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Analysis of Chemical Composition of Different Brands of Portland cement Used in Libya

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Abstract: **The chemical composition of cement has crucial impact on the performance of resulted concrete or mortar. Different brands of Portland cement are used in Libya by local contractors for various construction works without prior knowledge of their performances. In this study four different brands of Portland cement from Libyan market were analysed with X-Ray Fluorescence (XRF) spectrometer for their chemical constituents and compared with ASTM standard specifications. The results showed that there were no significant differences between chemical composition values specified in ASTM C150 standard and that of commercial Portland cements examined in this study. All the studied cements were found to be good for any construction works be it concrete or mortar formation especially where no particular properties are required.**

Keywords: **Cement brand, chemical composition, mineral composition, Libyan market.**

I. INTRODUCTION

The Cement is one of the most traditional construction materials in almost every part of the word. The understanding of the behaviour of cement can lead to design of high performance concrete and mortar for making solid and long life structure [1]. Portland cement derives its setting and hardening when mixed with water from chemical reaction called hydration.

A typical Portland cement clinker is produced by mixing limestone, clay, sand and iron oxide and heating them at elevated temperatures in rotary kilns were converted to major and minor oxides form [2]. The major oxides include CaO, SiO_2, Al_2O_3, and Fe_2O_3 whereas the minor oxides also include MgO, SO_3, and some alkali oxides (K_2O and Na_2O) [3]. Various properties of cement are considerably influenced by oxide compositions. Thus, during the proportioning of raw materials, the content of each oxide must be in the right quantity [4].

During burning (At 900 to 1450ºC) and blending of raw materials, the chemical reactions take place and four principal compounds which are normally referred to as minerals are resulted. These include tricalcium silicate (C_3S), dicalcium silicate (C_2S),tricalcium aluminate(C_3A), tetracalcium luminoferrite (C_4AF) (Fig.1). Silicates play the key role in gaining the strength compared to other components. C_3S easily reacts with water, results in more heat of hydration and responsible for early strength development, whereas, C_2S react slowly, produces less heat of hydration and responsible for later strength development [5].

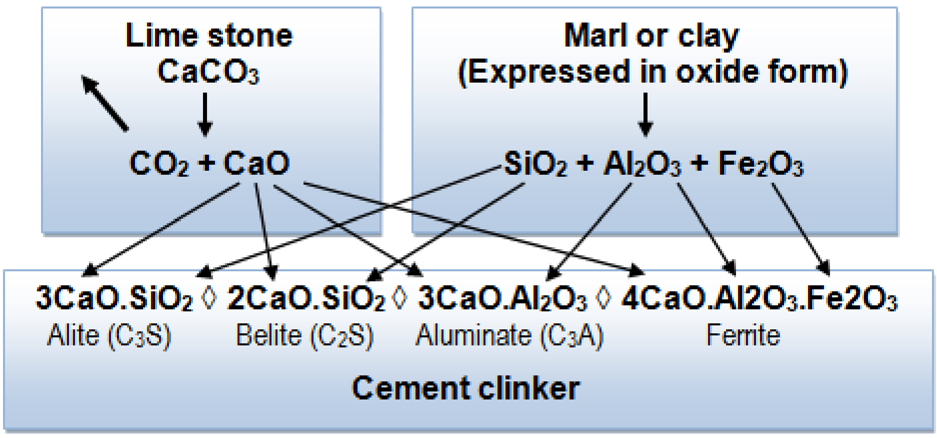

Fig 1: Mineral compositions of the cement clinker

Annually, a huge amount of cements is used for the construction of buildings and other purposes in Libya. However, most of the construction industries rely on the experience, availability and cost in selecting the brand of cement to be used in their projects. So, quality control has become an important and critical factor of cement production [6].

