Correlation Models Applications for Raw Materials Blending Proces in Cement Manufacturing

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Abstract

The blending process of raw materials such as limestone and clay of cement manufacturing play an important role in cement quality, it is aiming to mix a variety of materials to produce cement raw meal for the kiln. One cement manufacture is ensuring the appropriate chemical composition of the fundamental problems in the cement raw meal. A raw meal with a good fineness and well-controlled chemical composition by a control system can improve the cement quality. The first step in designing a control system for the process is obtaining an appropriate mathematical correlations.

This study has been conducted on the eastern region which parallel to the coastal strip in the northeastern of Libyan coast including four locations namely from west to east as follows; Martoba, Um Al Rozm, Ain Al Ghazalh and Beer Al Ashahb areas, between Longitudes 31º16'' 24' and 32º 56'' 28' and Latitudes 20º 18'' 53' and 25º 09'' 08'.

The objective of this study is the assessment the raw materials represented by limestone and clay throughout calculating the quality control models such as silica modulus (SM), alumina modulus (AM), hydraulic modulus (HM), lime saturation factor (LSF) liquid phase (L. phase) and Le Chatelier and Michaels Indices. On the other hand, the appropriate blending ratios have been calculated using Le Chatelier–Newberry and Eckel Formulae. The obtained results revealed that the raw materials under consideration can be used for cement manufacture because of they contain high amount of lime (CaO) and lower content of impurities.

Keywords: *Raw material, blending, chemical composition, correlations, cement.*

1. Introduction

Cement is the world's most widely used construction material and is a key ingredient in concrete. The cement manufacturing process includes the raw-materials blending process as well as the burning process, the cement clinker grinding process, and the packaging process. One of the main processes that effects cement quality is the raw-material blending process. The task of this process is to mix a variety of materials such as limestone, shale, sandstone, and iron, to produce cement raw meal for the kiln. Raw meal mainly contains four oxides: calcium oxide or lime (CaO), silica (SiO2), alumina (Al2O3) and iron oxide (Fe2O3). The oxide compositions of the raw meal significantly affect the quality and the properties of cement clinker. On the other hand, the chemical compositions of the raw materials vary from time to time and the feeder tanks do not contain chemically homogeneous raw materials. That is why blend estimating systems with quality control are needed to obtain the correct composition of the blend.

1.1. Process Overview

Cement is a solid material made of clinker, gypsum and other additives. It is mainly used to form concrete, a conglomerate of cement, water, fine sand and coarse aggregates, widely used for civil engineering constructions. Cement has a strong hydraulic binder power. Reacting with water it becomes a hard and durable material in a few days [1,7,8]. Global cement production has grown steadily from less than 200 million tons in 1950 to more than 2500 million tons in 2016. Today's growth is largely driven by rising production in emerging economies and developing countries, especially in Asia. In 2015, almost70% of the world production was in Asia (47.4% in China, 6.2% in India, 2.7% in Japan, 13.2% in other Asian countries), about 13.4% in Europe and the remainder in Africa (4%), in the US (3.9%), and in other American countries (5.8%). The EU-27 produced about 268 million tons of cement in 360 installations, of which 268 produce both clinker and cement, 90 produce only cement and 2 produce only clinker [1].

1.2. Cement Production

a. The manufacture of cement is a two-step process, notably, clinker production and cement grinding. In the first step, the raw materials are fed to the kiln system to produce clinker. Clinker consists of silicates, aluminates and ferrites of calcium obtained from the reduction of calcium, silica, alumina and iron oxides present in the raw materials. Clinker production starts with quarrying the main natural raw materials, typically limestone, chalk or marl (as a source of calcium carbonate) and clay, iron ore, sand or shale (as a source of silica, alumina and iron oxide). In the second step, clinker is ground (in a grinding mill) with calcium sulphates (gypsum or anhydrite) and with possible additions of other minerals (blast furnace slag, natural pozzolanas, fly ash, silica fume or limestone) to obtain cement with desired performance such as setting time and strength development [1,2,3,4].

2. Location of Study

This study has been carried out on the eastern region which parallel to the coastal strip in the northeastern of Libyan coast including for locations namely from west to east as follows; Martoba, Um Al Rozm, Ain Al Ghazalh and Beer Al Ashahb areas, between Longitudes 31°16" 24' and 32° 56" 28' and Latitudes 20° 18" 53' and 25° 09" 08' (Figure 1).

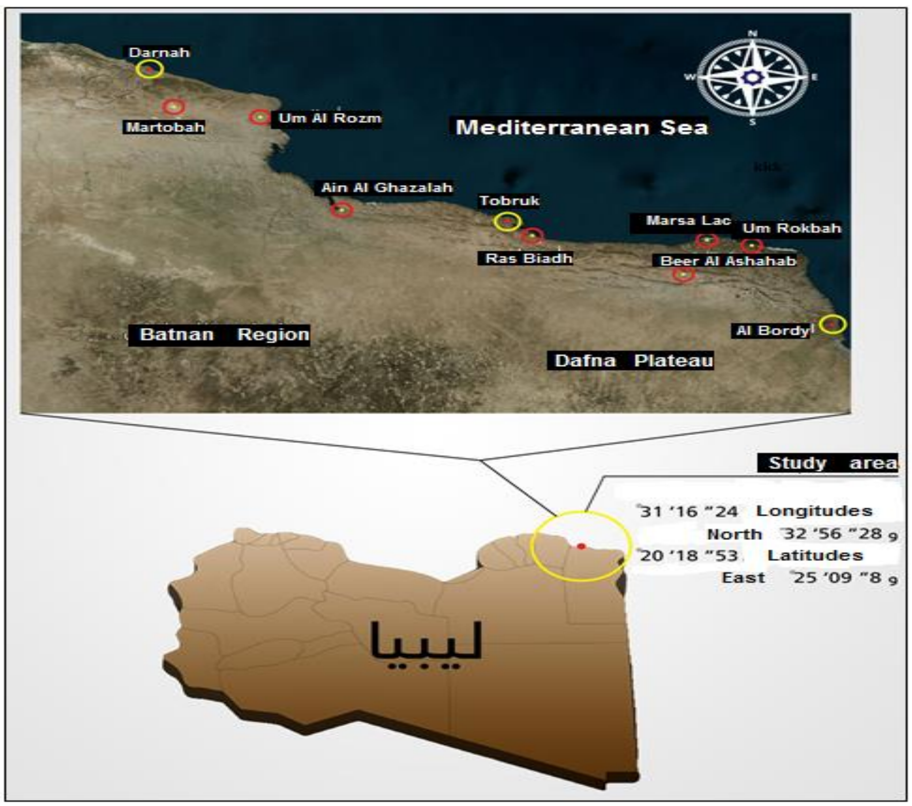

Fig. 1 Location map of the studied areas

3. Statement of Problem

This study highlights on the unused raw materials occurring over a very large distances and great thickness with very huge reserves of billions tons in Libya in spite of their good quality for cement manufacture to satisfy the requirements of this building material.

