Comparative Study of Limestone Resources from Different Areas of N.W.F.P for Industrial Utilization

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Summary: Good quality of huge limestone beds is 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 theses areas for chemicals analysis. The chemical composition was determined and compared to standard values for the industrial utilization. The chemical composition of the deposits of all the three areas indicate that these deposits could be utilized for production of cement, refining of sugar, glass, ceramic, paper and chemical industries.

Introduction

Limestone is a sedimentary rock, which is chiefly composed of calcium carbonate. The term Limestone is applied to rocks containing at least 50 percent calcium carbonate upto over 95 percent 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 (NWFP) has great reserves of limestone. In 2000-2001 its production was 4, 612, 556 metric tones [2].

Extensive deposits of limestone occur in Khyber Agency near Peshawar [3-5]. The area extends mostly to the east of Khyber pass highway, with a part extending to 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 [6]. Occurrence of red and pink variegated limestone and marble with veins and patches of white calcite has been reported [7] 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 [8]. 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 method to study their suitability for utilization in cement, sugar and chemical industries.

Results and Discussion

Twelve representative samples of limestone were collected from each of Khyber Agency, Cherat and Kohat areas and were analyzed by conventional as well as instrumental methods [9-11]. 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 in (Table-2) and C-6, C-10 in Cherat area (Table-3), deviate from rest of the samples, indicating that these samples are not suitable for cement manufacturing. For cement manufacturing, according to the British Standard Specification, (Table-4) 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 Khyber Agency varies from 31.05-55.10%, in Kohat area 38.01-53.05% and in Cherat area 45.01-54.42%. Results indicate that limestone of Khyber Agency and Cherat area are suitable than that of Kohat area. The results of the investigations show that quantity and quality of limestone of Cherat area is more suitable for industrial uses because it fully corresponds with the British Standard Specifications for cement manufacturing. Cherat limestone outcrops are easy to approach and are located close to road and

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Table -1: Chemical composition of limestone samples from Khyber Agency area.

Parameters	Sample Numbers												Range	Average
	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	A-9	A-10	A-11	A-12		
SiO_2	1.20	0.08	1.02	1.92	0.05	6.17	0.62	0.95	1.30	0.96	1.87	1.14	0.05-6.17	1.44
Al_2O_3	1.05	1.10	0.59	0.73	0.86	1.58	0.40	0.20	0.51	0.43	0.82	0.64	0.20-1.58	0.7425
Fe_2O_3	0.32	0.35	0.22	0.22	0.36	1.20	0.29	0.06	0.26	0.20	0.23	0.35	0.06-1.20	0.33
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	31.05	50.82	54.72	47.85	54.38	55.10	46.15	51.26	32.12	53.24	31.05-55.10	48.49
MgO	0.72	3.36	21.86	3.85	1.40	3.50	2.50	0.98	6.98	2.60	19.35	0.38	0.38-21.86	5.62
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	0.03	0.07	0.10	0.06	0.02	0.08	0.02	0.04	0.03	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	-	0.006	0.003	-	0.002	-	0.005	Traces	0.0-0.006	0.016
Moisture	0.06	0.04	0.05	0.06	0.05	0.04	0.06	0.09	0.12	0.05	0.04	0.05	0.04-0.12	0.059
Loss on ignition	43.15	43.29	45.46	42.27	42.52	39.67	41.95	42.19	44.43	43.65	45.63	43.91	39.67-45.63	43.17
Total	100.483	99.98	100.64	100.18	100.18	100.286	100.484	99.86	100.022	99.46	100.475	100.08	----	100.175

Table-2: Chemical composition of limestone samples from Kohat area.

Parameters	Sample Numbers												Range	Average
	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9	B-10	B-11	B-12		
SiO_2	12.56	1.85	2.60	6.60	7.28	2.13	2.42	1.64	2.98	1.06	1.78	1.84	1.06-12.56	3.72
Al_2O_3	0.68	1.26	0.62	0.67	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	38.01	53.05	51.34	48.00	46.16	52.16	51.64	52.85	50.05	51.00	52.28	49.63	38.01-53.05	49.68
MgO	6.98	0.79	2.75	3.36	4.19	1.78	1.95	1.30	2.61	2.47	1.76	3.6	0.79-6.98	2.79
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	-	0.04	Traces	Traces	0.00-0.04	0.02
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	40.05	42.36	42.68	40.46	40.43	43.20	42.53	42.86	42.26	43.00	42.48	42.37	40.05-43.20	42.05
Total	99.02	100.19	100.49	99.68	99.63	100.55	100.445	100.25	100.56	100.59	100.393	100.25	-	100.162

Table-3: Chemical Composition of limestone samples from Cherat area.

