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THE *OXIDATION OF *PYRITES ASSOCIATED WITH SOUTH AFRICAN COALS

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— *by* —

R. F. J. TEICHMANN, M.Sc.

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THE OXIDATION OF PYRITES ASSOCIATED WITH SOUTH AFRICAN COALS.

By R. F. J. Teichmann (Associate).
(Fuel Research Institute of South Africa).

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The influence of pyrites on the spontaneous heating of coal has been studied by many investigators, with results that are so conflicting that no general conclusions can be drawn therefrom. Much of the disagreement is probably due to variations in the properties of pyrites from different sources. Great differences in the rate of oxidation of pyrites, marcasite and pyrrhotite have been established and variations within these categories due to variations in physical structure or to the presence of impurities, which may act as catalysts, are also possible.

Review of Literature.

Macpherson, Simpkin and Wild (1) and Parr and Hamilton (2) conclude from their investigations that the main role of pyrites in the spontaneous oxidation of coal is a physical one in that the pyrites, on oxidation, expands and disintegrates the coal, thus rendering it more liable to self-ignition. Stopes and Wheeler (3), Winmill (4) and Davis and Reynolds (5) believe that, in general, the oxidation of the coal substance is by far the major factor in the ultimate self-ignition of coal, and that oxidation of pyrites associated with the coal is only a contributing factor and then only when the pyrites is present in a finely-divided state and in considerable proportions. Graham (6) and Miyagawa (7), however, conclude that frequently the oxidation of pyrites is the dominating factor in the initial heating of coal. Graham further says: "At the same time if it were possible to take a census of all underground heatings and ascertain the primary cause of each, the majority would, I believe, be traced to the oxidation of the carbonaceous constituents of the coal." Coals which contain a very small amount of pyrites (·5 per cent.) have been known to fire spontaneously. The presence of large proportions of pyrites are, therefore, not necessary for self-ignition. Drakeley (8) suggests that where a coal which contains only ·5 per cent. pyrites takes fire spontaneously, the pyrites may catalytically promote the oxidation of the coal substance. For such action to take place it would be necessary for ferrous sulphate to act as a carrier of oxygen. This catalytic action has not, however, been proved to take place in the oxidation of coal.

Li and Parr (9) conclude that, under certain conditions, the rate of oxidation of pyrites in stored coal may be sufficient to produce sufficiently high local temperatures (75–85° C.) to initiate the rapid oxidation of the carbonaceous material. They also show that the increase in the rate of oxidation with increasing temperature is greater for pyrites than for marcasite; but conclude that pyrites or marcasite is seldom responsible for cases of spontaneous ignition of coal underground. Davis and Byrne (10) also conclude that pyrites has but a small influence on the oxidation of coal.

Lomax (11) after studying the oxidation tendency of various forms of pyrites (crystalline, massive, nodular, stringy, granular, globulitic) finds that some of these forms oxidise rapidly and may be classed as dangerous, whereas others, under normal conditions, are harmless. The findings of the Committee on the Spontaneous Combustion of Coal in Mines (12) are that :—"Great differences exist in the relative oxidisability of different forms of pyrites in coal, some forms being rapidly converted into sulphate of iron, others being practically immune from oxidation, the crystals remaining bright and defined for many years."

A report of a similar nature was issued by the Fuel Research Station (13) in a special bulletin on "Fires in Steamship, Bunker and Cargo Coals." They state that "the physical condition of the pyrites is of great importance. Finely divided pyrites may oxidise rapidly owing to the rapid increase in its rate of oxidation with rise in temperature and to its low specific heat. Such local heating undoubtedly tends to assist the action taking place in the coal substance. Where pyrites occurs in lump or vein forms (coal brasses), the tendency to oxidation is reduced, and pyrites in this form may be regarded as practically inactive."

Winchell (14) found that some oxidation of pyrites, through which aerated water percolates, does take place, but the reaction is very slow. Segal (15) states that when pyrites, marcasite or pyrrhotite was treated with magnesium chloride solution (56 grms./100 grms. H_2O) the acidity increased. The reaction is rapid and quickly reaches equilibrium. Pyrites is most reactive; pyrrhotite least. Pyrites and pyrrhotite are more reactive at 90° than at 22° C., while the reverse holds with marcasite.

Lategan (16), in investigating the rates of oxidation of Witbank coals, could find no evidence of sulphate formation, and concluded that the pyrites in these coals plays no part in their spontaneous oxidation.

In reviewing the literature, it appears that most investigators agree that certain crystalline forms of pyrites when present in a finely divided state are amenable to oxidation, and may consequently contribute to the ultimate spontaneous ignition of coal. The presence of water is stated by certain workers to be necessary for the oxidation process. This process, according to Tideswell (17), is usually represented by the equation $2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2H_2SO_4 + 2FeSO_4$. They add that further oxidation to ferric sulphate may finally take place.

Winmill (4) gives the same equation, and also the following equation for the oxidation to ferric sulphate :—

$$4FeS_2 + 15O_2 + 2H_2O = 2Fe_2(SO_4)_3 + 2H_2SO_4$$

He states: "This (latter) reaction does not take place to any considerable extent until all the pyrites has disappeared, for ferric sulphate in a slightly acid solution to which pyrites has been added is fairly quickly reduced to ferrous sulphate, although the reduction is not complete. The reaction is a complex one in which some free sulphur is produced."

For pyrites to exert any appreciable effect on the spontaneous heating of coal, it must produce a considerable quantity of heat during its oxidation. From the heats of combustion of iron and sulphur, Haldane and Meachem (18) calculated the heat of oxidation of pyrites to be 4·5 calories per c.c. of oxygen absorbed. Parr and Kressman (19) calculated a value of 4·1 calories per c.c. of O_2 absorbed. Winmill (4) calculates a figure of 4·3 calories per c.c. of oxygen absorbed if no ferric salts are formed, and states that "if ferric salts are produced to any extent this quantity of heat would be increased, but probably only to a very slight extent."

A direct determination by Winmill (4) of the quantity of heat evolved by the oxidation of pyrites gave a value of 4·5 calories per c.c. of oxygen absorbed. Winmill concludes that "the best value for the heat of oxidation under conditions such as exist in a mine would seem to be 4·3 calories per c.c. of oxygen absorbed."

The specific heat of coal is 0·27 cals./grm. Under ideal conditions for the conservation of the heat produced, the heat required to raise the temperature of 100 grms. of coal from 20° C. to 80° C. would, therefore, be generated by the oxidation of 0·6 grms. of pyrites to ferrous sulphate.

