

Chemical Analysis of Available Portland Cement in Libyan Market Using X-Ray Fluorescence

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Abstract—This study compares the quality of different brands of Portland Cement (PC) available in Libyan market. The amounts of chemical constituents like SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , SO_3 and Lime Saturation Factor (LSF) were determined in accordance with Libyan (L.S.S) and American (A.S.S) Standard Specifications. All the cement studies were found to be good for concrete work especially where no special property is required. The chemical and mineralogical analyses for studied clinker samples show that the dominant phases composition are C3S and C2S while the C3A and C4AF are less abundant.

Keywords—Portland cement, Chemical Composition, Libyan market, X-ray fluorescence.

I. INTRODUCTION

PORTLAND cement is a hydraulic material composed primarily of calcium silicates, aluminates, and ferrites. In a rotary kiln, at temperature reaching the 1450°C , clinker nodules are produced from a finely ground, homogenized blend of limestone, shale and iron ore. The nodules are subsequently ground with gypsum, which serves to control setting, to a fine powder to produce finished Portland cement. The composition and texture of clinker phases result from complex interactions of raw feed chemical and mineralogical composition, particle size distribution, feed homogenization, and the heating and cooling regime [1] and [2]. In order to simplify these phenomena, [3] proposed an approach for the development of the clinker phases. The ferric oxide (Fe_2O_3) reacts with aluminum oxide (Al_2O_3) and lime (CaO) to form the tetracalcium alumino ferrite (Ferrite C_4AF or $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$). The remaining aluminum oxide reacts with lime to form the tricalcium aluminates (C_3A or $\text{Ca}_3\text{Al}_2\text{O}_6$). The lime reacts with the silicate oxide (SiO_2) to form two calcium silicates phases, the dicalcium silicate (Belite, C_2S or Ca_2SiO_4) and tricalcium silicate (Alite, C_3S or Ca_3SiO_5).

One of the important quality parameters of Portland cement is its chemical and phase composition. It is necessary to determine a complete mineralogy of clinker cement to correctly understand, interpret and predict the outcome of any plant production process [4], and [5]. Every year a huge amount of Portland cement is produced and used for the construction of building, roads and highways and other local

purposes in Misurata Libya. Use of poor quality cement in structural and constructional works may cause loss of lives and properties. So, quality assurance of PC has become an important and critical factor.

There are several brands of PC available in market but their chemical compositions are same. Variations in physical properties occur due to the variation in the amount of chemical constituents.

The chemical analysis of cement is carried out to check whether the supplied product conforms to standard specifications or not. In the analysis, each oxide is usually expressed as percentage. Wet chemistry is one of the methods that are employed in the composition determination of cement [6]. In addition to wet chemistry, there are various techniques that are utilized for the composition analysis of cement [7]-[11]. As an example, application of atomic absorption spectroscopy has been reported by a number of researchers for analysis of cement [7], [8]. Another group has determined aluminum oxid in Portland cement spectrophotometrically [11]. X-ray diffraction (XRD) has been used to estimate Portland cement [12]-[13].

In spite of various techniques that are used in analyzing the components of Portland cement, X-ray fluorescence (XRF) technique continues to have a wide popularity. The accuracy of (XRF) as well as the simplicity of procedures are the top reasons for making (XRF) is used by several investigators [14-16]. The study was aimed to conduct chemical analysis of PC. Chemical constituents like silica, Al_2O_3 , Fe_2O_3 , Lime Saturation Factor, CaO , MgO , SO_3 , and ALM were determined. No studies have been found yet in the literature regarding major components analysis of Portland cement that is used in Misurata –Libya.

II. MATERIALS AND METHODS

A. Sample Collection

Three types of cement were studied; the three types of cement were obtained from the Libyan market, as they are widely used in Libya. 50g of each sample was taken in clean labeled polythene bag as soon as the cement bag was opened to avoid surface contamination and kept for further analysis.

