Industrial applications of Abbottabad limestone; utilizing its chemical and engineering properties

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Abstract

Limestone is a commonly occurring rock in Pakistan and has got numerous industrial applications. Some of the limestone deposits of Abbottabad were studied to evaluate these for their use in construction and other industries. Sampling was done from Samana Suk, Kawagarh and Lokhart formations occurring in the vicinity of Abbottabad area. The results of various physical and chemical tests carried out on the collected samples show that these are suitable for use in cement making, agriculture, fertilizers, making animal feed, iron making, water treatment and for use in coal dust mines. Due to tight specifications required for the manufacture of glass and soda ash, acid gas removal, and sugar refining, all the samples of study area do not qualify to be used in the said industries.

Keywords: Abbottabad; Limestone; Industrial; Applications; Chemistry

1. Introduction

Limestone is a sedimentary rock composed largely of the mineral calcite (calcium carbonate). The deposition of limestone strata is often a by-product and indicator of biological activity in the geologic record. Calcium (along with nitrogen, phosphorus, and potassium) is a key mineral to plant nutrition: soils overlying limestone bedrock tend to be pre-fertilized with calcium. Limestone is an important stone for masonry and architecture. It is a key ingredient of quicklime, mortar, cement, and concrete and is being used in a number of industries worldwide.

The work on the industrial utilization of limestone dates back to 1935 when Searl (1935) carried out studies on the industrial products made from limestone. After that many people carried out work on limestone but prominent work is from Gillson (1960), who examined the physical and chemical properties of carbonate rocks and discussed some of the uses of limestone and dolomite. Boynton (1980), Tucker and Wright (1990), Wiersma (1990) and Oates (1998), all have contributed to the limestone production, technology, manufacturing processes and chemistry etc. In Pakistan, less research work has been carried out on the limestone utilization in the preparation of different industrial products and

there is only one group so far working on this subject. Various publications of the said group are those of Husain et al. (1989), Bilqees and Shah (2007), Jan et al. (2009) and Ramezanianpour et al. (2009). Present work is the extension of the research work done so far in order to evaluate the mineral resources of this country generally, and Khyber Pakhtunkhwa (KPK), especially; which has got huge reserves of limestone, ranging from Eocene to Precambrian (Hussain, 1995).

2. Geology of the Abbottabad area

The study area lies in southeast Hazara, a part of the Attock-Hazara Fold and Thrust Belt (Yeats and Lawrence, 1984). It lies southwest of Hazara Kashmir Syntaxis, south of Panjal Thrust, north of Main Boundary Thrust and west of Jhelum Fault (Murree Fault). To the south, crossing the Panjal Thrust (Coward and Butler, 1985), the Hazara Unit (Bossart et al., 1988) follows the Pre-Cambrian Hazara slates which are overlain tectonically by the Cambrian Abbottabad Group in the north and unconformably by Jurassic formations in the South. All the geologic structures present in the study area are northeast/southwest oriented and show a southeast tectonic transport direction. The area is structurally very complex and has experienced several episodes of deformation resulting in

various folds, and strike slip and thrust faults. Rocks are generally dipping towards northwest and southeast (Coward and Butler, 1985). The study area consists of rocks from Jurassic to Paleocene in age in Hazara area, these formations are Samana Suk Formation of Jurassic, Dowager Formation of Cretaceous and Lockhart Formation of Paleocene age. A general stratigraphy of Hazara area consists of rocks from Pre-Cambrian to Eocene in age; comprising a total of eight Formations.

The present sampling was done from Samana Suk, Kawagarh and Lokhart formations occurring in the vicinity of Abbottabad area. Samana Suk Formation refers to the Jurassic limestone in Samana Range. The lower contact is transitional with Shinawari Formation. The upper contact with the Chichali Formation is disconformable. The formation is middle Jurassic in age.

3.   Materials and methods

The limestone samples were analyzed on atomic absorption spectrometer A Analyst 700, PerkinElmer at National Centre of Excellence in Geology, University of Peshawar. For the analyses of different elements on atomic absorption, the wavelength, energy and lamp current varied from element to element. However, generally the wavelength ranged from 248.3 nm for Fe to 766.5 nm for K; energy varies from 25 to 92, slit width varies from 0.2H to 0.7H. Air/Acetylene flame was used and oxide flow was 17 L/min with fuel flow from 2.0 to 2.3 L/min.

