Kinetics of Cobalt Sulfide Reduction in the Presence of Calcium Oxide

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Kinetic measurements have been made on the hydrogen reduction of solid cobalt sulfide in the presence of calcium oxide. The cobalt metal yield was compared with that of the direct reduction reaction over the temperature range 600 to 800°C at various hydrogen flow rates, and calcium oxide to cobalt sulfide mixing ratios. It was found that the presence of calcium oxide caused a sharp increase in the reaction rate—for example a 15 fold increase in conversion was achieved at 700°C after 24 min of reaction. Low hydrogen flow rates were found to be desirable, and an optimum mixing ratio of 3.0 established.

THE direct reduction of metal sulfides to metal is industrially very attractive, but difficult to carry out because of unfavorable thermodynamics. The rate of reduction can be improved, however, since previous studies have shown that the yield of metal will be increased if the hydrogen sulfide evolved is continuously removed from the vicinity of the reacting mass. Alternatively, a chemical means of scavenging the hydrogen sulfide may be considered. In this case, for the direct reduction of sulfide to metal, the sulfur present is obtained in solid form, alleviating many of the pollution problems associated with gaseous sulfur compounds.

Rosenqvist[1] studied the absorbing power of calcium oxide for hydrogen sulfide. The thermodynamics of this reaction provide evidence of a high potential for calcium oxide to be used as a scavenging agent for hydrogen sulfide. Cech and Tiemann[2] took advantage of this fact and prepared metal fibers by hydrogen reduction of molten sulfides in the presence of calcium oxide. Barker[3] reduced pyrites and Kay[4] reduced molybdenite, in the presence of calcium oxide, to obtain the respective metals. More recently, Habashi and Dugdale[5] reported on the hydrogen reduction of chalcopyrite in the presence of calcium oxide.

THERMODYNAMIC CONSIDERATIONS

In the present work, the consecutive reaction

$$\tfrac{1}{8}Co_9S_8 + H_2 \rightleftharpoons \tfrac{9}{8}Co + H_2S \qquad [A]$$

$$CaO + H_2S \rightarrow CaS + H_2O \qquad [B]$$

was studied, to give overall

$$\tfrac{1}{8}Co_9S_8 + CaO + H_2 \rightarrow \tfrac{9}{8}Co + CaS + H_2O \qquad [C]$$

The thermodynamics of hydrogen reduction of metal sulfides are very unfavorable. For reaction [A] the equilibrium constant

$$K_A = \frac{p_{H_2S}}{p_{H_2}}$$

at 900 K is 2.2×10^{-3}, and this would give a low equilibrium conversion of cobalt. To shift the equilibrium to the right, H_2S has to be removed continuously from the vicinity of the sulfide. This is where reaction [B] plays an important role, in scavenging the H_2S formed. At 900 K the equilibrium constant of reaction [B]

$$K_B = \frac{p_{H_2O}}{p_{H_2S}}$$

is 4.08×10^3, which shows a strong tendency to replace H_2S by H_2O.

The equilibrium constant for the overall reaction [C] is the product of K_A and K_B

$$K_C = \frac{p_{H_2O}}{p_{H_2}} = K_A \cdot K_B,$$

which has a value of 8.98 at 900 K. Comparison of K_A and K_C shows a great improvement in the reduction thermodynamics of cobalt sulfide by hydrogen. Table I gives numerical values of the different equilibrium constants as a function of temperature.

The freshly reduced metal will be in contact with hydrogen having a high moisture content, and therefore a high oxidizing potential. If the moisture content, expressed as p_{H_2O}/p_{H_2} exceeds that which will oxidize the metal, then the reaction sequence depicted here would not occur, and metal sulfide would be converted directly to oxide. By checking the equilibrium constant for cobalt oxide formation with that for reation [C], it is clear that oxide formation is not possible under these conditions.[6]

Experiments were carried out on reaction [C], in powder form, over the temperature range 600 to 800°C, in order to examine the effect of gas flow rate and CaO/Co_9S_8 mixing ratio on the yield of metal.