Object of Investigation.

The present investigation was undertaken to determine the rates of oxidation of samples of pyrites obtained from South African coal seams in order to ascertain whether any of the forms of associated pyrites are likely to be contributing factors in the spontaneous ignition of the coal. The investigation was limited to the study of the rates of oxidation in the presence of moisture and air or oxygen at room temperature and at 105° C.

EXPERIMENTAL.

The investigation was carried out along the following lines :—

1. In the first series of experiments samples of pyrites, coal and coal-pyrites mixtures were oxidised at 105° C. in a stream of moist oxygen ; the rate of increase in the sulphate sulphur content of the pyrites was used as a measure of the rate of oxidation of the sample.

2. In the second series of experiments finely divided pyrites was kept in suspension in water or aqueous solutions by means of a constant stream of air passing through the solution. The oxidation of the pyrites formed sulphuric acid, and the rate of oxidation was measured by the rate of change of PH of the solution.

1. *Oxidation of Pyrites at 105° C.*

The samples of pyrites used in the tests were obtained from coals prepared for shipment and railway consumption and from freshly mined coal collected from the picking belts. The pyrites consisted of the crystalline and very finely divided stringy form associated with coals, and was usually finely disseminated throughout the coal substance.

The samples of pyrites from prepared coals were obtained by crushing samples of the coal to -60 mesh and separating the heavier, non-coaly fraction by means of carbon tetrachloride of a specific gravity of 1·6.

The pyrites from the freshly mined coal was obtained by selecting lumps of round coal in which finely divided pyrites was visible and shattering these by dropping them repeatedly from a height of about 6 ft. until 10 lbs. of $-\frac{1}{4}$ in. material was collected. This fine material, in which the visible pyrites was concentrated, was then ground to -60 mesh and the coaly constituents floated off in carbon tetrachloride of a specific gravity of 1·6.

TABLE 1.—ORIGIN AND DESCRIPTION OF SAMPLES.

Sample Number.	Origin of Coal and Pyrites.	Nature of Sample.
A	Landau Colliery, Witbank, Tvl.	Pure Pyrites
B	Coronation Colliery, Witbank, Tvl.	Pure Pyrites
C	Douglas Colliery, Witbank, Tvl.	Pyritic Coal
D	Douglas Colliery, Witbank, Tvl.	Pure Pyrites
E	Phoenix Colliery, Witbank, Tvl.	Pure Pyrites
F	Durban Navigation Colliery, Natal	Pure Pyrites
G	Durban Navigation Colliery, Natal	Pure Pyrites + Coal Mixture
H	Landau Colliery, Witbank, Tvl.	Pure Pyrites A + Coal Mixture
K	Cambrian Colliery, Klipriver, Natal	Pure Pyrites
L	Marsfield Colliery, Breyten, Tvl.	Pure Pyrites
M	Coronation Colliery, Witbank, Tvl.	Pure Pyrites
KC	Cambrian Colliery, Klip River, Natal	Coal
LC	Marsfield Colliery, Breyten, Tvl.	Coal
MC	Coronation Colliery, Witbank, Tvl.	Coal
KM	Cambrian Colliery, Witbank, Tvl.	50% Coal KC + 50% Pyrites K (Mixture).
LM	Marsfield Colliery, Breyten, Tvl.	50% Coal LC + 50% Pyrites L (Mixture)
MM	Coronation Colliery, Witbank, Tvl.	50% Coal MC + 50% Pyrites M (Mixture)
N	Northern Natal Navigation Colliery, Paulpietersburg, Natal	Pure Pyrites

To obtain the pure pyrites used in the oxidation tests, the sink from the separation at a specific gravity of 1·6 was ground to pass —200 mesh I.M.M. and floated in bromoform (S.G. 2·8). The pyrites which has a S.G. of 4·5 and therefore sinks, was washed well with alcohol, dried rapidly and stored in sealed containers. The pyrites obtained in this way is practically 100 per cent. pure. A microscopic examination revealed only traces of carbonaceous material and no marcasite was found in any of the samples examined.

Oxidation tests were made on samples of pure pyrites prepared in the manner described, on samples of the original coal before the pyrites had been removed and on mixtures of these. The coal was ground to —60 mesh for the purpose of these tests. The artificial mixtures consisted of equal parts of the original coals (—60 mesh) and the pure pyrites (—200 mesh) extracted from another portion of the same coal sample. Details of the samples used are given in Table 1.

Samples B, E, F, K, M and N were obtained from samples of coal as prepared for sale ; samples A, C, D, F and L were obtained from samples of coal, showing pyrites, selected from the picking belts.

Experimental Procedure.

Approximately 12 grms. of each sample was weighed out into a flat silica dish and spread out in a layer not more than ⅛ in. deep. The dishes were heated to 105° C. in an oven jacketed with a boiling solution of glycerine in water. The door of the oven was tightly closed and oxygen saturated with moisture was passed over the pyrites at a constant rate through a spiral pipe immersed in the jacket solution. The duration of each series of oxidation tests was six weeks. After the first, second, fourth and sixth weeks, the extent of the oxidation was estimated by determining the sulphate sulphur content of 1-gram samples taken from each dish. A representative sample for the sulphate determination was obtained by first pouring the whole contents of the silica dish through a funnel several times, then spreading the material in a thin layer and taking out 1 gram in ten increments spaced evenly over the surface of the material. The close agreement between duplicate samples taken in this way showed that they were truly representative of the whole mass.

The method at first employed for the estimation of the sulphate sulphur was that described by Powell and Parr (18). The method consists in extracting the coal or pyrites with 3 per cent. hydrochloric acid

TABLE 2.—INCREASE IN SULPHATE SULPHUR CONTENT OF SAMPLES DURING SIX WEEKS OXIDATION.

Sample Number.	Per Cent. Sulphate Sulphur.				
	Original.	After 1 Week.	After 2 Weeks.	After 4 Weeks.	After 6 Weeks.
A	1·99	2·55	2·86	3·12	3·32
B	2·72	3·11	3·27	3·35	3·46
C	3·29	3·82	4·19	4·43	4·75
D	1·71	2·31	2·63	2·89	3·03
E	1·35	1·64	1·87	2·08	2·31
F	Trace	·33	·63	·99	1·40
G	Trace	·27	·50	·73	·98
H	Trace	·43	·67	·90	1·07
K	·12	·25	·38	·58	·77
L	·16	·22	·53	·69	·84
M	·30	·35	·51	·77	1·00
KC	Nil	·22	·29	·37	·51
LC	Nil	·08	—	·37	·42
MC	Nil	·17	·30	·36	·45
KM	·06	·27	·43	·55	·76
LM	·08	·33	·45	·59	·69
MM	·15	·33	·55 3rd	·76	·90
N	·35	1·20	1·49 1·79	—	—

at 60° C. for 40 hours, and after filtration, the sulphate is determined as barium sulphate.

