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Evaluating the Suitability of Fa'tha Marl, Zurbatiyah Area-Wasit Governorate for Cement Industry

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Abstract: The marl rocks of Fat'haFormation in Wasit Governorate in the Zurbatiyah Area East-Iraq for the purpose of studying their suitability in the cement industries. Chemical, physical and engineering tests were carried out on the rocks of the study area. The chemical tests of the marl rocks showed that the calcium oxide range between 37.12-45.9% with average 41.42%. Silicaoxide ranged from 13.11-23.4 with average 17.37% as well as a appropriate percentage of iron and aluminum oxides and very low percentage of sulfur and magnesium oxides. The physical tests showed high values of dry density and true specific gravity. In addition, the porosity values are moderate while the values of water absorption are moderately too. The uniaxial compressive strength values classified as moderately strong. These results of the study are identical and within the permissible limits of the marl rocks in the cement industry.

Key words: FathaFormation, cement industry, geochemistry marl, petrophysicaltest, Zurbatiyah, moderately

INTRODUCTION

The marl is an important sedimentary rock which supply both carbonate and caly that are the essential components in raw mix. In this study, we have study the major oxides of marl in FathaFormation in order to assess it's validity for cement manufacturing. Clinker production requires a specific mix of limestone, clay and some additives in order to obtain a good mix for its production Fig. 1. The oxides in the marl must be accurately identify

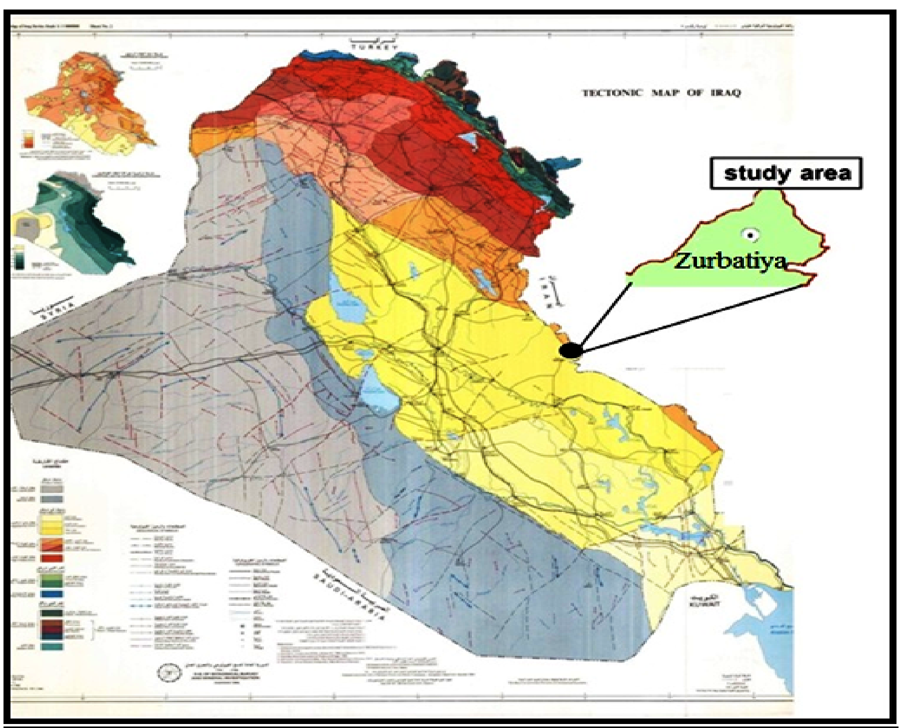

Fig. 1: Tectonic map of Iraq, modified from (Jassim and Goff, 2006), explain the location of the study area

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for the correct calculation of the potential clinker product. This study, looking for new resources (FathaFormation) can be used with some improvement additives in cement industries. The reserves of the marl in FathaFormation appear to be quite large (Neville and Brooks, 2010).

Geological setting: The study area is represented by one section in Zurbatiya area within the district of (Bedra) in Wasit Governorate, Southeast Iraq, Fig. 1 represent tectonic map of Iraq and location of study area. This area is located between latitudes (46°06’035”) and (46°06’ 286”) to the North and longitudes (33°16’275”) and (33°16’463”) to the East, it far 18 km from Badra district.

