STUDIES ON THE DESULPHURISATION OF BARIUM SULPHIDE WITH HEMATITE AND ACTIVATED IRON OXIDE

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(Received June 6, 1966; revised October 30, 1967)

The desulphurisation of BaS with iron oxide has been investigated. A maximum desulphurisation of 72% has been achieved in solution with activated iron oxide at 90°C in 30 min. The ratio of BaS to ferric oxide for this reaction has been found to be 1:5. Solid barium hydroxide of 95% purity is obtained by the fractional crystallisation of the desulphurised BaS solution at 0°C.

Attempts have been made for producing industrially important chemicals from the barytes occurring in West Pakistan. The barytes has been successfully reduced to barium sulphide by using Sui gas[1] and charcoal.[2] Ohshima *et al.*[3] have prepared barium hydroxide from barium sulphide using ferric oxide, obtained by the oxidation of iron pyrite.

The present investigation was undertaken to produce barium hydroxide by the desulphurisation of barium sulphide with indigenous hematite. Hematite is found in abundance in Kalabagh and Hazara districts.

Experimental

Materials.—The barytes of Kohala, District Hazara (91% barium sulphate) and the hematite of Langrial, District Hazara (76% Fe_2O_3) were used. The chemical analysis of these ores is given in Table 1.

Table 1.—Chemical Composition of Barytes and Hematite Ores.

	Barytes %	Hematite %
$BaSO_4$	91.03	—
Fe_2O_3	0.56	75.62
Al_2O_3	—	2.44
TiO_2	—	0.16
SiO_2	5.69	10.48
CaO	1.09	0.36
MgO	0.38	0.26
P_2O_5	—	traces
Loss on ignition	0.33	10.26

BaS (black ash) used for experiments was prepared by the reduction of barytes with charcoal.[2]

Activation of Hematite.—The natural hematite was not a good desulphurisation agent. The maximum desulphurisation was 7% (Table 4b). Hence the need for the activation of ore was realised and the activated iron oxide was prepared by the following methods.

(a) *Sodium Hydroxide Method.*[4]—Hematite was activated with 40% NaOH solution. The $Fe_2O_3.H_2O$ obtained was washed free from alkali and dried at 80°C.

(b) *Sodium Carbonate Method.*[4]—Hematite ore was fused with sodium carbonate in the ratio 1:1. The melt was kept at 850° for ½ hr. The resulting mass was extracted with water, filtered, washed and dried in air.

(c) *Yellow α-Fe_2O_3 by Balz Method.*[5]—The Balz method for the preparation of α-Fe_2O_3 from ferrous salts was modified. Hematite (100 g) was treated with 250 ml 1:1 HCl. The reaction mixture was heated on water bath to a small volume and then 250 ml 1:1 HCl was added. It was again heated to dryness on the water bath. The dry mass was dissolved in 250 ml hot water and filtered. It was further diluted to 1 l., heated on a hot plate and carbon dioxide-free air was bubbled through it for 2 hr. It was cooled and to it 3 l. 4% NaOH solution was added in small portions with constant stirring. The suspension was subjected to a brisk stirring for 2 hr and then filtered. The iron oxide obtained was again suspended in water and washed by decantation to remove excess chloride ions. The suspension was finally filtered, washed until free of chloride ions, drained and dried in air.

(d) *Ferric Oxide Hydrate by Oda Method.*[6]—Oda method was adopted and modified to get ferric oxide from hematite. Hematite (200 g) was treated with 250 ml 1:1 sulphuric acid on a hot plate for 2 hr, then cooled, diluted with 200 ml water and filtered. The filtrate was finally diluted to 4 l. Two litres of this stock solution was taken and to it 100 ml 1:1 NH_4OH was added. Through this suspension was passed CO_2-free air briskly for 4 hr. This aerated suspension of hydrated ferric oxide was then added to 1.25 l. of the remaining stock solution and the temperature raised

TABLE 2.—ABSORPTION OF SULPHIDE ION AND PERCENTAGE ACTIVATION OF THE OXIDES.

Oxide No.	Moisture %	Absorption of S″ ion from		% Activation of oxide for	
		BaS (moles/ mole of Fe_2O_3)	H_2S (moles/ mole of Fe_2O_3)	BaS	H_2S
O*	10.26	0.052	0.286	1.7	9.5
A	10.94	0.064	0.628	2.0	20.9
B	16.33	0.191	2.493	6.4	83.1
C	71.11	0.201	2.904	9.9	96.8
D	25.22	0.192	2.901	6.9	96.7

*Original hematite.