Preliminary tests disclosed that this method gave variable results, which were in all cases too high. This method was, therefore, abandoned and a method developed which gave consistent and correct results. This latter method consists in extracting the pyrites for 30 minutes with boiling hydrochloric acid of specific gravity 1·08, filtering and determining the sulphate in the filtrate as barium sulphate. (See Appendix 1.)

The results of the tests made are recorded in Table 2, and certain of them are shown graphically in Fig. 1.

From these results it is evident that the rate of oxidation is greatest during the first week. During the second week it decreases slightly to a value which remains practically constant from the third week onwards. This phenomenon may be due to the removal during the early stages of the oxidation of the finest portions of the material, or it may have its explanation in the observations of Li and Parr (10), who show that the rate of increase in the rate of oxidation with temperature is greater for pyrites than for marcasite. If the pyrites samples contained a proportion of marcasite, then the sulphate present in the samples at the beginning of the test might be due to the oxidation at room temperature of this easily oxidised variety. On heating to 105° C., the rate of oxidation of the pyrites variety becomes appreciable. During the first two weeks

Fig I

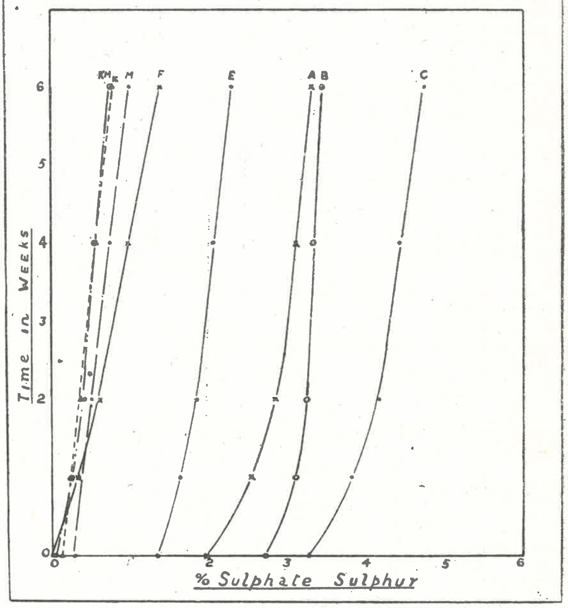
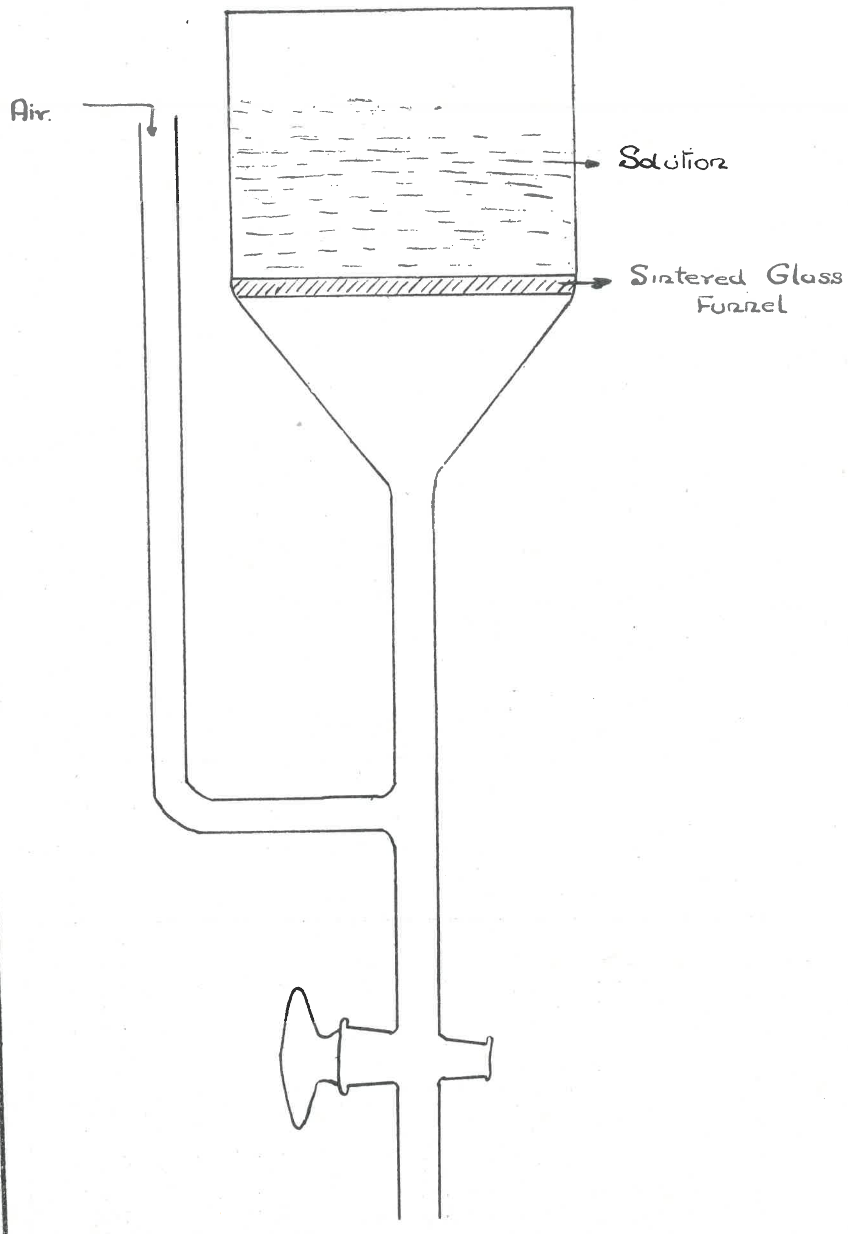


TABLE 3.—CALCULATED PER CENT. PYRITES OXIDISED AND PER CENT. SULPHATE FORMED.

