Applicability and characterization of clinker production from the raw materials of Sudr El-Hitan area, West Central Sinai, Egypt

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Abstract :- **The aim of our study is to give a feasibility report of the Sudr El-Hitan area West Central Sinai and declare a new field for manufacturing Portland cement. For this purpose, the studying limestone and clay available at different locations of the study area has been utilized in designing and preparation the raw mix. Various parameters are characterized the resulting of clinker samples, identify the surface morphological features and study characterization of produced clinker using SEM and thin section technique.**

Keywords: Cement; Sinai; Egypt; Clay; Limestone; Raw material

I. INTRODUCTION

At present, the manufacture of Portland cement is the largest consumer of carbonates in Egypt.Which are one of the leading country in the Middle East, Africa, and the Arabian Region with a total production capacity reach 48 million tons of clinker at 2011 according to [11] growing to 70 million tons of clinker at 2015 [10]. The construction sectors is witnessed the highest economy growth rate in real term over three years from (2006-2009) about 14.9% in Egypt [9]. About 84 million tons of limestone and 24 million tons of clay have been consumed to produce about 73 million tons of cement every year and still not satisfy the high demand of the cement market, so exploration for new material resource is imperative for the cement industry especially in Sinai which witness significant reserve from cement raw material and just have two factories in North Sinai.The study area is located in West Central Sinai between latitudes 29°40' N - 30°00' N and longitudes 32°55' E - 33°14'E, bounded be Sudr El-Hitan road from the North and Nekhel from the East and located 150 km north the Abu-Zenima city and 50 km east of Suez as shown in (Fig-1).

The present study is investigating the applicability of the carbonate and clay beds from the study area for the production of clinker as well as examining the characteristics of the produce clinker, this aim was accomplished through the following item:-

- Field study including a collection of carbonate and clay sample from the study area.
- Detailed interpretation of the chemical characteristics of the collected carbonate and clay rocks to outline their parameters that samples could be adequate for the cement industry.
-Detailed investigation of the petrography characteristics of the produced clinker.

II. SAMPLING AND METHODS

Thirty-eight samples were collected from a various place from the Sudr EI-Hitan area including both limestone and clay rock, in addition to samples from sand dunes from a nearby area and iron ore samples from iron ore mines at south Sinai in Abu-Zenima area.

Each collected sample is weights from 0.5 to 1.0 kg classified according to type of sample. The samples are dried then crushed and grinded at the El-Arish Cement Lab while chemical analyses were performed by X-ray Fluorescence technique (XRF-ARL9900) measuring the primary cement oxides including, SiO2%, Al2O3%, Fe2O3%, CaO%, MgO%, K2O%, Na2O% CL-%, and SO3% in order to establish raw mix design from collected samples.

The selected raw mix was burned in the El-Arish Cement Plant muffle furnace at 1450°C.The produced clinker Examined their morphological and petrography features by reflected microscope in Cairo University Geology Department lab and Examined by scanning electron microscopy (SEM) device (model Inspect SFEI company, Holland) at the Geological Research National Institute.

III. GEOLOGICAL SETTING

Central Sinai is one of the promising areas that contain a large reserve of limestone and clay deposits from late Cretaceous to Early Eocene age. The most common and widely used stratigraphic succession was classified the Upper Cretaceous into five Formations at sudr formation [7], they are from top to bottom.

1) Sudr Chalk

2) Matulla Formation (Santonian)
3) Wata Formation (Turonian)
4) Abu Qada Formation (Cenomanian)
5) Raha Formation (Cenomanian)

The Paleocene-Early Eocene Esna Formation overlies Upper Cretaceous rocks at Danian age according [13], then followed by Thebes Formation from early Eocene according to [1].

The sudr, esna and thebes formation are present in the northern part of area of study [5] after EL-Sheikh as shown in Fig, 2, while the Matulla Formation outcrops are found at southern part of the study area at Gabel.El-Risha as seen at in geological map of the study area (Fig 3).The formations present in the area of study Sudr EI-Hitan, West Central Sinai regions were discussed as following.

3.1-The Matulla formation is consists mainly of dark brown dolostone with clay and marl in the lower part while the upper part is made up of limestone, it thickness ranges from 85 to 120 m after Steen and Helmy,1982.

3.2- Sudr Formation outcrops are located in the northern part of the study area in Gabel El-Raha and Wadi Sudr, which considered the type section of this Formation [7]. The Sudr chalk formation is exposed and traced along the two-third of the El Egma scarp, and extent throughout the study area, the Campanian-Maastrichtian beds of the Sudr Formation [7] are composed of snow-white, hard, poorly bedded chalk and chalky limestone that attains l00-l20 m in thickness.

