

KINETIC STUDY OF NON-OXIDATIVE DISSOLUTION OF CALCIUM SULPHIDE FROM GYPSUM IN AQUEOUS ACID SOLUTION

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This study presents the results obtained from the kinetic study of non-oxidative dissolution of calcium sulphide in aqueous hydrochloric acid for the generation of hydrogen sulphide gas. It was found that dissolution rates were controlled by a chemical reaction on the surface of calcium sulphide. The temperature of 80° or higher and stirring speed above 700 rpm were found to be the optimum conditions for the generation of total H₂S gas from the reduced mass of gypsum containing 93.99 % of calcium sulphide. Reaction kinetics reveal that the type of reaction between calcium sulphide and hydrochloric acid is first order with respect to hydrogen ion activity. Activation energy of the reaction was 7.44 Kcal/mol.

Key words: Kinetics of calcium sulphide; Gypsum.

INTRODUCTION

Gypsum is one of the most abundant minerals available in Pakistan [1]. At present it is chiefly used in the cement industry, as fertilizer and in the manufacture of plaster of Paris. 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 countries where sulphur is not easily available. The US Bureau of Mines has 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, e.g. coal, natural gas, or carbon monoxide [6-7]. The calcium sulphide so obtained is further converted either into sulphur or sulphur compounds and sodium carbonate. In view of the shortage of natural deposits of elemental sulphur in Pakistan, it is imperative to develop techniques to utilize locally available gypsum and coal to produce chemicals of commercial importance and to establish optimum conditions for the reduction of gypsum to calcium sulphide and its subsequent conversion to sulphur. The objective is to work out optimum conditions to get maximum yield of sulphur and regulate other influencing factors to divert the direction of the reaction towards sulphur production.

MATERIALS

Calcium sulphide of the following composition was used throughout the present studies. It was obtained from

gypsum by a reduction method already described in our previous paper [7].

Table 1. Chemical analysis of calcium sulphide (%)

Ca	S	CaCO ₃	SiO ₂	C	R ₂ O ₃
52.22	41.77	2.96	0.30	2.39	0.36

where R = Fe, Al, Mg, etc.

Calcium sulphide was first ground into a fine powder and sieved through 100, 240 and 325 mesh sieves respectively. Deoxygenation of the acid solution and purging of the reactor was achieved by passing nitrogen gas.

EXPERIMENTAL

A flask (500 cm³) with a lid having four necks was used as the reaction vessel for all experiments. The central hole of the lid was used for the fixation of a condenser and the evolved hydrogen sulphide gas collected through the other end of condenser to the absorbing flask. The other three necks were used for the introduction of nitrogen gas, thermometer and the addition of the sample. A temperature-controlled water bath was used as a thermostat ($\pm 0.05^\circ$) as shown in Fig 1. Each dissolution medium was deoxygenated with nitrogen gas for 30 min. before each experimental study. 1 ± 0.05 g of calcium sulphide sample was added into the dissolution medium which was stirred with a magnetic stirrer. Nitrogen gas was bubbled into the dissolution medium through each run. The apparent linear

dissolution rate V_{Lin} ($\mu\text{m min}^{-1}$) was followed by the analysis of hydrogen sulphide [8] gas absorbed in a ($\text{NaOH} + \text{H}_2\text{O}_2 + \text{MoO}_3$) solution and calculated, using the following equation [9] which assumes the mono-dispersed shrinking particle system.

$$1-(1-X)^{1/3} = \frac{2V_{Lin}}{D_o} \times t$$

where X = fraction dissolved
 D_o = initial diameter diameter ($40.5 \mu\text{m}$)
 t = time (min.)

