Pak. J. Sci. Ind. Res. 2010 **53** (6) 303-310

Mineralogical and Textural Characteristics of Kakul (Hazara) Phosphate Rock, NWFP, Pakistan

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(received January 19, 2010; revised July 29, 2010; accepted August 6, 2010)

Abstract. Various types of minerals, present in phosphate rock of Hazara area of Khyber Pukhtoonkhwa Province of Pakistan, were identified and their concentration was determined using a suitable method. The characteristics of the rock were defined by petrography, X-ray diffraction, and chemical analysis and the textural characteristics such as grain size, grain shape and their arrangement in the rock body were also investigated. The degree of liberation of phosphate-bearing mineral was studied by the particle-counting method. Mineralogical and textural observations indicated that fine-grained rock may be suitable for beneficiation by the froth flotation separation technique.

Keywords: phosphate rock, mineralogy, mineral beneficiation, Hazara, Pakistan

Introduction

Phosphorous is an essential constituent of plant and animal tissues. Phosphate esters of nucleotides are of immense biological importance and play an important role in energy-related-functions of living systems. All living organisms fulfil their phosphorous need from soil directly as well as indirectly. The main source of phosphorous in soil is phosphate-bearing minerals which occur in small amounts in nearly all igneous and sedimentary rocks. There are about 200 minerals found that contain more than 1% P_2O_5. The most important phosphate mineral in igneous rocks is fluorapatite, while in sedimentary rocks, it is carbonate fluorapatite (Zanin, 2004).

Some phosphate-rock deposits are high-grade and are suitable for direct feed to fertilizer plants without beneficiation. However, most phosphate rocks are low-grade and are always subjected to beneficiation processes such as washing, screening, heavy media separation, gravity concentration, froth flotation and calcination and are later dried to reduce the moisture content to 3-4%. Phosphate rock or concentrate is graded according to its P_2O_5 content as furnace grade (16-24% P_2O_5), fertilizer grade (25-31% P_2O_5) and acid grade (>31% P_2O_5). The major use of phosphate rock (90-95%) is in the manufacture of phosphate fertilizers, while the rest is used in the preparation of phosphoric acid, elemental phosphorous, and other industrial phosphate chemicals (Ozer *et al.*, 2000).

Phosphate deposits are usually black or brown in colour and appear in different forms such as bones, nodules, granules, oolites, fragments, pellets, grains and shells (Hernainz *et al.*, 2003). Phosphate-rock deposits of economic importance are both igneous and sedimentary in nature. Important igneous deposits, containing apatite, are often found in alkaline rock complexes. Apatite also occurs in magmatic carbonatites (calcite, siderite, dolomite and ankerite). The sedimentary phosphate deposits (phosphorites) are of two types, namely guano and pelletal. Guano deposits are formed from the accumulation of animal excrement of large sea birds, but they constitute only a small percentage of total production. Pelletal phosphorites are the largest deposits, furnishing over 80% of the world phosphate rock requirement. They are marine in origin and are commonly associated with dolostone or limestone (Van Kauwenbergh, 2003).

Phosphate deposits have been reported to exist at various localities in Pakistan, but the significant deposits occur in Hazara Division, in an area of about 100 km^2 in the north-east of Abbottabad city. The most promising and prospecting locations are Kakul, Sherwan (Barkot) and Sirban Hill (Havellian), Lagarban, Kalu-di-Bandi and Dalola village (Garhi Habibullah). The average reserves of these areas have been estimated to be around 18 million tons (Ahmad and Siddiqui, 1992).

Phosphorite deposits of the Kakul area, Hazara Division are located within latitude of 34 °12′ to 34 °15′ N and longitude of 73 °16′ to 73 °30′ E (Fig. 1). These are early Cambrian sediments having 516 m strike length with an average thickness of 4.5 m. There are two main types; the uppermost cherty dolomite of Abbotabad formation and lowermost silty calcareous phosphorites of Hazara formation. The main phosphatic horizon is found in cherty dolomite of Abbotabad formation. Phosphorites developed in this area are usually

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*Author for correspondence; E-mail: voiceofrashid@hotmail.com pelletal, hard, compact and grey to black in colour. Abbotabad formation comprises of an upper unit of dolomite, limestone and shale, a middle unit of sandstone, shale and limestone and a lower unit of sandstone, variegated shale, quartzite and dolomitic limestone. Its contact with overlying Hazara formation seems to be gradational at most places (Hasan, 1989).

