Pak. J. Sci. Ind. Res. 2007 **50**(5) 293-298

Physical Sciences

Industrial Applications of Limestone Deposits of Kohat, NWFP: A Research Towards the Sustainability of the Deposits

Rubina Bilqees[a]* and Tahir Shah[b]

[a]PCSIR Laboratories Complex, Jamrud Road, Peshawar, Pakistan

[b]NCE in Geology, University of Peshawar, Peshawar, Pakistan

(received October 28, 2006; revised July 31, 2007; accepted August 3, 2007)

Abstract. Chemical analyses, petrographic studies and physical tests of limestone deposits in the vicinity of Kohat along Bannu Road, Hangu Road and Rawalpindi Road were carried out to categorize these reserves, locality-wise, for their specified industrial uses. Limestone of Kohat area was found to be generally good for construction purposes. The deposits on the Hangu Road were of good quality with more than 97% $CaCO_3$ and suitable for use in chemical, iron and steel industries, for glass making, soda ash manufacture etc. The deposit of Bannu Road with 96.5% $CaCO_3$ can be used for sugar refining, paint industry, flue gas desulphurization, animal feed etc. The limestone deposit of Rawalpindi Road is inferior in quality having 95.2 % $CaCO_3$. It can be utilized in rubber industry, as ceramic whiting, building materials, rock wool etc.

Keywords: limestone, Kohat (NWFP), industrial applications, sustainable development

Introduction

The North West Frontier Province (NWFP) of Pakistan limestone has huge reserves of limestone, besides of other minerals, comprising rocks dating back from Eocene to Precambrian period. This limestone is mostly used for construction purpose and in a few non-constructional industries, locally as well as in developed countries. The non-constructional uses or high purity applications include, in industries concerning manufacture of glass, paper, chemicals, sugar, animal feed, agriculture, paints, rubber, pharmaceuticals, foods and drinks etc. Searle (1935) was the first to carry out work on limestone. Gillson (1960) examined the physical and chemical properties of carbonate rocks and discussed some of the uses of limestone and dolomite. The major compilation work on the carbonate rocks employed directly (e.g. dimension stone) or indirectly in a manufacturing process (glass manufacturing or sugar refining) was done by Lamar (1961). Oates (1998) and Boynton (1980) worked on the chemistry, technology, production and uses of lime and limestone. Tucker and Wright (1990), Wiersma (1990) and Scoffin (1987), studied the geology of the carbonate sediments and rocks.

In Pakistan, some work on the Nizampur limestone of NWFP has been generally carried out by Husain *et al.* (1989), and on the limestone of NWFP for the cement industry by Husain (1995). Present work is a first step towards the detailed evaluation of limestones deposits for their various industrial applications and comprises, a series of studies to be carried out on different limestones deposit occurrences in NWFP. Present study includes limestones from different locations in and around the Kohat area. Detailed chemical, mineralogical and physical studies of these limestones suggest their potential for utilization in many industries. At present, limestones has been mined from the Babri Banda area at the Rawalpindi-Kohat road for the cement plant located in that locality.

Geology of the area. The Himalayas-Karakorum-Hindukush ranges in the northern Pakistan are considered to be a broad collision zone between the Asian plate in the north and the Indian plate, in the south. The first block to collide with southern margin of the Asian Plate was the Karakorum Plate, followed by the Afghan Block and in the end the Kohistan Island Arc came in contact with the system (Windley, 1983; Le Fort, 1975; Gannser, 1964). Main Karakorum Thrust (MKT) and Main Mantle Thrust (MMT) are the two major tectonic features formed as a result of these collisions in the Northern Pakistan (Fig. 1).

Kohat Province of the upper Indus Basin constitutes the western part of the Himalayan fold-and-thrust belt, which is the resultant of the ongoing collision between the Indian and Asian plates. The upper Indus Basin is divided into two areas, the Potowar Plateau to the east of the Indus River and the Kohat Plateau, west of the Indus River.

