DESULPHURISATION OF CALCIUM SULPHIDE

A. Rauf, J.I. Bhatty, Fayyaz Mahmood and Arjamand Khan

PCSIR Laboratories, Peshawar

(Received October 23, 1973; revised June 24, 1974)

Abstract. The decomposition of calcium sulphide with steam has been studied for different temperatures with a view to develop a process for the recovery of sulphur. The effect of varying particle size, reaction period, temperature and steam flow has been investigated. The maximum total recovery of sulphur as H_2S by steam was about 60%.

Pakistan depends entirely on imports for her requirements of sulphur due to the lack of indigenous resources of sulphur. Gypsum is one of the major sulphur bearing mineral occuring in abundance at various localities in Pakistan.[1]

Gypsum has been used as the raw material for H_2SO_4 in many of the European countries by sulphuric acid cement process.[2] In Pakistan the feasibility for the process has not been worked out as yet although the Clause process for the recovery of sulphur as adopted in Germany during the first world war has been reported.[3,4]

A process[5] for the reduction of Gypsum to CaS has already been developed. The CaS thus produced presented a lot of interest to undertake the studies so as to establish a method for its commercial exploitation for the production of S, possibily with steam or other gases.

In view of the fact that a very little attention has been paid on the winning of S from CaS, the present investigation deals with the reaction of steam with CaS by using analytically pure CaS.

Experimental

Experimental procedure consisted in heating 2 g pure CaS at the desired reaction temperature in a leak-proof atmosphere of steam. Flow of steam could be controlled by an attachment adjusted with the steam producer. Steam supply was cut off after it had passed for a definite period of reaction. The product gases were passed through a condenser to condense the hot vapours and then finally through an absorber containing aqueous normal NaOH solution. The solid product left, was analysed for compounds of Ca by chemical method and for residual sulphur by combustion method.[6] Hydrogen sulphide and SO_2 were estimated iodometrically.

Results and Discussion

To study the effect of particle size of CaS on conversion to H_2S in the steam, five different sizes (−5+22, −22+72, −72+120, −120+170 and −170+200) ASTM mesh, were used. It is seen from Table 1 that variation in the percentage of total sulphur elimination as H_2S is not much though the particle size was widely different; the conversion was independent of particle size above 120 mesh (Fig.1).

Hence in all the subsequent runs this particle size was used. The effect of temperature, time and steam flow is evident from the results presented in Tables 2 and 3. The influence of temperature is more pronounced at 1100–1150°C where most of the H_2S is obtained and maximum of the total S was eliminated within 40 min of reaction period. CaS–steam reaction may be stated as follows:

$$CaS + H_2O \longrightarrow CaO + H_2S$$

TABLE 1
(Time 30 min; temp. 1100°C).

Particle size (mesh)	weight of the sample (g)	Amount of S as H_2S evolved (%)
− 5+ 22	0.6831	29.00
− 22+ 72	0.4510	31.04
− 72+120	0.4567	32.21
−120+170	0.5013	35.71
−170+200	0.5944	36.21

TABLE 2
(Weight of the sample, 2/g; temp, 1150°C; time, 10 min.)

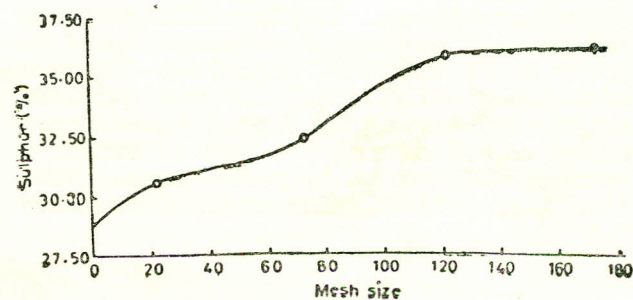| Rate of steam (g/min)	Difference in wt (g)	% S as H_2S
0.01153	0.2004	17.50
0.02306	0.3606	43.75
0.03473	0.1926	31.50
0.04612	0.1623	20.50

Fig. 1. Effect of particle size on the liberation of sulphur (Temp. 1100°C; Time 30 min).

TABLE 3

(Weight of sample 2 g; steam flow 0.02306 g/min; particle size 120 mesh.)

