

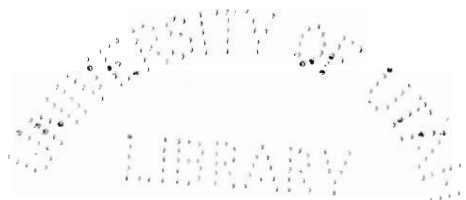
**A STUDY OF THE SULPHUR IN COAL AND ITS
DISTRIBUTION BETWEEN THE GASES AND THE
RESIDUE IN COKING**

ARTHUR W. WENGER

A STUDY OF THE SULPHUR IN COAL AND ITS DISTRIBUTION
BETWEEN THE GASES AND THE RESIDUE IN COKING

By

Arthur W. Wenger



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INTRODUCTION

Sulphur exists in metallurgical coke as a source of annoyance and difficulties in the economic progress of the metal industries. It is present in coal in several different forms under two heads as organic and inorganic sulphur. The percentage of the forms vary widely in different coals.

In the manufacture of coke, varying amounts of sulphur ^{are} ~~is~~ retained by the same coal under different methods of carbonization, and, by different coals under the same method of treatment.

It is desirable to know the factors that influence the distribution of the element between the gases and the residues of coal in the manufacture of metallurgical coke, and, for that reason it is an important problem at present which means a saving of millions of dollars to the metal industry.

Analyses of the forms of sulphur in several samples of Utah coals appear elsewhere in this paper. The samples were received from the offices of the yards in Salt Lake City and analyzed according to the methods used by Prof. S. W. Parr and A. R. Powell on several Eastern coals.

ACKNOWLEDGEMENTS. - Valuable data were obtained from the published works of S. W. Parr, A. R. Powell and others.

HISTORICAL

Recent investigations have shown that sulphur exists in coal in four different forms as pyritic, sulphate, organic, and humus sulphur. The organic form is considered to be in ashless organic substances, chiefly as resins. The humus sulphur is considered organic also, but the ground material with which it is separated from the coal substance contains very little ash.

A. R. Powell and S. W. Parr have contributed to science a reliable method of determining each form. These technical methods are useful to the coal technologist as indicating how much of the sulphur content of a particular coal will effect its heating value, and they also, enable him to follow the transformation of the sulphur during the coking processes.

PYRITIC SULPHUR

The sulphur in coal occurs in one of its most common form as iron pyrite or marcasite both of which are composed of sulphur and iron in the proportion of two to one respectively, but they are distinguished from each other by their physical forms. Pyrite is cubic in form while marcasite is orthorhombic and paler. The term pyrite is generally used in America when applied to FeS_2 in coal but most of the so-called pyrites are really marcasite. (1)

The knowledge that pyrite is omnipresent in the mineral kingdom is very old. J. F. Henckel (1725) termed it as "Jack in every street". (2)

The exact origin of the pyrite in the coal bed is not well known, but it is highly probable that it is the product of organic decomposition of the coal substance and the content of the percolating water. (13) Pyrite is found in the coal in all sizes ranging from finely disseminated microscopic crystals to boulders measuring several feet in diameter. The various physical forms in which they occur in the face of the mines are as follows:- cat faces, laminae, bands, lenses, balls or nodules, as films that coat the joint planes, as pyrite and marcasite crystals, and as vegetable fossil infiltrations. "Flake Sulphur" is not pyrite but calcium sulphate or gypsum. (3)

Most of the Pyrite bodies, especially those not in microscopic forms, can be mechanically removed by washing or by float and sink fractionation. These methods are the same in principle, being based on the principle of gravity partition, but for the latter zinc chloride solution (4) of specific gravity 1.35 is used instead of water as in the former. Coal is cleaned commercially by the washing method, while the use of the more expensive fractionating method is confined in the laboratory.

The distribution, in the coal seam, of sulphur in its pyritic form is not regular but very erratic. As a general rule most of this form is scattered in the floor and roof benches of the coal seam as shown by figures 1 and 2. (5)

In some instances the greatest amount of pyrite per unit of coal is found in the middle benches of the seam as shown by

