.

The quality of the cement products were calculated from the oxide concentrations of the cement using Bogue formulae [1,5]. The formulae are as follows:

$$C_3S = [(4.071 \cdot CaO) - (7.6 \cdot SiO_2) - (6.718 \cdot Al_2O_3) - (1.43 \cdot Fe_2O_3) - (2.852 \cdot SO_3)] \quad \text{eq.1}$$

$$C_2S = [(2.867 \cdot SiO_2) - (0.7544 \cdot C_3S)] \quad \text{eq.2}$$

$$C_3A = [(2.650 \cdot Al_2O_3) - (1.692 \cdot Fe_2O_3)] \quad \text{eq.3}$$

$$C_4AF = [3.043 \cdot Fe_2O_3] \quad \text{eq.4}$$

The Bogue calculation is a means of estimating the amount of the dominant minerals available in cement, based on its oxide composition. Notwithstanding, knowledge of the potential phase compositions is important in assessing the properties of cement [6].

Based on the concentrations of the chemical oxides (Table 2) and Bogue calculation, the percentage proportions of C_3S, C_2S, C_3A and C_4AF in CEM A, CEM B and CEM C were calculated. The results are presented in Fig 2. The percentage of C_3S in CEM A and CEM B cement are within the 50 % - 64 % range as recommended by the European standard specification (EN 197-1). CEM C is however, far below the recommended range. The standard specification for C_2S ranges from 14.2 % to 18.0 %, nonetheless, none of the cement brands lies within this range. Also, the percentage range of C_3A recommended by the European standard is 6 % - 9.5 %, an assessment of the results obtained indicates that only CEM A is within the recommended range. For C_4AF, all the cement brands are within the specified 8 % - 12 % range. Variation in the chemical constituent of cement affects the hardening/hydration, setting time, corrosion resistance, colour of cement [1, l1, 13]. Concrete made with cement having a relatively high C_3S content will tend to gain more strength and produce more heat of hydration at earlier ages, usually within the first week of placement. Concrete made with cement having a relatively high C_2S content tends to gain more of its strength at later ages, perhaps up to four weeks after placing. Cements with a relatively high C_3S content will have a relatively low C_2S content. Concrete made with cement having a relatively high C_3A content tends to exhibit faster setting times; more heat generation in the initial few hours after the concrete is poured [7]. Both C_3A and C_4AF make little contribution to strength [8].

