

Chemical Evaluation, Infrared Spectral, Thermal and Upgradation Studies of Batakna, Hazara (NWFP) Phosphate

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Summary: The present investigations were carried out on Batakna (BKN) phosphate deposits in Hazara (NWFP). Chemical, infrared spectral and thermogravimetric analyses showed these deposits to be of high-grade containing P₂O₅ mineral content greater than 30%. However, because of the presence of high content of undesirable impurities, especially magnesia (%MgO = 2.03 ± 0.15), the phosphate ore is not acceptable to NFC for phosphate fertilizer production in the country. In the present study, efforts have been made to upgrade BKN ore employing particle size reduction and flotation techniques. Details of these investigations along with the results of chemical analyses, infrared spectral and thermogravimetric studies carried out on the phosphate ore are described and discussed.

Introduction

To cater for the fast growing needs of fertilizers in Pakistan, large quantities of rock phosphate and phosphatic fertilizers are imported from Jordan, Morocco and Tunisia [1]. In NWFP, rock phosphate deposits of Hazara, spreaded over 155 sq.km. area and proven reserves of 10 million tons, are considered to be workable deposits. However, mining of the ore from a few localities in Hazara (including Batakna) has been abandoned because of the ore being low-grade due to its low P₂O₅ mineral content or due to undesirable amount of impurities such as SiO₂, Fe₂O₃ or MgO present in the ore [2-4].

All over the world a number of techniques have been employed for the upgradation of low-grade phosphate ores to enhance their economic worth [5-6]. Recent advances in the mineral processing have shown flotation or selective flocculation to be the most effective and versatile technique for removing undesirable impurities and upgrading the low-grade ores [7-9]. By employing this technique the impurities similar to those present in Hazara rock phosphate have been successfully reduced to acceptable limits in rock phosphates of Florida [10] and North Africa [11-12].

In view of the above, it was thought worthwhile to study the upgradation of low-grade Hazara rock phosphates by employing size reduction and flotation techniques. The present investigations were carried out on Batakna (Hazara) phosphate deposits which are at a few kilometers distance from Abbottabad city and are estimated over 3 million tons. To the best of our knowledge no analytical data has been reported on these deposits. The results of characterization of Batakna ore by chemical analyses, thermogravimetric, infrared spectral and upgradation/flotation studies are described and discussed in this paper.

Results and Discussion

A number of workers have reported the petrological and geochemical studies of some Hazara (NWFP) rock phosphates, which were first discovered by Latif [13]. Later on Bhatti *et al.* [14] and Hasan *et al.* [15] carried out detailed stratigraphic and other related investigations. The early Cambrian phosphate deposits of Hazara are generally hosted in Galdanian member of the Abbottabad Formation, which consists of a sequence of cherty dolomite in the upper part, quartzose sandstone in the middle part and

limestone and dolomite limestone in the lower part. Mineralogically these have been identified as hydroxylapatite and fluorapatite [16-17].

Thermogravimetric and infrared spectral analyses

Thermograms and infrared spectra of duplicate samples of Batakna (BKN) phosphate deposits are shown in Figure I and II.

Both samples A and B showed similar thermal characteristics. A very slow and gradual weight loss (< 1%) was observed upto 500°C for both the samples (Figure 1). For samples A and B maximum weight losses of 1.32% and 1.30% were observed around 556-764°C and 575-710°C, respectively. This weight loss may be attributed to loss of water, phosphorous oxyfluoride or chlorine, from hydroxy-, Fluoro- or chloro- apatites, respectively. The weight loss in this temperature range may also be possibly caused by the oxidation of organic matter or decomposition of the carbonate moiety of the small amount of host rock (calcite/dolomite) associated with the apatite [18]. A small increase in mass around 850°C (Figure I) may be caused by oxidation of minor metals in the rock samples. Thermograms showed total loss in

