

VALIDITY OF GABAL KHYLIA AND BIR GINDALY SEDIMENTS FOR CEMENT INDUSTRY NORTHERN EASTERN DESERT- EGYPT.

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ABSTRACT

Samples collected from both Gabal Khylia (Middle Eocene) carbonates and Bir Gindaly (Upper Eocene) shales to study their validity for cement industry. Cement is a finally ground hydraulic binding medium for mortar and concrete consisting substantially of compounds calcium oxide with silicon dioxide, aluminum oxide and ferric oxide.

The purpose of the present paper is to show how composition of raw mix for cement quality depends on chemical composition. To achieve this work; manufacture of Portland cement steps, raw material calculations, clinker process, reactions occurring in Rotary Kiln, calculation of clinker phases, properties of cement phases were done.

Age	Rock type	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃
Upper Eocene	Mudrocks	12.74	3.36	1.86	3.84	0.99	0.28
Middle Eocene	Carbonates	0.34	0.12	0.01	40.08	0.39	0.02
Sum		13.08	3.48	1.87	43.92	1.38	0.30

Lime saturation factor (L.S.F.), silica modulus (S.M) and Alumina Iron ratio (A/F) were computed showing that the studied raw materials are suitable for cement industry.

INTRODUCTION

The study area is located at Gebel kahaliya and Bir Gindali areas, North Eastern Desert. The aim of the present study is to test their rocks suitability for cement industry. The area under investigation represents the eastern parts of a larger region that extends from Cairo to western coast of the Gulf of Suez, a region which is dominated by Middle to Upper Eocene rocks. The areas examined (Fig. 1) lies between Latitudes 29°50' 00" and 30°00'00" N. and Longitudes 30° 00' 00" and 32°15' 00"E. approximately.

The Lithostratigraphic of Eocene exposures of Gebel kahaliya and Bir Gindali areas are shown in figs. (2 and 3).

The present definition of a cement as given in German standard, is as follows: "Cement is a finally ground hydraulic binding medium for mortar and concrete consisting substantially of compounds calcium oxide with silicon dioxide, aluminum oxide and ferric oxide. It is formed by sintering and fusion, by heating of a mixture of limestone and clay, or other materials of similar bulk composition in Portland cement clinker with an admixture of sulphate (Coulburn, D. 2001).

The purpose of the present work is to show how composition of raw mix for cement quality depends on chemical composition. The Sedimentary raw materials feed to a kiln consists in their simplest form of a calcareous component B) an argillaceous compound and C) Corrective ingredients.

A) - Calcareous (limestone):

Limestone is one of the abundant sedimentary materials in nature. Its rock formed under extreme pressure and the hardness ranges from comparatively soft and workable to granite-like structure (Haugh 2001). Calcium carbonate content varies within wide limits depending on its purity. Dolomite is limestone containing amounts of MgCO₃. In contrast to limestone, chalk is material characterized by a soft earthy texture, so it is qualified especially for the wet process of cement manufacture without blasting and Crushing process, so it lowers the cement production costs. Marls are rock comprising limestone with mixture of (SiO₂, Fe₂O₃ and clay), so it considers an excellent raw material for cement manufacture

(B) - Argillaceous (Clay or Shale)

