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journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	4
page range	538-544
year	1952
URL	http://hdl.handle.net/10097/26536

A Research on the Treatment of Complex Sulphide Ores. V On the Recovery of Sulphur*

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(Received August 2, 1952)

Synopsis

Hydrogen sulphide was oxidized with air in the presence of iron, manganese or vanadium oxide as catalyst. The main product of the oxidation was either elementary sulphur or sulphur dioxide according to the ratio of air to hydrogen sulphide. When hydrogen sulphide was mixed to about 29% with air, a maximum yield of sulphur was obtained amounting to about 90% and sulphur dioxide which was formed simultaneously was a little. Amount of sulphur formed decreased and that of sulphur dioxide increased as the ratio of air to hydrogen sulphide was increased. With a mixture containing 12% of hydrogen sulphide, 80% of the sulphur was oxidized to sulphur dioxide and the remainder was found as elementary sulphur. The oxidation took place at relatively low temperature. At 200~400°C, 90% of the sulphur was recovered as elementary sulphur with a mixture which contained 28% of hydrogen sulphide. An effect of flowing rate on the reaction was little.

I. Introduction

Most of the metals form sparingly soluble sulphides but the concentration of acids which can be present when they are precipitated varies widely from metal to metal. For example, sulphides of arsenic, antimony, silver and copper are precipitated even in the presence of concentrated sulphuric acid, but those of iron and manganese are not precipitated unless the solution is made alkaline. Cadmium and lead sulphides are not completely precipitated in a hydrochloric acid solution, if the concentration of the latter is above 0.2N. Zinc sulphide can be precipitated from acetic acid solution but not from sulphuric acid solution if the concentration of the latter is above 0.01N. So when treated with mineral acids, sulphides of zinc, iron and manganese dissolve readily, while those of arsenic, copper, etc. are not affected by sulphuric acid, even in high concentration, and cadmium and lead sulphides are dissolved when the concentration of the acid is adjusted to an appropriate value. Accordingly, when various complex sulphide ores are treated with sulphuric acid of appropriate concentration, avoiding oxidation as described in the preceding paper (III) of this series, iron pyrite and chalcopyrite remain undissolved, while zinc blende and galena are converted into sulphate and combined sulphur is evolved as hydrogen sulphide. In a few samples of copper concentrates authors examined, 9~13% of such combined sulphur was found contained.

* The 40th report of the Research Institute of Mineral Dressing and Metallurgy.

The generated hydrogen sulphide may be utilized for recovery of copper, for example, in mine water by the process of sulphidization, or for production of elementary sulphur by oxydation or again for production of sulphur dioxide by further oxydation.

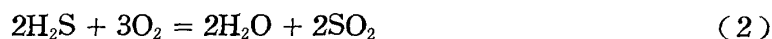
Authors carried out here some experiments on the oxidation of hydrogen sulfide with air.

II. Method and apparatus used

Many attempts have been made to recover elementary sulphur from hydrogen sulphide. When hydrogen sulphide is heated, it is decomposed.⁽¹⁾ Contact with a heated platinum⁽²⁾ or molybdenum⁽³⁾ filament promotes the decomposition. Oxidation with air of it after it is absorbed in ammoniacal arsenate solution⁽⁴⁾ will precipitate sulphur. Direct oxydation with air has also been studied. Two volumes of hydrogen sulphide react with one volume of oxygen according to the equation :



and with three volumes of the latter sulphur dioxide is generated :



In the reaction (1), ferric oxide⁽⁵⁾ silica gels either alone or treated with salts of iron, manganese, or iron and manganese, or iron and copper, or bricks impregnated with these salts may be used as catalyst.⁽⁶⁾ According to Kharmandar'yan and Kopeliovitch high active catalyst is prepared by igniting freshly precipitated manganese carbonate at 400~500°C.⁽⁷⁾

Sulphur is also liberated by the action of sulphur dioxide on hydrogen sulphide.



A mixture of hydrogen sulphide and air in certain ratio explodes on ignition. During sulphatization, hydrogen may also be accompanied with hydrogen sulphide. Therefore, a few preliminary tests for explosion were made on such points.

