Journal homepage www.jzs.univsul.edu.iq
Journal of Zankoy Sulaimani
Part-A- (Pure and Applied Sciences)

Geochemical assessment of Naopurdan limestone for cement making - Chwarta area, Kurdistan Region, NE Iraq

Tola A. Mirza[1], Ibrahim M. J. Mohialdeen[1], Salim H. Al-Hakarri[1], and Chro M. Fatah[1]

[1]University of Sulaimani, School of Science, Department of Geology
E-mail: tola.merza@univsul.edu.iq

Article info

Original: 06.10.2015
Accepted:01.04.2016

Key Words:
Naopurdan, Red Bed Series, Limestone, Cement, Lime saturation factor.

Abstract

The Naopurdan limestone klippe is covering about 19.28 Km^{2}of Chwarta area-Sulaimani City. Fifteen samples were collected from this limestone body and analyzed by X-ray fluorescence technique. The analysis was carried out in Mass Cement Company. The Petrographical study revealed the presence of different fossil content such as Nummulitesspp (*N. perforates; N.milliucaput; N.globulosa; N.atacicus; N.bahyranses*)., Alvelinaspp(*A. eleptica; A. aragoensis; A. oblonga; A. fusiformis*)., Miliolina ; Algae (*Lithothaminum sp.; Cympolina sp.*); echinoid bioclasts; corals; and Orbitolites; Coskinolinasp; Somalina sp. Index fossils indicate the Middle Eocene age for this limestone body. The formaniferal wackestone and packstone microfacies are the most common facies in the studied samples, as well as recrystallized limestone observed in two samples. The depositional environment as deduced from lithology and fossil content is shoal marine environment.

Petrological study indicated that the limestone samples are crystalline and dominantly composed of calcite with $CaCO_3$ content more than 95 %. Geochemical analysis results of fifteen handpicked samples indicated that the limestone from the Naopurdan Formation shows LOI range between (38.50% to 43.29%), $Si0_2$ (0.11% to 7.92%), CaO (55.19% to 45.82%), $A1_2O_3$(0.01% to 0.97%), Fe_2O_3(0.02 % to .46%) and MgO 0.37 % to 4.29 %, K_2O, Na_2O, and SO_3 are present in traces. The lime saturation factors (LSF) of studied samples have widely differing values ranging from 188.64 to 7543.52, but most have values above the limits required for high quality cement. Thus a claystone rocks from Red Bed Series have been added to reach the best point of LSF of clinker. All materials after mixing proved that they meet the specification required for clinker production.

1. Introduction

Chwarta Town is located about 30Km to the NE of Sulaimani (*Figure:1*). It was directly build on a limestone body forming a high and steep cliff, this isolated body is called Naopurdan Limestone (sometimes series). This rock unit was defined for the first time by Bolton [1958] in Buday [1980] from Naopurdan Village in the Rawanduz River Valley. The Naopurdan Series consists of a heterogeneous sequence contains limestone, sandstone and shale. At least five units were distinguished [Buday, 1980], but not necessary all units appeared at the same place.

The limestone unit which is mostly composed of coralline limestone and nummulitic limestone is the subject of this study. There are some studies have been done on the Naopurdan Series such as; [Al-Hashimi, 1975; Surdashi, 1997; Al-Qayim et al., 2012], mostly dealing about stratigraphy, sedimentology, and paleontology of these rocks. There is no detailed geochemical work on these rocks, especially the limestone unit.

The main aim of this study is to examine this isolated limestone body to determine their suitability for the manufactureing of Portland cement.

Portland cement (often referred to as OPC, from Ordinary Portland Cement) is the most common type of cement in general use around the world because it is a basic ingredient of concrete, mortar, stucco and most non-specialty grout. Cement is a fine powder produced by grinding Portland cement clinker and adding about 3 % of Gypsum. Portland cement clinker is a hydraulic material which shall consist of at least two-thirds by mass of calcium silicates ($3CaO.SiO_2$ and $2CaO.SiO_2$), the remainder consisting of tricalcium silicate (C_3S) and tetra calcium aluminum ferrite (C_4AF) phases and other compounds.

The raw materials for Portland cement production are the mixture (as fine powder in the 'Dry process') of minerals containing calcium oxide, silicon oxide, aluminum oxide, ferric oxide, and magnesium oxide (Limestone and clay) which is produced by firing to partial fusion, at a temperature of approximately 1500°C. The raw materials are usually quarried from local rocks, which in some places is already practically the desired composition and in other places require addition of the clay and limestone, as well as iron ore, bauxite or recycled materials [Alemayehu and Sahu, 2013]. There are three fundamental stages in the production of Portland cement [Johansen etal, 2002]: (a) Preparation of the raw mixture, (b) Production of the clinker, (c) Preparation of the cement**.** This study focuses on the suitability of using limestone of Naopurdan Formation and clay from Red bed Series as main raw materials for manufacturing Portland cement. These two materials are present in huge amount as well as its close to the Sulaimani city in Chwarta area therefore this study examine these materials as essential raw materials for Portland cement.

2. Geological Setting:

The study area is located about 30 km to northeast of Sulaimani city, close to Chwarta Town *(Figure:1& 2)*. The area has complexity in structure and stratigraphy as it is located in the Penjween-Walash Zone of the Zagros Suture Zone [Jassim and Goff, 2006]. The central part of the area is occupied by ophiolite and Naoperdan Series while the northern and southern parts are covered partly by Qulqula Group and Cretaceous Rocks respectively [Karim, 2005].

The Penjween-Walash Zone is a unit of the main (Central) Neo-Tethys *(Figure:2).* It composed of volcanosidimentary sequences formed during Cretaceous ocean spreading in the Neo-Tethys, and Paleogene arc volcanic and syn-tectonic basic intrusions formed during the final closure of this ocean. The zone is thus a remnant of the Neo-Tethys which was thrust over the Arabian Plate during Miocene- Paleocene time. The main structural features of the zone are thrust sheets sometimes dislocated by reverse faults [Jassim and Goff, 2006]. The Penjween-Walash Zone consists of three thrust sheets: the structurally lowest Naopurdan, the middle Walash and the upper Qandil (structurally highest).