Few studies have been carried out to analysis the major components of cement which is used in Libya. Chemical analysis of different cement brands used in Libya was conducted by Elbagermia et al.[6]. The results indicated that although the studied samples showed different percent composition of constituents, however, in general they can be used for concrete work if no special properties are required. Other study by Abdunnabi [7] was carried on to determine the major and traces elements in the Libyan and imported Portland cement. This study showed that the Libyan cement is comparable to the imported ones and also meets the requirements of the international specifications of the Portland cement.

The most key factor for most civil engineers when choosing cement brand is its strength specification. However, other information such as chemical and mineral composition could be used to corroborate with strength in making right decisions to choose the best quality of cement [8].

Several techniques have been used for chemical analysis of cement, however, X-ray fluorescence (XRF) is the most popular technique used today. Because of its accuracy and simplicity of procedures, XRF is used by several researchers [6, 8-10]. The objective of this study was to conduct a chemical analysis of some cement brands available in Libyan market using X-ray fluorescence (XRF). This is important to determine whether the cement brands meet the standard requirements.

II. METHODS AND MATERIALS

A. Cement samples

Four different brands of cement ratifying the criteria of CEM I (El Borge Zliten, Al Borge Egypt, Helwan Egypt and Dernah) were collected from the Libyan market and labelled as BL, BE, HE and DC respectively. El Borge Zliten and Dernah cements are Libyan products whereas Al Borge Egypt, Helwan Egypt are Egyptian products. After collection, each cement bag was kept in an air-tight plastic bag to avoid surface contamination and unwanted hydration with the moisture present in the air.

B. Chemical composition of the cements

The chemical compositions in the four types of cement were performed with the sequential X- ray fluorescence technique model ARL 9400, Switzerland. In this method, about 10 g of each cement sample was mixed with boric acid in 10: 1 ratio and then the mixture was milled in a milling machine for two minutes with 800 rpm to produce a homogeneous mixture. The sample was placed in dice and pressed by a briquetting press machine for one minute and then transferred to the x-ray fluorescence for analysis.

C. Chemical composition of the cements

The mineral compositions were determined using Bogue's equation [11] The equations are reproduced as Equations (1) – (4).

$$C_3S = 4.0710\ (CaO) - 7.6024\ (SiO_2) - 6.7187\ (Al_2O_3) - 1.4297(Fe_2O_3) \quad (1)$$

$$C_2S = 8.6024\ (SiO_{2)} + 1.0785\ (Fe_2O_3) + 5.0683\ (Al_2O_{3)} - 3.0710\ (CaO) \quad (2)$$

$$C_3A = 2.6504\ (Al_2O_3) - 1.6902\ (Fe_2O_3) \quad (3)$$

$$C_4AF = 3.0432\ (Fe_2O_3) \quad (4)$$

D. Quality of cements

Cement control parameters were calculated based on oxide concentrations of the studied cements using equations from (5) to (7).

$$\text{Silica Ratio (SR)} = \frac{Si\ O2}{Al2O3 + FeO3} \quad (5)$$

$$\text{Alumina Ratio (AR)} = \frac{Al2\ O3}{Fe\ O3} \quad (6)$$

$$\text{Lime Saturation Factor (LSF)} = \frac{\text{CaO}}{2.8\ \text{SiO2} + 1.65\ \text{Al2O3} + 0.35\ \text{FeO3}} \quad (7)$$

III. RESULTS AND DISCUSSION

A. Oxides composition

The results of the analysis carried out on the samples are listed in TABLE I. The oxides composition of the studied cement brands were almost at the limits given by ASTM C150 [12]

TABLE I: PERCENT CHEMICAL COMPOSITION OF THE SELECTED CEMENTBRANDS ANALYSED BY XRF METHOD

Parameter	BL	BE	HE	DC	ASTM C150-12
CaO	62.36	61.47	61.84	63.03	61 - 67
SiO_2	22.06	19.83	20.69	20.06	19 - 23
Al_2O_3	4.80	3.75	3.45	5.17	2.5 – 6.0
Fe_2O_3	3.68	4.39	3.50	3.07	6 Max
MgO	2.01	2.23	1.92	1.41	5 Max
K_2O	0.63	0.27	0.22	0.91	<1.0
SO_3	2.47	2.94	3.14	2.46	3 Max
Na_2O	0.08	0.38	0.34	0.18	<1.0