Taking the content of oxygen in air to be 20%, it would necessary to add hydrogen sulphide to 28.6 and 11.8% respectively for obtaining sulphur or sulphur dioxide under equation (1) or (2). Igniting, therefore, the mixtures containing 5~30% hydrogen sulphide with a heated nicrome wire or passing the mixtures over the heated pieces of bricks impregnated with vanadium pentoxide,

(1) G. Preuner, *Z. anorg. Chem.*, **55** (1907), 279.

(2) H. A. Taylor and C. F. Pickett, *J. phys. Chem.*, **31** (1927), 1212.

(3) F. E. T. Kingman, *Trans. Farad. soc.*, **32** (1936), 903.

(4) G. E. Foxwell and A. Grounds, *J. Soc. Chem. Ind.*, **50** (1939), 163.

(5) C. F. Claus, *Brit. pat.* 3606, 1882; G. Lunge, *Sulphuric Acid and Alkali*, Vol. II, part II, 971 (1909).

(6) M. O. Kharmandar'yan, E. L. Kopeliovich and A. E. Buryak, *Ukrain. Khim. Zhur.* **8** *Wiss-Tech.*, Teil 72 (1933); *Chem. Abst.*, **28** (1934), 1819.

(7) M. O. Kharmandar'yan and E. L. Kopeliovich, *J. Applied Chem. (U. S. S. R.)* **9** (1936), 23; *Chem. Abst.*, **30** (1936), 6141.

tests on explosion were made. The result is give in Table 1.

Table 1. A Preliminary Test for Explosion.
Mixed gases were ignited with Ni-Cr wire in sealed vessel.

H ₂ S %	Reaction
5	Reacted quietly.
10	Reacted with slight noise. H ₂ S could not be recognized in the products.
20	Reacted with noise. SO ₂ , H ₂ S and S were observed.
30	Reacted without noise. „

Mixed gases were passed over heated catalyst.

H ₂ S %	Reaction
10	Flame was observed traveling backward.
15	Flame was observed when the mixed gas was flowed at high velocity.
20	No flame was observed.
30	„

When ignited with microme wire, the mixture contining 20% of hydrogen sulphide reacted vigorously with an explosive report. Mixtures of under 5% or over 30% hydrogen sulphide content did not give out noise in buruing. When a mixture containing 10% of hydrogen sulphide was passed over catalysts heated at 300~400°C, flame was observed arising in the vicinity of the catalysts and traveling backward in the reaction tube. Springing apart of the catalyst was seen, with 15% of hydrogen sulphide when the flow rate was great.

A mixture of hydrogen and air will explode, when hydrogen is present within the scope of 9.45~66.40%.⁽⁸⁾ Now, under the assumption that sulphur may be recovered under reaction (1) by admixture of about 28% of hydrogen sulphide, a test was made for the quantity of hydrogen permissible in hydrogen sulphide-air mixture and arrived at the result shown in Table 2.

Table 2. Explosibility of Mixtures of H₂S, H₂ and Air.

H ₂ S (%)	H ₂ (%)	Air (%)	Reaction
20	8	72	Explosion
22	6	„	Flammation with noise
24	4	„	„

Presence of hydrogen in a quantity less than 6% caused no explosion, though the reaction took place with noise. With hydrogen exceeded 8%, violent and dangerous explosion took place. However, installation of a water safety valve was effective in preventing explosion.

The appartus used for the recovery of sulphur is given in Fig. 1.

A and A' are 10 litre flasks used as auxiliary tanks. The mixed gas is alternately fed into the two flasks and alternately sent out into the reaction tube D. Paper gauges are pasted on the outside of the flasks. C is a flowmeter. In the lower parts of the reaction tube catalysts were placed and heated by an

(8) J. W. Mellor, Modern Inorganic Chemistry 910, London (1927).

electric furnace E. The sulphur liberated was collected in a receiver G. H is a cooling tube. Amount of sulphur which was condensed therein was negligibly small. The gases generated by the reaction were let off through I, except when they were collected in the absorbing bottles J_1 , J_2 , K_1 and K_2 , for subsequent analysis. In J_1 and J_2 , the unreacted hydrogen sulphide was caught by cadmium sulphate. In K_1 and K_2 , sulphur dioxide was oxidized to sulphate by alkaline peroxide solution in the presence of molybdenum oxide as catalyst. After a definite amount of escaping gas was passed, the cock L was turned and hydrogen was introduced through M, while J_1 and J_2 was lightly boiled. Thus sulphur dioxide dissolved in the solution in J_1 and J_2 was transferred into K_1 and K_2 .