TABLE 3.—DESULPHURISATION OF BaS BY THE OXIDES.

Oxide No.	Wt. of oxide (g)	Conc of BaS soln %	Iodine soln used in ml*	Absorption ratio‡ [BaS]/ Fe_2O_3
O	2.0	3.34	0.45	0.05
A	2.0	3.34	0.55	0.07
B	2.0	3.34	1.64	0.20
C	2.0	3.34	1.73	0.21
D	2.0	3.34	1.65	0.20

*Weight of BaS absorbed per g. Fe_2O_3.
‡0.1N soln used (difference before and after desulphurisation) is against 10 ml BaS solution.

TABLE 4(a).—EFFECT OF BaS CONCENTRATION/ ON [BaS]/Fe_2O_3, ABSORPTION RATIO.

Oxide No.	Wt. of oxide (g)	Conc of BaS soln %	Iodine soln used in ml*	% age desulphurisation	Absorption ratio [BaS]/ Fe_2O_3
B	2.0	0.33	1.29	41.0	0.16
B	2.0	0.67	1.30	20.6	0.16
B	2.0	1.00	1.64	17.7	0.20
B	2.0	1.33	1.69	13.7	0.21
B	2.0	1.67	1.59	10.0	0.20
B	2.0	2.00	1.70	9.2	0.21
B	2.0	3.34	1.64	5.3	0.20
B	2.0	5.00	1.62	3.5	0.20
B	2.0	10.50	1.68	1.7	0.21

*0.1N soln used (difference before and after desulphurisation).

to 60°C. Then pH was adjusted to 5 and again air was blown for 6 hr. The suspension was then allowed to settle and the supernatant liquid was poured off. The residue was washed by decantation until it had only traces of SO_4'' ions. It was finally filtered off, washed free of sulphate ions and dried in the air.

Effect of Temperature on Desulphurisation.—As a result of preliminary investigations it was observed that the rate of reaction is slow up to 60°C and that the reaction took about 1 hr to complete. Between 80–90°C the reaction took about 20 min. This temperature range was beneficial also because the BaS and barium hydroxide were readily soluble under these conditions and have much low solubility at lower temperatures. Hence the desulphurisation studies in solution were carried out at 90°C and the reaction was allowed to proceed for 30 min to ensure completion.

Comparative Study of the Activity of Iron Oxides.—Various air-dried samples of the iron oxides prepared by different methods were studied for their activity by the following procedure.

Black ash (BaS) (10 g) was dissolved in 120 ml hot water (~90°C) and the solution filtered to remove any insoluble material. The filtrate was received in a 500-ml stoppered conical flask. A slurry of iron oxide, obtained by mixing 2 g iron oxide and 40 ml hot water, was added in small portions to the sulphide solution and the total volume of the solution was then made up to 200 ml. A blank was also prepared from the black ash without adding the iron oxide. The concentration of the BaS in 200 ml of the blank solution was taken as the original sulphide content 'before desulphurisation'. The sulphide content was determined by the standard iodometric method. The mixture of the BaS solution and iron oxide was shaken vigorously for ½ hr. The contents were filtered, washed and the volume of the filtrate made up to 250 ml in a volumetric flask. Aliquot portions of the solutions were analysed for the sulphide content iodometrically. The difference between the sulphide content of the blank and the filtrate was used to calculate the extent of desulphurisation. The reactions involved in the procedure are:

$$BaS + H_2O = Ba(SH)(OH)$$

$$3Ba(SH)(OH) + Fe_2O_3.H_2O = 3Ba(OH)_2 + Fe_2S_3.H_2O$$

The H_2S absorption capacity of the oxide was also determined by the method of Ali and Yunis[7] for comparison. The results are given in Tables 2 and 3.

Effect of BaS Concentration on the Activity of Iron Oxide.—The activities of the iron oxides were found to be very low towards BaS as compared to H_2S (Table 2) when the two reactants were mixed in the solution in the theoretical ratio, e.g. BaS/Fe_2O_3 3:1 mole ratio. The activity of iron oxide with different concentrations of barium sulphide was then studied in order to find an optimum ratio of the reactants which could give the maximum desulphurisation of the sulphide. The results are given in Table 4(a).

