LXXIII.—*The Liberation of Hydrogen Sulphide from Gob Fires in Coal Mines.*

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EXPERIMENTS described in an earlier paper (T., 1916, **109**, 723) have shown that iron pyrites favourably influences to a small extent the oxidation, and therefore spontaneous ignition, of coal.

Lewes (Second Report of the Royal Commission on Coal Supplies, 1904 [Cd. 1991], Vol. 2, 232), however, expressed the view that iron pyrites has no connexion whatever with the spontaneous heating of coal. This inference is based on the fact that, in an inspection of a case of spontaneous combustion where the coal was heated, the sulphur was found to be evolved as hydrogen sulphide and not as sulphur dioxide, as would have been the case "if the pyrites had anything to do with" the fire.

The fact that hydrogen sulphide is evolved during the initial stages of a gob fire is indisputable; but the assumption that if iron pyrites favoured the heating, the sulphur would be given off necessarily as sulphur dioxide appeared to need verification. There is the reasonable possibility that the sulphur dioxide may be reduced to hydrogen sulphide by contact with the heated coal.

Experiments were conducted to investigate this question, and a detailed account is given in the following pages.

The investigation has shown that hydrogen sulphide may be formed from heated coal and iron pyrites in a number of ways, as, for example, by heating coal, by passing sulphur dioxide over heated coal, by heating mixtures of coal with sulphur or iron pyrites, by passing water vapour or hydrogen over heated iron pyrites, etc.

Therefore, at the seat of a gob fire, it would appear to be quite possible for sulphur dioxide to be formed, but, previous to an external outbreak of the fire, there would be very little likelihood of this sulphur dioxide being liberated into the mine atmosphere. If the sulphur dioxide were not reduced completely to hydrogen sulphide by contact with heated coal in the immediate vicinity of the fire, it would encounter the larger volumes of hydrogen sulphide that would be issuing from the gradually heated material in the locality, and thereby would be decomposed to give sulphur. In consequence of such reactions, no sulphur dioxide would reach the external air.

In view of this, Lewes's statement, that if iron pyrites assisted in the ignition of the coal the sulphur would be liberated as sulphur dioxide, seems to be erroneous.

The Formation of Hydrogen Sulphide by Passing Sulphur Dioxide over Heated Coal.

In order to reproduce to a certain extent the conditions of the liberation of the gas from the gob, a moist mixture of four volumes of carbon dioxide and one volume of sulphur dioxide was passed over 20 grams of powdered coal contained in a glass tube. The tube (45 cm. long and 2 cm. in diameter) was gradually heated in a 28 cm. platinum-wound electric furnace until the temperature reached 500°. The temperature was maintained at 500° until no further evolution of gas from the coal could be detected. During this time, the mixture of carbon dioxide and sulphur dioxide was passed over the coal at the rate of 2 litres per hour.

The gases evolved were delivered, first, into a Woulfe's bottle, where tarry oils were deposited, through a spiral tube immersed in water at 10°, and then through pure concentrated sulphuric acid.

After this treatment, the hydrogen sulphide in the gases was absorbed by passing them through a train of four bottles, each containing a solution of copper sulphate acidified with hydrochloric acid. A duplicate absorption train was arranged so that by means of a three-way tap the gases could be diverted from one train to the other.

At the commencement of an experiment, the air in the glass tube in the furnace was displaced by a stream of carbon dioxide. The heating was started, and the mixture of carbon dioxide and sulphur dioxide was passed through the tube. At first, no precipitate appeared in the copper sulphate solution, but as soon as the slightest trace was discernible the tap was turned so that the gases were washed with fresh copper sulphate solution in the second absorption train. This was to eliminate any possible errors that might arise from a reaction between the hydrogen sulphide and any soluble gases with which the copper sulphate solution had been contaminated during the initial stage of the experiment.

After the temperature of the furnace had been 500° for about two hours, the mixture of carbon dioxide and sulphur dioxide was turned off to test whether the evolution of volatile products was continuing. When this ceased, the precipitated copper sulphide was collected, washed, dried, and detached from the filter paper. The filter paper was ignited, and the ash was added to the main part of the precipitate, which was mixed with sulphur, heated to redness in an atmosphere of coal gas, cooled, and weighed.