3.3- The Esna Shales formation is located above the white Maastrichtian chalks and below Eocene limestone after Beadnell. (1905), The thickness unit reach 35 m and composed of light green to gray highly fossiliferous soft shale with minor carbonate thin beds, gypsum veins, and brownish iron concretions in the middle part.

3.4- The Thebes Formation outcrops are located along the Nile Valley and over vast areas of the Western Desert of Upper Egypt and also found in Central Sinai Egypt. The Thebes highlighting the influence of stratified bedding-parallel elongate cherty nodules on fracturing at mechanical interfaces[16], which has a thickness from 70 to l30 meter of well bedded grey-white limestone with the abundant chart in certain horizons after (Said,1960) .

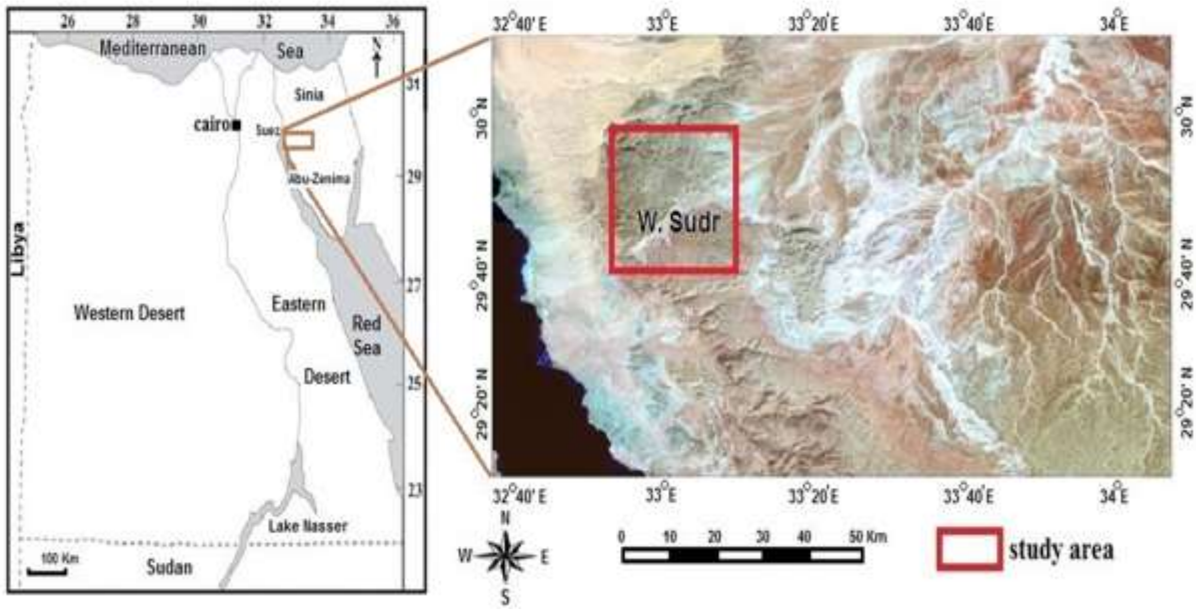

Fig-1: Location map and landsate image of the area of study wadi sudr West Central Sinai