It is evident from this table that [BaS]: Fe_2O_3 ratio (absorption ratio) remains almost constant within the concentration range of 1 to 10.5%. At high concentrations there is an increase in the ratio from 0.2–0.92. But in concentrated solutions the un-reacted BaS crystallizes out with the slight lowering of temperature and its handling in filtration and washing becomes difficult. Hence BaS solutions of low concentrations were used for the desulphurisation studies. The effect of concentration of BaS on the activity of original hematite is shown in Table 4(b).

Maximum Desulphurisation of BaS.—The study of the maximum percentage conversion of BaS into $Ba(OH)_2$ in solution was studied in successive steps using aliquot amounts of iron oxide. The results are shown in Table 5(a). A maximum desulphurisation of 72% was achieved. The amount of iron oxide used depended upon the original amount of BaS present in the solution. The w/w ratio of BaS and Fe_2O_3 for maximum desulphurisation was found to be about 1/5. By adding 5 parts by weight of activated iron oxide to 1 part by weight of BaS in the solution and shaking for ½ hr gave maximum desulphurisation of 72% in one step. The maximum desulphurisation achieved with inactive hematite ore, when taken in the ratio hematite BaS 5:1 with different BaS concentration, is shown in Table 5(b).

Revivification of Spent Oxide.—The activity of the used iron oxide, after its revivification, was studied and it was observed that the oxide could be used over and over again for 10–15 times with almost the same activity as that of the fresh sample. The oxide became inactive when the sulphur content reached a maximum of 30–34%. The results are shown in Table 6.

Effect of Pressure on Desulphurisation of BaS.—The desulphurisation was studied at higher pressures in

TABLE 4(b).—EFFECT OF BaS CONCENTRATION ON ABSORPTION RATIO OF ORIGINAL HEMATITE.

Oxide g	Conc of BaS %	Total BaS in soln g	Iodine soln used in ml*	% De-sulphurisation	Absorption ratio
2.0	0.67	1.33	0.45	7.1	0.05
2.0	1.00	2.00	0.45	4.9	0.05
2.0	1.33	2.67	0.45	3.6	0.05
2.0	1.67	3.34	0.45	2.9	0.05
2.0	2.00	4.00	0.44	2.4	0.05
2.0	3.34	6.68	0.45	1.5	0.05
2.0	5.00	10.00	0.45	1.0	0.05
2.0	10.50	21.00	0.44	0.4	0.05

*0.1N iodine soln used (difference before and after desulphurisation).

TABLE 5(a).—MAXIMUM DESULPHURISATION OF BaS.

Oxide No.	Conc of BaS soln %	BaS in soln g.	Min. Amount of oxide used (g)	Oxide: BaS	% desulphurisation
B	0.67	0.67	4	6.0	69
B	2.00	2.00	10	5.0	72
B	3.33	3.33	16	4.8	72
B	4.00	4.00	20	5.0	72
C	0.67	0.67	3	4.5	72
C	2.00	3.33	10	5.0	72
C	3.33	3.33	15	4.5	72
C	4.00	4.00	18	4.5	72
D	0.67	0.67	4	6.0	72
D	2.00	2.00	10	5.0	72
D	3.33	3.33	16	4.8	72
D	4.00	4.00	18	4.5	72

TABLE 5(b).—DESULPHURISATION BY HEMATITE WHEN USED IN THE RATIO OF HEMATITE BaS 5:1

Conc of BaS soln %	Desulphurisation %
1.00	13.6
2.00	11.9
3·34	12.2
4·00	11.9
Mean	12.4

TABLE 6.—DESULPHURISATION BY THE REVIVIFIED OXIDE B, ABSORPTION RATIO $[BaS]/Fe_2O_3$ OF THE ORIGINAL SAMPLE 0.20.

Conc. BaS soln %	After revivifications										Mean
	1st		2nd		3rd		4th		5th		
	Iodine soln (ml)*	$\frac{[BaS]}{Fe_2O_3}$	Iodine soln (ml)*	$\frac{[BaS]}{Fe_2O_3}$	Iodine soln (ml)*	$\frac{[BaS]}{Fe_2O_3}$	Iodine soln (ml)*	$\frac{[BaS]}{Fe_2O_3}$	Iodine Iodine (ml)*	$\frac{[BaS]}{Fe_2O_3}$	$\frac{(BaS)}{Fe_2O_3}$
1.00	1.64	0.20	1.33	0.16	2.07	0.25	1.33	0.16	1.61	0.20	0.20
1.33	2.09	0.26	1.57	0.19	1.61	0.20	1.46	0.18	1.62	0.20	0.21
1.67	1.59	0.20	2.22	0.27	1.23	0.15	1.80	0.22	1.53	0.19	0.21
2.00	2.12	0.26	1.12	0.14	1.84	0.23	1.64	0.20	1.68	0.21	0.21

*0.1N iodine soln used (difference before and after desulphurisation).