The age of FathaFormation is middle Miocene, their type locality is located at the area of Al-Fat’ha 15 km North of Biji city in the region where the Tigris river crosses the mountain Makhul-Himren, it consist of strata of anhydrite, gypsum and limestone (Jassim and Goff, 2006). The lower contact is conformable, the underlying unit usually Euphrates and Jeribe Formations taken at the appearance of first gypsum bed, upper contact of Fatha Formation is always overlain gradationally and conformably by Injana Formation, the upper contact is taken on top of last gypsum bed and the appearance of sandstone (Buday and Jassim, 1984). The formation is representing by neritic limestone at the base passing into not evaporate silt-grad clastic (Al-Naqib, 1959).

MATERIALS AND METHODS

In this study, 15 stations has been selected to study it. 15 samples were collected for chemical, physical, mechanical and mineralogical analysis, each sample weighting about 5-7 kg.

Geochemical analysis was carried out by weighting method in applied Geology Department Laboratories-University of Babylon.

Physical test which including; dry bulk density, true specific gravity, porosity and water absorption was carried out in Applied Geology Laboratories, University of Babylon. And-mechanical properties only the uniaxial compressive strength also carried out in Geology Department, University of Babylon.

RESULTS AND DISCUSSION

Geochemistry of raw materials: Table 1 shows the results of chemical analysis for marl and compared with (Chatterjee, 2018) in Table 2 which represent the typical limits of oxides for cement industry. Portland cement is mainly composed of CaO, SiO_2, Al_2O_3 and Fe_2O_3. The combined content of these four oxides (main components) is about 90% of the weight of the cement and the remaining 10% is composed of Magnesium (MgO), alkali (Na_2O and K_2O), Chloride (CL), SO_3, TiO_2, P_2O_5 and MnO (Al-Dabbas *et al*., 2013).

The percent of oxides in marl is near from the acceptable range which lead us to add some material as a corrected additive as limestone from the adjacent area as given in Table 3. For this correction four sample of limestone have been analyzed from the adjacent area to use it for design a mixture with good oxides boundaries.

Geochemistry of marl: The major chemical oxides of marl (Free LOI) is given in Table 2. Calcium oxide (CaO) Calcium Oxide (CaO) is the highest component of the studied marl. The concentration of calcium oxide is high in all studied stations, ranging between 53-65.43% with average 60.27%. These ratios are close to the natural limits according to Chatterjee (2018) as shown in Table 2 CaO is the primary oxide used in the cement industry to interact with oxides; Al_2O_3, SiO_2 and Fe_2O_3. Lime content is very effected component because low lime content lead to lower early strength and unsoundness at high lime content (Duda, 1985). Early strength associated with high lime content. To increase strength, it is necessary to raise lime content or fine grinding or both

Table 1: Results of chemical analysis (wt.%) of the studied marl

St. No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	Mgo	SO_3	Na_2O	K_2O	LOI	Total (%)
1	15.76	3.82	5.10	41.00	0.66	0.39	0.23	0.12	31.16	98.24
2	18.32	4.60	0.93	42.47	0.96	0.30	0.34	0.21	30.54	98.67
3	13.11	3.64	3.92	42.11	0.71	1.50	0.05	0.03	33.21	98.28
4	16.66	4.32	0.68	44.98	0.94	0.29	0.06	0.043	31.26	99.233
5	13.93	4.38	4.21	45.90	0.46	0.03	0.11	0.24	29.59	98.85
6	15.11	6.64	3.36	43.41	0.44	0.06	0.23	0.39	29.32	98.96
7	19.54	2.59	3.40	41.39	0.31	0.13	0.41	0.63	31.27	99.67
8	21.38	5.81	0.74	37.12	0.96	0.14	0.43	0.31	32.61	99.50
9	16.76	3.62	3.04	42.67	0.83	0.49	0.67	0.06	32.27	100.41
10	14.13	6.36	4.36	38.79	0.88	0.10	0.73	0.29	32.43	98.07
11	17.47	5.40	3.21	41.29	0.35	0.14	0.45	0.43	29.73	98.47
12	15.61	2.81	5.96	42.61	0.96	0.30	0.29	0.17	30.12	98.83
13	20.12	2.23	3.38	40.11	0.56	0.12	0.16	0.22	31.22	98.12
14	19.25	2.19	2.40	40.32	0.51	0.42	0.25	0.31	34.27	99.92
15	23.4	4.60	2.40	37.19	0.13	0.31	0.54	0.67	30.13	99.37
Average	17.37	4.20	3.14	41.42	0.644	0.314	0.33	0.27	31.27	98.97