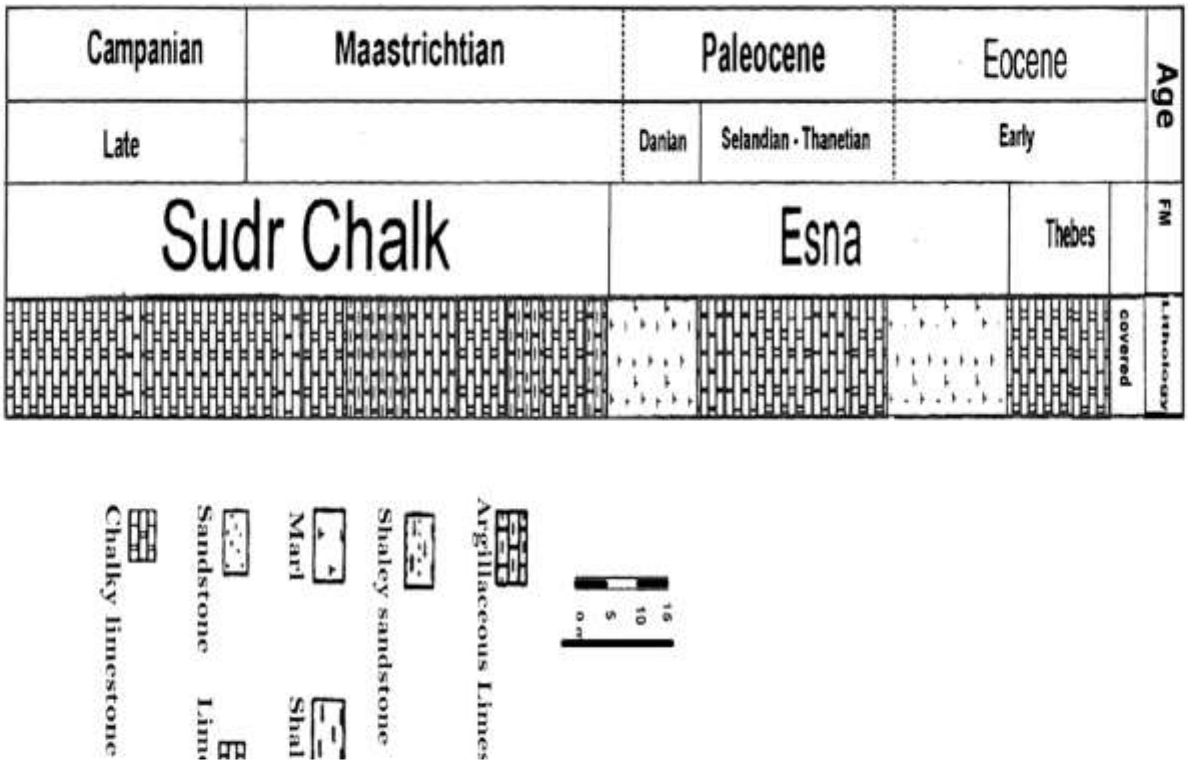

Fig-2: Stratigraphic section of Sudr EI-Hitan after EL-Sheikh et al. (1987).

