Iraqi Bulletin of Geology and Mining Vol.12, No.1, 2016 p 65 – 72

SHIRANISH FORMATION IN GAROTA (SHAQLAWA, NORTH IRAQ) AS RAW MATERIAL FOR PORTLAND CEMENT MANUFACTURING

Rzger A. Abdula[1] and Rebwar N.S. Khailany[2]

Received: 10/ 03/ 2015, Accepted: 03/ 09/ 2015
Key words: Portland cement, Shiranish Formation, Garota, Kurdistan, Iraq

ABSTRACT

Limestone, the main raw material for cement production, is readily available in the Kurdistan Region. This study tries to evaluate the usage of the limestone from the Shiranish Formation for Portland cement production. Samples of limestone of this formation in Garota Village, Shaqlawa area are selected and analyzed for the major elemental oxides and the data are evaluated and compared with the available standard chemical analysis of raw limestones for Portland cement. In the sampled locality, the Shiranish Formation has a thickness and geomorphologic conditions that can easily be excavated and transferred to the site of cement production. The obtained data shows that only one sample among the selected samples is suitable for Portland cement production, but with minor addition of gypsum to enhance the SO_3 content, while the other samples are slightly below the lower limit of the usual range of Portland cement manufacture due to high content of silica.

تكوين شيرانش في منطقه گروته (شقلاوه شمال العراق) كمواد أوليه في صناعه السمنت البورتلاندي

رزگار عبد الكريم عبد الله و ريبوار نوري سعيد خيلاني

المستخلص

الحجر الجيري هو المادة الخام الرئيسية لإنتاج السمنت، متوفر بكثرة في إقليم كردستان. تحاول هذه الدراسة تقييم استخدام الحجر الجيري من تكوين شيرانش لإنتاج السمنت البورتلاندي. تم اختيار عينات من الحجر الجيري لهذا التكوين في قرية گروتة بمنطقة شقلاوة، وتم اختبارها مختبريا لمعرفة محتواها من أكاسيد العناصر الرئيسية، وتم تقييم البيانات الناتجة ومقارنتها مع المعايير القياسية المتوفرة للتحليل الكيميائي للحجر الجيري الخام المستخدم لانتاج السمنت البورتلاندي. وتكوين شيرانش في المنطقة لها سمك وظروف جيومورفولوجية تساعد في سهولة حفرها ونقلها إلى موقع لإنتاج السمنت. وتظهر البيانات التي تم الحصول عليها أن عينة واحدة فقط من بين العينات المختارة مناسبة لإنتاج السمنت البورتلاند بعد اضافه طفيفه من الجبسم لزيادة نسبة SO_3، في حين أن العينات الآخرى أقل قليلا من الحد الأدنى للنطاق المعتاد لصناعة السمنت نظرا لمحتواها العالي من السيليكا.

INTRODUCTION

Al-Sayyab *et al.* (1982) stated that the Shiranish Formation could be utilized for cement manufacture without giving any details. Later, Thanoon (1999) assessed the Shiranish Formation from Sinjar Area – NW Iraq for Portland cement manufacturing.

[1] Soran University, Department of Petroleum Geosciences, Soran, Kurdistan Region, Iraq, e-mail: rzger.abdula@soran.edu.iq
[2] Diroctorate of Geological Survey, Erbil, Kurdistan Region, Iraq, e-mail: rkailani@yahoo.com

The Garota Village is located in the High Folded Zone, five Km to the east of Shaqlawa Town and 50 Km northeast of Erbil (Fig.1).

Fig.1: Map of Iraq showing the study area

- **Geological Setting**

The Shiranish Formation has a wide geographic distribution in Iraq and surrounding countries, having outcrops in several localities within the High Folded Zone, and also recognized in NE Syria (Buday, 1980; Litak *et al*., 1998).

In the study area, the Shiranish Formation conformably overlies the Bekhme Formation, and underlies the Kolosh Formation (Fig.2). The thickness of the formation varies greatly, being 227.8 m thick in the type section (Bellen *et al*., 1959). In other areas, the isopach varies greatly as a result of subsidence related to the basin and its depositional environment (Buday, 1980). In the study area, the apparent thickness is about 24 m.

