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STUDIES ON THE REDUCTION OF GYPSUM TO CALCIUM SULPHIDE WITH MINERAL COAL AS THE REDUCTANT

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The optimum conditions for maximum reduction of gypsum ($CaSO_4.2H_2O$) by using mineral coal as reductant carbon source have been described. The particle size of 325 mesh of both gypsum and coal, the temperature of 850° and one hour heating time have been found to be the best conditions to achieve the maximum yield of calcium sulphide of 96.1 % purity. The process has been made economical by establishing conditions which allow the use of lowest carbon to gypsum ratio of 1:5.

INTRODUCTION

Pakistan inherits huge deposits of gypsum of reasonable good quality [1]. At present it is chiefly used in the cement industry and in the manufacture of ammonium sulphate of fertilizer grade. Gypsum has bright prospects in the production of a number of chemicals. Numerous methods [2–4] have been developed to produce sulphur, sulphuric acid and ammonium sulphate particularly in those countries where sulphur is not easily available. Two major units of U.S.A. have developed processes to get sulphur from gypsum [5]. The basic step of the above process is roasting of gypsum to calcium sulphide in the presence of carbonaceous matter i.e. coal, natural gas, carbon monoxide or hydrogen [6,7]. The calcium sulphide so obtained is further converted either into sulphur or sulphur compounds with calcium carbonate [8–11]. In view of the shortage of natural deposits of elemental sulphur and sulphides in Pakistan, it is imperative to develop techniques to utilise locally available gypsum and coal to produce chemicals of commercial importance and to establish optimum conditions for the reduction of gypsum to calcium sulphide.

MATERIALS

Gypsum. Gypsum of the Kohat variety was used throughout the present study. Its chemical composition is given in Table 1. Three different grades of gypsum were prepared by first grinding it to a fine powder in a pulveriser and then sieving it through 100, 240 and 325 mesh screens respectively. About 25 kg of each mesh size was collected for the studies.

Coal. Makerwal coal with a fixed carbon content of 40 %, was used for reduction studies. Analysis of this variety is given in Table 2. The coal was ground in a ball mill to a fine powder and graded to 100, 240 and 325 mesh sizes by the procedure similar to that used for gypsum.

Table 1. Chemical analysis of gypsum (%).

CaO	SO_3	Moisture	$CaCO_3$	SiO_2	R_2O_3
33.2	46.0	17.0	2.96	0.30	0.35

where R= Fe, Al, Mg, etc.

Table 2. Chemical composition of coal (%).

Moisture	Carbon	Volatile matters	Sulphur	Ash
7.6	40.00	30.00	7.4	15.00

EXPERIMENTAL

Reduction Studies. 500 g of powdered gypsum of each mesh size was mixed with 200 g coal powder of the same mesh size in a pestle and mortar. This mixture was then placed in a Groge crucible covered with lid and heated to 250° in an oven to drive out free and molecular water. The mixtures were then heated at 700, 750, 800, 850 and 900°. The samples were kept at each temperature for 30, 60, 90 and 120 min respectively, removed from the furnace and allowed to cool at room temperature. The calcium sulphide formed was determined iodimetrically [12].

RESULTS AND DISCUSSION

Effect of Particle Size. The reduction studies on gypsum (Table 3) have shown that the formation of the reduced product calcium sulphide is dependent upon the particle size of both gypsum and coal. The optimum conversion of gypsum into calcium sulphide takes place with 325 mesh size in one hour at 850°. 100 mesh size gypsum powder shows only 40.7 % conversion in 30 min heating period; this reaches the maximum value of 81.7 % in 90 min. Further heating up to 120 min caused decrease to 75.11 % value. Studies with 240 mesh size powder show 67.35 % conversion to calcium sulphide in 30 min which increases to 88.6 % in 60 min and finally to a value of 94.34 % in 90 min. In this case also heating up to 120 min caused decrease to 85.25 % value.

Studies with 325 mesh size show 82.11 % conversion into calcium sulphide in 30 min, increasing to 96.01 % in 60 min. In this case decrease in percentage conversion is apparent after 90 min heating period as compared to 120 min in case of 100 and 240 mesh studies. This decrease could be due to the exhaustion of carbonaceous matter which allows reoxidation of calcium sulphide to calcium sulphate.

$$CaS + 2O_2 \ldots\ldots\ldots CaSO_4$$

The results show that more or less the same yield of calcium sulphide (94.34 %) could be obtained with 240 mesh size gypsum powder by increasing the heating period from 60 to 90 min. It therefore seems to be more economical to use 325 mesh size which permits yield up to 82 % calcium sulphide even in 30 min heating period. Better yield of calcium sulphide obtained with 325 mesh size could be interpreted as due to the larger surface area offered by the ingredients for interaction.

Table 3. Effect of particle size of gypsum on the yeild of calcium sulphide at 850°.

Particle size (mesh)	Calcium sulphide (%)	Heating time (min)
100	40.73	30
240	67.35	30
325	82.11	30
100	60.62	60
240	84.12	60
325	96.01	60
100	81.78	90
240	94.34	90
325	73.29	90
100	75.11	120
240	85.25	120
325	57.27	120

Effect of Temperature. The effect of temperature on the rate of reduction was also examined using selected particle size of 325 mesh. The results in Table 4 indicate a marked improvement in the yield of the reduced mass as the temperature was raised from 700–850°. Temperatures lower than 800° do not yield good result even on prolonged heating. This is probably due to high activation energy required for the reduction of the sulphate of gypsum into the sulphide radical. The apparent activation energy for the reduction of gypsum with coal was computed from the value of rate constant by the use of Arrhenius equation. The apparent activation energy was calculated to be 57.28 kcal/mol. The reaction seems to be temperature dependent. The value of rate constant was calculated by the equation reported by Zhitkov *et al.* [13].

$$X = 1 - e^{-Kc^n}$$

Where X is the proportion of reduced calcium sulphate in time T.K. is the rate constant for the reaction, n is the order of reaction (first order) and c is the initial concentration.

Table 4. Effect of temperature on the reduction of gypsum during 60 min heating period.

Temperature (°C)	Calcium sulphide (%)
700	3.50
750	43.39
800	82.50
850	96.01
900	59.43

The reduction studies on gypsum have been carried out by Reddy [6] and All *et al.* [7]. In these studies, the reduction of gypsum was attempted with wood charcoal and animal charcoal which required the use of higher percentage of carbon due to low reduction value.

Moreover, the low bulk density of wood charcoal causes excessive losses of carbon during heating. The present work utilizes mineral coal which has the advantage of having fixed carbon with high reduction value. Mineral coal produced results as good as other sources of carbon

reported, but with the advantage that the gypsum to carbon ratio as low as 5:1 could be used which made the processes economical. The present studies reveal that the temperature of 850° and one hour heating period are the best conditions with mineral coal as the carbon source. The reaction takes place at lower temperature than that of 900–100° reported by Hull *et al.* [3] and Reddy *et al.* [6].

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