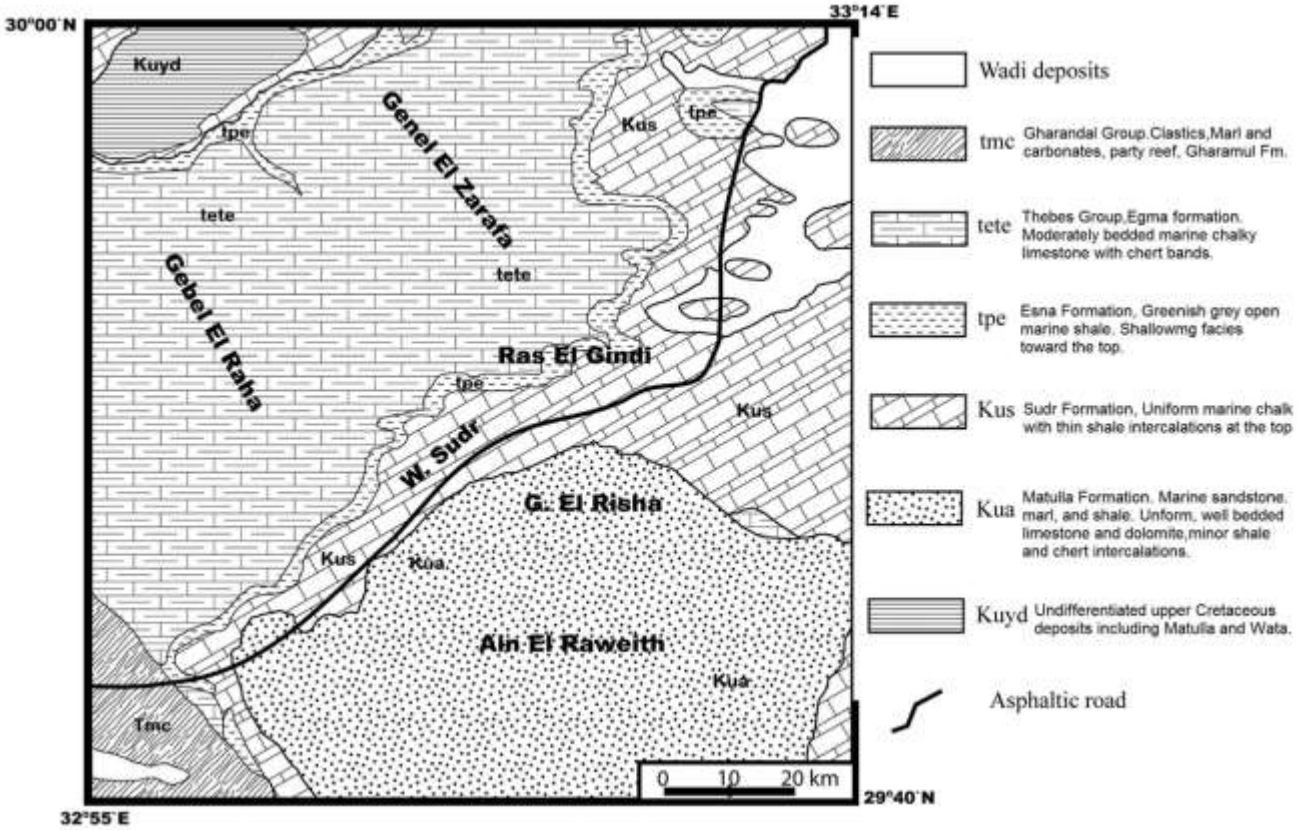

Fig-3: Geological map of the area of study [4]

IV. CLINKER RAW MATERIALS

In the comprehensive investigations of raw materials, the quality and the quantity of the deposit are appraised, [6]. The chemical analysis was carried out to determine the type and percentage of the principal oxides present in the examined samples by X-ray fluorescence (XRF).

The raw materials utilized in the manufacture of Portland cement and control clinker formation consist mainly of four oxides calcium, silica, alumina and iron oxides.These compounds interact with one another in the kiln to form a series of more complex products and a small apart from the residue of uncombined lime, the raw material are supplied by various kinds of raw materials as following.

4.1- Calcareous material ($CaCO_3$) is wide spread in nature. Calcium carbonate of all geological formations qualifies for the production of Portland cement according to content of calcium oxide (CaO%) The purest grades of limestone are chakly limestone which present at area of study, the slection of the best sample is determine the according highest value of CaO % and the lower chlorine percent (Cl%) in different samples as shown in Table 1 ,the CaO% range in chakly limestone of Sudr EI-Hitan area between 44.68%and 53.26%, while chlorine ranges between 2.9% to 0.01% the most acceptable limestone samples are L4 and L6. The hardness of limestone depends on it geological age; usually, the older the geological formation, the harder the limestone. The hardness of limestone is between 1.8 and 3.0 of the Mohs'scaIe of hardness.

However, sample number L6 has a better chemical composition where it contains a lower percent of chlorine with a higher percent of CaO than L4.

4.2- Argillaceous material, The scond most important raw material for cement manufacture is clay with percent reach 23.0±5%. The clay is formed by the weathering of alkali and alkaline earth containing aluminum silicates and of their chemical conversion products, mainly feldspar and mica, The chemical composition of clay are varying and contain different amount of chemical admixtures as iron hydroxide, iron sulfide, sand and calcium carbonate. The quality of clay is determined according to more than one factor, the percent of Al_2O_3, SiO_2 the highest value is required and the lower chlorine (Cl^-) percent is preferable while the other percent of CaO% and SO_3% must be considered in mix design, Eight mix designs formed by every clay sample shown in Table 2 to select the better clay sample, that show clay sample code C8 formed applicable mix design and formed clinker comply with international stander as shown in Table 5.

4.3- Siliceous material, mainly sandstone used in raw meal up to 3% as corrective material at the mix design as a source of silica. Eleven sand samples were collected from local sandy dunes covering wide areas especially in the depressions present between the hills and hillocks where the thickness of the sand accumulations may reach up to 10 meters or more, the average chemical composition of sandstone samples are shown in Table 3.

4.4-The ferric material, mainly iron ore (hematite) are used as corrective material at the mix design with percent up to 3% as a source of iron oxide FeO, iron ore samples were collected from Abu-Zenima iron ore mines near the area of study that supply all cement plants in Sinai.The average chemical composition of iron ore samples shown in Table 4.

V. RESULT AND DISCUSSION

The produced clinker is consisting of four main phases Alite (C3S), Belite (C2S), Tricalcium Aluminate (C3A) and Ferrite (C4AF) which had been discovered by petrographic investigations of Tornebohm [15] that phases have been affect the potential physical parameter of the produced clinker.The clinker had produced by burning the designed raw mix by increasing the temperature gradually up to 1450°C and stay still at kiln for 30 min then cooling at a fast rate to fixed phases .The raw mix shown in Table 5 formed according to fixed parameters that are known as hydraulic modulus (Lime saturation factor (LSF) =93± 2, Silica modules (SM) =2.2 $\pm .2$, Alumina modules (AM) =1.55$\pm .2$ this value used at El-Arish Cement Plant).