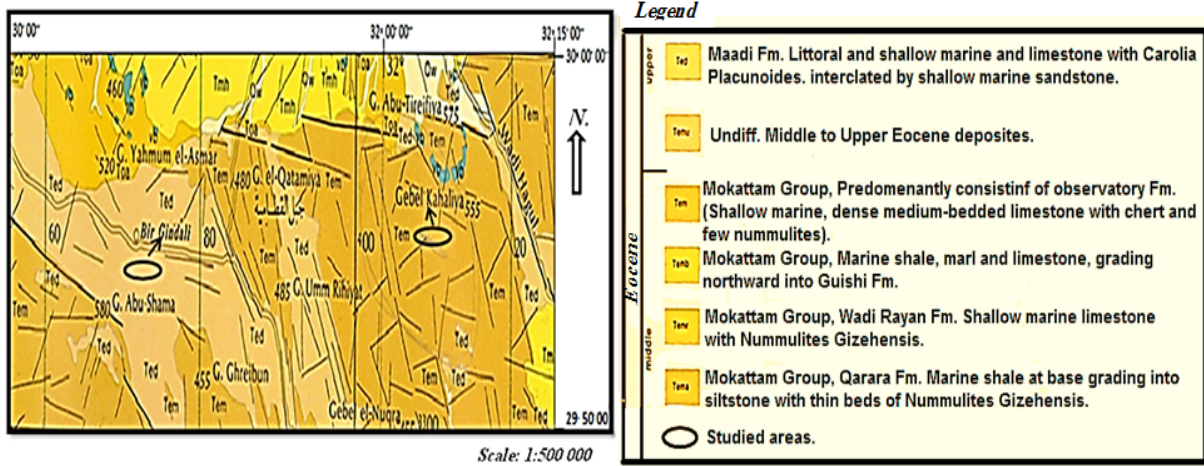


Figure (1) : Geologic map of the studied areas, Gebel kahaliya and BirGindali, (after

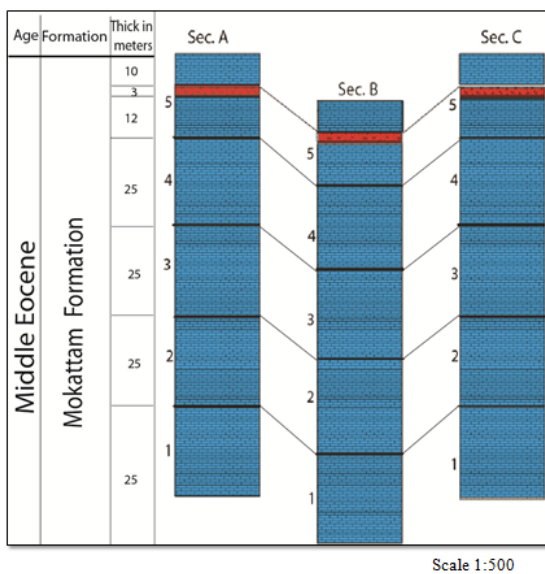


Fig (2): Measured columnar lithic log of Middle Eocene (Mokattam Formation) recorded at Gebel Kahaliya limestone quarry.

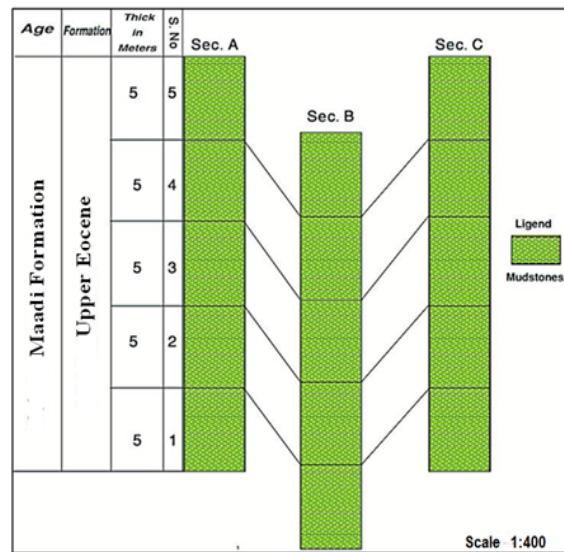


Fig (3): Measured columnar lithic log of Gebel Gendali mudstone quarry (Upper Eocene, Maadi Fm.).

Clay is formed by weathering of alkali and alkaline conversion products mainly feldspar and mica. Clay particles are plate-shaped and arranged in a lattice which is able to bind water in the molecule. Clay can absorb surface water which will evaporate at room temperature. The ability to take up water determines the plasticity of clay.

(C) Corrective ingredients

For the completion of the silica content sand, high silica clay, diatomic is used as additives. Pyrite cinders, iron ore are applied as corrective material to compensate deficiency in iron oxide

Manufacture of Portland cement:-

The steps of cement industry are start with

the quarrying of limestone and clay for crushing, transportation to the mixed bed, grinding raw material at raw mill and burning at rotary kiln (1450° C) where partial fusion occurs. (The product named nodules clinker). Two methods of grinding are detected; the dry and wet method the dry method is economically preferable. The grind clinker is mixed with a small percent of calcium sulfate (controls the rate of strength development) at cement Mill and the final product transfers into cement silo and packing.

