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Characterization of Phosphate Rock of Garhi Habibullah, District Mansehra, Pakistan

Naseer M. Khan[1*], Ishaq Ahmed[2], Sajjad Hussain[2], Imtiaz Ali[3]

[1]Mining Engineering, Balochistan University of Information Technology, Engineering and Management Sciences, Quetta, Pakistan
[2]Mining Engineering, University of Engineering and Technology, Peshawar, Pakistan
[3]Petroleum and Gas, Balochistan University of Information Technology, Engineering and Management Sciences, Quetta, Pakistan

*****Email: engrnaseer1@gmail.com

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Abstract: Phosphate rock is essential and basic raw material for fertilizer and chemical based industries. In this research work, characterization of Ghari Habibullah (GHU) phosphate rock samples, were carried out. Aim of the study is to determine mineralogy of the ore deposits by using thin sections, X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) techniques. Elemental composition was determined by X-ray Fluorescence (XRF), assay of ore minerals and various gangue minerals were determined by chemical analysis. Mineralogical study results showed that the major gangue minerals present with ore mineral (apatite) are silica, hematite and calcite. The SEM analysis revealed that apatite (fluorapatite) was sandwiched between silica and calcite. X-ray Fluorescence indicated apatite grade is 22.85% which is below the marketable cutoff grade and main gangues are quartz 40% and hematite grade greater >2% is more than the required limit of fertilizer. The iron content should be kept low in the fertilizers, reduces the solubility efficiency of water, which have a diverse effect on the production of Single Super Phosphate.

Keywords: Phosphate rock, optimum liberation, single super phosphate, Garhi Habibullah, mineralogy, quartz.

Introduction

Phosphate rock is the raw material which is basic source of phosphorous, playing a vital role in the fertilizer, medicine and food industries (Cordell et al., 2009). Phosphorous does not exist itself in nature due to its high reactivity (Alsafasfeh and Alagha, 2017). Phosphate plays an important role in national economy due to its wide range of uses like fertilizer, animal food, foodstuff, clarifying agent for sugar and other industries. Mining and mineral processing plays a vital role in phosphate required demand (Soetan et al., 2010). The demand for phosphate is increasing continuously due to population increase. In 2013 phosphate production was 224 million tons and it is predicted to reach 260 million tons in 2017 (Shariati et al., 2015). Most of the phosphate deposits origin is sedimentary. It contains apatite matrix in significant quantity of impurities like carbonate and silicate (Abouzeid, 2008). Phosphate uses are increasing in the industry while the high-grade reserves are depleting day by day. As a result, the demand for high grade and beneficiation methods are increasing to overcome the complexity of sedimentary deposits (Cordell et al., 2009). Phosphate deposits with sedimentary origin contain a low content of P_2O_5 mineral with various impurities. The most challenging assignment is the reduction of impurities from low-grade apatite ore (Smit et al., 2009). The phosphate rock contains P_2O_5 with different mineralogical composition, made it a complex raw material. The chemistry of the rock varies from origin to origin. The behaviors of these different chemistry rocks were different in acidulation processes (McConnel, 2012). Fundamentally, phosphate deposits composed of the apatite group with various minerals compositions, mainly calcium oxide, chert, mud, quartz, silicates and metal oxides (Zafar et al., 1995). Some researchers have worked in the last decade on the origin of different phosphate deposits and their beneficiation techniques and various methods (Abouzeid, 2008; Issahary and Pelly, 1985). The percent of phosphate mineral in phosphate rock is known as phosphorous pentoxide (P_2O_5). Calcium phosphate ($Ca_3(PO_4)_2$) also known as Bone Phosphate of Lime (BPL) which were usually used in the industries of fertilizer (Notholt et al., 1979). Cut size is used to determine whether the material is economical or not. It is a size above which the minerals are considered economical (Garcia and Staniek, 1993). Phosphate rock ranges from 20 to 60% or 80% BPL (28-39% P_2O_5) are considered as economical (El-Rahiem, 2013). Phosphate rock which is used directly for the end product generally contains more than 65% BPL or 30% P_2O_5 (Wingate and Kohmuench, 2016). Delolaha area of Garhi Habibullah contains a large number of phosphate deposits. According to the previous estimate, these reserves are 9.1 million tons but contains low grade, not meeting the standard of fertilizers industries. These deposits are different from the Kakul deposits geologically and mineralogically. Kakul deposits beds are continuous in both dip and strike in hundred and 5-10 ft respectively. Mineralogical deposits contain a significant amount of gangue in the form of calcium oxide (40-50%), hematite (1-2%) and quartz (10-25%) (Notholt et al., 2005). Ghari Habib Ullah (Delolaha) deposits area is faulted and highly fractured. Overall formations of deposits are dolomitized. Stratigraphy of the deposit is not constant due to fault in the bed of that area. Garhi Habibullah phosphate deposits mineralogically consist of major gangues; quartz (35-50%), calcium oxide (15-25%) and hematite (5-10%). Different tools and technique for mineral identification, usually used are Optical microscopy, X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Energy Dispersive X-Ray (EDX) and chemical analysis are the most common methods (Liu et al., 2016). Characterization of bauxite ore was carried by SEM, XRD and XRF (Shariati et al., 2015; Ahmad et al., 2014). Optical microscopy is the main and significant instrument used for mineralogical studies and it has advanced to an electron microscope. The most precise identification of mineral and gangue in country rocks are achieved through X-ray diffraction technique. Microstructures characterization of valuable mineral and gangue minerals in the country rocks are determined by SEM worldwide (El-Aal and Masoud, 2017). SEM images are evaluated for examination of grain size and to understand the minerals interlocked profile. Elemental analysis is achieved through EDX which is an easy and fast technique. Optimum liberation size was determined through sieve analysis. In samples, mineral identification was carried out through both thin section and XRD in country rock. Due to the complex nature of ore, the minerals were not precisely recognized by optical microscopy and X-ray diffraction. Complete minerals identification was carried out through chemical analysis. The present study is focused on the characterizations of Garhi Habibullah phosphate deposits.