Table I. Values of Equilibrium Constants

T(K)	K_A	K_B	K_C
800	5.2×10^{-4}	1.2×10^{4}	6.33
900	2.2×10^{-3}	4.08×10^{3}	8.98
1000	6.65×10^{-3}	1.7×10^{3}	11.31
1100	1.33×10^{-2}	8.31×10^{2}	11.05

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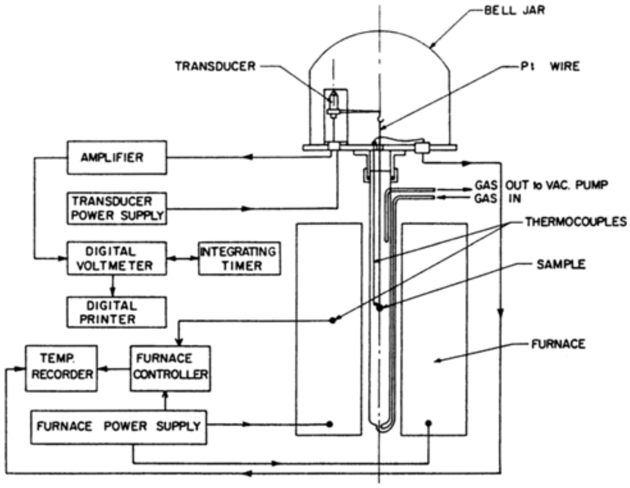

Fig. 1—Schematic diagram of apparatus.

EXPERIMENTAL

(a) Apparatus

The conversion-time data were obtained using a thermogravimetric technique. The schematic diagram of the apparatus is given in Fig. 1. The basic weighing unit was a transducer cell, supplied by the Statham Co., California (model #UC3). The top part of the apparatus consisted of a 1/2 in. thick brass flange, through which the main accessories were connected. The electrical connections were sealed to this flange via two vacuum seal connectors, which carried the output voltages of the transducer and the thermocouples respectively. The reactor chamber was a 1.5 in. inside diameter × 33 in. long quartz tube, packed at the bottom with ceramic Raschig rings, for even heating of the inlet gases. The upper end of the reactor tube was connected to the top flange by a water-cooled brass tube and sealed by an O-ring connector. The gas and powder temperatures were measured by chromel/alumel thermocouples (contained in 1/16 in. outside diameter stainless steel sheaths). Powder temperature measurements were only possible when the weight change was not being followed. A split-type vertical furnace was used. The furnace provided a uniform temperature zone of 6 in. at the center, where temperatures could be controlled to within ±3°C, and the solid samples were therefore placed in that zone.

To minimize the effect of external mechanical vibrations, the whole apparatus was mounted on a heavy iron frame with a concrete base. Ultra high purity hydrogen, helium and argon were used in this work. Each gas emerging from the cylinder was metered by Matheson flowmeters, which were calibrated over a wide range of flow rates. After passing through individual constant flow controllers, gases were fed in at the bottom of the reactor.

(b) Materials Used

Pure calcium oxide was supplied by Baker Chemical Co., the surface area as determined by the Ontario Research Foundation being 2.26×10^4 g/cm^2.

Cobalt sulfide was prepared by reacting sulfur with pure metal powder as follows. Fine powders of sublimed sulfur and high purity cobalt metal were mixed intimately in the molar stoichiometric ratio corresponding to Co_9S_8, and placed in a quartz ampoule, which was then sealed under vacuum. The tube was heated slowly to 950°C, and held at this temperature for two hours. It was then cooled to 700°C and held for 12 hours. After cooling slowly to room temperature, a homogeneous rod of sulfide was obtained. X-ray diffraction showed the product to be essentially pure Co_9S_8. This solid rod was crushed and screened into powders of different particle sizes.