In the Kohat district, several outcrops of Lockhart and Kohat limestone are found along the Indus Highway, the Kohat-Pindi Road and Kohat-Hangu Road. The limestone occurrences at Kohat-Bannu Road, Kohat-Pindi Road and Kohat-Hangu Road were selected for the present study. All these limestones belong to Kohat formation which represents the top of the Eocene sequence within Kohat plateau. The three-fold subdi-

*Author for correspondence; E-mail: rubina_bilqees@hotmail.com

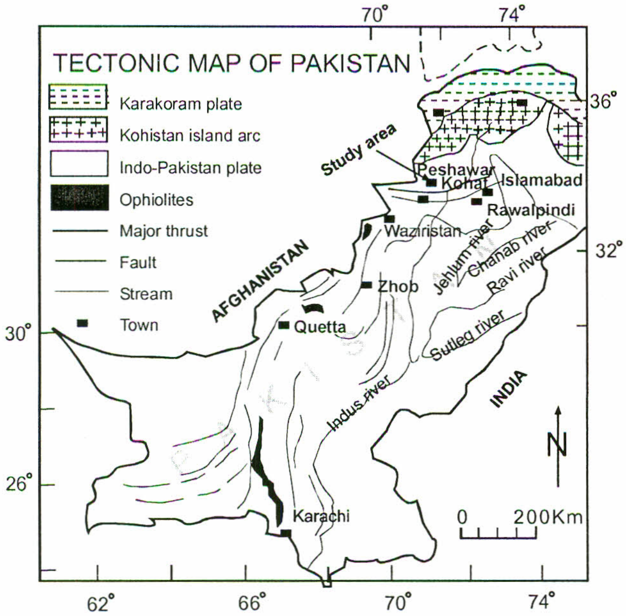

Fig. 1. Tectonic map of Pakistan.

vision of the Kohat formation into various members by Meissner *et al.* (1974) does not persist throughout the plateau. The reserves of limestone are of several hundred million tons.

Materials and Methods

Fieldwork was conducted and about 40 grab samples were collected from three localities: Kohat-Rawalpindi Road, Kohat-Bannu Road and Kohat-Hangu Road (Fig. 2). Thin sections were prepared for the petrographic studies. Various physical tests were carried out to study the suitability of these limestones for building material whereas, chemical analyses were carried out to study their suitability for different industrial uses.

The standard methods of the American Society for Testing Materials (ASTM) for testing the physical properties of rock materials were adopted for the physical tests of Kohat limestone.

Results and Discussion

Petrography. Physically these limestones are generally gray to dark gray and medium to thick bedded and have nodular structures at places. Solution weathering is common along fractures and joints. The formation attains maximum thichness in the northern Kohat plateau, southwest of Kohat city (180 m) and varies between 1-5 m in southern Kohat plateau. At its type locality the Kohat formation is composed of thin bedded foraminiferal limestone and yellow-green shale at the base. In the middle part the Formation is dominantly foraminiferal grainstone which is composed of numulites. Towards, the top it comprises of thick-bedded limestone of Kohat formation (Davies, 1941), which makes ridges throughout the Kohat plateau. Its lower contact is conformable with the underlying Mamikhel clay and is unconformably overlain by the Miocene series. It is fine to medium-grained, well-bedded, compact and hard. The majority of the samples have microfossils, which are visible in the field with the help of a hand lens.

Microscopic studies show that these limestones are granular, fine to medium-grained and are bioturbated with microfos-