Sample Number.	Per Cent. Pyrites in Sample.	Per Cent. Sulphate S. Formed in 6 Weeks.	Per Cent. Original Pyrites Oxidised to Sulphate in 6 Weeks.	Calculated Per Cent. Sulphate Sulphur Formed.
A	100	1·33	1·33	—
B	100	0·74	0·74	—
C	—	1·46	—	—
D	100	1·32	1·32	—
E	100	0·96	0·96	—
F	100	1·40	1·40	—
G	100	0·98	0·98	—
K	100	0·65	0·65	—
L	100	0·68	0·68	—
M	100	0·70	0·70	—
KC	2·43	0·51	21·00	—
LC	1·87	0·42	22·50	—
MC	1·12	0·45	40·20	—
KM	51·2	0·70	1·37	1·13
LM	50·9	0·61	1·20	1·08
MM	50·6	0·75	1·48	1·14

Fig. II



both pyrites and marcasite oxidise until the marcasite is consumed and thereafter the pyrites alone oxidises at a constant rate. This hypothesis assumes the presence of marcasite (which was not detected under the microscope) or of some other modification having similar properties.

The rate of oxidation of mixtures of pyrites and coal is, in most cases, more rapid than the rate obtained by calculation from the individual constituents. A similar phenomenon may often be observed in lumps of coal containing visible pyrites which have partly been oxidised by exposure to the air. In such lumps the oxidation of the pyrites is generally concentrated at the contact between pyrites and coal. That freshly ground coal adsorbs oxygen is well known, and it is possible that the increased oxidation of the pyrites is due to contact with the oxygen adsorbed on the surface film of the coal. In Table 3 are recorded the percentages of the pyrites in the test materials which had been oxidised after six weeks.

From the figures it is evident that pyrites associated with coal (KC, LC and MC) oxidises at a rate which is twenty times as great as the rate at which pure pyrites oxidises (A–M).

If the percentages of sulphur oxidised individually in the coal and in the pyrites are used to calculate what the percentage sulphur oxidised in the 50 : 50 mixtures of coal and pyrites (KM, LM and MM) would be, the values given in the fifth column of Table 3 are obtained. The percentages of oxidised sulphur actually found by experiment in the synthetic mixtures are shown in the fourth column of Table 3. These figures are greater than the calculated ones and the discrepancy is too large to be attributed to experimental error. It is evident, therefore, that the artificial mixing of coal and pyrites accelerates the oxidation to some extent. In the more intimate natural mixtures of coal and pyrites (KC, LC, MC) the acceleration is much greater. It would, therefore, appear that deductions made from the behaviour of pure pyrites cannot be directly applied to mixtures of coal and pyrites.

In all the tests made the actual amount of oxidation in six weeks is small, and in no case did the amount of sulphate sulphur formed exceed 1·5 per cent. of the original material. The oxidation of 1·5 per cent. sulphur is observed in the case of the natural pyritic coal C and is equivalent to the liberation of $\frac{(7 \times 22400 \times 4{\cdot}3 \times 1{\cdot}5)}{128} =$ 7,900 calories per 100 grms. of material in six weeks. If all this heat were retained by coal C, its temperature would have been raised 293° in six weeks.

From a visual examination of the oxidised pyritic coal C, however, the pyrites in it appears to be far less oxidised than lumps of oxidised pyritic coal observed underground in mines which at no time during their oxidation reached a temperature anywhere near 293° C. It is probable, therefore, that under any conceivable practical set of conditions by far the greater part of the heat generated would be dissipated, and the rise in temperature of the coal would be too small to promote spontaneous combustion.

2. *Oxidation of Pyrites suspended in Water and in Magnesium Chloride solutions.*

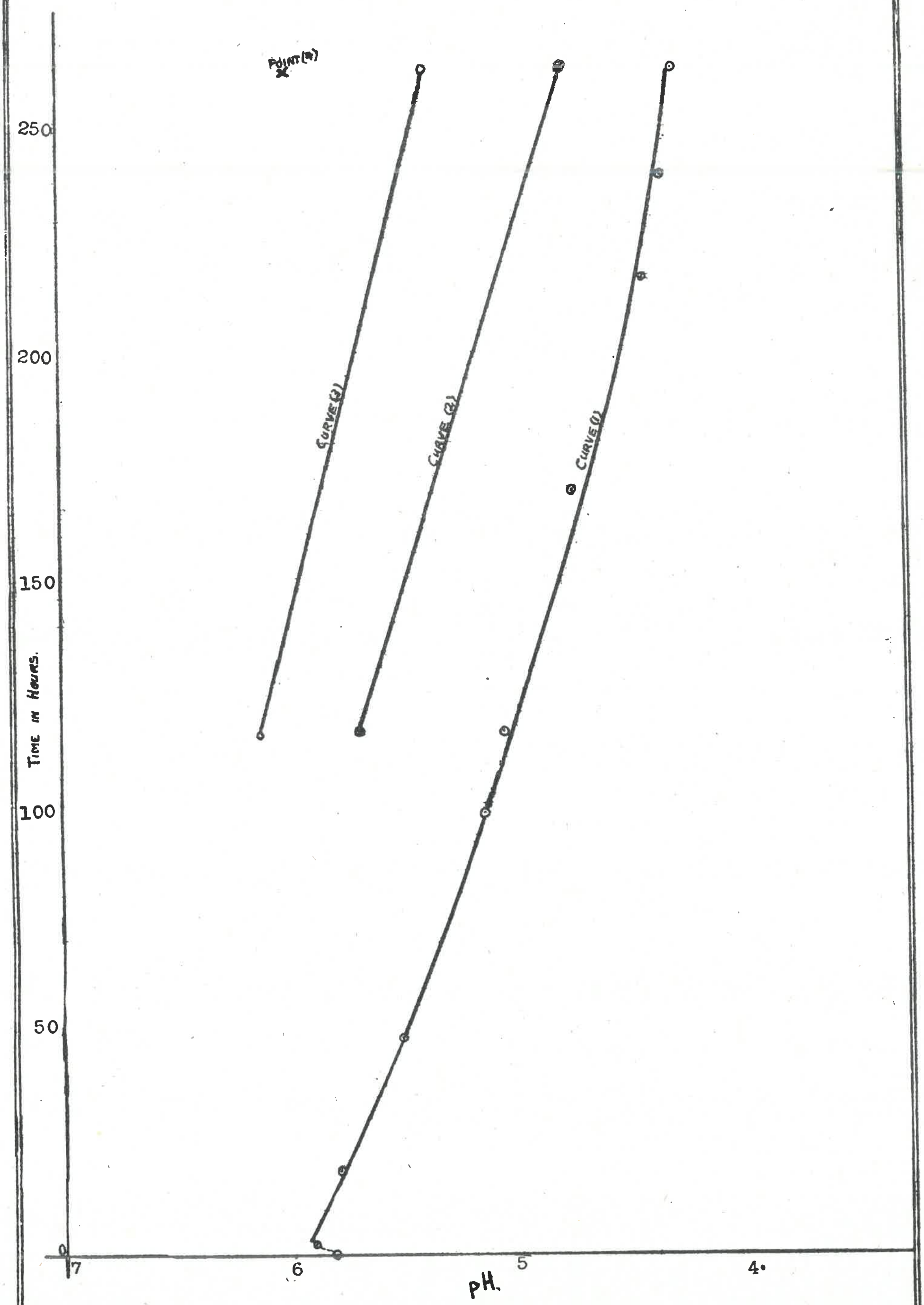
Segal (16) found that on stirring pyrites ground to −90 mesh with a solution of magnesium chloride a definite reaction takes place, resulting in an increase in the acidity of the solution. He measured the change in acidity of the solution with time by means of a quinhydrone electrode. The reaction was very rapid, the greatest change taking place in the first minute.