B. X-ray Analysis of the Sample

The amount of each of the studied oxides in the three types of cement was determined by using sequential x-ray fluorescence technique model **ARL 9400**, Switzerland. In the used method, each cement sample (10g) was mixed with boric acid in 10:1 ratio in a milling machine for two minutes with 800rpm. The sample is then pressed by a briquetting press

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machine for 1 minute and then transferred to the X-ray fluorescence for analysis.

C. Mineral Content of the Cements

The mineral content of the cements were calculated based on Bogue's formula as outline by Taylor [17].

$$C3S = 4.07CaO - 7.6024SiO_2 - 6.7187Al_2O_3 - 1.4297Fe_2O_3$$

$$C2S = -3.07CaO + 8.6024SiO_2 + 5.0683Al_2O_3 + 1.08Fe_2O_3$$

$$C3A = 2.6504Al_2O_3 - 1.692 Fe_2O_3$$

$$C4AF = 3.0432 Fe_2O_3$$

III. RESULT AND DISCUSSION

The results of the analysis carried out on the samples as shown in Tables I and II. As shown in Table I, the percentage compositions of the various major and minor constituents of the cement samples are within the specifications of American Standard for testing materials (ASTM C150). This means that the cement samples were of certain quality.

The SiO₂ content for all the samples is in the range of 20.87– 25.89% with Al-Ethadiah recording the highest value i.e. Al-Ethadiah > Adana Cemento > AS Çimento > Al-Qumeas. SiO₂ content is an index for fineness or coarseness and it determine the grind ability of the cement clinker, level of water intake and strength of concrete [18]. Percentage of the studies oxides AS Çimento is illustrated in Fig. 1. It can be seen from Fig. 1, the CaO present with the greatest amount, while MgO appeared with the smallest quantity.

Al-Ethadiah cement had the highest Al₂O₃ content which will lead to high content of C₃A (Table II) that contribute to early strength development, while Adana Cemento cement had the least Al₂O₃ content. Thus more setting decelerating additives are needed for Al-Ethadiah in a long period of cementing job.

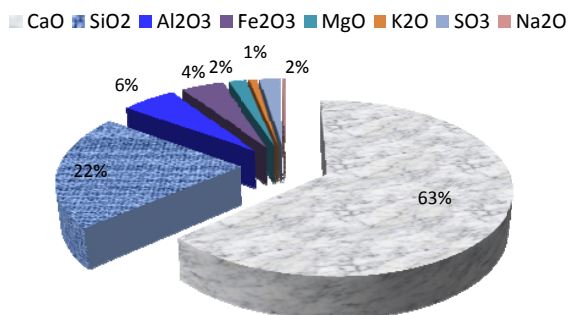


Fig. 1 Oxides in AS Çimento

Adana Cemento had the highest value of SO₃ and AS Çimento the least SO₃ content which also favors formation of C₃S mineral compound which is responsible for initial set and early strength. The lower the SO₃ value the better [17].

Adana Cemento had the highest value of Lime Saturation Factor (LSF), whilst Al-Ethadiah had the least (LSF). The LSF controls the ratio of alite to belite in the clinker. A clinker with a higher LSF will have a higher proportion of alite to belite than will a clinker with a low LSF. Adana Cemento cement

shows the highest percentage of Fe₂O₃. The Fe₂O₃ is one of the parameters responsible for cement colouration which explain why Adana Cemento Cement is darker grey than all the cements. High free lime content results in expansion due to formation of Ca(OH)₂, Adana Cemento is therefore unsound due to the higher content of free CaO. It can be seen from Table I that CaO is present with the greatest amount (50.52-63.36%), whereas Na₂O appeared with the smallest quantity (0.22 -0.61%).