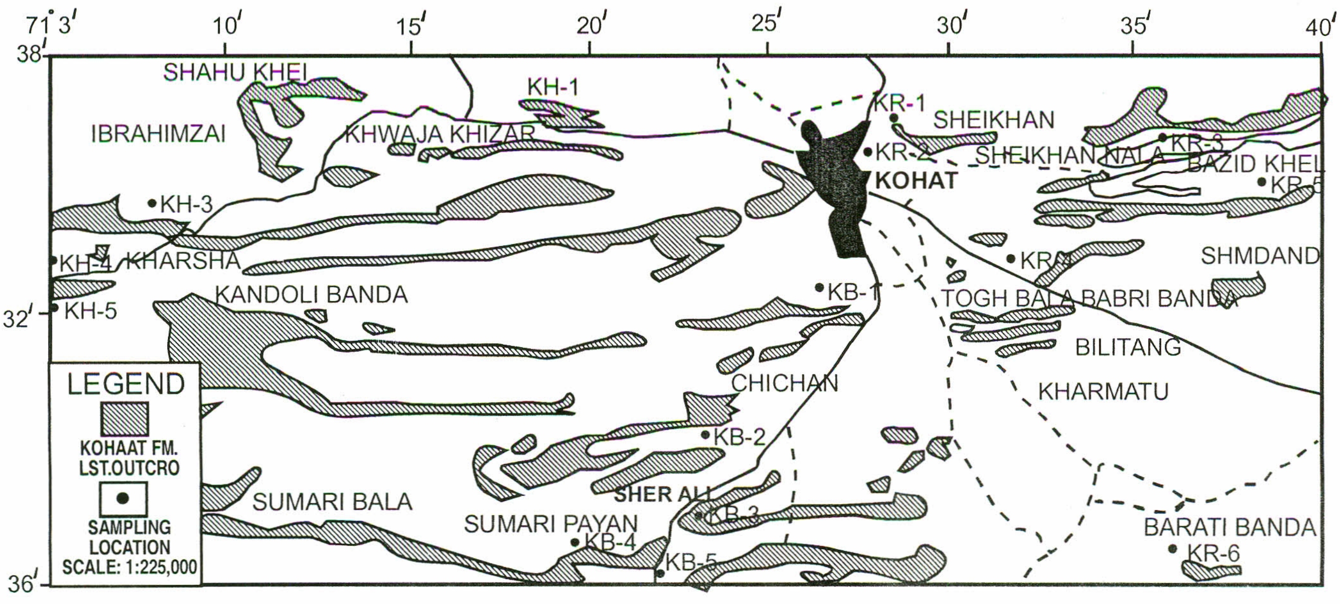

Fig. 2. Map of the study area.

sils. They are composed mainly of calcite and fossil shells, with lesser amounts of dolomite, quartz, clay and opaque minerals. Calcite is generally fine-grained, but patches of medium to coarse-grained anhedral calcite in the fine-grained ground mass is also common. The fine-grained calcite seems to be authegenic (primary) in origin and has been deposited *in situ*. The coarse grained calcite has interlocking texture and grains show well- developed cleavages. Microfractures filled with fine to medium grained calcite, forming micro-veins, are also common in these rocks that are considered to be diagenetic (secondary).

Dolomite is intimately associated with calcite in the micro-veins and is, therefore, considered as the secondary phase. It is difficult to distinguish dolomite from limestone visibility, however, it can very easily be recognized after staining the sections. Dolomite is medium grained having rhombohedral habit. Quartz is either absent or is present in traces in almost all the thin sections; however, one sample (KH-6) collected from Ghulam Banda, Rawalpindi Road, has more quartz and thin sections show dissemination of quartz throughout the sample. Some times, chalcedony is present in the form of sphelurite in the fossil's tests. Clay is present in trace amounts in few thin sections. Opaque minerals are also present in traces, distributed throughout the rock. Iron leaching is seen along some micro fractures.

The petrographic study of these limestones show the absence of deleterious substances except minute chalcedony, dolomite and quartz in the argillaceous variety of limestone. The limestone was further examined by ASTM C 289-94 (chemical method), to ensure its feasibility for concrete.

The limestone chemistryhas been summarised in Tables 1a-c at each location. The limestones have SiO_2 in the range of <0.5-1.5 except two samples which are from siliceous limestone on the Rawalpindi Road. Al_2O_3 is not more than 0.74% by weight. Fe_2O_3 is less than 0.5% by wt. and MnO is negligible. MgO is generally less than 1%, however, some samples show MgO as high as 3.52% by wt. Among alkalies Na_2O is less than 0.50% by wt. while K_2O is negligible. The loss of ignition is more or less constant about 43 weight %, by wt.

Table 1a. Chemical analyses of Kohat eocene limestone (Kohat-Hangu Road)

Samples	KH-1	KH-2	KH-3	KH-4	KH-5	KH-6	KH-7	KH-8	KH-9	Average
CaO	55.20	52.2	53.51	53.74	54.59	54.11	55.52	55.42	55.62	54.43
MgO	0	1.24	0.62	1.14	1.97	2.69	0.93	1.35	3.52	1.49
SiO_2	<0.5	1.5	<.50	<0.05	<0.5	<0.5	0	0	0	<0.5
Fe_2O_3	0.5	.15	0.08	0.22	0.15	0.06	0.06	0.14	0.12	0.16
Al_2O_3	0.49	.47	0.46	0.51	0.58	0.51	0.49	0.52	0.48	0.50
Na_2O	0.43	.36	0.39	0.43	0.36	0.39	0.40	0.41	0.42	0.399
K_2O	0.02	.03	0.02	0.02	0.03	0.02	0.02	0.04	0.03	0.02
MnO	0.01	.01	0.01	0.02	0.02	0.01	0	0	0.007	0.009
L.O.I.	42.88	43.21	43.53	43.35	43.41	42.67	43.08	42.68	42.07	42.98
$CaCO_3$	98.57	93.20	95.56	95.97	97.49	96.64	99.16	98.98	99.34	97.2