Worldwide, the deposits of high-grade phosphate rock are declining and the beneficiation of low-grade deposits is becoming more widespread. The mineralogical and textural characteristics of different deposits vary greatly, thereby requiring use of different flow sheets for their beneficiation. The main object of this investigation is to identify various types of mineral constituents present in the phosphate rock of Hazara and to determine the textural characteristics which are useful for the evaluation of a suitable beneficiation process to be adopted for this kind of rock.

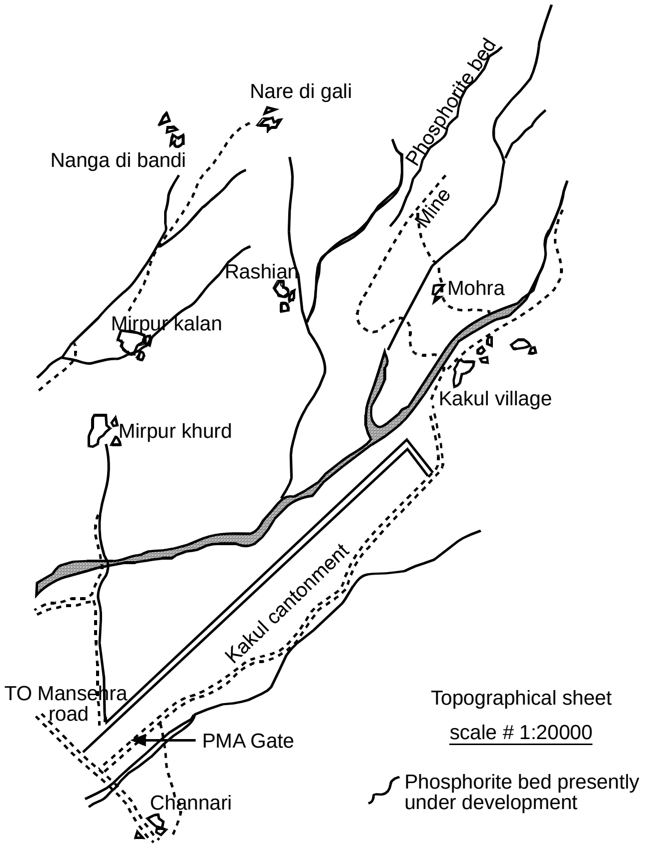

Fig. 1. Location map of Kakul (Hazara) phosphate rock.

Materials and Methods

Sample preparation. A representative sample of the phosphate rock was provided by Pak-American Fertilizer Ltd. It consisted of lumps of various sizes ranging from 50 mm to 150 mm. Some of the rock was kept for mineralogical study while the remainder was crushed using a laboratory jaw crusher set at 20-25 mm and a roll crusher set at 4-5 mm. A head sample for chemical analysis and X-ray diffraction studies was prepared by applying sampling techniques of coning-quartering and riffling on the crushed rock. This was further pulverized to 100% - 200 mesh # (74µm) with the help of disc pulverizer (Denver, USA).

Chemical evaluation. Chemical analysis of the representative sample was performed in accordance with ASTM methods of chemical analysis. Silica and sulphate were determined gravimetrically (ASTM, 2005a), while phosphorous was determined volumetrically using ammonium molybdate (ASTM, 2005b). Iron and manganese were determined by oxidation-reduction titration (ASTM, 2005c; 2005d). Alumina was determined by complexometric titration using EDTA (ASTM, 2005e). Calcium and magnesium were estimated by atomic absorption spectrophotometer (Model: Z-8000, Hitachi, Japan) while sodium and potassium were determined by flame photometer (Model: PFP7, Jenway, England) (ASTM, 2005f; 2005g). Fluorine was estimated by gravimetric method.

Petrography. Rock chips were cut out of the representative samples to a thickness of about 1.0 mm with the help of a diamond thin section cut-off saw and glued to a glass slide with one or two drops of Canada balsam. These were then ground on a metal lap wheel utilizing progressively decreasing silicon carbide grit abrasives (# 120, 240, 320, 400 and 600) followed by polishing on cloth laps using 7, 3 and 1 micron diamond pastes. After grinding to a final thickness of about 0.03 mm, these were covered with cover slips and examined with the polarizing microscope (Nikon, Japan).

