STUDIES ON THE REDUCTION OF BARYTES WITH CHARCOAL

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The conditions for the reduction of barytes with carbon have been studied. The use of 35 percent carbon at 850°C. for duration of 2.5 hours gives 90 percent reduction. At 900°C., 97 percent reduction is obtained in 2 hours with 35 percent carbon.

Introduction

The barytes (Heavy Spar) deposits in mineable quantities occur in West Pakistan. The principal deposits are found in Hazara, Khuzdar and Lasbela Districts.[1] Most of the mineral is at present being utilised by the domestic petroleum and paint industries. However, high grade ore with 86-98 percent $BaSO_4$ content has a great prospect for the manufacture of industrially important chemicals of barium such as $BaS, BaSO_4$, $BaCl_2$, $BaCO_3$, $Ba(OH)_2$ and lithophone pigment.

Barium sulphide is the "basic material" for the preparation of all other barium compounds. Hence various workers have used either carbon or gas reduction method for the preparation of barium sulphide from the barytes mineral. M. Savul *et. al.*[2] have worked on the utilisation of Romanian Barytes and found that among the various forms of carbon the charcoal gives the best reduction of the barytes at 750°-800°C. in 2-hour duration. Besides Iqbal and Gupta,[3] Steinmetzer,[4] S. Hani,[5] Shushunov,[6] Budnikov[7] and a number of other workers [8-13] have studied the conditions for maximum reduction of barytes with carbon at elevated temperatures. No fixed conditions of temperature and ore: carbon ratio have been established. The conditions for the reduction of barytes vary from ore to ore. The temperature and the amount of carbon used in each case varies, mainly depending upon the nature of the ore, the purity of carbon and the impurities present in the ore.

The gas reduction technique has been used by Sakhtakhtinskii,[14] Salvi,[15] Culver, [16-17] Mirev[18] and R.A. Shah and I.A. Khan.[19] Shah and Khan have used Sui gas in the presence of various catalysts for reducing barytes to barium sulphide. They achieved~93 percent reduction at 950°C. in 4 hours with $FeSO_4$ as a catalyst.

It was thought of interest to investigate the optimum conditions of reduction of the Pakistani Barytes with carbon and compare with the similar work reported in the literature and also to compare the efficiency of the carbon-reduction with that of the Sui gas-reduction (loc. cit). The studies on barytes reduction by carbon were also prompted by the fact that the Sui gas is not at present available for the reduction in Hazara region, where chemical grade baryte deposits mainly occur.

Experimental

Materials.—Barytes ore from Kohala deposits (Hazara District) with $BaSO_4$ content 88-96 percent was used. The ore was purchased through M/S Zia Mining Corporation, Rawalpindi. The chemical analysis of the three samples of ore used are given in Table 1.

TABLE 1.—CHEMICAL ANALYSIS OF THE BARYTES ORE.

		Sample A %	Sample B %	Sample C %
$BaSO_4$	..	95.504	87.623	91.025
SiO_2	..	2.167	6.182	5.690
Fe_2O_3	..	0.663	1.515	0.556
CaO	..	—	1.528	1.091
MgO	..	0.234	0.857	0.386
$Al2O_3$	..	0.881	0.968	—
Ignition loss at 850°C.	..	0.516	2.141	0.334
Total	..	99.965	100.814	99.082
Solubility in water (at room temperature).	..	0.057	0.147	0.106
Specific gravity	..	4.44	4.10	4.23

Ordinary 'Kikar' charcoal having 5-7 percent ash content was used for reducing barytes.

