



Comparative study of ordinary portland cement from different production (Al Fatiah and Al Huary cement factories), NE Libya

F. F. Fares*, O. R. Shaltami, Saad K. Elebaidi, Fathi Mohamed and Mohammed Sh. El Gahmi

University of Benghazi, Faculty of Science, Department of Earth Sciences, P. O. Box 9480, Benghazi-Libya

ARTICLE INFO

Article history:

Received 07 January 2017

Revised 30 January 2017

Accepted 18 February 2017

Available online 20 February 2017

Keywords:

Clinker, Cement Quality, Portland Cement, Al Fatiah Quarry, Al Huary Quarry

* Corresponding author:

E-mail address: faresfathi2222@gmail.com

F.F. Fares

ABSTRACT

This study will discuss the evaluation of clinkers and cement powdered chemistry during manufacturing process from Al Fatiah and Al Huary Cement Factories then matching with British standard. The bulk geochemical analysis has been carried out using X-ray fluorescence (XRF) and inductively coupled plasma-mass spectrometry (ICP-MS) techniques. The chemical analyses data showed that the limestone at the Al Fatiah Cement Quarry is classified as a high pure limestone and the limestone at the Al Huary Cement Quarry is a low pure limestone. The studied terra rossa samples showed a suitable composition and could be a good source for SiO_2 and Al_2O_3 . The results of homogeneous samples of clinkers and cement powdered were compared to the British Standard.

© 2017 University of Benghazi. All rights reserved.

1. Introduction

Al Jabal Al Akhdar is a highland area which encompasses the northern most part of Cyrenaica north east Libya, it consists of Upper Cretaceous to Tertiary marine deposits. The Jurassic and Lower Cretaceous marine deposits are known from the exploratory oil wells. The Al Jabal Al Akhdar is more than 200 Km long and 75 Km wide. Al Faiadiyah and Benghazi formations represent a portion of Al Jabal Al Akhdar region. The ages of these two formations are Oligo-Miocene to Middle Miocene respectively were deposited in shallow marine environments (Berggren, 1974; and Klen, 1974).

Fig. (1) shows that the first section is located at Al Fatiah cement quarry between latitude $32^\circ 35' 46''$ N and longitude $22^\circ 43' 21''$ E of about 25 km east of Darnah City. The terra rossa in this section is located at latitude $32^\circ 36' 50''$ N and longitude $22^\circ 42' 08''$ E of about 40 Km east of Darnah City and about 20 Km south of Al Fatiah limestone cement quarry. The second section is located at Al Huary cement quarry of about 18 Km south west of Benghazi City. This section is represented by limestone and terra rossa soil between latitude $31^\circ 59' 59''$ N and longitude $73^\circ 32' 00''$ E.



Fig. 1: Location map of the study areas

The Al Faiadiyah Formation is the only detected rocks in the Al Fatiah Cement Quarry. It is composed of skeletal limestone. The

Benghazi Formation is the only detected rocks in the other quarries. It is composed of fossiliferous limestone in the Al Huary Cement Quarry. Cement is typically made from limestone and clay, these raw materials are extracted from the quarry crushed to a very fine powder and then blended in the correct proportions. The blended of raw material is called the raw feed or the raw kiln and is heated in a rotary kiln where it reached temperature of about at 1400°C to 1500°C . The rotary kiln is a tube up 200 meters long 6 meters in diameter which long flame one at the end, the raw materials enter the kiln at the cool end gradually passes down to the hot end then falls out of the kiln and cools down. The raw materials formed in the kiln are described as clinker and is typically composed rounded nodules between 1mm and 25 mm across after cooling, the clinker may be sorted temporarily in the clinker store or may be pass directly to the cement mill. The cement mill grinds the clinker to a fine powder. A small amount of gypsum in a form of calcium sulfates normally ground up with the clinker (Fig. 2). The gypsum controls the setting properties of the cement when water is added (Winter, 2013).