(c) Procedure

The microbalance was first calibrated with standard weights. Then the sample was placed in a quartz tray, which was suspended on a platinum wire. The platinum wire in turn was attached to the transducer by a short gold chain.

After the sample was in place, the reactor was evacuated, flushed with helium, and then brought to a pressure slightly greater than atmospheric. The reaction temperature was now set, and held for at least 1/2 h, under a steady flow of helium. To start the reaction, helium was cut off, and pure hydrogen switched on. At the end of the reaction, hydrogen was switched off, and helium switched on, for flushing. The sample was cooled in the helium atmosphere. The microbalance was protected from product gases and heat during the run by flushing the bell jar with argon. All runs were carried out at atmospheric pressure.

The gas flow rate was changed from 0.05 l/min to 2.0 l/min and the reaction temperature varied from 600 to 800°C according to the experimental conditions.

RESULTS AND DISCUSSION

In the early stages, reaction [C] was carried out with the stoichiometric molar mixing ratio of 1.0. However, hydrogen sulfide could be detected in the exit gas stream. The amount of hydrogen sulfide evolved at 737°C after 36 minutes, could have contained as much as 4 pct of the total sulfur present in the unreacted sulfide. This could introduce an error of up to 5 pct in the calculated conversions, based on the assumption that all initial sulfur would be transferred to calcium oxide in accordance with reaction [C]. Thus it was important as a first step to minimize hydrogen sulfide evolution, by using more calcium oxide.

Effect of Mixing Ratio

The appropriate amounts of calcium oxide and cobalt sulfide were mixed, suspended in the microbalance, and the weight recorded in the usual manner. The exit gases were passed through a two stage scrubber containing cadmium acetate solution to precipitate the sulfur as cadmium sulfide. The time-conversion results are presented in Fig. 2, at different mixing ratios.

There was a limiting mixing ratio, above which there was no further increase in reaction rate. It seems that above this ratio, the remaining calcium oxide becomes essentially an inert filler. Fig. 3 shows that the H_2S evolution dropped as the mixing ratio increased. At first sight,

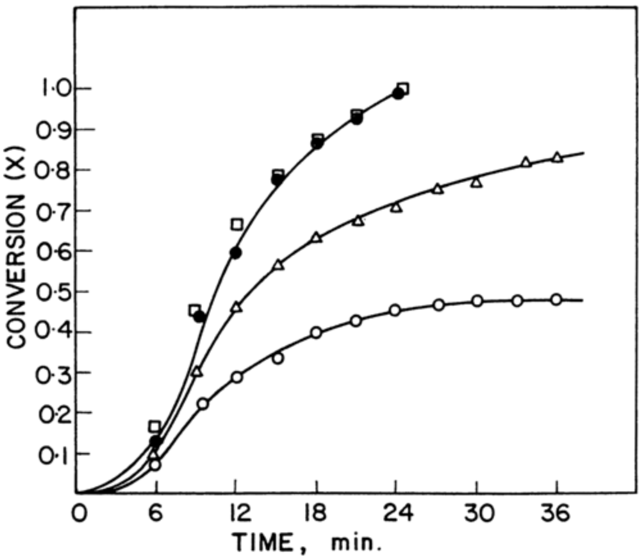

Fig. 2—Effect of the molar mixing ratio. Reaction temperature = 737°C; Average Co_9S_8 particle diam = 0.0125 cm; Hydrogen flow rate = 0.1 l/min. Mixing Ratio: ○ = 1.0, △ = 2.0, ● = 2.6, □ = 6.6.