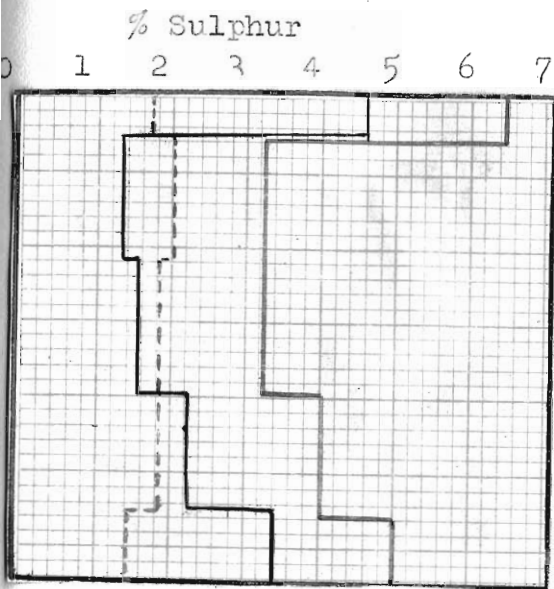


Fig. 1

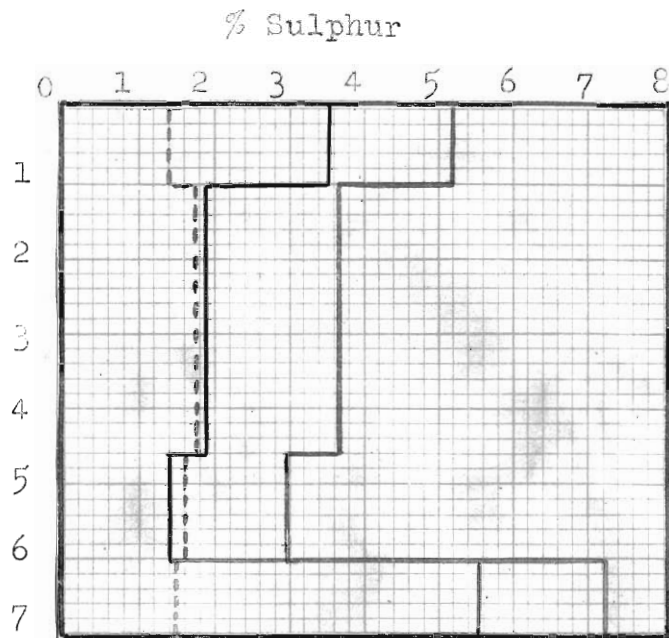


Fig. 2

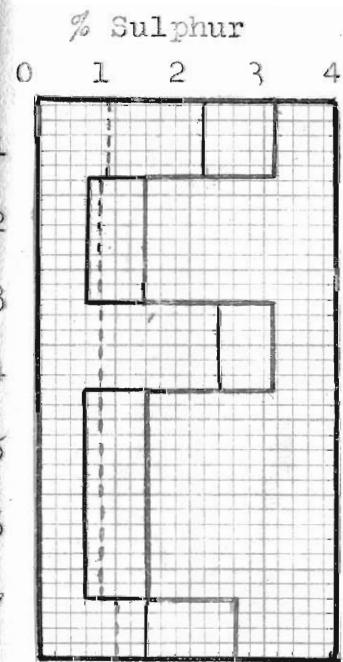


Fig. 3

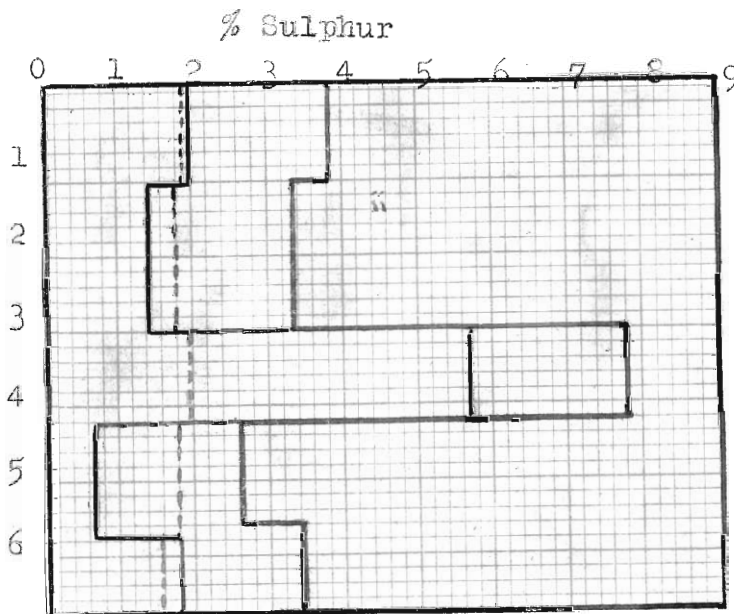


Fig. 4

— Total Sulphur

- - - Pyritic Sulphur

· · · Organic Sulphur

Charts Showing the Distribution of the Forms of Sulphur in a Coal Bed of Illinois. (5)

figures 3 and 4.

Explanation of Figure 2. - The thickness of the seam is shown to be seven feet and one inch. The samples were obtained by picking a straight, narrow groove from top to bottom of the seam. This groove is divided according to natural benches that are separated by great partings or unconformities. In this case there were four benches; therefore four separate samples were taken from the face of this seam.

This curve in the figure is square or rough probably because only a few samples were taken. It is likely that we shall obtain a rounded and more significant curve if the groove is divided into a greater number of parts.

ORGANIC SULPHUR

Our attention was called, by Bradsbury (1878) to the presence of organic sulphur in coal. (6)

Organic sulphur exists in coal as a real part of the coal substance, because it is a natural constituent of the plant and animal proteins from which the coal was originally formed. This pure organic matter, may, however, contribute a part of its sulphur content to the formation of iron sulphides that change thence to pyrite.

By comparing the curves of organic sulphur with the curves of pyritic sulphur in figures 1, 2, 3, and 4, it will be seen that the distribution of organic sulphur is almost uniform

throughout the coal seam. This contrast strongly sustains the theory that organic sulphur is a natural constituent of the coal while the pyritic form is extraneous. The finely disseminated form, "black pyrite", is the exception because, being evenly distributed, the sulphur is derived from the decomposition of the organic form.

Since our knowledge of inorganic chemistry is almost well established it is easily demonstrated that sulphur occurs in certain inorganic forms. Hence, the study of these forms is short. But in the case of organic chemistry it is the contrary. Therefore, the study of organic sulphur remains open and offers a great deal of interest.

Numerous experiments have been made to determine the organic compound in which sulphur exists as a constitutional part. The organic compounds as they exist in coal are only surmised to be very complex.

There are several laboratory procedures by which all or part of the organic sulphur may be followed up or isolated.

Most of the sulphur is removed by extraction with phenol. The substance extracted by phenol is proven to be organic in nature by its lack of an ash.

When the phenol extract is dried by evaporation and then the residue is treated with anhydrous ether (7) all of the sulphur is found in the insoluble substance.

The substance that is removed from coal by phenol consists

of a resinic nature which is thought to be the binding material of coke because the residues after the phenol extraction would not coke.

SULPHATE SULPHUR

Freshly mined coal contains sulphate sulphur chiefly as gypsum (calcium sulphate). The sulphate content of coal increases as the coal stands in storage when oxidation of the pyrite occurs. This sulphate is water soluble and is easily leached off by rain. No importance is attached to the sulphate form. It is the form that exists in the smallest quantity.

