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Comparative Study of Limestone Resources of Different Areas of NWFP for Industrial Utilization

Hamidullah Khan and M. Akhyar Farrukh
P.C.S.I.R. Laboratories Complex, Jamrud Road, Peshawar-25120, Pakistan

Abstract: Good quality of huge limestone beds are found in many parts of N.W.F.P, Pakistan, particularly in Khyber Agency, Kohat and Cherat Areas. Limestone samples were collected from different localities of these areas for chemical analysis. Results of different areas were compared to each other for the industrial utilization. The chemical composition of the deposits of all the three areas indicate that these deposits would be utilized for production of cement, refining of sugar, glass, ceramic, paper and chemical industries. Percentage of lime was found to be in the range of 31.18-55.10, 38.61-53.05, 44.28-54.42% and average percent composition of SiO_2 is 1.45, 3.82, 3.75%, Al_2O_3, 0.76, 1.157, 0.71%; Fe_2O_3, 0.34, 0.44, 0.415%; TiO_2, 0, 0, 0%; MnO, 0, 0, 0%; P_2O_5, 0.008, 0.004, 0.024%; CaO, 48.30, 49.77, 52.284%; MgO, 5.60, 2.80, 0.366%; Na_2O, 0.23, 0.15, 0.439%; K_2O, 0.056, 0.07, 0.227%; SO_3, 0.003, 0.002, 0.001%; Cl^-, 0.002, 0.001, 0.003%; moisture, 0.065, 0.08, 0.095% and l.O.I, 43.25, 41.97, 41.47% in Khyber Agency, Kohat and Cherat Areas, respectively.

Key words: Limestone, NWFP, chemical analysis, industrial utilization

INTRODUCTION

Limestone is a sedimentary rock, which is chiefly composed of calcium carbonate. Limestone term is applied to rocks which conation as little as 50% calcium carbonate upto over 95% in its pure form.

There are virtually inexhaustible deposits of good quality limestone in all the four provinces of Pakistan and a reserve of five billion tons is available in open pit mining[1]. North West Frontier Province has great reserves of limestone.

Extensive deposits of limestone occur in Khyber Agency near Peshawar[2]. The area extends mostly to the east of Khyber pass highway, with a part extending to south-east. The composition of the rocks of the area ranges from magnesia to dolomitic limestone and are composed of calcite, dolomite and subordinate amounts of quartz and illite. The Khyber Agency area is underlain by sequence of sedimentary and metamorphic rocks intruded by plutonic and volcanic bodies. Deposits of limestone are also found in Cherat at about 20 km south of Nowshera[3]. Occurrence of red and pink variegated limestone and marble with veins and patches of white calcite has been reported[4] in the vicinity of Cherat area near Nowshera. Cherat area has extensive deposits of raw materials such as limestone, slate, shale and clay. Very large deposits of limestone ranging in age from Juarassic to Eocene are found in Kohat area about 64 km south of Peshawar[5]. These limestones are mainly composed of calcite, dolomite and subordinate amount of quartz, illite and some times kaolinite.

A number of representative limestone samples were collected from these three areas for evaluation by chemical and physical methods to study their suitability for utilization in cement, sugar and chemical industries.

MATERIALS AND METHODS

Twelve representative samples of limestone were collected from Khyber Agency, Cherat and Kohat Areas and were analyzed by conventional as well as instrumental methods[6-8].

Nearly 1 g of sample was taken in a platinum crucible, heated in an electric oven at 115°C for 2 h to find the moisture content. The same crucible was heated in electric furnace at 950°C for 1 h to determine the loss on ignition.

0.5 g of each sample was dissolved in 30 mL HCl, dehydrated and dissolved in 5 mL HCl, added some water, heated on sand bath for 15 min, filtered and washed with water. Residue on the filter paper was ignited in a weighed platinum crucible and reported as silica. The filtrate was collected in 250 mL v. flask. In 100 mL of above filtrate combined oxides were precipitated by adding ammonium chloride and ammonium hydroxide. The precipitates were digested, filtered, washed, ignited in a platinum crucible and weighed. The filtrate was collected in an

Corresponding Author: Dr. M. Akhyar Farrukh, P.C.S.I.R. Laboratories Complex, Jamrud Road, Peshawar-25120, Pakistan
E-mail: drmafarrukh@yahoo.com

other volumetric flask and make the volume 250 mL. Calcium and magnesium were determined in the filtrate by titration with standard EDTA solution. 100 mL of this solution was taken in a beaker, made slightly acidic with dilute HCl and precipitated the sulfate as barium sulfate from the hot solution, filtered, ignited in weighed crucible and determined as sulfate.