Procedure

The reduction of barytes in the temperature range of 650 to 900°C. with 20 to 45 percent charcoal for the period of 1-4 hours was studied. 10 g. of 200 mesh ore mixed with the required amount of charcoal (200 mesh) was placed in a china crucible. The crucible and its contents were heated in a muffle furnace at the desired temperature for the fixed period. At each selected temperature and time six such charged crucible

were ignited. After ignition the crucible and its contents were cooled to room temperature and then leached with hot water at~90°C. The following chemical reactions occur during reduction and leaching:-

$$BaSO_4 + 4C = BaS + 4CO\uparrow$$
$$BaS + H_2O = \underline{\quad Ba(SH)(OH)}$$
$$\text{(Water soluble)}$$

The volume of the leached solution was made 500 ml. in each case. The amount of barium in the solution was determined volumetrically using excess of standard H_2SO_4 solution and back titrating the unreacted acid with a standard alkali solution. The volume of sulphuric acid used was corrected for the alkalinity present in the coal ash by doing the blank experiments and substracting the volume of the acid used for the coal ash from the total volume of the acid used for precipitation. The results were also confirmed by the standard gravimetric procedures. The volumetric method was preferred because of its rapidity and convenience. The results of reduction of barytes at various temperatures and with varying amount of charcoal at different periods are shown in Tables 2, 3 and 4.

Discussion

Fig. 1 shows the relationship between the percentage reduction of barytes and temperature. The reduction starts at about 650°C. and it reaches to maximum at temperatures 850-900°C., indicating the last two temperatures to be most suitable for the quantitative reduction of the barytes ore.

In Figs. 2 and 3 the percentage reduction at 850 and 900°C., respectively have been plotted against the percentage of carbon in order to establish the optimum ore: carbon ratio. The graph shows that 35-40 percent carbon gives the maximum reduction (90-97 percent). At 850°C.

TABLE 2.—PERCENTAGE REDUCTION OF BARYTES "A".

Temperature °C.	% C.	Time in Hours						
		1.0	1.50	2.0	2.5	3.0	3.5	4.0
		Percentage Reduction						
700	20	7.98	—	16.50	13.20	4.89	3.73	2.93
	25	9.75	—	26.83	16.50	14.05	5.44	3.64
	30	10.39	—	31.59	15.40	22.85	6.20	4.98
	35	10.91	—	30.55	24.44	29.70	6.91	5.81
	40	11.82	—	28.51	28.35	25.09	7.79	5.87
	45	9.78	—	25.60	24.32	22.49	6.84	7.09
750	20	23.46	36.36	32.00	25.54	22.34	—	19.92
	25	33.98	39.35	36.66	29.33	27.86	—	20.53
	30	35.44	35.75	37.89	28.72	26.52	—	18.94
	35	32.63	33.36	49.37	31.16	24.20	—	21.14
	40	36.66	45.69	52.06	31.90	28.48	—	19.80
	45	39.72	32.39	45.46	29.64	27.86	—	22.73
800	20	46.68	41.16	39.50	34.44	29.00	—	24.72
	25	46.44	43.36	41.17	36.65	30.45	—	26.56
	30	46.61	43.61	41.79	37.63	36.89	—	27.36
	35	42.78	57.30	55.45	40.86	38.23	—	30.68
	40	40.94	61.96	67.15	40.75	38.90	—	30.97
	45	37.82	58.18	55.96	39.97	37.02	—	30.12
850	20	73.60	67.83	58.41	41.24	28.43	—	21.32
	25	71.53	86.47	62.64	53.16	38.74	—	32.87
	30	78.53	80.56	87.69	83.71	58.86	—	53.48
	35	80.35	74.86	88.00	90.50	87.68	—	68.48
	40	80.35	75.16	88.30	89.10	93.76	—	83.78
	45	72.11	61.41	81.88	88.60	93.14	—	84.20

TABLE 3.—PERCENTAGE REDUCTION OF BARYTES "B".

Temperature in °C.	% C.	Time in Hours					
		1.0	1.5	2.0	2.5	3.0	4.0
		Percentage Reduction					
850	20	70.39	65.28	56.48	29.57	26.31	25.71
	25	74.59	76.79	69.26	45.95	36.51	33.43
	30	73.92	83.36	83.38	87.38	59.48	50.27
	35	71.66	84.65	87.98	**90.04**	85.13	71.95
	40	71.79	83.36	82.98	89.77	**94.30**	81.25
	45	68.86	82.85	81.92	88.31	93.70	82.99
900	20	70.73	50.08	39.96	24.57	9.72	6.72
	25	81.65	74.32	57.54	34.90	14.92	10.26
	30	87.24	87.23	77.39	49.15	23.65	20.79
	35	86.98	95.64	**96.91**	65.67	42.63	40.09
	40	82.25	**95.50**	94.04	90.77	68.46	54.88
	45	75.25	86.84	88.58	94.70	69.13	56.85

TABLE 4.—PERCENTAGE REDUCTION OF BARYTES "C".