HUMUS SULPHUR

When the sum of the above three forms - phenol soluble, pyritic and sulphate sulphur - is compared with the total sulphur, it will be observed that there is some sulphur which is still unaccounted for. This absent quantity of the sulphur, calculated by difference, is designated as humus sulphur in order to differentiate it from the resinic sulphur which dissolves in phenol.

Friswell (9) has produced evidences to show that there is some nitric acid insoluble sulphur in this humus-like material. Some powdered coal is digested with dilute nitric acid (1 pt. nitric acid to 3 pts. water) to remove all of the inorganic sulphur forms. Further treatment will show no

sulphur in the filtrate. The residue is then treated with concentrated ammonia or sodium peroxide solution. The mixture is diluted and filtered. The filtrate contains nearly all of the sulphur while but a small trace is held in the residue by occlusion. As soon as the filtrate is acidified with Hydrochloric acid the sulphur will fall out of the solution as a brown flocculent precipitate.

The steps followed in the treatment of the coal as just described is similar to Grandeau's "Matiere Noire" method for the estimation of humus in soil. (10) The weak nitric acid, as used in the case of soil, liberates the humic acids from their union with lime and magnesia. These humic acids are removed by subsequent extraction with dilute ammonia or alkali solution. Upon evaporating the ammonia or alkali extract a black lustrous substance, "Matiere Noire" is obtained.

If, instead of the weak alkali, a strong solution is used, not only will the freed humic acids be removed, but more will be formed. "Humic acids" apply to the extract of humus from soil and peat but in the case of coal it is called "coal acid". These two acids have characteristically different properties that serve to distinguish them.

Coal Acid		Humus Acid (of peat)
Not hygroscopic	:	Hygroscopic

Continued

Dissolves after drying	:	Will not dissolve after drying
Does not yield acetic acid on dry distillation	:	
Does not yield ammonia when boiled with alkalies even when evidence shows that it is a nitro compound	:	Yields ammonia when boiled with alkalies

OTHER FORMS OF SULPHUR

Four chief forms of sulphur as found in all coals have been described and are now determined by standard methods of analysis which will be outlined later on.

Other possible forms of sulphur which might be present in coal have been investigated, but without satisfactory results.

Extraction of coal with carbon tetrachloride yielded no sulphur; therefore, it is not found in the free state.

Investigations failed to determine the phenol-soluble compound in which the sulphur is found. Even Powell tried to secure a more specific knowledge of the organic sulphur present in coal but obtained negative results. Powdered coal and also the ammonia extract (after digestion with nitric acid) fail to give a positive Smiles test for presence of sulphinic acid and sulphoxides.

The substance is treated with concentrated sulphuric acid and then a drop of anisole is added. A blue color is a positive indication that sulphinic acid or sulphoxide is present.

A test with isatin (oxidized indigo) also failed to show presence of thiophen. The latter result is interesting in view of the fact that coal by dry distillation yields thiophen in the tarry distillate. This proves without a doubt that the organic compound of coal is very complex. It also sustains R. Meyers theory that the main part of the organic substance in coal is composed of compounds which are polymers of acetylene. These polymers of acetylene break up readily into simple acetylene that undergoes secondary reaction with hydrogen sulphide to form thiophen. This last result is not a valid proof that the sulphur exists as a constituent of cyclic organic compounds in coal.

METHODS OF QUANTITATIVE ANALYSIS

TOTAL SULPHUR. Total sulphur is determined by the Eschka method as follows:- One gram of finely powdered sample (50 mesh and air dried) is intimately mixed with three grams of Eschka mixture (2 parts, by weight, of light calcined magnesium oxide and 1 part anhydrous sodium carbonate. See foot note) in a 50 c.c. porcelain or platinum crucible and then covered with a layer of the Eschka mixture by sprinkling. The mixture is slowly ignited in an electric furnace and then the heat is gradually raised to maximum temperature. The maximum heat is maintained for 1 1/2 hours or until all of the black particles of the coal have disappeared. The crucible is allowed to cool in the muffle and its content is leached out into a beaker with 100 c.c. of hot water. The mixture is digested 30-45 minutes and filtered. A thorough washing of the residue in the filter will remove all of the sulphur. 10 c.c. of bromine water is added to the combined filtrate and washings. The solution is made slightly acid with HCl and brought to boiling after which 10 c.c. of hot 10% barium chloride solution

Hundeshagen (12) recommended the use of calcined potassium carbonate instead of the sodium carbonate because, he contended, that loss of some sulphur as hydrogen sulphide occurs when the latter is used.

are added to precipitate the sulphur as barium sulphate. The mixture (200-300 c.c.) is allowed to stand hot over night and then filtered through a high grade ashless filter. The barium sulphate and the filter are washed several times until silver nitrate shows no cloudiness in the washings and, then ignited to a white ash. The percentage of the sulphur is calculated from the weight of the ash as barium sulphate. A blank determination should be made simultaneously with the determination of sulphur in all its forms and correction made according to the blank determination. The quantity of sulphur in the reagents is certainly not negligible.

TOTAL IRON. 15 c.c. of concentrated hydrochloric acid is added to the ash from 1 gram of powdered coal. The mixture is boiled for three minutes and allowed to stand over night. Hydrofluoric acid treatment to remove the silica can be applied but in most cases only negligible quantities of iron occur as iron silicate. The yellow acid solution is heated and then decolorized with at least two or three drops of saturated stannous chlorid solution and made up to about 100 c.c. The excess of stannous chloride is removed from solution by precipitation with 5 c.c. of saturated Mercuric chloride after which the iron is immediately titrated against N/40 potassium dichromate solution with drops of potassium ferricyanide as indicator.