Table 2: Chemical analysis for marl (free LOI) and compared with oxides boundaries of typical raw mix material (Chatterjee, 2018)

Oxides	Min	Max	Average	Typical oxides boundaries
CaO	53	65.43	60.27	63-65
SiO_2	19.62	33.49	25.28	20-23
Al_2O_3	9.41	3.24	6.1	4-8
Fe_2O_3	0.98	7.4	4.56	3-5
MgO	0.18	1.42	0.94	2-3
SO_3	0.08	2.24	0.46	2.0-3.5
(Na_2O+K_2O)	0.07+0.04	1.08+0.95	0.48+0.4	0.4-1.2

Table 3: Chemical composition of limestone in surrounding area

St. No.	SiO_2	Cao	MgO	SO_3	Al_2O_3	Fe_2O_3	LOI	K_2O	Na_2O	Percentage
1	4.61	51.09	0.96	0.30	1.37	0.58	40.50	0.29	0.22	99.92
2	4.20	52.70	0.61	0.31	1.02	0.48	41.07	0.23	0.22	100.84
3	3.50	51.86	1.03	0.35	1.68	0.78	39.32	0.36	0.38	99.26
4	3.98	51.90	0.46	0.10	0.89	0.46	41.53	0.25	0.36	99.93
Average	4.07	51.88	0.76	0.26	1.24	0.575	40.60	0.28	0.29	99.98

Table 4: The designed raw material calculation (%)

Oxides	Raw material free LOI		Percent of raw material		Raw mix design		
	Marl (%)	Lime (%)	Marl (%)	Limestone (%)	Marl (%)	Limestone (%)	Total
CaO	60.27	87.35	79	21	47.6100	18.39	66.00
MgO	0.93	1.28			0.750	0.27	1.02
SO_3	0.45	0.44			0.350	0.1	0.45
SiO_2	25.27	6.85			19.96	1.44	21.40
Fe_2O_3	4.95	0.96			3.910	0.21	4.12
Al_2O_3	6.65	2.08			5.250	0.44	5.69
Na_2O	0.33	0.5			0.265	0.105	0.37
K_2O	0.27	0.47			0.210	0.1	0.31
Total	99.12	99.93			78.30	21	99.36

Table 5: Result of calculated kiln feed parameters

LSF	SSF	HM	AR	SR	CS
0.95	0.915	2.11	1.38	2.18	3.08

(Al-Uwaidi, 2013). However, high temperatures are required to burn high lime mixtures (Neville and Brooks, 2010). The marl loss about 31.27% of it's weight in calcination as show in Table 1.

Silica (SiO_2) after some additives material this percentage can be acceptable to produce Portland cement according to Chatterjee, 2018, respectively (Table 2). SiO_2 percentage ranging 19.62-33.49% with average 25.28% estimated for free LOI. Alumina oxide ranging between 9.41-3.24% with average 6.1% in marl.

The iron oxide (Fe_2O_3) the iron come as oxides and sulphides form as impurity in marl which at high amount can lead to deterioration in the building (Ali and Shah, 2008).The studied marl samples has concentration of Fe_2O_3 ranging 0.98 to 7.4 with average 4.56. This percentage is reasonable according to (Chatterjee, 2018) (Table 2).

Magnesium oxide the source of MgO is the thermal disintegration of dolomite at (700-750°C) which consist the MgO (Al-Samarrai, 2010).The maximum limit of this oxide is (6%) according to (ASTM C 150-02 a, 2002). The permitted percentage of this oxide in Portland cement varies from case to case depended on nature and availability of raw material. Most of studied sample has low concentration of MgO ranging 0.18-1.42% with average 0.94, this indicates that all samples are acceptable for national specifications for the production of (Ordinary Portland Cement) and (IQS, No. 5, 1984).