Petrographic study of the limestone of the study area shows that these are composed of medium- to coarse-grained equigranular calcite grains. Larger portion of the samples are composed of calcite grains occurring in aggregates of rounded to subrounded grains with no matrix seen, but few larger discrete calcite grains are also present within the matrix of very fine grained calcite. No or very few pore spaces can be seen. No flaky minerals or sulfide-bearing minerals are present showing the suitability of these limestones for use as aggregates. Though most of the samples are of pure limestone but some dolomitic limestone is also present. Dolomite rhombs mostly occur in aggregates along with calcite, however, some are found in micritic groundmass also.

Various engineering properties of these limestone samples were studied following the experimental methodology of American Society for Testing Materials (ASTM) standards (Table 1). For water absorption ASTM C121-06 was used for this purpose a known weight of oven dried sample at 105°C was immersed in water for 24 hours. Then known weight of this sample was taken and immersed in water completely for about 24 hours and then weighed again. From the difference in weight percent water absorption was calculated. Bulk density was determined by using ASTM C29/C29M-07 method in which oven dried samples were tamped in three layers in a steel mould of known volume and weight. By subtracting the weight of the mould we got the weight of the sample and the bulk density value was calculated by taking the ratio of mass to volume. Soundness was determined according to AASHTO T 104 method in which sodium sulfate solution is used. For compressive strength ASTM C 39 /C 39M method was adopted. Concrete cubes of size 4"x4"x4" were made with cement, sand and limestone in a ratio of 1:2:4 by mass and placed in water tub for curing till the time it was tested. The samples were dried for an hour or two in the open air on the 7th day, and then tested for uniaxial compression test in universal testing machine. Similarly, the same test was also performed after 28 days of curing.

4.   Results and discussion

Field work was conducted, about fifteen samples were collected from limestone of Samana Suk, Kawagarh and Lokhart formations (Fig. 1) in Abbottabad area. Samples were divided into two portions; the larger one (about 8-10kg each) for studying engineering properties and the smaller one for mineralogy and chemistry. Chemical analyses were carried out for major elements (Table 2) as well as for trace elements (Table 3). For mineralogy, petrographic study was conducted.
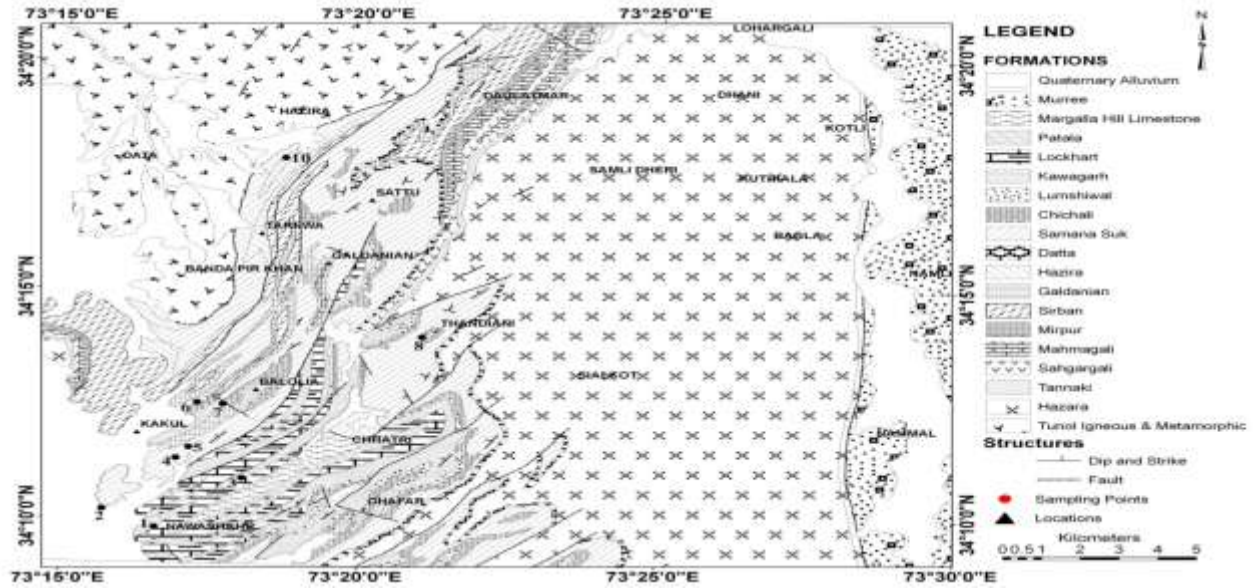
Fig. 1. Geological map of area around Abbottabad showing sample locations (after Latif, 1970)

Table 1. Physical properties of Abbottabad limestone.