SULPHATE SULPHUR.- Sulphate sulphur is determined by boiling in a beaker, 5 grams of powdered coal in 100 c.c. of dilute hydrochloric acid (1 part conc. HCl and 2 parts water) for 15-20 minutes. Small quantities of water ^{are} ~~is~~ added from time to time to replace that which is evaporated. Complete extraction of the sulphate sulphur is secured without any of the pyrite going into solution to effect the quantitative result. The mixture is diluted and filtered. The filtrate is made up to about 200 c.c. so that the H Cl concentration is diminished. From this point the rest of the procedure for the sulphate sulphur determination is the same as that for total sulphur beginning where the solution is "brought to boiling". The reagents are measured so that corresponding amounts can be used in running a blank determination.

PYRITIC SULPHUR.- The pyritic sulphur is determined by extracting 1 gram of the powdered coal with 80 c.c. of dilute nitric acid of specific gravity 1.12 (1 volume of conc. nitric acid, Sp. G. 1.42 plus 3 volumes of water). (11) The mixture is allowed to stand at room temperature for one day or longer and then filtered. The filtrate is evaporated to dryness and the residue dissolved in dilute H Cl. The iron is precipitated with ammonium hydroxide and removed by filtration. The filter is punctured and the ferric hydroxide washed through into a clean beaker. 5 c.c. of conc. H Cl is added by pouring over the filter and the iron is quantitatively determined by the same procedure as for total iron determination, beginning where the "H Cl solution is heated". The pyritic sulphur is determined in the ammonical filtrate by the

same procedure as for total sulphur, beginning where "the solution is made slightly acid and brought to boiling". A blank determination is run at the same time. The sulphur obtained in this determination represents the sulphate sulphur, which has been previously determined by the H Cl extraction, plus the pyritic sulphur. Sometimes the extraction is over-done that is, part of the organic sulphur is taken in solution. The iron in the nitric acid extract (21) minus the H Cl soluble iron, is assumed to be pyritic iron. This pyritic iron is quantitatively determined in conjunction with the pyritic sulphur determination so that the sulphur-iron ratio may be used in checking on the result of the latter determination.

The weight of pyritic iron (nitric acid soluble iron minus H Cl soluble iron) times 1.145 give the weight of pyritic sulphur in close approximation to the result of direct determination as shown by the following table

Table 1

Constituents	%	%
Total sulphur, as determined	3.06	
Sulphur soluble in dilute nitric acid	2.31	
Sulphur soluble in dilute hydrochloric acid	.32	
Pyritic sulphur by direct extraction		1.99
Iron soluble in dilute nitric acid	2.25	
Iron soluble in dilute hydrochloric acid	.49	
Pyritic iron by direct extraction	1.76	
Pyritic sulphur calculated from iron		2.01
Difference of Pyritic sulphur value from calculation		-.02

RESINIC SULPHUR. Resinic sulphur is determined by extraction of the resinic substance of coal with hot phenol.

One half gram of powdered coal is soaked in 25 c.c. of phenol in a small Erlenmeyer flask to which is fitted a two foot reflux air condenser. The flask is placed in an electric hot box* in such a manner that the greater length of the condenser protrudes outside the box through the top. The inside of the box is maintained at a regulated temperature of 140°C for twenty hours.

Foot note-

* The electric oven used in the phenol extraction consists of a heavy iron cylinder, 12 inches long and 5 inches in diameter, with a wrap of nichrome resistance coil, which is covered with fire clay - waterglass cementing material, and a five gallon oil can. The space between the cylinder and the sides of the can is stuffed with ^s asbestos insulating material. A sixty foot #18 nichrome wire is coiled into a quarter inch spiral, doubled over at the middle and then wound several times on the cylinder which is previously covered with asbestos paper. While winding the wire is stretched a little, and the two ends fastened on terminal posts at the top. An asbestos board, with four holes for the air condensers and a thermometer is used for a cover.

At the end of the extraction time the flask is removed while warm and the contents immediately filtered through a Gooch crucible. The flask and the residue in the crucible are washed with absolute alcohol followed by ether.

Resinic sulphur is represented by the sulphur in the filtrate but its analysis is more difficult and time consuming, so recourse is had by determining the undissolved sulphur in the residue as follows:- The washed residue is dried and treated by the Eschka method as outlined for total sulphur. The difference between the total sulphur and this phenol-insoluble sulphur represents the sulphur removed by phenol as resinic sulphur.

HUMUS SULPHUR.- Humus sulphur can be determined directly by the following procedure: One gram of powdered coal is treated with 15 c.c. of concentrated nitric acid for about 30 minutes. The mixture is diluted and filtered. The washed filter and residue are allowed to stand in 25 c.c. of concentrated ammonium hydroxide over night. The mixture is diluted and filtered on a fluted filter. The filtrate is evaporated to dryness and the sulphur in the residue is determined as humus sulphur by the Eschka method as outlined for total sulphur. This humus sulphur is generally determined by the difference between the phenol insoluble sulphur and the sum of the inorganic sulphur.

Table 2. Results of analysis on several Utah Coals

	Sunny Side		Mutual		Standard	
	%	%	%	%	%	%
Total Sulphur (Direct Analysis):		.68		.635		.556
Phosphate Sulphur " "	.02		.005		.005	
Chromitic " " "	.43		.412		.359	
Organic " " "	.02		.059		.082	
Residual " " "	.20		.159		.109	
Sum Total		.67		.635		.555
Difference		-.01		.00		-.001

* Determined by difference between phenol insol. sulphur and dilute nitric acid soluble sulphur.

Table 3.