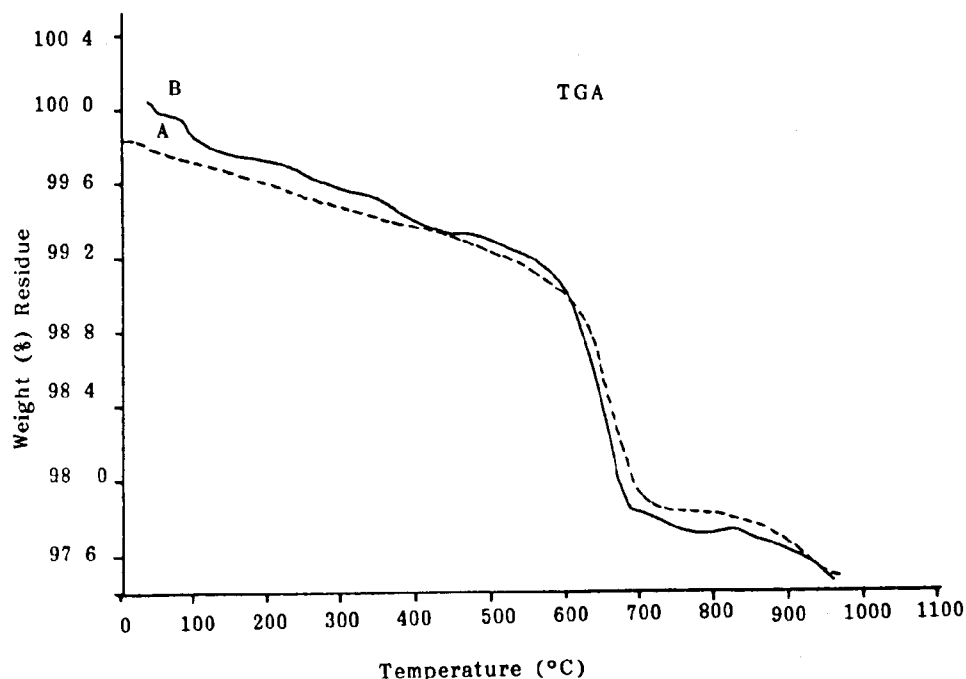


Fig.1 Thermogravimetric analyses (TGA) curves for Batakna phosphate samples.

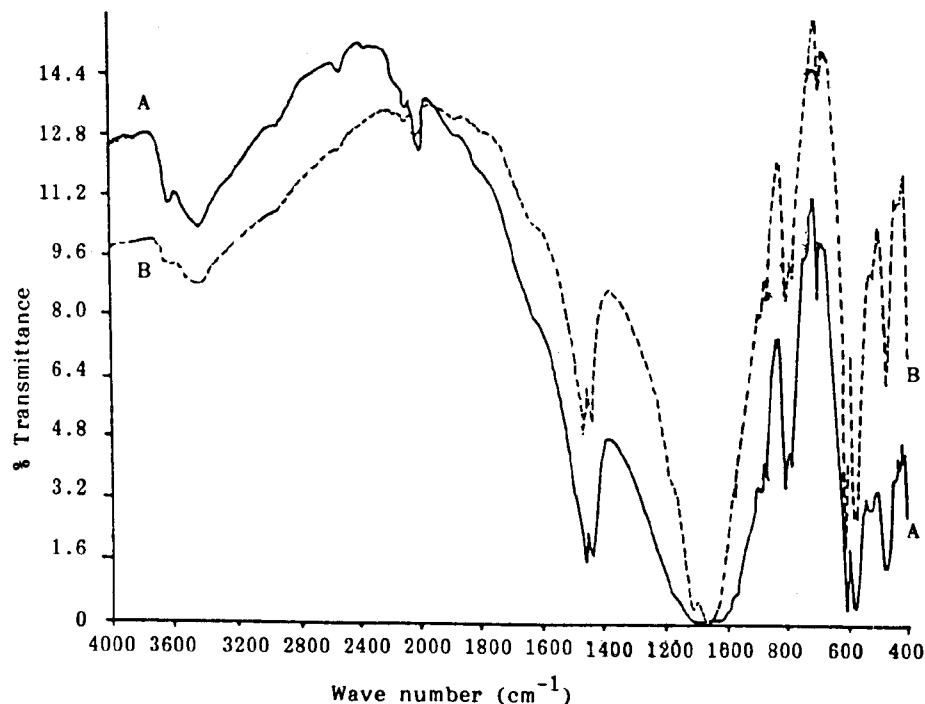


Fig.2: Infrared spectra of Batakna phosphate samples.

weight of 2.85% and 2.44% for sample A and B, respectively. No characteristic differential thermal analyses (DTA) peak was observed in the thermogrammes of either of samples A or B.