X-ray diffractometery. The ground sample of rock was examined with an X-ray diffractometer (Model: D-5000, Siemens, Germany). X-ray diffraction was done with a 0.02° step size per second. The scan angle ranged from 15-60°. The spectrum obtained was matched with standard data to identify the mineral phases.

Degree of liberation. Degree of liberation was measured by grain mounts using the stereomicroscope (Hausen, 1983). The roll crusher product was ground in a rod mill (Denver, USA) for 15 min and was subjected to a sieve shaker (International Combustion, England) for separating into a number of size fractions using different sieves. The fractions obtained were examined with the stereomicroscope to measure the degree of liberation of mineral grains of interest using the particle-counting method. The number of liberated and locked mineral grains in each sieve fraction was noted and the percent particle liberation was calculated using the following relation.

Collophane liberation (%) = [Free collophane (%) × 100/ [Free collophane (%)+Locked collophane (%)]

Bond work index. Bond work index (Wi) of phosphate rock was determined using a standard Bico-Braun grinding ball mill (Denver, USA). A fixed volume (700 mL) of ore was weighed and ground repeatedly in the ball mill to obtain the constant grindibility and A mesh size 200 was selected for grinding. Graph was plotted between particle size in (μm) and cumulative weight percent passing to get 80% passing of feed and product (Fig. 8). The Work Index (Wi) was calculated using the F. C. Bond formula (Diester, 1987).

$$\mathrm{Wi} = \frac{44.5}{(P_1)^{0.23} \times (\mathrm{Gbp})^{0.82} \times [10/\sqrt{P_2} - 10/\sqrt{F_2}}$$

$$\mathrm{Gbp} = 1.036\ \mathrm{gm/rev}\ P_1 = 74\ \mu\ P_2 = 64\ \mu\ F_2 = 1750\ \mu$$

$$\mathrm{Wi} = \frac{44.50}{(74)^{0.23} \times (1.036)^{0.28} \times [10/\sqrt{64} - 10/\sqrt{1750}} = 15.27$$

where:

Gbp signifies the average grams of undersize produced per revolution

P_1 = opening size (μm) of the test sieve used

P_2 = product size (μm) at which 80% of last grinding cycle sieve undersize passes

F_2 = feed size (μm) at which 80% the new ball mill feed passes

Results and Discussion

The chemical analysis of the representative sample (Table 1) shows that the phosphorus pentaoxide (P_2O_5) content is around 23%. The obtained grade is sufficient to exploit the rock on a commercial scale to produce phosphate concentrate. However, silica (SiO_2) and alumina (Al_2O_3) appear to be the main impurities and must be removed. For general use in the fertilizer industry, phosphate rock or its concentrates preferably have levels of 30% (P_2O_5), reasonable amounts of calcium oxide (5%) and < 4% combined iron and aluminium oxides (Ozer *et al.*, 2000). Therefore the percentage value of iron oxide (Fe_2O_3) also needs to be minimized. The rock seems to belong to the furnace grade and is suitable for the production of phosphorous. However, after concentration, this rock can also be utilized to produce phosphate fertilisers and chemicals (Van Kauwenbergh, 2003).

Table 2 shows the mineralogical composition of the rock, obtained by microscopic examination of thin sections. The main phosphate-bearing mineral identified in the rock sample is collophane (carbonate fluorapatite), a member of the apatite group. The petrographic examination shows disseminated rounded to sub-rounded grains of collophane which look reddish black in plane polarized light and rounded to sub-rounded under crossed nicols (Fig. 2-6). The view taken with crossed polar shows the isotropic nature of collophane and the high-order interference colour of calcite. The small grains of collophane (0.01-0.05 mm) as well as large rounded to sub-rounded grains (0.05-4.0 mm) are present. The petrographic examination of the samples shows rounded to sub-rounded grains of quartz (0.5-2.0 mm). Many small grains up to 0.05 mm (microcrystalline) are disseminated throughout the matrix. Calcite is present as anhedral colourless grains. The collophane contains 5-30% inclusions of small quartz and carbonate grains of less than 0.01 mm. Dahllite (carbonate hydroxyl apatite) is granular, disseminated in thin sections, reddish brown in plane

