# Technology

# BENEFICIATION OF HAZARA BARITE AS RAW MATERIAL FOR DIFFERENT BARITE UTILIZING INDUSTRIES

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Three barite deposits of economic importance occur near Haripur, Havelian and Kohala in Hazara Division. Beneficiation studies of eighteen representative samples from these deposits were undertaken by chemical method. The objective of this study was to upgrade the quality of barite to acceptable limit for utilization in various industries. Simple treatment for 15 min with commercial hydrochloric acid has been suggested to obtain the required specification for 80% barite utilizing industries.

Key words: Beneficiation, Barite, Hazara.

## Introduction

Pakistan is rich in mineral resources particularly industrial minerals like gypsum, rock salt, silica sand, limestone, dolomite, barite, phosphate rock, soap stone and nepheline syenite (Hussain *et al* 1991).

Heavyspar or barite (BaSO<sub>4</sub>) which is 65.7% barium oxide and 34.3% sulphur trioxide is an important industrial mineral. It has many fold uses. It is used in oil and water well drilling muds, in pharmaceutical industry, for the preparation of several barium chemicals, manufacture of paint, lithophone, glass, artificial ivory and insecticides. Paper, rubber and plastic industries use barite as filler. (Crookshank 1954; Ahmad 1969).

Large stratiform barite deposits occur in Khuzdar and Lasbela districts of Balochistan along the axial belt. Barite deposits of Khuzdar are being mined at the rate of 30.000 tons per annum by Bolan mining company. Barite deposits also occur in various localities of NWFP. A few studies (Marks and Ali 1961; Killinger and Richards 1967; Iqbal and Shah 1980; Afridi 1986) were done covering regional and local geological aspects of some of these barite deposits. Later (Aurangzeb *et al* 1988; Hussain *et al* 1991; Khan *et al* 1994) carried out studies related to petrographic and geochemical characteristics of barite deposits of Haripur and Havelian. Three principal occurrences i. e., Haripur, Havelian and Kohala barite deposits have been reported in Hazara.

Presence of small deposits have also been reported in Swabi, Swat and Salt Range (Shah and Khan 1963; Ali and Aziz 1965).

The present paper deals with the up-gradation of the barite samples, from Hazara deposits, with hydrochloric acid to improve their characteristics for utilization in various industries in the light of international standard specification.

#### **Materials and Methods**

Brief description of barite depsoits in Hazara is as follows: Haripur barite deposits that lie around Haripur village have been recorded in 12 localities spreading over an area of about 30 km<sup>2</sup> (Fig 1). The promising barite deposits are Kag, Aluli, Darwaza, Chinjiala, Kachi Bir, etc. All the barite deposits are accessible through Haripur - Bir road. These barite occur in quartzite, quartz-mica and dolomite. In the Kag Aluli under ground mine up to 300 feet deep several feet thick barite veins occur.

Havelian barite deposits lie in the southern area of Hazara Districts. In the thick sequence of limestone with subordinate shale, barite occurs in veins, varying in thickness from few inches to several feet.

In this region Chandomera, Faqir Muhammad and Batagrain are three important barite deposits. In Chandomera, reddish white barite veins occur in grey colour argillaceous limestone and reddish shale (Aurangzeb 1991). The barite veins are irregular throughout the region but have a sharp contact with the host rock.

Kohala deposit is the largest deposit of Hazara district. It is located at about 3 miles to the South West of the Kohala village, near Nithiagali. The barite occurs in large and small dilation veins and is the highest grade of all other barite deposits nearby in Hazara district, and reserves of all catego-

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ries have been estimated up to 30,000 tonnes (Ahmad 1969).

*Genesis of barite.* Field observations have established that Havelian barite occur as veins in shale and limestone in narrow and steeply incline zones. The structural control of mineralization is noticed as barite deposits in Havelian which show linear trends controled by small faults, strongly jointed and sheared zones present throughout the district. Barite veins in the area show pinhing and swelling behaviour and persistance with depth. The fractures are often seen filled by fine grained recrystallised calcite and goethite. Presence of secondary fine grained are sparry calcite and release of iron oxide solution seen filling the fratures may be the result of diagenesis and low grade regional metamorphism of thick sedimentary sequence exposed in the mineralized area.