It was found that the CaO content in all studied samples are almost the same and within the specified limits of ASTM C150 standard. High lime content makes the cement unsound and decreases strength when it is too low [9]. While CaO were present in greatest quantities (61.47 – 63.03), K_2O and Na_2O appeared with the smallest quantities (0.22 – 0.91%) and (0.08 – 0.38%) respectively. Quick setting, strength reducion and increase shrinkage under drying conditions can be happened due to excess alkalis content in clinker [13].

The SiO_2 content for all samples are in the range of ASTM C150 standard with BL and BE cements recording the highest and lowest value respectively. SiO_2 gives strength to cement due to formation of dicalcium and tricalcium silicate. Furthermore, SiO_2 is an indicator for fineness and determine the grind ability of the cement clinker and impart strength to cement [14].

It can be seen from Table 1, the content of Al_2O_3 in all cements was found to be within the limit given by ASTM C150 standard. High alumina cement is used when early strength development is required [6]. However, cements with high content of alumina are not suitable for mass concreting.

It has been observed that the Fe_2O_3 content in all the cement samples was found to be within the stipulated limits given by ASTM C150 standard. BL and BE cements have higher MgO content compared to HE and DC cements. However, all the cement samples are having the MgO within the limits specified in ASTM C150 standard. Excess magnesia will reduce the strength of the cement and may be damaging the soundness of the cement especially at late ages [9]. Almost the content of SO_3 for all cement samples was within the range of ASTM C150 standard. SO_3 makes cement unsound or sound if present in excess or very small quantities respectively [15].

B. Mineral composition

The mineral composition of cement samples were computed based on Bogue's equations and presented in Fig. 2. The mineral composition of the cement is more useful than its oxide composition regarding determination of cement performance [16].

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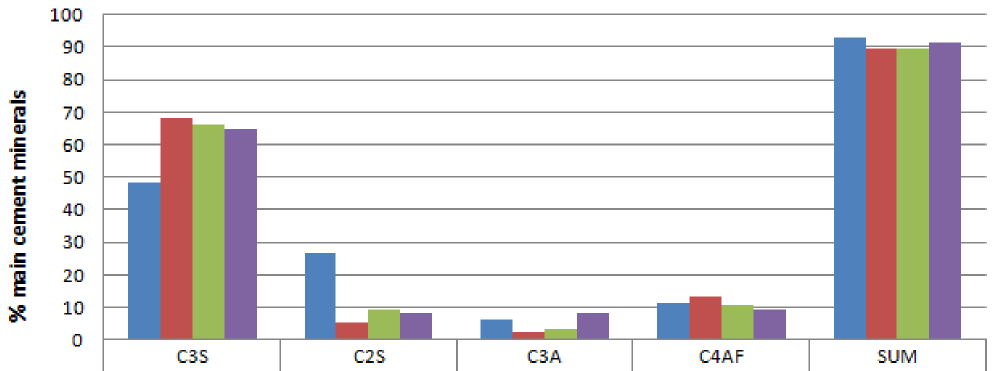

	C3S	C2S	C3A	C4AF	SUM
BL	48.65	26.56	6.50	11.20	92.91
BE	68.02	5.55	2.52	13.36	89.45
HE	66.27	9.33	3.23	10.65	89.49
DC	64.97	8.51	8.51	9.34	91.34
ASTM C150 AND BS 12:1991	45 – 65	7 – 32	8 – 12	10 – 11	

Fig 2: Percent mineral composition of cement samples according to Bogue's equation

The mineral compositions of the cements varied from one to another. This could be due to the differences that exist with individual factory proportioning of raw materials. The composition of C_3S in BL and DC cements (Libyan product) were 48.65 and 64.97% respectively. These values are within the 45 – 65% limits as specified by ASTM C 150. However, the C_3S values for BE and HE cement (Egyptian product) were found 68.02 and 66.27% which is slightly higher than the limits given by ASTM C150 (Fig. 2).