Table 1. Chemical composition of the rock

Constituents	Wt (%)
Loss on ignition (LOI)	4.58
Phosphorous oxide(P_2O_5)	23.38
Calcium oxide (CaO)	38.65
Magnesium oxide (MgO)	0.89
Aluminum oxide (Al_2O_3)	15.20
Iron oxide(Fe_2O_3)	4.07
Silica(SiO_2)	10.86
Sulphate (SO_4)	0.88
Potassium oxide (K_2O)	0.30
Sodium oxide (Na_2O)	0.04
Fluoride (F)	2.31
Total	101.16

Table 2. Mineralogical composition of the rock

Minerals	Percentage (%)	Specific gravity
Collophane Ca_{10} (PO_4) CO_3 F_{15} (OH) $_{0.5}$	36-40	3.1-3.4
Dahllite Ca_5 [(OH,O) (PO_4, CO_3)$_3$]	9 -12	3.1-3.5
Quartz (SiO_2)	9-10	2.6
Calcite (Ca CO_3)	7-8	2.7
Dolomite Ca Mg $(CO_3)_2$	5-6	2.9
Boehmite (γ-AlOOH)	4-5	3.0-3.1
Diaspore (β-AlO(OH)	2-3	3.2-3.5
Fluorite(Ca F_2)	1-2	3.2
Gypsum (Ca $SO_{4.}2H_2O$)	1-2	2.9-3.0
Goethite [FeO(OH)]	2-3	4.0-4.4
Hematite ($Fe_2O_{3.}$)	1-2	5.0
Siderite ($FeCO_3$)	<1	3.7-3.9
Pyrite (FeS_2)	<1	4.5-5.2
Glauconite (K(Fe,Al)$_2$ (Si,Al)$_4$O$_{10}$(OH)$_2$)	<1	3.0-3.2

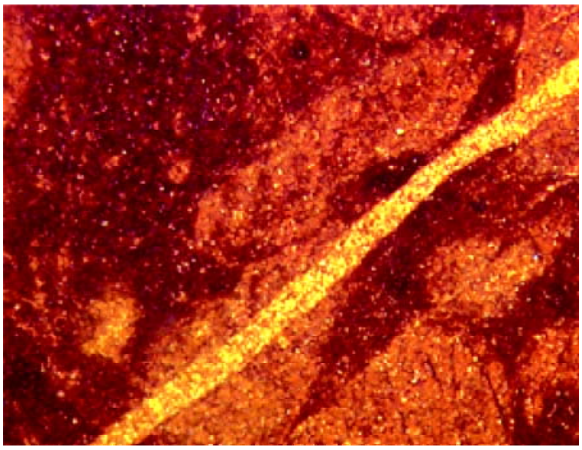

Fig. 2. (×200) Calcite vein with darker and brownish pellets of isotropic collophane.

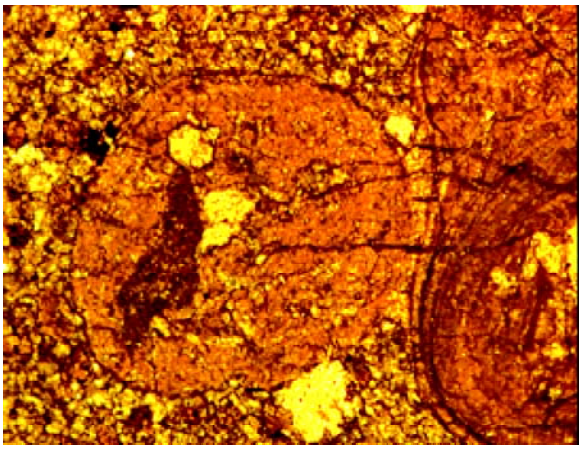

Fig. 3. (×200) Rounded pellets of collophane (darker in colour).

