STUDIES ON THE REDUCTION OF INDIGENOUS GYPSUM WITH CHARCOAL

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Reduction of Pakistani gypsum with carbon (wood charcoal) has been investigated at different temperatures and percentages of carbon by weight. The optimum conditions found for this reduction are 850–900°C, 20–25% carbon and 0.5–1.0 hr duration.

Extensive deposits of good quality gypsum occur in West Pakistan.[1] It is chiefly used in the cement industry and in the manufacture of ammonium sulphate at the Daudkhel Fertilizer Factory. In view of the shortage of natural deposits of elemental sulphur and sulphides in Pakistan it is imperative that attempts should be made to utilise this important economic mineral as a source of sulphur and sulphur compounds.

Calcium sulphide is an industrially important chemical, used in the production of sulphur by the Chance-Claus[2] process, in the treatment of waste liquor from paper mills,[3] as an insecticide and germicide, and as a depilatory in the leather industry. It is usually prepared by the reduction of gypsum with carbon[4–10] or reducing gases [11–15] Varying conditions of temperature and carbon–to–gypsum ratio have been reported in the literature for the reduction of gypsum with carbon. The percentage of carbon used for the reduction varies between 30–80% and the temperature variation reported are between 800–1100°C. This is mainly because these conditions vary from ore to ore depending upon the nature of the ore, impurities present in the ore, and the form of carbon used for the reduction. The present investigation was undertaken to investigate the optimum conditions of the reduction of the indigenous gypsum with charcoal with a view to develope a method for the production of calcium sulphide from the locally available raw materials.

Experimental

Materials.—The gypsum ore of Daudkhel was used. The chemical composition of these different samples used is given in Table 1.

Wood charcoal of the following composition was employed: carbon, 89.95%; ash, 5.14%; moisture, 4.90%.

Procedure.—Mixtures of gypsum (200 mesh) and charcoal (200 mesh) containing 15–30% of the latter by weight were prepared. Each mixture (10 g) was placed in a china crucible. Thus 15 crucibles were charged for each temperature study. The crucibles with contents were first heated to 250°C for 0.5 hr to expel most of the water in order to prevent the spurting at elevated temperatures. Then they were placed in a muffle furnace at the fixed temperature for a definite period. Three crucibles were withdrawn at intervals of 15 min. ½hr, 1hr, 1½hr and 2hr. The studies were undertaken at 700, 800, 850 and 900°C. Thus reduction of gypsum was investigated by taking samples in triplicate for every time interval at the fixed composition and temperature.

Table 1.

	Sample A %	Sample B %	Sample C %
Humidity at 50°C	0.05	0.18	0.23
$CaSO_4,2H_2O$	96.10	86.40	92.40
$CaCO_3$	3.10	5.02	0.99
$MgCO_3$	—	6.30	2.80
SiO_2	0.30	0.70	0.90
R_2O_3	0.30	1.29	2.62
Total	99.85	99.89	99.94

After ignition the crucibles were cooled in a desiccator and reweighed. The sulphide formed was determined iodometrically.[15]

The reduction of calcium sulphhate to calcium sulphide takes place through two different reactions as shown below:

$$CaSO_4+4C-CaS+4CO \quad (H-103.89) \qquad \text{I}$$
$$CaSO_4+2C-CaS+2CO_2 \quad (H-187.8) \qquad \text{II}$$

Reaction I is favoured by the excess of carbon while the second reaction predominates with low amount of carbon.

The calcium sulphide formed in the absence of carbon on prolonged heating may be reoxidized to calcium sulphate.

$$CaS+2O_2 \qquad CaSO_4$$

Results of the reduction studies of gypsum with varying amounts of charcoal at different temperatures are given in Tables 2,3, and 4.

TABLE 2.—PERCENTAGE REDUCTION OF GYPSUM, SAMPLE A.

Carbon (%)	Time (hr)	Conversion % at 800°C	850°C	900°C
	0.25	28.8	27.9	—
	0.50	51.1	56.1	78.2
15	1.00	64.5	67.2	76.2
	1.50	73.5	71.5	67.2
	2.00	56.4	53.5	56.0
	0.25	55.9	83.4	84.2
	0.50	85.2	92.9	94.9
20	1.00	95.1	97.0	91.3
	1.50	89.4	89.1	79.2
	2.00	81.2	79.3	66.1
	0.25	55.3	88.3	88.9
	0.50	81.1	94.4	98.1
25	1.00	96.4	98.6	93.9
	1.50	90.8	92.0	84.1
	2.00	85.1	83.7	72.2
	0.25	34.8	86.2	92.4
	0.50	56.0	89.5	94.2
30	1.00	87.6	92.8	91.2
	1.50	86.4	92.6	82.2
	2.00	77.7	86.0	68.1

TABLE 3.—REDUCTION OF GYPSUM, SAMPLE B.

