

LXI.—*The Influence of Iron Pyrites on the Oxidation of Coal.*

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THE effect of the presence of iron pyrites on the oxidation of coal is a subject on which various opinions are held. Some authorities maintain that its influence is favourable (Meyer, *J. pr. Chem.*, 1872, [ii], **5**, 407; Lamplough and Hill, *T. Inst. Min. Engrs.*, 1913, **45**, 645; Louis, *ibid.*, 651; Hall, *ibid.*, 1914, **46**, 571), some that it has nothing whatever to do with the spontaneous ignition of coal (Threlfall, "Second Report of the Royal Commission on Coal Supplies," 1904 [Cd. 1991], **2**, 227; Lewes, *ibid.*, 232; Lawton, *T. Inst. Min. Engrs.*, 1904, **27**, 112), whilst others regard its presence as detrimental to the oxidation of the coal (Fayol, *Bull. Soc. Ind. Min.*, 1879, [ii], **8**, iii, 3487; Dennstedt and Büinz, *Zeitsch. angew. Chem.*, 1908, **21**, 1825).

It may be recalled that years ago the popular idea was that the spontaneous combustion of coal was due solely to the presence of pyrites in the coal. This theory was overthrown mainly by the classical researches of Richters (*Ding. Poly. J.*, 1868, **190**, 398; 1869, **193**, 54, 264; 1870, **195**, 315, 449; **196**, 317; for summary see Wagner's "Jahresbericht über die Fortschritte der Chemischen Technologie," 1870, **16**, 758) and Fayol (*loc. cit.*), but was brought into prominence again by the investigations of Haldane and Meachem (*T. Inst. Min. Engrs.*, 1898, **16**, 491; compare, however, Harger, *ibid.*, 1913, **44**, 318) and upheld by Jeffries (*T. Inst. Min. Engrs.*, 1905, **29**, 532).

The generally accepted view among coal-mining men at the present time seems to be that little importance is to be attached to the presence of pyrites and that a sufficient explanation of spontaneous combustion is to be found in the rapidity with which coal absorbs oxygen and heats. Interesting information on this point is contained in the Minutes of Evidence (February 12th—July 16th, 1913) given before the Departmental Committee on Spontaneous Combustion in Coal Mines.

Dissemination throughout the rock of carbonaceous matter intimately mixed with finely divided pyrites is regarded as a determining factor in the production of fires in iron mines (compare Higgins, Bureau of Mines, U.S.A., Technical Paper 59), yet despite the fact that the conditions of its occurrence are largely identical with those in a coal mine, many investigators protest

against the inclusion of pyrites even as a contributory factor in coal-mine fires.

A series of experiments was devised therefore to ascertain definitely the effect produced by the presence of iron pyrites on coal. Before conducting the experiments, the question arose as to whether moist or dry air should be the oxidising medium, and on seeking information on this point the conclusions arrived at by various investigators are as conflicting as those given in regard to the question of the iron pyrites. Thus moisture is considered to act as a deterrent to spontaneous combustion by Richters (*loc. cit.*) and the New South Wales Commission, 1896—1900 (see Threlfall's description of the experiments, *J. Soc. Chem. Ind.*, 1909, **28**, 759); Fayol (*loc. cit.*) states that its influence is unobservable; whilst the weight of the evidence given by witnesses before the British Royal Commission, 1876 (inquiring into the causes of spontaneous combustion of coal) is heavily in favour of the opinion that moist coal is more liable to ignite than dry coal (compare letter to Commission from Mr. Poole, Inspector of Mines of Nova Scotia). This view is upheld by Lewes (*loc. cit.*), Mahler (*Ann. des Mines*, 1913, [ii], **4**, 163), and Winmill (*T. Inst. Min. Engrs.*, 1915, **48**, iii, 503). Recently Graham (*T. Inst. Min. Engrs.*, 1915, **49**, 35) has shown that coal-dust when moist absorbs oxygen at a rate approximately half as great again as that of dry dust.

