Studies on the Beneficiation of Gunga Barite with Different Concentrations of Hydrochloric Acid

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Summary: Beneficiation conditions of Gunga (Baluchistan) Barite using different concentrations of hydrochloric acid, in the range of (5-30%), at room temperature and for the same interval of time have been studied. With the use of 25% hydrochloric acid the world standard specifications of barite for most of barite utilizing industries can be achieved and the process is suggested to be used for other barite deposits in the country.

Introduction

Barite (heavyspar) is an important mineral. Chemically it is 67.7% barium oxide and 34.3% sulphar trioxide. [1,2]. Its deposits in Pakistan are concentrated in Baluchistan and North West Frontier province. In 1984-85 Baluchistan produced 20699 tones and NWFP 437 tones of barite[3]. About eleven million metric tones of barite deposits occur at Gunga 16 Km South West of Khuzdar (Baluchistan) [4].

Barite has range of applications. It is used in oil and water drilling mud, in the manufacture of lithophone($BaSO_4$ + ZnS), glass, artificial ivory, insecticide, as extender in paint, as filler in paper, rubber and plastic and for the preparation of barium chemicals such as BaS, $BaCl_2$, $Ba(OH)_2$ and $BaCO_3$. These chemicals are used for paint and heavy chemical industry.[1,2,5,6,7,8]. Besides barite is used infrequently in electronic products, lubricant, fluxing agents and welding [9,10]

In Pakistan most of barite is consumed as drilling mud additive during boring of water wells and in the petroleum drilling industry with the rest going in raw state to the paint industry in Lahore and Karachi [4,7]. The analar; grade barium chemicals requirements are met through import and also products of international level in other industries like glass, paint and plastic is demand of the day.

The barite is neither, processed nor categorized for drilling and non drilling purposes. The dominant Gunga mineral is quartze which is not easily separated from the ore. Other impurities are from the presence of calcite, dolomite, pyrite and limonite which cause calcium, magnesium, aluminium and iron contents to exceed the limit specified for certain industrial applications [7]. To fulfil the increasing demands of pure barite for non drilling purposes, beneficiation of raw barite is necessary to reduce the concentration of above impurities to the desired level.

The main purpose of the study is to improve the quality of the barite of Gunga deposits to the internationaly specified level for different barite utilizing industries to produce high quality products (Table-3)

Geological Setting:

Barite deposits are locatd in the narrow metallogenic zone of Baluchistan, known as the Khuzdar-Lasbela belt. This belt is about 300 km long and is reported to contain several stratabound and vein type barite occurences.

The Gunga barite deposits occur about 16 km South West of Khuzdar city, which is 400 km from karachi on Quetta Karachi road. These deposits lie within latitude of 27° 44' N and longitude 66° 32' E. These deposits extend for about 1500 to 2000 m within jurassic limestone comprising a series of disconnected barite lenses of 3 to 5 m thickness [11].

The barite deposits of Gunga are associated with interbedded Jurassic limestone and shale belonging to the Angira formation of Ferozabad group. The term Ferozabad group given by Fatimi et al [12] is divided into three formations, Spingwar, Lorali and Angira of Jurrassic age. The Ferozabad Group is intensely folded and is disconformable with the overlying Sember Formation of early Cretacous

Table I:Chemical Composition of Gunga Barite Samples (in wt %)

No	SiO_2	BaO	SO_3	Fe_2O_3	Al_2O_3	CaO	MgO	Moist	LOI at 950°C	Total	$BaSO_4$
1	3.82	61.36	31.98	0.70	0.92	0.23	0.18	0.07	0.25	99.51	93.24
2	3.22	61.28	32.07	0.82	1.01	0.30	0.22	0.05	0.43	99.40	93.50
3	3.84	61.17	31.90	0.73	0.95	0.28	0.21	0.06	0.38	99.52	93.00
4	3.60	61.16	32.12	0.84	1.04	0.24	0.21	0.03	0.39	99.63	93.64
5	3.86	61.09	31.93	0.91	1.11	0.26	0.16	-	0.38	99.70	93.09
6	7.92	58.64	30.32	0.87	1.09	0.30	0.14	-	0.39	99.67	88.39
7	2.82	60.81	31.65	1.20	1.88	0.40	0.19	0.03	0.71	99.69	92.27
8	2.84	60.22	31.38	1.35	3.21	0.23	0.16	0.07	0.25	99.71	91.49
9	3.06	60.87	31.80	1.22	2.38	0.30	0.18	0.09	0.45	100.35	92.71
10	4.06	62.01	31.88	0.52	0.60	0.27	0.16	0.05	0.34	99.89	92.94
11	2.88	61.58	32.10	0.68	0.80	0.66	0.25	0.06	0.71	99.72	93.58
12	4.68	60.32	31.52	0.58	0.62	0.62	0.53	0.02	1.67	100.56	91.89
13	2.48	61.84	31.92	0.61	0.79	0.61	0.45	0.09	1.36	100.15	93.06
14	3.80	61.08	31.85	0.60	0.76	0.68	0.50	0.11	1.15	100.53	92.85
15	2.00	70.54	06.38	0.31	0.45	0.68	0.46	0.07	19.69	99.58	18.60

