Study of Limestone from Nizampur Area for Industrial Utilization

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Summary: The present research was designed to study the chemical composition of Nizampur limestone and to compare it with the already published data of Khyber Agency, Kohat and Cherat areas of NWFP for industrial utilization. Thirteen samples of limestone were collected from different areas of Nizampur for chemical analysis. The results of the study indicate that as compared to these other areas, Nizampur limestone is most suitable for use in glass, paper, pottery and cement industries.

Introduction

Limestone is a naturally occurring mineral that consists principally of calcium carbonate. Many limestonnes are remarkably pure with less than 5 % of non-carbonate impurities. Limestone is found in many forms and is classified in terms of its origin, chemical, composition, structure and geological formation. It occurs widely throughout the world, and is an essential raw material for many industries [1, 2]. Limestone and calcium carbonate are used in a wide range of products *e.g.* glass, ceramics, paper, sugar, plastic, paint, rubber, polishes, dentifrices, putty, insecticides, as a filler in adhesives, matches, pencils, food, cosmetics, pharmaceuticals and antibiotics [3].

There are virtually inexhaustible deposits of good quality limestone in all the four provinces of Pakistan and a reserve of five billion tonns is available by open pit mining [4]. In Pakistan its annual production is 8,697,573 metric tonnes, while in 2000-2001 its production was 11, 783, 813 metric tonnes [5]. North West Frontier Province (NWFP) has great reserves of limestone. In 2000-2001 its production was 4, 612, 556 metric tonnes and revenue generated was 50, 738, 116 rupees [6].

Limestone occurs in rocks, which vary in age from Pre-cambrian to Paleocene and Eocene eras.

Geology of Nizampur Limestone

The Nizampur area is dominantly a sedimentary belt in the Himalayan foothill region of northern Pakistan (Fig. 1). The area under investigation is located on the survey of Pakistan Toposheet No. 43C between the latitude 33°-45' to 33°-47'-12" and longitude 72° to 72° 2' 3". The rock sequences in the area range from Triassic to Quatelnary in age. The oldest rocks in the area are thin-bedded limestone, dolomitic limestone, marl, sandstone and siltstone of Mianwali and Tridian formations of early Triassic age. This sequence is succeeded by dolomite, dolomitic limestone with interbreds of shale and marl of chalk Jabbi and Kingriali formations of middle Triassic age. These rocks are unconformably overlain by continental origin ironstone with exotic blocks of dolomite, hematite and quartzose sandstone and fireclay and claystone of Datta formation of early Jurassic age. The contact of Datta formation with the overlying shinawari/samana suk formations of middle Jurassic is transitional. The shinwari formation is represented by limestone, marl and subordinate shale, while the overlying Sama suk formation is dominantly yellowish grey limestone, dolomitic limestone with pelloidal and oolitic beds. This sequence is overlain by black shale and glauconitic sandstone of chichali formation.

The cretaceous rocks are comprised of sandstone, quartzite and subordinate limestone of lumshiwal formation and thin-bedded marl and calcareous shale of Kawagarh formation. An Uniformity is marked at the top of the cretaceous sequence, which is represented by 1-2 m of laterite. Paleocene rocks containing Hangu formation dominated by coal bearing clastic sediments, middle Lokhart limestone, dominantly nodular and massive limestone and subordinate carbonaceous shale, and upper shale and limestone forms Patala formation.