Scope and limitation of the study

- 1) To describe clinkers and cement powdered chemistry of Al Fatiah and Al Huary Cement quarries during manufacturing process.
- 2) Make comparison for quality of clinkers and cement powdered of Al Huary and Al Fatiah Cement quarries with British standard of Ordinary Portland Cement Industry.

2. Methodology

About twelve samples of limestones and six samples of terra rossa were collected from the studied quarries. The collected samples were washed thoroughly in distilled water to remove the contamination. Bulk geochemical analyses for major oxides and trace elements were performed using the inductively coupled plasma-mass spectrometry (ICP-MS) technique, which is widely used, at present, for determination of elements in various materials with high precision.

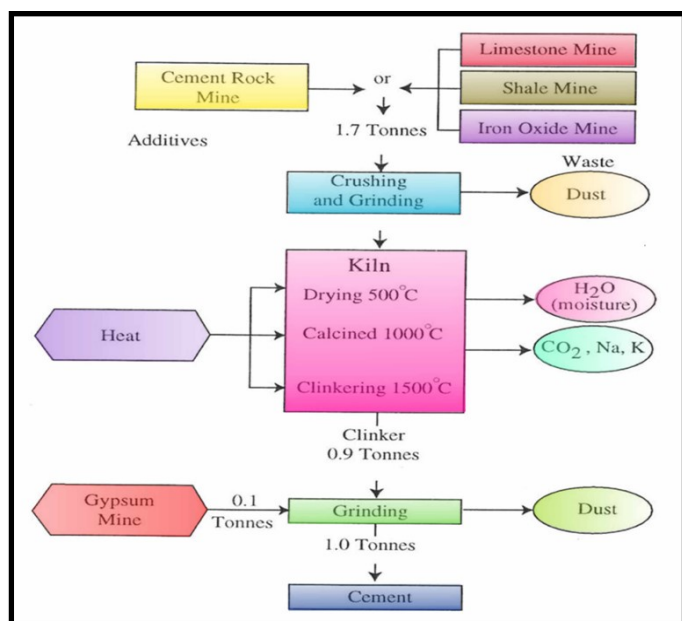


Fig. 2: Flow chart of cement producing progress (Kesler, 1994)

The analytical procedure depends on the decomposition of exact weight of 0.2 g powdered fine sand size sample in 50 ml Teflon beaker. Decomposition was done by 4 ml HNO₃, 3 ml HClO₄ and 5 ml HF, and evaporated to dryness under 200°C. The residue was dissolved with 5 ml (1:1) HNO₃ by heating and 5 ml of 4 ppm indium solution was added as an internal standard. The sample, as well as reference, solutions were introduced by peristaltic pump with 0.18 rpm. Before each measurement, nebulizer and spray chamber were washed by introducing the solution for 3 min with 0.5 rpm and 30 seconds with 0.18 rpm. The analysis was done in the Nuclear Materials authority of Egypt.

Another nine homogeneous samples as well as for clinkers and cement powdered were washed thoroughly in distilled water to remove the contamination, drying, grinding, compression and analyses for major oxides in the XRF (X-ray fluorescence) Laboratory, Cement Factory of Benghazi, Libya. Many authors agree to the efficiency of this method for major oxide determination (Al Jaboury and McCann, 2008).

3. Results and discussion

3.1. Raw materials

Tables (1 and 2) shows that the limestone from Al Fatiah Cement Quarry is classified as high pure limestone (CaO = 55%, using classification of Harris, 1983) and the limestone from Huary Cement Quarry is classified as low pure limestone (CaO = 49.5 %, using classification of Harris, 1983), with some impurities of SiO₂ and Al₂O₃. The studied terra rossa samples show high content of SiO₂, Al₂O₃, Fe₂O₃ and K₂O with low contents of CaO and MgO. These terra rossa samples show a suitable composition and could be a good source for SiO₂ and Al₂O₃ (see Tables 1 and 2).