4. Objectives of Study

The main aim of this study is to focus on the assessment of the raw materials required for cement industry in the investigated locations throughout:

1. Study the chemical composition of raw materials particularly limestone and clay.
2. Determination the potentiality for cement manufacture.
3. Calculation the appropriate blending ratios of mix.
4. Highlight on the raw materials as natural resources in Libya.
5. Correlation between these raw materials and the standard ones to distinguish their quality for cement clinker.

5. Importance of Study

The importance of this study can be summarized as:

1. Libya has a great quantities of raw materials estimated as billions of tons.
2. The raw materials characterized by the lower contents of impurities.
3. The most locations of these materials located on or nearby the highways.
4. The easy of transportation by trucks or belt conveyor.
5. To achieve the sustainable development and support the national income.

6. MATERIALS AND METHODS

To assessment the quality of the raw materials in the studied areas for cement manufacture, samples were collected from different and chemically analyzed in Libyan National Cement Company at Al Fataih area to determine the different constituents using XRF instrument.

The following correlations and models were applied:

6.1. Quality Control Coefficients for Raw Meal Evaluation

6.1.1. Bogue's Formula for Cement Constituents

If alumina modulus (AM) > 0.64

C3S = 4.071(CaO) - 7.60 (SiO2) - 6.718 (Al2O3) – 1.430(Fe2O3) - 2.852(SO3) [1]

C2S = 2.867(SiO2) – 0.7544(C3S) [2]

C3A = 2.65(Al2O3) - 1.692(Fe2O3) [3]

C4AF = 3.043 (Fe2O3) [4]

If alumina modulus (AM) < 0.64

C3S = 4.071(CaO) - 7.602 (SiO2) – 4.479 (Al2O3) – 2.859 (Fe2O3) - 2.852(SO3) [5]

C2S = 2.867(SiO2) – 0.7544(C3S) [6]

C3A = 0 [7]

C4AF + C2F) = 2.1 Al2O3 +1.702 (Fe2O3) [8]

6.1.1.1 Hydraulic Modulus (HM)

$$H.M = \frac{CaO\ \%}{SiO_2\% + Al_2O_3\ \% + Fe_2O_3\ \%} \quad [9]$$

6.1.1.2. Lime Saturation Factor (LSF)

If MgO $< 2\%$

$$LSF = \frac{100\ (CaO\ \% + 0.75MgO\ \%)}{2.8SiO_2\ \% + 1.2\ Al_2O_3\ \% + 0.65Fe_2O_3\ \%} \quad [10]$$

If alumina modulus (AM) $> \mathbf{0.64}$

$$LSF = \frac{CaO}{2.8SiO_2\ \% + 1.65\ Al_2O_3\ \% + 0.35Fe_2O_3\ \%} \quad [11]$$

If alumina modulus (AM) $< \mathbf{0.64}$

$$LSF = \frac{CaO}{2.8SiO_2\ \% + 1.1\ Al_2O_3\ \% + 0.7Fe_2O_3\ \%} \quad [12]$$

6.1.1.3 Silica Modulus (SM)

$$SM = \frac{SiO_2\ \%}{Al_2O_3\ \% + Fe_2O_3\ \%} \qquad [13]$$

6.1.1.4. Alumina Modulus (AM)

$$AM = \frac{Al_2O_3\ \%}{Fe_2O_3\ \%} \qquad [14]$$

6.2. Le Chatelier and Newberry Formula

Many attempts have been made to put the calculation of cement mixtures on a scientific basis. If the theories of Le Chatelier and Newberry are taken as the basis, and Portland cement considered as composed of definite chemical' compounds, then it becomes a comparatively easy matter and is simply a question of molecular or combining weights. Our knowledge, at the present time, however, as regards the composition of Portland cement, is very unsatisfactory, and it is impossible to express scientifically in mathematical formulas, the proportions of the different substances in it. Nevertheless, formulas have been proposed at different times by Le Chatelier, Newberry and others, by which to calculate mixtures of cement materials.

In the case of new and untried materials, it is necessary to rely entirely on the chemical analyses, and formulas enable us to arrive at a close approximation of the ultimate composition of Portland cement. The formula 3CaO, $Si0_2$+2CaO, $A1_20_3$, proposed by Newberry, has been used extensively in the proportioning of raw materials. In this formula one part of silica corresponds by weight to five parts of calcium carbonate, and one part of alumina to two parts of calcium carbonate. In the calculation, the percentage of iron oxide is added to the percentage of alumina, the total being considered as alumina [5].

6.3. Eckel Formula

Eckel presents a formula which differs from Newberry's only in the fact that it takes into account the iron and the magnesia. The different steps in the process following this rule are given below:

a- Operation 1: Multiply the percentage of silica in the clayey material by 2.8, the percentage of alumina by 1.1, and the percentage of iron oxide by 0.7; add the products; subtract from the sum thus obtained the percentage of lime oxide in the clayey materials plus 1.4 times the percentage of magnesia, and call the result n.

b- Operation 2: Multiply the percentage of silica in the calcareous materials by 2.8, the percentage of alumina by 1.1, and the percentage of iron oxide by 0.7; add the products and subtract the sum from the percentage of lime oxide plus 1.4 times the percentage of magnesia in the calcareous material, calling the result m.

c- Operation 3: Divide *n* by *m*. The quotient will be the number of parts of calcareous material required for one part of clayey material.