The outcrops of these rocks form a tongue, which elongates from the north (from Iranian border) towards the south and ends near Chwarta Town. Its central part consists of ophiolite and metamorphic rocks surrounded by the outcrops of Red Bed Series and Naopurdan Series. This tongue is called MawatNappe by Al-Mehaidi[1975] who studied that this Nappe is underlain by Red Bed Series and Cretaceous rocks.

The Chwarta- Mawat area consists of a large graben which was formed by two transverse normal faults. Geographically, the northern part of the area is occupied by ophiolite (Late Cretaceous) and Naoperdan Series thrust sheets while the northeastern part is covered by the Qulqula Formation (Early Cretaceous). This front (as a nappe) is most probably attributed to the subsidence due this graben [Karim, 2005].

The Red Bed Series and Naoperdan Series have relatively wider distribution of outcrops *(Figure:2)*, than in the neighboring areas. In these areas such as Qandil Mountain toe and Penjween area these units have narrow outcrops. The wide outcrops of the two units are indirect evidence to the subsidence of the area which preserved these two series from more tectonic deformations and erosion.

Naoperdan rocks in this region closes to Chwarta Town, is forming a Klippe *(Figure: 3)*.Klippe is an erosional outlier of a thrust sheet (nappe) that is completely surrounded by footwall rocks [Fossen, 2010]. The main raw materials in manufacturing Portland cement are limestone and clay, therefore for this study in addition to limestone two clay samples from the Red Bed series were taken: one sample from the middle part of Red Bed Series at Qallachwalan area which consists of brown to pale brown clay deposits with thickness of 10-12 m and represented by sample R1, the second sample R2 took from the upper part of Red Bed Series at ShakhaSur resort which composed of red claystone and siltstone with the thickness of about 10 m and extend over the large area as well as thick beds of conglomerate present at the top the clay sample.

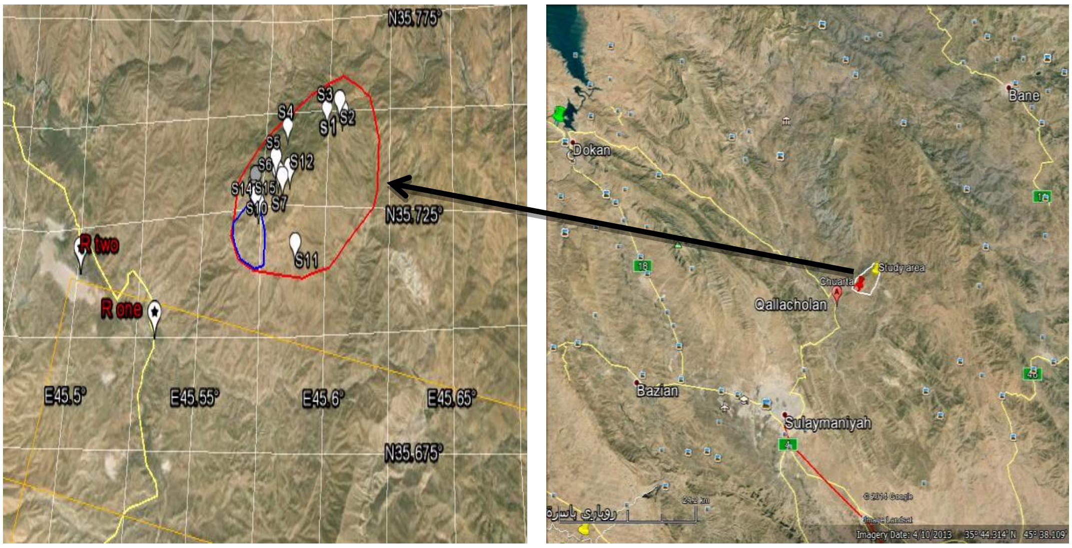

Figure-1: Satellites images of the studied area show the location of samples, Sulaimani Governorate, Kurdistan

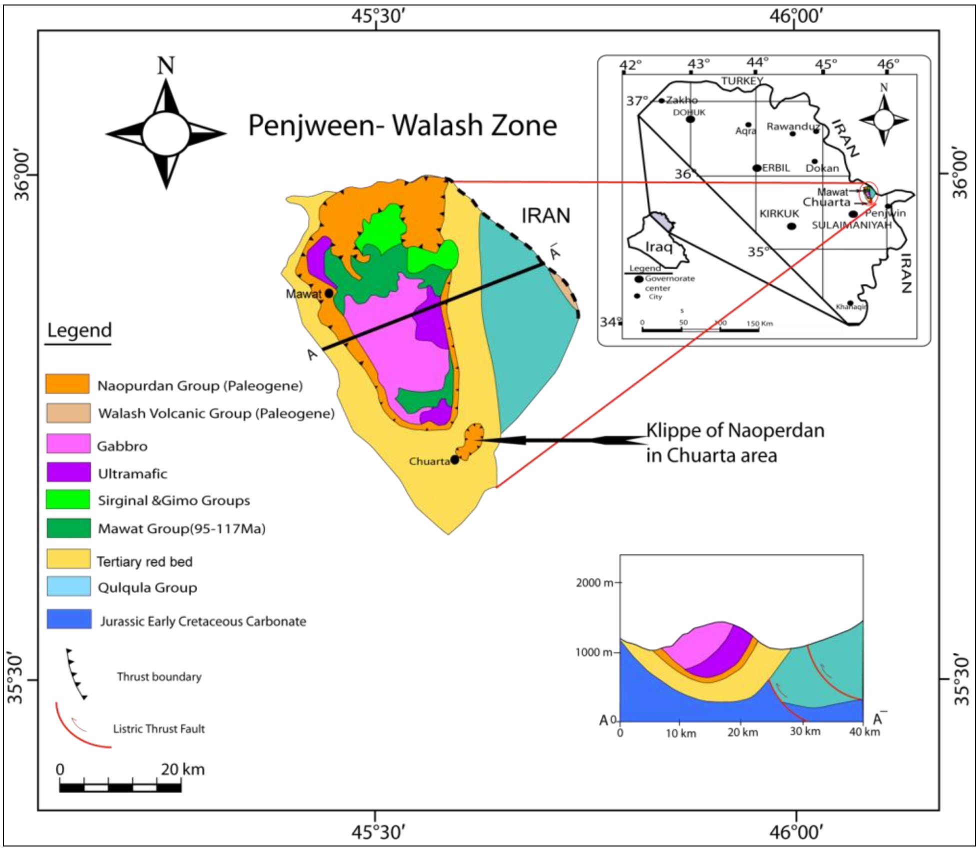

Figure-2: Geological map and cross section of Penjween-Walash Zone (Modified from Jassim and Goff, 2006) shows the Klippe of Naoperdan in Chwarta area.