The oxidation obtained by Segal is much greater than that shown in the tests recorded in Table 2 (see page 5). It was, therefore, decided to investigate the rate of oxidation of pyrites samples obtained from coal under similar conditions to those used by Segal.

Experimental Procedure.

The apparatus used is sketched in Fig. 2. It consists of a sintered glass funnel (Schott and Gen. 17 G3) of 150 c.c. capacity, to the stem of which a side tube and tap had been fused. One or two grams of pyrites, together with 100 c.c. of water or solution, were placed in the funnel and the pyrites kept in suspension in the solution by means of a slow stream of air blown through the side tube. The acidity of the solution in the funnel was measured electro-metrically by

FIG. 3.


POINT (4)
250
200
150
100
50
TIME IN HOURS.
CURVE (3)
CURVE (2)
CURVE (1)
7
6
5
4
pH.

inserting a quinhydrone or glass electrode and connecting the solution by means of an agar-agar bridge to a saturated calomel electrode.

In order to determine whether, during the duration of a test, the continuous stream of air through the solution affected the stability of a quinhydrone electrode, the following tests were carried out. (*a*) 100 c.c. of a solution containing 43 grms. $MgCl_2$ per 100 c.c. were placed in the sintered glass funnel, quinhydrone was added and the solution aerated for 264 hours. The acidity of the solution was measured periodically by using a platinum electrode and an agar-agar bridge and measuring the potential difference of the cell. The electrode and bridge were removed after each measurement. The change of acidity of the solution with time is shown in curve 1, Fig. 3. (*b*) A similar solution to which the same amount of quinhydrone had been added was allowed to stand without aeration for the same period of time and the acidity measured at the start and after 116 and 264 hours. The results are shown in curve 2, Fig. 3. (*c*) A further quantity of the same solution was allowed to stand for 116 hours, quinhydrone was then added and the acidity measured then and after 264 hours. (*d*) A further quantity of the solution was allowed to stand for 264 hours, quinhydrone added and the acidity measured. The results of tests (*c*) and (*d*) are shown in curve 3 and point 4 respectively in Fig. 3 (see page 9). Fig. 3 shows that the acidity of the solution aerated with quinhydrone for the whole period apparently changed steadily from PH 5·8 to PH 4·3. Without aeration the PH changed from 5·8 to 4·8. The solution to which quinhydrone was added after 116 hours (curve 3) had a PH at this stage of 6·1,

TABLE 4.—ORIGIN AND NATURE OF SAMPLES.

Sample Number.	Origin of Sample.	Nature of Sample.
C	Museum specimen from Pretoria University	Crystalline pyrites (−200 mesh I.M.M.)
P	Northfield Colliery	Pure pyrites, separated from slurry (−120 mesh)
Q	Phoenix Colliery	Pure pyrites, separated from coal (−200 mesh)
R	Durban Navigation Colliery	Pure pyrites, separated from coal (−200 mesh)
S	Landau Colliery	Pure pyrites, separated from coal (−200 mesh)
T	Coronation Colliery	Crystalline pyrites (−200 mesh)
U	Douglas Colliery	Oxidised pyritic coal (−60)
V	Tweefontein Colliery	Oxidised pyritic coal (−60)
W	Northfield Colliery	Pure pyrites, separated from coal (−200)
X	Cambrian Colliery	Pure pyrites, separated from coal (−200)

TABLE 5.—NATURE AND STRENGTH OF SUSPENDING MEDIUM AND METHOD OF MEASURING PH.

Experiment No.	Volume of Solution Used c.cs.	Nature of Solution.	Conc. of Salt Per 100 c.c. Solution.	Pyrites Oxidised Sample Number.	Weight of Pyrites.	Electrode Used.
1	100	$MgCl_2$ soln.	± 60 grms.	O	1 grm.	Quinhydrone
2	100	Dist. H_2O	—	P	1 ,,	,,
3	100	Bi-dist. H_2O	—	Q	1 ,,	,,
4	100	Dist. H_2O	—	R	1 ,,	Glass
5	100	Dist. H_2O	—	S	1 ,,	,,
6	100	Bi-dist. H_2O	—	T	1 ,,	,,
7	100	$MgCl_2$ soln.	± 56 grms.	W	2 ,,	Quinhydrone
8	100	$MgCl_2$ soln.	± 56 grms.	X	2 ,,	,,
9	100	Dist. H_2O	—	U	1 ,,	,,
10	100	$MgCl_2$ soln.	± 56 grms.	U	2 ,,	,,
11	100	Dist. H_2O	—	V	1 ,,	,,
12	100	$FeCl_3$ soln.	± ·1 grm.	R	1 ,,	Glass

which decreased to 5·4, 148 hours later. The solution which stood for 264 hours before the addition of quinhydrone had a PH of 6·0. These tests were repeated with a similar solution and the above results were confirmed.

These tests show that the PH of the solutions which contain quinhydrone decrease with time, and that aeration of the solution causes a further lowering of the PH value. In the tests to be described in which quinhydrone is used for determining the rate of oxidation of pyrites this change must be allowed for.

Oxidation tests in the apparatus described above were made on samples of finely-ground pyrites, particulars of which are given in Table 4.