The variety of opinion regarding the influence of moisture seems to be due to the meaning to be attached to the term "dry" coal. Coal containing its natural moisture is, from a chemical point of view, wet, but is considered dry by the New South Wales Commission. In fact, it is doubtful whether the results of the experiments conducted by this Commission are so conclusive that the views of the British Commission, 1876, "must now be definitely abandoned," for the coal used as dry coal contained its natural moisture, amounting to 2·2 per cent., whilst the wet coal was saturated by playing a stream of water on it.

Probably the view held at present in the mining world is correct, namely, that moisture plays an important part in, and accelerates, the oxidation of the coal. It is considered, however, that an excessive amount of water retards spontaneous combustion in two ways. First, the water enters the pores of the coal and so renders it less pervious to the air, and secondly, the temperature is kept low by evaporation.

A moist atmosphere is practically essential for the oxidation of the iron pyrites, and the author judges that it would also be favourable for the oxidation of the coal. With a moist atmo-

sphere the coal would not become unduly wetted or dried, but would retain its natural moisture throughout the experiment.

### EXPERIMENTAL.

The experimental work is divided into two sections.

Part I. deals with the influence of iron pyrites on the oxidation of coal to carbon dioxide.

Part II. gives an account of the effect of iron pyrites on the absorption of oxygen by the coal.

### PART I.

In order to ascertain the influence of iron pyrites on the oxidation of coal to carbon dioxide, the oxidation products of:

- (i) Pyrites;
- (ii) Coal;
- (iii) An artificial mixture of pyrites and coal;
- (iv) Ferrous sulphate;
- (v) A mixture of ferrous sulphate and coal;
- (vi) A mixture of sulphuric acid and coal,

were determined.

The coal used in the experiment was a specially selected sample of "King" coal from the Pemberton Colliery, near Wigan. In this seam of coal no case of spontaneous combustion has ever occurred.

Owing to the possibility of the coal absorbing oxygen rapidly when freshly mined, this sample was kept from 1913 to 1915. In this way it was thought possible to have eliminated any uncontrollable factor which might have caused a variation in the coal between the experiments.

A complete analysis of the coal was made in 1915.

#### *Ultimate Analysis.*

Carbon.....	76.020	per cent.
Hydrogen .....	5.076	" "
Nitrogen .....	1.364	" "
Sulphur .....	1.358	" "
Ash .....	4.750	" "
Oxygen, etc. (by difference) .....	11.432	" "
	<u>100.000</u>	

#### *Proximate Analysis.*

Coke .....	62.99	per cent.
Ash .....	4.75	" "
Moisture .....	1.329	" "

*Analysis of Ash.*

Silica .....	38.72	per cent.
Alumina .....	25.15	" "
Iron sesquioxide.....	21.87	" "
Sulphate (SO <sub>4</sub> ) .....	6.71	" "
Lime .....	3.96	" "
Magnesia .....	trace	
Undetermined constituents .....	3.59	" "
	<hr/>	
	100.00	
	<hr/>	
Specific gravity of coal =	1.280	

The pyrites was a selected sample and was free from carbonates.

*Analysis of the Pyrites.*

Silica.....	1.20	per cent.
Iron .....	46.38	" "
Sulphur.....	51.84	" "
Copper.....	trace	
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	99.42	
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Specific gravity of pyrites =	4.97	

The analysis of the pyrites showed an excess of 1.02 per cent. of iron, and if it is assumed that this excess is present in the pyrites as the sesquioxide, an additional 0.44 per cent. of oxygen is introduced. This would bring the total for the analysis to 99.86.

A finely divided sample of the pyrites was exposed to the air of the laboratory for three months. A microscopic examination then showed that about one quarter of the powder was completely oxidised, whilst the remainder still retained the brassy lustre. The pyrites therefore seemed to be mixed, so far as its resistance to the oxidising action of the air was concerned.

