GEOCHEMICAL INVESTIGATION OF MUSAKHEL LIMESTONE

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Six representative samples of limestone were selected for the study of the effects of their mineral components and proportion and their various uses in industry. The samples were collected from Musakhel in the Salt Range, West Pakistan.

Limestone and related rocks are the most important carbonate sedimentary rocks. It is proposed to designate those sedimentary rocks as limestone in which the carbonate fraction is composed primarily of calcite.

The minerals forming the calcareous rocks are few in number, and the great variation in the appearance and proportion of different limestones arises principally from the almost endless variety of chemical, organic and other structures into which the crystals of these minerals are aggregated. Calcite is the stable form of calcium carbonate at ordinary temperatures, and may be regarded as the principal mineral of limestone. Aragonite is the form which calcium carbonate normally adopts when inorganically precipitated from sea-water, and is unstable. Dolomite is another important constituent of calcareous rocks. Other minor limestone rock-forming minerals are magnesite, phosphorite, glauconite, quartz, feldspar, clay minerals, gypsum, limonite, pyrite and chalcedeny.

The calcium carbonate of a limestone may originate from the debris of calcareous organism or as a chemical precipitate from solution or as fragmental material derived from older limestones. It is convenient, therefore, to name them as follows:-

1. Organic limestones.
2. Precipitated limestones.
3. Plastic limestones.

The chemical composition of limestones as might be expected, reflect closely their mineral composition. The limestones are mainly calcite, and the contents of CaO and CO_2 is in some cases more than 95%. Magnesium limestones contain 1 to 2% MgO, indicating the presence of mineral dolomite. Excessive silica indicates the presence of much detritus or the presence of chert. If alumina is also high the silica is probably a constituent of associated shaly matter in argillaceous limestone.

Experimental

Geological Investigation.—Large deposits of limestones are found in the bare and well-exposed mountains of Chidru, Marmandi, Sakesar, Nammal, Daudkhel and other areas of the Salt Range.[1,2] The out-crops extend for a distance of more than one hundred miles from Katha in the east and beyond Kalabagh in the west. Limestone can be found in many hundred feet thickness in the Permian to Eocene Systems in and around the Nammal gorge area which can be approached directly by metalled road from Mianwali. The lithology of all formations is quite distinct from one another in all the system. The limestones are light grey and yellowish in colour and they are somewhat soft to compact. The deposits of limestone are not successively overlain by one another but are intercalated by sandstone, clay-stone, marl and shales. The whole geology is very briefly discussed in the following lines[3] with reference to the samples collected.

MURREE SERIES OF L. MIOCENE.

System	Thickness ft.	Sample Ref.	Description
(1)	(2)	(3)	(4)
Eocene			*Bhadrar beds.* Olive-green foraminiferal shales and bedded limestone.
	160-500	1	*Sakesar Limestone.* Massive and nodular, white and grey foraminiferal l. st. with subordinate marls and shales.
	120-250	2	*Nammal Limestone & Shales.* White and light grey calcareous shales with limestones.
	100-250		*Patala Shales.* Olive green foraminiferal shales and coal seams.
	1000	3	*Khairabad limestone.* Grey and yellowish brown, semi-nodular foraminiferal limestones.

(*Continued*:-)

(*Continued*:-)

(1)	(2)	(3)	(4)
	150		*Dhak Pass beds.* Impure limestones and shales, often carbonaceous.
	Unconformity		
Cretaceous	330		*Lumshiwal Sandstone.* Massive white and light coloured sandstones.
	440		*Belemnite beds.* Grey, dark, green and almost black shales and sandstones.
Jurassic	1000		*Baroch Limestone:* Grey and purplish bedded limestones often semi-porcellaneous.
	1500		*Varigated stage.* Alternating marine shelly limestone with plant-bearing carbonaceous shales. Also red shales and laterite.
	Unconformity		
Triassic	300-400		*Kingriali dolomite.* Massive light coloured dolomitic limestones and sandstones.
	200		*Kingriali sandstones.* Massive yellow-grey, purple and verigated sandstones.
	600	4	*Ceratite beds.* Green and brown sandstones and shales with thin limestone underlain by olive-green shales and thin limestones with Ceratites.
Permian	250		*Upper Productus beds.* Yellow-grey limestones, marls and calcareous sandstones very fossiliferous; with dull green shales.
	300	5,6	*Middle Products limestones.* Massive fossiliferous light-grey limestones passing down into dark-grey shales.
	150		*Lower Productus beds.* Brown and greenish grey calcareous sandstones and impure limestone.