3. Samples and Methods:

Fifteen samples from limestone of Naopurdan Klippe (S1-S15) and two clay samples from Red Bed Series (R1 and R2) were collected to study their suitability for normal Portland cement manufacturing. The limestone body of Naopurdan Series is allochthonous, hence it is difficult to divide the body to lower and upper parts, as well as the collected samples will be random and not in a stratigraphic sequence. The collected samples represent most outcropped parts of these rocks, as 15 samples were collected from limestone of Naopurdan and two samples from claystone of Red Bed series *(Figure: 1).*

Geochemical analysis for limestone samples were carried out in Mass Cement Company using XRF typeMDX1000 Cox ford Model EG50H (RH) and for the claystone samples R12 and R6 the geochemical analyses were done in Washington State University using XRF type Thermo-ARL Advant´XP+ X-ray fluorescence spectrometer (XRF) at GeoAnalytical laboratory, School of Earth and Environmental Sciences, Washington State University.

Mineralogical analysis of the clay samples was carried out by X-Ray Diffraction (XRD) technique in X-Ray Laboratories of the Iraqi Geological Survey- Baghdad. Many types of clay and non-clay minerals have been identified on the basis of their diffraction pattern.

Ten of the limestone samples were subjected to petrographical study by preparing thin sections in order to study these samples under polarized microscope.

4. Results and Discussion

4.1 Petrography:

After collecting limestone samples from the Naopurdan Limestone body, location for each sample was defined on Figures 1, and 2. From total of 15 samples, thin sections were made from ten of them. The limestones as examined in the field are mostly pure calcium carbonate, sometimes fossiliferous and recrystallized with no effect of dolomitization. According to the description of Bolton [1958] in Buday, [1980] this limestone body is representing the coralline limestone horizon with coral-rich lower part and nummulitic upper part. He estimated the thickness of this unit as 150m and the age as Paleocene-Lower Eocene.

The petrographical examination of thin sections clearly indicates that the samples are mostly pure limestone, which different types of fossils have been recognized. The main constituents are foraminifera *(Figure:3Aand B),* algae (blue-green algae) (*Figure:.3C),* corals *(Figure:3D),* and Echinodermata bioclasts *(Figure:3E).* Different species of Nummulites, such as (*N. perforates; N.milliucaput; N.globulosa; N.atacicus; N.bahyranses*) have been recognized, which indicates shoal environment. Also different species of Alveolinaspp(*A. eleptica; A. aragoensis; A. oblonga; A. fusiformis*) have determined, in addition to few Miliolina species. Other fossils such as coral, algae (*Lithothaminum sp.; Cympolina sp*.); *Orbitolites; Coskinolinasp; Somalina sp.* These components together with the groundmass forming three major microfacies types which are foraminiferal wackestone and packstone as well as foraminiferal floatstone (*Figure:3B).* The major distributed microfacies are nummulitic packstone and Alveolina floatstone.

As the collected samples were from this allochthonous body, there is no indication for the upper and lower part of the body. Hence interpretation of microfacies will not be in a sequence or from lower to upper part. All these microfacies indicting a depositional environment of shoal/slope conditions [Flugel, 2010]. The presence of Nummulites, Alveolina, corals, and sandy facies are good indicator for the shoal environment [Al-Hashimi, 1975; Surdashy, 1997]. Two of samples were recrystallized limestones *(Figure:3F)* without any observing of dolomite crystals (after staining). This isolated body of limestone interpreted by Al-Qayim et al. [2012] as shallowing-upward sequence of slope to shallow platform facies.