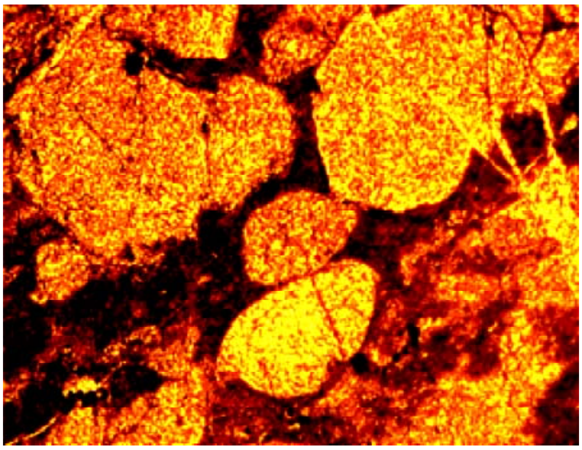

Fig. 4. (×200) Disseminated dahllite crystal with darker rounded pellets of collophane.

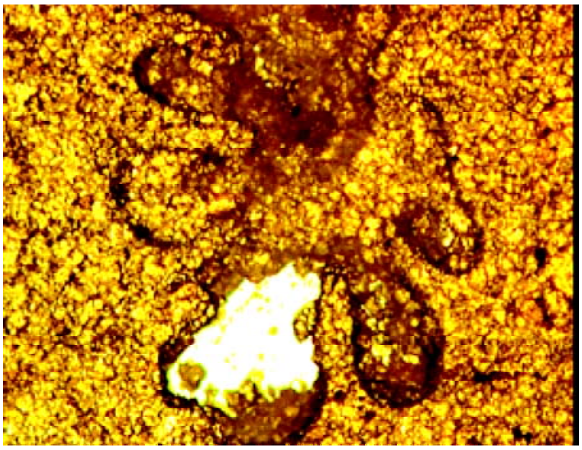

Fig. 5. (×200) Fine grained matrix (microcrystalline) with a few brownish-green glauconite grains.

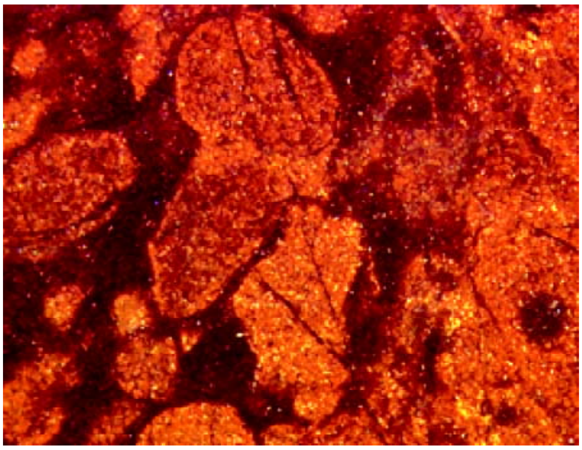

Fig. 6. (×200) Disseminated dahllite crystals.

polarized light and has weak birefringence under crossed nicols. Both collophane and dahllite are associated with iron and aluminum minerals. The rare grains of glauconite are present in quartz cement which shows that the rock is marine and pelletal in nature. Pellitic origin confirms that the phosphate is of sedimentary origin.

The major X-ray diffraction peaks (Fig. 7) confirm the presence of considerable amount of collophane (carbonate fluorapatite) and quartz (SiO_2) minerals, as *d*-values of 2.794, 2.696 and 2.242, correspond to the standard *d*-values of carbonate fluorapatite (Ca_{10} $(PO_4)CO_3F_{15}(OH)_{0.5}$) and *d*-values of 4.249, 3.335 and 1.814 correspond to the standard *d*- values of quartz. This was confirmed by the JCP.CAT search/match programme provided with the X-ray diffractometer which also showed that the minor peaks correspond to dahllite ($Ca_5[(OH,O)(PO_4,CO_3)_3]$), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$),