Solution of other 0.5 g portion of each sample was made with the help of HF and $HClO_4$. Sodium and potassium were determined by flame photometry (Corning 400 flame photometer) and iron, titanium, phosphate and manganese by spectrophotometry (Schimadzu-UV-200S spectrophotometer). Aluminium was calculated by subtractions of these constituents from combined oxides.

Chloride was determined by titrating the water extract of the samples with standard silver nitrate.

RESULTS AND DISCUSSION

Limestone has a wide range of uses, which are discussed in accordance with the results obtained from all three areas, namely, Khyber Agency, Kohat Area and Cherat Area.

Chemical compositions are very consistent in each series of three areas. However few of them A-3, A-6, A-9, A-11 in Khyber Agency (Table 1) and B-1, B-4, B-5 in Kohat Area (Table 2) and C-6, C-10 in Cherat Area (Table 3), deviate from the rest of the samples, indicating that these samples are not suitable for cement manufacturing. For cement manufacturing, according to the British Standard Specification, limestone should have the composition as, CaO (lime) 54.84%, MgO (magnesia) 0.20%, R_2O_3 (alumina and iron oxide) 0.41%, SiO_2 1.14% and loss on ignition 43.26%. Lime content (CaO) in Kayber Agency varies from 31.18-55.10%, in Kohat Area 38.61-53.05% and in Cherat Area 44.28-54.42%. Results indicate that limestone of Khyber Agency and Cherat Area are more suitable than that of Kohat Area.

Limestone is used in sugar refining, having magnesia content, MgO, not more than 3% to precipitate impurities from juices. Magnesia content of Khyber Agency, Kohat Area and Cherat Area varies from traces-22.04%, 0.82-7.10% and 0-1.26%, respectively (Table 1-3). Results indicated that limestone of Cherat Area may be used for this purpose. While that of Khyber Agency and Kohat Area are not suitable due to more magnesia content.

According to USA specification, limestone used for manufacturing of alkali like soda ash should not have silica and magnesia content. So limestone resources of these three areas are not recommended for these purposes.

High calcium lime with less than 2% MgO is used for paper manufacturing. Limestone is used for producing paper pulp from woods during the process of sulfite and sulfate. Only Cherat Area limestone having a limited range of magnesia (MgO) can be used for this purpose (Table 1-3).

Dolomite limestone with no more than 0.2% Fe_2O_3 and other specification like 55.20% CaO, 1.00% silica is used for certain special glasses. A-10 of Khyber Agency (Table 1), C-3, C-4 of Cherat Area (Table 3) for this may be used.

High lime content with no more than 0.3% Fe_2O_3, 2% SiO_2 and 0.1% SO_4^{2-} is used for pottery purposes.

Alumina in a combined state is an important constituent of cement in which it behaves as an acid[9]. Alumina content in Khyber Agency, Kohat and Cherat Areas series ranges from 0.20-1.68, 0.62-2.02 and 0.13-1.815%, respectively.

Iron content in some of the sample is high in comparison to the other samples, which makes these samples unsuitable for the use of cement making.

Alkalies are objectionable in cement as they enter in reaction with certain types of aggregates[10]. Alkalies present in the samples are lower than the objectionable limit for the use in cement industries. Low amounts of Cl^- and SO_4^{2-} in the samples are also not objectionable for cement making.

The results of the investigations show that suitable quantity and quality of limestone near Cherat exist for industrial uses. Limestone fully corresponds with the British Standard Specifications (i.e. CaO should be 50% and MgO should be less than 3%) for cement manufacturing. Allowed percentage of silica content is found mostly in the form of clay (Kaolinite and illite) and to a lesser degree as quartz. High percentage of Fe_2O_3 in Cherat limestone does not permits its use in glass industries. Cherat limestone outcrops are easy to approach and are located close to road and rail links. Other raw materials used in the industries are also abundantly available at hand.