TABLE 7.—EFFECT OF PRESSURE ON DESULPHURISATION OF BaS WITH OXIDE B.

Wt of oxide	Strength of BaS soln %	Total BaS in soln g	Pressure lb/in$_2$	Time (min)	Iodine soln (ml)*	[BaS] / Fe_2O_3
2.00	3.03	6.06	20	20	2.60	0.32
2.00	2.99	5.97	40	20	3.00	0.37
2.00	2.99	5.97	60	20	3.00	0.37
2.00	4.34	8.68	70	20	3.00	0.37
2.00	2.99	5.97	80	20	3.00	0.37
2.00	4.34	8.68	100	20	2.90	0.36
2.00	4.34	8.68	120	20	2.80	0.34
2.00	3.03	6.06	140	20	2.80	0.34

*0.1N iodine soln used (difference before and after desulphurisation).

TABLE 8.—PERCENTAGE PURITY OF $Ba(OH)_2$ AFTER CRYSTALLISATION.

Crystallisation	Total $Ba(OH)_2$ + BaS g	BaS	$Ba(OH)_2$	%BaS	% purity of $Ba(OH)_2$
Before crystallisation (in solution)	—	—	—	—	72.0
1st	3.26	0.60	2.66	18.38	81.6
2nd	3.25	0.57	2.68	17.49	82.5
3rd	3.08	0.26	2.82	8.53	91.5
4th	3.02	0.19	2.83	6.26	93.8
5th	2.92	0.15	2.77	5.23	94.8

the range of 20–140 lb/in^2 in an autoclave, specially designed for this purpose. It was observed that there is an increase in the activity of iron oxide in the pressure range of 40–80 lb/in^2. The activity is almost doubled at this pressure range but there is no effect of pressure on the maximum desulphurisation of BaS which remains 72% even at high pressure. The results are given in Table 7.

Desulphurisation Studies in Solid State at High Temperature.—The reaction between BaS and activated iron oxide was also studied in the solid phase in the temperature range of 200–800°C with a duration of 15 min to 3 hr. The activity of the oxide was in general reduced from 6.4% in the wet state to 3.0–0.2% in the dry phase. The activity decreased with rise of temperature and at 800°C it was negligible.

Preparation of Pure Barium Hydroxide.—With a maximum desulphurisation of 72% the resulting solution contained unreacted barium hydrosulphide in addition to barium hydroxide. Attempts were made to prepare pure barium hydroxide crystals by fractional crystallisation at 0°C. The results are shown in Table 8. The fifth crystallisation gave barium hydroxide of about 95% purity.

Discussion and Conclusion

The optimum conditions for the desulphurisation of BaS in solution were established as 90°C temperature and 30 min duration of reaction. The activated iron oxide were found to be much more active than the original hematite. The maximum desulphurisation with original hematite was 7.0%, while with the activated iron oxide it was 72%. The iron oxide activated by the Na_2CO_3 method is preferable because it is economical and easy to prepare although it is slightly less active than the oxideprepared by the Balz method. The activity of the iron oxide was found to be independent of the concentration of barium sulphide and a maximum desulphurisation of 72% could be achieved by taking BaS and iron oxide in the ratio of 1:5 by weight. The spent iron oxide can be revivified and re-used until it has reached a sulphur content of 30–34%. From this spent oxide sulphur can be extracted by the standard methods and the oxide can be re-used for desulphurisation.

Studies at high pressure reveal that there is no effect of pressure on the maximum desulphurisation of BaS in solution. In the dry state the reaction between BaS and iron oxide shows little progress and the activity of the iron oxide decreases with the increase in temperature, and at 800°C the oxide becomes inactive.

Barium hydroxide crystals of about 95% purity can be obtained from the solution by fractional crystallisation at 0°C.

Acknowledgement.—The authors are thankful to Dr. S.A. Warsi, Director, North Regional Laboratories, P.C.S.I.R., Peshawar, for his encouragement and advice throughout this investigation.

Thanks are also due to Mr. N.U. Khan, Senior Technician, for his help in designing and making of the autoclave.

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