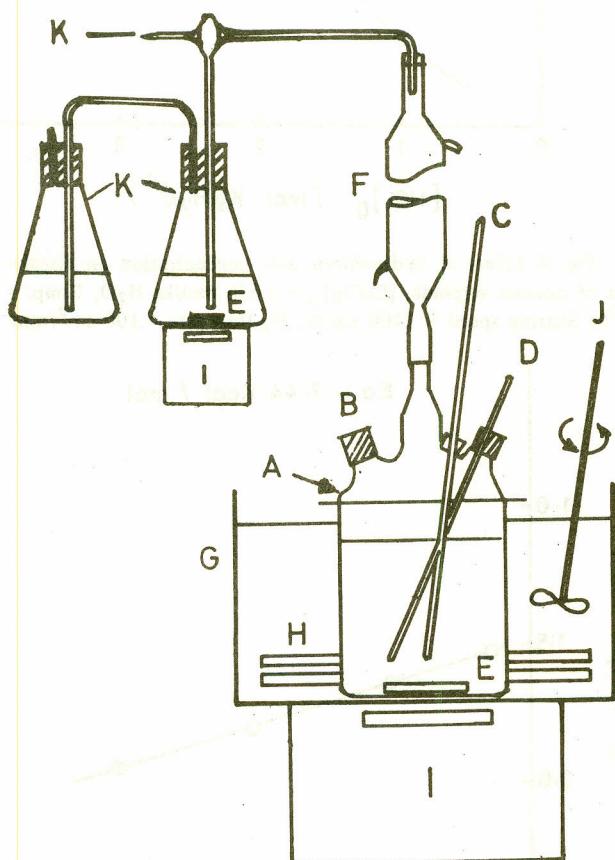


Fig. 1. Experimental apparatus. (A. Reaction flask (500 cm^3 Inner dia. 85 mm). B. Sample feed & sampling hole; C. Thermometer; D. Bubbling tube; E. Stirrer. F. Condenser; G. Water bath. H. Heater; I. Magnetic stirrer; J. Bath agitator; K. Absorption bottle).

RESULTS AND DISCUSSION

Effect of N_2 -flow rate. In order to study the effect of nitrogen flow rate on the dissolution of calcium sulphide, the system was examined at nitrogen flow rate of 100 and $1000 \text{ cm}^2/\text{min}$. The other variables such as temperature and calcium chloride concentration were kept constant. The

results are shown in Fig. 2 and Table 2. It can be seen that the dissolution rate was not effected by nitrogen flow rate.

Effect of stirring speed. In order to examine the effect of stirring speed, experiments at different stirring speeds were performed. The results are shown in Fig. 3 and Table 3. Linear dissolution rates corresponding to the slope in Fig. 2 at the stirring speed of 700 and 1100 rpm were independent of the stirring speed and slightly higher than that at 500 rpm. This independent behaviour of the dissolution rate from stirring speed seems to suggest that diffusion process is not a rate controlled step.

Effect of hydrochloric acid concentration. The dissolution rate of calcium sulphide was examined at different concentrations of hydrochloric acid at 80°C and at a constant stirring speed of 1100 rpm. The results are shown in Figure 4 and Table 4. The dissolution rate increased with increasing hydrochloric acid concentration in which the rate was accelerated slightly with increasing acid concentration. A similar tendency in the dissolution rate of Sphalerite was also reported by Majima and Awakura [10].

Effect of temperature. Effect of temperature was examined at values ranging from 50°C to 80°C (Table 5). The solution of hydrochloric acid contained 0.026 G mol .

Table 2. Effect of nitrogen flow rate on dissolution of calcium sulphide at $[\text{CaCl}_2]_0$ $0.026 \text{ mol kg H}_2\text{O}^{-1}$ $[\text{HCl}]_0$ $1 \text{ mol kg H}_2\text{O}^{-1}$ temp. 80° and stirring speed 1100 rpm.