Samples P, Q, R, S, T, W and X were obtained from the collieries named and purified by flotation with bromoform and subsequent washing with alcohol and water to remove traces of oxidation products. Sample O was a museum specimen of pyrites which was purified in a similar manner. Samples U and V consisted of specimens of pyritic coal which had been exposed to the air for two years and were visibly oxidised.

Portions of each of the samples were oxidised in the sintered glass apparatus, and the change of acidity measured either by means of a quinhydrone electrode or a glass electrode. The details of the tests are shown in Table 5.

The results of tests 1 to 8 and No. 12 are given in Table 6.

The results in Table 6 show that in every test the increase in acidity as a result of the oxidation of pyrites is small. The observed

TABLE 6.—CHANGE IN PH OF SOLUTIONS WITH TIME.

Time.	Experiment Numbers.								
	1 PH.	2 PH.	3 PH.	4 PH.	5 PH.	6 PH.	7 PH.	8 PH.	12 PH.
O *	4·88	5·05	6·50	5·8	5·5	5·33	5·17	5·01	3·15
1 hour	3·24	4·83	5·64	4·8	4·98	3·99	5·14	4·76	3·15
1 day	—	—	—	3·8	4·08	3·80	—	4·31	3·11
2 days	3·57	4·62	—	3·6	3·60	—	—	3·92	3·05
3 ,,	3·59	4·44	6·17	3·47	—	3·59	—	3·68	3·01
4 ,,	3·61	4·27	6·00	3·40	3·30	—	—	—	2·99
5 ,,	3·63	—	5·90	—	3·18	3·54	—	3·51	2·97
6 ,,	3·64	4·11	5·76	3·23	—	3·54	—	3·39	—
7 ,,	—	—	—	3·14	—	3·50	4·61	3·31	2·85
8 ,,	—	—	—	—	—	3·50	—	—	2·81
9 ,,	3·63	4·01	5·26	—	—	3·49	4·42	3·20	2·79
10 ,,	3·62	—	5·15	—	—	—	4·31	—	—
11 ,,	—	3·96	—	—	—	—	4·19	—	—
12 ,,	—	3·91	4·92	—	—	—	3·81	—	—
13 ,,	—	—	—	—	—	—	3·65	—	—
14 ,,	—	—	—	—	—	—	3·54	—	—
15 ,,	—	3·84	—	—	—	—	—	—	—
16 ,,	—	—	4·59	—	—	—	—	—	—
17 ,,	—	3·80	4·53	—	—	—	—	—	—
18 ,,	—	—	4·52	—	—	—	—	—	—
19 ,,	—	3·80	—	—	—	—	—	—	—
20 ,,	—	—	4·38	—	—	—	—	—	—
21 ,,	—	—	—	—	—	—	—	—	—
22 ,,	—	—	—	—	—	—	—	—	—
23 ,,	—	—	—	—	—	—	—	—	—
24 ,,	—	—	4·25	—	—	—	—	—	—
25 ,,	—	—	—	—	—	—	—	—	—
26 ,,	—	—	—	—	—	—	—	—	—
27 ,,	—	—	4·15	—	—	—	—	—	—
Equivalent % S.	·04	·03	·11	·12	·11	·05	·03	·05	·15

* Pyrites added.

increase in acidity is due to the sulphuric acid formed by the oxidation of the pyrites together with sulphuric acid formed by the hydrolysis of the iron sulphate also formed. The sulphur equivalent to the final increase in acidity was calculated as a percentage of the pyrites for each test, and is also recorded in Table 6.

If Tideswell's (17) equation represents the oxidation reaction, then this sulphur represents more than half of the total sulphur rendered soluble. With Winmill's (4) equation the sulphur represents more than 33⅓ per cent. of the soluble sulphur. In either case the proportion of pyrites oxidised is small and very much less than that observed by Segal (15). Furthermore, there is no appreciable difference in the amount of oxidation which occurs when magnesium chloride solution is substituted for water. This latter conclusion is also at variance with those of Segal (15).

In experiment No. 12 a very dilute solution of ferric chloride was substituted for water and magnesium chloride solutions as suspending medium. It will be noted that the increase in acidity in this case is about 26 per cent. higher than in the case where the same pyrites was dissolved in water. Cammerer (20) suggests that the reaction takes place according to the following equation :—

$$FeS_2+2FeCl_3=3\ FeCl_2+2S.$$

TABLE 7.

Time Mins.	Experiment Numbers.				
	9 PH.	10 PH.	11 PH.	Segal 3 PH.	Segal 4 PH.
0 *	4·41	5·83	5·41	4·85	6·67
1	2·44	1·31	3·15	1·72	0·55
2	2·44	1·29	3·17	1·57	0·76
3	2·42	1·29	3·19	1·57	0·85
4	”	”	3·20	1·55	0·89
5	”	”	3·20	1·49	0·90
6	”	”	”	1·49	0·91
7	”	”	”	1·45	0·91
8	”	”	”	1·44	0·90
9	”	”	”	1·43	0·90
10	”	”	”	1·39	0·90
11	”	”	”	1·35	0·90
12	”	”	”	1·31	0·90
13	”	”	”	1·31	0·91
14	”	”	”	1·31	0·91
15	”	”	”	1·31	0·92
16	”	”	”	1·31	0·92
17	”	”	”	1·31	0·93
18	”	”	”	1·31	0·93
19	”	”	”	1·31	0·93
20	”	”	”	—	0·93
21	”	”	”	—	0·94
22	”	”	”	—	0·94
23	”	”	”	—	0·94
24	”	1·29†	”	—	0·95
25	”	—	”	—	—
26	”	—	”	—	0·95
27	”	—	”	—	—
28	”	—	”	—	0·95
29	”	—	”	—	—
30	”	1·49	”	—	0·95
35	”	1·94	—	—	—
40	”	—	—	—	—
45	” †	—	—	—	—
90	4·37	—	—	—	—

* Added pyrites.
† Added Fe filings.

If the $FeCl_2$ formed were oxidised back to $FeCl_3$, the reaction between the $FeCl_3$ and the FeS_2 would continue until all the pyrites had disappeared. These statements lend added weight to the theory of Drakeley (8) in which he suggests that $FeSO_4$ may act as an oxygen carrier by alternate oxidation to $Fe_2(SO_4)_3$ and subsequent reduction of the $Fe_2(SO_4)_3$, in the oxidation of pyrites.