The mineralization in faults and joint zone imply outward fluid movements from the structures. Fluids utilizing these structures moved out into potous and permeable sediments



Fig 1 Map showing the location of barite deposits of Hazara NWFP.

 Table 1

 Chemical composition(%) of Haripur barite in raw state.

Sample No.	$SiO_2$	BaO	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SO3	LOI	Total	$BaSO_4$	Sp.Gr
Kag	2.62	61.37	1.15	0.80	0.18	0.26	32.34	0.71	99.43	93.71	4.23
Aluli	2.44	59.99	3.65	0.52	0.14	0.51	31.48	1.55	100.28	91.47	4.12
Darwaza	2.87	59.28	1.70	0.86	0.25	0.62	31.26	2.63	99.47	90.54	4.07
Kachi	2.26	58.70	1.68	1.61	0.36	2.19	30.90	1.75	99.45	89.60	4.02
Bir	0.98	60.77	1.48	0.56	0.18	2.20	32.03	1.20	99.40	92.80	4.18
Hil	2.61	60.78	1.26	0.85	0.11	0.14	32.06	1.40	99.21	92.84	4.17
Mean	2.29	60.14	1.82	0.86	0.20	0.98	31.68	1.54	99.51	91.82	4.139

which are widely exposed in Havelian and precipitated barite in the available open space (Charles and William 1997). The oxidation of fluid rich in barium and reduced sulphur would lower the pH and would lead to the dissolution of carbonate host rocks (Plummer 1971). Barite was deposited in preexisting openspace such as breccice deposits and solution channels (Leach 1980). Eighteen representative barite samples were collected from Hazara deposits, selecting six each from Haripur, Havelian and Kohala respectively. For chemical analysis each sample was crushed to 150-180 µm after conning and quartering. Percentage composition of silica, iron, aluminium, calcium, magnesium, barium and loss on ignition was determined by conventional methods (Scott and Furman 1962). Iron was also

Table 2
Chemical composition (%) of Haripur barite after HCl treatment

Sample No.	SiO <sub>2</sub>	BaO	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SO3	LOI	Total	$BaSO_4$	Sp.Gr
Kag	2.96	62.40	0.63	0.42	0.07	0.12	32.82	0.16	99.58	95.22	4.27
Aluli	2.88	62.36	1.49	0.20	0.05	0.13	32.81	0.23	100.15	95.17	4.27
Darwaza	3.69	62.22	0.33	0.15	0.06	0.18	32.67	0.35	99.64	94.89	4.27
Kachi	3.88	60.55	0.83	0.84	0.09	1.03	31.87	0.32	99.41	92.42	4.16
Bir	2.40	62.37	0.57	0.22	0.06	1.00	32.88	0.20	99.70	95.25	4.29
Hil	2.88	62.52	0.40	0.32	0.04	0.05	32.94	0.28	99.43	95.46	4.29
Mean	3.11	62.07	0.71	0.36	0.06	0.41	32.66	0.36	99.74	94.74	4.26

 Table 3

 Chemical composition (%) of Havelian barite in raw state

Sample No.	SiO <sub>2</sub>	BaO	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SO3	LOI	Total	BaSO <sub>4</sub>	Sp.Gr
Chandomera 1	4.84	61.01	0.60	0.14	0.08	1.23	32.01	0.31	100.22	93.02	4.18
Chandomera 2	5.30	60.00	1.12	0.38	0.14	1.42	31.48	0.42	100.26	91.48	4.12
Fagir Mohd 1	0.88	55.52	5.56	1.26	0.16	2.11	29.03	5.88	100.40	84.55	3.81
Faqir Mohd 2	0.75	60.67	2.58	0.92	0.15	1.02	31.83	2.54	100.46	92.50	4.15
Batagram 1	6.82	59.04	0.82	0.52	0.09	0.40	30.83	1.66	100.17	89.87	4.04
Batagram 2	6.62	56.83	1.84	1.56	0.12	0.45	29.67	3.57	100.66	86.50	3.89
Mean	4.20	58.84	2.08	0.79	0.12	0.93	30.81	2.39	100.16	89.65	4.31