It can be seen from figure 2, lower contents of C_2S content were observed in BE cement compared to the ranges specified in ASTM C150. The reason could be that some C_2S may have converted to C_3S during clinker heating [17]. C_2S hydrates in a similar manner to that of C_3S but is much slower as it is a less reactive compound than C_3S [18]. Among various cement chemical compositions, C_3S and C_2S provide most of the strength developed by Portland cement. It was observed that, the both of C_2S and C_3S in all cements account for over 73% of the total cement composition.

The results indicated that the C_3A value for DC cements was found within the limits given by ASTM C150 while those of BL, BE and HE were lower the standard (Figure 2). C_3A in cement had different impacts. Firstly, cement with high C_3A generates higher heat of hydration than cement contains lower C_3A. Secondly, the reactivity of C_3A and the solubility of gypsum play a crucial role in controlling the setting of cement. Thirdly, low level of C_3A cement is a sulphate resistance whereas high level C_3A cement is non-sulphate resistance [11].

As it can be noted that the content of C_4AF in BL and BL cements are slightly above the limits specified by ASTM C150. HE and DC cements on the other hand have C_4AF contents being in agreement with the standard of ASTM C150 (Fig. 2). C_4AF does not play an important role in affecting the behaviour of cement [19]. However, with C_3A, can lower corrosion risk arising from chloride and sulphate ions [11].

C. Cement control parameters

Lime saturated factor (LSF), silica ratio (SR) and Alumina ratio (AR) were also determined. Each of these parameters influences performance of cements and is often used for control purposes [11, 20].

Amount of LSF was found to vary in between 0.895 to 0.984 among the different brands of cements as shown in Fig.3. The LSF controls the ratio of C_3S to C_2S in the clinker. A clinker with a higher LSF has a higher proportion of C_3S to C_2S than will a clinker with a low LSF. Typical LSF values as reported by Taylor [11] is 0.92 – 0.98 but if it is 0.8, it does not create any problem in cement manufacturing process and cement strength [9]. The possibility of existence of free lime in clinker is more likely if LSF value above 1.0. At LSF equal 1.0; all free lime should have combined with C_2S to form C_3S, but if the LSF is higher than 1.0, the excess free lime could not combine and remain as free lime [19, 21].

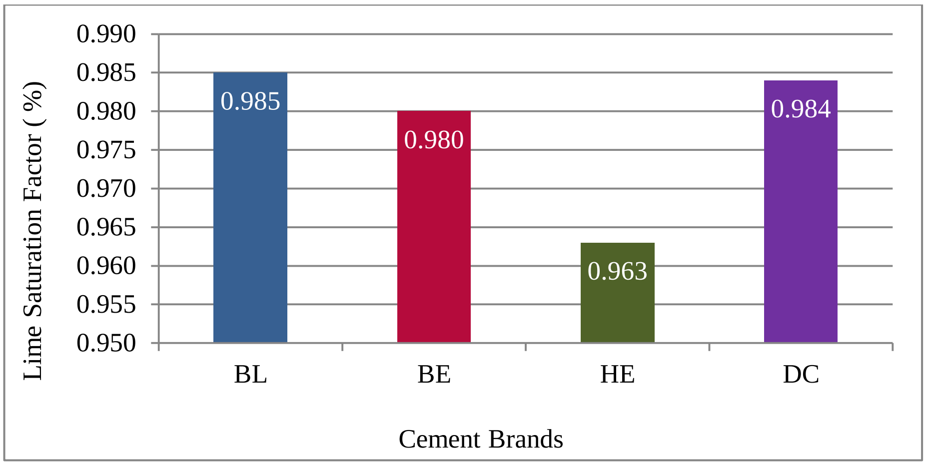

Fig 2: Percentage of LSF in the studied brands of cement

As shown in Fig. 4, the values of SR of all cement brands are within the typical limits (2 – 3) reported by Taylor [11]. When SR less than 2, burning become very easy with extra liquid phase and low strength cement is obtained. Conversely, if the SR reached up to 3, the burning becomes very difficult and high strength is obtained. Moreover, with SR more than 3, no clinkerisation will take place [9].