age in Lasbela area but in the vicinity of Khuzdar, either the Sember Formation is absent or scarcely exposed [13].

In Gunga two mineralized zones are recognized. The upper zone is mainly composed of barite, but significant concentration of Sphalerite and Galena are found in the lower mineralized zone. The mode of barite mineralization in Gunga is divided into following four types, statabound replacement associated with 1) Fracture filling 2) Open space filling in solution collapsed breccia 3) Replacement in faults, and 4) Veinlets associated with all these types [14]

Results and Discussion

It is evident from the reported results of fifteen barite samples (Table 1) that $BaSo_4$ varies from 18.60 to 93.64 % iron oxide, 0.31 to 1.35 aluminum oxide, 0.45 to 3.21, calcium oxide, 0.23 to 0.68 and magnesium oxide, 0.14 to 0.53 in Gunga barite.

Deviation is observed in the sample No.15. In this sample barite is 18.6%. The remaining barium is present as witherite ($BaCO_3$) which causes increase in percent loss on heating and barium oxide content in the sample.

Composite sample which actually represents all the fifteen samples of Table I. The chemical composition in raw state is indicated in Table 2. It contains 3.50 % SiO_2, 91.02% $BaSO_4$, 0.86% Iron oxide, 1.08% aluminium oxide, 0.53% calcium oxide and 0.28% magnesium oxide.

Treatment of this composite sample with hydrochloric acid causes increase of $BaSO_4$ from 91.02 to 95.23% and decrease of unwanted iron oxide 0.86 to 0.043, aluminum oxide 1.08 to 0.054, calcium oxide 0.53 to 0.027, and magnesium oxide from 0.28 to 0.013 (Table 2 and figures 1,2).

This upgradation of barite is the result of partial reaction of iron and aluminium with hydrochloric acid to form $FeCl_2$ and $AlCl_3$. Similarly calcium and magnisium which are domenantly present as carbonates react with hydrochloric acid and form calcium and magnesium chlorides as below.

$$CaCO_3 + 2HCL \longrightarrow CaCl_2 + H_2O + CO_2$$

$$MgCO_3 + 2\ HCL \longrightarrow MgCl_2 + H_2O + CO_2$$

These chlorides of unwanted elements are soluble in water which are washed away, and

Table-2 Chemical Composition of Barite in Raw State and After Treatment with Hydrochloric Acid of Different Concentration.

Sample	SiO_2	BaO	SO_3	Fe_2O_3	Al_2O_3	CaO	MgO	H_2O	L.O.I.	Total	$BaSO_4$
Raw state	3.50	61.13	31.22	0.86	1.08	0.53	0.28	0.06	1.88	100.54	91.02
After 5% HCl	3.55	61.90	31.66	0.61	0.77	0.38	0.20	0.013	0.93	100.013	92.30
After 10% HCl	3.610	62.956	32.208	0.301	0.478	0.186	0.098	0.011	0.46	100.008	93.87
After 15% HCl	3.645	63.470	32.513	0.129	0.262	0.08	0.042	0.009	0.28	100.33	94.78
After 20% HCl	3.66	63.815	32.637	0.060	0.080	0.038	0.020	0.01	0.130	100.450	95.15
After 25% HCl	3.662	63.770	32.665	0.043	0.054	0.027	0.014	0.012	0.094	100.341	95.23
After 30% HCl	3.661	63.768	32.663	0.044	0.053	0.028	0.013	0.010	0.093	100.333	95.22