Raw Material Calculations

Suppose the degree of purity of CaO in limestone and clays are 96% and 4% respectively to gain from them CaO% amount equal to 65% in the clinker. To gain 100 Kg. of CaO from lime-

stone and clays, calculation according to the following formula must be done.

$$Z = 100 (P - Y) = 100 (0.04 - 0.65) = 66.3 \text{ Kg.}$$

$$P - Q = 0.04 - 0.96$$

Whereas,

Z (CaO % of both limestone and clays supposed to use in clinker).

P (CaO % the degree of purity of CaO in clay sample).

Y (CaO % recorded limestone sample supposed to use in clinker).

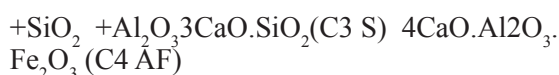
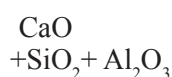
Q (CaO % the degree of purity of CaO in limestone).

According to the previous equation and to gain 100 Kg. of CaO we must use an amount equal to 66.3% of CaO (from limestone after burning to 1000 C o) and 33.7% of CaO (from clay after burning to 1000 C o).

The clinker process:

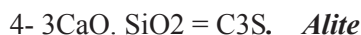
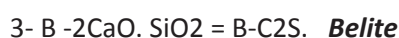
The burning of cement clinker consists of a series of reactions between chemically dissimilar finely divided particles. In general the reactions can be listed as follow; evaporation of the free water, loss of combined water from clay minerals and combination between lime and clays. The reactions may be formulated as follows:-

Reactions



Calculation of clinker phases

Clinker four phases can be written in abbreviation forms as follows;



To determine the phases percent in analyzed samples use the following rules:-

1 – To determine CaO used in the formation of anhydrite (CaSO₄) mineral, multiply the SO₃ content by 0.7 (factor). Reduce the total amount of CaO by an amount equal to CaO used.

2- To determine CaO used in the formation of Celite, C4AF (4CaO·Al₂O₃·Fe₂O₃), multiply all the amount of Fe₂O₃ content by 1.41 (factor) and Al₂O₃ content by 2.20 (factor). Reduce the total amount of CaO by an amount equal to CaO used. Reduce the total amount of Al₂O₃ by an amount equal to Al₂O₃ used.

3- To determine CaO used in the formation of Tri-calcium Aluminate, C3A (3CaO·Al₂O₃), multiply all the amount of Al₂O₃ content by 1.65

Table (1): Reactions occurring in Rotary Kiln (After Austria, U. 1997)

Temperature C°	Reaction Type
20-100 C°	Loss of free water (moisture)
100-300 C°	Loss of adsorbed water (clays)
400 – 900 C°	
Loss of combined water (L.O.I)	
>500 C°	Meta-kaolin formation
600 – 900 C°	Carbonate destruction (calcination)
>800 C°	Belite (B-C2S), Aluminate (C3A) and Celite (C4AF) formation
>1250 Co	Formation of Alite (C3S). Aluminate and Celite dissolved
1450 Co	Reactions are complete. Alite and Belite recrystallized.
1300-1240 Co	Recrystallization of soluble Celite and Aluminate

(factor) Reduce the total amount of CaO by an amount equal to CaO used. Reduce the total amount of Al_2O_3 by an amount equal to Al_2O_3 used.

Multiply the amount of SiO_2 content by 1.87 (factor). Reduce the total amount of CaO by an amount equal to CaO used. Reduce the total amount of SiO_2 by an amount equal to SiO_2 used.

5- To determine CaO used in the formation of Alite, C3S ($3CaO \cdot SiO_2$). Multiply the amount of SiO_2 content by 2.80 (factor). Reduce the total amount of CaO by an amount equal to CaO used. Reduce the total amount of SiO_2 by an amount equal to SiO_2 used.