It has been noticed that the AR content in DC and BL cements were found to be within the typical set limits (1 – 4) described by Taylor [11], however, BL and HE cements were slightly less than the limits (Fig. 5). Low AR is associated with low heat of hydration, slow setting of cement. Conversely, High AR with low silicate ratio leads to quicker settings of cement. Consequently, an addition of gypsum is required to control the setting time [22].

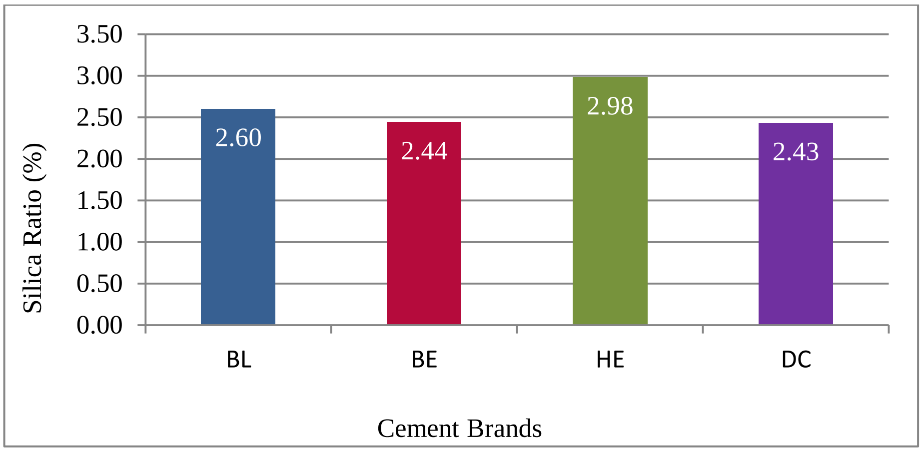

Fig 4: Percentage of SR in the studied brands of cement

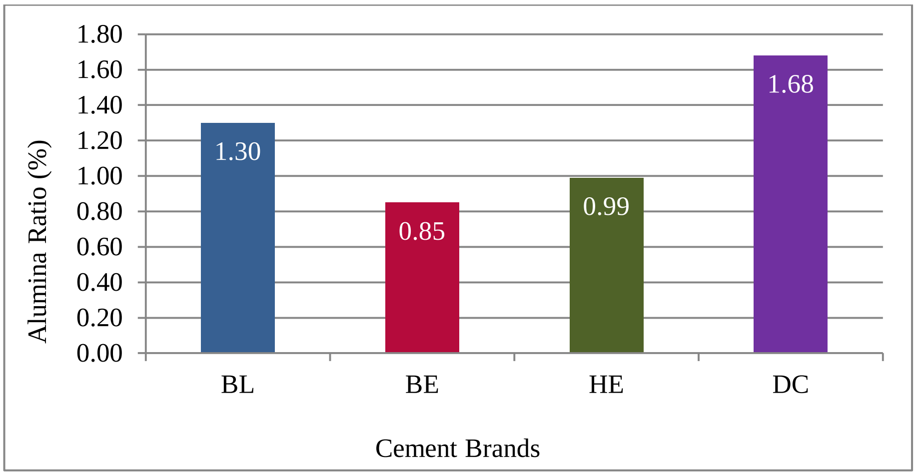

Fig 3: Percentage of AR in the studied brands of cement

IV. CONCLUSION

The chemical compositions of commonly used Portland cement in Libyan market were analysed with X-Ray Fluorescence (XRF) spectrometer. Although the results indicated that each brand of studied cement has an individual variation with regard to chemical composition. However, the outcome showed that the studied samples have no significant deviation from values specified in ASTM C150 standard. This therefore shows that any of the studied cement brands could be acceptable for normal construction works.

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