From the weight of cuprous sulphide, the quantity of sulphur evolved as hydrogen sulphide was calculated.

Blank experiments (in which only carbon dioxide was passed over the coal) were made for each sample of coal.

Three samples of different coals were used in the experiments.

Coal "A" was a selected sample of Arley coal from a local colliery. The coal was black, possessing considerable lustre and a brown streak. It fractured along lines chiefly defined by "mother of coal" (charcoal). The seam is not subject to spontaneous combustion. The sample was picked carefully, and all visible impurity excluded.

Coal "B" was a selected sample of "Five Feet" coal from a colliery near Chester. The coal was moderately dull black, and was exceptionally close and compact. The fracture was mainly splinty. From its properties it would appear to be a canneloid coal. The seam is not subject to gob fires. The sample was freed carefully from all visible impurity.

Coal "C" was from a local colliery, and was a deliberately chosen inferior sample from the Ravine Seam, which is subject to spontaneous combustion. The coal consisted of alternate lustrous black and comparatively dull black layers; it fractured easily along planes which contained considerable deposits of calcium carbonate. Iron pyrites was present in the finely disseminated form. The sample was obtained from the neighbourhood of a gob fire.

Analyses of the coals gave the following results:

Estimation.	Coal "A."	Coal "B."	Coal "C."
Specific Gravity.	1·248.	1·247.	1·341.
Ultimate Analysis :—	Per cent.	Per cent.	Per cent.
Carbon	80·937	75·761	67·730
Hydrogen	4·815	5·783	2·992
Nitrogen	1·365	1·487	1·015
Sulphur	1·412	0·953	4·017
Ash	1·660	3·646	12·084
Oxygen, etc. (by diff.)	9·811	12·350	12·162
	100·000	100·000	100·000
Proximate Analysis :—			
Fixed Carbon	66·475	47·606	51·637
Ash	1·660	3·646	12·084
Moisture	0·828	0·566	3·738
Volatile matter	31·037	48·182	31·541
	100·000	100·000	100·000
Yield of Volatile Matter on heating to 500°	14·421	25·830	20·516

The results of the experiments are given in the accompanying table, and are calculated for a weight of 100 grams.:

Result.	Sample.	Time. Mins.	Weight of sulphur in coke residue. Grams.	Weight of sulphur evolved as H_2S. Grams.
1	Coal "A."	30	1·352	0·032
2		60	1·351	0·035
3		30	1·373	0·172
4		60	1·379	0·194
5	Coal "B."	30	0·618	0·049
6		60	0·609	0·049
7		30	0·711	0·316
8		60	0·703	0·351
9	Coal C."	30	2·878	1·096
10		60	2·879	1·098
11		30	4·186	2·065
12		60	4·205	2·619

In the above table, each result represents the average of five experiments.

The time mentioned in the second column gives the number of minutes taken to raise the temperature of the furnace from 15° to 500°. Subsequently, the temperature of the furnace was maintained at 500° until the end of the experiment, which occupied from two to two hours and a-half.

Results 1—4 were obtained with coal "A," 5—8 with coal "B," and 9—12 with coal "C." Results 1, 2, 5, 6, 9, 10 were blank determinations, and give the weight of sulphur that was eliminated as hydrogen sulphide when 100 grams of the coal were heated in a current of moist carbon dioxide. Results 3, 4, 7, 8, 11, 12 were obtained by passing the mixture of carbon dioxide and sulphur dioxide over the heated coal.

In the blank experiments, the temperature of the furnace reached the following values before any appreciable quantity of hydrogen sulphide was evolved from the samples of coal.

	Coal "A."	Coal "B."	Coal "C."
Temperature	290°	270°	275°

It was observed, however, that when the mixture of carbon dioxide and sulphur dioxide was passed over the coal, no hydrogen sulphide was evolved until a much higher temperature had been reached. The values are given below.

	Coal "A."	Coal "B."	Coal "C."
Temperature	440°	435°	445°

During this time, the coal in the tube appeared to have become coated with a whitish-yellow powder. No doubt this was a slight deposit of sulphur which, probably, had been formed by the reaction between the sulphur dioxide passing over and the hydrogen sulphide evolved from the coal. Possibly the organic tarry liquids from the coal may have influenced the interaction of the hydrogen sulphide and the sulphur dioxide (compare Klein, *J. Physical Chem.*, 1910, **15**, 1, who also showed that water was a catalyst).