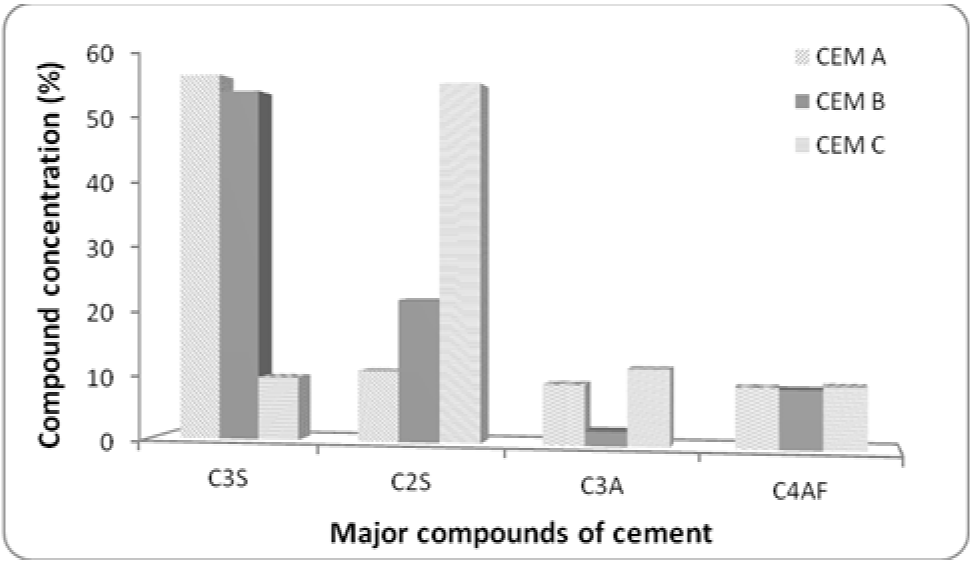

Fig 2: Variation of cement potential in different brands of cement

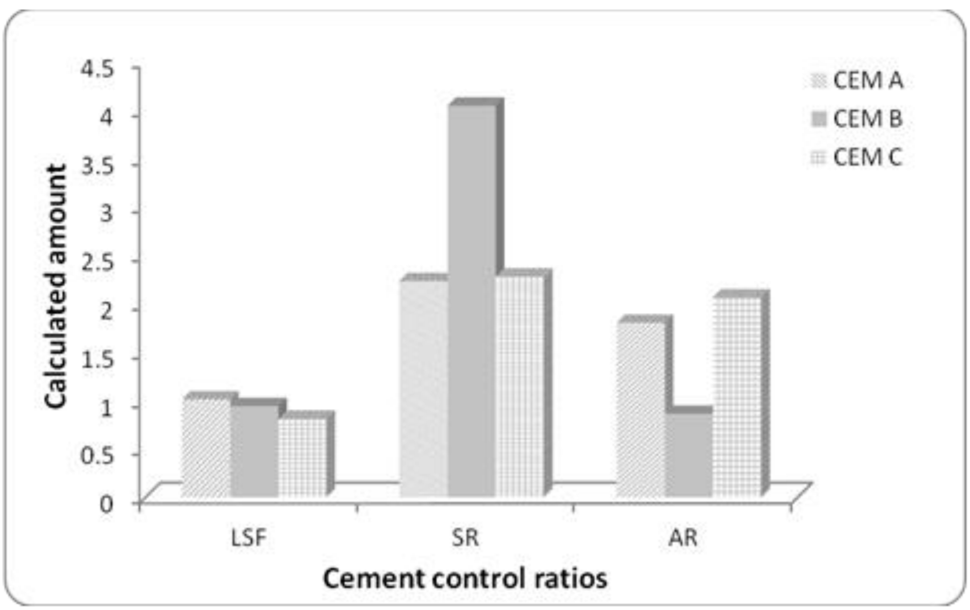

Fig. 3: Variation of cement ratio in different cement brands

According to Nasir and Eletr (1996), the lime saturation factor, the silica and aluminum ratios (formulae stated below) are important factors for chemical control in cement [8]. Based on the formulae, the lime saturation factor, the silica and aluminum ratios were calculated from the percentage oxide compositions. The results obtained are presented in Fig. 3. The formulae for the calculation are as follows:

Lime Saturation factor (LSF) = $\{(CaO)/ [(2.8SiO_2) + (1.2Al_2O_3) + (0.65Fe_2O_3)]\}$ eq.5

Aluminum/iron ratio (AR) = $[(Al_2O_3)/ (Fe_2O_3)]$ eq.6

Silica ratio (SR) = $[(SiO_2)/ (Al_2O_3 + Fe_2O_3)]$ eq.7

The cement control ratios are shown in Figure 3. The normal range of AR is 1.3-2.5. If it goes above 2.5, viscous slag and high early strength occur and if it goes below 1.3, then fluid slag, low early strength and low heat of hydration occur. The usual range of SR is 2-3. For SR less than 2, burning become very easy but excessive liquid phase and low strength cement is obtained. On the other hand if the SR reaches up to 3, then the high strength cement is obtained, however the burning become very difficult. For SR more than 3, no clinkerization takes place. The normal range of LSF is 0.90 - 0.98, on the other hand if it is 0.8, then it does not create any problem in cement manufacturing process and cement strength. It is therefore recommended that it should not go below 0.80 [10, 13]. From the calculated results; CEM A and CEM C have AR within the range, except CEM B cement which falls below it (Fig. 3). CEM B cement is within the acceptable range for the LSF, CEM A has LSF above the acceptable limit and CEM C has LSF far below the acceptable limit. For SR, CEM A and CEM C are within the limit while CEM B is far above the range. The potential for C_3S formation is given by the lime saturation factor (LSF). The AR influences the characteristics of the molten flux, whereas, the SR is a controlling factor that determines the possible amount of calcium silicates formed in the clinker (C_3S + C_2S) [8].

4. CONCLUSION

The chemical oxide composition, major compounds and the control ratios of three brands of cement products on the Ghanaian market have been determined successfully. The chemical oxides (CaO, Fe_2O_3, Al_2O_3, SiO_2, SO_3 and MgO) contents in CEM A and CEM B cement brands meet European Standard EN 197-1 specification except CEM C. The compound concentrations (C_3S, C_2S, C_3A and C_4AF) of the two brands of cement (CEM A and CEM B) conform to European standard EN 197-1 specification for CEM I (Portland cement), while CEM C did not meet EN 197-1 specification for CEM I (Portland cement). From the analysis, CEM A and CEM B cements are of good quality, while the third cement brand (CEM C) is of lower quality.

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