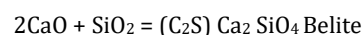
3.2. Chemical reaction of mixture in the kiln

At 900 to 1450°C the chemical reactions take place and formed four mineral phases; alite (C₃S), belite (C₂S), aluminate (C₃A) and aluminate ferrite (C₄A₂Fe₂O₁₀ C₄AF) (Fig. 3). Alite (C₃S) is the most important constituent, 38-60% in normal Portland cement clinkers. It is responsible for the setting characteristics and development of the early strength of cement from 1 to 28 days.



Belite (C₂S) this phase has a content of 15-38 % (Brandt, 2009) of the clinker. It is hardened slowly and is contributed largely to the beyond one week (Tennis and Kosmatka, 2011). It

reacts slowly with water, thus contributing little to the strength during the first 28 days.



Aluminate (C₃A) this phase has a content in clinker is approximately 7-15 % (Brandt, 2009). It liberates a large amount of heat during the first days of hardening. It also contributes slightly for early strength development. C₃A hydrates very rapidly and will influence early bonding characteristics.



Ferrite (C₄AF) the average composition and constitutes is about 6 to 18 % of a typical clinker (Brandt, 2009). It reduces the clinkering temperature and acts as a flux in burning the clinker. It hydrates rather rapidly but contributes very little to strength development. The iron content is mainly responsible for the dark coloring of cement (Kohlhaas, 1983).

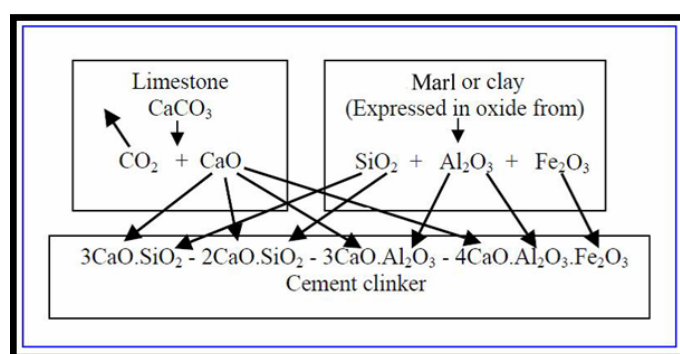
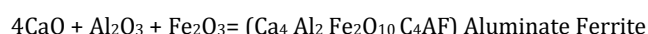


Fig. 3: Mineral compositions of the cement clinker

Table 1: Chemical analysis data (major oxides in wt. %) of the Al Fatiah quarry samples

Formation	Soil			Al Faidiyah Formation					
Sample No.	10	12	14	1	3	4	6	7	9
SiO ₂	40.31	44.41	50.66	17.05	16.35	1.49	1.33	1.18	0.97
TiO ₂	0.63	0.55	0.82	0.21	0.17	0.02	0.02	0.04	0.01
Al ₂ O ₃	20.20	17.91	14.00	2.44	2.13	0.54	0.41	0.73	0.23
Fe ₂ O ₃	15.51	10.53	6.09	1.38	1.29	0.43	0.50	1.72	0.57
MnO	0.25	0.19	0.11	0.02	0.02	0.03	0.02	0.01	0.03
MgO	2.00	0.77	0.93	0.95	0.88	1.12	1.41	0.91	1.24
CaO	5.73	4.86	12.12	43.00	42.77	54.87	55.80	53.92	55.53
Na ₂ O	0.08	0.09	0.05	0.06	0.04	0.03	0.03	0.06	0.03
K ₂ O	5.18	2.81	3.33	0.60	0.47	0.14	0.09	0.11	0.06
P ₂ O ₅	0.08	0.06	0.02	0.01	0.02	0.01	0.01	0.01	0.01
SO ₃	0.32	0.21	0.11	0.05	0.04	0.15	0.21	0.05	0.25
Cl	0.07	0.06	0.03	0.04	0.04	0.02	0.02	0.04	0.02

The estimation of alite (C₃S), belite (C₂S), aluminate (C₃A) and aluminate ferrite mineral phases (C₄Al₂Fe₂O₁₀ C₄AF) in clinker and cement samples (see Tables 3 and 4). These values coincide with the mineral percentage content in Ordinary Portland Cement specification described by Kohlhaas et al. (1983). The X-ray fluoresces (XRF) analyses of the clinkers have been calculated. This calculation shows that both of the studied quarries contain alite and belite as major a mineral phases, aluminate and aluminate ferrite as a minor mineral phases, while free lime and periclase representative as trace phases in Al Fatiah and Al Huary quarries, respectively.