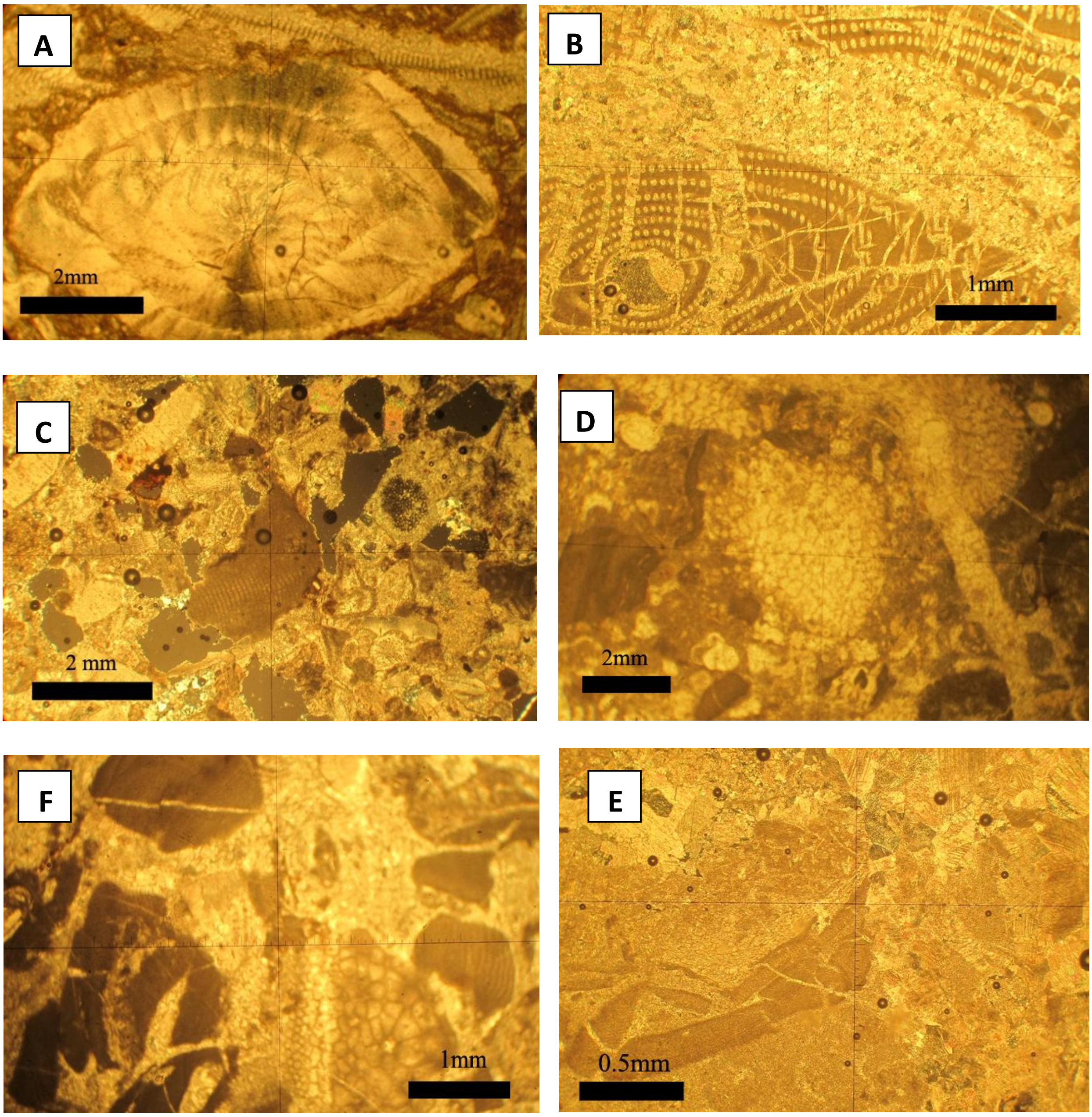

Figure-3.Photomicrographs of different constituents and microfacies of Naopurdan limestone body from Chwarta Area, Sulaimani, Kurdistan. **(A)**Nummulitic limestone (*N. perforates*) Sample No.9, PPL. **(B)** Foraminiferal floatstone (*Alveolinarugoza*), Foraminiferal Floatstone, Sample No. 10,PPL **(C)** Blue-green algae (*Lithothaminumsp*), Sample No.2,XP. **(D)** Coral patch, Sample No.1, PPL**. (E)** Echinodermata bioclasts within algae-rich limestone, Sample No.8, PPL. **(F)** Recrystallized limestone with few patches of algae, Sample No.3, XP.

4.2 Mineralogy of clay samples:

The mineralogical composition of clay samples consists of clay minerals and non-clay minerals. The clay minerals are represented by smectite, Illite, as a major proportion, and chlorite as a minor proportion *(Figure. 4 B)*. The non-clay minerals are dolomite, as a dominant mineral followed by quartz and very few percentages of plagioclase, hematite and calcite *(Figure. 4 A).*