The calculation procedure is illustrated in Table 2 as following:

Table 2 Calculation procedure

	Operation (1): Clay	Operation (2): Limestone	Operation (3):
Silica	SiO_2 % × 2.8 =	SiO_2 % × 2.8 =	$\frac{n}{m}$ =
Alumina	Al_2O_3 % × 1.1 =	Al_2O_3 % × 1.1 =	Parts of limestone should be used to parts of clay
Iron	Fe_2O_3 % × 0.7 =	Fe_2O_3 % × 0.7 =	
Total	$= \sum_1$	$= \sum_1$	
Lime	CaO % × 1.1 =	CaO % × 1.1 =	
Magnesia	MgO % × 1.4 =	MgO % × 1.4 =	
Total	$= \sum_2$	$= \sum_2$	
	$\sum_1 - \sum_2 = n$	$\sum_1 - \sum_2 = m$	

7. THE MANUFACTURING PROCESS

Portland cement is made by heating raw materials rich in oxides of silicon, calcium, aluminium and iron to temperatures of around 1200 - 1400ºC. The chemical reactions that occur within the partially molten mass result from the formation of the four main cement materials (Table 3).

Table 3 Approximate composition of the cement clinker

Compound	Formula	Notation	wt.%

Celite (tricalcium aluminate)	$Ca_3Al_2O_6$ [$3CaO·Al_2O_3$]	C_3A	10
Brownmillerite (tetracalcium aluminoferrite)	$Ca4Al_2Fe_2O_{10}$ [$4CaO·Al_2O_3·Fe_2O_3$]	C_4AF	8
Belite (dicalcium silicate)	$Ca2SiO_4$ [$2CaO·SiO_2$]	C_2S	20
Alite (tricalcium silicate)	$Ca3SiO_5$ [$3CaO·SiO_2$]	C_3S	55
Sodium oxide	Na_2O	N	≤ 2
Potassium oxide	K_2O	K	
Gypsum (calcium sulphate dihydrate)	$CaSO_4·2H_2O$ [$CaO·SO_3·2H_2O$]	CSH_2	5

Adapted from[6]

Of these compounds, C_3S and C_3A are mainly responsible for the strength of the cement. High percentages of C_3S (low C_2S) results in high early strength but also high heat generation as the concrete sets. The reverse combination of low C_3S and high C_2S develops strengths more slowly (over 52 rather than 28 days) and generates less heat. C_3A causes undesirable heat and rapid reacting properties, which can be prevented by adding $CaSO_4$ to the final product. C_3A can be converted to the more desirable C_4AF by the addition of Fe_2O_3 before heating, but this also inhibits the formation of C3S. C_4AF makes the cement more resistant to seawater and results in a somewhat slower reaction which evolves less heat.

There are several different types of cements of which Portland cement, Siliceous (ASTM C618 Class F) Fly Ash, Calcareous (ASTM C618 Class C) Fly Ash, slag cement, and silica fume are the major types. 0ey differ from their chemical composition. Table 4 gives the compositions of the above cement types in terms of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, and SO_3, and the remaining can be other materials such as Na_2O and K_2O[7,8].

The cement manufacturing process involves four distinct stages, and these are outlined below.

Step 1 - Quarrying

The raw material for cement manufacture is a rock mixture which is about 80% limestone(which is rich in $CaCO_3$) and 20% clay or shale (a source of silica, alumina and Fe_2O_3).

Table 4 Components as wt.% used to make different types of cements

Component	Portland cement	Siliceous fly ash	Calcareous cement	Slag cement	Fume silica
SiO_2	21.9	52.0	35.0	35.0	85-97
Al_2O_3	6.9	23.0	18.0	12.0	0
Fe_2O_3	3.9	11.0	6.0	1.0	0
CaO	63.0	5.0	21.0	40.0	< 1
MgO	2.5	0	0	0	0
SO_3	1.7	0	0	0	0
SSA ($m^2 \cdot g^{-1}$)	0.37 Blaine	0.42 Blaine	0.42 Blaine	0.40 Blaine	15–30 BET
SG	3.15	2.38	2.65	2.94	2.22

SSA = specific surface area; SG = specific gravity. Adapted from[9–11].

Step 2 - Raw material preparation

The steps involved here depend on the process used. There are two main cement manufacturing processes: the dry and the wet processes. The dry process uses more energy in grinding but less in the kiln, and the wet process has lower overheads than the dry process.

Step 3 - Clinkering

This is the step which is characteristic of Portland cement. The finely ground material is dried, heated and then cooled down again. While it is being heated various chemical reactions take place to form the major mineral constituents of Portland cement.

Breaking the reaction processes into a number of simple zones means we can make some approximations about the cement formation process.

Zone 1: 0 - 35 min, 800 - 1100°C
Decarbonation. Formation of $3CaO \bullet Al_2O_3$ above 900°C. Melting of fluxing compounds Al_2O_3 and Fe_2O_3.

$$CaCO_3 \xrightarrow{Heat} CaO + CO_2$$

Zone 2: 35 - 40 min, 1100 - 1300°C
Exothermic reactions and the formation of secondary silicate phases as follows:

$$2CaO + SiO_2 \xrightarrow{Heat} 2CaO \bullet SiO_2$$

Zone 3: 40 - 50 min, 1300 - 1450 - 1300°C
Sintering and reaction within the melt to form ternary silicates and tetracalcium aluminoferrates:

$$2CaO \bullet SiO_2 + CaO \xrightarrow{Heat+time} 3CaO \bullet SiO_2$$

$$3CaO \bullet Al_2O_3 + CaO + Fe_2O_3 \xrightarrow{Heat+time} 4CaO \bullet Al_2O_3 \bullet Fe_2O_3$$

Zone 4: 50 - 60 min, 1300 - 1000°C
Cooling and crystallization of the various mineral phases formed in the kiln.

8. RESULTS AND DISCUSSION

8.1. Limestone Raw Materials

The chemical analyses are very important for the assessment of the studied raw materials for cement industry. So the raw materials in this study represented by limestone and clay are chemically analyzed. The results of chemical analysis for the studied areas of limestone and clay rocks were presented in Table 5.