In Table 7 the results of tests 9, 10 and 11 are given. The pyritic coals used in these tests had been exposed to the air for two years and the pyrites was appreciably oxidised. In addition to the above results, two tests given by Segal (15) are reproduced in the table. In these latter tests (Segal 3 and Segal 4) 2 grm. samples of pyrites were suspended in 100 c.c. portions of magnesium chloride solutions containing 37 grms. $MgCl_2$ per 100 ccs.

The increase in acidity of tests 9, 10 and 11 is in each case much greater than was found in the tests using unoxidised or only slightly oxidised pyrites. This increase occurs in the first minute after addition of the pyrites to the solution and is obviously due to the solution of the acid oxidation products adhering to the pyrites. The similarity of the above tests with those of Segal suggests that his samples were also oxidised when the tests were made, although the analyses given for these samples show practically no water soluble sulphur at the time of the analysis.

The increase in acidity observed in test 10 in which $MgCl_2$ solution was used, is 14 times greater than that observed in test 9, in which water was the solvent. This difference may be due to the presence of basic ferric sulphates which are less soluble in water than in magnesium chloride. Segal (15) observed a similar difference. The pyrites used in tests "Segal 3" and "Segal 4" increased the acidity of water from PH 6·85 to PH 6·60 and PH 5·2 respectively; in both cases a much smaller increase in acidity than was observed when magnesium chloride was used.

Both methods of estimating the rate of oxidation of pyrites (*a*) oxidation by moist oxygen at 105° C. and (*b*) air oxidation of pyrites suspended in magnesium chloride solution and water; show clearly that pyrites does oxidise to some extent; but that the rate of oxidation is slow. It is doubtful whether the rate of oxidation is rapid enough and produces enough heat, to play a major part in the spontaneous ignition of coal under any practical conditions.

It would appear that oxidation takes place most rapidly when pyrites is well mixed with coal, or when pyrites occurs in lump coal, at the coal-pyrites interface. In the latter case, the initial and greatest danger that would be caused by the oxidation, would be the disintegration of the coal mass itself.

APPENDIX 1.

THE ESTIMATION OF SULPHATFS IN PYRITFS.

As has been previously stated, the methods of Powell and Parr (21) for the determination of sulphate sulphur, when applied to pyrites, gave variable results which were, in all cases, too high. An investigation was therefore undertaken to ascertain a more satisfactory method of analysis.

Samples of —200 mesh pyrites were refluxed with excess hydrochloric acid containing 1 per cent. and 16 per cent. HCl for varying periods and at temperatures of 60° C. and at the boiling point. The percentages of sulphur extracted were determined by precipitation as barium sulphate. Details of these tests are shown in Table 8. The tests recorded under the same sample number were made concurrently.

The data in Table 8 shows that the same amounts are extracted by boiling 1 per cent. and 16 per cent. HCl, and that the extraction is not increased by increasing the time beyond half an hour. Extraction at 60° C. gives higher results than at the boiling point and the amount extracted increases with increasing time of extraction.

In order to determine whether pyrites, completely extracted with boiling acid, will yield a further amount of sulphate on extraction at 60° C., a series of pyrites samples were extracted with boiling 16 per cent. HCl, filtered and washed free of soluble sulphur. The residual pyrites was again extracted for 40 hours at 60° C. with varying strengths of hydrochloric acid. Table 9 shows the original sulphate sulphur

TABLE 8.

PER CENT. SULPHATE EXTRACTED.—(*a*) VARYING PERIODS OF TIME. (*b*) DIFFERENT TEMPERATURES.

Sample Number.	Conc. of HCl %	Extraction Time Hours.	Temp. of Extraction.	S. Extracted (Duplicate Determinations—%).	
F 1	16	½	Boiling Pt.	1·11	1·10
	16	1	,,	1·11	1·11
	16	3	,,	1·11	1·11
F 2	16	½	,,	1·12	1·12
	16	1	,,	1·14	1·15
	1	3	,,	1·12	1·12
	1	6	,,	1·13	1·15
F 3	16	½	,,	1·17	1·17
	16	1	,,	1·15	1·15
	1	½	,,	1·15	1·15
	1	1	,,	1·19	1·19
	1	3	,,	1·18	1·18
	1	6	,,	1·15	1·15
	1	24	60° C.	1·30	1·31
	1	48	60° C.	1·89	1·97
	1	60	60° C.	2·01	2·00
E	16	½	Boiling Pt.	1·22	1·20
	16	1	,,	1·21	1·21
	16	3	,,	1·20	1·21
	1	60	60° C.	1·93	2·07
Z	16	½	Boiling Pt.	·14	·14
	16	1	,,	·16	·16
	1	½	,,	·15	·15
	1	1	,,	·16	·16

extracted by the first treatment and the additional sulphate extracted by the subsequent treatment at 60° C.

These results show that after complete extraction with boiling hydrochloric acid, a further quantity of sulphate is extracted at 60° C. and that this amount increases with increasing dilution of the hydrochloric acid. It further appears from Tables 8 and 9 that the agreement between duplicate tests is less close when extracting with dilute acid at 60° C.

In order to determine whether the phenomena previously observed also occur when pyrites is extracted with acid in the presence of coal, a series of samples of coal and artificial mixtures of coal with 5 per cent. of pyrites were extracted for one hour with boiling 16 per cent. HCl (method 1)

TABLE 9.—RE-EXTRACTION OF PYRITES WITH HYDROCHLORIC ACID.

Sample No.	Original Extraction.	SECOND EXTRACTION WITH HCl OF STRENGTH SHOWN. 16% HCl % S.	11% HCl % S.	6% HCl % S.	4% HCl % S.	2% HCl % S.	1% HCl % S.
V	·15, ·16	·08, ·07	—	—	—	—	·35, ·43
W	2·45, 2·45	—	·11, ·11	·15, ·15	·16, ·19	·33, ·33	—
X	1·40, 1·40	—	·09, ·08	·16, ·16	·22, ·23	·25, ·32	—
Y	1·44, 1·44	—	·18, ·15	·21, ·22	·26, ·25	·48, ·48	—

and for 48 hours at 60° C. with 1 per cent. HCl (method 2). The results of these tests are shown in Table 10.

TABLE 10.

EXTRACTION OF COAL+PYRITES WITH HCl.