Carbon (%)	Time (hr)	Conversion % at 850°C	900°C
	0.25	57.0	80.8
15	0.50	79.5	85.2
	1.00	74.5	75.8
	0.25	66.5	85.0
	0.50	84.4	91.2
20	1.00	82.8	86.0
	2.00	68.2	80.2
	0.25	69.6	86.6
	0.50	88.2	92.8
25	1.00	92.0	91.1
	2.00	90.6	88.0

TABLE 4.—REDUCTION OF GYPSUM, SAMPLE C.

Carbon (%)	Time (hr)	Conversion % at 850°C	900°C
	0.25	90.1	95.0
	0.50	93.8	96.1
20	1.00	95.3	96.2
	2.00	78.0	80.1
	0.25	93.2	95.6
	0.50	95.3	96.5
25	1.00	96.5	94.5
	2.00	88.5	86.6

TABLE 5.—REDUCTION OF GYPSUM USING LARGER QUANTITIES OF THE MIXTURE.

Mixture taken g	Reduction %
10	98.6
20	98.6
50	98.2
100	97.1

Discussion

The effect of percentage of charcoal on the reduction of gypsum (Sample A) to CaS at the temperatures of 800° and 850° and 900°C is shown in Table 2. At 700°C the reduction is very small even after heating for 3 hr.

At 800°C the percentage reduction of gypsum is 95.1% with 20% charcoal and 96.4% with 25% charcoal. At 850°C maximum reduction of 97.0% is achieved with 20% charcoal while it rises to 98.6% with 25% charcoal. The percentage reduction is 94.9% with 20% charcoal and 98.1% with 25% charcoal at 900°C.

The decrease in the percentage reduction beyond 25% charcoal might be due to the endothermic reaction:

$$CO_2 + C \longrightarrow CO \quad (H = +39 \text{ kcal})$$

This reaction predominates with a higher amount of carbon. This is borne out by the fact that with higher percentage of carbon on increasing the temperature the yield of the product increased, showing the supression of the endothermic reaction.

The time required for the maximum reduction of gypsum is 1 hr for 800°C and 850°C while it decreases to $\frac{1}{2}$ hr for 900°C.

The percentage reduction of gypsum increases upto 25% charcoal content but it decreases when more than 25% charcoal is used.

In ½ hr for 25% charcoal there is a continuous increase in percentage reduction with the rise in temperature from 800 to 900°C e.g. 81.1, 94.4 and 98.1% respectively. However, on increasing the time of reaction from ½ hr to 1 hr the percentage reduction decreases from 98.6 at 850°C to 93.9 at 900°C. The decrease in the percentage yield with increase of temperature and time may be due to the reoxidation of CaS to $CaSO_4$ which may be caused by the high rate of reaction at 900°C when the reaction reaches completion in ½ hr (98.1%).

The maximum reduction at 850°C is achieved in 1 hr. At 900°C the maximum reduction takes place in ½ hr due to increased rate of reaction at higher temperature.

The optimum conditions which could be fixed for the reduction of gypsum (containing 96.1% $CaSO_4$) to calcium sulphide are 20–25% charcoal, 850°C reaction temperature and 1 hr duration of reaction. The product obtained under these experimental conditions has a purity of 94.8%.

The results of the reduction samples B and C of gypsum, containing 86.4% and 92.4% $CaSO_4$, are given in Tables 3 and 4. For both these samples the optimum conditions for the maximum reduction could be set as 20% charcoal at 900°C in ½ hr. With the lower percentages of $CaSO_4$ in these samples, higher temperature is required for the reduction. The percentage of maximum reduction is also less in these two samples as compared to that of sample A. The initial rate of reaction in case of sample C is much higher which may be due to the catalytic effect of R_2O_3 which is present in greater quantity in this sample.

The results of the reduction of gypsum using larger quantities of the mixture at 850°C with 25% charcoal are shown in Table 5. There is no marked difference in the percentage yield while using the large-scale set up.

Conclusion

The optimum conditions of the reduction of the indigenous gypsum with carbon (wood charcoal) to produce calcium sulphide have been established. These are 850–900°C temperature, 20–25% carbon and 0.5–1.0 hr duration of reaction as against the reported value of 1000–1100°C, 40–50% carbon and duration of 1.5–2.0 hr/.[4–6]

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