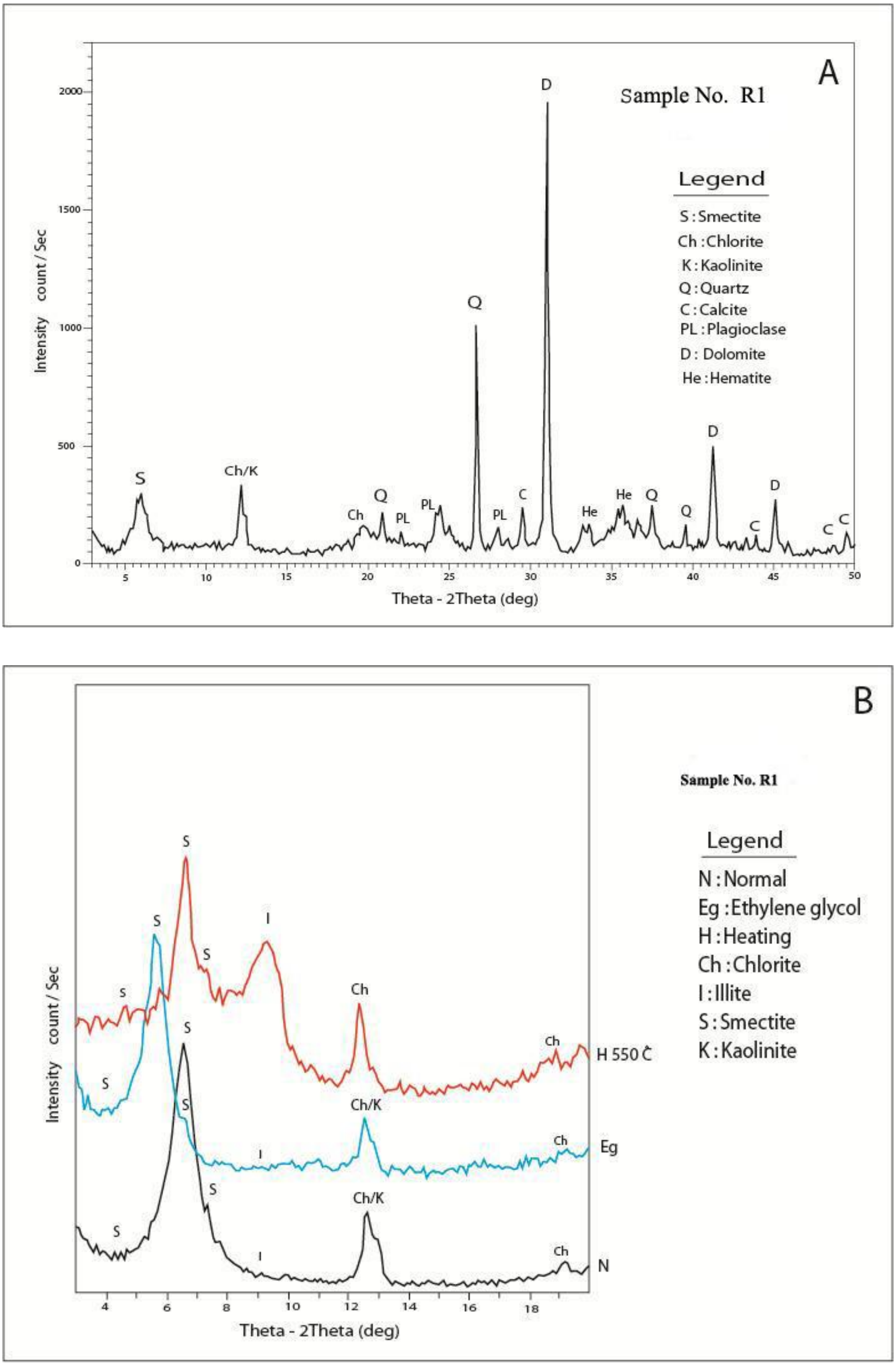

Figure- 4: X-Ray Diffraction pattern of clays from Red Bed Series, sample No.R1. A: Bulk sample B: Oriented sample

4.3Geochemistry

The chemistry of the cement in general and Portland cement in particular largely depends upon the geochemistry of its raw materials, i.e., limestone and clay. About 75 % of Portland cement raw materials consist of lime (CaO) – bearing materials [Lea, 1976 and Raoet. al. 2011].The major elemental chemistry of the limestone samples from Naopurdan Formation are represent in Table 1**.** Geochemical analysis revealed that the limestone contain lime as major constituent varies between 45.82 % to55.11 % and is due to calcite content in limestone, followed by Loss On Ignitions LOI (Table 1). The LOI content is generally contributed with carbonate minerals. Silica, Alumina, iron and Magnesia form the minor constituents, as alkalis (soda and potash) and SO_3 are present in traces. The SiO_2 content in limestone vary between 0.11 % to 7.92 % which is may be due to detrital quartz grains.

It seems that the limestone samples can be directly used in cement industries as the samples contain silica less than 8 %. Along with the other constituents that are usually important is MgO it ranges between 0.37 % to 4.29 % (Table 1) which might have been resulting from the magnesium –rich calcite shells or due to post depositional digenesis (dolomitization). High magnesium concentration in the clinker is limited to less than about 5% because it might cause destructive expansion in mortar and concert [Thanoon, 1999].SiO_2, $A1_2O_3$, Fe_2O_3 beside CaO of the limestone form the main ingredients that compose the cement but should be within permissible limits. Total alkali content (Na_2O+K_2O) should not exceed 0.6% [Duda, 1985] because during burning process in rotary kiln parts of alkalis evaporate in burning zone causing the so- called alkali circulation which reacts with amorphous silica in aggregate that are sensitive to alkalis such as opal , chalcedony and obsidian result in alkali expansion (alkali aggregate reactivity). The total alkali content of studied limestone samples is below 0.2 % and that means all samples within permissible limits.

The major elemental constituents of studied clay samples R1 and R2show that the SiO_2 is the most abundance oxide and varies from 50.7% to 55.07 % (Table 1). The composition of studied clayey samples were compared to normal clay (N.C) (Table 1) it appears that all oxides in these two samples have more or less comparable to that normal clay except CaO % manifold higher in the studied clay as compared to that of normal clay.

4.4Lime saturation factor (LSF)

The LSF is a ratio of CaO to the other three main oxides. Applied to clinker, it is calculated as: LSF=100 CaO/ ($2.8\ SiO_2+1.2\ A1_20_3+0.65\ Fe_2O_3$). Often, this is referred to as a percentage and therefore multiplied by 100 and this is mostly applied to clinkers. The LSF factor is limited – to assure that the lime in the raw materials, used in the cement manufacturing is not so high, so if the LSF exceeds 100% then there is likely to be uncombined free lime in the clinker [Al-Obaidy, 2010]. The higher the LSF (up to 100% the more C_3S there will be in the clinker, but the higher will be the thermal energy consumption of the kiln. While too low a LSF would make the burning in the kiln difficult and the proportion of C_3S in the clinker would be too low. Typical LSF values in modem clinkers are 92-98. Values above 100 indicate that free lime is likely to be present in the clinker [Rao, et al, 2011 and Amin, 2014]. This is because in principle at LSF=100 all the free lime should have combined with belite to form alite. In practice, the mixing of raw materials is never perfect and there are always regions within the clinker where the LSF is locally a little above, or a little below, the target for the clinker as a whole. This means that there is always some residua1 free 1ime, even where the LSF is considerably below 100. It also means that to convert virtually all the belite to alite, an LSF slightly above 100 is needed. Referring to Table 1, it can be shown that the samples have widely differing LSF values ranging from 188.64 to 7543.5 but most have values above the limits required for high quality cement. Thus a claystone rocks have to be added to reach the set point of LSF in the clinker. For this, the range of raw mixes (Clay and limestone) can be obtained from the materials to give a cement clinker with LSF of 94 are shown in Table 2

4.5 Silica modulus (SM)

The silica modulus represents the proportion of SiO_2 to the total Al_2O_3 and Fe_2O_3. The amount of melt phase in the burning zone is a function of SM. When SM is high the amount of melt is low & vice versa [Alemayehu and Sahu, 2013]. Therefore, higher the silica modulus harder to burn and exhibits poor coating properties as well as a high silica modulus means that more calcium silicates are present in the clinker and less aluminate and ferrite. SM is typically between 2.0 and 3.0 for Portland cement clinker. The SM governs the proportion of silicate phases in the clinker. The SM for the most current samples less than 3 except samples S3,S6, S13, and S15 (Table 1) which indicate that these samples are higher in SiO_2 content and needs to be bring down to under the specified limits for cement production. Lower the silica modulus there may be more melt phase and coating can become thick and leads to ring formation and low early strength (3-7days) in the cement. The SM of some of the present samples is below 2 (Table 1) therefore needs to increase to specified limits sequentially to avoid ring formation in the cement. The chemical compositions of the limestone were adjusted by addition clay to keep the SM within the mentioned limits (Table 2).