When the temperature of the furnace reached about 450°, the evolution of hydrogen sulphide became so rapid that the stream of sulphur dioxide was insufficient to react with it completely, and a rapid precipitation of copper sulphide occurred.

It may be noted that a deposit of sulphur is observed frequently in the initial stages of an actual occurrence of a gob fire (compare Henshaw, Departmental Committee on Spontaneous Combustion in Coal Mines, Minutes of Evidence, 12th Feb.—16th July, 1913, p. 26); but this slight yellow deposit in the cracks of the coal, where the heating is evidenced, may be due, in addition, to other causes than the one stated above. However, the similarity between the actual gob fire and the experiment was striking.

The percentage of sulphur in the coke residue, which was slightly more friable when sulphur dioxide was passed over the coal, would indicate that a quantity of the sulphur becomes fixed in the coke. This may be due to an interaction between the sulphur dioxide and the ash constituents.

It is possible that if the mineral matter of the coal contained lime at 500°, a little sulphur may have been formed by the action of the sulphur dioxide on the lime (Veley, T., 1893, **63**, 821; compare Hammick, this vol., 379).

The results indicate that the evolution of the hydrogen sulphide is increased where sulphur dioxide is passed over heating coal. The observed fact that the sulphur is evolved as hydrogen sulphide and not as sulphur dioxide from a gob fire does not, therefore, decide the question whether or not iron pyrites assists in the spontaneous ignition of coal.

The Formation of Hydrogen Sulphide by Heating Mixtures of Coal and Sulphur.

From the results obtained in the previous section, it would appear that the production of hydrogen sulphide resulted from heating the coal with the sulphur which previously had been deposited upon it. To investigate this question, mixtures of 20 grams of coal with various proportions of sulphur were heated in a glass tube in an electric furnace to 500°.

In the first series of experiments a stream of moist carbon dioxide was passed through the tube, and was interrupted only to test whether all the volatile gases had been liberated from the coal.

In the second series of experiments, the air was displaced from the glass tube containing the mixture of coal and sulphur by means of a stream of dry carbon dioxide. The carbon dioxide was turned off until all volatile matter had been expelled from the mixture, then the residual gases were swept into the absorption train by means of the current of dry carbon dioxide.

Dry carbon dioxide was driven regularly over the heated mixtures in the experiments comprising the third series. The current of carbon dioxide was interrupted only to test for the cessation of the evolution of gas from the mixtures.

The apparatus and the method of collecting the hydrogen sulphide have been described in the previous part of the paper.

The following table gives the weight (in grams) of sulphur that was eliminated as hydrogen sulphide and the weight of sulphur in the coke from mixtures of 100 grams of coal with different quantities of sulphur:

Result.	Sample.	Weight of sulphur mixed with 100 grams of coal. Grams.	Series 1.		Series 2.		Series 3.	
			S in coke. Grams.	S as H_2S. Grams.	S in coke. Grams.	S as H_2S. Grams.	S in coke. Grams.	S as H_2S. Grams.
1	Coal "A."	0	1·352	0·032	1·361	0·031	1·363	0·031
2		1	1·373	0·801	1·394	0·605	1·394	0·515
3		2	1·374	1·652	1·401	1·151	1·391	0·997
4		3	1·371	2·302	1·393	1·572	1·404	1·354
5		4	1·379	3·109	1·402	2·095	1·395	1·736
6		5	1·370	4·036	1·401	2·097	1·397	1·831
7		6	1·373	4·783	1·395	2·103	1·403	1·987
8	Coal "B."	0	0·608	0·049	0·618	0·049	0·619	0·049
9		1	0·613	0·872	0·617	0·693	0·623	0·604
10		2	0·618	1·801	0·835	1·502	0·871	1·025
11		3	0·617	2·673	1·201	1·712	1·114	1·513
12		4	0·615	3·397	1·439	2·383	1·503	2·007
13		5	0·612	4·413	1·423	2·524	1·501	2·188
14		6	0·617	5·216	1·457	2·591	1·512	2·436
15	Coal "C."	0	2·877	1·098	2·878	1·097	2·905	1·097
16		1	3·054	1·897	3·082	1·803	3·085	1·802
17		2	3·236	2·633	3·298	2·516	3·284	2·517
18		3	3·509	3·189	3·611	3·167	3·627	3·091
19		4	3·605	4·314	3·828	3·591	3·971	3·388
20		5	3·892	4·846	3·909	3·807	4·426	3·645
21		6	3·955	5·684	4·136	4·070	4·518	3·923