Table 5 Chemical composition of limestone rocks

Comp. (%)	Martoba		Um Al Rozm		Ain Al Ghazalh		Beer Al Ashahb	
	Limest-one	Clay	Limest-one	Clay	Limest-one	Clay	Limest-one	Clay
SiO_2	2.86	10.24	0.41	39.56	0.00	12.90	2.75	50.40
Al_2O_3	0.82	2.95	0.33	5.73	0.166	4.38	0.64	7.30
Fe_2O_3	0.33	2.22	0.19	4.64	0.020	3.01	0.74	3.60
CaO	52.35	32.90	53.25	21.72	54.97	24.96	44.63	12.10
MgO	1.03	11.86	1.07	1.20	0.60	14.32	8.31	1.83
Cl	0.05	1.00	0.52	0.22	0.053	1.71	0.09	0.12
SO_3	0.20	0.50	0.22	0.34	0.29	0.79	0.52	0.01
Na_2O	0.00	0.30	0.00	0.22	0.00	0.37	0.22	0.35
K_2O	0.00	0.25	0.00	0.92	0.00	0.81	0.00	1.14
TiO_2	0.01	0.27	0.00	0.66	0.00	0.42	0.03	0.70
MnO	0.01	0.03	0.01	0.10	0.008	0.035	0.03	0.050
P_2O_5	0.21	0.16	0.22	0.17	0.204	0.130	0.21	0.08
LOI*	42.01	39.25	43.5	24.22	43.61	35.95	41.8	22.24
$\sum$	99.88	99.93	99.72	99.7	99.92	99.78	99.97	99.92
$CaCO_3$	93.43	58.70	96.23	38.80	98.10	44.55	79.85	21.60
$MgCO_3$	2.20	24.81	4.16	25.51	1.26	29.95	17.40	28.82

LOI* = Loss on ignition

8.2. Quality Control Coefficients of Raw Materials

8.2.1. Bogue's Formula

The assessment of raw materials of this study based on the calculations of apparent values of clinker constituents such as C_2S, C_3S, C_3A and C_4AF using Bogue's formulae, that rely on the typical chemical composition of limestone rocks suggested by Klieger (1985)[12], Bayles (1985)[13] and Moore (1996)[14] Table 6, and the results are presented in Table 7.

The calculation of these parameters revealed that there a variance of these values for the studied areas, and this owing to the different of chemical composition of raw materials in these areas, and within the range of requirements as raw materials for cement industry.

The comparison between Bogue apparent values and the calculated values of studied limestone of the investigates areas for parameters C_2S and C_3S show a wide variance through the investigated parameters of Klieger (1985), Bayles (1985) and Moore (1996), also, for the examined rocks (Figure 2).

Table 6 Typical chemical composition of limestone and Bogue apparent values

Limestone	A	B	C	D	E
SiO_2	4.00	13.60	2.00	12.05	2.96
Al_2O_3	0.77	2.50	0.80	3.19	0.79
Fe_2O_3	0.30	0.90	0.20	1.22	0.30
CaO	51.4	43.4	52.90	43.50	52.30
MgO	1.30	3.20	0.90	1.68	1.30
SO_3	0.10	0.10	0.20	0.56	0.03
LOI	42.0	35.6	42.50	36.21	42.18
Na_2O	0.01	-	-	0.12	0.04
K_2O	0.02	0.60	0.20	0.72	0.23
$\sum$	99.90	99.60	99.70	99.25	100.13
Apparent values					
C_3S	173.0	55.0	155.9	60.7	184.6
C_2S	119.0-	2.5-	111.9-	11.30-	130.80-
C_3A	1.5	5.10	1.50	6.40	1.60
C_4AF	0.9	2.70	0.60	3.70	0.90
Reference	Moore	Bayles	Bayles	Klieger	Klieger

	1996	1985	1985	1985	1985

Table 7 Bogue parameters for cement constituents

Bogue parameters	Martoba	Um Al Rozm	Ain Al Ghazalh	Beer Al Ashahb
C_3S	184.80	210.50	221.80	153.94
C_2S	95.74-	156.70-	166.35-	107.56-
C_3A	1.62	0.55	0.39	0.45
C_4AF	1.01	0.58	0.06	2.25

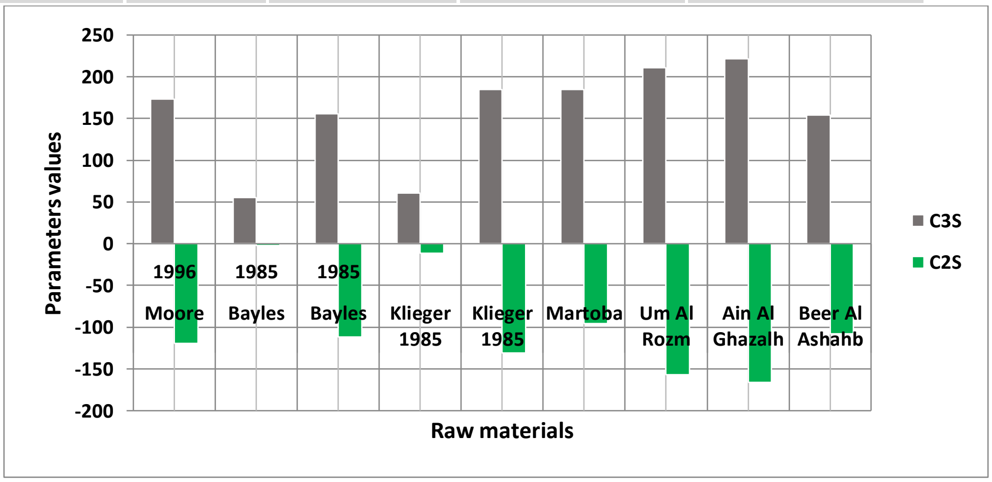

Fig. 2 Comparison between Bogue C2S, C3S and studied areas

The comparison between C_3A and Bogue values and the studied areas is depicted in Figure 3, it reveals that some values are close to the values of typical limestones and are lowers for others e. g. Klieger (1985), Moore (1996) and Bayles (1985). While the comparison of C_4AF values exhibit a clear variation in the studied areas with Bogue values (Figure 4).