4.6 Aluminum Modulus (AM)

The aluminum ratio characterizes the cement by the proportion of alumina to iron oxide: $AM= Al_2O_3/Fe_2O_3$. Generally the values of AM values are in the range from 1.5 to 2.5 and more (Duda, 1985). An increase in clinker AM means there will be proportionally more aluminate and less ferrite in the clinker. Clinker with higher the Alumina modulus results in cement with high early strength. The AM for the present samples ranges from 0.01 to 1.83 (Table 1) and generally are low therefore the chemical composition of the limestone were adjusted by addition clay to keep the AM within the mentioned limits (Table 2).

4.7 Hydraulic Modulus (HM):

The hydraulic modulus has the following form: $CaO / SiO_2 +Al_2O_3 +Fe_2O_3$. The hydraulic modulus of excellent quality cements was about 2. Cements with HM less than 1.7 showed mostly insufficient strength; cement with HM = 2.4 and more had poor stability of volume [Rao, et al., 2011]. In general the HM values for the studied samples are of excellent quality which is around 2.1 (Table 2).

4.8 Raw mixture composition:

If an essential component needed in cement raw mixture is no present in required amount, corrective ingredients are used as additives. Thus example for the completion of silica content sand and high silica clay are used as additives ingredients [Duda 1985].

The purpose of calculating the composition of raw mixture is to determine the quantitative proportionsof the raw component in order to give the desired chemical and mineralogical composition for the clinker. For the present samples the proportion of raw mix composition where calculated depending on the final equation limestone saturation factor (LSF) which was supposed by [Lea and parker, 1935] and mentioned in [Alao,1979] and modified by many, especially [Duda, 1977] and the required LSF is 0.94 (Table 2). The expected mixing ratio of both claystone of Red Bed Series with limestone was 1:3 (Table 2). The studied samples have widely differing LSF values ranging from 188.64 to 7543.5 but most have values above the limits required for high quality cement, therefore the claystone from Red Bed Series have been added to limestone in proportion 1:3 to set pointing clinker. Comparing the composition of raw mixture with the required standard specification for normal Portland cement it have been proved that all of the materials meet the specification required for clinker production and have a composition close to that of so called normal Portland cement (Table 2). The LSF value range between (93.83 - 94.18) in a raw mixture composition while without mixing all samples have widely differing LSF values ranging from 188.64 to 7543.5 and most have values above the limits required for high quality 83 - 94.19),therefore the mixing of raw materials were perform. The SM, AM are ranges between 2.26 to 2.93 and 1.42 to 2.49 respectively in raw mixture which are indicate within mixing all studied samples keep within standard limits.

4.9 Clinker Phases:

The properties of Portland cement are mainly determined by the proportion of its four principle clinker phases which are the impure forms of Ca_3SiO5 (alite), Ca_2SiO_4 (belite), Ca_3Al_2O6 (tricalcium aluminate) and C_4AF (tetracalcium aluminate ferrite). Other phases such as periclase (MgO), quartz (SiO_2), free lime (CaO), etc. may also be present in minor quantities, usually less than 1%w **[**Dutta, 2011]**.**

The C_3S and C_2S in the studied samples range between (42.99 -52.75), (23.62-31.92) respectively when LSF is equal to 0 .94 (Table 2). Comparing this result with typical constituents of C_3S in normal Portland cement [Newman, 2003, and Brand, 2009] (Table 3), it becomes clear that the C_3S and C_2S content of all the studied samples is within the range. The C3A and C4AF are ranges between (7.11-13.12) and (7.25 10.72) respectively. This indicates that all the studied samples are in agreement with typical constituent of normal Portland cement by Newman [2003] and Brandt [2009] (Table 3).

Table-1: Geochemical analysis of Naopurdan limestone samples (S1-S15), clay samples from Red Bed Series (R1, R2) and normal clay composition **(N.C)**

S. No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	L.O.I	Total	$CaCO_3$ %	LSF	SM	AM
S1	0.25	0.44	0.24	55.08	0.37	0.06	0.08	0.02	42.98	99.52	98.31	3979.77	0.37	1.83
S2	0.34	0.36	0.27	54.43	0.73	0.06	0.09	0.02	43.29	99.59	97.15	3490.22	0.54	1.33
S3	5.11	0.44	0.36	50.42	2.26	0.09	0.10	0.08	40.53	99.39	89.99	334.57	6.39	1.22
S4	6.21	0.59	1.45	48.85	2.94	0.09	0.11	0.12	39.84	100.20	87.19	256.59	3.04	0.41
S5	0.62	0.06	0.34	54.33	0.88	0.06	0.08	0.03	43.02	99.42	96.97	2677.67	1.55	0.18
S6	0.77	0.02	0.03	54.15	1.47	0.06	0.09	0.02	43.36	99.97	96.65	2461.92	15.40	0.67
S7	1.92	0.36	0.27	53.85	1.10	0.08	0.10	0.07	41.79	99.54	96.11	899.98	3.05	1.33
S8	1.10	0.31	0.36	53.75	1.35	0.08	0.10	0.07	42.76	99.88	95.93	1458.22	1.64	0.86
S9	0.22	0.01	0.73	55.19	0.49	0.05	0.08	0.02	42.61	99.40	98.50	5005.90	0.30	0.01
S10	0.11	0.01	0.63	55.03	0.94	0.05	0.08	0.02	43.01	99.88	98.22	7543.52	0.17	0.02
S11	0.64	0.34	0.29	55.03	0.98	0.06	0.08	0.02	42.60	100.04	98.22	2303.96	1.02	1.17
S12	7.92	0.97	1.46	45.82	4.29	0.10	0.13	0.11	38.50	99.30	81.78	188.65	3.26	0.66
S13	0.98	0.10	0.02	54.34	0.92	0.04	0.08	0.01	42.76	99.26	96.99	1888.77	4.26	0.77
S14	0.48	0.07	0.19	55.11	0.95	0.04	0.07	0.03	43.11	100.04	98.36	3552.05	1.85	0.37
S15	1.90	0.01	0.24	53.96	0.87	0.06	0.09	0.01	42.61	99.75	96.31	983.24	7.60	0.04
R1	55.07	13.69	5.99	6.97	3.06	1.58	1.89	0.01	10.15	98.41				
R2	50.70	14.80	6.00	9.5	3.17	0.97	3.04	0.03	10.03	98.24				
N. C	**50.33**	**19.17**	**6.50**	**1.43**	**3.77**	**0.81**	**2.32**							

Table -2: Cement clinker composition with LSF of 94 calculated from binary combination of Naopurdan limestone S1-S15) and clay of Red bed series sample (R1) with SR,AR, main miner phase component in clinker.

