

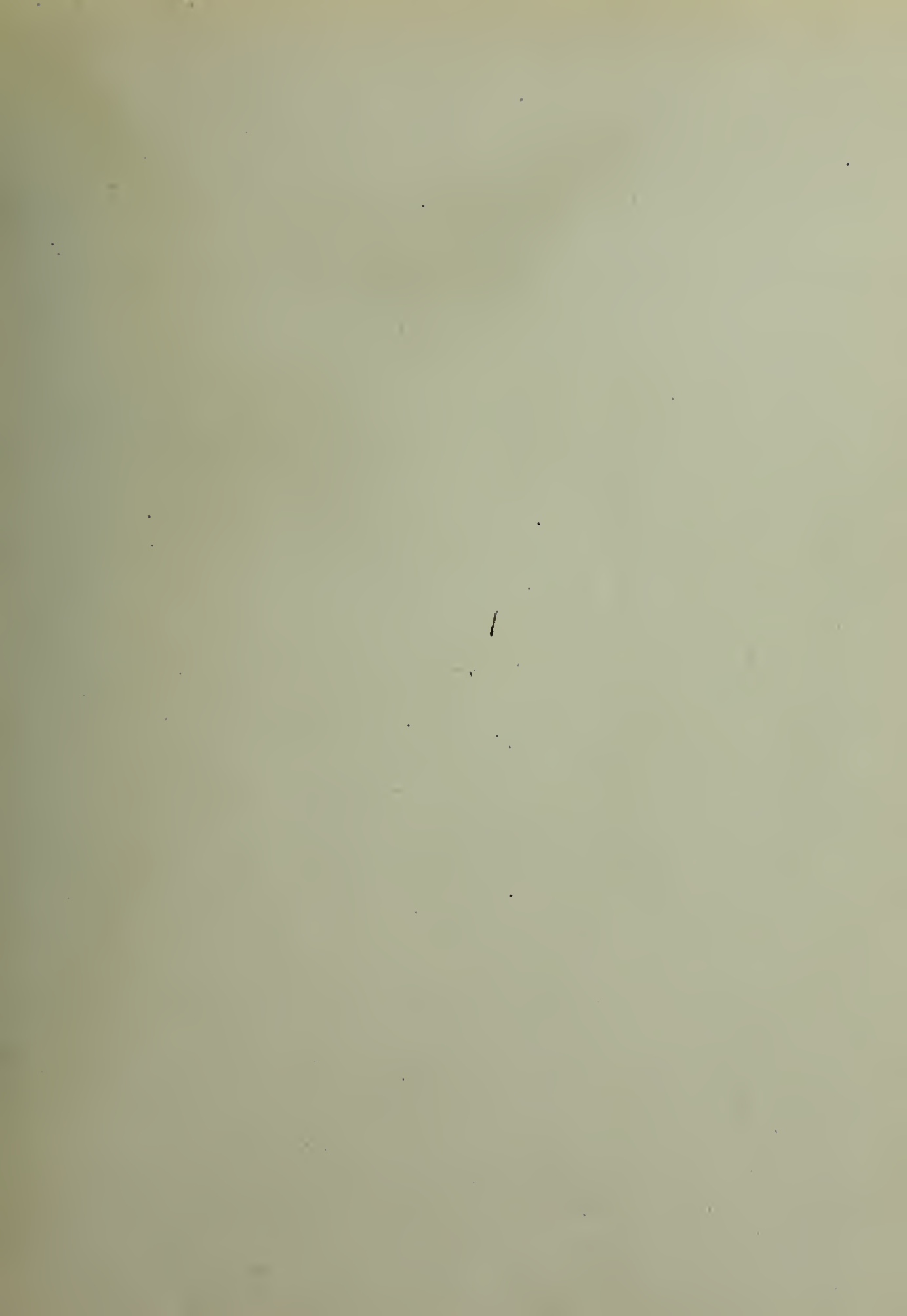
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Sulphur compounds in coke.

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SULPHUR COMPOUNDS IN COKE

BY

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THE SULPHUR IN COAL AND COKE

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THE SULPHUR IN COAL AND COKE

I. Introduction

The study of the changes in combination which sulphur undergoes in the coking of coal is one of vital importance. Sulphur in coke which is to be used in most metallurgical processes, as well as the sulphur in coal gas is detrimental, as it produces undesirable properties in the ultimate material. Sulphur in steel causes it to become weak and brittle or hot short, and for that reason the sulphur in the coke used for the manufacture of steel should be kept as low as possible. The sulphur in coal gas is present as hydrogen sulfide and as carbon bisulfide or other organic sulphur compounds. These on burning oxidize to sulphur dioxide, which is very obnoxious.

If the forms into which sulphur changed during the process of coking were known, it might be possible to control the change and drive the sulphur over into the gas or tar as desired.

The main procedure in this study was based on the theory that the iron or the iron pyrites in the coke was reduced to pyrrhotite, the magnetic sulphide of iron, and evidence of this combination would give at least one view-point as to some of the sulphur transformations which occur in the coking process.

II. Historical.

The origin of pyrite in coal has been the object of much speculation. The underground circulating waters contain considerable amounts of iron salts, hydrogen sulphide, and salts in solution. ⁽¹⁾ Some of the pyrite is in large enough bands or lenses so that it can be separated by picking at the mines, while other particles are so small that they cannot be eliminated. However, all of the sulphur in the coal is not in the pyritic form, but is present in the sulphate and organic forms.