Parameters	Sample Numbers												Range	Average
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12		
SiO_2	1.40	2.20	1.006	0.592	0.642	15.10	2.26	2.78	5.40	8.84	2.30	2.68	0.592-15.10	3.76
Al_2O_3	0.215	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	0.659
Fe_2O_3	0.145	0.322	0.13	0.12	0.100	0.855	0.60	0.560	0.75	0.85	0.37	0.32	0.1-0.855	0.415
TiO_2	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MnO	-	-	-	-	-	-	-	-	-	-	-	-	-	-
P_2O_5	Traces	0.012	-	-	-	-	0.092	0.180	-	-	-	-	0.00-0.180	0.023
CaO	54.12	53.36	54.00	54.33	54.42	45.01	52.08	52.58	52.08	47.97	54.26	53.88	45.01-54.42	52.284
MgO	0.27	Traces	0.63	0.46	0.54	1.35	0.73	0.51	Traces	Traces	Traces	Traces	0.00-1.35	0.38
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	0.02	0.03	Nil	Nil	0.00-0.03	0.0041
Cl^-	-	-	0.006	0.005	0.004	0.006	0.003	0.009	Nil	Nil	Nil	0.0011	0.00-0.01	0,0028
Moisture	0.13	0.12	0.09	0.75	0.05	0.10	0.07	0.12	0.08	0.07	0.15	0.11	0.05-0.15	0.097
Loss on ignition	42.87	42.20	43.13	43.02	43.36	35.50	42.22	42.03	40.31	38.12	42.20	41.66	35.50-43.13	41.38
Total	99.74	99.68	99.10	99.603	99.862	100.05	100.579	99.90	100.28	99.20	99.94	99.93	-	99.822

rail links. Other raw materials used in industries are also abundantly available at hand.

Limestone having magnesia content, MgO, not more than 3% is used to precipitate impurities from juices in sugar refining. Magnesia content of Khyber Agency, Kohat area and Cherat area varies from 0.38-21.86%, 0.79-6.98% and 0-1.35% respectively (Table 1-3). These results indicated that the 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.

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. The results presented in table 1,2 and 3 show that only Cherat area limestone

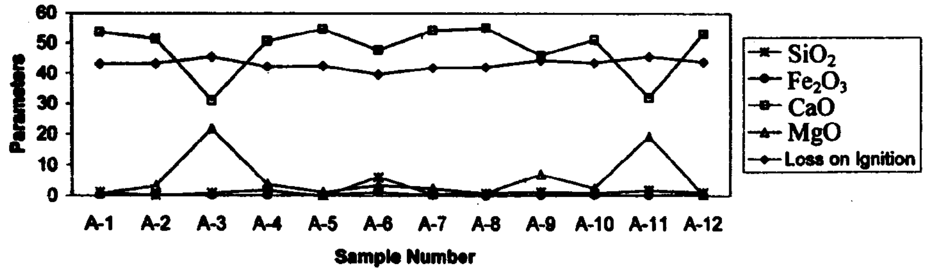

Fig. 1: Chemical composition of limestone samples from Khyber Agency area.

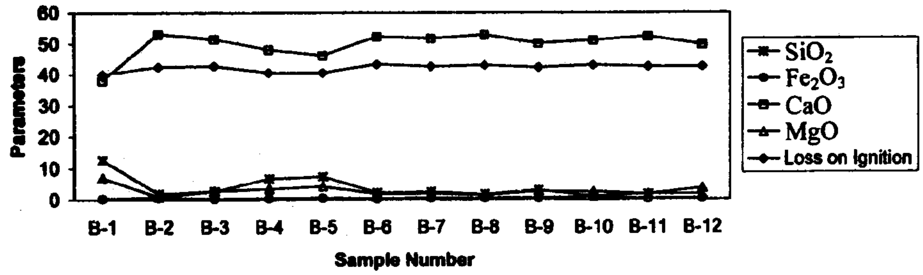

Fig. 2: Chemical composition of limestone samples from Kohat area.