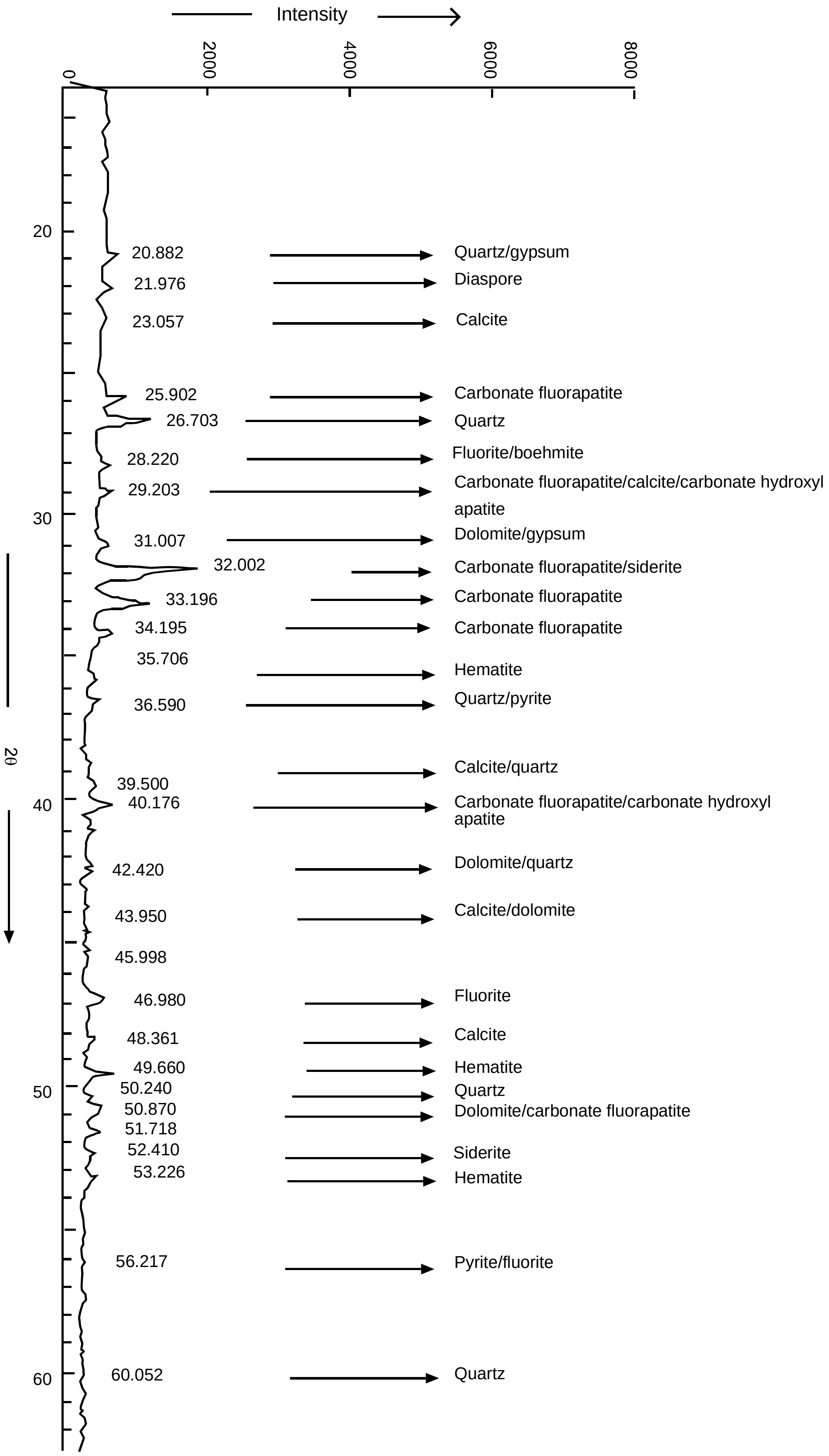

Fig. 7. X-ray diffractrogram of Kakul (Hazara) phosphate rock.

siderite ($FeCO_3$), boehmite (γ-AlOOH), goethite [FeO.(OH)], hematite (Fe_2O_3), pyrite (FeS_2), fluorite (CaF_2), gypsum ($CaSO_4 \cdot 2H_2O$) and glauconite ($K(Fe,Al)_2(Si,Al)_4O_{10}(OH)_2$) minerals.