The results obtained from Khyber Agency indicate that the magnesia contents of the limestone samples except A-6, A-9, A-11, are within the recommended limits of British Standard Specification for cement manufacturing. Due to shortage of water in the area cement factory based on dry method manufacturing is recommended.

Table 1: Chemical composition of limestone of Khyber Agency Area

Sample No.	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	A-9	A-10	A-11	A-12	Range	Average
SiO_2	1.16	0.08	1.00	1.92	0.05	6.07	0.62	0.95	1.20	0.96	1.87	1.14	0.05-6.07	1.45
Al_2O_3	1.12	1.10	0.62	0.73	0.86	1.68	0.40	0.20	0.52	0.43	0.82	0.64	0.20-1.68	0.76
Fe_2O_3	0.32	0.35	0.21	0.22	0.37	1.20	0.29	0.06	0.26	0.20	0.23	0.35	0.06-1.20	0.34
TiO_2	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MnO	-	-	-	-	-	-	-	-	-	-	-	-	-	-
P_2O_5	Traces	Traces	-	Traces	0.02	0.03	Traces	-	0.02	Traces	0.03	Traces	-	0.008
CaO	53.72	51.53	30.04	50.82	54.72	47.64	54.38	55.10	46.02	51.26	31.18	53.24	31.18-55.10	48.30
MgO	0.72	3.36	22.04	3.85	1.40	3.50	2.50	0.98	6.98	2.60	19.35	Traces	Traces-22.04	5.60
Na_2O	0.23	0.16	0.28	0.22	0.19	0.14	0.26	0.25	0.22	0.27	0.22	0.34	0.14-0.34	0.23
K_2O	0.02	0.07	0.10	0.06	0.03	0.08	0.02	0.03	0.04	0.04	0.16	0.03	0.02-0.16	0.056
SO_3	Traces	Traces	0.01	0.03	-	Traces	-	-	Traces	Traces	Traces	Traces	0.00-0.03	0.003
Cl^-	0.003	0.003	Traces	Traces	-	0.005	0.004	-	0.002	-	0.005	Traces	0-0.005	0.002
Moisture	0.05	0.06	0.05	0.07	0.05	0.04	0.08	0.09	0.12	0.05	0.08	0.05	0.04-0.12	0.065
Loss on ignition	43.15	43.29	46.58	42.27	42.52	39.37	41.95	42.19	44.20	43.65	46.03	43.91	39.37-46.58	43.25
Total	100.493	100.003	100.93	100.19	100.20	99.755	100.504	99.85	99.582	99.46	99.975	99.70	-------	99.98

Table 2: Chemical composition of limestone of Kohat Area

Sample No.	B-1	B -2	B -3	B -4	B -5	B -6	B -7	B -8	B -9	B -10	B -11	B -12	Range	Average
SiO_2	13.90	1.85	2.60	6.60	7.31	2.13	2.42	1.64	2.76	1.06	1.78	1.82	1.06-13.90	3.82
Al_2O_3	0.70	1.26	0.62	0.65	0.83	0.75	1.24	0.85	1.82	1.85	1.30	2.02	0.62-2.02	1.157
Fe_2O_3	0.38	0.59	0.19	0.35	0.47	0.22	0.44	0.49	0.42	0.86	0.39	0.49	0.19-0.86	0.44
TiO_2	Traces	Traces	-	Traces	Traces	Traces	-	-	-	Traces	-	-	-	-
MnO	-	-	-	-	-	-	-	-	-	-	-	-	-	-
P_2O_5	Traces	-	Traces	Traces	-	-	0.03	0.02	Traces	Traces	Traces	Traces	0.00-0.03	0.004
CaO	38.61	53.05	51.34	48.40	46.23	52.16	51.64	52.85	50.05	51.06	52.28	49.63	38.61-53.05	49.77
MgO	7.10	0.82	2.75	3.36	4.19	1.78	1.95	1.30	2.61	2.47	1.76	3.6	0.82-7.10	2.80
Na_2O	0.20	0.15	0.12	0.12	0.20	0.13	0.16	0.12	0.21	0.16	0.15	0.12	0.12-0.21	0.15
K_2O	0.11	0.08	0.10	0.05	0.07	0.06	0.03	0.07	0.07	0.04	0.12	0.06	0.03-0.12	0.07
SO_3	Traces	Traces	-	Traces	Traces	-	Traces	Traces	-	0.03	Traces	Traces	0.00-0.03	0.002
Cl^-	-	-	Traces	-	Traces	Traces	0.005	Traces	0.004	-	0.003	Traces	0.00-0.005	0.001
Moisture	0.05	0.06	0.09	0.07	-	0.12	-	0.05	0.14	0.11	0.13	0.12	0.00-0.14	0.08
Loss on ignition	39.22	42.36	42.68	40.86	40.80	43.20	42.53	42.86	42.26	42.62	42.48	42.37	39.22-43.20	41.97
Total	100.27	100.22	100.49	100.46	100.10	100.55	100.445	100.25	100.344	100.26	100.393	100.23	-	100.33