Temperature °C.	% C.	Time in Hours					
		1.0	1.5	2.0	2.5	3.0	4.0
		Percentage Reduction					
850	20	68.34	59.88	28.86	21.16	11.16	7.68
	25	75.65	75.91	67.58	52.32	30.51	25.76
	30	77.52	78.86	78.99	64.88	56.93	46.42
	35	79.18	78.47	81.17	**89.76**	71.55	57.38
	40	79.37	77.16	84.63	87.71	**91.17**	79.92
	45	77.45	76.94	80.14	87.07	90.91	80.38
900	20	63.70	42.83	27.03	10.98	10.46	8.02
	25	74.32	56.04	48.82	34.46	23.78	14.25
	30	85.35	68.54	61.41	58.08	26.92	21.38
	35	92.16	92.18	**94.98**	58.99	39.24	30.68
	40	91.29	**93.95**	92.87	73.38	63.48	51.08
	45	90.10	89.88	91.70	94.78	88.89	62.77

the 35 percent proportion of carbon is preferable, firstly because the increase in reduction is only 4 percent with the addition of 5 percent carbon and increase of half an hour in the reduction time; secondly the excess of unreacted carbon lowers the quality of the "black ash" (barium sulphide). At 900°C. there is 1 to 3 percent decrease in the percent reduction of the barytes by increasing the percentage carbon from 35 to 40. This may be due to reoxidation of the sulphide to sulphate.

The third variable (time duration) has been plotted against percentage reduction of the barytes in Figs. 4 and 5. at 850 and 900°C. The graphs show that at 850°C. maximum reduction of 90 percent is obtained after 2.5 hours with 35 percent carbon. The use of 40 percent carbon at this temperature gives the maximum reduction of 94 percent in duration of 3 hours. At 900°C. the percent reduction is increased to 97 percent for the duration of 2.0 hours with 35 percent carbon.

With 40 percent carbon at 900°C. the maximum reduction is 95.5 percent for the duration of an hour and a half.

Conclusion

As a result of the present investigations it has been established that the optimum conditions of the reductions of the indigenous barytes to barium sulphide with charcoal are:-(i) 850°C. and 35 percent carbon which give 90 percent reduction

in the duration of two hours and a half, and (ii) 900°C., 35 percent carbon and duration of two hours which gives upto 97 percent reduction.

At 850°C. the use of 40 percent carbon gives a slightly increased percentage reduction but the quality of the product is poorer and moreover, it needs more time for completion of the reduction, which means greater consumption of the reducing agent and the fuel.