The apparatus in which the oxidation was carried out was of the form of a large horizontal condenser, and consisted of a glass tube (140 × 3.75 cm.) surrounded by an iron tube (125 × 5 cm.) as jacket. Steam was passed through the annular space between the two tubes.

Fifty grams of the material for oxidation were placed in the spaces between five wet glass-wool plugs, which were introduced to keep the air moist during its passage through the inner tube. The air was drawn through the tube by means of a filter pump at the rate of about 1½ litres per hour, and was freed from carbon dioxide and sulphur dioxide before entering. On leaving the inner tube, the air bubbled through three absorption bulbs containing potassium hydroxide, in which the carbon dioxide and

sulphur dioxide resulting from the oxidation of the material in the tube were collected.

During the experiments, each of which occupied thirty-six hours, steam was blown through the iron jacket, with the result that the temperature of the air leaving the inner tube varied from  $36^{\circ}$  to  $39^{\circ}$ , having entered at  $15-18^{\circ}$ .

At the close of each experiment the contents of the tube and the absorption bulbs were tested for oxidised products. The results were corrected for the "blank" estimations which were made in all possible cases.

In experiments (i) to (iii) the oxidised iron and sulphur in the residue in the tube were extracted with air-free, dilute hydrochloric acid, whilst in experiments (iv) to (vB) the amount of iron oxidised to the ferric state was estimated volumetrically, and is given as a percentage of the total iron present.

The results, calculated for the specified weights of the substances, are tabulated below.

EXPERIMENT	i.	ii.	iii.	iv.	vA.	vB.	vi.
Substances for oxidation.	100 Grams of pyrites.	100 Grams of coal.	Mixture of 100 grams of pyrites and 100 grams of coal.	100 Grams of ferrous sulphate.	Mixture of 100 grams of coal and 100 grams of ferrous sulphate.	Mixture of 100 grams of coal and 5.26 grams of ferrous sulphate.	Mixture of 100 grams of coal and 10 c.c. of dilute sulphuric acid (1 in 10).
Iron oxidised ...	Gram. 0.6510	c.c. —	Gram. 0.5240	Per cent. 82.39	Per cent. 79.68	Per cent. 52.79	c.c. —
Sulphur oxidised to $\text{SO}_4$ .....	0.5730	—	0.3225	—	—	—	—
Sulphur oxidised to $\text{SO}_2$ .....	0.1405	—	0.2786	—	—	—	—
Total sulphur oxidised .....	0.7135	—	0.6011	—	—	—	—
Carbon dioxide.	—	24.17	c.c. 82.8	—	c.c. 8.17	c.c. 45.6	18.8

*Discussion of the Results.*

(i) In this experiment it would be expected that if 0.7135 gram of sulphur of the iron pyrites were oxidised, 0.6243 gram of iron would become soluble in the acid. The amount actually determined was higher. This may be due to the pyrites becoming more finely divided, so that a larger quantity of the excess of iron (1.02 per cent.) in the pyrites would be available to the action of the acid than in the blank determination on the ordinary sample.

An analysis of the solution extracted with the air-free, dilute hydrochloric acid from the pyrites left in the tube indicated the presence of almost pure ferric sulphate.

From this it may be concluded that under the conditions of the experiment and in the absence of carbonaceous matter the pyrites oxidises to form ferric sulphate.

(ii) No oxidation of the iron and sulphur, which occur naturally in the coal in small quantities, could be detected.

(ii and iii) The analysis of the solution extracted in experiment (iii) indicated that the oxidation of pyrites under the conditions of the experiment and in the presence of carbonaceous matter is mainly to give ferrous sulphate.