Properties of cement phases:-

Alite (Ca_3SiO_5) is the most important constituent of all normal Portland cement clinkers for strength development; it reacts relatively quickly with water and consists of 50 – 70% tri-calcium silicate. Silicatemodified in composition and crystal structure by ionic substitutions

Belite(Ca_2SiO_4) constitutes 15 – 30% of normal Portland cement clinkers. It is di -calcium silicate modified by ionic substitutions. It reacts slowly with water, thus contributing little to the strength during the first 28 days, but substantially to the further increase in strength that occurs at later ages. The *strengths* obtainable from pure alite and pure belite are about the same under comparable conditions.

Aluminate ($Ca_3Al_2O_6$) constitutes 5 - 10 % of most normal Portland cement clinkers. It is tri-calcium aluminate substantially modified in composition and sometimes also in structure by ionic substitution.

Calculations of some important factors

Three factors affect the quality of raw mixes and also on the crystalline constituents of clinker; lime saturation factor (L.S.F.), silica modulus (S.M) and Alumina Iron ratio A/F.

The effect of lime saturation L.S.F.

This ratio affects the relative potential proportions of Alite and belite. Increasing clinker L.S.F at constant free lime, increase the quality of Alite at the expense of belite.

Lime saturation formula (L.S.F) factor in Portland cement must do not exceed than 1.02 and not less than 0.66.

Lime saturation formula (L.S.F)

2- The effect of silica modulus (S.M):

The major effect of S.M. is on the quantity of flux or liquid potentially present at clinkering temperature. At low S.M. the quantity of liquid is high and vice versa. Reducing the quantity of liquid by increasing S.M., increases the proportion of silicate and at constant L.S.F., this means the increase of Alite quantity. Silica modulus

Table (2) Properties of the Major Constituents of Portland cement(After Rother, W. 1996 January,).

Compound	Alite(C3s)	Belite(C2s)	Aluminate(C3A)	Celite(C4AF)
Approx.				
Chem. composition	$3CaO \cdot SiO_2$	$2CaO \cdot SiO_2$	$3CaO \cdot Al_2O_3$	$4CaO \cdot Fe_2O_3 \cdot Al_2O_3$
Rate of Hydration	Rapid(hours)	Slow(days)	Instantaneous	Very rapid(min)
Strength Development	Rapid (days)	Slow (weeks)	Very rapid (one day)	Very rapid (one day)
Ultimate Strength	High: tens N/mm ²	Probable: tens N/mm ²	Low: few N/mm ²	Low: few N/mm ²
Heat of Hydration	Medium 530 J/g	Low 250 J/g	Very High 850 J/g	Medium 420 J/g
Remarks	Characteristic constituent. Of Portland Cement	Characteristic constituent. Of low heat P.C	Unstable in water, sensitive to sulphate attack	Imparts to the cement. Its characteristic grey colour.

(S.M) factor in Portland cement reveals that ranges from 1.7 to 2.0 for low silica cement and from 2.5 to 3.5 for high silica cement. In Portland cement factor range from 2.0 to 2.5.

Silica modulus (S.M) =

3-The effect of Alumina Iron ratio A/F:

The flux consists potentially of C, A and ferite with small quantities of silica, magnesia, lime and alkalis. The higher the A/F ratio the greater is the proportion of Al₂O₃ relative to Fe₂O₃. The viscosity of the flux is affected by the composition; the higher ratio gives more viscosity. The factor detect the ratio between Al₂O₃ and Fe₂O₃

Alumina ratio (A.R)

The following paragraphs deals with results of the studies area: To calculate the ratio of limestone and clay used in Portland cement industry supposes that the purity degree of limestone is 96% CaO or the required limestone saturation factor (L.S.F) of the mixed bed is 0.96.

So, when the L.S.F equal one, the factor for SiO₂, Al₂O₃ and Fe₂O₃ are 2.8, 1.2 and 0.65 respectively. To calculate the modified factors of

SiO₂, Al₂O₃ and Fe₂O₃; each factor must be multiplied by 0.96.

$$FS = 2.8 \times 0.96 = 2.688$$

$$FA = 1.2 \times 0.96 = 1.152 \quad (\text{Modified factors})$$

$$Ff = 0.65 \times 0.96 = 0.624$$

To calculate the CaO % used, from both limestone and clay, to combine with SiO₂, Al₂O₃ and Fe₂O₃; follow this steps:-

A- For limestone analyzed samples:-

Multiply the modified factors by SiO₂, Al₂O₃ and Fe₂O₃ relative percent recorded for limestone analyzed sample (table 5).