In Garota, only limestone beds are obvious and the upper marls are covered by soil. The lithology of the formation in this type area is divided into two units: the upper unit is comprised of blue pelagic marls sometimes dolomitic with occasional thin marly limestone beds rich in microfauna; and the lower unit is comprised of thin bedded marly limestone (Bellen *et al*., 1959; Buday, 1980).

The outcrop is located within the northeastern limb of Safin anticline. There are several geomorphological forms that were formed by erosion, deposition, mass movement and solution, such as karst, cleavage and rock fall. The effect of gully erosion; freezing and thawing; gravitational erosion and mass movement can be observed.

The ever growing need for cement nationwide requires a continuous supply of raw material of which limestone is the most important. The Shiranish Formation has been studied for this purpose and in the present study the formation outcrop of Garota Village is studied to:

– Compare the chemical composition of all limestone samples with the usual range accepted for Portland cement.
– Find a suitable mixture of all samples directly or with minor additions to reach a better clinker composition for cement manufacture.

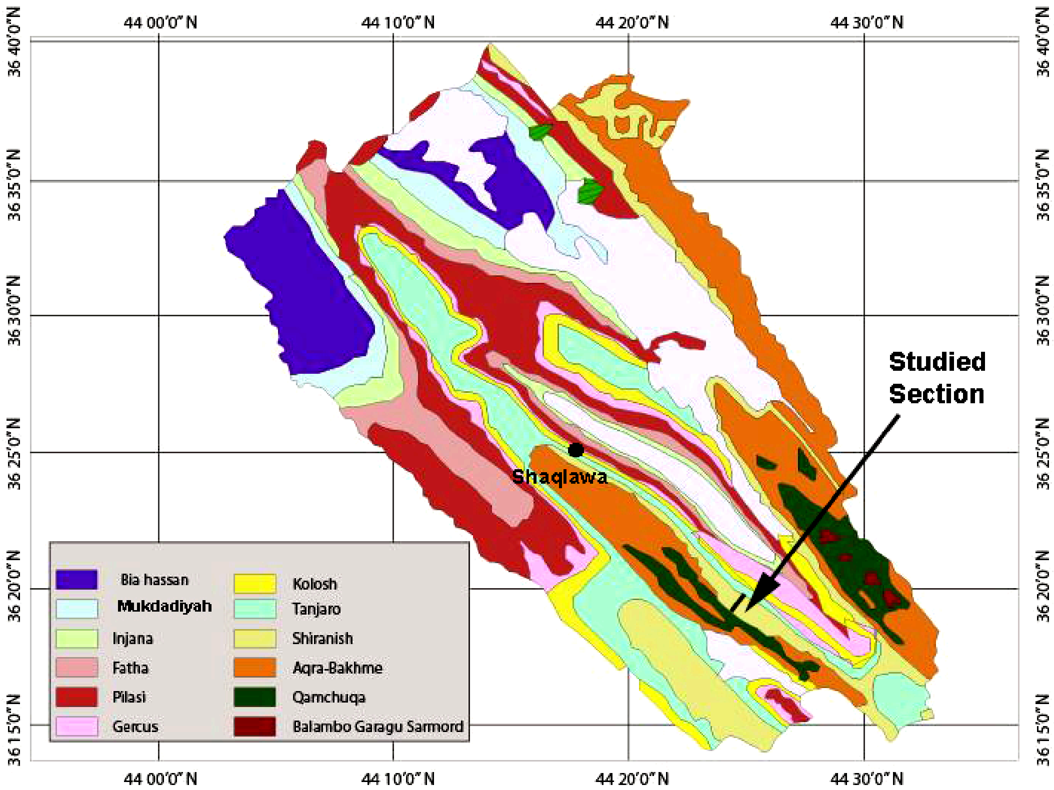

Fig.2: Geological map of Shaqlawa area (Sissakian, 1998)

- **Methodology**

A total of eight samples of limestone were collected from the Shiranish Formation outcrop near Garota Village (Table 1). Samples were taken from different points within the same horizon to observe the lateral change within the horizon.

The chemical analyses were carried out in the National Center of Construction Laboratories (NCCL), Erbil, to determine the percentages of major oxides in the bulk samples. The 20 gram dried rock samples were grounded to a particle size of < 50 µm (capable of passing through a sieve of 325 mesh). Five grams of the resulting powdered samples were transferred to a pellet pie and pressed at a minimum of 15 ton pressure. The samples were pressed into a boric acid backed pellet. Then they were analyzed using Oxford Instruments X-Supreme 8000.