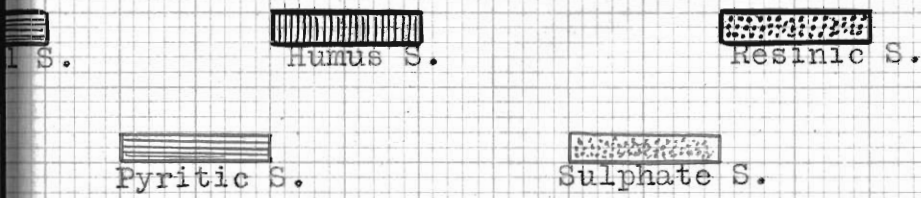
	Aberdeen		Peerless		King	
	%	%	%	%	%	%
Total Sulphur (Direct Analysis):		.330		.506		.400
Phosphate Sulphur " "	.006		.009		.000	
Chromitic Sulphur (Calculated from Fe)	.063		.056		.094	
Organic Sulphur	.04		.152		.064	
Residual Sulphur	.265		.289		.242	
Sum Total		.374		.506		.400
Difference		.044		.000		.000



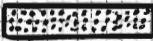
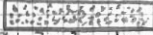
RESULTS.- The results of the above determinations for the sulphur forms in Utah coals are listed in Tables 2 and 3.

The coal samples of table 3 respond in a characteristically different manner to the reaction of the dilute nitric acid treatment for pyritic sulphur determination. The nitric acid extract gives sulphur in larger amount than the amount not soluble in phenol. This indicates that the organic sulphur has been attacked by the acid, therefore, the pyritic form of sulphur was calculated from the iron which gives a low figure for pyritic sulphur and a higher one for the humus form.

The relative quantities of the sulphur forms in a variety of coals are delightfully compared by chart Fig: 5.

Graphic comparison of the various forms
with the total sulphur of the different coals.



 Pyritic S.
  Humus S.
  Resinic S.
  Sulphate S.

---Pennsylvania, Upper Freeport. (21)
 ---Pennsylvania, Pittsburg Seam. (21)
 ---Kansas, Cherokee. (21)
 ---Utah, Sunnyside
 ---Utah, Mutual
 ---Utah, Peerless

RESIDUAL SULPHUR IN COKE

It seems that we are quite satisfied with the results of our studies of the forms of sulphur in the raw coal and their distribution in the coal seam.

We now enter into an advanced field of research which is a chapter of great theoretical interest that will probably lead to a new coking method designed to reduce or eliminate the sulphur content of metallurgical coke.

The original forms of sulphur in coal possess different behavior towards heat as applied in the destructive distillation of coal.

The forms of the sulphur in coke are determined by the same methods as for the forms in raw coal.

The wide divergence of results obtained by different investigators on the amount and forms of the residual sulphur in coke tends to show that there are many factors that influence the transformation of sulphur during the carbonization process. On the basis of these different results the several investigators presented different theories as to the reaction undergone by the coal sulphur. This caused confusion so Powell (14) undertook to carbonize different coals under what he supposed to be carefully controlled conditions, with the idea of studying the character and amount of the various sulphur forms obtained in coke.

The results of analysis for the different forms of sulphur in the residues at different temperatures of carbonization are shown in the following table.

Table 4. Distribution of Sulphur in a Tennessee coal at various temperatures. (17)

Temperature	0°	300°	400°	500°	600°	1000°
Pyritic Sulphur	1.75	1.75	1.42	0.31	0.00	0.00
Organic Sulphur	1.79	1.63	1.51	1.70	1.87	1.81
Sulphate Sulphur	0.71	0.55	0.44	0.01	0.01	0.00
Sulphide Sulphur	0.00	0.13	0.44	0.93	0.82	0.84
Sulphur as H ₂ S	0.00	0.19	0.39	1.20	1.39	1.44
Tar Sulphur	0.00	0.00	0.05	0.10	0.16	0.16
Sulphur as CS ₂	0.00	0.00	0.00	0.00	0.00	0.00
Total Sulphur	4.25	4.25	4.25	4.25	4.25	4.25

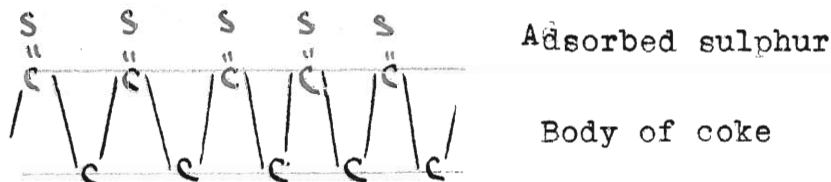
(Values given in % by weight of original and dried coal)

The figures in the table give an interesting account of how the sulphur in its different forms behaves at different periods of coking. The figures in the 0° column represent the percentages of the different forms in the raw coal, and the last column shows the distribution of the sulphur in its final forms where two of its original ones disappear while two new ones appear.

Since the sulphate form is mostly on the surface it is one of the earliest forms that decompose at a low temperature, but there is some that still persists up to 600°C as indicated by the

table. This is so small that it is unimportant.

Organic sulphur begins to decompose early. It is observed in the table that, according to the method of analysis employed the % of the so-called organic form decreases until above 400°C when it begins to rise to a value greater than the % originally present in the raw coal. This leads to a discrepancy as pointed out by Parr (16), who stated that the sulphur does not exist in chemical combination as a compound according to the rule of chemical proportion but in an adsorbed condition on the surface of the carbon according to Langmuir's (22) theoretical construction of a surface compound as follows:



Further study of this subject will be found in the Journal of the American Chemical Society for January 1923.

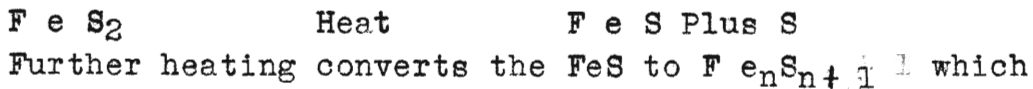
Before studying the decomposition of pyritic sulphur in coal a study of the results obtained by heat decomposition of mineralogical pyrite will make the subject clear.

Mineralogical pyrite is completely decomposed at 1000°C to form free sulphur, ferrous sulphide and hydrogen sulphide as seen in table 5.

Table 5.