The results of homogeneous samples of clinkers and cement powdered were done by comparing with the British Standard Specification. The composition of clinkers is relatively similar to British standard clinker composition. However is slightly different from cement composition due to addition of gypsum latter (see Table 4).

Table 2: Chemical analysis data (major oxides in wt%) of the Al Huarry quarry samples

Formation	Soil			Benghazi Formation					
Sample No.	27	28	30	16	18	19	21	22	24
SiO ₂	39.11	34.34	53.00	1.43	2.00	1.05	1.91	1.20	1.18
TiO ₂	0.87	0.49	0.76	0.02	0.05	0.01	0.03	0.02	0.01
Al ₂ O ₃	19.70	20.55	12.41	0.18	0.24	0.15	0.21	0.16	0.13
Fe ₂ O ₃	14.13	12.00	5.03	0.13	0.22	0.08	0.05	0.08	0.14
MnO	0.30	0.18	0.13	0.01	0.01	0.02	0.01	0.03	0.01
MgO	2.39	0.95	1.27	9.21	11.60	8.23	12.59	7.76	13.73
CaO	9.40	7.32	13.81	41.33	44.49	40.93	45.52	41.00	46.42
Na ₂ O	0.18	0.12	0.09	0.02	0.04	0.01	0.03	0.01	0.01
K ₂ O	4.44	1.67	2.50	0.15	0.27	0.12	0.19	0.10	0.09
P ₂ O ₅	0.12	0.08	0.05	0.02	0.03	0.02	0.01	0.01	0.01
SO ₃	0.17	0.55	0.08	0.39	0.13	0.26	0.34	0.36	0.25
Cl	0.16	0.11	0.06	0.02	0.01	0.01	0.02	0.03	0.02

Table 3: Chemical and mineral compositions of the clinker samples (major oxides in wt. %)

Location	Al Fatiah Quarry			Al Huarry Quarry			BS 12 -78
Sample No.	1	2	3	1	2	3	
SiO ₂	21.86	23.00	22.00	22.59	22.03	21.60	21 – 22
Al ₂ O ₃	5.61	5.86	5.57	4.71	4.66	4.78	5.36
Fe ₂ O ₃	3.51	3.19	4.19	2.69	2.50	2.90	0.03
CaO	65.61	64.00	64.59	63.56	64.02	64.30	64 – 66
MgO	1.41	1.61	1.39	3.22	2.95	2.60	0.01
Na ₂ O	0.02	0.01	0.06	0.01	0.03	0.02	0.58
K ₂ O	1.10	0.90	0.07	0.02	0.10	0.50	0.36
Na ₂ O ⁺	1.12	0.91	0.13	0.30	0.13	0.52	< 2
SO ₃	0.17	0.12	0.14	0.20	0.22	0.15	< 3.5
L.O.I	0.71	1.31	2.03	2.73	3.50	3.15	< 5
Total	99.29	98.69	97.97	97.27	96.60	96.85	-
SR	2.30	2.50	2.27	3.05	2.90	2.80	1.5 – 4.0
AR	1.54	1.50	1.32	1.75	1.90	1.60	1.4 – 3.5
HM	2.12	2.00	2.00	2.12	2.19	2.20	1.7 – 2.3
L.S.F	94.00	87.70	90.00	90.00	92.00	87.00	66 – 102
CaO _{free}	2.46	1.88	1.51	2.24	1.30	1.22	< 2
C ₃ S	59.43	59.09	49.19	51.87	52.40	47.30	40 – 80
C ₂ S	17.19	21.36	26.40	25.50	25.61	23.47	0 – 30
C ₃ A	8.80	10.13	8.13	7.93	8.01	7.90	7 – 15
C ₄ AF	10.91	9.70	12.74	8.18	9.10	9.09	4 – 15

Amount of CaO as specified in British stander should be within the range (from 64 to 66 %), all the samples of Al Fatiah and Al Huarry quarries formed clinker are ranging from 63.56 to 65.61 %. These values of CaO content within clinker produced are acceptable industrially due to lesser than 66%. In which a result of hard is burning throughout the rotary kiln. As shown it closes to British Standard (see Tables 3 and 4).