		Sample Nombers														
	Requirment	**S1+R1**	**S2+R1**	**S3+R1**	**S4+ R1**	**S5+R1**	**S6+ R1**	**S7+R1**	**S8+ R1**	**S9+R1**	**S10+R1**	**S11+R1**	**S12+R1**	**S13+R1**	**S14+R1**	**S15+R1**
	X=	X=0.272	X=0.270	X=0.208	X=0.187	X=0.269	X=0.269	X=0.253	X=0.262	X=0.274	X=0.276	X=0.270	X=0.154	X=0.266	X=0.273	X=0.255
Raw Mix	Y=	Y=0.728	Y=0.730	Y=0.792	Y=0.813	Y=0.731	Y=0.731	Y=0.747	Y=0.738	Y=0.726	Y=0.724	Y=0.730	Y=0.846	Y=0.734	Y=0.727	Y=0.745
	SiO_2	14.51	14.18	14.78	14.70	14.34	14.45	14.49	14.33	14.30	14.32	14.40	14.65	14.45	14.44	14.58
	Al_2O_3	3.89	4.33	3.48	3.30	4.10	4.07	4.08	4.18	4.14	4.17	4.32	3.14	4.08	4.16	3.85
	Fe_2O_3	1.74	1.85	1.56	2.32	1.89	1.66	1.75	1.87	2.20	2.14	1.86	2.18	1.64	1.81	1.74
	CaO	42.79	42.34	41.94	41.52	42.32	42.18	42.67	42.20	42.72	42.51	42.78	40.25	42.46	42.70	42.67
	MgO	1.07	1.40	2.46	2.99	1.51	1.94	1.64	1.84	1.24	1.57	1.59	4.13	1.53	1.57	1.47
	SO_3	0.02	0.02	0.07	0.10	0.03	0.02	0.06	0.06	0.02	0.02	0.02	0.10	0.02	0.03	0.02
	Na_2O	0.46	0.31	0.28	0.26	0.31	0.31	0.31	0.32	0.31	0.31	0.31	0.24	0.29	0.30	0.30
	K_2O	0.55	0.90	0.72	0.67	0.89	0.90	0.86	0.88	0.91	0.91	0.89	0.59	0.88	0.90	0.86
	L.O.I	34.62	34.36	34.22	34.30	34.19	34.44	33.80	34.23	33.73	33.96	33.85	34.14	34.10	34.13	34.35
	ToTal	99.64	99.70	99.52	100.16	99.58	99.98	99.66	99.91	99.56	99.91	100.03	99.41	99.45	100.04	99.81
Clinker	SiO_2	21.68	21.70	22.64	22.32	21.93	22.04	22.00	21.82	21.72	21.72	21.76	22.44	22.11	21.91	22.26
	Al_2O_3	6.74	6.63	5.33	5.01	6.27	6.21	6.20	6.36	6.28	6.32	6.52	4.81	6.24	6.32	5.88
	Fe_2O_3	2.80	2.83	2.38	3.52	2.89	2.54	2.65	2.84	3.35	3.25	2.81	3.33	2.51	2.74	2.65
	CaO	65.15	64.80	64.24	63.04	64.72	64.37	64.80	64.25	64.89	64.45	64.65	61.68	64.97	64.79	65.17
	MgO	1.75	2.15	3.77	4.55	2.31	2.96	2.49	2.80	1.88	2.38	2.40	6.32	2.35	2.38	2.25
	SO_3	0.03	0.03	0.11	0.16	0.05	0.03	0.09	0.09	0.03	0.03	0.03	0.15	0.02	0.05	0.02
	Na_2O	0.48	0.48	0.42	0.39	0.47	0.47	0.47	0.48	0.47	0.47	0.47	0.36	0.45	0.45	0.45
	K_2O	1.37	1.38	1.11	1.01	1.36	1.37	1.30	1.35	1.38	1.38	1.35	0.90	1.35	1.36	1.31
	L.O.I															
	ToTal	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ratio	LSF*	94.12	94.12	94.01	93.88	93.87	94.04	94.19	94.02	94.00	93.96	94.14	93.83	93.95	94.18	94.01
	LSF**	94.00	94.00	94.00	94.00	94.00	94.00	94.00	94.00	94.00	94.00	94.00	94.00	94.00	94.00	
	SR	2.27	2.30	2.93	2.62	2.39	2.52	2.49	2.37	2.26	2.27	2.33	2.76	2.53	2.42	2.61
	AR	2.41	2.35	2.24	1.42	2.17	2.44	2.34	2.24	1.88	1.94	2.32	1.44	2.49	2.31	2.22
Clinker Phases	C_3S	51.09	50.20	49.93	47.92	50.48	49.10	50.88	48.69	51.99	50.17	49.87	42.99	50.87	50.80	52.75
	C_2S	23.62	24.36	27.24	27.83	24.78	26.15	24.70	25.84	23.06	24.41	24.78	31.92	25.00	24.48	24.04
	C_3A	13.12	12.78	10.10	7.30	11.71	12.15	11.93	12.04	10.98	11.24	12.53	7.11	12.30	12.11	11.09
	C_4AF	8.52	8.60	7.25	10.72	8.80	7.73	8.07	8.64	10.19	9.88	8.56	10.14	7.63	8.34	8.07
Clinker Properties	H.M.	2.09	2.08	2.12	2.04	2.08	2.09	2.10	2.07	2.07	2.06	2.08	2.02	2.11	2.09	2.12