Nitrogen ($\text{cm}^3 \text{ min}^{-1}$)	Time (min.)	Hydrogen sulphide (mol %)
100	2	0.034
100	4	0.041
100	6	0.073
100	10	0.163
100	20	0.310
100	30	0.440
100	40	0.500
100	50	0.545
100	60	0.620
1000	2	0.033
1000	4	0.043
1000	6	0.081
1000	10	0.162
1000	20	0.300
1000	30	0.440
1000	40	0.500
1000	50	0.545
1000	60	0.620

calcium chloride kg H_2O^{-1} . The logarithm of the linear dissolution rate obtained from experimental results was plotted against $1/T$ Figure 5. A linear relationship was observed over the entire temperature range studied. The activation energy obtained from the Arrhenius plot was about 7.44 Kcal/mol.

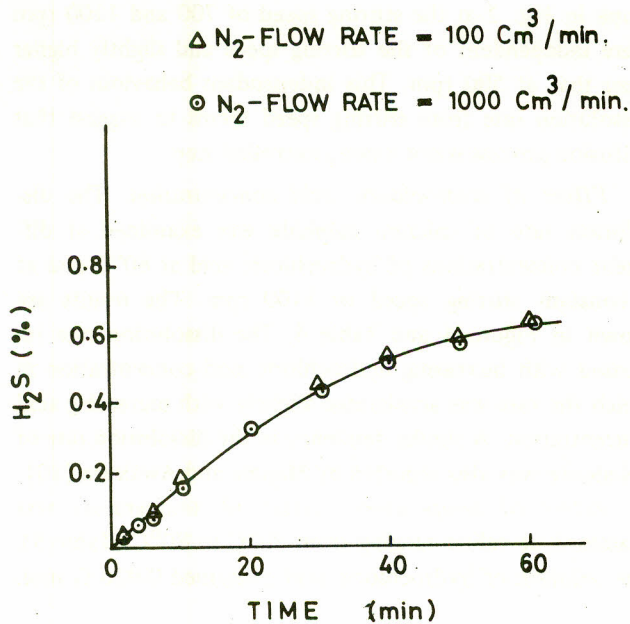


Fig. 2. Effect of N_2 -flow rate on dissolution of calcium sulphide. $[\text{HCl}]_0 = 1 \text{ mol/kg H}_2\text{O}$; $[\text{CaCl}_2]_0 = 0.026 \text{ mol/kg H}_2\text{O}$; Stirring speed = 1100 r.p.m.

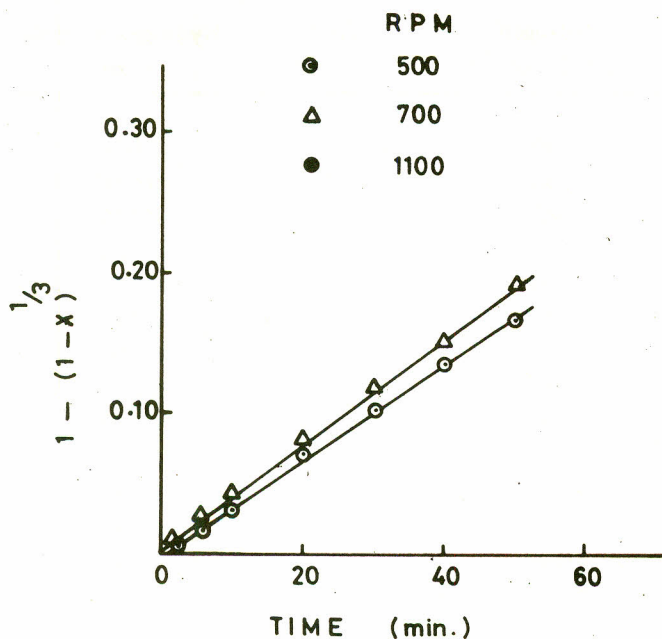


Fig. 3. Effect of stirring speed on dissolution of calcium sulphide. $[\text{HCl}]_0 = 1 \text{ mol/kg H}_2\text{O}$; $[\text{CaCl}_2]_0 = 0.026 \text{ mol/kg H}_2\text{O}$; Temp. = 80°C ; N_2 -flow rate = $100 \text{ cm}^3/\text{min}$.