	Table 4		
Chemical composition	(%) of Havelian	barite after HO	Cl treatment

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Sample No.	SiO <sub>2</sub>	BaO	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SO3	LOI	Total	BaSO <sub>4</sub>	Sp.Gr
Chandomera 1	5.51	61.44	0.29	0.04	0.03	0.50	32.09	0.11	100.01	93.53	4.21
Chandomera 2	5.83	60.95	0.56	0.27	0.06	0.65	31.89	0.23	100.44	92.84	4.18
Faqir Mohd 1	2.23	62.44	0.75	0.39	0.05	0.83	32.61	0.85	100.15	95.05	4.26
Faqir Mohd 2	1.43	63.34	1.08	0.25	0.04	0.43	33.18	0.58	100.33	96.52	4.34
Batagram 1	7.24	60.50	0.12	0.15	0.02	0.05	31.58	0.42	100.08	92.08	4.14
Batagram 2	6.92	60.65	0.34	0.28	0.03	0.06	31.66	0.65	100.60	92.31	4.14
Mean	4.86	61.55	0.52	0.21	0.04	0.42	32.16	0.47	100.23	93.72	4.21

determined by spectrophotometric method. Chemical analysis of raw samples is given in Table 1, 3 and 5.

Then 50 g of each sample was taken in 500ml beaker, washed two times with distilled water by decantation and 50ml commercial hydrochloric acid was added. Stirring was done with mechanical stirrer. After 15 min reaction, acid was decanted. Sample was washed with distilled water by decantation and then by filtration till the filtrate was free from chloride and iron. Washed sample was dried in the oven at 110°C and chemical analysis was carried out, using the same procedures as were used for the sample in crude form. Results are tabulated in Table 2, 4 and 6 respectively. Specific gravity of all samples was also determined and reported (Table 1-6).

## **Results and Discussion**

Table 1, 3 and 5 show that  $BaSO_4$  varies from 89.6% to 93.71% iron from 0.11 to 0.36% and aluminium from 0.14 to 2.2%. in Haripur barite samples.  $BaSO_4$  ranges from 84.55 to 93.02% iron from 0.08 to 0.16% and aluminium from 0.4 to 2.11% in Havelian barite while  $BaSO_4$  varies from 88.92 to 92.68%,

iron from 0.12 to 0.26% and a luminium from 0.28% to 0.82% in Kohala barite.

 $BaSO_4$  is up-graded from 92.42 to 95.46% in Haripur barite, from 92.08 to 96.52% in Havelian barite and from 94.32 to 95.90% Kohala barite after hydrochloric acid treatment of the samples. The quantity of iron, aluminium, calcium and magnesium decreased and silica contents increased in all samples after the crude mineral is treated with the acid. HCl reacts only with the impurities of iron, aluminium, calcium and magnesium and has no effect on silica contents and therefore, the silica contents in the treated samples increase with the decrease of other impurities.

Barite contains calcium, magnesium, iron and aluminium as impurities. It is obvious that some iron, aluminium and the part of the calcium and magnesium (present as carbonates) reacts with the hydrochloric acid to form soluble chlorides causing the reduction of these elements. These can be represented by the following reactions:

$$XCO_3 + 2HCI \rightarrow H_2CO_3 + XCI_3$$

where X : Ca, Mg

Sample No.	SiO <sub>2</sub>	BaO	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SO3	LOI	Total	BaSO <sub>4</sub>	Sp.Gr
Kohala 1	3.20	58.57	2.58	1.02	0.18	0.28	30.58	3.16	99.57	89.15	4.02
Kohala 2	2.65	58.32	3.23	0.86	0.16	0.45	30.60	2.96	99.23	88.92	4.00
Kohala 3	3.32	60.49	1.48	0.62	0.12	0.32	31.61	1.50	99.46	92.10	4.14
Kohala 4	2.08	59.16	1.95	1.32	0.26	0.82	30.89	3.22	99.70	90.05	4.04
Kohala 5	1.88	60.88	1.83	0.84	0.13	0.63	31.70	2.16	99.79	92.32	4.16
Kohala 6	2.02	60.88	1.47	0.56	0.15	0.52	31.80	1.87	99.27	92.68	4.17
Mean	2.52	59.67	2.09	0.87	0.16	0.50	31.19	2.47	99.47	90.86	4.09