$$\text{SiO}_2\% \text{ used in cement} = 2.668 (\text{modified factor}) \times 0.48 (\text{SiO}_2\%) = 1.28$$

$$\text{Al}_2\text{O}_3\% \text{ used in cement} = 1.152 (\text{modified factor}) \times 0.16 (\text{Al}_2\text{O}_3\%) = 0.18$$

$$\text{Fe}_2\text{O}_3\% \text{ used in cement} = 0.624 (\text{modified factor}) \times 0.02 (\text{Fe}_2\text{O}_3\%) = 0.01$$

So, the total CaO % used from limestone sample in cement = 1.47

Table (3): Averages of the major chemical oxides of the studied Sections (G. Kahylia Area).

Age	ROCK TYPE	Chemical Oxides	SEC.A	SEC.B	SEC.C
			Average	Average	Average
Middle Eocene	CARBONATES	SiO ₂	0.3	0.55	0.60
		Al ₂ O ₃	0.16	0.16	0.15
		Fe ₂ O ₃	0.02	0.01	0.02
		CaO	55.75	55.70	55.37
		MgO	0.54	0.50	0.57
		SO ₃	0.03	0.03	0.04

Table (4): Averages of the major chemical oxides of the studied Sections (G. Gendali area).

Age	ROCK TYPE	Chemical Oxides	SEC.A	SEC.B	SEC.C
Upper Eocene	MUDROCKS	SiO ₂	43.49	48.59	44.74
		Al ₂ O ₃	13.02	11.31	11.74
		Fe ₂ O ₃	6.66	6.22	7.09
		CaO	14.43	13.30	13.54
		MgO	3.22	3.19	4.17
		SO ₃	1.71	0.36	0.94

Table (5): Averages of the major chemical oxides of the studied area.

Age	Rock type	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃
Upper Eocene	Mudrocks	45.60	12.02	6.65	13.76	3.53	1.00
Middle Eocene	Carbonates	0.48	0.16	0.02	55.61	0.54	0.03

The CaO remained = 55.61(CaO in limestone) - 1.47 = 54.14

For clay analyzed samples:-

SiO₂% used in cement

= 2.668 (modified factor) x 45.60 (SiO₂ %)=121.66

Al₂O₃% used in cement

= 1.152 (modified factor) x 12.02 (Al₂O₃ %) =13.85

Fe₂O₃% used in cement

= 0.624 (modified factor) x 6.65 (Fe₂O₃%)=4.15

So, the total CaO % used from clay sample in cement =139.66

The CaO required = 139.66 -13.76 (CaO in clay) = 125.90

Calculate the ratio between the CaO required for clay and the remained CaO in limestone.

Ratio = 139.66 / 54.14 = 2.58

Ratio= 2.58: 1

= 0.7207: 0.2793

To determine the required amounts of chemical oxides from both limestone and clay, aiming to calculate Silica modulus (S.M), Alumina ratio (A.R) and Lime saturation formula (L.S.F).

A- For limestone:-

Multiply the factor 0.7207 x SiO₂%, Al₂O₃%, CaO%, MgO% and SO₃%.

B- For clay:-

Multiply the factor 0.2793 x SiO₂%, Al₂O₃%, CaO%, MgO% and SO₃%.

The computed values are shown in table (6).

Age	Rock type	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃
Upper Eocene	Mudrocks	12.74	3.36	1.86	3.84	0.99	0.28
Middle Eocene	Carbonates	0.34	0.12	0.01	40.08	0.39	0.02
Sum		13.08	3.48	1.87	43.92	1.38	0.30

Table (6) required amounts of chemical oxides from both limestone and clays

Silica modulus (S.M) =
= 13.08 / 3.48 + 1.87 = 2.44 (Low silica content)

Alumina ratio (A.R)

= 3.48 / 1.87 = 1.86

Lime saturation formula (L.S.F)

= 43.92 - 0.7 x 0.30 / 2.8 x 13.08 + 1.2 x 3.48 + 0.65 x 1.87

= 43.71 / 42.02 = 1.04 (fall in range).

From the previous studies, it clear that the studied raw materials are very suitable for cement industry.

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