HCl	Fe2O3
0%	0.86
5%	0.61
10%	0.301
15%	0.129
20%	0.06
25%	0.043
30%	0.044

HCl	Al2O3
0%	1.08
5%	0.77
10%	0.478
15%	0.262
20%	0.08
25%	0.054
30%	0.053

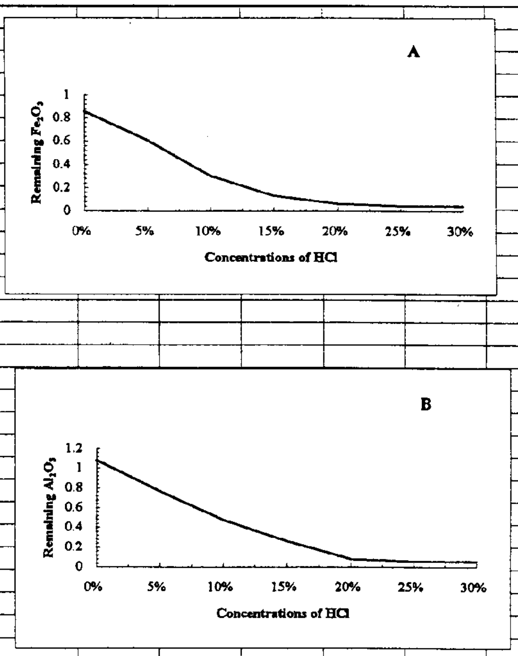


Fig. 1: Plot of (A) remaining iron and (B) Aluminium vs HCl concentrations.

upgradation of the barite to the desired level [15] for different industries can be produced. (Table-3)

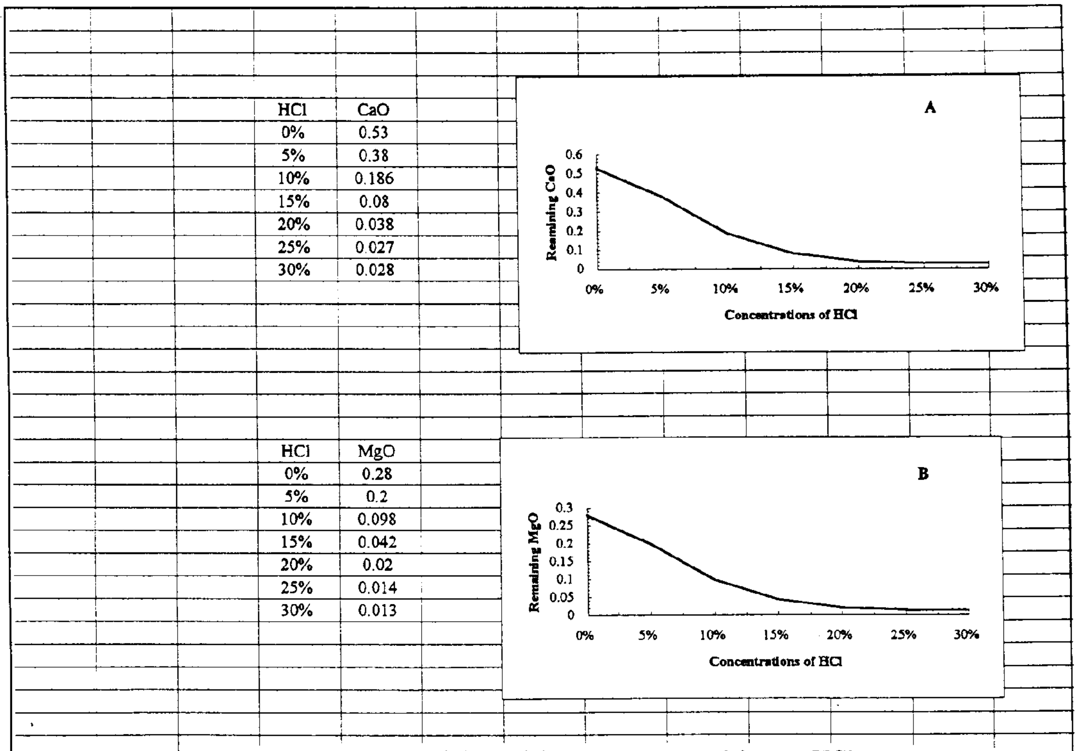
On reducing the barite to barium sulphide by charcoal [5] or natural gas [6] at 800-950°C and 2-4 hours duration, sufficeient reducing agent and fuel shall be consumed. These cause to increase the cost and the process is applicable to chemical and paint industries only. In the present study barite is purified simply by treating with 25% hydrochloric acid at room temperature and for 15 minutes only. This upgraded barite can be used in several industries. Hence it is obvious that this is a low cost and multipurpose process as aompared to the above reducing procedures.