Time (min)	Difference in wt (g)	% S as H_2S
Temperature 900°C		
5	—0.0903	0.57
15	—0.0949	1.03
20	—0.1903	2.44
30	—0.0073	3.63
40	—0.0321	4.90
Temperature 1000°C		
10	—0.0397	2.95
20	—0.0393	6.63
30	—0.0469	11.04
40	—0.0215	21.20
50	—0.0703	23.82
Temperature 1100°C		
7	—0.0207	14.16
20	+0.2139	36.10
30	+0.6290	44.80
40	+0.5748	50.20
50	+0.5661	51.00
Temperature 1150°C		
15	+0.7276	40.40
30	+0.7476	54.20
45	+0.7832	60.20
60	+0.7771	59.20

Fig. 2. Effect of steam flow rate on the liberation of sulphur. (Temp. 1150°C; time 10 min; size 120 mesh).

The results given in Table 2 reveal that the maximum recovery of S in the form of H_2S from CaS is feasible only at a steam flow of 0.02306 g/min. The reason for this is perhaps the easy release of S and other gaseous products from CaS from the reaction zone. The effect of reaction period on particle size distribution at 1100–1150°C is shown in Table 3. It is observed that the conversion reaches 54.00 and 60.20% in 30 and 45 min respectively at 1150°C and a flow rate of 0.02306 g/min. In the beginning the conversion is very sharp but above the time period of 40 min the conversion becomes almost steady. Moreover, trend of two graphs drawn at adjacent temperatures shows slight difference. They have a little percentage variation in the maximum as compared to that of the graphs at 900 and 1000°C respectively. The mode of conversion of CaS to H_2S thus more specifically can be judged from the Fig. 2 which relates the percentage of H_2S conversion vs temp. of reaction at optimum conditions. A temperature range of 1000–1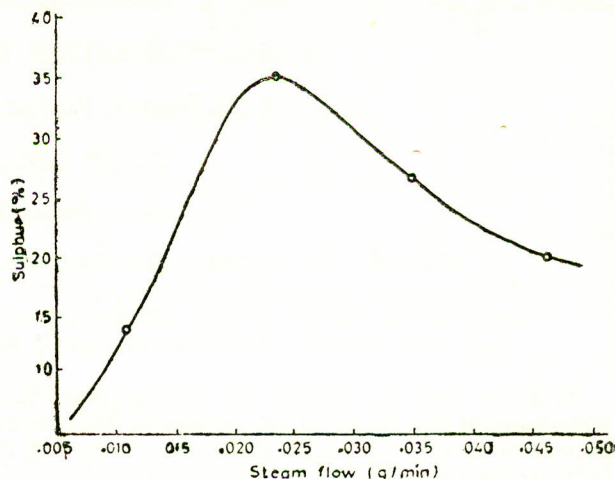100°C seems to be of significance which shows a sharp uplift in the conversion. Beyond this the conversion seems steady. Notable amount of SO_2 is also confirmed in the product gases.

The SO_2 so produced, partially reacts with the H_2S resulting in the formation of elemental sulphur.

$$2 H_2S + SO_2 \longrightarrow 2H_2O + 3S.$$

Sulphur vapours are so meager in amount that they stick inside the extended end of the tube, thus making it impossible to estimate it analytically.

Dejahn reported that in the steam–sulphide reactions[7] only labile sulphur, i.e. 50% of the total sulphur present in sulphides, was distilled off as H_2S and SO_2. But we got the conversion mainly in the form of H_2S (60%) alongwith SO_2. In exceptional cases sulphur was found to be in traces in the remaining products.

References

1. *Directory of Mineral Deposits of Pakistan* (Geological Survey of Pakistan, 1969).
2. S.N. Ganz, Zh. Prikl. Khim., **26,** 464 (1953); Chem. Abstr., **48,** 3646D (1954).
3. E. Terres, Z. Angew. Chem., **44,** 356 (1931), Chem. Abstr., **25,** 4362 (1931).
4. *Thorpes Dictionary of Applied Chemistry* (Longman Green, 1956), p. 424.
5. S.M. Ali, Izharul Haque and Bashir Ahmad, Pakistan J. Sci. Ind. Res., **11,** 172 (1968).
6. W.W. Scotts, *Standard Methods of Chemical Analysis* (Van Nostrand, Princeton, 1939), fifth edition, vol. 1, p.915.
7. F.W De. Jahn, Canadian Patent No. 581,565 (18 Aug. 1959), Chem. Abstr., **54** 1232 (1960(.