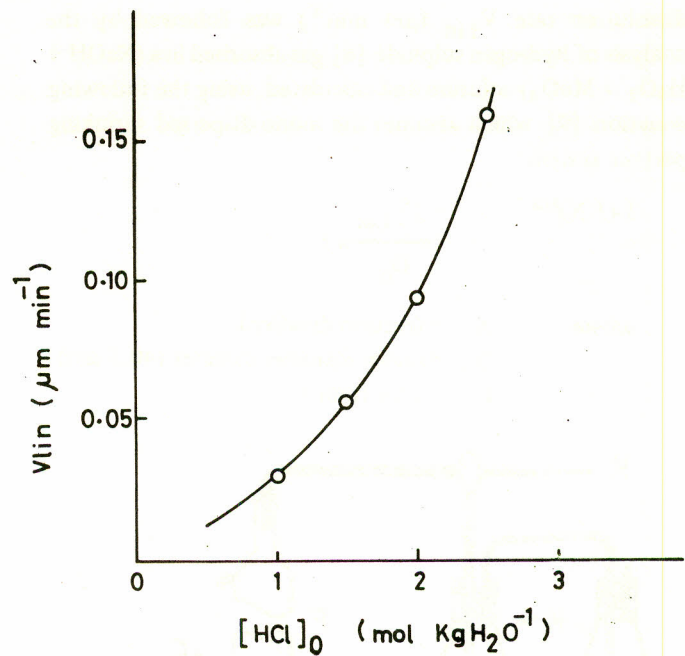


Fig. 4. Effect of hydrochloric acid concentration on dissolution of calcium sulphide. $[\text{CaCl}_2]_0 = 0.026 \text{ mol/kg H}_2\text{O}$; Temp. = 80°C ; Stirring speed = 1100 r.p.m.; N_2 -flow rate = $100 \text{ cm}^3/\text{min}$.

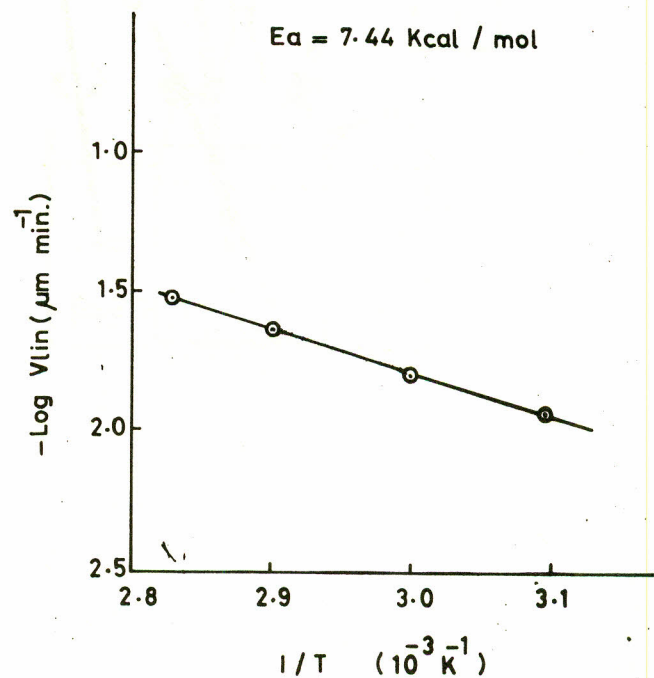


Fig. 5. Arrhenius plot for non oxidative dissolution of calcium sulphide. $[\text{HCl}]_0 = 1 \text{ mol/kg H}_2\text{O}$; $[\text{CaCl}_2]_0 = 0.026 \text{ mol/kg H}_2\text{O}$; Stirring speed = 1100 r.p.m.; N_2 -flow rate = $100 \text{ cm}^3/\text{min}$.