Field Sampling.—The samples were collected from different formations of limestone from the bottom contacts to the top contracts in intervals of about five feet from comparatively thin beds and of ten feet for thick beds. The lateral variations were noted at about 200-300 at intervals. In this way the samples collected were in an area of about 30 square miles.

Laboratory Sampling.—In the laboratories the samples were mixed and crushed. The crushed bulk was quarter-coned, and then about 200 g of

TABLE 1.— CHEMICAL ANALYSIS %.

No.	Insoluble matter including silica	CaO	Fe_2O_3	Al_2O_3	MgO	SO_3	P_2O_5
L-1	1.29	54.20	0.399	0.311	Traces	Traces	Traces
L-2	3.64	50.80	0.399	0.921	,,	0.05	,,
L-3	1.33	51.68	0.439	0.781	,,	0.04	,,
L-4	0.53	51.48	0.271	0.499	0.76	0.05	,,
L-5	0.46	55.04	0.159	0.481	0.68	Traces	,,
L-6	0.47	55.10	0.127	0.198	Traces	,,	,,

sample was further ground, spread out in a layer, and portions taken from different parts to yield a sample of approximately 20 g. This sample was further finely ground in an agate mortar, dried at 110°C in an oven, put in stoppered bottle and stored in a dessicator.

Chemical Analysis.—Samples were analysed chemically, according to British Specifications.[4] The constituents determined were non-volatile matter including silica, Al_2O_3, CaO, SO_3, P_2O_5 and MgO; Fe_2O_3 was determined colorimetrically using the thiocyanate method. Al_2O_3 was found out by difference. Results are given in Table 1.

Petrography.—In handspecimen[5] the limestone L-5 and L-6 are almost white with some iron oxide stains. Both these limestones are structurally compact and hard, i.e., highly cemented medium to coarse grained rocks. Due to compaction the grains of calcite have been corroded at the corners. Hardness is 3.0 in both cases. Limestones L-1 and L-3 are white and grey coloured respectively. L-1 shows some bluish tints while L-3 has yellowish and brownish tints. L-1 and L-3 have 3.0 hardness. The grains in both cases are fine but there are some coarse grains of calcite in L-1. In L-3, veins of pure white calcite are also present. Anyhow the rocks are compact. L-2 is light-grey and cream coloured earthy limestone. In this rock the grains of rock-forming minerals are very fine and not very compact. But some microfossils are distinctly medium grained. Due to earthiness the hardness decreases to 2.5. The limestone L-4 is light grey with occasional yellowish and bluish tints. The hardness is again 3.0. Some coarse grains are visible for the identification of calcite. Again in this case the compaction has made the interlocking of calcite grains which make the rock compact and hard.

Under the microscope[6] the limestone L-1 and L-3 consists of calcite, quartz and ore minerals (magnetite, hemetite, limonite and pyrite). Calcite is colourless and fine to medium grained. Quartz and ore minerals are about 2% each in both limestones. The rocks form a compact, texture. L-2 is not very compact and the grains of calcite are somewhat of earthy colour. The modal composition is same as in L-1. The ore minerals are in the form of fine grains and specks. The texture of L-4 is fine to coarse-grained and compact but medium to coarse grains are predominant. Ore minerals and quartz contents are about 1% each respectively. L-5 and L-6 are from Productus Series and are very much rich in calcite. They do contain authigenic mineral like dolomite which is hardly 1%. Quartz and other ore minerals are less than in L-1 to L-4 limestones.

Apparent Porosity and Specific Gravity.—Apparent porosity was determined by the water saturation method according to the A.S.T.M. specifications.[7]

Specific gravity of the limestone was determined by the pycnometer method.

Table 2.— Results of Apparent Porosity and Specific Gravity.