Table 1: List of samples showing sample number, lithology, location and coordinates

Sample No.	Lithology	Location	Coordinates
1	Calcareous Limestone	Garota Village, Shaqlawa	36° 18' 31" N 44° 26' 35" E
2	Calcareous Limestone	Garota Village, Shaqlawa	36° 18' 46" N 44° 26' 31" E
3	Calcareous Limestone	Garota Village, Shaqlawa	36° 18' 29" N 44° 26' 07" E
4	Calcareous Limestone	Garota Village, Shaqlawa	36° 18' 46" N 44° 26' 37" E
5	Calcareous Limestone	Garota Village, Shaqlawa	36° 18' 44" N 44° 26' 37" E
6	Calcareous Limestone	Garota Village, Shaqlawa	36° 18' 48" N 44° 26' 35" E
7	Calcareous Limestone	Garota Village, Shaqlawa	36° 18' 44" N 44° 26' 31" E
8	Calcareous Limestone	Garota Village, Shaqlawa	36° 18' 46" N 44° 26' 32" E

RESULTS AND DISCUSSION

The results of chemical analyses for the collected samples are shown in Table 2. The raw material factor (default = 1.54) is used for converting raw material constituents to a Portland cement clinker constituent, with the resultant clinker composition calculated as shown in Table 3 (Szabo *et al*., 2003). The data from Table 3 is used in order to compare its percentages with the usual range in cement and to figure out if it is within, above, or below the usual range.

The percentage of calcium oxide (CaO) of six samples: 1, 4, 5, 6, 7 and 8 is within the acceptable range, but samples 2 and 3 are below and above the range, respectively. The CaO wt. % average is 41.27 which is at the mid of the acceptable range (Table 2). The averages of $CaCO_3$ wt. % and raw mix are 73.61 and 0.62, respectively (Table 4). These values are within the acceptable limits.

Generally, all samples have high content of silicon oxide (SiO_2); four samples: 1, 3, 6 and 7 have SiO_2 contents within the acceptable range but higher than the median value. The other four samples: 2, 4, 5 and 8 contain silica above the acceptable range. The average SiO_2 content is slightly above the acceptable. The contents of aluminum oxide (Al_2O_3) and iron oxide (Fe_2O_3) in the resulting clinker for all samples are within the acceptable limits. The magnesium oxide (MgO) content in resultant clinker for sample 3 is slightly below the acceptable range, whereas MgO content in all other samples is within the range. Samples 2, 4, 5 and 6 show slightly higher MgO concentrations than the median value of usually acceptable range, whereas, samples 1, 7 and 8 have slightly lower MgO content than the median value. However, the average of all samples is within the acceptable range.

The content of sulfur oxide (SO_3) in the resultant clinker for all samples are below the acceptable range for clinker. Sulfate is usually added to the raw material mix in cement industry. The role of SO_3 in the cement is to prevent sulfate expansion; the sulfate added to clinker is mostly in the form of gypsum to control the setting time; thus the content of SO_3 should be adjusted in the mix to conform to the usual range and to prevent the extensive sulfatization of the alkalis (Duda, 1976; Austin, 1985; Neville, 1996).

Table 2: Results of chemical analysis of the studied samples

Sample No. / Element Oxides	1 Wt.%	2 Wt.%	3 Wt.%	4 Wt.%	5 Wt.%	6 Wt.%	7 Wt.%	8 Wt.%
Na_2O	0.06	0.04	0.05	0.04	0.06	0.03	0.05	0.05
MgO	1.01	1.43	0.32	1.53	1.76	1.68	1.25	1.09
Al_2O_3	4.10	4.42	2.04	3.51	4.28	3.71	4.17	4.10
SiO_2	15.80	17.45	14.78	16.30	17.98	15.65	16.06	18.06
P_2O_5	0.08	0.15	0.08	0.10	0.06	0.11	0.11	0.08
SO_3	0.32	0.15	0.19	0.33	0.21	0.34	0.28	0.18
K_2O	1.24	1.08	0.74	0.66	0.86	0.73	0.93	0.97
CaO	40.93	38.20	45.50	42.26	39.93	41.82	41.01	40.47
MnO	0.04	0.07	0.01	0.07	0.08	0.06	0.05	0.04
Fe_2O_3	1.94	2.48	0.81	2.04	2.48	2.24	2.33	2.09
Total oxides	65.52	65.47	64.52	66.84	67.70	66.37	66.24	67.13
LOI	34.47	34.54	35.49	33.41	32.69	33.11	34.94	33.21
Total	99.99	100.01	100.01	100.25	100.39	99.48	101.18	100.34