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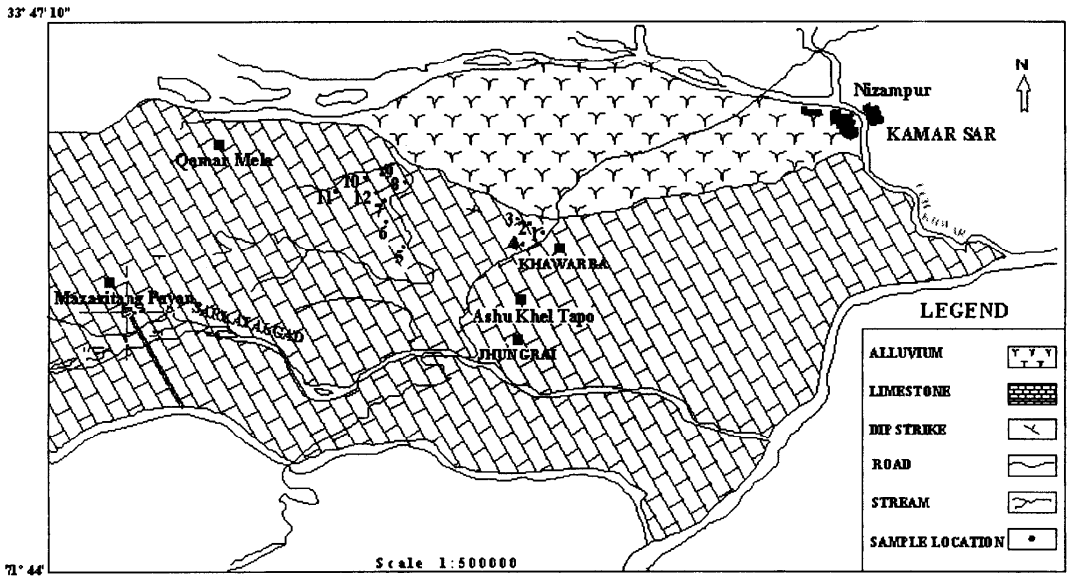

Fig. 1: Location map of limestone and clay deposits at Daro Khula, Nizampur District, Nowshera, (Modified after McDougall and Hussain, 1991.

Semi consolidated gravel silt and clay of Quaternary age unconformably overlie the older rock sequence.

The samples for the present work were collected from the Lokhart formation exposed near Shekhai village. It has uniform lithological character throughout its extent. This limestone is generally light grey to dark grey in colour and is medium to thick bedded. It is hard, finely crystalline and nodular. Numerous calcite veins and veinlets traverse these massive deposits [7]. A number of representative limestone samples were collected for evaluation by chemical and physical method to study their suitability for utilization in cement, sugar and chemical industries.

Results and Discussion

Thirteen representative samples of limestone were collected randomly from Nizampur area and analyzed physically and chemically for SiO_2, Al_2O_3, CaO, MgO, Na_2O, K_2O and loss on ignition (Table-1) by conventional as well as instrumental methods [8-10].

Limestone samples analyzed were subjected to study their suitability for industrial utilization and compared with already published data of the Khyber, Kohat and Cherat areas of NWFP (Tables 2-4) [11].

According to British standard specifications for cement manufacturing, 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 % (Table-5). Chemical analysis of Nizampur limestone shows the content of CaO as 30.17 %-57.24 % (Table-1). While that of Khyber Agency varies from 31.05-55.10 %, of Kohat area 38.01-53.05 % and of Cherat area 45.01-54.42 % (Tables 2-4). Analysis of sample N-3 and N-7 deviate from the rest of the samples in their CaO content 30.17 % and 44.28 % CaO, while all the samples are well above the 50 % CaO. Like that of the Khyber Agency, Kohat and Cherat areas, Nizampur limestone is also suitable for cement manufacturing.

Limestone having magnesia content, MgO, not more than 3 % is used in sugar industry. Paper industry use high calcium lime with less than 2 % MgO during the process of sulfite and sulfate to produce paper pulp from the wood and $Ca(HSO_3)$ liquor which remove components of the pulp other than the cellulose. Magnesia content of Nizampur limestone shows the composition as 0.40 %-9.61 % (Table-1). While Khyber Agency, Kohat area and Cherat area varies from 0.38-21.86 %, 0.79-6.98 % and 0-1.35 % respectively (Tables 2-4). Most of the samples (N-1, N-3, N-7, and N-9) showed high