It is well known that sulphur below its boiling point combines with hydrogen, and when heated to 200° reacts with paraffin or vaselin, forming hydrogen sulphide. Even if little free hydrogen is evolved from coal at 500°, the action of sulphur on bituminous coal would explain the production of hydrogen sulphide.

Evidence that the coal behaved differently when heated with sulphur was noted by the change in the character of the coke.

When coal "A" was heated alone to 500°, a firm, hard coke with submetallic lustre was produced, but as the quantity of sulphur admixed with the coal increased, the coherence of the coke residue diminished. Indeed, in the experiments of series 1, when the coal was heated with 6 grams of sulphur, the resulting coke was quite pulverulent. The cokes were less powdery in series 2 than in series 1, and in series 3 than series 2. The above statements were true also for coals "B" and "C."

The influence of moisture on the production of hydrogen sulphide was particularly noticeable (compare Jones, *Mem. Manchester Phil. Soc.*, 1904, **48**, No. XVI.). In the experiments in series 1, in which moisture was admitted, the sulphur evolved as hydrogen sulphide exceeds the quantity collected in the corresponding experiments in series 2 and 3. In series 3, dry carbon dioxide was passed continually over the mixtures, and the production of hydrogen sulphide was the smallest.

It is impossible, however, to state definitely how far moisture is responsible for the formation of hydrogen sulphide, as water is one of the decomposition products on heating coal, and therefore its elimination is incapable of being accomplished. That it is a very important factor is demonstrated by the greater production of hydrogen sulphide in series 1 than in either series 2 or 3. Furthermore, with coal "C," which contained more than 3 per cent. of moisture, the difference between the results in series 2 and 3 and those in series 1 is not so marked as with the comparatively dry coals "A" and "B." That moisture is probably not the sole factor is substantiated by the production of hydrogen sulphide on heating such a mixture as sulphur and paraffin.

The decomposition of the moisture by the heated sulphur would produce oxygen and hydrogen sulphide, and the loss of the caking power would appear to be explained satisfactorily as the result of the oxidation to inert substances of those particular compounds which endow the coal with this property. This was upheld by the fact that the coke increased in hardness from series 1 to 3, that is, as the moisture admitted to the reaction was diminished. No attempt was made to determine whether any carbon dioxide was reduced by the heated coal to carbon monoxide (see Meyer and Schuster, *Ber.*, 1911, **44**, 1931).

The weight of sulphur fixed in the coke showed no marked variation with the different mixtures containing coal "A"; but the cokes from coals "B" and "C" exhibited a gradually increasing fixation of sulphur. The presence of moisture tends to reduce the quantity of sulphur left in the coke.

During each experiment there accumulated a precipitate of sulphur in the sulphuric acid wash-bottle. This was noticeable particularly with the coal mixtures containing the larger quantities of sulphur. At the conclusion of an experiment the sulphuric acid was found to emit a pungent and disagreeable garlic-like odour.

The experiments indicate that where mixtures of sulphur and coal are heated, the sulphur is evolved largely as hydrogen sulphide and that its formation is increased by the presence of moisture.

These conditions are fulfilled admirably during the initial stage of a gob fire; for sulphur becomes mixed with the coal, moisture is present, and the temperature gradually rises. Therefore it is not surprising that hydrogen sulphide is liberated from the gob and that sulphur dioxide is not observed until the fire breaks externally. Incidentally, the author may add that he has been assured by one who has had experience of gob fires that the odour produced in the room by heating coal with sulphur is almost identical with the peculiar and characteristic "gob stink."

Hence it may be argued that such a series of reactions as the following take place in the gob. First, iron pyrites assists the ignition and liberates sulphur dioxide. The materials in the locality are heated and evolve hydrogen sulphide, which reacts with the sulphur dioxide to form sulphur. The sulphur is deposited on the coal which is being heated gradually, and from this mixture the sulphur is disengaged as hydrogen sulphide.