Table 3: Calculated Clinker chemical composition of the studied raw material samples. The usual composition limits are based on Neville (2012)

Element Oxides	Usual Composition Limits	Sample Number and Clinker (RM * 1.54) Wt.%							
		1 Wt.%	2 Wt.%	3 Wt.%	4 Wt.%	5 Wt.%	6 Wt.%	7 Wt.%	8 Wt.%
Na_2O	0.3 – 1.2	0.09	0.06	0.08	0.06	0.09	0.05	0.08	0.08
MgO	0.5 – 4.0	1.56	2.20	0.49	2.36	2.71	2.59	1.93	1.68
Al_2O_3	3 – 8	6.31	6.81	3.14	5.41	6.59	5.71	6.42	6.31
SiO_2	17 – 25	24.33	26.87	22.76	25.10	27.69	24.10	24.73	27.81
P_2O_5		0.12	0.23	0.12	0.15	0.09	0.17	0.17	0.12
SO_3	2.0 – 3.5	0.49	0.23	0.29	0.51	0.32	0.52	0.43	0.28
K_2O	0.3 – 1.2	1.91	1.66	1.14	1.02	1.32	1.12	1.43	1.49
CaO	60 – 67	63.03	58.83	70.07	65.08	61.49	64.40	63.16	62.32
MnO		0.06	0.11	0.02	0.11	0.12	0.09	0.08	0.06
Fe_2O_3	0.5 – 6	2.99	3.82	1.25	3.14	3.82	3.45	3.59	3.22

Table 4: Calculation of $CaCO_3$ of raw mix (RM) of the studied samples

Sample No.	CaO wt.%	$CaCO_3$ wt.%	$CaCO_3$ of Raw Mix
1	40.93	72.86	0.62
2	38.20	68.00	0.58
3	45.50	81.21	0.71
4	42.26	75.43	0.63
5	39.93	71.27	0.59
6	41.82	74.64	0.63
7	41.01	73.20	0.62
8	40.47	72.23	0.60
Average	41.27	73.61	0.62

All samples have low content of sodium oxide (Na_2O). Three samples: 3, 4, and 6 are within the acceptable range of potassium oxides (K_2O), but they are above the median value of acceptable range, whereas the other five samples; 1, 2, 5, 7, and 8 are above the acceptable range. Furthermore, the average of all samples is also above the range (Table 2). The alkalis, total sodium and potassium oxides (Na_2O, K_2O) are expressed as Na_2O equivalent (Na_2O + 0.658 K_2O); their amount in the produced Portland cement clinker is mostly derived from clay minerals present within the raw mix and coal if present. Approximate range of alkalis in Portland cement is 0.3 – 1.2 (Neville, 1996); thus the calculated Na_2O equivalent for all samples is within the acceptable range (Table 2 and Table 5).

The concentration of three main element oxides (Al_2O_3, Fe_2O_3, and CaO) for the resulting clinker is within the acceptable range of Portland cement standards, whereas (SiO_2) is slightly above the range. By calculating the average for the four main components of all samples in the resultant clinker, the collected samples would have a clinker composition with slightly high percentage of SiO_2 above the acceptable range (Table 6).