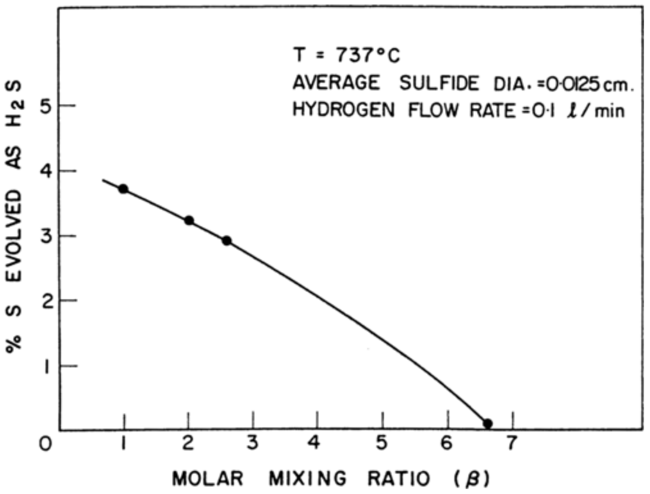

Fig. 3—Effect of mixing ratio on amount of H_2S evolved.

it would appear that a mixing ratio of 6.0 was needed to absorb all H_2S evolved. However tests showed that a mixing ratio of 3.0 was satisfactory, in that H_2S evolution essentially ceased. The ratio of 6.0 was really only necessary to ensure that metal sulfide particles did not lie on the surface of the powder. Therefore all runs were done at a mixing ratio of 3.0.

It is possible to follow the effect of the mixing ratio, by plotting the time required for say 40 pct conversion as a function of mixing ratio. The result, presented in Fig. 4, shows that there was very little decrease in the time required for 40 pct conversion, when using a mixing ratio above three.

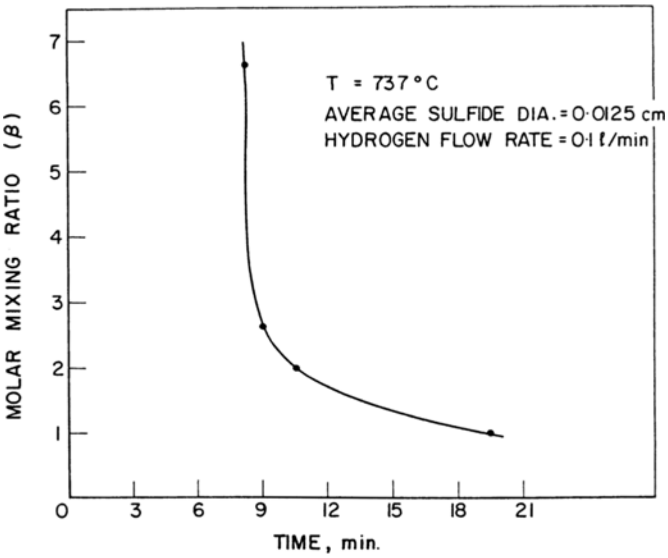

Fig. 4—Time required for 40 pct conversion—reaction [C].

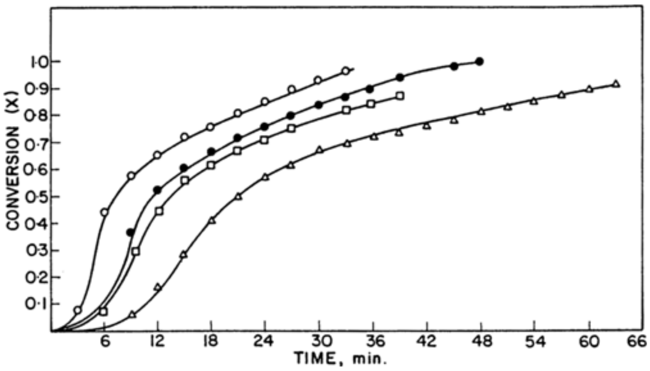

Fig. 5—Effect of hydrogen flow rate. Reaction temperature = 737°C; Molar mixing ratio = 3.0; Average particle diam = 0.0125 cm. Hydrogen Flow Rate (l/min): △ = 0.05, □ = 0.10, ● = 0.15, ○ = 0.20.