Banerjee *et. al.* have reported infrared spectra of some phosphate ores of Udaipur and Jhabua in India [19]. In the present study, infrared absorption spectra of Batakna ore samples (Fig. 2) showed strong absorption bands at 1060 cm^{-1} and 580 cm^{-1} which were thought to be resulting from (P-O) bonding and (P-O) weak modes and regarded as characteristic of phosphate ion [19-20]. Medium intensity absorption bands at 800 cm^{-1} and weak intensity absorption band at 700 cm^{-1} observed in the spectra, have been assigned to various modes of vibrations from P-O linkages in PO_2 , PO_3 and PO_4 groups [19-20].

Medium intensity absorption bands at 1480 cm^{-1} and 1440 cm^{-1} in the infrared spectra have been considered by some workers [19] to be characteristics of phosphorites concentrates. From a study of infrared spectra, chemical and TGA/DTA analyses of fourteen rock phosphate samples from different localities, Khawaja and

Khattak [21] have recently reported that ores with high phosphate content showed in their infrared spectra, a set of two characteristic medium intensity absorption bands around $1460\text{--}1440\text{ cm}^{-1}$ and on heating total loss in weight $< 3\%$. In the present investigations, Batakna ore samples which showed medium intensity absorption bands at 1460 cm^{-1} and 1440 cm^{-1} in their infrared spectra and loss in weight of 2.65% and 2.44% on ignition, appeared to be high-grade phosphate ore. This was also confirmed by the results of chemical analyses of the ore, described below:

Chemical analyses

The analytical data obtained from the chemical analyses of four samples from Batakna (BKN) phosphate ore deposit is shown in Table-1. As also evident from IR, DTA and TGA data, the ore appeared to be high grade phosphate ore. The average chemical composition (%) was found to be:- moisture = 0.07 ± 0.01 ; LOI = 3.04 ± 0.04 ; silica = 17.46 ± 0.11 ; P_2O_5 = 31.26 ± 0.28 ; CaO = 40.04 ± 1.13 ; MgO = 2.03 ± 0.15 ; Fe_2O_3 = 1.66 ± 0.01 ; Al_2O_3 = 4.32 ± 0.27 . A comparison of chemical composition of BKN deposit with those of

Table-1: Chemical analyses of Batakna (NWFP) Rock Phosphate (%)

Constituents	Sample I	Sample II	Sample III	Sample IV	Average
Moisture	0.06	0.08	0.05	0.09	0.07 ±0.01
LOI	3.16	2.98	3.01	3.02	3.04 ±0.04
Silica	17.71	17.05	17.75	17.35	17.46 ±0.11
P ₂ O ₅	30.51	31.32	31.48	31.73	31.26 ±0.28
CaO	40.32	41.52	39.28	39.03	40.04 ±1.13
MgO	2.03	1.83	2.10	2.17	2.03 ±0.15
Fe ₂ O ₃	1.65	1.66	1.65	1.66	1.66 ±0.01
Al ₂ O ₃	4.43	4.19	4.38	4.75	4.32 ±0.27

Table-2: Effect of Grinding modes on various Sieve Fractions % Wt. (Corrected) Retained.