Table 5: Calculated % of Alkali content (Na_2O)

Sample No.	**Na_2O %**	**K_2O %**	**Total Alkali content Na_2O (Na_2O + 0.658 K_2O)**
1	0.06	1.24	0.88
2	0.04	1.08	0.75
3	0.05	0.74	0.54
4	0.04	0.66	0.47
5	0.06	0.86	0.63
6	0.03	0.73	0.51
7	0.05	0.93	0.66
8	0.05	0.97	0.69

Table 6: Average of main raw material and clinker component for all eight samples. The usual composition limits PC after Neville (2012)

Element Oxides	**Usual Composition Limits PC**	**Raw Material for 8 samples**	**Clinker (RM × 1.54) wt.% for 8 Samples**
Na_2O (Alkalis)	0.3 – 1.2	0.05	0.07
MgO	0.5 – 4	1.26	1.94
Al_2O_3	3 – 8	3.79	5.84
SiO_2	17 – 25	16.51	25.43
P_2O_5		0.10	0.15
SO_3	2 – 3.5	0.25	0.39
K_2O (Alkalis)	0.3 – 1.2	0.90	1.39
CaO	60 – 67	41.27	63.55
MnO		0.05	0.08
Fe_2O_3	0.5 – 6	2.05	3.16
Total		66.22	101.98

The Lime Saturation Factor (LSF) modulus represents saturation of lime in the mixture. The acceptable range of LSF is 0.90 to 0.98 while up to 1.02 is practically acceptable and a range of (0.80 – 0.90) does not cause any problem in the cement manufacturing process or affect cement strength. However, it should not go below 0.80 (Carpio, 2005). Table 7 presents calculated LSF for the raw material samples. Table 6 shows calculated averages of CaO, SiO_2, Al_2O_3, and Fe_2O_3 in raw material.

LSF average for samples = CaO / [(2.80 × SiO_2) + (1.18 × Al_2O_3) + (0.65 × Fe_2O_3)]
LSF average for 8 samples = 41.23 / [(2.80 × 16.51) + (1.18 × 3.79) + (0.65 × 2.05)] = 0.80

The normal range of Silica Ratio (SR) is 2 – 3. If the SR value is less than 2, the burning process becomes very easy although excessive liquid phase and low strength cement will occur. However, if the SR value reaches up to 3, the burning become very difficult and the high strength cement is obtained. If the SR exceeds 3, then no clinkerization process occurs at all (Taylor, 1997). Table 7 shows calculated SR for samples. SR for raw material samples = SiO_2/ (Al_2O_3 + Fe_2O_3) = 2.99, which is towards the higher limit of the acceptable SR range.

The Aluminum Ratio (AR) is used to determine ratio of aluminum oxide to ferric oxide (Al_2O_3/ Fe_2O_3). AR acceptable range is between 1.3 and 2.5; if the obtained value is greater than 2.5, it indicates a viscous slag and occurrence of high early strength, but if it is less than 1.3, then this leads to fluid slag with low early strength and low heat of hydration (Taylor, 1997). Table 7 shows calculated AR for samples. The average of AR for all samples is 1.91, which is within the acceptable range.

Further studies should include petrography and/or X-ray diffractometry to determine the occurrence of free quartz and its grain size.

Table 7: Calculated LSF, SR and AR for studied samples, with averages

Sample No.	LSF (range: 0.90 – 0.98)	SR (range: 2.0 – 3.0)	AR (range: 1.3 – 2.5)
1	0.81	2.62	2.11
2	0.69	2.53	1.78
3	1.03	5.19	2.52
4	0.83	2.94	1.72
5	0.70	2.66	1.73
6	0.84	2.63	1.66
7	0.80	2.47	1.79
8	0.71	2.92	1.96
Average	0.80	2.99	1.91

CONCLUSIONS

- The chemical compositions for all samples of limestones show differences in mass percentages for the main constituents.
- The average of $CaCO_3$ for all samples is 73.60.
- The mass percentages of SO_3 for all samples are below the acceptable range for manufacturing grey and black Portland cement clinker and needs to be adjusted by adding gypsum to increase SO_3 percentage to meet at least the lower limit for usual range.
- The mixture of all samples gives a resultant clinker with a high percentage of SiO_2 and low percentage of SO_3. The Na_2O equivalent and the remaining chemical components are within the acceptable range of Portland cement manufacture.
- Although the LSF is below the acceptable range, this would not make any problem in cement manufacturing process and cement strength.
- A mixture of all samples can be utilized for cement manufacture with minor additions of SO_3 to reach a better clinker composition with acceptable specifications.

REFERENCES

Al-Sayyab, A., Al-Ansari, N., Al-Rawi, D., Al-Jassim, J., Al-Omari, F. and Al-Shaikh, Z., 1982. Geology of Iraq: Mosul University Press, Mosul, Iraq, 280pp, (in Arabic).