Amount of SiO₂ in British stander specify in Ordinary Portland Cement within the range 21 to 22%, it has been observed that in Al Fatiah and Al Huarry quarries within specified range limit(see Tables 3 and 4). Specify amounts of MgO in Ordinary Portland Cement not more than 2 %, it was found in all the samples of Al Fatiah Quarry were within the specified range while in Al Huarry Cement Quarry more than 2% (see Tables 3 and 4). The magnesia content is limited by the standard specifications not to exceed 2% because higher magnesia contents may be detrimental to the soundness of the cement, especially at late ages (Deborah et al. 2009). Beyond that limit it appears in the clinker as free MgO (periclase). Periclase reacts with water to form Mg(OH)₂, and this is the slowest reaction among all other hardening reactions.

Since Mg(OH)₂ occupies a larger volume than the MgO and is formed on the same spot where the periclase particle is located, it can split apart the binding of the hardened cement paste, resulting

in expansion cracks commonly known as magnesia expansion (Khan et al. 2008).

Table 4: Chemical and mineral compositions of the cement powdered samples (major oxides in wt. %)

Location	Al Fatiah Quarry			Al Huarry Quarry		
Sample No.	1	2	3	1	2	3
SiO ₂	21.05	21.66	21.37	19.73	20.51	20.80
Al ₂ O ₃	5.45	5.48	5.48	4.72	4.59	4.64
Fe ₂ O ₃	3.19	3.79	3.78	2.99	3.18	2.79
CaO	62.50	62.10	62.60	63.64	63.27	64.16
MgO	1.41	1.61	1.17	2.40	2.44	2.22
SO ₃	2.80	2.32	2.32	2.25	2.10	2.02
L.O.I	1.64	1.60	1.57	2.76	2.33	2.50
Total	97.90	96.95	97.40	95.73	96.09	96.61
SR	2.36	2.34	2.35	2.56	2.64	2.77
AR	1.80	1.45	1.45	1.58	1.44	1.60
HM	2.02	1.95	1.96	2.01	2.02	2.08
L.S.F	0.89	0.87	0.87	0.88	0.88	0.89
CaO _{free}	2.02	3.30	2.10	0.28	0.37	0.73
C ₃ S	42.27	42.19	42.40	45.00	49.24	50.13
C ₂ S	28.33	27.80	28.10	23.20	22.90	23.90
C ₃ A	9.82	10.22	10.11	7.45	7.90	8.01
C ₄ AF	9.70	10.00	9.85	9.09	9.50	9.80

The amounts of Al₂O₃ and Fe₂O₃ in Al Fatiah and Al Huarry quarries were within specified limit (see Tables 3 and 4). If the lime content is fixed, and the silica becomes too high, which may be accompanied by a decrease in alumina and ferric oxide, the temperature of burning will be raised and the special influence of the high lime will be lost. If the lime content is too low, which means an increase in the alumina and ferric oxide; the cement may become quick-setting and contain a larger amount of alumina compounds, which appear to be of little value for their cementing qualities. Rapid setting is undesirable, and is not permitted by the standard specifications, because the cement sets up so rapidly that it cannot properly be worked in the forms before stiffening occurs. A high loss on ignition indicates pre-hydration and carbonation, which may be caused by improper and prolonged storage or adulteration of Ordinary Portland Cement during transport or transfer (Khan et al. 2008).