L.O.I. = loss of Ignition

Table 1b. Chemical analyses of Kohat eocene limestone (Kohat-Bannu Road)

Samples	KH-1	KH-2	KH-3	KH-4	KH-5	KH-6	Average
CaO	53.03	54.76	55.12	53.74	53.6	54.03	54.06
MgO	0.21	0.31	0.83	0	0	0.31	0.27
SiO_2	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	0	< 0.5
Fe_2O_3	0.19	0.1	0.10	0.15	0.12	0.13	0.13
Al_2O_3	0.15	0.62	0.47	0.53	0.58	0.57	0.49
Na_2O	0.4	0.44	0.41	0.46	0.42	0.43	0.43
K_2O	0.03	0.02	0.02	0.02	0.02	0.03	0.02
MnO	0.01	0.1	0	0	0	0.02	0.02
L.O.I.	43.15	43.21	43.12	43.21	43.17	42.92	43.13
$CaCO_3$	94.71	97.80	98.44	95.98	95.73	96.50	96.5

Table 1c. Chemical analyses of Kohat eocene limestone (Kohat-Rawalpindi Road)

Sample	KH-1	KH-2	KH-3	KH-4	KH-5	KH-6	KH-7	KH-8	KH-9	Average
CaO	54.61	55.54	54.8	52.79	54.91	46.07	52.43	55.75	54.91	53.51
MgO	0.93	1.24	0.62	0.73	1.04	0.62	0.62	1.55	0.41	0.86
SiO_2	1.3	0.60	<0.5	3.5	<0.5	13.90	<0.5	0	0	-
Fe_2O_3	0.27	0.19	0.24	0.30	0.13	0.25	0.25	0.17	0.09	0.21
Al_2O_3	0.67	0.52	0.53	0.52	0.47	0.74	0.57	0.46	0.61	0.56
Na_2O	0.37	0.47	0.46	0.43	0.43	0.45	0.35	0.43	0.49	0.42
K_2O	0.04	0.04	0.03	0.04	0.01	0.02	0.05	0.02	0.02	0.03
MnO	0	0	0	0.01	0.02	0.25	0.01	0.004	0	0.03
L.O.I.	41.88	42.33	42.78	42.36	42.81	35.74	42.36	42.44	42.3	41.65
$CaCO_3$	97.53	99.19	97.87	94.26	98.05	82.26	96.27	93.63	98.05	95.2

with the exception of one sample (KH-6) which has a lesser L.O.I., circa 35% by wt.

Industrial applications. Carbonate minerals and rocks, or the products derived from them have a myriad of uses. Indeed, industrial development in the United States and other developed countries in the world, is in part reflected in the number of tons of the raw material carbonate produced and sold each year. The uses to which carbonate rocks and minerals can be put is a function of their physical and chemical properties. The physical, chemical, mineralogical and other properties of carbonate rocks influence (within certain limits) their economic potential, that is, the maximum number of uses they might serve.

Uses based on the physical properties of Kohat limestone. The applications of physical properties of limestone are mainly for constructional uses, however, there are other additional uses.

Physical properties such as strength and durability influence the characteristics of concrete but, impermeability, resistance to abrasion and soundness are vital to concrete aggregates in order to withstand the pressure to which concrete is stressed and the shrinkage caused by dehydration. Table 2 shows the soundness, water absorption and Los Angeles Abrasion values of the Kohat samples, which are within permissible limits for concrete aggregates given by ASTM.

Harder limestone is commonly used in highway construction and, in Pakistan and many other countries, road stone is the largest single end use of limestones. Different physical tests carried out for the evaluation of these limestones (Table 2) show that these rocks fulfil the requirements of road-stone. Besides, these limestones are also suitable as rip rap (used in spillways of dams, construction of docks and piers and for filling in low places on land or in roads), as asphalt filler, as roofing shingles and as other construction products.