TABLE I
PERCENT COMPOSITION OF MAJOR CONSTITUENT OF THE CEMENT SAMPLES BY XRF METHOD

Parameter	AS Çimento	Al-Ethadiah	Adana Cemento	Al- Qumeas
CaO	62.16± 0.05	50.52± 0.02	63.36± 0.07	63.19± 0.05
SiO ₂	21.16± 0.01	25.89± 0.04	21.72± 0.05	20.87± 0.03
Al ₂ O ₃	5.50± 0.02	8.05± 0.01	4.20± 0.03	5.53± 0.07
Fe ₂ O ₃	4.30± 0.05	3.52± 0.02	4.34± 0.01	3.31± 0.01
MgO	1.78± 0.07	1.30± 0.05	1.30± 0.01	2.14± 0.05
K ₂ O	0.75± 0.04	1.45± 0.07	0.90± 0.02	1.32± 0.03
SO ₃	2.09± 0.01	2.54± 0.05	2.60± 0.04	2.14± 0.02
Na ₂ O	0.22± 0.01	0.50± 0.05	0.31± 0.03	0.61± 0.01
LSF	88.59± 0.03	57.83± 0.08	90.58± 0.05	83.65± 0.06
SIM	2.16± 0.02	2.24± 0.04	2.88± 0.06	2.69± 0.05
ALM	1.28± 0.02	2.29± 0.03	1.26± 0.05	1.27± 0.04

where are: SIM: silica ratio; ALM: Alumina ratio

In the hydration of the cement powder, it is C₃A that causes the sudden hardening of the cement paste. Hence it is usually retarded by addition of gypsum. High amount of C₃A is undesirable. The C₃S and C₂S hydrate to form the calcium silicate hydrate that brings about the adhesive and the cohesive strengths of the cement structure. [19] The calcium aluminoferrite (C₄AF) does not have significant role in the hydration of cement. However along with C₃A, it serves as a reservoir for the removal of some deleterious ions like Cl⁻ and SO₄²⁻ that cause the rusting of steel reinforced concrete. [17]

TABLE II
PERCENT MINERAL COMPOSITION OF CEMENT SAMPLES (%)

Sample	C3S	C2S	C3A	C4AF	SUM
AS Çimento	49.02490	23.71518	7.30160	13.08576	93.12744
Al-Ethadiah	-50.3173	112.2114	15.37988	10.71206	87.98604
Adana Cemento	59.75973	17.2229	4.5786	10.16428	91.72551
Al Qumeas	56.6345	17.14127	9.0539	10.0729	92.90257

As shown in Table I and Fig. 2, the SIM and ALM contents for all the samples is in the range of 2.16-2.88 and 1.26-1.29 respectively, a high silica ratio means that more calcium silicates are present in the clinker and less aluminate and ferrite. SIM is typically between 2.0 and 3.0. An increase in ALM means there will be proportionally more aluminate and less ferrite in the clinker. In ordinary Portland cement clinker, the ALM is usually between 1 and 4.

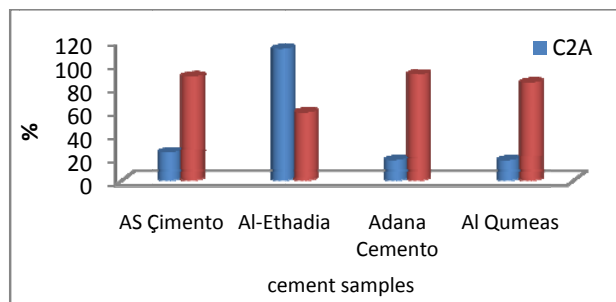


Fig. 2 Percentage of LSF and C₂S in the studied types of Cement

IV. CONCLUSION

The result of the analysis indicates that the cement samples under study are generally good for concrete work especially where no other special properties are required AS Çimento seems to be the best one having the lowest SO₃, whereas Al-Ethadia had the lowest Lime Saturation Factor and highest percentage of C₂A. As shown in Tables I and II, the cement has high LSF and highest C₃S while C₂S is decreased with increasing the LSF but it still an important strength-giving compound.

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