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

Parameters	Sample Numbers													Range	Average
	N-1	N-2	N-3	N-4	N-5	N-6	N-7	N-8	N-9	N-10	N-11	N-12	N-13		
SiO_2	1.22	1.16	9.89	0.60	0.08	0.32	1.50	0.98	0.64	1.84	0.98	3.46	0.58	0.08-9.89	1.78
Al_2O_3	4.51	0.33	10.32	4.71	7.98	8.39	12.96	3.53	6.61	6.10	9.23	3.54	2.74	0.33-12.96	6.23
Fe_2O_3	0.017	0.017	0.023	0.053	0.14	0.07	0.20	0.05	0.27	0.50	0.37	0.06	0.02	0.017-0.50	0.13
CaO	50.24	57.24	30.17	51.28	50.96	50.38	44.28	51.76	51.86	50.19	50.14	50.76	54.70	30.17-57.24	49.53
MgO	4.37	0.87	9.61	2.14	2.84	0.87	5.20	1.31	4.37	0.43	0.73	0.40	0.41	0.40-9.61	2.58
Na_2O	0.35	0.07	0.10	0.15	0.10	0.15	0.09	0.10	0.15	0.10	0.10	0.15	0.10	0.07-0.35	0.13
K_2O	0.01	0.01	0.01	0.03	0.02	0.03	0.06	0.07	0.03	0.09	0.06	0.05	0.04	0.01-0.09	0.04
Loss on ignition	40.14	40.42	38.39	41.46	39.74	40.07	34.29	42.18	37.15	41.18	37.32	41.06	42.00	34.29-42.18	39.68
Total	100.85	100.13	98.51	100.42	101.86	100.28	99.14	99.98	101.08	100.43	98.93	99.48	100.59	---	100.13

Table-2: Chemical composition of limestone samples from Khyber Agency area [11].

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
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
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-3: Chemical composition of limestone samples from Kohat area [11].

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
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
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-4: Chemical Composition of limestone samples from Cherat area [11].

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
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
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

Table-5: Standard specification of limestone for different industries [14, 15].

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 %	_
Colorless glass	1.00 %	0.035 %	_	55.20 % min	_	_	_	_	2.00 %
Sodalime glass	68-75 %		_	14 %	0-10 %	10-15 %	_	_	_
Pottery	2 %	0.30 %	_	_	_	_	_	_	_

concentration of MgO contents, and therefore found unsuitable for sugar refining and paper manufacturing.

In glass industry both high calcium limestone and dolomite are used in glass manufacture. Limestone containing less than 0.2 % Fe_2O_3, 55.20 % CaO, 1.00 % silica is used for certain special glasses (Table-5). Comparison of the result of Nizampur limestone (Table-1) with Khyber Agency, Kohat and Cherat limestone (Tables 2-4) showed that due to low iron and high CaO, limestone of all selected areas are suitable for glass industry.

Limestone having high lime content alongwith 0.3 % Fe_2O_3, 2 % SiO_2 and 0.1 % SO_4 is

used for pottery purposes (Table-4). Results show that along with Khyber Agency, Kohat and Cherat area (Tables 2-4), Nizampur limestone (Table-1) is also suitable for pottery purpose.

Alumina in combined state is an important constituent of cement in which it behaves as an acid. In cement industry Al_2O_3 and Fe_2O_3 are used to produce liquid (flux) in the kiln burning zone, insufficient Al_2O_3 and Fe_2O_3 lead to difficult burning of clinker while excessive amount lead to low strength due to dilution of silicates by aluminate and ferrite [12]. Alumina content in Nizampur limestone varies from 0.3 %-12.96 % while Khyber Agency, Kohat and Cherat areas series ranges from 0.20-1.58, 0.62-2.02 and 0.13-1.815 % respectively, which is high in most of the samples.

High Alkalies are objectionable in cement industry, which cause deterioration of concrete and enter in reaction with certain types of aggregates [13]. So it is recommended to use a low alkali limestone [14, 15]. Nizampur limestone is in the range of 0.07 %-0.35 and 0.01-0.09 Na_2O and K_2O while Khyber Agency, Kohat and Cherat areas vary from 0.14 %-0.34 % and 0.02 %-0.10 %, 0.12 %-0.21 % and 0.03 %-0.12 %, 0.27 %-0.60 % and 0.035 %-0.70 % respectively. The results of Nizampur shows that the alkalies are lower than the objectionable limit for the use in cement industries.

Experimental

The carbonates samples were analyzed for their major and minor elements. The silica and combine oxide were determined by conventional gravimetric methods, where as calcium oxide and magnesssium oxide were determined by EDTA titrimetric method, as well as gravimetric method for comparing the results. Sodium and Potassium were determined by flame photometric method using Corning 400 Flame photometer, while iron by spectrophotometric method using Schimadzu Double Beam Spectrophotometer UV-200S. Loss on ignition was determined at 950 °C in muffle furnace for 1 hour.

Conclusions

The results of chemical analysis of Nizampur limestone showed that it is suitable for glass, paper, pottery and cement industries. However, detail work is recommended for determining the economic feasibility of these deposits for different industrial purposes.

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