Austin, G.T., 1985. Shreve's Chemical Process Industries, 5th edition, McGraw Hill Book Company, Singapore, 854pp.

Bazian Cement Plant, 2012, https://www.facebook.com/pages/Bazian-Cement Company/284615178231635?id=284615178231635&sk=info, accessed on 15 Aug 2012.

Bellen, R.C., van Dunnington, H.V., Wetzel, R. and Morton, D., 1959. Lexique Stratigraphic International. Asie, Fasc. 10a, Iraq, Paris, 333pp.

Buday, T., 1980. The Regional Geology of Iraq. Vol.1. Stratigraphy and Paleogeography. In: I.I., Kassab and S.Z., Jassim (Eds.). GEOSURV, 445pp.

Bye, G.C., 1999. Portland cement composition; production and properties, 2nd edition: Thomas Trelford Publishing, London, UK, 225pp.

Carpio, R.C., 2005. Optimization in the co-processing of waste in the cement industry comprising cost, quality and environmental impact, PhD Thesis: Federal University of Itajubá-UNIFEI, Institute of Mechanical Engineering

Duda, W.H., 1976. Cement Data Book. Vol. 1, 3rd Edition: Berlin: Bauverlag GmbH, 538 p.

Hewlett, P.C. (ed.), 2004. Lea's chemistry of cement and concrete, 4th edition: Butterworth-Heinemann, UK, 1057pp.

Izdihar-USAID, 2007. An over view of Iraq cement industry, Iraq Private Sector Growth and Employment Generation: United States Agency for International Development, 31pp.

Karol, R.H., 2005. Chemical grouting and soil stabilization, 3rd edition: CRC Press, USA, 584pp.

Kreh, D., 1998. Building with masonry break, block and concrete: Taunton Press USA, 183pp.

Litak, R.K., Barazingi, M., Brew, G., Sawaf, T., Al-Imam, A. and Al-Youssef, W., 1998. Structure and evolution of the petroliferous Euphrates Graben system, southeast Syria: AAPG Bulletin, Vol.82, No.6, p. 1173 – 1190.

Ministry of Industry and Minerals (Iraq), 1975. Sarchinar Cement Factory: History and Production, 36pp.

Neville, A.M., 1996. Concrete Technology, 4th edition: Long man Singapore Publishers Ltd, Singapore, 452pp.

Neville, A.M., 2012. Properties of Concrete, 5th edition: Prentice Hall, 872pp.

Punmia, B.C., Jain, Ashok, K., and Jain, Arun. K., 2003. Basic civil engineering: Laxmi Publications, India, 446pp

Sisakian, V.K., 1998, The Geology of Erbil and Mahabad Quadrangle Sheet NJ-38-14 and NJ-38-15 (GM 5 and 6), Scale 1:250 000. Iraq Geological Survey: Baghdad, Iraq.

Szabó, L., Hidalgo, I., Císcar, J.C., Soria, A. and Russ, P., 2003. Energy consumption and CO_2 emissions from the world cement industry, Report EUR 20769 EN: European Commission, Joint Research Center, Institute for Prospective Technological Studies, Spain, 59pp.

Taylor, H.F.W., 1997. Cement chemistry: Thomas Telford Publishers, UK.

Thanoon, T.A., 1999, Assessment of Shiranish Formation from Sinjar Area – NW Iraq for Portland cement manufacturing: Proceedings of the 4th International Conference on Geochemistry in Alexandria – Egypt.

About the Authors

Rzger Abdulkarim Abdula, graduated from University of Salahaldin in 1987, with B.Sc. degree in geology; he got his M.Sc. in 2010 from Colorado School of Mines in Geology and currently he is a Ph.D. student. He joined Soran University in 2012. He has two published papers.

e-mail: rzger.abdula@soran.edu.iq
Mailing address: Iraq, Soran University, Kawa Street, Soran, Iraq

Rebwar N. Khailany, graduated from University of Salahaldeen in 1988, with B.Sc. degree in Geology. He joined Directorate of Geological Survey - Erbil in 1994 and currently, is working as Geologist in the Petroleum Division. His major field of interest is Petroleum Geology.

e-mail: rkailany@yahoo.com