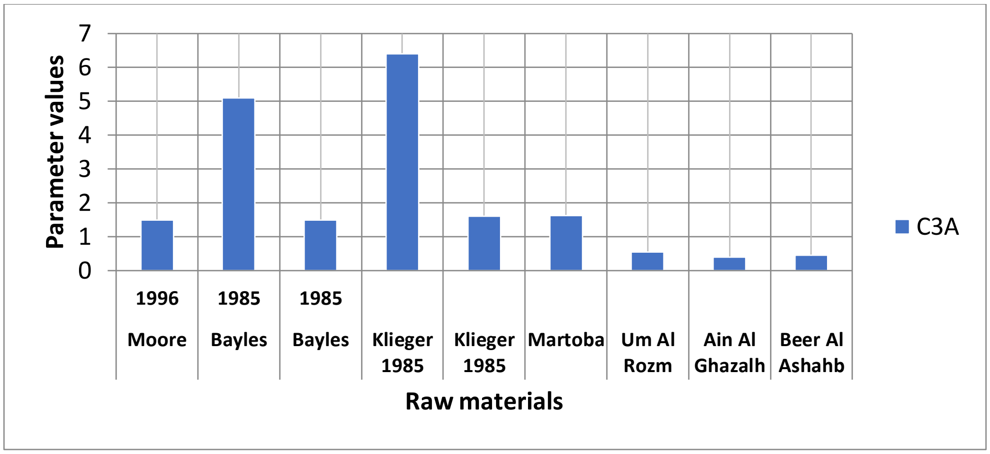

Fig. 3 Comparison between Bogue C3A and studied areas

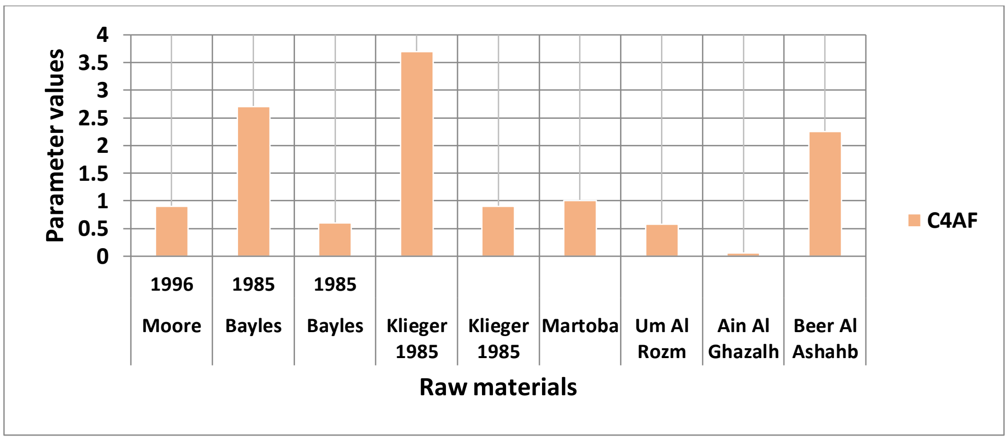

Fig. 4 Comparison between Bogue C4AF and studied areas

8.2.2. Evaluation Moduli of Raw Materials

There are other moduli can be used for the assessment of the investigated raw materials e. g. silica modulus (SM), alumina modulus (AM), Hydraulic Modulus (HM), Lime Saturation Factor (LSF) and Le Chatelier, liquid phase & Michaels Indices. The calculation results are presented in Table8.

Table 8 calculations moduli of raw materials

Modulus values	Martoba	Um Al Rozm	Ain Al Ghazalh	Beer Al Ashahb
HM	13.05	57.25	305.39	10.81
LSF	5.52	30.27	202.84	4.95
SM	2.49	0.79	0.00	1.99

AM	2.48	1.74	8.0	0.86
L. phase	10.55	2.71	1.42	12.64
Le Chatelier index	14.50	73.40	347.31	15.61
Michaelis index	13.05	57.25	305.39	10.80

The calculated values of HM and LSF parameters show a variation from locality to anther as illustrated in Figure 5, whereas, the highest values were recorded in Ain Al Ghazalh area and the lowest ones in Martoba and Beer Al Ashahb areas. This attributed to the chemical composition of the raw materials. In spite of this variation they are within the range of specification of raw materials for cement industry. Figure 6 also, depicted the differences in values of SM, AM and L. phase moduli in the studied areas.

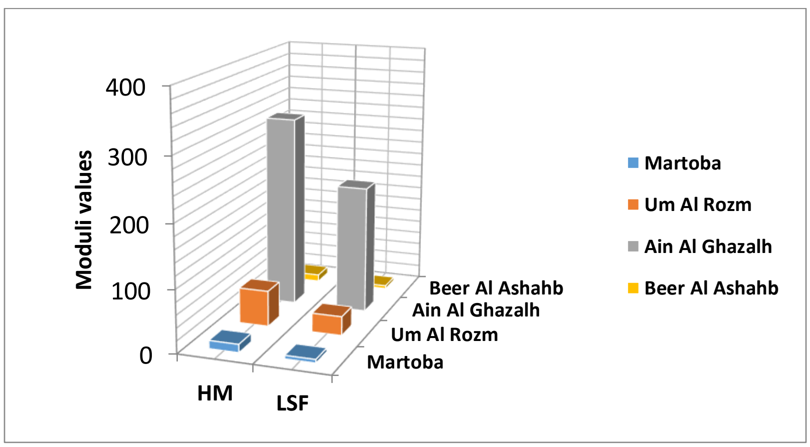

Fig. 5 The variance of HM and LSF moduli in the studied areas

8.3. CEMENT RAW-MATERIALS BLENDING PROCESS

The cement manufacturing process consists broadly of mining, crushing and grinding, burning, and grinding with gypsum. In the dry process of cement production, the raw materials are proportioned, stored, ground, mixed, pulverized, and fed into the kiln in a dry state [15].

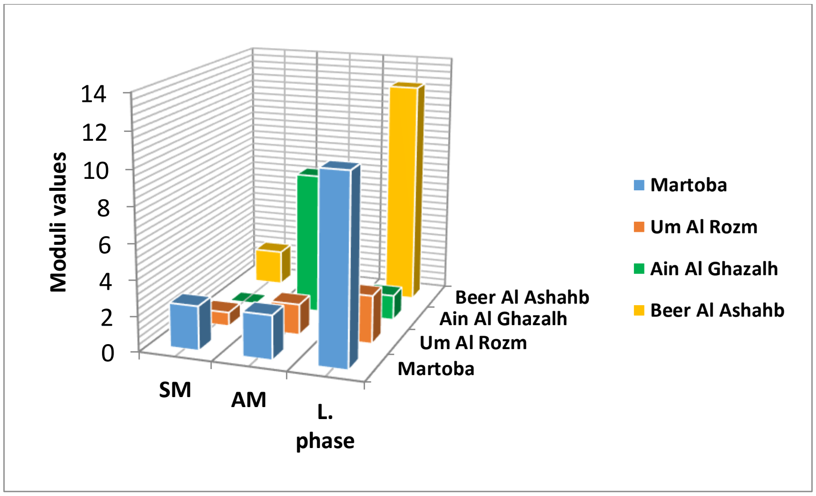

Fig. 6 The variation of SM, AM and L. phase moduli in the studied areas

In this study, the raw material blending process was investigated. The quality of raw meal depends on the relative rates of CaO, SiO_2, Fe_2O_3 and Al_2O_3. The relative rates can be expressed by the so-called modulus values [15,16].