The concentration of Na_2O and K_2O the argillaceous and calcareous are the main source of alkalis (sodium and potassium enter in the crystalline structure) (Al-Samarrai, 2010). Some alkaline volatilities occur during combustion and dust from cement kilns with a relatively higher alkaline ratio than the raw mixture that feeds the kiln. The concentration of alkalis is within the acceptable range according (Chatterjee, 2018) (Table 2)

The sulpher added as gypsum $CaSO_4{\cdot}2H_2O$ to the clinker during the grinding process. The content of sulpher is 3.5% depending on the (ASTM C 150-02a, 2002). The marl rock has low content of sulpher oxides (0.08-2.24%) with average 0.46%. This percent is acceptable according to Chatterjee (2018) (Table 2).

Raw mix design: The raw mixture is an important stage of cement production. The purpose of raw mix is to supply the kiln with high quality raw and to ensure the produced cement have good quality. If the essential compound is not existed in the required amount, must use additives-materials to correct it (Duda, 1985), (Table 4) represent the designed raw mix and Table 5 represent the result of calculated kiln feed parameters.

Limestone saturation factor: This parameter have a great important in cement industry. The (LSF) represent the degree of Silica, Iron and Alumina convertion to the primary calcium compounds (Taylor, 1997). (LSF) is a critical contral ratio which determined by ratios of lime (C) to Alumina (A), Silica (S) and Iron (F). The range of (LSF) must be between (0.66-1.2) (Taylor, 1997) at calculation from the following equation:

$$LSF=\frac{100°C}{2.8(SiO_2)+1.18(Al_2O_3)+0.65(Fe_2O_3)} \quad (1)$$

This equation control the relative proportion of C3S and C2S. Clinker with higher LSF will have a C3S to C2S ratio higher than clinker with low LSF (Kebede, 2010). LSF's best limits in standard Portland cement according to Duda (1985) is range from 0.90-0.95. The range used in Iraq cement factories ranges within (0.88-0.90) for (LSF) according to the manufacturing process in these factories. LSF value is 0.95 as estimated for designed mix is with acceptable ranges according to Duda (1985).

Silica saturation factor: It efficiently combines silica with residual lime after formation of C_3A and C_4AF. Which is maintained between 0.85 and 0.95 can give a very satisfactory cement (Kebede, 2010).The estimated value for the designed mixture 0.915 is within the acceptable range. The equation use it to calculate SSF is:

$$SSF=\frac{\left[CaO-(1.65Al_2O_3+Fe_2O_3+0.7SO_3)\right]}{2.8SiO_2} \quad (2)$$

Hydraulic Modulus (HM): The hydraulic modulus represent the perfect lime content which ranges between 1.7-2.3 but the good quality is 2 (Ghosh, 2002). Increasing of HM mean more heat required for clinker burning. This lead to increase strength and heat of hydration but reduce the resistance for chemical attack (Rao *et al*., 2011). Hydraulic modulus calculating by the following equation:

$$HM=\frac{CaO\%}{(SiO_2+Al_2O_3+Fe_2O_3\%)} \quad (3)$$

The hydraulic modulus for this mixture is 2.11 which give the best lime content, generally, the cement with low HM (<1.7) shows low strength and cement with high HM (>2.3) shows poor stability of volume (Aldieb and Ibrahim, 2010).

Alumina Ratio (AR): This factor is also called "alumina modulus". Its represent ratio of alumina oxide to iron oxide:

$$AR=\frac{A\%}{F\%} \quad (4)$$

The alumina ratio value is 1.38 according to the designed mixture. This modulus shows the composition of the liquid phase in the clinker. The suitable value for (AR) should range between 1.3-2.8 but the perfect value is restricted between 1.4 and 1.6 (Peray, 1986). The AR is very important in order to determine the potential ratio of C_3A and C_4AF in the clinker which the increase of AR means more of C_3A and less C_4AF in the clinker (Kohlhaas, 1983; Kebede, 2010).

Silica Ratio (SR): This factor is also called "silica modulus" which is the percentage ratio by silica weight to the proportion of total alumina and ferric oxides (Czernin, 1980). Silica ratio shows if the cement is rich or weak in silica. In Portland cement, the average value of silica ratio ranges between (2.0-2.5). A high proportion of silica containing the value of convergence between (2.5-3.5) and the ratio is almost low silica (1.7-2.0):

$$SR=\frac{s\%}{(A+F\%)} \quad (5)$$

The silica ratio for designed mix is 2.18 lie within acceptable ranges. According to Duda (1977) the best range for the (SR) value in cement is between (2.2-2.6).