Materials and Methods

Total 20 rock samples were collected from an area of Dawlat Mar (Delolaha) located in Ghari Habib Ullah having 34°19'3.91"N, 73°21'23.69"E. These samples were collected from the trench which was 12 cm wide, 12 cm deep and 12 cm thick. The samples after collection were properly packed in the plastic bag to reduce the contamination and oxidation. A large part of each sample was collected, mixed with each other and then subjected to (crushing and grinding) up to 250 µm size powder, a representative sample was achieved through coning and quartering method. The samples were divided into two parts. One part was used for XRD, chemical analysis, SEM and EDX in the form of powder while other parts were used for petrographic study in the form of the thin sections. Ground samples were used for XRD and chemical analysis.

Optical reflected microscope (Nikon Microphoto-FXA, Type 118) was used for mineral identification. Minerals were identified on the basis of color property. X'Pert PRO MPD instrument (Cu Kα, 40 mA current, 40 kV voltage) was used for XRD analysis to determine minerals crystalline phase. Scanning Electron Microscope hyphenated with an energy dispersive X-ray spectrometer (SEM-EDX) (6610LV+ OXFORD X-max, Japan, with energy range 0-20 KV) was used for determination of morphology and mineral microstructure element distribution in the phosphate rock.

Major oxides element percentages were determined in the phosphate rock samples including SiO_2, Fe_2O_3, CaO, Al_2O_3, MgO, MnO, Na_2O and K_2O by X-ray Fluorescence (XRF).