It certainly cannot be inferred that iron pyrites has no influence on the spontaneous ignition merely because hydrogen sulphide, and not sulphur dioxide, is liberated from the gob.

The Formation of Hydrogen Sulphide by Heating Mixtures of Coal and Iron Pyrites.

The experiments in this section were made in the same manner as those just described. The mixtures of coal and iron pyrites were heated in a glass tube in an electric tube furnace to 500°. Previous to the heating, the air was displaced from the tube by a stream of carbon dioxide, whilst at the conclusion the residual gases were swept into the absorption train, containing acidified copper sulphate solution, by again turning on the current of carbon dioxide.

The analysis of the iron pyrites gave the following results:

Silica	1·416 per cent.
Iron	45·902 ,, ,,
Sulphur	51·978 ,, ,,
Copper	trace

The weight of sulphur evolved as hydrogen sulphide from various mixtures of coal and iron pyrites is given in the accompanying table.

Result.	Sample.	Weight of iron pyrites mixed with 100 grams of coal. Grams.	Weight of sulphur evolved as hydrogen sulphide. Grams.
1	Coal "A"	0	0·031
2		2	0·208
3		4	0·387
4		6	0·533
5		8	0·666
6		10	0·876
7	Coal "B"	0	0·049
8		2	0·604
9		4	0·685
10		6	0·789
11		8	0·901
12		10	1·013
13	Coal "C"	0	1·089
14		2	1·620
15		4	1·953
16		6	2·194
17		8	2·576
18		10	3·058

Hence, the liberation of hydrogen sulphide from a gob fire may be due, to a certain extent, to the effect of the coal being heated in the presence of iron pyrites.

The Formation of Hydrogen Sulphide by Passing Moist Carbon Dioxide over Heated Iron Pyrites.

A stream of dried carbon dioxide was passed over iron pyrites heated as in the previous experiments to 500° in an electric tube furnace, and no hydrogen sulphide could be detected in the issuing gases.

When, however, a current of moist carbon dioxide was passed over the heated iron pyrites it resulted in the immediate production of hydrogen sulphide (compare Jones, *loc. cit.*). A considerable accumulation of sulphur collected in the cooler parts of the glass tube.

This experiment indicates that some of the hydrogen sulphide liberated from a gob fire may owe its origin to the action of moisture on heated iron pyrites. In the gob there would be oxidisable material, which would acquire with avidity the oxygen produced by the decomposition of the moisture, and would thereby tend to promote the formation of the hydrogen sulphide.

The Formation of Hydrogen Sulphide by Passing Hydrogen over Heated Iron Pyrites.

For the experiments in this part 2 grams of iron pyrites were placed in each of two tubes (48 cm. long and 1 cm. in diameter), which were introduced simultaneously into an electric tube furnace at 500°. Through one tube was passed a stream of dry hydrogen at the same rate as moist hydrogen was driven through the other.

The gases leaving the tube were delivered direct into acidified copper sulphate solution. The precipitated copper sulphide was collected every fifteen minutes, and the sulphur estimated as previously described.

The quantity of sulphur emitted as hydrogen sulphide is given in the following table [under (*a*) when dry hydrogen was passed,

Time.	Sulphur evolved as hydrogen sulphide	
	(*a*)	(*b*)
Minutes.	Grams.	Grams.
15	0·436	0·779
30	0·608	1·140
45	0·705	1·388
60	0·753	1·518
75	0·773	1·590
90	0·792	1·628
105	0·796	1·632
120	0·801	1·636

under (*b*) when wet hydrogen was used. The results are calculated for a weight of 10 grams of iron pyrites.]

The values clearly demonstrate the paramount importance of moisture in the reduction of iron pyrites by hydrogen.

In the coal mine the gob may reach a high temperature when hydrogen will form a considerable proportion of the gases emitted from the coal (Burgess and Wheeler, T., 1910, **97**, 1917).

In these circumstances, should it pass over heated iron pyrites, hydrogen sulphide would constitute one of the gases emitted from the gob.

The author's thanks are due to Mr. George William Farmer for assistance in the last series of experiments.

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[*Received, July 14th,* 1917.]