DISCUSSION

The facts obtained from the experimental results were as described below.

Table 3. Effect of stirring speed on dissolution of calcium sulphide at $[\text{CaCl}_2]_0$ 0.026 mol kg H_2O^{-1} , $[\text{HCl}]_0$ 1 mol kg H_2O^{-1} temp. 80° and N_2 -flow rate $100 \text{ cm}^3 \text{ min}^{-1}$.

Stirring speed (rpm)	Time (min.)	$1-(1-X)^{1/3}$
500	2	0.005
500	6	0.015
500	10	0.030
500	20	0.070
500	30	0.100
500	40	0.132
500	50	0.165
700	2	0.010
700	6	0.020
700	10	0.040
700	20	0.080
700	30	0.115
700	40	0.150
700	50	0.190
1100	2	0.010
1110	6	0.020
1100	10	0.040
1100	20	0.080
1100	30	0.115
1100	50	0.190

Table 4. Effect of hydrochloric acid concentration on dissolution of calcium sulphide at $[\text{CaCl}_2]_0$ 0.026 mol kg H_2O^{-1} , temp. 80° , stirring speed 1100 rpm and N_2 -flow rate $100 \text{ cm}^3 \text{ min}^{-1}$.

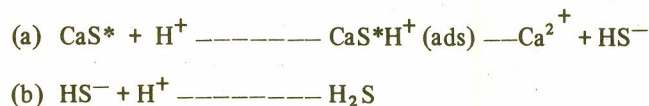
HCl mol kg H_2O^{-1}	$V_{\text{lin}} (\mu\text{m min}^{-1})$
1	0.030
1.5	0.055
2	0.095
2.5	0.160

The reaction rate was independent of the nitrogen flow rate and stirring speed above 700 rpm. Under vigorous stirring speed of 1100 rpm, the higher value of 7.44 Kcal/mol was obtained for activation energy. From these facts, it appears that the dissolution of calcium sulphide in this study is not controlled by diffusion in liquid phase. In contrast, the dissolution rate seems to be directly propor-

Table 5. Effect of temperature on dissolution of calcium sulphide at $[\text{CaCl}_2]_0$ 0.026 mol kg H_2O^{-1} $[\text{HCl}]_0$ 1 mol kg H_2O^{-1} , stirring speed 1100 rpm and N_2 -flow rate $100 \text{ cm}^3 \text{ min}^{-1}$.

Temperature ($^\circ\text{C}$)	$1/T \cdot 10^3 \text{ K}^{-1}$	$V_{\text{lin}} (\mu\text{m min}^{-1})$	$-\text{Log } V_{\text{lin}} (\mu\text{m min}^{-1})$
50	3.095	0.0115	1.9393
60	3.003	0.0160	1.7958
70	2.915	0.0237	1.6252
80	2.832	0.0300	1.5230

tional to the hydrogen ion activity. This system was also studied by Majima and Awakura [10] for the non-oxidative dissolution of sphalerite. They observed that the dissolution rate of sphalerite is proportional to the activity of hydrogen ion as determined by e.m.f. method at 25° . Acid concentration vs dissolution rate plot in our studies are similar to that of Majima and Awakura [10]. Therefore, with the analogy to their system, it appears that the rate controlling process in these studies postulates the adsorption of hydrogen ion onto solid surface. Hence, the reaction mechanism for the dissolution of calcium sulphide in hydrochloric acid could be as follows :



$\text{CaS}^* \text{H}^+ (\text{ads})$ designates the electrostatically charged surface of calcium sulphide with H^+ adsorbed. Step(a) is a rate controlling process. From these studies we can conclude that the temperature of 80° or higher and stirring speed above 700 rpm are the optimum conditions for the generation H_2S gas from the reduced mass of gypsum containing 93.99 % calcium sulphide. This information is of great value for designing a manufacturing plant of sulphur from gypsum.

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