When compared to the reduction of indigenous barytes with Sui gas (loc. cit) which requirs 4 hours and gives a maximum reduction of 93 percent at
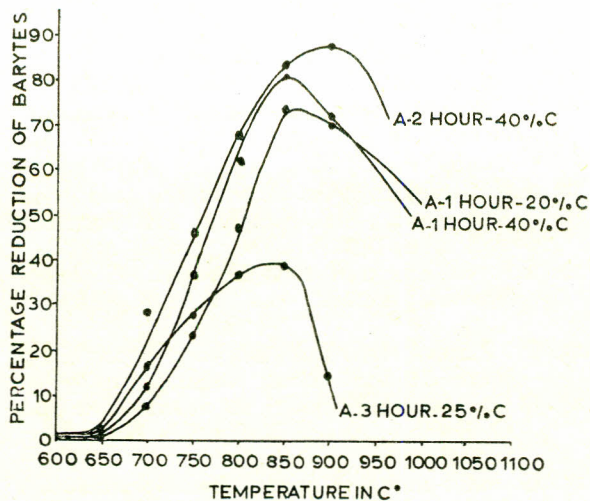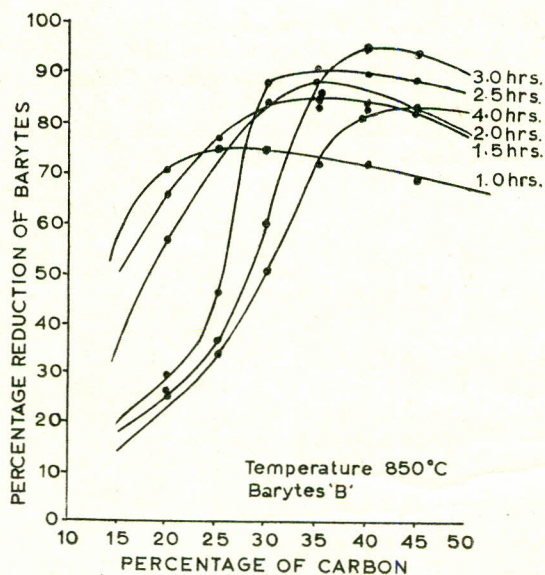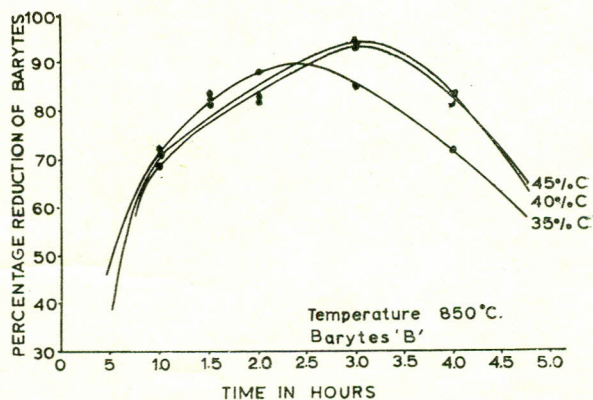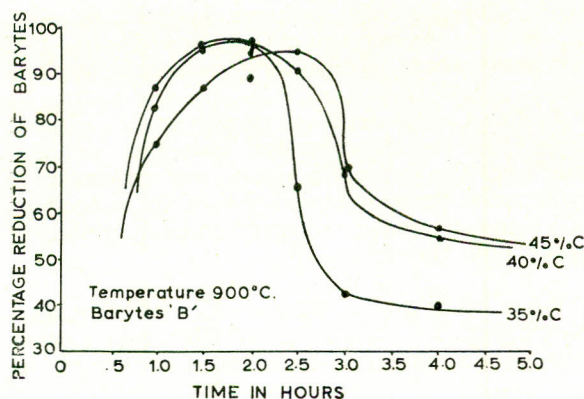
Fig. 1.
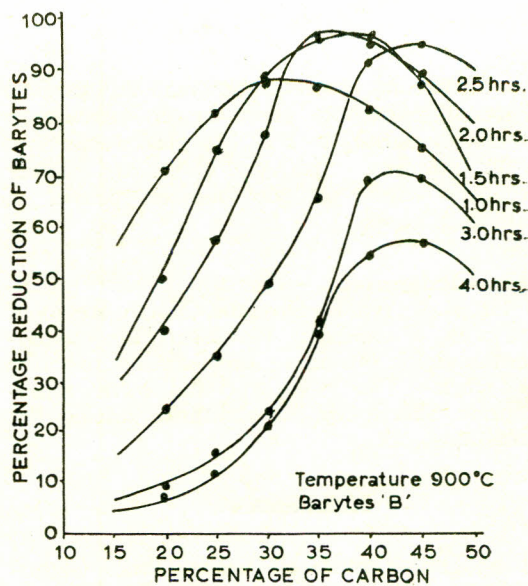
Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

950°C., the present studies show that the method of charcoal reduction gives better percentage conversion of $BaSO_4$ to BaS (94 percent at 850° and 97 percent at 900°C.) at lower temperatures and in the shorter period of time (2 to 3 hours).

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