The most notable point was the increase in the evolution of carbon dioxide from 24.17 c.c. to 82.8 c.c. The liberation of carbon dioxide seemed peculiar, for some investigators (compare Parr and Kressmann, Bulletin No. 46, University of Illinois) state that there is no liberation of oxidised gaseous products from coal until the temperature reaches 100° or above. Contrary views are also held (compare Cox, *Philippine J. Sci.*, 1912, **7**, 297; Winmill, *T. Inst. Min. Engrs.*, 1914, **46**, 563). It may be noted that the portion of the coal in contact with the tube might have its temperature raised to this value, although the temperature of the air passed over it never exceeded 39°.

Another point to be noted is that in the experiment with the pyrites alone, more of this mineral was oxidised than when it was mixed with coal. This may be due to two factors: first, the coal may have exercised a deterrent effect by absorbing the oxygen; secondly, the ventilation of the mixture may not have been so effective, for the volume of 50 grams of the mixture exceeded the volume of the same weight of powdered pyrites.

(iv and v) These experiments were conducted in order to determine whether the iron compounds produced by the oxidation of the pyrites caused an increase in the volume of carbon dioxide liberated.

In experiment (vA) a small volume was obtained, but this was probably due to the fact that after a few hours the coal was saturated, and was finally submerged. The experiment was repeated (vB) with a mixture containing 5 per cent. of ferrous sulphate, and from this mixture the volume of carbon dioxide collected rose to 45.6 c.c., whilst the percentage of iron oxidised to the ferric state only reached 52.79. Again, in this experiment the coal appeared moist after about twenty-nine hours, but the result seems sufficient to show that the ferrous sulphate increases the liberation of carbon dioxide by the coal.

(vi) The results of this experiment indicate that any sulphuric acid produced by the oxidation of the pyrites would not aid in the production of carbon dioxide. The volume of carbon dioxide liberated in this case was far below that obtained from the coal alone. This may be due to the dilute sulphuric acid filling the pores, and thus preventing the oxygen of the air from penetrating the coal-dust.

## PART II.

Experiments were conducted to determine how the admixture of iron pyrites, ferrous sulphate, and sulphuric acid with the coal influenced its absorption of oxygen.

Six large flasks of almost equal volume were clamped horizontally and fitted with rubber stoppers, through which passed glass tubes 120 cm. long. These were bent at right angles 10 cm. from the flask and their ends dipped under water so that the absorption of oxygen could be measured by the rise of the water up these tubes. Had the absorption proved large, the ends could be immersed in mercury so that the flasks should not be flooded with water. The absorption of oxygen by the sample of "King" coal, however, was exceptionally small; incidentally, this may account for the fact that no case of spontaneous ignition has occurred in this seam.

Into five of the flasks were placed 50 grams of the following powders: "King" coal, iron pyrites, a mixture of equal weights of iron pyrites and coal, ferrous sulphate, and a mixture of coal with five per cent. of ferrous sulphate, whilst the sixth flask contained a mixture of 50 grams of coal with 5 c.c. of dilute sulphuric acid (1 in 10).

The sample of "King" coal was mined in the morning and brought to the laboratory early in the afternoon. Four large pieces of coal (about 22.5 cm. cube) were broken open and the central portions of about 70 grams were taken from each. This coal was rapidly powdered, sieved, mixed as stated above, and

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placed in the flasks. The time taken for this operation amounted to about eleven minutes. An analysis of the sample is given below.

*Ultimate Analysis.*

Carbon.....	81.069	per cent.
Hydrogen .....	5.666	" "
Nitrogen .....	1.088	" "
Sulphur .....	1.042	" "
Ash .....	3.338	" "
Oxygen, etc. (by difference) .....	7.797	" "
	<u>100.000</u>	

*Proximate Analysis.*

Coke .....	62.085	per cent.
Ash .....	3.338	" "
Moisture .....	2.269	" "

Specific gravity of the coal = 1.291

A wide boat containing freshly slaked lime was placed in each flask to absorb any carbon dioxide which might be evolved, and to keep the air moist a wet glass-wool pad was introduced into each of the necks of the flasks. At the close of the experiments a test made for methane showed it to be entirely absent.