Temperature	0°	1000°
Pyritic Sulphur	48.52	0.00
Sulphate Sulphur	00.16	0.00
Free Sulphur	00.00	21.88
Sulphide Sulphur	0.00	24.24
Sulphur as H ₂ S	0.00	2.56
Total	48.68	48.68

The pyritic form has retained half of its pyritic sulphur to form ferrous sulphide. This substantiates the following equilibrium that takes place when pure pyrite is decomposed.



is not a chemical compound but a solid solution of sulphur in ferrous sulphide called pyrrhotite. (18)

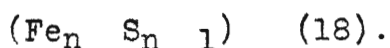
Now when pure mineralogical pyrite is intimately mixed with an equal quantity of coal of known sulphur content and the mixture is coked at a temperature of 1000°C, we obtain the following table of results, which is entirely different from the previous one. This shows that secondary reactions take place when coal is carbonized.

Table 6. Decomposition of Pyrite-coal Mixture

Temperature	0°	1000°
Pyritic Sulphur	25.14	0.00
Sulphate Sulphur	.39	0.00
Organic sulphur	.90	1.93
Free sulphur	.00	5.22
Sulphide sulphur	.00	13.12
Sulphur as H ₂ S	.00	6.08
Tar sulphur	.00	.08
Total	26.43	26.43

The hydrogen sulphide and the organic sulphur are materially increased, while the free sulphur is moderately reduced. These changes are conditioned by the simultaneous decomposition of the coal that liberates hydrogen which combines with a proportion of the free sulphur. We note in table 5 that the decomposition of pure mineralogical pyrite begins at once and is completed at 1000°C. But table 4 shows that pyrite sulphur in coal does not begin to decompose until the temperature reached 300°C and then runs through to completion at a little above 500°C. This shows that the decomposition of the pyrite is accelerated by the gases or the product of organic decomposition.

While the decomposition of the pyrite is in progress ferrous sulphide and hydrogen sulphide are formed. At a higher temperature the ferrous sulphide is decomposed to form pyrrhotite.



Free iron does not exist as a decomposition product of pyrite in coke. This is proved by the absence of metallic copper when an acid solution of a copper salt is added to the finely powdered coke.

When hydrogen travels through a red hot coking mass some sulphur of the latter will combine with the hydrogen to form hydrogen sulphide and is thereby removed from the mass.

Powell (19) undertook to determine the equilibrium between the sulphur in the hydrogen gas and the sulphur in the coke.

He found that hydrogen over coke containing 1.2% sulphur, at 900°C, reaches saturation when it contains about .24 pound of sulphur per 1000 cu. ft. of the gas/

If the by-product oven gases is purified from the sulphur and then passes back through the red hot coking mass the sulphur content of the latter will be greatly reduced. The efficiency of the removal is improved when the gases are allowed to travel in longer contact with the hot coke. An excellent illustration of the mechanism of the carborization processes that occur in commercial by-product oven is given by Bacon & Hamer. (20) By passing through the red hot coke the gases of primary reaction undergo secondary reaction. This secondary reaction does not occur when a small quantity of coal is coked in a laboratory furnace because the gases of primary reaction are swept away as soon as produced. The difference in sulphur contents between the cokes of the laboratory and by product ovens is shown in table 7.

Table 7.

Coal	% Organic S.	% Inorg. S.	% S in coal	% S in coke (Lab)	% S in coke (by-prod)
Pocahontas	85.5	14.5	.55	.45	
Washed Vandalia	78.2	21.8	1.15	1.14	
Joliet Coking	68.3	31.7	.82	.75	.64
Upper F Freeport	58.8	41.2	1.14	1.09	
Tennessee Raw	50.6	49.4	3.54	3.22	
Vandalia	48.1	51.9	1.35	1.30	
Pittsburg	47.0	53.0	1.49	1.51	

Relation of the Sulphur Forms of the Coal to Sulphur in the coke.

This table contains another interesting fact: That coal washing will reduce the sulphur in the coke, but the reduction of the sulphur in the coke is not as good as the corresponding reduction of the sulphur in the washed coal. The ratio between the sulphur in the coal and coke of washed Vandalia is almost the same as the ratio between the sulphur in the coal and coke of the raw Vandalia. This shows that the quantity of sulphur in the coke is determined by the total sulphur in the coal used and not by the relative quantities of the different forms.

	Sulphur in coal	Sulphur in coke
Aberdeen	.330%	.236%
Sunnyside	.660%	.464%
Mutual	.635%	.339%
Peerless	.506%	.250%
Standard	.556%	.294%
King	.400%	.242%

TABLE 8. The percentage of the sulphur in the coke as given in this table is calculated from the weight of the corresponding coal.

The above table shows the quantity of sulphur that remains in the coke after driving off the volatile matter in the laboratory electric muffle. Sunnyside coal, which is the coking coal that is utilized as such on a large commercial scale for consumption in the intermountain and Pacific coast states, shows the greatest quantity of residual sulphur.

The most recent report on the study of the sulphur in coke

was published by Powell (23).

It is known that the organic sulphur in coke is greater than that originally contained in the coal, but the condition under which it exists can not be determined by distillation or wet chemical examination. So Powell undertook to determine the conditions by observing the phase-rule effects of the sulphur.

There are three possible conditions under which the sulphur may exist:- 1st. As one or more chemical compounds neither dissolved in nor adsorbed by the carbon. 2nd -As free sulphur or as a carbon-sulphur compound in solid solution with the carbon. 3rd. As sulphur either free or as one or more compounds that are absorbed by the carbon.

A solid solution follows Henry's law and therefore its isotherm would be a straight slanting line. A compound under constant temperature undergoes constant dissociation and its isotherm would be a straight horizontal line as shown by ferrous sulphide in Fig. 6. Since adsorption is a surface phenomenon the sulphur would be given off at a rapid rate as indicated by the steep curve, whereas a solid solution would give up its sulphur slowly.

The concentration-pressure isotherm is plotted by recording the pressure after each withdrawal of the sulphur in known quantity, hence the curve is produced from top to bottom.