It should be mentioned that the clinker composition shown in Table 5 calculated according to this method was denoted by Bogue calculation that is a well know cement industry standard method for estimating the mineralogical composition of produced clinker shown in Table 6 [2].

Table 1- Chemical composition of limestone samples

Number of samples	SiO_2%	Al_2O_3%	Fe_2O_3%	CaO%	MgO%	K_2O%	Na_2O%	Cl-%	SO_3%	L.O.I%
L1	8.96	0.42	0.43	44.68	1.04	0.3	0.03	0.09	0.027	41.48
L2	9.20	0.13	0.17	45.38	0.91	0.3	0.03	0.12	0.021	41.37
L3	4.60	3.60	0.11	48.4	0.68	0.36	0.03	0.31	0.017	37.00
L4	3.69	0.34	0.2	50.63	0.77	0.15	0.03	0.03	0.048	42.32
L5	0.92	0.14	0.14	50.26	0.82	0.4	0.03	2.90	0.043	42.35
L6	1.89	0.33	0.18	53.26	0.85	0.36	0.02	0.01	0.05	41.34

L7	1.62	0.41	0.13	52.41	0.81	0.36	0.03	0.17	0.041	42.57
L8	7.20	0.17	0.1	47.2	0.70	0.36	0.01	0.08	0.055	42.83

Table 2 - Chemical composition of clay samples.

Number of samples	SiO_2%	Al_2O_3%	Fe_2O_3%	CaO%	MgO%	K_2O%	Na_2O%	Cl-%	SO_3%	Moisture
C1	51.33	16.4	7.94	6.85	0.578	1.8	0.09	2.7	1.88	22.49
C2	47.41	13.8	5.20	6.2	0.62	0.06	0.04	0.98	1.33	14.3
C3	50.20	9.9	7.94	10.09	0.59	0.63	0.66	0.705	1.56	17.31
C4	49.97	15.12	8.34	8.47	0.54	0.67	1.17	1.9	1.76	15.12
C5	45.00	13.65	6.57	6.54	0.58	2.1	0.04	5.3	1.69	18
C6	45.20	14.71	8.01	10.18	0.98	1.2	0.60	1.1	1.71	18.2
C7	34.33	12.2	9.86	16.00	1.552	0.03	0.04	0.552	3.74	18.1
C8	51.96	15.37	7.56	3.41	1.162	0.03	0.04	0.65	2.1	18.1

Table 3- The average chemical composition of eight sand samples

Oxide	SiO_2%	Al_2O_3%	Fe_2O_3%	CaO%	SO_3%	MgO%	K_2O%	Na_2O%	Cl-%
A.vg	88.99	2.56	0.76	4.32	0.57	0.19	0.88	0.25	0.06

Table 4- XRF for iron ore samples from The Abu-Zinama area

Oxide	SiO_2%	Al_2O_3%	Fe_2O_3%	CaO%	SO_3%	MgO%	K_2O%	Na_2O%	Cl-%
A.vg	10.556	4.485	63.416	6.866	6.836	4.145	1.825	0.339	0.472

Table 5 -Raw mix design for C8

$$L.S.F = \frac{100Ca}{2.8\,SI + 1.18Al + 0.65Fe} \qquad S.M = \frac{SI}{Al + Fe} \qquad A.M = \frac{Al}{Fe}$$

MATRIAL	PERCENT	L.O.I	Si	Al	Fe	Ca	MgO	SO3	K	Na	Cl	lsF	SM	AM
LIME STONE	75.354	41.34	1.89	0.33	0.18	53.26	0.05	.85	.36	0.02	0.014			
CLAY	23.174	18.1	51.96	15.37	7.56	3.41	2.1	1.162	0.03	0.04	0.65			
SAND	0.5154	1.4	88.99	2.56	0.76	4.32	0.57	0.19	0.88	0.25	0.06			
IRON	0.9571	2.3	11.67	5.67	63.78	7.05	6.84	4.24	1.87	0.34	0.47			
RAW Meal		35.4	14.0	3.9	2.5	41.0	0.6	0.3	0.03	0.029	0.166	93.0	2.2	1.55
clinker			21.6	5.9	4.0	64.8	0.8	0.8	0.28	0.3	0.04	90.6	2.2	1.5