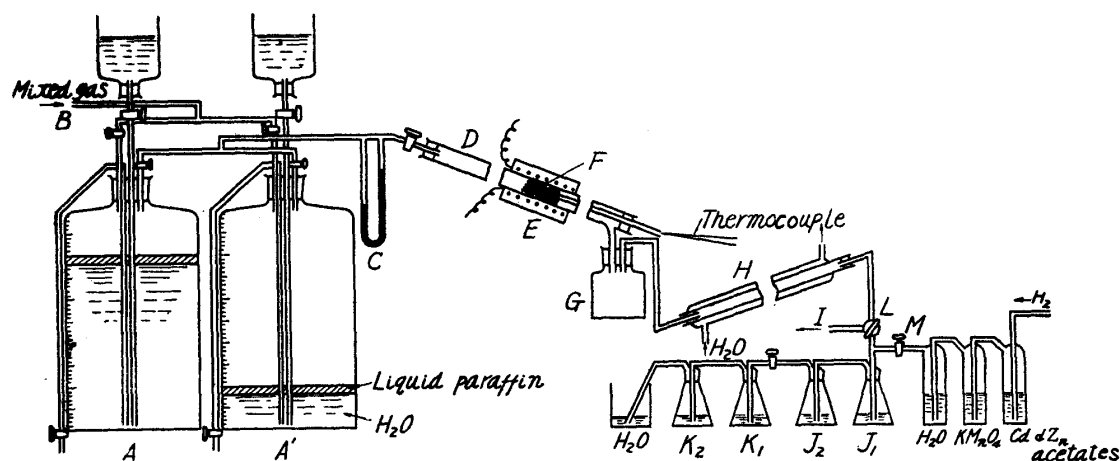


Fig. 1. Apparatus

A, A' : Tanks	C : Flow meter	D : Reaction tube
E : Electric furnace	F : Catalyst	G : Receiver for S formed
H : Cooler	J_1, J_2, K_1, K_2 : Absorbing bottles	

The amount of hydrogen sulphide remaining in the escaping gas was determined by titrating the sulphuric acid produced in J_1 and J_2 with alkali after filtering off the cadmium sulphide. For the determination of sulphur, iodometry is liable to give unduly low results when the sulphide is present in rather large quantity.

The sulphur dioxide was absorbed in a solution containing potassium hydroxide (0.1N) and hydrogen peroxide (6%), oxidized into sulphate in the presence of 40 γ of molybdenum oxide per 50 ml of the absorbent, and the remaining alkali was titrated.

During the reaction, if sulphur dioxide was generated by equation (2) in the presence of hydrogen sulphide, they would react forthwith, according to the equation (3), so that, in the escaping gas coexistence of both in large quantity could not be considered. Actually only a very small amount of sulphur was deposited in H.

The catalysts were prepared by immersing pumice stones crushed to 2~3 mm in diameter in a dense suspension of ferric oxide or solutions of manganese acetate or ammonium vanadate and igniting at 500~600°C. The process was repeated several times. The catalysts may become coated with sulphur, when they are cooled after use and color may change, but no reactivation is needed.

They may be reused without detracting from their efficiency.

III. Results

After replacing the air in the reaction tube, etc. with standardized mixture of hydrogen sulphide and air, electric furnace E was heated to appropriate temperature and the reaction initiated with the introduction of the same gas at a definite flow rate. As the temperature in the vicinity of the catalyst rises in the course of the reaction, the catalyst was preheated to a certain temperature, so that the temperature at F was kept within the range of 400~450°C throughout the reaction. The last litre of every 10 litres of the escaping gas was analysed.