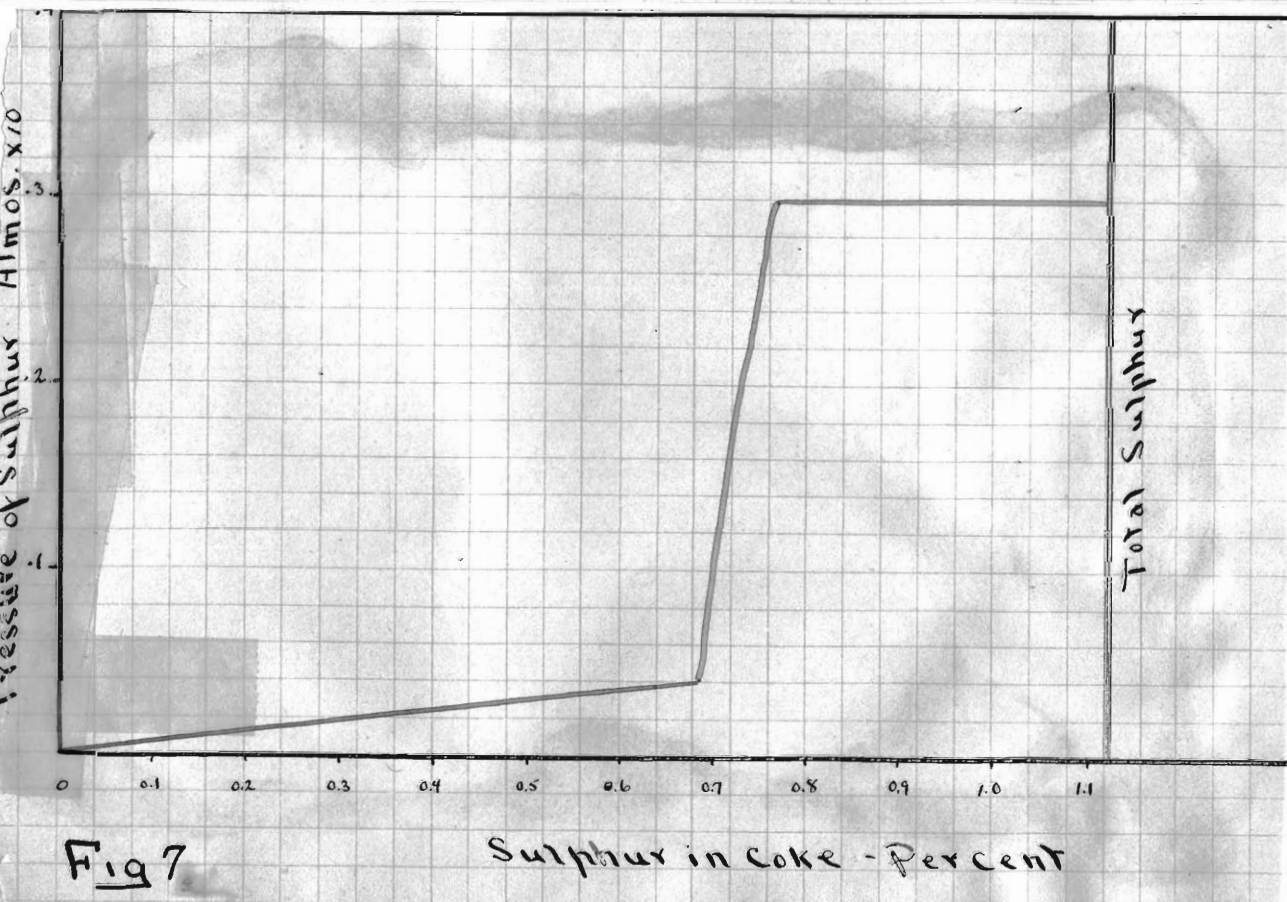
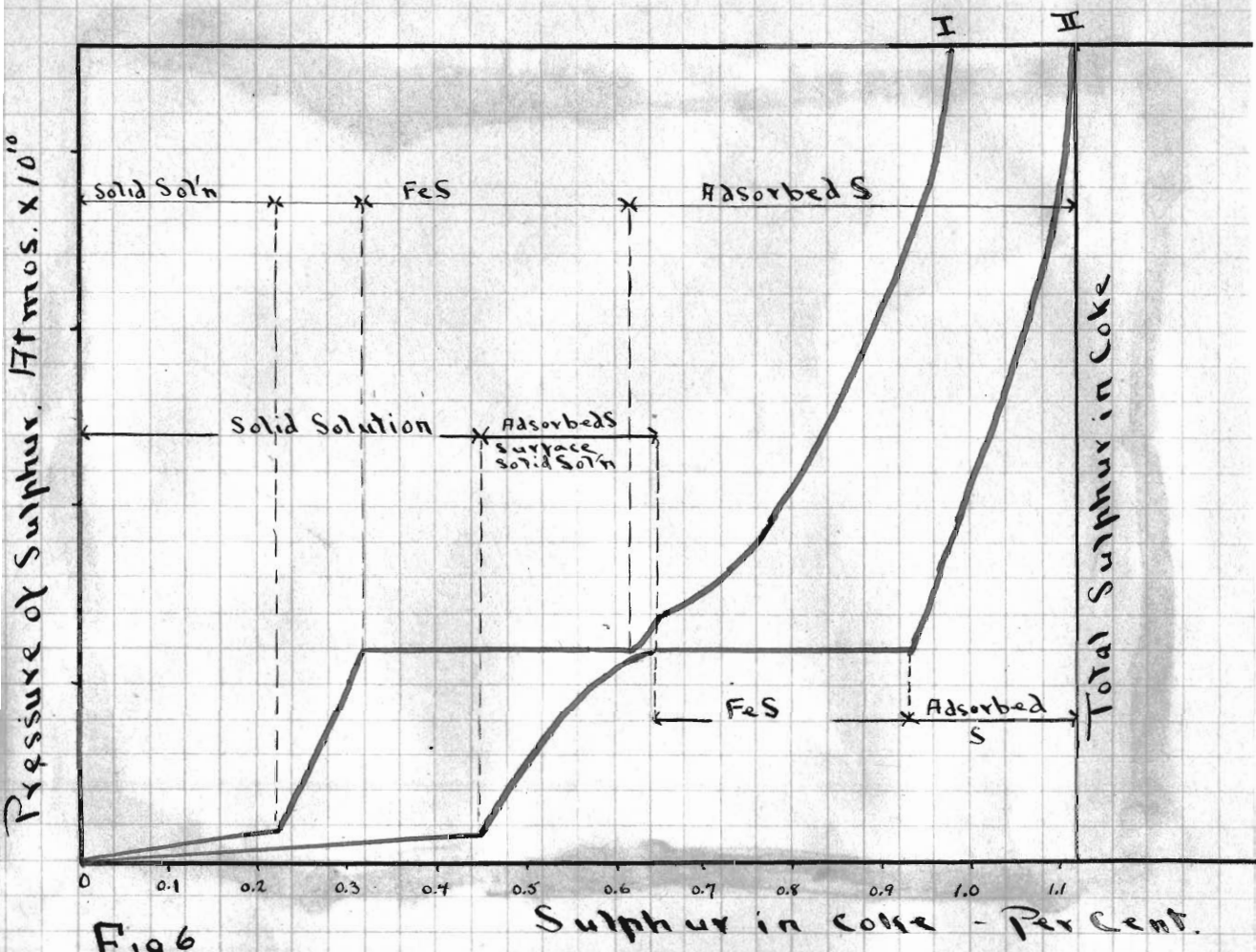