8.3.1. Raw Materials Mix Ratios Calculations

8.3.1.1. Le Chatelier - Newberry Formula

The calculations were carried out for the studied locations according to this equation: 3CaO, SiO_2 + 2CaO, Al_2O_3

Table 9 gives the chemical constituents of raw materials for Martoba area and Um Al Rozm areas.

Table 9 Chemical composition of raw materials

Constituents	Chemical formula	Martoba area		Um Al Rozm area	
		Limestone	Clay	Limestone	Clay
Silica	SiO_2	2.86	10.24	0.41	39.56
Alumina	Al_2O_3	0.82	2.95	0.33	5.73
Iron	Fe_2O_3	0.33	2.22	0.19	4.64
Lime	CaO	52.35	32.90	53.25	21.72
Magnesia	MgO	1.03	11.86	1.07	1.20

Alkalies	Na_2O	0.00	0.30	0.00	0.22
	K_2O	0.00	0.25	0.00	0.92
Loss on ignition	LOI	42.01	39.25	43.50	24.22
Total	$\sum$	99.40	99.97	98.75	98.21
Calcium carbonate	$CaCO_3$	93.43	58.70	96.23	38.80

This clay requires, according to Le Chatelier - Newberry formula:

		Martoba area		Um Al Rozm area	
Parts of Clay		Ration of $CaCO_3$	$CaCO_3$ Required	Ration of $CaCO_3$	$CaCO_3$ Required
Silica	SiO_2	$= 5 \times 10.24$	52.70	$= 5 \times 39.56$	197.80
Alumina	Al_2O_3	$= 2 \times 2.95$	5.90	$= 2 \times 5.73$	11.46
Iron	Fe_2O_3	$= 2 \times 2.22$	4.44	$= 2 \times 4.65$	9.30
$\sum$			63.04		218.56
Calcium carbonate ($CaCO_3$)			58.70		38.80
Residue			4.34		179.76

The limestone of Martoba area contains low amounts of silica, and low amounts of alumina and iron; and a small part of the lime in it will be required to satisfy these constituents:

		Martoba area		Um Al Rozm area	
Silica	SiO_2	$= 5 \times 2.86$	14.30	$= 5 \times 0.41$	2.05
Alumina	Al_2O_3	$= 2 \times 0.82$	1.64	$= 2 \times 0.33$	0.66
Iron	Fe_2O_3	$= 2 \times 0.33$	0.66	$= 2 \times 0.19$	0.38
$\sum$			16.60		3.09

This subtracted from the total $CaCO_3$ (93.43 – 16.60), leaves 76.83 parts of $CaCO_3$ in each unit of limestone and, as 4.34 parts of $CaCO_3$ are required for each unit of clay, the units of limestone required per unit of clay will be:

$$\frac{4.34}{76.83} = 0.06$$

In other words, .006 ton of limestone are required for each ton of clay. This quantity regards as small to be added to the mix due to the high content of lime (CaO) in clay material (32.90%) and the decrease of silica content (10.24%).

In the raw material of limestone in Um Al Rozm area contains small quantity of silica, alumina and iron, and small amount of lime in it is required to satisfy these constituents.

This value subtracted from the total $CaCO_3$ (96.23 – 3.09), leaves 93.14 parts of $CaCO_3$ in each unit of limestone and, as 179.76 parts of $CaCO_3$ are required for each unit of clay, the units of limestone required per unit of clay will be: $\frac{179.76}{93.14} = 1.93$

In other words, 1.93 tons of limestone are required for each ton of clay. Whereas, the lime percent in clay material is 21.72%, and the silica percent is 39.56% to form the suitable blend for cement material.

On the other hand, Table 10 gives the chemical constituents of raw materials for Ain Al Ghazalh and Beer Al Ashahb areas.

Table 10 Chemical composition of raw materials

Constituents	Chemical formula	Ain Al Ghazalh area		Beer Al Ashahb area	
		Limestone	Clay	Limestone	Clay
Silica	SiO_2	0.00	12.90	2.75	50.40
Alumina	Al_2O_3	0.166	4.38	0.64	7.30
Iron	Fe_2O_3	0.020	3.01	0.74	3.60
Lime	CaO	54.97	24.96	44.63	12.10
Magnesia	MgO	0.60	14.32	8.31	1.83

Alkalies	Na_2O	0.00	0.37	0.00	0.35
	K_2O	0.00	0.81	0.03	1.14
Loss on ignition	LOI	43.61	37.95	41.80	22.24
Total	$\sum$	99.37	98.70	98.90	98.96
Calcium carbonate	$CaCO_3$	98.10	44.55	99.97	21.60

This clay requires, according to Le Chatelier - Newberry formula:

		Ain Al Ghazalh area		Beer Al Ashahb area	
Parts of Clay		Ration of $CaCO_3$	$CaCO_3$ Required	Ration of $CaCO_3$	$CaCO_3$ Required
Silica	SiO_2	$= 5 \times 12.90$	64.50	$= 5 \times 50.40$	252.0
Alumina	Al_2O_3	$= 2 \times 4.38$	8.76	$= 2 \times 7.30$	14.60
Iron	Fe_2O_3	$= 2 \times 3.01$	6.02	$= 2 \times 3.60$	7.20
$\sum$			79.28		273.80
Calcium carbonate ($CaCO_3$)			44.55		21.60
Residue			34.73		252.20

The limestone of Ain Al Ghazalh area contains small amounts of silica, alumina and iron, and a small part of the lime in it will be required to satisfy these constituents:

		Ain Al Ghazalh area		Beer Al Ashahb area	
Silica	SiO_2	$= 5 \times 0.00$	0.00	$= 5 \times 2.75$	13.75
Alumina	Al_2O_3	$= 2 \times 0.166$	0.33	$= 2 \times 0.64$	1.28
Iron	Fe_2O_3	$= 2 \times 0.02$	0.04	$= 2 \times 0.74$	1.48
$\sum$			0.37		16.51

This value subtracted from the total $CaCO_3$ (98.10 – 0.37), leaves 97.73 parts of $CaCO_3$ in each unit of limestone and, as 34.73 parts of $CaCO_3$ are required for each unit of clay, the units of limestone required per unit of clay will be: $\frac{34.73}{97.73} = 0.36$

In other words, 0.36 tons of limestone are required for each ton of clay. This is regards as high quantity to be added to the mix because of the lower content of lime CaO in both raw materials of limestone (24.96%) and clay (12.90%) respectively.