Sample ID	Soundness (%age loss in Weight)	Compressive Strength (psi)	Bulk Density (lb/ft3)	Water Absorption (%)
1	0.55	11023	167.42	0.38
2	0.74	11850	162.31	0.44
3	0.52	5126	178.36	0.14
4	0.35	8488	156.07	0.59
5	1.27	6614	166.47	0.79
6	0.56	11023	166.47	0.45
7	1.00	6068	156.07	0.47
8	2.12	2039	166.47	0.37
9	0.20	9480	166.47	0.46
10	0.29	12125	164.99	0.28
11	0.48	11574	156.07	0.72
12	0.34	12125	156.07	1.31
13	0.17	10637	166.47	0.42

Soundness = AASHTO T104 method
Compressive Strength = C 39/C39M method
Bulk Density = ASTM C29/C 29-07 method
Water absorption = ASTM C121-06 method

Table 2.   Chemical composition of major elements (in %) of limestone samples from Abbottabad area.

Parameters	1	2	4	5	6	9	10	11	12	13
SiO_2	22.9	3.3	1.6	27.5	0	0.1	1.4	7.1	4.1	0.1
Al_2O_3	3.92	< 1	< 1	4.58	< 1	< 1	< 1	< 1	< 1	< 1
Fe_2O_3	0.98	0.23	0.21	1.49	0.05	0.05	0.42	0.32	0.62	0.21
CaO	26.74	50.76	53.69	28.12	53.72	52.9	53.76	48.8	50.72	55.32
MgO	14.78	2.04	4.94	7.16	1.29	2.34	1.17	1.92	4.07	0.98
Na_2O	0.2	0.07	0.08	0.2	0.05	0.06	0.08	0.2	0.14	0.08
K_2O	2.58	0.06	0.06	3.66	0.03	0.05	0.05	0.27	0.44	0.07
MnO	0.02	0.01	0.02	0.03	0.01	0.01	0.01	0.03	0.01	0
LOI	26	42.58	40	25.75	42.77	41.76	42.3	38.7	40.89	42.78
Total	98.12	99.05	100.6	98.49	97.92	97.27	99.19	97.34	100.99	99.64
$CaCO_3$	59.09	96.77	90.91	58.52	97.2	94.91	96.14	87.95	92.93	97.22

Table 3. Trace elements (ppm) of limestone samples from Abbottabad area.

Parameters	1	2	4	5	6	9	10	11	12	13
Pb	2	15	15	19	12	11	20	20	20	14
Co	8	3	4	17	3	3	9	1	4	4
Cr	25	8	5	31	9	14	18	18	26	10
Cd	2	2	2	1	2	2	3	1	2	1
Zn	21	7	8	23	10	9	8	14	13	8
Cu	124	34	4	293	6	7	2	5	11	3
pH	8.4	8.3	8.3	8.9	8.3	8.4	8.4	8.5	8.3	8.2

4.1. Building material

Table 1 shows the results of different engineering properties of the present samples. The results of soundness, water absorption, bulk density and compressive strength, all show that these limestone have the durability for use in aggregate and other construction purposes. If we see the specifications for the suitability of limestone for use as building material, the sample Nos. 2, 6, 9, 10, 11 and 13 (Table 2) are suitable for cement making because of their high CaO and low MgO contents. While sample Nos. 2, 4, 6, 13, are suitable for use as aggregate material because of their being even-grained and fracture-less texture studied under the microscope. However, sample Nos. 1and 5 because of the presence of quartz are rendered not suitable to be used as aggregate. Sample Nos. 10 and 12 though are even grained but are too fine to be used as aggregate.

4.2. Agriculture, fertilizers and animal feed

The use of marl and limestone as fertilizer dates back to first century AD and Romans were aware in those days of the long-term benefits of this rock to use in their lands for the better growth of their cereals. The MgO content of all the samples, except for sample No. 1, is less than 10 % so they are suitable for agriculture purposes (Oates, 1998).