Table 6-mineralogical composition of produced clinker

F-CaO	C3S	C2S	C3A	C4AF
0.6	49.9	24.2	9.0	12.1

$C3S = 4.07 (CaO\text{-}F.cao) - 7.6\ SiO_2 - 6.72\ Al_2O_3 - 1.43\ Fe_2O_3 — 2.85\ SO_3$
$C2S = 2.87\ SiO_2 - 0.754\ C_3S$
$C3A = 2.65\ Al_2O_3 - 1.69\ Fe_2O_3$
$C4AF = 3.04\ Fe_2O_3$

A. Petrographical characterization of the produced clinker.

The clinker phase's composition and texture (crystal size, abundance,) of clinker result from complex interactions of raw feed particle size, feed homogenization, and the heating then cooling regime.
The mineralogical percent of produced clinker fit the normal clinker average according to [3] Alite comprises from 40 to 70 percent of normal Portland cement clinker, while Blite said to compose approximately from 10 to 30 percent of most Portland cement clinker [8]. Tricalcium Aluminate (C3A) may comprise up to 18 percent in ordinary clinker and Ferrite percent up to 20 according to [3], Free lime (CaO) limit up to 2.0 percent in ordinary Portland cement according to Egyptian standard.

1) Alite.

The microstructures of alite under a microscope in photomicrographs image reflect gray color and amber yellow belite as shown in Fig 4A but after etching with nital (1% nitric acid in isopropyl alcohol), alite crystals reflect blue color as shown in Fig 4b. Nital etches color is to some extent, a function of a length of etching time, temperature, and reactivity of the crystal [12]. Alite is the principal constituent of cement clinker occurs most frequently as idiomorphic hexagonal crystals under scanning electron microscope as be seen in (Fig 5A), the feature that commonly observed within alite crystals is the presence of inclusions of small rounded belite crystals, Pure alite is unstable below 1250°C and tends to decompose into belite as shown in (Fig 5B) and sub-microscopic free lime.

2) Belite

The belite solid-solution is a series of trigonal, orthorhombic, and monoclinic varieties of impure dicalcium silicate, usually termed as C_2S in the cement industry after [3]. The rounded crystal form is the most regular habit of belite as shown in (Fig 5A).
Secondary belite is developed as a result of slow clinker cooling after reaching the maximum temperature; the SiO2 comes out of solution in the form of small secondary belite crystals as shown in (Fig 5B) with free lime as a result of following equation C3S ↔C2S+F-CaO.

3) Tricalcium Aluminate (C_3A)

The tricalcium aluminate (Ca3Al2O6) has a melting point of approximately 1242ºC which is coded as C3A in the cement industry. C3A is consisting of uniform small xenomorphous to rectangular crystals [3]. The principal clinker minerals alite and belite are surrounded at clinkering temperature by a liquid phase (matrix) as shown in (Fig 6A), which is principally aluminates and ferrite, the aluminates phase tend to form well-separated idiomorphic shape.

4) Ferrite

Ferrite or tetracalcium alumino- ferrite which is known as C4AF in the cement industry, Ca2 (Al, Fe)O5) comprise about 12.1 % of the total composition of the clinker,. The ferrite and aluminate phases are sometimes as the interstitial or matrix phases as they occur between alite and belite as shown in (Fig 6B) [15].

5) Sulfate

Alkali sulfates and calcium sulfates are occur as patches on crystal lattices of clinkers, as shown in (Fig 5A) and as a substituent in the major phases especially alite and belite, which have gotten an interest since they have been found to affect hydration rates and strength development[15].