Experimental

Fifteen barite samples were collected from Gunga Barite deposits and studied for their chemical characteristics by conventional methods mentioned below.

Nearly 1 gm of sample was taken in a platinium crucible, heated in an electric oven at 115 °C for two hours to find the moisture content. The same crucible was heated in an electric furnance at 950°C for one hour to determine loss on ignition.

An other 0.5 gm portion of the sample was disintegrated by fusing with about six times its weight of sodium carbonates at 900°C. The resultant cake was leached out in hot water and filtered. The sulphate was determined from the filtrate by precipatating with barium chloride. The precipitates on the filter paper were dissovled in dilute hydrochloric acid and ratained as a stock solution for determination of iron and aluminium by precipitating with ammonium hydroxide and calcium and magnisium by titration with a standard EDTA solution. Residue on the filter paper was washed throughly, ignited in a weight crucible and reported as SiO_2. Iron was also checked spectrophotometrically by making solution of 0.2 gm sample in



HCl	CaO
0%	0.53
5%	0.38
10%	0.186
15%	0.08
20%	0.038
25%	0.027
30%	0.028

HCl	MgO
0%	0.28
5%	0.2
10%	0.098
15%	0.042
20%	0.02
25%	0.014
30%	0.013

Fig. 2: Plot of (A) remaining calcium and (B) magnisium vs HCl concentrations.

Table 3 Standard Specification of Barite for Different Barite Utilising Industries.

Industries	$BaSO_4$	SiO_2	Fe_2O_3	Al_2O_3	Colour	Particle size
Glass	95 % min	1.5 % max	0.15 % max	0.15 max	White	100% - 850 μ m with less than 5% 150 μ m
Chemicals	92 - 96 % mim.	-	1.0 % max	-	-	-5.0 + 0.5 mm
Paint	95% mim	-	0.05% max	-	White	37 μ m (400 mesh)
As heavy aggregate	95% mim	-	-	-	-	Gravel size.
As Filler	95 % mim	-	-	-	Near white	95% 45 xm
Drill Mud Barite	92 % mim.	-	-	-	-	95% (325 mesh) 45 μ m

P.R.A. Andrews and R.K. Collings "Barite in Canada" Industrial Minerals 46-57 (1990).

hydrofluoric and perchloric acid [16,17]. Results are given in Table-1.

50 gms of the samples was mixed homogenously using small ball mill to prepare a composite representative sample. This homogenous miixture was analysed in its raw state. for SiO_2,BaO, SO_3, Fe_2O_3, Al_2O_3, CaO, MgO, moisture and loss on ignition.

50 gms of this composite sample was taken in a beaker and treated with 50 ml 5% hydrochloric acid with a constant stirring. After 15 minutes, acid was decanted. Sample was washed with distilled water first by decantation and finally by filteration till free from chloride and iron. Chloride was tested with silver nitrate which if present, gives white precipitates of silver chloride and iron gives red color with ammonium thiocynate or blue color with potasium thiocynate. Final mxiture was dried.

Similar procedure was adopted for other 50 gms fractions of the composite sample by treating with 10%, 15%, 20%, 25% and 30% hydrochloric acid respectively. All oven dried samples were chemically evaluated by using the same methods as used for the raw samples. These results are summarized in Table-2. The results indicate that 25%

concentration of hydrochloric acid is more favourable and optimum concentration.

Conclusions

Different barite deposits available in the country are being utilized by the petroleum industry, for manufacturing of low standard barium chemicals, paint and in glass industry. Similarly barite of Gunga deposits is mainly used as drilling mud additive by local petroleum industry. It can be used in other industries, but the products are not of international standard. As a result of present investigation it has been concluded that by HCl beneficiation procedure desirable standard specifications can be acheived for manufacturing of high quality products.

Moreover, hydrochloric acid is abundantly available in the country and its use is economical for the process. Hence this process can be fruitfully employed to remove Fe, Al, Ca and Mg impurities from Gunga barite, and may be suggested for other barite deposits in Pakistan.

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