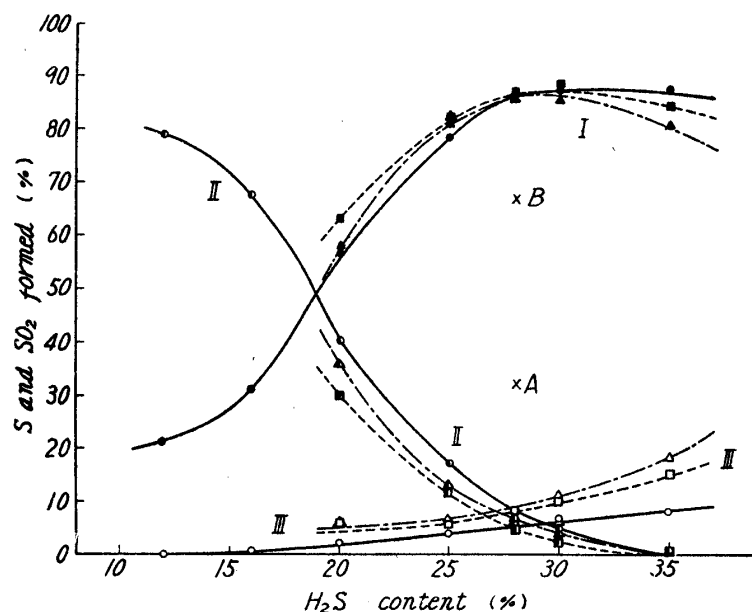


Fig. 2. Oxidation of Hydrogen Sulphide with Air.

Curve I : Amount of S liberated. ● ■ ▲
 Curve II : Amount of SO₂ formed. ○ □ △
 Curve III : Amount of H₂S remained. ○ □ △
 Catalyst : V, ● ○ ○, Fe, ■ □ □, Mn, ▲ △ △

As it was feared that a larger error would creep in by direct measurement of the liberated sulphur, the recovery of sulphur was indirectly estimated by subtracting the sulphur in the escaping gas. The result is shown in Fig. 2.

Curves I and II in the figure show the amount of sulphur and sulphur dioxide formed, respectively. Hydrogen sulphide remaining in the escaping gas is represented in curve III.

As is seen, there was little difference whether

iron oxide or manganese oxide or again vanadium oxide was used as catalyst. Taking the oxygen content in air at 1/5, the theoretical amount of hydrogen sulphide required to produce sulphur in accordance with the equation (1) is 28.6%. The recovery of sulphur showed the maximum of 88% when the content of hydrogen sulphide was 28~30%. However, the oxidation was not complete. A small amount of hydrogen sulphide remained unreacted. When the content of hydrogen sulphide was raised to 35%, the recovery of sulphur fell, due to the deficiency of oxygen. Sulphur dioxide could not be detected in the escaping gas. On the contrary, when the hydrogen sulphide content was lowered to 25% or under, the quantity of unreacted hydrogen sulphide decreased and the reaction (2) became more active, due to the increase of the oxygen content, that is, more sulphur dioxide and less elementary sulphur was produced. When the air content came up to 81%, about an equal amount of sulphur and its dioxide was formed, an increase of air thereabove causing production of

more and more sulphur dioxide and less and less elementary sulphur. When the hydrogen sulphide content was decreased to 12%, 79% of the total sulphur was found oxidized into sulphur dioxide. As no free hydrogen sulphide was found remaining in the escaping gas, the remainder of sulphur, 21%, was estimated to have been liberated as elementary sulphur. As the theoretical quantity of hydrogen sulphide required for production of sulphur dioxide according to the equation (2) above being calculated as 11.8%, an excessive quantity of oxygen is required for the oxidation of the total sulphur into sulphur dioxide, if the result of the above test is followed. When the amount of air was further increased to 90% of the mixture, oxidation took place energetically, and on frequent occasions, flame burst out in the vicinity of the catalyst, which would travel backwards toward the reservoir. In the case where air content was 15%, flame was also observed, but only under a higher rate of gas flow.

A reaction without catalysis of a 28% hydrogen sulphide dilution at a temperature of around 430°C resulted in liberating about 32% of total sulphur as elementary sulphur (point A in Fig. 2), about 67% remaining as hydrogen sulphide unreacted (point B).