		Ta	ble	5				
Chemical	composition	(%)	of	Kohala	barite	in	raw	state

		T	able 6				
Chemical composition	(%)	of	Kohala	barite	after	HCI	treatment

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Sample No.	SiO <sub>2</sub>	BaO	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SO3	LOI	Total	BaSO <sub>4</sub>	Sp.Gr
Kohala 1	3.54	62.10	0.54	0.32	0.06	0.16	32.43	0.52	99.67	94.53	4.24
Kohala 2	3.00	61.84	0.86	0.34	0.05	0.21	32.48	0.45	99.23	94.32	4.21
Kohala 3	3.57	62.10	0.38	0.29	0.03	0.17	32.58	0.26	99.38	94.68	4.25
Kohala 4	2.73	62.59	0.42	0.43	0.07	0.36	32.68	0.62	99.90	95.27	4.28
Kohala 5	2.34	63.00	0.39	0.30	0.04	0.28	32.90	0.36	99.61	95.90	4.32
Kohala 6	2.40	62.93	0.35	0.21	0.05	0.25	32.87	0.32	99.38	95.80	4.30
Mean	2.93	62.42	0.49	0.31	0.05	0.23	32.65	0.42	99.50	95.09	4.27

	1	2	3	4	5	6
	Drill mud barite	Filler application	Glass grade barite	Barite as heavy aggregate	Barium chemicals manufacture	Paint grade barite
Sp. gravity	4.2					144
BaSO <sub>4</sub>	92% min	95% min	95% min	95% min	92-96% min	95%
SiO,			1.5 max			
Fe <sub>2</sub> Õ <sub>2</sub>			0.15 max	1071	1% max	0.05
Al,O,		300	0.15 max			
Color		near white	white			white
Particle size	95% 45 µm	95% 45max	100%-8.5µm	gravel size	-5.0+0.5 mm	37µm

 Table 7

 General specifications of barit

Ref: Andrew and Collings (1990).

$$Y_2(CO_3)_3 + 6HCl \rightarrow 3H_2CO_3 + 2YCl_3$$

where Y: Al, Fe

This up-gradation of barite has shown that unwanted impurities go along with washings and only minor impurities remain in the acid treated barite. Thus chemical composition of all samples except sample from Kachi, sample no. Chandomera 2 and Batagram 1 and 2 reaches the recommended limit of international standard specification (Table 7) for most of industries. If this beneficiation procedure is undertaken with increasing temperature, or other beneficiating methods are used, the quality of barite could be obtained which can be used for pharmaceutical purposes but that may be uneconomical. By this simple 15 min acid treatment, Hazara barite can be made suitable for 80% industrial applications according to the world standard specification (Endrew and Kollings 1990).

The mean specific gravity of Haripur barite is 4.139, Havelian barite is 4.037 and Kohala barite is 4.092 in the crude form. In the beneficiated samples mean specific gravity changes to 4.463, 4.215 and 4.277 respectively. This increase in specific gravity confirms the increase in the purity of the mineral. The specific gravity of pure barite is 4.5 (Hurlbut 1956).

#### Conclusion

Though barite produced in Hazara is already utilized in petroleum drilling industry, manufacture of paint and chemical industry, this barite in original form is not suitable for high quality products. The present study show that suitable quality of barite exists in Hazara which after simple acid treatment can be utilised for the international standard production of chemicals, paint and glass, and for application as heavy aggregate and filler in rubber, paper and plastic industries. It can also be used in petroleum drilling industry.

Since commercial hydrochloric acid is abundantly available in Pakistan from the chemical industries, this process can be economically and fruitfully employed to reduce the unwanted constituents.

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