3.3. Kiln feed parameters

A set of parameters (modules) is currently used in cement manufacturing to characterize the quality of the raw materials and to ensure the quality of the produced cement (Kebede 2010).

3.2.1. Silica Ratio (SR)

Increasing silica ratio impairs the burn ability of the clinker, by reducing liquid phase content and tendency toward formation of coating in the kiln. An increasing silica ratio causes a slow setting and hardening of the cement. With decreasing silica ratio the content of liquid phase increases, this improves the burnability of the clinker and the formation of coating in the kiln (Aldieb et al. 2010). Generally in depending on British standard the silica ratio runs between 1.5 to 4.0, low values for silica ratios can be accepted as low down to 1.5, for the all studied clinker and cement powder samples of silica ratio runs between 2.3 to 3.05, these values accepted in which that improves the burnability of the clinker and the formation of coating in the kiln the silica ratio (SR) can be calculated as: $SR = SiO_2 / (Al_2O_3 + Fe_2O_3)$.

3.2.2. Alumina Ratio (AR)

Alumina Ratio (AR) is characterizing the cement by the proportion of alumina to iron oxide values of alumina ratio are in the range from 1.4 to 3.5. British standard, the AR determines the

composition of liquid phase in the clinker, when it's lower than 1.4 both oxides are present in their molecular ratios and therefore only tetracalcium aluminoferrite can be formed in the clinker, consequently the clinker cannot contain tricalcium aluminate. This is the case called Ferrari-cement which is characterized by low heat of hydration, slow setting and low shrinking. A high alumina ratio together with a low silica ratio results among other things, in a fast setting of the cement; this requires the addition of a higher gypsum rate to control the setting time requirements for cement. The data of alumina ratio runs between in the acceptable ranges (from 1.4 to 1.9). The alumina ratio (AR) can be calculated as: $AR = Al_2O_3 / Fe_2O_3$.

3.2.3. Hydraulic modulus (HM)

Hydraulic modulus (HM) is represented the optimum lime content which ranges (from 1.7 to 2.3) but the good quality is 2 (Ghosh, 2002). Increasing HM more heat is required for clinker burning the strengths, especially the initial set up and also the heat of hydration rises and simultaneously the resistance to chemical attack decrease (Rao et al. 2011). The hydraulic modulus of good quality cements were approximately 2 as shown in the tables and located in the permitted range (from 1.96 to 2.12) (see Tables 3 and 4). The hydraulic modulus can be calculated as: $HM = CaO / (SiO_2 + Al_2O_3 + Fe_2O_3)$.

To attain complete lime saturation in the clinker the total silica must be combined as C_3S , all iron oxide must combine with the equivalent amount of alumina to C_4AF , and the remaining alumina must combine to C_3A . For technical purposes good values of LSF range between 80 to 95, and the all studied samples have a good value of LSF which are ranges between 87 to 94%. As a result of market requirements for cements from different sources to have similar properties and also to optimize clinker production there has been a trend to converge on a 'standard' clinker chemistry of lime saturation factor (LSF) is Lime saturation factor is measure the ability of the blend to react leaving no free lime. The lime saturation factor can be calculated as: $LSF = CaO / (2.8 SiO_2 + 1.2 Al_2O_3 + 0.65 Fe_2O_3)$.

At most plants the achievement of this ideal chemistry will require the use of corrective materials such as sand and iron oxide all modulus estimated for formed clinker run an acceptable ranges and their accuracy of them closed to the British standard.

4. Conclusion

About twelve samples of limestones and six samples of terra rossa were subjected to inductively coupled plasma-mass spectrometry (ICP-MS) technique as well as of nine homogeneous samples for clinkers and cement powdered were subjected to X-ray fluoresces (XRF) technique. The chemical composition shows that Al Fatiah Quarry is classified as high pure limestone and Al Huaryr Quarry is classified as low pure limestone, but after treatment and adds high grade limestone can be used for cement production. The studied terra rossa samples show a suitable composition and could be a good source for SiO_2 and Al_2O_3 . The XRF analysis of clinkers and cement powdered showed that the alite and the belite represented as a major mineral phases aluminate and the aluminate ferrite represented as a minor mineral phases while periclase phase and free-lime occurred as fine very fine grain or trace mineral phases and they are not effected in quality of cement. All the amounts of CaO , SiO_2 , Al_2O_3 and Fe_2O_3 and all the modulus estimated for formed clinkers are running an acceptable ranges and their accuracy of them closed to British standard. The comparative study between Al Fatiah and Al Huaryr Factories are recommended to encourage quality production.