Results and Discussions

Petrographic studies show that the samples contain a large percent of chert also known as cryptocrystalline silica (Fig. 1A). Apatite with direct alleviation and parallel eradication were present inside the dolomitic lime mud lattice (Fig. 1B-C) respectively. These specimens are fractured, contains a number of joints in which few cracks are extensive and some are little. Cracks and joints are occupied by quartz which gives high obstruction shading (Fig. 1C). Coarse grain of apatite fractured staining ferruginous with parallel

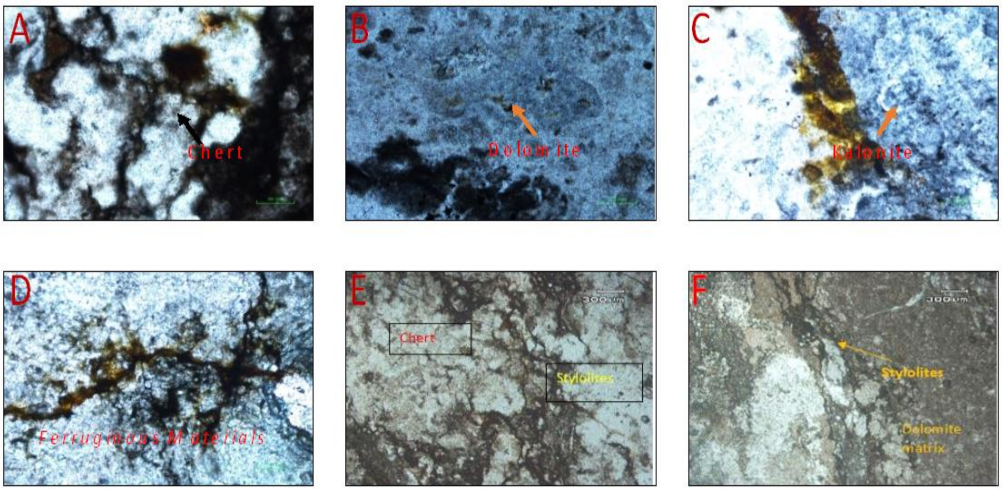


Fig. 1 Thin section of samples: **(A)** Disseminated chert with appetite; **(B)** Dolomite matrix embedded in the apatite; **(C)** Quartz occupied fracture which gives interference; (D) ferruginous mineral filled in fracture; **(E)** Stylolite place in the chert; **(F)** Stylolite embedded in the dolomite matrix.

extension, Inclusions are present in apatite grain, ferruginous matrix at places. Ferruginous rich lamination or bands (Fig. 1D). Stylolite is filled with ferruginous materials and chert inserted in dolomitized lime mud matrix (Fig. 1E-F).

The result obtained from the petrographic study shows that the deposits were of dolomitized formation and were formed in a deep environment with mudstone. The main gangue minerals associated with phosphate are quartz embed dolomitized lime mud matrix.

Mineralogy

The main mineral found in phosphate rock with percentage greater than 5% were determined by XRD. The major mineral, include calcite, fluorapatite, hematite and quartz (Fig. 2). It can be inferred from the relative peak sizes that the amount of quartz is greatest in small size fraction (+325 mesh). The quartz peaks increasing in size along with the particles size fractions, indicating that the amount of quartz present decreases as the particles size increases. A sample of 580g was taken from representative samples. This sample size was reduced by the roll and disc crusher. The size of the sample was further reduced by a mortar mill that passed through 300 mesh (BBS) Screen. The sample was run through XRD unit Cu.K, radiation-having wavelength 1.540598 Å. Peaks of the ore mineral and gangue mineral give an idea at a different point in the XRD graph with different intensity values. The mineral was identified on the basis of 2θ and lattice space. Variation in peaks was identified due to variation in mineral composition and intensity. Different minerals were identified on the basis of peak variation (Fig. 2).

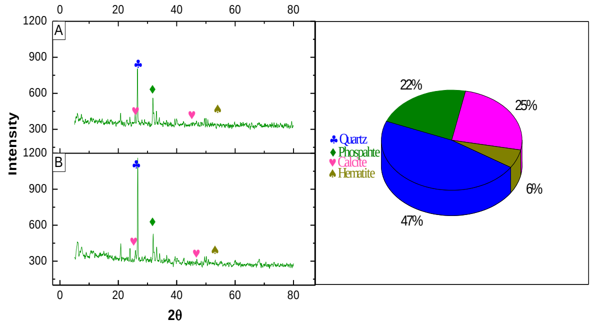


Fig. 2 X-ray diffraction of phosphate ore.