Sample.	% S. Extracted By	
	Method 1.	Method 2.
Coal A	Trace	Trace
Coal A+5% Pyrites	·140, ·140	·162, ·159
Coal B	·037, ·034	·117, ·117
Coal B+5% Pyrites	·219, ·221	·306, ·297
Coal C	Trace	Trace
Coal C+5% Pyrites	·072, ·082	·100, ·102
Coal D	1·990, 2·010	1·990, 2·010
Coal E	·022, ·027	·037, ·037
Coal E+5% Pyrites	·026, ·026	·076, ·076

Coal D, Table 10, was a sample of pyritic coal which was badly weathered and in which all the pyrites had apparently been oxidised to sulphate. Table 10 shows that extraction at 60° C. with dilute acid also gives higher soluble sulphur values than extraction with boiling acid. The only exception is coal D in which all the pyrites was dissolved by both methods.

Rousseau (22) obtained similar results when extracting South African coals and torbanites with 3 per cent. HCl at 60° C. for 40 hours and with boiling concentrated HCl (S.G. 1·12) for 20 minutes. These results are shown in Table 11, which includes also the total percentage of pyritic and sulphide sulphur in the samples.

TABLE 11.

Sample Number	Pyritic+ Sulphide Sulphur %	% S. Extracted with HCl.	
		3% HCl at 60° C.	Conc. HCl at B.P.
1	·169	·012	·003
2	·386	·016	·010
4	·532	·313	·306
5	·538	·201	·122
6	·003	·198	·198
7	·076	·123	·141
8	·262	·055	·060
9	·024	·016	·017

In these tests the extraction with dilute acid at 60° C. gives results either equal to or higher than the extraction at the boiling point except in the one case of sample 7. Rousseau concludes that the correct results are given by extraction with 3 per cent. acid at 60° C., and discounts the probability that oxygen dissolves in the acid and oxidises the pyrites during the extraction.

From the experiments reported it can be concluded that with boiling acid, a definite quantity of sulphate is rapidly extracted and that increasing the extraction time does not increase the amount extracted. On the other hand, extraction at 60° C. yields a higher but indefinite quantity of soluble sulphate, which increases with increasing extraction time. Furthermore, the amount extracted by boiling acid is independent of the acid strength between 1 per cent. and 16 per cent., whereas at 60° C. the weaker acid extracts the greater amount in the same time.

The most probable explanation of the phenomena is that, during the extraction at 60° C., the pyrites is slowly oxidised by oxygen dissolved from the air, probably through the agency of the alternate oxidation and reduction of the ferrous chloride present in solution. On the other hand, boiling solutions in which the oxygen is not soluble, do not promote this oxidation to any appreciable extent.

That ferric chloride solutions dissolve pyrites under certain conditions is known—Cammerer (20). The following series of tests to ascertain whether, under the conditions of the determination of sulphate sulphur, soluble iron salts had any appreciable solvent action, were carried out.

Samples of pyrites were extracted for one hour with boiling 16 per cent. HCl and the soluble salts completely separated by repeated centrifuging with hot water. The sulphate sulphur in the combined wash liquors was determined. The extracted samples were then re-extracted with solutions containing 1 per cent. of ferric chloride ($FeCl_3$, $6H_2O$) and either 1 per cent. or 16 per cent. HCl for varying times at both 60° C. and at the boiling point. The extracting solution was free from sulphates. The percentage sulphate sulphur dissolved in the first extraction was 1·3 per cent., the additional sulphate sulphur extracted by the second treatment is shown in Table 12.

TABLE 12.—EXTRACTION OF PYRITES WITH $FeCl_3+HCl$.

Test Number.	Extracting Solution.	Time of Extraction Hrs.	Temp. of Extraction ° C.	Soluble S. %
1	1% $FeCl_3$+ 1% HCl	1	Boiling Pt.	1·41
2	1% $FeCl_3$+ 1% HCl	48	60° C.	2·20
3	1% $FeCl_3$+16% HCl	1	Boiling Pt.	Trace
4	1% $FeCl_3$+16% HCl	48	60° C.	0·88

These tests clearly show the oxidising effect of ferric chloride and also the retardation of the oxidation by strong hydrochloric acid solution. Since boiling 1 per cent. and 16 per cent. HCl solutions have been shown to extract the same amounts of sulphur from pyrites, the sulphur extracted in test No. 1 must, therefore, be entirely due to the ferric chloride.

Since chlorides of iron are formed when partly oxidised pyrites is extracted with hydrochloric acid, their oxidising action on the pyrites cannot be ignored, especially when the pyrites is originally appreciably oxidised and the concentration of iron salts in the extracting solution is significant. The solution of the pyrites by ferric salts should at first be rapid until all the original ferric salt is reduced, and thereafter slow as oxygen becomes available for the re-oxidation of the ferrous ions. Factors tending to retard the slow oxidation are the gradual accumulation of acid in the extracting solution and the gradual decrease in the surface area of the pyrites through the complete solution of the finest and most reactive particles. The combined effect of these factors is shown in the results recorded in Table 8.

From the data available it must be concluded that, contrary to the conclusions of Rosseau (22), the extraction of partly oxidised pyrites with dilute acid at 60° C. does not give the true sulphate content, and that a more accurate value is obtained by extracting with boiling 16 per cent. HCl (1 volume conc. hydrochloric acid+1 volume water) for one hour. The difference between the results obtained by the two methods when applied to pyritic coals is, however, generally small and of no great significance except where exceptional accuracy is required.

SUMMARY.

1. Pure pyrites and pyrites-coal mixtures oxidise when subjected to a stream of moist oxygen at 105° C. over a period of six weeks. The actual amount of oxidation is small. The rate of oxidation is greatest during the first week. During the second week it decreases slightly to a value which remains practically constant from the third week onwards.

The rate of oxidation of pure pyrites is appreciably less than when the pyrites is associated with coal.

2. Wet oxidation of pyrites was determined by measuring the rate of change in PH of a solution in which the pyrites was kept in suspension by a current of air. Quinhydrone and glass electrodes were used for determining the PH values. Tests showed that the PH value of a quinhydrone solution decreases with time. Aeration of the solution increases the change observed.

(*a*) In every test made the increase in acidity as a result of the oxidation of pyrites is small.

(*b*) When the oxidation of the pyrites is carried out in a dilute solution of ferric chloride, the increase in acidity is appreciably higher than when other solutions are used.

Appendix 1.

Powell and Parr's method of estimating sulphate sulphur in coal was found to give high values when used for estimating the sulphate sulphur in pyrites.

(*a*) It has been shown that the presence of ferric chloride in the solvent solution gives high results.

(*b*) A more accurate method of extracting the sulphate has been suggested.

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