Table 2. Physical (geotechnical) properties of Kohat limestone

Group nos.	L.A. abrasion	Soundness	Water absorption
A	21.2	2.7	0.6
B	20.40	0.8	0.3
C	20.7	1.0	0.4
D	20.8	0.4	0.7
E	21.3	0.4	1.2
F	18.2	0.5	0.7

Group A comprised of geochemical samples no.RK-1. RK-3/b, RK-6 & RK-7; Group B comprised of geochemical samples no.RK-2/a, Rb-2/b & RK-4; Group C comprised of geochemical samples No.RK-8, RK-10 & RK-12; Group D comprised of geochemical samples No.RK-11, RK-14a, & RK-14/b; Group E comprised of geochemical samples No.RK-13/a, RK-13/b, RK-15&RK-4;Group F comprised of geochemical sample No.RK-9; for L.A. (Log Angeles) abrasion value, ASTM method no. C-131 (max. limit 50.0), for soundness; ASTM method no.C-88 (max. limit 12.0) and for water absorption, ASTM method no.C-127 (max. limit 0.8) were used.

Uses based on chemical properties of Kohat limestone. The chemical composition of carbonate determines most of its potential uses. Strict control has to be maintained on the chemical composition of the limestone for use in the manufacture of many economically important products. Limestone for is used in a number of industries where chemical properties (basic oxide, neutralizing agent, calcium content, flux etc.) are important. Lime is produced when pulverized high purity limestone is heated at an elevated temperature, volatilizing nearly half of the stone's weight as CO_2. Hydrated lime in turn is produced by reacting quicklime with sufficient water to form a dry, white powder.

$$CaCO_3 \xrightarrow{(1000\,^{\circ}C)} CaO + CO_2$$

$$CaO + H_2O \longrightarrow Ca(OH)_2 \text{ (lime)}$$

Lime is neither toxic to workers in lime manufacturing or lime consuming plants, nor its air-borne particles are harmful to the public. Next to steel-making, the most extensive use of lime is for environmental cleaning of water, waste water (Lewis and Gutschick, 1980), air and solid wastes. This basic chemical is materially aiding mankind in its environmental clean-up.

Limestone or lime is used as a flux to assist smelting in the extraction of iron from ore. Lime reacts with silica and alumina impurities in the ore and forms a slag, which floats on the surface of the melt. Different specifications of limestone are used, depending upon the particular iron/steel plant, but generally pure limestone with low sulphur and phosphorus contents are specified for this process. Silica is less than 2 % in samples from Eocene limestone of Kohat-Hangu Road section, Kohat-Rawalpindi Road section and most samples from the Kohat-Bannu Road section; thus it is suitable for this use.

Soda ash (sodium carbonate) is an important raw material for the chemical industry and requires limestone of high purity (> 98.5% $CaCO_3$). The analyses of Eocene limestone of Kohat (Table 1) shows that $CaCO_3$ content of the Kohat-Rawalpindi Road is lesser than this specification; this limestone, therefore, does not qualify for this purpose unless processed. The limestone of Kohat-Bannu Road has $CaCO_3$ in the range of 94.7 to 98.4% which, though slightly low may serve the purpose. But the limestone of Kohat-Hangu Road has $CaCO_3$ content suitable for the manufacture of soda ash (with the exception of one sample which is too low in $Ca CO_3$).

Limestone and lime used in the sugar industry, as part of the purification process, need to be high-grade, containing at least 96 % $CaCO_3$ and < 1% SiO_2, < 0.35 % Al_2O_3 and < 0.3 % Fe_2O_3. Al_2O_3 content in all the studied samples is little higher than the required specification; hence, if these limestone are processed to reduce this content, they can be utilized in the sugar manufacture.

The proportion of lime and limestone used in the glass industry is close to that of soda ash and it is the third major ingredient of different types of soda-lime-glass. Major ingredients of different types of soda-lime-glass are:

SiO_2: 68-75 %
CaO : 5-14 %
Na_2O : 10-18 %
MgO : 0-10 %

Limestone is used to render the glass more insoluble for uses in contact with water and chemical solutions, to improve the mechanical properties of glass by making it less brittle and stronger, and to improve the appearance of glass by providing a more enduring lustre. Limestone and lime are the lowest-cost fluxing materials for glass. They flux the silica sand, forming chemically fused calcium silicates. For some general uses, preferences are made. A decided trend is to employ high calcium stone for flat or window glass and dolomitic stone or lime for glass containers and tumblers. Due to Mg content, glass acquires greater resistance to the etching effect of certain chemical solvents and acids that may cause discoloration in consumer products packed in glass. Moreover, MgO has slightly improved resistance to heat shock. High purity limestone with $CaCO_3$ >98% is required. Fe_2O_3 content should be less than 0.05%, hence the Kohat limestone cannot be used unless processed.