The volume of air in each of the flasks was determined. Readings of the atmospheric pressure, temperature (which varied from 13.2° to 15.8°), and the level of the water in the tubes were taken every three hours during the daytime for seven days. From these readings the volumes of oxygen absorbed by the specified weights of material were calculated, and are recorded in c.c. in the table on page 731.

In the diagram (p. 732) only the results up to the forty-eighth hour are shown, as from the thirty-sixth hour the graphs become almost straight lines. The curves are obtained by plotting the results as follows: curve I from the results in column (c), II from the sum of (a) and (b), III from (e), IV from (f), and V from (b).

*Discussion of the Results.*

Since curve I rises more rapidly than curve II, it would appear that mixing the iron pyrites with the coal causes the absorption of oxygen to be more vigorous at first. After the absorption of about 34 c.c. of oxygen the two curves become almost parallel straight lines, showing that the iron pyrites has ceased to increase the rate of oxidation.

The course of the oxidation of iron pyrites is first to form



HOURS.	(a) 50 Grams of coal.	(b) 50 Grams of iron pyrites.	(c) Mixture of 50 grams of coal and 50 grams of iron pyrites.	(d) 2.5 Grams of ferrous sulphate.	(e) Mixture of 50 grams of coal and 2.5 grams of ferrous sulphate.	(f) Mixture of 50 grams of coal and 5 c.c. of dilute sulphuric acid (1 in 10).
3	3.8	0.3	6.1	—	6.5	2.5
6	7.5	0.7	11.1	—	12.0	3.3
18	23.2	0.8	29.3	—	23.9	8.1
21	26.2	0.9	30.9	—	24.5	8.7
24	29.0	1.0	32.5	—	24.6	8.9
27	30.5	1.0	34.0	0.05	24.7	9.9
30	31.8	1.2	35.0	—	24.8	10.3
42	33.1	1.4	36.6	—	25.1	11.0
45	33.2	1.5	37.1	—	25.3	11.0
48	33.5	1.5	37.6	0.01	25.5	11.3
51	33.6	1.6	37.9	—	25.6	11.4
54	33.8	1.7	37.9	—	25.7	11.5
66	34.8	2.1	39.5	—	26.0	11.7
69	35.0	2.2	39.7	—	26.1	12.0
72	35.3	2.2	40.2	—	26.3	12.4
75	35.5	2.3	40.3	—	26.5	12.5
78	35.6	2.5	40.7	0.15	26.5	12.5
90	36.3	2.7	41.6	—	27.0	12.6
93	36.7	2.8	42.2	—	27.0	12.6
96	36.7	2.9	42.4	—	27.0	12.7
99	37.0	3.0	42.6	—	27.1	12.8
102	37.2	3.0	42.9	—	27.5	12.9
114	38.2	3.4	44.1	—	28.0	13.4
120	38.6	3.5	44.8	0.2	28.1	13.5
144	40.3	4.2	47.0	0.25	28.8	14.6
168	41.2	5.0	49.1	0.3	29.7	15.2