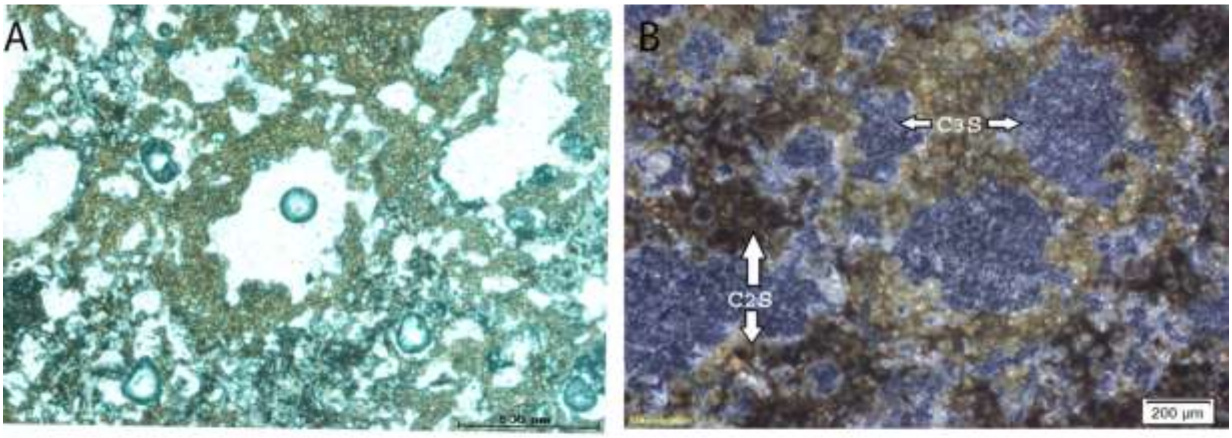

Fig-4: Photomicrographs showing microstructures of clinker (A) Regular distribution of C_3S (light gray) and amber yellow nested belite (B) Nital etched, tabular C_3S (light blue) crystals and yellow anhedral rounded C_2S nest.

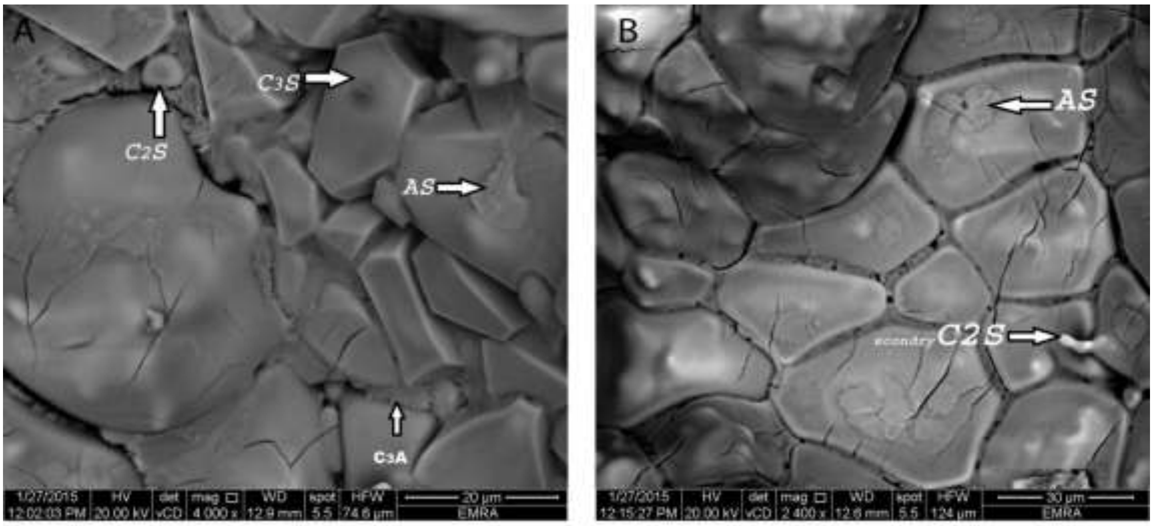

Fig 5- SEM Micrographs showing the produced clinker microstructure including (A) angular hexagonal C_3S crystals with patched Alkalis sulfate (AS) (B) rounded C_2S and secondary belite with free lime crystals.

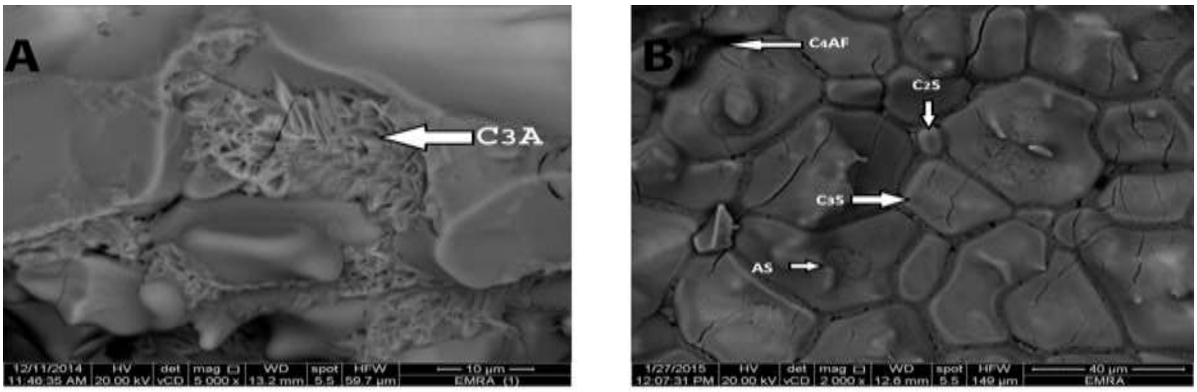

Fig-6 SEM Micrograph of produced clinker showing (A) a framework of needle-like C_3A crystals (B) perfect hexagonal C_3S with Interstitial Ferrite between alite and belite and alkali sulphates (AS) substituted.