Limestone is used in the sulphite process for making paper pulp where it reacts with SO_3 to form the calcium bisulphite pulp-cooking liquor in the Jennsen tower system. A high calcium limestone is required in this process. Generally specified are the minimum $CaCO_3$ content 95-97 %, and stone as large as 20.3-35.6 cm. Top size is preferred for use in the tower. Limestone of all the three localities studied is suitable for paper pulp industry.

Consumption of minerals as fillers and extenders in the paint and other coatings industries is of the order of 7,50,000 tpa, about one third of which is calcium carbonate. Kohat limestone has high calcium content, low Mg and Al_2O_3 and acid insolubles are less than 2%. So it fulfils the requirements of filler used in paint industry. Brightness is an important parameter for whiting and precipitated calcium carbonate.

Kohat limestone is a high calcium limestone so it may be used in the manufacture of chemicals. It can be used in the recovery of acetic acid from the destructive distillation of wood. These limestones could also be used in the manufacture of alkali, aluminum oxide, soda ash, ammonia and asphalt filler, calcium carbide, calcium nitrate, mono-calcium phosphate, carbon dioxide, pharmaceuticals and ammonium nitrate. It is also suitable for use in the manufacture of dyes.

Limestone at all the studied localities of Kohat are suitable for use in liming the soil, for copper purification, manufacture of explosives, manufacture of rock wool, and as ceramic whiting. Generally, the Kohat limestone can be used as barnstone/barn lime, brick glazing, fertilizer filler, filler stone, etc. It can be used as mineral feed for livestock if fluorine content is less than 0.1% (not determined here).

Conclusion

The physical and chemical properties of Kohat limestone reveal that it could be used for a variety of purposes. The purpose of this study was to categorize these deposits for specific potential uses. Though limestone resources are immense at this time, the burden of ever-growing population on these limited resources is increasing day by day, and all these resources have to be saved for the generations to come. So awareness must be created through publications and seminars etc. towards the sustainability of these mineral resources. Moreover, conducting similar studies is suggested for all the mineral resources to meet the present as well as the future needs of the country.

References

Boynton, R.S. 1980. *Chemistry and Technology of Lime and Limestone*, John Wiley & Sons Inc., New York, USA.

Davies, L.M. 1941. The Dungham limestone and Ranikot beds in Baluchistan. *Geol. Mag*. **78:** 316-317.

Gansser, A. 1964. *Geology of the Himalayas*, pp. 289. Interscience Publishers, John Wiley & Sons, London, UK.

Gillson, J. L. 1960. The carbonate rocks. In: *Industrial Minerals and Rocks*, pp. 262-263, 3rd edition, Am. Inst. Min. Eng., New York, USA.

Hussain, A. 1995. Cement raw materials in the North West Province, Pakistan. In: *Proc. Int. Symp. and Field Workshop on Phosphorites and other Industrial Minerals, Segmite International Geologist Project, Abstracts Volume,* pp. 19.

Husain, V., Bilqees, R., Nasreen, S. 1989. Petrological and industrial applications of Nizampur limestone, NWFP, Pakistan. *Pak. J. Sci. Ind. Res.* **12:** 775-779.

Lamar, J.E. 1961. *Uses of Limestone and Dolomite. Illinois State Geol. Survey. Circ.* 321, pp. 1-44.

LeFort, P. 1975. Himalayas, the collided ranges, present knowledge of the continental arc. *Am. J. Sci.* **275-A:** 1-44.

Lewis, C.J., Gutschick, K.A. 1980. Lime in Municipal Sludge Processing. *National Lime Assoc. Bull.* No. 217.

Meissner, C.R., Master, J.M., Rashid, M.A., Hussain, M., 1974. Stratigraphy of the Kohat Quadrangle, Pakistan. *US. Geol. Surv. Prof. Pap.* 716- D, pp.1-30.

Oates, J.A.H. 1998. *Lime and Limestone, Chemistry and Technology, Production and Uses,* Wiley-VCH, Weinheim.

Scoffin, T.P. 1987. *An Introduction to Carbonate Sediments and Rocks*, Chapman & Hall, New York, USA.

Searle, A.B. 1935. *Limestone and its Products.* Ernst Benn. Ltd., London, U.K.

Tucker, M.E.,Wright, V.P. 1990. *Carbonate Sedimentalogy*, Blackwell Sci. Publ. London, UK.

Wiersma, M. 1990. The geology of carbonate rocks. In: *Proc. Int. Lime Cong.* Rome, Italy.

Windley, B.F. 1983. Metamorphism and tectonics of the Himalaya. *J. Geol. Soc. Lond.* **140:** 849-865.