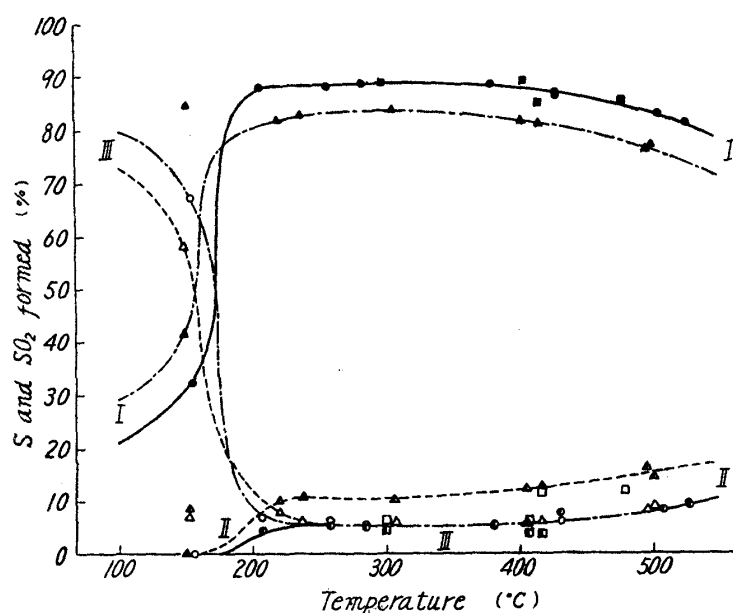


Fig. 3. Effect on the Oxidation of Hydrogen Sulphide of Temperature.

Curve I : Amount of S liberated. ▲ ● ■
 Curve II : Amount of SO₂ formed. ▲ ● ■
 Curve III : Amount of H₂S remained. △ ○ □
 Amount of H₂S mixed with air ; 25%, ▲ △ △ ;
 28%, ● ○ ○ ; 30%, ■ □ □.

Tests for the effect of reaction temperature, changing from 150°C to 550°C, were conducted next. Manganese oxide was used as catalyst. The result is shown in Fig. 3, wherein the curve I represents the amount of sulphur liberated, curve II that of the sulphur dioxide and curve III that of the hydrogen sulphide remained. An oxidation at 150°C converted only about 30~40% of sulphur as elementary sulphur, but when the temperature was raised over 200°C, the recovery was increased abruptly, 80~90% of the sulphur being liberated as elementary sulphur. The recovery changed little up to 400°C, but when the temperature exceeded 500°C, it tended to decrease, sulphur dioxide increasing correspondingly. For the purpose of efficient oxidation, a comparatively low temperature gave satisfactory results, 89% of the total sulphur being converted into free sulphur at a temperature of 207°C with a mixture of 28% hydrogen

sulphide.

Using a 28% hydrogen sulphide mixture, another test was conducted for ascertaining the effect of the flow rate on the sulphur recovery. Iron oxide was

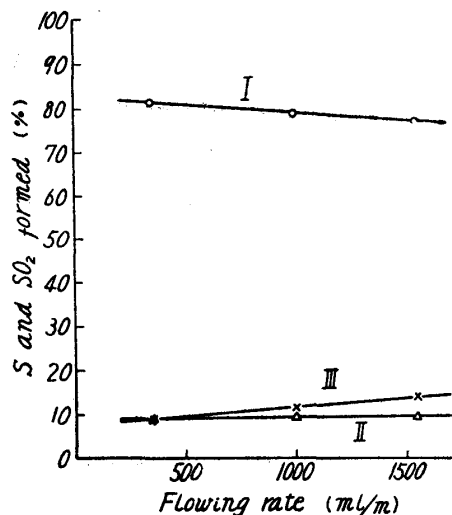


Fig. 4. Effect on the Oxidation of Hydrogen Sulphide of flowing Rate.
Curve I : Amount of S liberated.
Curve II : Amount of SO₂ formed.
Curve III : Amount of H₂S remained.

used as catalyst. The result is shown in Fig. 4.

Temperature in the vicinity of catalyst was affected by the flow rate. Accordingly, to assure maximum constancy of temperature during the reaction, the catalysts used were preheated to about 400°C, 358°C and 296°C and the mixture was passed through at the varying rates 350 ml/min, 1000 ml/min and 1550 ml/min, respectively, to keep the temperature of the catalysts at about 510~530°C throughout. I shows the recovery of free sulphur, II shows the amount of sulphur dioxide formed and III that of the hydrogen sulphide remained. Although, as may be seen from the figure, the effect of change in

flowing rate on the recovery of sulphur was small, but as a slight rising amount of the hydrogen sulphide remained unreacted with a rise in the rate of flow, the recovery was diminished that much

The present investigation has been supported partly by the grant in aid for fundamental scientific research from the Ministry of Education.