X-ray diffraction analysis shows that the samples contain major mineral quartz, calcite, fluorapatite, and hematite. The analysis also contains some minor mineral such as sodium oxides, aluminum oxides, potassium oxide and magnesium oxides (Table 1).

XRD analysis shows that quartz is the major gangue associated with ore mineral. The phosphate rock contains phosphate-bearing mineral grade is in the range 22-25% that is below marketable grade. Hematite was also >2% which are not directly used in fertilizer production.

The texture of grain was determined by using SEM. Different areas of each sample were analyzed with different range 0-20 keV. The result shows that most area of the samples occupies quartz, calcite, and apatite (Fig. 3,4). Each sample area was a scan by SEM at varies resolution. This different resolution gives that the apatite grain size varies between 22-25 μm (Fig. 4,5). SEM analysis and thin section study confirmed that the apatite grains are varying in size (0.075-0.15mm) that is greater than clay size 0.002mm.

Table 1. XRD analysis of a representative phosphate ore.

Mineral Type	Fluorapatite	Quartz	Calcite	Other Minerals	Total
%	22	49	27	2	100

Table 2. XRD angle and wavelength base analysis of phosphate rock.

Set of Peaks	2 Theta [2θ]	d [Å]	Mineral
1.	20.88	4.251	Quartz
	22.94	3.8741	
	31.98	2.7961	
2.	32.41	2.7602	Flourapatite
	51.66	1.7689	
	53.39	1.7146	
3.	46.86	1.9371	Flourapatite, Hematite
	51.60	1.7698	
4.	31.97	2.7970	Flourapatite, Hematite, Calcite
	33.11	2.7033	
5.	34.20	2.6197	Hematite
	52.28	1.7483	
	18.17	4.8772	
6.	36.52	2.4585	Quartz, Flourapatite, Hematite, Calcite
	68.07	1.3762	

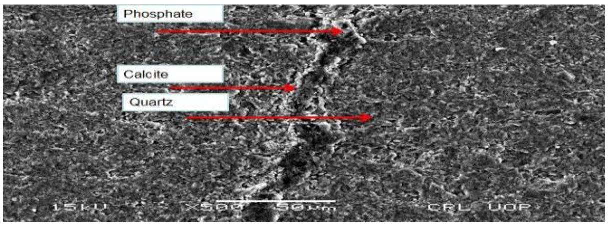
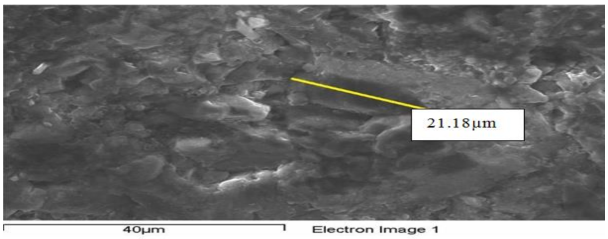


Fig. 3 Mineralogical analysis of ore mineral and gangue mineral.



fracture of the deposits particularly ferruginous mineral. The range of the phosphate mineral of 0.075-0.15mm. Therefore, it needs optimum grinding to liberate it from gangue minerals (Table 1). Each peak of the XRD analysis represents one or more minerals (Table 2). The values of peaks change with diffraction angle and intensity of the light. Mineral composition of the ore is given (Table 1, fig. 2). Mineral with different peaks, 2θ angles and intensity are described in Table 2. Apatite peaks were absorbed in a different range of 2θ angles but the dominant peaks angle is 31.98 and 32.42 respectively, (Fig. 2). The dominant 2θ angles value 20.88, 28.10 are absorbed in figure 2 show the high percentage of quartz contents in the sample.

SEM confirmed the presence of quartz, which is the major gangue, associated with ore mineral (Fig. 3).

Table 3. The composition of phosphate rock by XRF.