Generally pulverized dolomitic limestone in the size range 0.2-1mm is frequently added to compound fertilizers at levels of up to about 10 % for achieving the benefits (Oates, 1998) like it conditions the fertilizer making it less prone to caking, it helps to neutralize acidity arising from nitrogenous compounds (ammonium sulfate/nitrate and urea), neutralizes any 'free' acid in the superphosphate components and contributes small amounts of Ca and Mg as plant nutrients.

High-calcium limestone is not widely used in fertilizer formulations as it can release ammonia from, nitrogenous compounds (Oates, 1998). Therefore, in this regard samples 1 and 5 are suitable for fertilizing purposes because these have lower contents of CaO as compared to the rest of the samples. All the samples when fine ground can be used as animal feed as these contain low level of toxic impurities and the lead levels are below 10mg/kg (Oates, 1998).

4.3. Iron production and glass manufacture

Iron is produced by the reduction of iron ore (oxides of iron) by coke in blast furnace. Limestone or lime is used as a flux to assist melting 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. The limestone required should have silica less then 0.1%. Limestone is widely used as flux in smelting of copper, lead, zinc and antimony. It is charged into smelters with the concentrated ores. The limestone calcines and resulting lime react with silica, alumina and other impurities to form a molten slag. The limestone should be high in calcium carbonate and low in silica and alumina. Therefore, according to this specification, sample Nos. 4, 6, 9, 10, and 13 are suitable for this purpose (Jackson, 1967, 1969).

Glass manufacturing is generally carried by fusing a mixture of silica sand, soda ash, limestone, dolomite and other materials. Limestone, like in iron and steel production, also acts as a flux in glass manufacturing. Moreover, as the mixture enters the bath, the carbonates decompose and evolve carbon dioxide which helps to agitate the bath and to disperse the solids into melt. The solids react to produce the sodium/calcium/magnesium silicate which is the principal constituent of most glasses. Stringent chemical specifications for limestone and dolomite used in glass making are usually specified. Iron with less than 0.1% Fe_2O_3 is specified but for colorless glass its level must be less than 0.02% (Oates, 1998). In the studied limestone Fe_2O_3 content is usually high, however, samples 6 and 9 may be used, but not for manufacture of very transparent glass (Oates, 1998).

4.4. Acid gas removal and rock dust for coal mines

Recent times have put constraints on industries to limit their emissions of acidic gases to a certain level. Limestone reacts with most common acidic gases (i.e. SO_2, HCl and HF) and thus acts as an absorbent. Limestone is less expensive as compared to other alternative alkaline materials like sodium carbonate/bicarbonate and caustic soda (Oates, 1998). All the samples contain high amounts of MgO and SiO_2 so are unacceptable for this use. Only sample No. 13 can be used for this purpose (Oates, 1998)

Finely ground (>1mm, with 70 % less than 75 m) rock is used in mines particularly in coal mines to dilute the coal dust and thereby to reduce explosion risk. No other specifications are found except that the content of silica in limestone should be low. Therefore, all the samples in Table-2 except No. 1 and No. 5 are suitable for this purpose (Oates, 1998).

4.5. Water treatment

Hydrated lime is used in the treatment of potable water to adjust the pH and to remove impurities. Lime is also used to condition sewage sludge and neutralize industrial effluents. Chemical and physical constraints on the type of limestone used to produce the lime are not usually specified, however, those limestone which have

CaCO$_3$ from 98-88% and SiO$_2$ < 6% can be used (Bilqees and Shah, 2007). Hence taking into consideration the toxic elements (Table 3), sample Nos. 2, 4, 6, 9, 11 and 13 seem suitable for this purpose (Oates, 1998).

4.6. Sugar refining and soda ash manufacture

Limestone and lime used in the sugar industry for the purification purpose should be of high grade (Bilqees and Shah, 2007; Jan et al., 2009). According to the specifications the sample Nos. 10 and 13 are suitable.

Soda ash (sodium carbonate) is an important raw material for the chemical industry and involves the reaction of carbon dioxide with a solution of brine and ammonia to produce ammonium chloride and a sodium bicarbonate precipitate. The precipitate is recovered and heated to produce sodium carbonate. As it needs high grade limestone so only sample No. 13 is suitable for this purpose.

Acknowledgement

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