Calcium to Silica ratio (CS): The ratio of Calcium to Silica (CS).This ratio calculated in the following equation:

$$CS=\frac{c}{s} \quad (6)$$

The value of this ratio is 3.08 as estimated for the designed mix. Generally, in cement industry This ratio should be not <2 (Kebede, 2010).

Petrophysical properties of marl: Basic properties considered very important in the assessment of rock. Also, it gives a full description about type and validity of these rock as raw material which is represented by bulk density, specific gravity, water adsorption and porosity according to Anonymous (1984).

Porosity: The studied sample porosity ranges between 8.7-19.23%, Table 6 decreasing porosity produce high compressive strength which leads to difficulties in crushing and grinding of marl.

Table 6: Physical properties of marl

Station No.	Dry dencsity (gm cm^{-3})	Specific gravity	Porosity (%)	Water abs (%)
1	2.195	2.57	14.8	6.7
2	2.17	2.51	13.54	6.23
3	2.13	2.64	19.23	8.99
4	2.22	2.59	14.02	6.28
5	2.22	2.66	16.41	7.38
6	2.25	2.63	14.4	6.38
7	2.34	2.63	10.8	4.6
8	2.3	2.57	11.5	5.11
9	2.37	2.607	8.7	3.69
10	2.22	2.56	13.09	5.87
11	2.19	2.53	10.12	4.23
12	2.216	2.53	15.97	6.57
13	2.36	2.6	12.14	5.17
14	2.12	2.5	15.72	7.8
15	2.32	2.63	13.67	6.85
Avg	2.2414	2.5838	13.60733	6.123333

Table 7: Result of compressive strength for marl samples

St. No.	Load (N)	Area (mm)	qu (MPa)
1	150700	30.75510	4900
2	122200	24.93878	4900
3	115400	23.55102	4900
4	137500	28.06122	4900
5	119300	24.34694	4900
6	104300	21.28571	4900
7	160500	32.75510	4900
8	152400	31.10204	4900
9	223000	45.51020	4900
10	188000	38.36735	4900
11	150700	30.75510	4900
12	992000	20.24490	4900
13	137000	27.95918	4900
14	112000	22.85714	4900
15	107700	21.97959	4900
Average	138660	28.29800	4900

Dry density: Dry density of the studied samples ranging between 2.13-2.37 gm cm^{-3} (Table 6). Low porosity sample give high value of dry density.

Water absorption: The water absorption for the studied sample ranged between 3.69-8.99% (Table 6) water absorption increasing with increasing porosity.

True specific gravity: True specific gravity of marl ranges between 2.64-2.5 (Table 6). The differences between true specific gravity and density indicated a moderately porous for a study samples.

Uniaxial compressive strength: Compression strength is defined as the resistance of the rock to the stress applied on it. It is measured by placing an load on the body in two opposite directions and continuously until the collapse occurs. Stress is the resistance of the body and the unit of measurement is N/m^2 or Pascal (Pa) and depends on the mineral composition of the rock, fabric, hardness, porosity and water adsorption. Moreover fracture and joints affect the compressive strength of sample.

The compressive strength was obtained for 15 sample of marl using uniaxial compressive strength (CCT 200 Model) in Babylon University (Table 7) the compressive strength of the studied samples ranges between (21.97-45.51 MPa). The marl classified as moderately strong. According to Dearman *et al*. (1972), the UCS of all studied samples are acceptable with standered world range.

CONCLUSION

The chemical analysis of the marl proved that the marl contains the ratio of oxides close to the limits required for the cement industry where it can be used as a raw material for the cement industry after adding a certain percentage of limestone to obtain the best ratios of oxides.

The value of the LSF for the prepared mixture is 0.95 which is appropriate with the wordly standard ranges for the cement industry petrophysical test of all samples show high specific-gravity, dry density and moderated porosity and water absorption which are in agreement with required standard ranges for cement industry. The UCS test for marl indicate that the marl classifing as moderatly strong in hence its require a sutable force for extraction and crushing process.

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