VI. SUMMARY AND CONCLUSIONS

1-The Sudr El-Hitan area contains sufficient material could be used in cement industry. sudr Formation is containing chalky limestone with elevation reach l00-l20 m and Esna Shale thickness reaches 35 m presence along El-Egma plateau.

2-the suggested raw meal composed of four material, limestone from location L6 (29°51.00´43.34" N, 33°07.00´ 44.51" E) which have the most suitable chemical composition (high CaO percent and lower Cl%), sandstone used from local sandy dunes covering Sudr El-Hitan and iron ore come from Abu zinama are used as corrective material at mix design to achieve the raw meal modulus.

3-Eight modulus are created using programmable calculator to select the better clay location. Which shown the clinker formed from using clay sample code C8 locate at 29°43.00´25.76"N 32°59.00´07.92"E which show theoretically high hydraulic properties that responsible of strength of cement after 28 days which will affect the efficiency mortar in construction and chemical analysis don't exceeds the limit of Egyptian stander.

4-petrographical analysis (Photomicrographs and SEM) are showing formation typical gray hexagonal crystals of alite and rounded belite when burning raw meal at 1450°C then formation secondary belite due to the reverse reaction during clinker cooling and transformation alite to belite and free lime, alkali sulfates present as patches on crystal lattices of alite crystal .

REFERENCES

[1]-Aubry, M.P., Salem, R.(2013): The Dababiya Core, A window into Paleocene to Early Eocene depositional history in Egypt based on Coccolith Stratigraphy. Stratigraphy vol.9,pp.287–346.

[2]-Bogue, R.H (1929): Calculation of the Compounds in Portland Cement, Ind. Eng. Chem., Anal. Ed. 1, .pp 192-197.

[3]-Campbell, D.H. (1986): Microscopical Examination and Interpretation of Portland cement and clinker Association. Library of Congress 85-63563. 201p.

[4]-Conoco, CH.S. (1987): Geological Map of Egypt 1:500000- NH 36 SE South Sinai.The Egyptian General Petroleum Corporation., Cairo, Egypt.

[5]-Eid, M.A.(1995: Geological and Studies of Cretaceous Rock East Central Sinai.Cairo University., M.Sc, Egypt . 255 P.

[6]- ES 4756-1(2009): Cement Part :(1) Composition, Specifications And Conformity Criteria For Common Cements,Egyptian Organization for Standardization and Quality .

[7]-Ghorab, M.A. (1956): A summary of proposed rock Stratigraphic Classification for the Upper Cretaceous rocks in Egypt. Geol. Soc., of Egypt, 324p.

[8]-Ghosh, S.K., (1983): Portland Cement Phases: Polymorphism, Solid Solution, Defect Structure, and Hydraulicity. Advances in Cement Technology, Pergamon Press., New York, pp. 289-305.

[9]-Hasan, F. (2009): Egypt Cement Sector, Global Investment House KSCC,121p.

[10]-Hussien, A. (2015): Egyptian Regulations for Coal Related Activities and Cement Industries in Egypt. Arab Republic of Egypt Ministry of Environment,.Egypt, 27p.

[11]-Oss,G.v.(2012):cement, U.S. Geological Survey, Mineral Commodity Summaries http://minerals.usgs.gov/minerals/pubs/commodity/cement/mcs-2012-cemen.pdf.

[12]-Ono, Y. (1980): Microscopical Estimation of Burning Condition and Quality of Clinker. Seventh International Congress on the Chemistry of Cement, Paris, Vol. 2, Thcmc I, pp. 206-211.

[13]-Said, R. (1962): The Geology of Egypt. Elsevier, New York, 377 pp.

[14]-Steen, G., Helmy, H. (1982): Pre-Miocene Evolution in the Gulf of Suez GUPCO Internal Report.

[15]-Stutzman, Paul (2004): Scanning Electron Microscopy Imaging of Hydraulic cement microstructure. Cement and Concrete Composites, Vol No. 26,. pp .957-966.

[16]-Temraz, M (2005): Mineralogical and Geochemical Studies of Carbonaceous Shale Deposits from Egypt. M.Sc, 124p.