The success of mineral processing operation, to a great extent, depends upon the grain size and the distribution of individual mineral grains in the host rock (Nachev, 2002). XRD record of rock giving angle (2θ), intensity, *d*-values and mineral phases identified are given in Table 3. The microscopic study of thin sections of the rock reveals that the grain size of collophane shows wide variations under the microscope, however, the average grain size is about 150 µm. Rock is ground to a size at which maximum mineral grains are liberated at the coarsest possible size, avoiding over-grinding which can lead to slimming problems, resulting in heavy losses in achieving the desired grade and recovery (Ryshchenko *et al*., 2002). Table 4 shows the degree of liberation of collophane in various size fractions and hence, indicates the extent of its concentration during beneficiation. It is evident from this Table that about 95% of collophane grains are liberated when the rock is ground to minus 200 mesh (74 µm) and that finer grind size results in considerable decrease in collophane locked with gangue. Therefore, in order to avoid over-grinding and to obtain the economic degree of liberation, the rock should be carefully ground to nearly 80% passing 200 mesh sieve so that it may have a fair proportion of free valuable mineral particles in subsequent mineral processing operations.

Table 3. Interpretation of XRD record of Kakul (Hazara) phosphate rock

Angle (2θ)	Intensity	*d*-value	Mineral phase
14.592		6.110	Boehmite
20.882	695	4.249	Quartz, Gypsum
21.976	629	4.041	Diaspore
23.057	631	3.854	Calcite
25.902	1007	3.436	Carbonate fluorapatite,
26.703	1271	3.335	Quartz
28.220	644	3.159	Boehmite, Fluorite
29.203	691	3.056	Carbonate fluorapatite, Calcite, Gypsum
31.007	692	2.881	Dolomite, Gypsum
32.002	1918	2.794	Carbonate fluorapatite, Siderite
33.196	1237	2.696	Carbonate fluorapatite, Hematite, Pyrite, Goethite
35.706	498	2.512	Hematite,
36.590	452	2.454	Quartz, Goethite, Pyrite
39.500	476	2.278	Calcite, Quartz,
40.174	673	2.242	Carbonate fluorapatite, Carbonate hydroxylapatite Quartz, Goethite
42.420	404	2.129	Quartz, Dolomite, Siderite
43.950	397	2.058	Calcite, Dolomite
45.498	379	1.992	Quartz,
46.980	656	1.932	Fluorite
48.361	476	1.880	Calcite
49.660	759	1.834	Hematite,
50.240	414	1.814	Quartz, Dolomite
50.870	559	1.793	Carbonate fluorapatite, Dolomite
52.410	450	1.744	Siderite
53.226	505	1.719	Goethite
56.217	331	1.634	Pyrite, Fluorite
60.052	342	1.539	Quartz

Table 4. Mesh of liberation of collophane mineral

Size fractions (ASTM)	Free collophane grains (%)	Locked collophane grains (%)	Free gangue grains (%)	Collophane liberation (%)
+50	22.58	27.62	49.80	44.98
-50+70	27.99	19.98	52.03	58.34
-70+100	28.39	16.05	55.56	63.88
-100+150	32.23	8.95	58.82	78.27
-150+200	33.15	5.56	61.29	85.64
-200+250	36.12	1.83	62.05	95.18
-250	36.43	0.92	62.65	97.54

The moisture content is also of importance as it affects the ease with which the phosphate rock can be ground. The maximum limit of the moisture content varies with type of phosphate rock, but is generally from 2% to 5%. The Bond work index (Wi) of phosphate rocks generally ranges from 10-16 depending upon the nature of minerals present and moisture content (Couper *et al*., 2005.). The bond work index (Wi) of the Kakul phosphate rock was determined with a standard Bico-Braun grinding ball mill using F.C. Bond formula as follows with

$$\text{Gbp} = 1.036\ \text{g/rev}; \quad P_1 = 74\mu; \quad P_2 = 64\mu; \quad F_2 = 1750\mu$$

$$\text{Wi} = \frac{44.50}{(74)^{0.23} \times (1.036)^{0.28} \times [10/\sqrt{64} - 10/\sqrt{1750}]} = 15.27$$

Wi was found to be 15.27 kWh/ton. The value is slightly on the higher side because the phosphorites are sufficiently massive and hard and create problems during grinding and size reduction operations (Fig. 8).