Sample	Average apparent porosity	Average sp. g.
L-1	2.33%	2.74
L-2	11.34%	2.64
L-3	2.33%	2.74
L-4	1.29%	2.73
L-5	0.60%	2.72
L-6	0.80%	2.72

Results and Discussion

Geological investigation shows that the limestone formation occurred by chemical and organic processes. The detrital limestone is hardly available. Some other interbedded deposits are of shallow-water conditions. Thus the entire formations from Permain to Eocene were deposited sometimes in the deep sea and sometimes in the shallow-water conditions. The respective fauna of that age, such as Criniods, Ceratites, Forumus etc. show the formation in deep sea while ripple marks and cross-bedding is the evidence of shallow-water formations.

Physical properties show that the limestones of various systems have different characters. L4, L5, and L6 are medium to coarse-grained and highly compact and white to grey in colour. Further, from Table 2 it is clear that the porosity of the limestones is low. Uniform texture of this type is usually specified for monumental and structural buildings, since high porosity affects the durability of the stone due to infiltration of water, which may freeze and cause the stone to spall. For attractive monuments the fessiliferous limestones can be cut into beautiful polished tiles as well.

Petrographic examination of the samples shows that impurities present in limestones are chiefly in the form of quartz, dolomite and ore minerals.

As already observed, commercial exploitation of limestones greatly depends on their mineral contents. Keeping the results of chemical analysis (Table 1) in view, the industrial utility[8] of different limestones is discussed as follows.

1. For use in the blast furnace, limestone should not contain more than 1.5% SiO_2. Sulphur should not exceed 0.5% for which L-1, L-3, L-4, can be used, but L-5 and L-6 are the best for the purpose. The amount of magnesia in L-5 is also not objectionable. Basic, open hearth steel makers require a stone having a high lime content with low sulphur and phosphorus. Silica is more objectionable in limestone for this purpose than in limestone used as a flux in blast furnace work and should, therefore, be low, preferably not over 1%, for which L-5 and L-6 are more useful.

2. For manufacture of soda ash a specification proposed by an American authority suggests that the following percentage composition is desirable. $CaCO_3$ 90-99; $MgCO_3$ 0.6; $Fe_2O_3+Al_2O_3+SiO_2$, 0.3. No limestone can be used as such for this purpose, any how, after beneficiation L-5 and L-6 can be taken into consideration.

3. L-5 and L-6 can be used in the manufacture of both cane and beet sugars as they have low silica and iron contents. Silica is objectionable in limestone as it may become collodial in the juices, form film on the crystals, and retard their growth. Iron oxide tends to colur the finished sugar.

4. For the soda and sulphate pulp processes of paper manufacture a high calcium lime with less than 2% MgO is usually preferred, and although lime containing upto 7% total $Fe_2O_3+Al_2O_3+SiO_2$ is used purer lime is to be preferred. So L-1, L-3, L-4, L-5, and L-6 are proposed for this purpose.

5. For the production of high grade glass, limestone should not contain more than 0.2% iron oxide but for flint glass the limit is about 0.03%. Calcium carbonate should be 98.5%,

and non-volatile matter not exceeding 1.0%. For this purpose L-5 and L-6 are the most suitable. They require a little beneficiation for flint glass.

6. Calcium carbonate is used as a constituent of certain pottery glazes and enamels. The mineral should not contain less than 97% total carbonate, not more than 0.3% Fe_2O_3, 2% of silica and 0.1% of SO_3. L-5 and L-6 are readily preferable while L-1 can be considered as well.

7. In textile industry, lime is used in boiling out, scouring and bleaching of vegetable fibres and for liming kiers. The lime must contain a minimum of 94% CaO with the following maximum percentages: MgO 0.3; R_2O_3 2 and insoluble matter, 2.5. L-1, L-5 and L-6 fulfil these requirements.

8. In the manufacture of silica bricks quicklime or slaked lime should not contain less than 90% CaO, and the following percentages maximum: MgO 4.5; $Fe_2O_3+Al_2O_3$ 1.5, SiO_2 and insoluble matter 3. All the limestones after calcination can be used.

9. For agricultural uses, no special specifications are needed as the function of limestone is to ameliorate soil conditions. Thus L-1 to L-6 can be utilised.

10. Cement industry is probably the largest consumer of limestone. Specification for limestones are CaO 42% minimum, MgO 0.4%, Fe_2O_3 0.2%. All the samples are readily useable after calcination.

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