5. Recommendations

The uses of limestone are widely utilized in many industries such as general constructions and non-constructions: glasses and aggregates, mind dust, paper, paints, rubbers, iron steels, plastics soda ash and oil drilling fluid materials. This project it may need further study using other techniques such as Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD).

Acknowledgement

First of all, we would like to thank Allah for all benefits. Authors are thankful and acknowledge to all staff members of Nuclear Materials Authority of Egypt and Al Fatiah and Al Huaryr Cement factories of Libya for their supports and encouragements for Department of Earth sciences.

References

- Aldieb, M.A. and Ibrahim, H.G. (2010): Variation of feed chemical composition and its effect on clinker formation-simulation process. World Congress on Engineering and Computer Science (WCECS); Vol. II, San Francisco, USA.
- Al Juboury, A. I and McCann, T. (2008): The Middle Miocene Fatha (Lower Fans) Formation, Iraq. GeoArabia, Middle East Petroleum Geoscience; 13(3):141-174.
- Berggren, W. A. (1974): Late Paleocene-Early Eocene benthonic foraminifera biostratigraphy and paleoecology of Rock all Ban, Micropaleontology; 20: 462-448.
- Brandt, A. M. (2009): Cement-Based Composites. 2nd ed. Taylor and Francis, London, UK. 536P
- Deborah, N. H. and Thomas, D. E. (2009): A life-cycle assessment of Portland cement manufacturing: comparing the traditional process with alternative technologies. Journal of Cleaner Production; 17: 668-675.
- Ghosh, S. N. (2002): Advances in cement technology; Chemistry, Manufacture and Testing. 2nd ed., Tech. books international, New Delhi, India. 804P.
- Harries, P. T. (1983): Limestone and dolomite mineral resources consultative committee. minerals strategy and economics research. Unit. Institute of Geology Science. Mineral Dossier. pp. 23 - 111.
- Kebede, M. A. (2010): Investigation of calcite and volcanic ash for their utilization as cement filling and additive materials. MSc. Thesis; Addis Ababa University, Ethiopia, 75P.
- Kesler, S. E. (1994): Mineral resources, economics and the environment. Macmillan college publishing company, New York, 391 pp.
- Kohlhaas, B. (1983): Cement engineer's handbook. 4th ed. Bauverlag GMBH, Wiesbaden and Berlin, Germany, 794P.
- Khan, M. I.; Hossain, M. S. and Ali, I. A. (2008): Chemical analysis of ordinary Portland cement of Bangladesh. Chemical Engineering Research Bulletin; 12: 7 -10.
- Klen, I. (1974): Geological map of Libya 1:250000. Sheet. NI 34-14, Benghazi Explanatory Booklet. Indust. Resear. Cent. Tripoli, 56 pp.
- Rao, S. D.; Vijayakumr, T. V.; Prabhaka, S. and Raju, B. G. (2011): Geochemical assessment of a siliceous limestone sample for cement making. Chinese Journal of Geochemistry. 30: 30-39.
- Tennis, P. D. and Kosmatka, S. H. (2011): Cement characteristics in innovations in Portland cement industry. 2nd ed., Portland Cement Association (PCA). Illinois, USA. 1734P.
- Moore, C. (1982): (BS 12-78) British standard for cement Portland grey grade 42.5 chemical control of Portland cement clinker. Ceramic Bulletin; 61(4): 511-515.
- Winter, B. N. (2013): Understanding cement. WHD Microanalysis Consultants Ltd. United Kingdom. P.5.