Also, the limestone of Beer Al Ashahb area contains small amounts of silica, alumina and iron, and a small part of the lime in it will be required.

This value subtracted from the total $CaCO_3$ (99.97 – 16.51), leaves 83.46 parts of $CaCO_3$ in each unit of limestone and, as 252.20 parts of $CaCO_3$ are required for each unit of clay, the units of limestone required per unit of clay will be: $\frac{252.20}{83.46} = 3.02$

In other words, 3.02 ton of limestone is required for each ton of clay. This quantity regards as high to be added to the mix due to the low content of lime (CaO) in limestone material (44.63%) and also in clay (12.10%).

8.3.1.2. Eckel Formula

The blend ratios of raw materials have been calculated for the studied locations by applying Eckel formula as following:

1. Martoba Area

The chemical constituents of both limestone and clay of Martoba and Um Al Rozm areas are presented in Table 11.

Table 11 Chemical composition of limestone and clay raw materials

Constituents	Chemical formula	Martoba area		Um Al Rozm area	
		Limestone	Clay	Limestone	Clay
Silica	SiO_2	2.86	10.24	0.41	39.56
Alumina	Al_2O_3	0.82	2.95	0.33	5.73
Iron	Fe_2O_3	0.33	2.22	0.19	4.64

Lime	CaO	52.35	32.90	53.25	21.72
Magnesia	MgO	1.03	11.86	1.07	1.20
Alkalies	Na_2O	0.00	0.30	0.00	0.22
	K_2O	0.00	0.25	0.00	0.92
Loss on ignition	LOI	42.01	39.25	43.50	24.22
Total	$\sum$	99.40	99.97	98.75	98.21
Calcium carbonate	$CaCO_3$	93.43	58.70	96.23	38.80

Calculations procedure as illustrated below:

Operation (1). Clay				
	Martoba area		Um Al Rozm area	
	Operation (1) Clay		Operation (1) Clay	
Silica	$= 2.8 \times 10.24$	28.67	$= 2.8 \times 39.56$	110.77
Alumina	$= 1.1 \times 2.95$	3.25	$= 1.1 \times 5.73$	6.30
Iron	$= 0.7 \times 2.22$	<u>1.55</u>	$= 0.7 \times 4.64$	<u>3.25</u>
$\sum$		33.90		120.32
Lime	$= 1.0 \times 32.14$	32.14	$= 1.0 \times 21.72$	21.72
Magnesia	$= 1.4 \times 11.86$	<u>16.60</u>	$= 1.4 \times 1.20$	<u>1.68</u>
$\sum$		<u>48.74</u>		23.40
	$n = 48.74 - 33.90 = 14.84$		$n = 120.32 - 23.40 = 96.92$	
Operation (2). Limestone				
	Martoba area		Um Al Rozm area	
	Operation (2). Limestone		Operation (2). Limestone	
Silica	$= 2.8 \times 2.86$	8.01	$= 2.8 \times 0.41$	1.15

Alumina	$= 1.1 \times 0.82$	0.90	$= 1.1 \times 0.33$	0.36
$\sum$		8.91		1.51
Lime	$= 1.0 \times 52.35$	52.35	$= 1.0 \times 53.25$	52.35
Magnesia	$= 1.4 \times 1.03$	1.44	$= 1.4 \times 1.07$	1.50
$\sum$		62.70		53.85
$m = 62.70 - 8.91 = 53.79$			$m = 53.85 - 1.51 = 52.34$	
Operation (3)				
Martoba area			Um Al Rozm area	
Operation (3)			Operation (3)	
$\frac{n}{m} = \frac{14.84}{53.79} = 0.27$			$\frac{n}{m} = \frac{96.92}{52.34} = 1.85$	

The raw material mix of Martoba area, for each part of clay, by weight, 0.27 parts of limestone (0.27 ton of limestone/ton of clay) should be used. This, however, represents low amount of lime due to the high content of (CaO) in limestone (52.35%) and also in clay (32.90%).

2. Um Al Rozm Area

The raw material mix of Um Al Rozm area for each part of clay, by weight, 1.85 parts of limestone (1.85 ton of limestone/ton of clay) should be used. This quantity considered good for mix because of the high content of CaO in limestone (53.25%).

3. Ain Al Ghazalh Area

The chemical constituents of both limestone and clay of Ain Al Ghazalh and Beer Al Ashahb areas are presented in Table 12.

Table 12 Chemical composition of limestone and clay raw materials

Constituents	Chemical formula	Ain Al Ghazalh area		Beer Al Ashahb area	
		Limestone	Clay	Limestone	Clay
Silica	SiO_2	0.00	12.90	2.75	50.40
Alumina	Al_2O_3	0.166	4.38	0.64	7.30
Iron	Fe_2O_3	0.020	3.01	0.74	3.60
Lime	CaO	54.97	24.96	44.63	12.10
Magnesia	MgO	0.60	14.32	8.31	1.83
Alkalies	Na_2O	0.00	0.37	0.00	0.35
	K_2O	0.00	0.81	0.03	1.14
Loss on ignition	LOI	43.61	35.95	41.80	22.24
Total	$\sum$	99.37	96.70	98.90	98.96
Calcium carbonate	$CaCO_3$	98.10	44.55	99.97	21.60

Calculations procedure as illustrated below:

Operation (1). Clay				
	Ain Al Ghazalh area		Beer Al Ashahb area	
	Operation (1). Clay		Operation (1). Clay	
Silica	$= 2.8 \times 12.90$	36.12	$= 2.8 \times 50.40$	141.12
Alumina	$= 1.1 \times 4.38$	4.82	$= 1.1 \times 7.30$	8.03
Iron	$= 0.7 \times 3.01$	<u>2.11</u>	$= 0.7 \times 3.60$	<u>2.52</u>
$\sum$		43.05		151.67
Lime	$= 1.0 \times 24.96$	24.96	$= 1.0 \times 12.10$	12.10