Sieve Size (Mesh)	3B 25S T = 20	3B 25S 15 M T = 20	3B 25S 20 M T = 20	6B 25S 10 M T = 20	6B 25S 15 M T = 20	6B 25S 20 M T = 20
+ 30	7.44	9.22	8.81	6.77	8.79	9.06
- 30 + 130	38.89	38.57	39.14	41.29	37.93	40.60
- 130-	53.67	52.79	52.70	51.98	53.30	50.27
Sieve Size (Mesh)	3B 15 T = 20	3B 15M 25S T = 20	3B 15M 50S T = 20	3B 15M 50S T = 10	3B 15M 50S T = 20	3B 15M 50S T = 30
+ 30	5.59	9.22	6.47	11.44	6.47	7.79
- 30 + 130	40.46	38.57	38.48	40.49	38.46	41.12
- 130	53.89	52.80	55.05	48.06	55.05	51.08

T = Grinding time (minutes)

B = Big size ball (diameter = 40.66± 0.17 mm)

M = Medium size ball (diameter = 30.30 ±0.37 mm)

S = Small size ball (diameter = 19.68± 0.28 mm)

imported rock phosphate from Jordan and Morocco indicated a high content of undesirable impurities such as SiO₂ and MgO present in BKN deposit. Studies were carried out using size reduction and flotation techniques to upgrade and to reduce the amount of undesirable impurities present in Batakna phosphate ore.

Upgradation by particle size reduction

Table-2 shows grinding and sieving results of 1.5 kgm ore sample using different combination of small, medium and big sizes balls in the Ball Mill. A combination of three big(B), fifteen medium(M) and fifty small (S) sizes balls [3B15M50S] was found to be most suitable for obtaining the maximum amount of a desired sieve fraction. The results of detailed sieve analyses of the powdered ore between +5 -230 mesh are shown in Table-3. A, B, C and D correspond to each of the quarters of the ore sample obtained after its adequate mixing, conning and quartering. Six sieve fractions between -5 +10, -10 +18, -18 +30, -30 +60, -60, +130, and -130 +230 mesh were subjected to chemical analyses for SiO₂ and P₂O₅ contents. However, with the decreasing mesh size, none of the sieve fractions showed any appreciable

decrease or increase in SiO₂/P₂O₅ content, indicating little upgradation of BKN ore with particle size reduction.

Flotation studies

For the removal of excessive amounts of undesirable impurities such as magnesia and to a lesser extent silica and iron, flotation tests were carried out on BKN phosphate ore and the results are summarized in Table-4.

The use of Kerosine oil was beneficial not only in reducing the collector consumption but also in accelerating the flotation rates. The promoters added before the addition of collector aided in increasing the rejection of magnesia, while sodium silicate and starch were the selective depressants in the flotation of apatite from silicate and iron oxide minerals.

It is evident from the data in Table-4 that the use of sodium carbonate, ammonium hydroxide and their combination, as a promoter showed an increase of 0.11 to 0.34% in P₂O₅ content and a decrease of 0.47 to 0.82% in magnesia content in the concentrates (Tests 2-4). Maximum decrease of

Table-3: Sieve analysis of BKN rock phosphate (quarters A,B,C,D)

Sieve Size (Mesh)	Sieve Size (Mesh)	Commulative oversize Wt. (%)				Commulative Undersize Wt.(%)				Average Commulative Oversize (% Wt.)	Average Commulative Undersize (% Wt.)
		A	B	C	D	A	B	C	D		
+5	4 mm	0.14	0.43	0.29	0.00	99.86	99.57	99.71	100	0.21	99.78
-5 +10	2 mm	1.40	1.65	1.50	1.22	98.60	98.35	98.50	98.78	±0.19	±0.15
-10 +18	1 mm	6.91	7.46	7.30	7.18	93.09	92.54	92.70	92.82	±0.18	±0.18
-18 +30	0.5 mm	20.05	20.24	21.43	20.08	79.95	79.76	78.57	79.92	7.21	92.79
-30 +60	0.25 mm	40.36	39.11	40.25	40.19	59.64	60.89	59.75	59.81	±0.23	±0.23
-60 +130	0.125 mm	65.25	62.60	61.09	60.86	34.75	37.40	38.91	39.15	±0.65	±0.66
-130 +230	0.0625 mm	77.91	74.30	74.28	74.67	22.09	25.70	25.72	25.33	±0.58	±0.58
-230		99.96	99.97	99.95	99.99	-	-	-	-	±2.02	±2.02
										75.29	24.71
										±1.8	±1.67
										99.97	-
										±0.02	