Fig. 6 shows two isotherms of laboratory cokes produced differently. #1 represents the sulphur forms in coke made by the ordinary method of determining volatile matter. This isotherm indicates .24% of the sulphur in solid solution, .32% in the form of a compound and .55% as adsorbed sulphur.

Curve #II. shows the effect of treating the same coke for 24 hours at 800°. The solid solution form is increased at the expense of the absorbed form and the curve of adsorption between solid solution and compound forms is lengthened but the percentage of the FeS form remains the same.

Powell demonstrated that there was no sulphur in the absorbed condition in standard by-product coke except in small quantity whose vapor pressure is greater than that of the sulphur in solid solution but less than the decomposition pressure of ferrous sulphide as shown by Fig. 7.

-CONCLUSIONS-

Sulphur exists in coal in four different forms, i.e., as pyrite sulphur, sulphate sulphur, resinic sulphur, and humus sulphur. These forms are distributed in various quantities throughout the coal seam.

The organic sulphur is distributed in constant quantities in each natural bench of the same locality.

The distribution of the pyritic form is erratic because it occurs mostly as chance inclusions: therefore, a representative sample of a coal seam should be obtained by cutting a straight groove from the roof to the floor of the seam.

The quantity of sulphur that remains in the coke is determined by the method of coking and by the total quantity of the sulphur in the raw coal. These conditions includes the size of the coking mass.

In laboratory coke the sulphur exists in solid solution and is adsorbed by the carbon and also as a compound. But in by-product coke it exists in only two of the three conditions, i.e. in solid solution and as a compound with adsorbed sulphur present in very small quantity or almost nil.

The quantitative analysis of total sulphur in the residues of the several Utah coals after driving off the volatile matter do not give any more information than that the sulphur content of coke is dependent on the total sulphur in the corresponding coal.

REFERENCES

- (1) Encyclopeida Britanica
- (2) "Pyritologia" by J. F. Henckel, or
Mineral Kingdom by Dana.
- (3) Bulletin 23, page 144, U.S. Bureau of Mines.
- (4) A.C. Feldner and F.D. Osgood
Bulletin U.S. Bureau of Mines
- (5) H. F. Yancey and Thos. Fraser, "Distribution of the Forms
of Sulphur in the coal bed". Bulletin 125, University of
Illinois Experiment Station.
- (6) Chemical News, Vol. 38, Page 147.
- (7) Frazer and Hoffman. Tech. P. #5.
U. S. Bureau of Mines
- (8) White, Prof. P. #85 U. S. Geol: Survey
- (9) Proceedings of the Chemical Society. Vol. #8, P. 9 (1892)
- (10) Soil, by E. W. Hilgard
- (11) Powell and Parr. "A study of the Forms in which Sulphur
occurs in Coal." Bulletin 111, University of Illinois,
Engineering Experiment Station (1919)
- (12) Journal on Anal. and App. Chem., Vol. VI, p.385
- (13) "The origin of coal" Bulletin #38, p. 34 and 58.
U. S. Bureau of Mines.
- (14) Journal of Ind. and Eng'g. Chem. Vol. 12, p. 888.
- (15) Ibed. P. 1069

References continued -

(16) Parr and Layng.

Journal Ind: and Eng'g Chem: Vol. 13, p. 14 (1921)

(17) Powell, "A study of the reaction of coal sulphur in
the coking process. Journal of Ind. Eng'g Chem. Vol. 12,
p p. 1069.

(18) E. T. Allen, J. L. Crenshaw and John Johnson. "The mineral
Sulphides of Iron", Am. J. Sci. 33, 169 (1912)

(19) Some Factors Affecting the Sulphur content of Coke and
Gas. Journal Ind. and Eng'g Chem: Vol. 13, p. 33.

(20) American Fuels, Bacon and Hamor. Vol. 1, p. 88.

(21) Tech. P. 254 U. S. Bureau of Mines

(22) Langmuir, Jour: Am. Chem. Soc. 37, 1154 (1915)
38, 2285 (1916)

(23) Powell, Jour: Am. Chem. Soc. 45, 1 (1923)

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