With beneficiation technology, often the most difficult rock types (e.g., siliceous, dolomitic and Fe-Al-rich) can be upgraded satisfactorily (Zafar *et al*., 1995). Selection of the beneficiation technique depends upon the type of minerals present in the rock and their degree of intergrowth. Gravity concentration

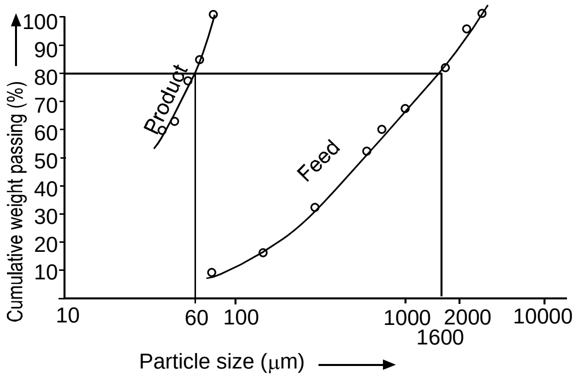

Fig. 8. Bond work index (Wi)of the phosphate rock.

methods operate well when the differences in density of valuable and gangue minerals is more than 2.0 (Wills, 1992). In this rock, the specific gravity of the principal phosphorous-bearing mineral (carbonate fluorapatite) ranges from 3.0 to 3.5 whereas, gangue mineral such as quartz, aluminum and iron oxide and carbonate minerals have specific gravity ranging from 2.5 to 4.0. Due to this small difference in specific gravity, it is difficult to beneficiate this rock by gravity concentration techniques. Moreover, gravity methods work satisfactorily only when the liberation of valuable minerals from gangue minerals takes place at a coarser size. This is because, at finer size, the density difference between valuable and gangue materials becomes less effective. As this rock is fine-grained and liberation of collophane from the host quartz requires adequate grinding, therefore, it is difficult to beneficiate this rock by gravity concentration, wet screening and cyclone methods.

The phosphorous-bearing minerals in the rock i.e., collophane and dahllite can be separated by froth flotation. Flotation is a widely utilized unit operation in mineral processing and is based upon the principle that different minerals have different wetting characteristics that can be used as a basis for their separation. It separates the grains of valuable minerals from the gangue minerals by making valuable minerals hydrophobic and aerophilic and gangue minerals hydrophilic with the help of flotation reagents (Wills, 1992). Fatty acids, such as oleic acid, are good collectors for phosphate minerals because of their high selectivity. The associated gangue minerals can be depressed using selective depressants which reduce their flotation tendency by rendering them hydrophilic.

The phosphate rocks with calcareous and siliceous gangue minerals are beneficiated by direct flotation with fatty acid collector in alkaline circuit. The carbonate gangue minerals (calcite, dolomite, and siderite) are depressed with quebracho, tannins, lignin sulphonate or causticized starch while silica is depressed by sodium silicate (Zafar *et al.*, 1995). Silica in this rock is present as chert and quartz inclusions in phosphate pellets and as a part of matrix. The presence of silica inclusions in phosphate grains complicates the use of flotation technique for beneficiation. Such rocks are beneficiated by double float method. The process involves direct flotation of phosphate minerals with oleic acid collector in alkaline medium to produce phosphate values rich rougher concentrate. The phosphate concentrate is then cleaned by reverse flotation in acidic medium using fatty amine collector to remove silica into the froth. The phosphate minerals are depressed with depressant such as ACCOPHOS 950.Multiple stage cleanings are often required to produce specific grade concentrate. Iron minerals (hematite, goethite etc.), if present in phosphate concentrate, can be removed by high intensity magnetic separation technique.

Conclusion

On the basis of the present investigation, it is concluded that the phosphate rock of Kakul area contains mainly collophane as the major phosphate-bearing mineral along with subordinate amount of dahllite, while the remaining minerals such as quartz, calcite, dolomite, siderite, fluorite, boehmite, goethite, hematite, pyrite, glauconite, gypsum are associated gangue minerals. Thin section study reveals that rock is fine-grained in texture and mineral phases are finely disseminated in the microcrystalline quartz matrix. The distribution of free and locked collophane grains in various size fractions of the rock shows that it should be ground to more than 80% minus 200 mesh size to have an economic degree of liberation. Mineralogical and textural characteristics of the rock indicate that froth flotation is the most suitable technique for its up-gradation while gravity concentration methods cannot be used due to the finely disseminated texture of the rock.

Acknowledgement

The authors are highly thankful to Pak-American Fertilizer for providing a representative sample of phosphate rock.

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