Table-4: Flotation tests

Test No.	Reagents	Up-gradation in concentrates (%)			Apatite Recovery (%)
		SiO ₂	MgO	P ₂ O ₅	
1.	Oleic acid/ Kerosine oil	-1.35	+0.06	-0.37	98.00
2.	Oleic acid/ Kerosine oil +Na ₂ CO ₃	+0.12	-0.82	+0.34	90.00
3.	Oleic acid/ Kerosine oil +NH ₄ OH	0.12	-0.47	+0.11	91.60
4.	Oleic acid/ Kerosine oil +Na ₂ CO ₃ +NH ₄ OH	+0.11	-0.47	+0.11	91.00
5.	Oleic acid/ Kerosine oil + Sod. silicate	-0.89	-0.52	+0.02	87.86
6.	Oleic acid/ Kerosine oil + Sod. Silicate + Starch	0.16	-0.57	-0.04	85.00

magnesium (0.82%) was observed with the use of sodium carbonate promoter. Silica content was slightly increased in all these tests. With the use of depressants sodium silicate and starch, a decrease of 0.52% to 0.57% and 0.16% to 0.89% in magnesium and silica contents was observed, respectively (Tests 5-6), while P₂O₅ content almost remained unchanged. Studies are in progress for further improving the process parameters (Table-4) and optimizing the dosage of collectors mixtures, promoters and depressants.

Experimental

In dry weather, 20 kg, sample from Batakna (BKN) deposits was hand picked and collected in a bag from inside the mine (No. M-1),

300-400 feet deep. In the laboratory, the light-gray ore was not crushed as it was soft and brittle and was powdered directly in a KHD Industrieanlagen AH Humboldt Wedage type Ball Mill. After adequate conning and quartering, representative samples of the ore were taken for various studies. Sieve analysis was carried out using KHD Humboldt Wedag type sieve shaker.

Both the fusion and acid decomposition methods were used to digest and dissolve the ore for chemical analyses [22,23]. Standard analytical methods were used for the estimation of phosphorus, magnesium, aluminium, SiO₂, iron and magnesia contents [22-24].

Spectra were recorded on a Hitachi Model-270-50 infrared spectrophotometer in the range 4000-250 cm⁻¹ using KBr disc techniques.

Thermogravimetric (TGA) and Differential Thermal (DTA) analyses of samples weighing 20-25 mg were carried out in platinum boat, at a heating rate of 10°C per minute under inert atmosphere (purified nitrogen) and a gas flow rate of 50 ml per minutes, on Dupont TGA-Model 951 with temperature range 25-1000°C, coupled with a Dupont 1090 computer controlled thermal analyzer and controller.

Flotation studies

All flotation tests were carried out by classic flotation technique using WEADAGE laboratory

flotation machine with a cell capacity of one litre. Before the flotation, 200 gms (200 mesh) dolomitic phosphate rock of Batakna, Hazara (NWFP) was conditioned for five minutes with 1.25 Kg/ton of Sodium Carbonate, ammonium hydroxide separately or in combination. This material was then conditioned with 1.5 Kg/ton Kerosine oil and 2.5 Kg/ton Oleic acid mixture, followed by 2-3 drops of polyethylene glycol frother. The pH was adjusted to 9.5, then floated until the froth was barren of mineral particles. The flotation time was normally less than ten minutes. The rotor speed was fixed at 1200 RPM and the pulp density at about 20%. The phosphate concentrates and the tailings were dried, weighed and assayed for P_2O_5 , MgO and SiO_2 , by standard analytical methods. Details of the reagents and % recovery alongwith variation in P_2O_5 , MgO and SiO_2 contents of the concentrates, expressed as % upgradation are given in Table-4.

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