Table-3: Mineralogical composition percent Portland cement, [after Newman, 2003 and Brandt, 2009]

Cement Notation	**Mineral Name**	**Typical level (Mass %)**	**Typical range (Mass %)**	**Chemical composition**
C_3S	Alite	57	38- 60	$3CaO.\ SiO_2$
C_2S	Belite	16	15- 38	$2CaO.\ SiO_2$
C_3A	Aluminate	9	7- 15	$3CaO.\ Al_2O_3$
C_4AF	Ferrite	10	6- 18	$4CaO.\ Al_2O_3.\ Fe_2O_3$

Conclusions:

1- Petrological studies indicated that the Naopurdan limestone samples are pure calcium carbonate, sometimes fossiliferous (The main constituents are formanifera) and recrystallized with no effect of dolomitization and dominantly composed of calcite. They have a simple mineralogy, and yet they have very small variation in lime contents and having a composition close to that of natural cement rock.

2- The geochemical results reflect the rising of the concentrations of CaO and loss on ignition, and the decrease of the concentrations of SiO_2, Al_2O_3, MgO, Fe_2O_3, SO_3, Na_2O, and K_2O. According to these geochemical properties, the tested samples are reliable as carbonate component for cement industry.

3- Silica modulus, Aluminum modulus and lime saturation factor from geochemistry data indicated that the limestone samples from the Naopurdan Formation can be utilized for cement industry process provided they are processed for beneficiation for silica, alumina and iron addition to required level by adding claystone from Red Bed Series to limestone in proportion 1:3 to set point in clinker.

Acknowledgements

The authors would like to thank Mass Cement Company for help with geochemical analyses. Also we would like to thank Professor Imad, M. Gafor (Department of Geology-University of Sulaimani) for his help in identification of micro fossils.

References:

- Alemayehu, F. Sahu, O. *"Minimization of variation in clinker quality":* Advances in Materials, Science Publishig Group, 2(2) :pp.23-28. (2013)
- AlObaidy,S.A.H.*"Geochemical,PetrographicandPetrophysicalstudiestoevaluatethesuitabilityoflimestoneforcementindustryintheoutcropsof Fatha Formation Sukkariaarea, westofBaiji":* Iraqi Journal of Science, Vol. 51, No. 1, pp. 107-122. (2010)
- Al-Hashimi, H.A. *"Contribution to the Stratigraphy and Micropaleontology of the NaopurdanShaly Group in Chwarta are, northeastern Iraq"*: Journal of the Geological Society of Iraq, special issue, pp. 27-36. (1975).
- Al- Mehiadi, H., *"Geological investigation of Mawat ñ Chwarta area, NE Iraq":* unpublished report, SOM Library, No. 609.(1 975).
- Al-Qayim, B. Omer, A. and Koyi, K. *"Tectono stratigraphic overview of the Zagros Suture Zone, Kurdistan Region, Northeast Iraq":*GeoArabia, v. 17, no. 4, p. 109-156. (2012).
- Amin, C. M. F. *"Assessment ofAvroman limestone Formation for Portland cement industry, Halabja area south-east Sulaimani, Kurdistan Region NE-Iraq":* Unpublished MSc. Thesis, University of Sulaimani, Department of Geology, 164p. (2014).
- Brandt, A. M. "Cement-Based Composites.2ndᵉd": Taylor& Francis, London, UK. 536P (2009).
- Buday, T. *"The regional geology of Iraq , Stratigraphy and paleogeography":* edited by Kassab, I.M. and Jassim S.Z., Dar Al- Kutib publishing house ,Mosel, Iraq, 445p. (1 980).
- Duda, W. H.*"Cement –Data Book'' International process engineering in the cement industry,3rd ed":*Bauverlag, GmbH, Wiesbaden and Berlin, Macdonald and Evans, London, 636P. (1985).
- Dutta, D.*"Utilization of Blast Furnace Slag as a Raw Material for Manufacturing of Portland Cement Clinker":* MS.C, thesis, National Institute of Technology Rourkela, Ceramic Engineering, p 67. (2011).
- Flugel, E. *"Microfacies of carbonate rocks":* Springer, Berlin, 984p. (2010)
- Fossen H. *"Structural geology":* Cambridge University Press, New York. USA. 479p.(2010)
- Karim, K.H. *"Some sedimentary structural evidence of possible graben in Mawat-Chuarta area, NE-Iraq"*: Iraqi Jour. Earth Sci., Vol. 5, No. 2, pp. 9-1 8. (2005)
- Jassim, S.Z. Goff, J.C.*"Geology of Iraq"*: published by Dolin, Prague and Moravian Museum, Brno, 341p.(2006).
- Johansen ,V.C. Hills, L.M. Miller F.M. and Stevenson, R.W. *" The Importance of Cement Raw Mix Homogeneity":* International Cement, Chicago, USA, online on America's Cement (2002)
- Lea F. M. *"Chemistry of Cement and Concrete (3 Edition) [M]":* Edward Arnold (Publishers) Ltd., U.K. (1 976).
- Newman, J. and Choo, B.S. *"Advanced Concrete Technology; Constituent Materials. 1st ed.":* Butterworth Heinemann, Elsevier, UK. 288P. (2003).
- Rao D . S. Vijayakumar, T_V.PrabhakarS.andBhaskar RajuG.*"Geochemical assessment of a siliceous limestone sample for cement making":*ChinJ.Geochem Vol. 30: pp.033-039. (2011).
- Surdashy, A. *"Depositional environment and post-depositional deformation of Naopurdanlimestone unit from Chuwarta-Mawat area, northeast of Iraq":* Iraqi Geological Journal, v. 30, p. 118-127. (1997).
- Thanoon, T. A. *"Assessment of Sheranish Formation from Sinjar area, NW Iraq for Portland cement Manufacture":* 4th Inter. Conf. On Geochemistry, Alex, Univ., Egypt. Sept., PP. 237-243 (1999).