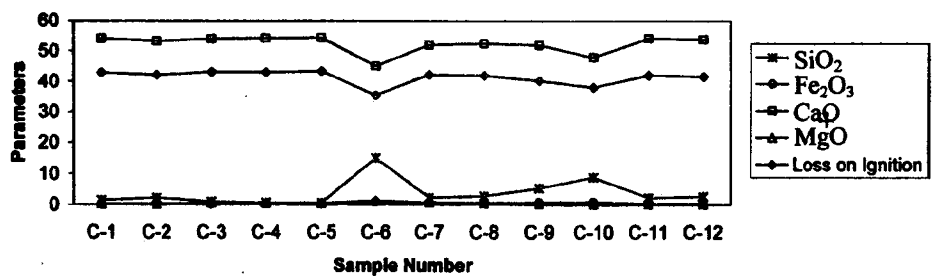

Fig. 3: Chemical composition of limestone samples from Cherat area.

having a limited range of magnesia (MgO) can be used for this purpose.

Dolomite limestone containing less than 0.2% Fe_2O_3, 55.20% CaO, 1.00% silica is used for certain special glasses (Table 4). A-10 of Khyber Agency (Table-1), C-3, C-4 of Cherat area (Table 3) may be used for this purpose.

Limestone having high lime content with 0.3% Fe_2O_3, 2% SiO_2 and 0.1% SO_4 is used for pottery purposes (Table-4).

Alumina in combined state is an important constituent of cement in which it behaves as an acid [12]. Alumina content in Khyber Agency, Kohat and Cherat areas series ranges from 0.20-1.58, 0.62-2.02 and 0.13-1.815%, respectively.

Iron content in some of the samples e.g A-6, B-10, C-6, C-9, C-10, is high in comparison to the other samples, which make these samples unsuitable for the use of cement manufacturing.

Alkalies are objectionable in cement as they enter in reaction with certain types of aggregates [13]. Alkalies present in the samples are lower than the objectionable limit for the use in cement industries.

Experimental

Loss on ignition and Moisture content

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

Table 4: Standard specification of different limestone for different limestone utilizing industries.

Industries	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O	Loss on ignition.	Moisture
Cement	1.14%	_	0.41%	54.84%	0.20%	_	_	43.26%	
Colourless glass	1.00%	0.035%	_	55.20% min	_	_	_	_	2.00%
Sodalime glass	68-75%		_	14%	0-10%	10-15%	_	_	_
Pottery	2%	0.30%	_	_	_	_	_	_	_

Industrial mineralogy "Materials, processes and uses by Luke L.Y. chang prentice hall upper Saddle river, New Jersey Page 195-203 (2002).

Silica content

Silica content was determined by taking nearly 0.5g of each sample and dissolved in 30ml HCl (1+1), 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 diluted to 250 ml.

Combined oxide

Combined oxides were precipitated by adding ammonium chloride and ammonium hydroxide in 100 ml of above filtrate. The precipitates were digested on sand bath, filtered, washed ignited in a platinum crucible and weighed. The filtrate was collected in an other volumetric flask and diluted to 250 ml. Calcium and magnesium were determined in the filtrate by titration with standard EDTA solution using Erichrome black T and Muroxide indicators.

Sulfate

Sulphate contents were determined by taking 100 ml of solution in a beaker, it was made slightly acidic with dilute HCl and the sulfate was precipitated as barium sulfate from the hot solution, filtered, ignited in weighed crucible and determined as sulfate.

Sodium and Potassium

Sodium and Potassium contents were determined by taking nearly 0.5 g portion of each sample and made the solution with the help of HF and $HClO_4$, in which Sodium and Potassium were determined by flame photometry (Corning 400 flame photometer) while iron, titanium, phosphate, manganese by spectrophotometry (Schimadzu double beam spectrophotometer UV-200S). For spectrophotometric analysis solutions were prepared by taking volume of 2ml from 250ml and diluted to 100ml. Reagents used were hydroxyl ammine hydrochloride, orthophenanthrolein, sodium periodate, potassium pyrosulphate, ammonium metavanadate and ammonium molybdate. Calibration curve drawn for all four elements by concentration versus absorbance were statistically analyzed using fitting of straight line by least square method. Distilled water is used as blank. Aluminium was calculated by subtractions of these constituents from combined oxides.

Chloride

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

Conclusions

The results of the investigations show that suitable quantity and quality of limestone near Cherat exist for industrial uses. Limestone chemical composition is consistant with the British Standard Specifications for cement manufacturing. Permitted percentage of silica content is found mostly in the form of clay (kaolinite and illiite) 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 material used in industries are also abundantly available at hand.

However, detail work 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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