Area	P_2O_5 (%)	Fe_2O_3 (%)	SiO_2 (%)	Al_2O_3 (%)	CaO (%)	MgO %	LOI (%)	MnO_2 (%)	Na_2O (%)	K_2O (%)	Total
GHU	22.85	5.09	39.45	3.50	19.4	2.5	2	0.08	4.85	0.28	99.96

Table 4. Sieve fraction chemical analysis and their recovery

Sieve (µm)	+150	-150+106	-106+75	-75+63	-63+53	-53+45	-45	Total
P_2O_5 %(G)	30.8	25.62	20.7	2.2	1	1.7	17.98	100
Bulk (B), gm	36.6	9.18	7.5	3.6	3	1.8	25.62	87.3
G × B, gm	11.27	2.35	1.55	0.08	0.03	.03	4.60	19.91

Fig. 4 SEM textural investigation.

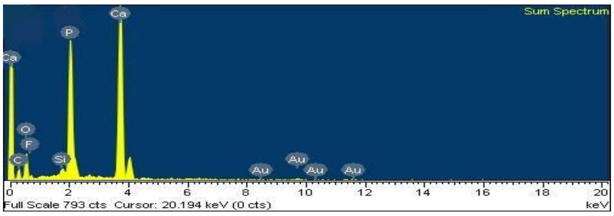


Fig. 5 Elemental analysis of phosphate rock by SEM-EDX.

Grinding weight of samples was used for sieve analysis by passing a known weight of 87.3 g of material through sieves nest to determine the percentage weight of each fraction. All the sieve fractions were analyz ed chemically by UV-visible spectrophotometer for P_2O_5.

Ghari Habibullah phosphate ore mineralogical result shows the presence of apatite, quartz and calcite. The overall formation of the phosphate ore is dolomitic in nature. The content of the ore mineral P_2O_5 (fluorapatite) is less than 30%. The ore is low grade and it is not used directly for the industrial purposed. The phosphate mineral grains interlocked with gangue minerals are like quartz, calcite and hematite. These gangue minerals play a vital role in the degradation of phosphate mineral. The deposits are highly fractured, the gangue mineral, are disseminated and filled in the

Quartz distributions are in disseminated form in the phosphate rock samples, which affect the separation technique due to it is the difficult liberation of apatite from quartz. SEM with EDX analyses show the elemental composition of the sample (Fig. 5) such as Ca, Al, P etc (Fig. 5).

XRF analysis shows the existence of quartz, fluorapatite calcite and hematite in the represented sample (Table 3). Sieve fraction chemical analysis (Table 4) show the P_2O_5 percent in each fraction and their corresponding bulk. Sieve analysis data (Table 4) were used to determine optimum liberation size, which is in the range of 53-150µm.

The result obtained from the petrographic study shows that the deposits were of dolomitized formation and are formed in a deep environment with mudstone. The main gangue associated with mineral is quartz embedded in dolomitized lime mud matrix.

XRD analysis shows that quartz is the major gangue associated with ore mineral. The phosphate rock contains phosphate-bearing mineral grade in the range 22-25% that is below the marketable grade. Hematite was also >2% which is not directly used in fertilizer production. SEM analysis and thin section study confirmed that the apatite grains are varying in size

(0.075-0.15mm), which is greater than clay size (0.002mm). XRF analysis gives an idea that the mineralogical Ghari Habibullah phosphate contains quartz as main gangue minerals (Table 3). Sieve analysis shows optimum grain size is in range of 150-75µm (0.075-0.15mm).

Conclusion

The quantity of fertilizer production depends upon the P_2O_2 and Fe_2O_3 contents. Ghari Habibullah phosphate rock contains 22.85% P_2O_2 that are not used directly for fertilizer. It needs upgradation for the fertilizer industry, which uses phosphate rock containing <2% Fe_2O_3. These deposits contain greater than 2% Fe_2O_3. Therefore, it cannot be directly used with such content of Fe_2O_3 before using it for industrial uses, Fe_2O_3 values should be reduced to <2% Fe_2O_3 by using a high-intensity magnetic separator. Ghari Habibullah phosphate will be upgraded through froth flotation, shaking table or any concentration methods because it contains quartz and calcium oxide.

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