Table 3: Chemical composition of limestone of Cherat Area

Sample No.	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	Range	Average
SiO_2	1.39	2.20	1.006	0.592	0.642	14.862	2.26	2.78	5.40	8.84	2.30	2.74	0.592-14.862	3.75
Al_2O_3	0.205	0.914	0.284	0.359	0.221	1.096	1.815	0.462	0.87	1.35	0.13	0.20	0.13-1.815	0.71
Fe_2O_3	0.145	0.322	0.103	0.103	0.100	0.855	0.609	0.560	0.75	0.85	0.37	0.32	0.1-0.855	0.415
TiO_2	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MnO	-	-	-	-	-	-	-	-	-	-	-	-	-	-
P_2O_5	Traces	0.014	-	-	-	-	0.098	0.178	-	-	-	-	0.00-0.178	0.024
CaO	54.12	53.36	54.00	54.33	54.42	44.28	52.08	52.58	52.08	48.28	54.26	53.62	44.28-54.42	52.284
MgO	0.27	Traces	0.63	0.46	0.54	1.26	0.73	0.51	Traces	Traces	Traces	Traces	0.00-1.26	0.366
Na_2O	0.53	0.49	0.495	0.602	0.490	0.440	0.57	0.49	0.27	0.27	0.33	0.15	0.27-0.602	0.439
K_2O	0.06	0.07	0.066	0.040	0.035	0.598	0.13	0.18	0.50	0.70	0.20	0.30	0.035-0.7	0.227
SO_3	Traces	Traces	Traces	Traces	Traces	Traces	-	Traces	0.03	0.02	Nil	Nil	0.00-0.3	0.004
Cl^-	-	-	0.006	0.005	0.004	0.007	0.003	0.010	Nil	Nil	Nil	0.0011	0.00-0.01	0.003
Moisture	0.13	0.12	0.09	0.08	0.05	0.10	0.07	0.10	0.08	0.07	0.14	0.11	0.05-0.14	0.095
Loss on ignition	42.87	42.20	43.13	43.02	43.36	36.14	42.22	42.03	40.31	38.97	42.20	41.20	36.14-43.13	41.47
Total	99.72	99.69	99.81	99.591	99.862	99.638	100.585	99.88	100.29	100.35	99.93	99.271	-	99.80

The limestones having higher SiO_2 (>1%) or higher Fe_2O_3 (>.035%) are unsuitable for glass manufacture. Hence, the Khyber limestone is not suitable for this purpose. This limestone may be used for ceramics as having more than 79% of $CaCO_3$ with permissible amounts of Fe_2O_3 and SiO_2. The samples having 3-2% MgO may be used in sugar refining, paper industry and for the manufacture of precipitated calcium carbonate.

However, further study is recommended for determining the economic feasibility of these deposits for different industrial purposes. A close interval channel sampling of the carbonate rocks, exposed in these areas, will have to be conducted to delineate different zones according to chemical composition. The present study is only a preliminary effort to spotlight the possible industrial uses of the resources available in these areas.

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