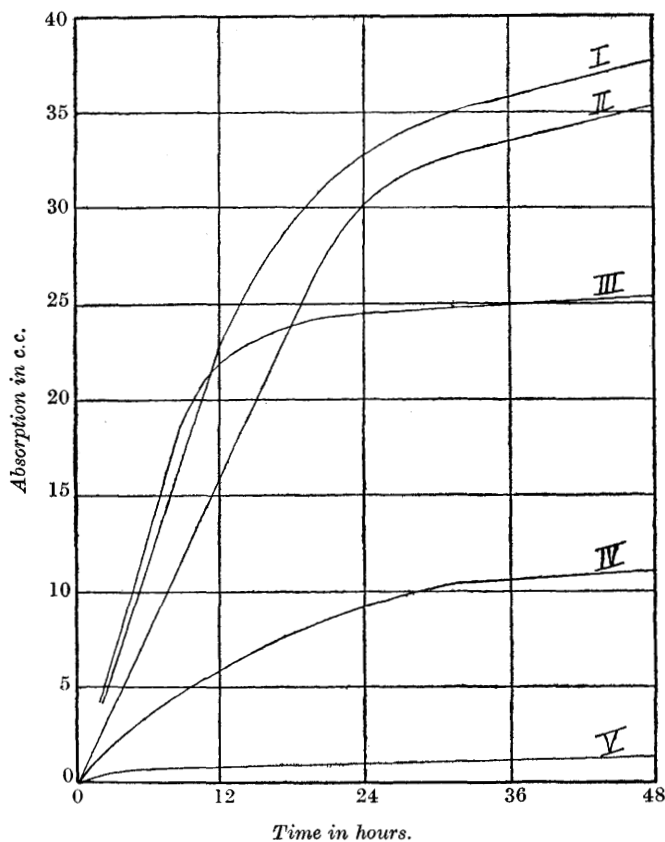
ferrous sulphate and finally to give ferric sulphate. Richters' suggestion that the ferric sulphate is reduced by contact with the coal seems feasible, for by alternate oxidation and reduction the iron may act as an oxygen carrier to some particular compound in the coal. When this compound is oxidised, the iron ceases to possess catalytic properties and the oxidation becomes an additive process.

Another point in connexion with this suggestion is that apparently the most readily oxidised material of the coal is the one to which the iron behaves as an oxidising agent. (For the catalytic effect of ferruginous compounds in coal, compare Dennstedt and Hassler, D.R.-P., 203848.)

If it is assumed that the presence of iron compounds increases

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the rate of oxidation (compare von Meyer, Lamplough, and Hill, *loc. cit.*), it is difficult to explain satisfactorily the curve III. At first the oxidation took place the most rapidly, but then fell off to a slower rate than for coal alone. This peculiarity may be due to the fact that the ferrous sulphate tended to cause the



mixture to form into a cake, and thus may have considerably reduced the rate of absorption of oxygen.

Curve IV indicates that sulphuric acid is a deterrent to the oxidation of the coal. An explanation of this may be that the coal, by being moistened with the acid, was rendered less pervious to the air, and therefore the absorption proceeded at a slower rate.

*Conclusion.*

Iron pyrites has a minor effect (compare Porter and Ovitz, Bureau of Mines, U.S.A., Technical Paper 16), but because coals which cannot be regarded as pyritic are among those most liable to spontaneous ignition (compare Commission of the New South Wales Government, 1896—1900; *T. Inst. Min. Engrs.*, 1900, **19**, 546) it cannot be inferred that its presence may be ignored.

It is very difficult to draw any conclusions from the percentage of sulphur which a coal contains, for pyrites disseminated throughout the coal in microscopical particles will act more effectively than larger quantities of nodular pyrites.

To make any inferences from the analyses of coals from various collieries, even though the samples be from the same seam, is almost impossible, for great differences may exist in the physical conditions under which the coal occurs. Any one of these conditions, for example, a fault or a poor roof, may have a more predominating influence on the question of the ignitibility of the coal than its percentage of sulphur. It is therefore with the view of drawing no conclusions that the author points out that in the majority of cases of spontaneous combustion mentioned in the Minutes of Evidence (February 12th—July 16th, 1913) given before the Departmental Committee on Spontaneous Combustion in Coal Mines, in which the pyrites question is broached, this mineral is stated to be found in the finely disseminated form.

The results of the experiments appear to indicate that pyrites, although a subsidiary factor, is not entirely negligible. A protest therefore may be made against the common practice of disregarding the influence of pyrites on the spontaneous ignition of coal.

In concluding, the author wishes to express his thanks to E. B. Naylor, Esq., Head of the Chemistry Department, and to G. Hunter, Esq., Head of the Mining Department, for the interest they have shown during the course of the experiments.

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