Magnesia	= 1.4 × 14.32	20.05	= 1.4 × 1.83	2.56
∑		45.01		14.66
n = 45.01 - 43.05 = 1.96			n = 151.67 – 14.66 = 137.01	

Operation (2). Limestone				
	Ain Al Ghazalah area		Beer Al Ashahb area	
	Operation (2). Limestone		Operation (2). Limestone	
Silica	= 2.8 × 0.00	0.00	= 2.8 × 2.75	7.70
Alumina	= 1.1 × 0.166	1.83	= 1.1 × 0.64	0.71
∑		1.83		8.41
Lime	= 1.0 × 54.97	54.97	= 1.0 × 44.63	44.63
Magnesia	= 1.4 × 0.60	0.84	= 1.4 × 8.31	11.64
∑		55.81		56.26
m = 55.81- 1.83= 53.98			m = 56.26 – 8.41 = 47.85	

Operation (3)	
Ain Al Ghazalah area	Beer Al Ashahb area
Operation (3)	Operation (3)
$\frac{n}{m} = \frac{1.97}{53.98} = 0.04$	$\frac{n}{m} = \frac{137.01}{47.85} = 2.86$

For this raw material of Ain Al Ghazalah area the ratio required 0.04 part of limestone to be added to the blend. This, however, represents the very low because of the high content of lime (CaO) in limestone (54.97%), and also in clay material (24.96%).

4. Beer Al Ashahb Area

To form the blend of raw materials of Beer Al Ashahb area, it is required to add 2.86 ton of limestone per one ton of clay, and this regard as acceptable quantity due to the decreasing content of lime in the raw material limestone (44%) and clay substance (12.10%).

On the other hand, a comparison between Le Chatelier-Newberry and Eckel formulae for raw materials mix ratios $\frac{n}{m}$ (calcareous & argillaceous rocks) for the investigated areas to distinguish what is the differences between the two methods. Results are presented in Table 13.

The results revealed that some variation between Le Chatelier-Newberry and Eckel methods for the studied locations, while others show no much difference e. g. Ras Biadh area (1.48) and (1.62) respectively, whereas the same values for Al Bordy area (0.74). The differences refer to the chemical composition of raw materials.

Table 13 Raw material mix ratios based on Le Chatelier–Newberry and Eckel formulae

Formula / Area	Le Chatelier-Newberry formula $\frac{n}{m}$	Eckel formula $\frac{n}{m}$
Martoba	0.06	0.27
Um Al Rozm	1.93	1.85
Ain Al Ghazalah	0.36	0.04
Beer Al Ashahb	3.02	2.86

Figure 7 depicts a comparison between the obtained results from the calculations of raw material mix ratios based on Le Chatelier–Newberry and Eckel formulae. It is obviously that Um Al Rozm and Beer Al Ashahb required more of raw material of lime stone to be added compared with the other locations, and this attributed to the decrease of CaO content in the in limestone rock and increasing in clay minerals.

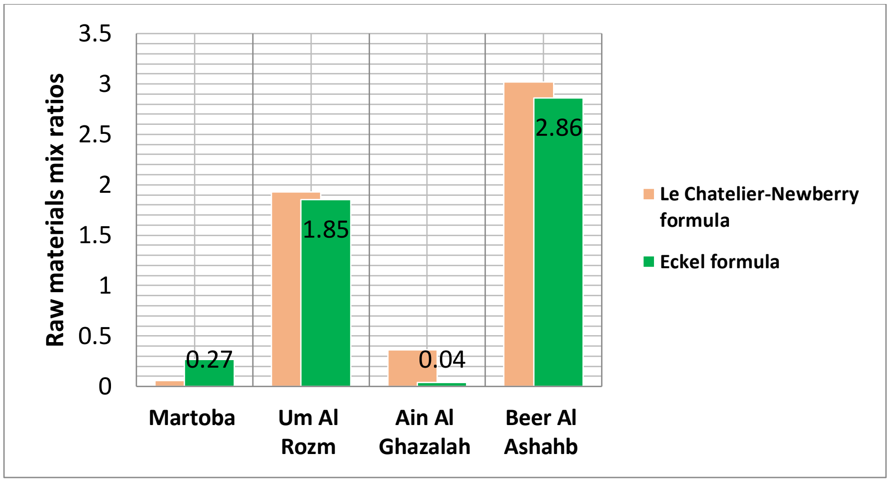

Fig. 7 Comparison between Le Chatelier-Newberry and Eckel formulae for $\frac{n}{m}$

In general, we can say that these raw materials in the studied areas can be characterized by a good quality for cement manufacture to form the clinker because of the high content of lime (CaO) and the lower content of undesired compounds e. g. alkalies and phosphrous that cause a problems in kiln during burning process.

9. CONCLUSION

Based on the results obtained from this study of raw material rocks, the following conclusion could be drawn:

The chemical analysis of raw materials under investigation revealed that contained high content of lime (CaO) reached to 54.97% and 53.25% in both Ain Al Ghazalh and Um Al Rozm areas respectively, and low content of magnesium and silica.

- The lime content exceeds 50% in the studied raw materials indicates their good quality for cement manufacture.
- The low amount of impurities such alkalies and sometimes absent in some areas as well as sulphates.
- The highest content of calcium carbonate ($CaCO_3$) was recorded in Ain Al Ghazalh area (98.10%), while the lowest content in Beer Al Ashahb area (79.85%).

- The chemical analysis of clay materials exhibit acceptable results, whereas the silica reached 24.96% in Ain Al Ghazalh area.
- The calculations moduli of quality control coefficient show some difference that attributed to the chemical composition.
- The variation of the estimated parameters with the compared ones of Bayles (1985), Klieger (1985) and Moore (1985) for the apparent values of clinker C_3S, C_2S, C_3A and C_4AF owing to the chemical constituents.
- The comparison between Le Chatelier-Newberry and Eckel formulae for $\frac{n}{m}$ exhibit some differences for some areas and similarity for the others.
- Generally, the raw materials under investigation characterized by a good chemical quality for cement clinker.

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