Effect of Hydrogen Flow Rate

The effect of hydrogen flow rate was investigated by mixing the powders in a molar ratio of three and carrying out the reduction runs at different flow rates at the same temperature. As the flow rate was increased the reaction rate increased. However at a flow rate of 0.2 l/min, hydrogen sulfide containing as much as 10 pct of the sulfur present in the unreacted sulfide was evolved. At lower flow rates hydrogen sulfide evolution was negligible. It seems that at high flow rates, there are two competing mechanisms for the reduction. The reduction can go *via* reaction [A], which has now less gas film resistance, or *via* reaction [C]. The contact time between calcium oxide and hydrogen sulfide is very short and the gas could be carried out without reaction into the bulk gas stream. Based on this behavior, it seems that the success of reaction [C] depends on the use of lower hydrogen flow rates. The time-conversion curves for the runs described above are shown in Fig. 5.

Effect of Temperature

The effect of temperature was investigated at a mixing ratio of 3.0 and flow rate of 0.1 l/min. Another set of runs was carried out under identical conditions using the metal sulfide alone. The results of both runs were very useful in comparing the scavenged system with the unscavenged one. These results are given in Fig. 6. It is quite clear that the reduc-

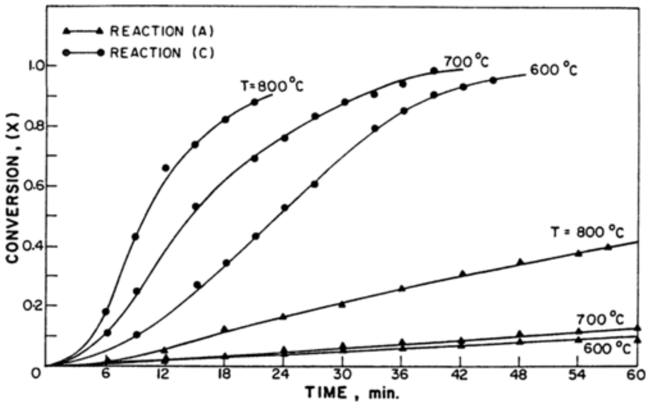

Fig. 6—Effect of temperature on reactions [A] and [C]. Mixing ratio = 3.0; Hydrogen flow rate = 0.1 l/min; Average diam of Co_9S_8 = 0.011 cm.

tion rate for the scavenged system was much higher than that for the unscavenged one. For example, at 700°C, the ratio of the two rates was 15 after 24 minutes of reaction. At high temperatures, the scavenged system became slightly sensitive to temperature changes, indicating development of diffusional effects, which is quite understandable at such small flow rates.

There was always an induction period at the beginning of the reaction (of the order of a few minutes). This phenomenon could be explained by a slow nucleation process occurring in the metal sulfide. Cobalt sulfide is a metal deficit compound[7] and on exposure to a hydrogen atmosphere, sulfur atoms are first removed, and thus the metal deficiency decreases. According to Wagner[8] the metal ions diffuse to the bulk of the metal sulfide, which gradually becomes supersaturated with respect to the metal. Accordingly nucleation of the metal becomes possible. Once metal nuclei are formed, they start to grow on the surface of the sulfide, forming a shell of cobalt metal. At higher temperatures these nuclei may grow into whiskers. At 800°C, needle-like whiskers of cobalt metal were formed. These whiskers were also observed in the direct reduction of cobalt sulfide by hydrogen.[6] However, the whiskers obtained in the scavenged system were shorter in length.

CONCLUSIONS

From the results obtained in this study, it can be concluded that:

1) Considerably enhanced cobalt sulfide reduction rates are achieved in the presence of CaO. For example, at 700°C, the ratio of the two rates was 15, after 24 minutes of reaction.

2) The effect of excess CaO becomes small beyond a CaO/Co_9S_8 ratio of 3.0.

3) The successful use of a scavenging agent (CaO) depends on a low hydrogen flow rate being maintained during the reaction.

ACKNOWLEDGMENTS

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