It is a recognized fact that during the coking of coal the sulphur undergoes some radical changes. As far back as 1878, Bradbury showed that there was no sulphate sulphur in coke, and that the sulphur remaining in the coke was very stable, since he could not remove it even with the aid of aqua regia and potassium chlorate. He was able to find a very small amount of sulphide sulphur, which he liberated with hydrochloric acid.

In the coking of coal the sulphur of FeS_2 is partly volatilized, but a portion of it is left. ⁽²⁾ The sulphate is reduced to the sulphide in the hot reducing atmosphere of the coking oven, and some of the organic sulphur as well as some of the sulphur of FeS is changed into a more stable form and retained by the coke. Powell says that sulphur in the coke is present in two forms, sulphide sulphur and a more stable form which is released only with great difficulty. ⁽²⁾ This, he says, is probably a carbon-sulphur compound which is stable at the temperature of the coking oven. He was able to remove part of this sulphur with nascent hydrogen.

Jeude has shown that carbon has a certain avidity for sulphur

at a given temperature, and that as the temperature increases the amount of sulphur retained by carbon decreases.⁽³⁾

Dr. M. Tidy says that if pyrite is heated below the fusion point, pyrrhotite will be formed and sulphur will be volatilized.⁽⁴⁾

In 1916, A. Rowen and S. C. Lilja took out a patent on a process whereby certain ore constituents such as the sulphides of iron and nickel were rendered magnetic by reduction with coal, sulphur, and their compounds, and with superheated steam.⁽⁵⁾ In the same year C. S. Brooks patented a process for reducing ferric oxide to the magnetic oxide with the aid of carbon monoxide at a temperature of 700 degrees Centigrade.⁽⁶⁾ Later Brooks patented a process for converting pyrites into pyrrhotite by heating in the absence of air. After farther experiments, he conceived the idea of reducing pyrite to pyrrhotite in a reducing flame of methane and ethane assisted by the action of steam, and later he patented the process. The reaction zone was kept at a temperature of about 800 degrees Centigrade, which corresponds closely to the temperature of the coke oven. The atmosphere of reducing gases is also similar to that present during the coking process.

The conditions used by the above men in the reduction of pyrites nearly approaches the conditions in the low temperature coke oven, and this leads to the possible hypothesis that the sulphides of iron are reduced to pyrrhotite, and to the farther possibility of the existence of a carbon-sulphur compound with magnetic properties.

The conclusions to be drawn from a historical review of these investigations are as follows:

1. The sulfide of iron in coke is not present as FeS_2 , but

as a lower sulfide.

2. Conditions such as temperature and reducing atmosphere of gases favor the reduction of FeS_2 to Fe_2S_3 , the magnetic sulfide.

3. Sulfate sulphur is reduced to sulfide sulphur or to a carbon-sulphur compound.

4. All available evidence points to the existence of a carbon-sulphur compound without magnetic properties.

5. There are two forms of sulphur in coke, sulfide sulphur, and a compound of carbon and sulphur which is very stable. The sulphur from this compound can partly be released by nascent hydrogen.

III. Experimental

About 600 grams of a low temperature coke, Laboratory number 147, from a Saline County, Illinois, coal, were pulverized so that the product would pass a sieve with 100 mesh to the inch. A coke with a high sulphur and iron content was chosen, as these were the elements with which the work was chiefly concerned. The temperature at which the coking took place was about 700 degrees Centigrade, the same temperature, as previously noted, at which most of the reduction of the pyrite took place.

About 50 grams of the pulverized coke was spread out on a sheet of paper and a powerful horseshoe magnet was passed through the coke until no more particles would attach themselves to the magnet. In this manner about 6.5 grams of magnetic material was obtained. This will be referred to as the magnetic extract.

The extraction was also tried by placing about 50 grams of the coke in 300 c.c. of water and alcohol respectively. The solution was agitated by vigorous stirring while the magnet was suspended therein. The wet particles could be removed from the magnet only with great difficulty, so that wet methods for obtaining the extract were discarded.

By scattering this magnetic extract on a sheet of paper, all of it could be picked up again with the magnet, so that as far as possible the carbon that was brought down mechanically with the magnetic material was eliminated by this method. The magnetic material had all of the appearances of the original coke except that it seemed to be a little finer grained. As nothing could be ascertained from the outward appearance of this magnetic material,

a proximate analysis of the coke, the non-magnetic material, and the magnetic extract was made.

It must be noted at this point that the coke was ground on a buckboard, and it is reasonable to suppose that some iron was introduced from this source. Some of the same sample was, however, pulverized in a porcelain mortar, and yielded a magnetic material which exactly resembled in its properties the extract from the sample ground on the buckboard. It is assumed, therefore, that no appreciable quantity of magnetic material was introduced in grinding.

Proximate Analysis

The proximate analysis was made according to the standard methods.⁽⁷⁾ One gram samples of the substance to be analyzed were used in each case.

Total Moisture. One gram of the substance was weighed into a glass capsule, and this was heated for one hour at 104 degrees Centigrade. The capsule was then cooled and weighed, and the loss recorded as moisture.

Ash. The one gram sample used above for the determination of moisture was transferred to a crucible and heated over a low flame for thirty minutes, and then heated over a blast until no farther loss in weight occurred. The difference between the weight of the crucible plus the ash and the weight of the ignited crucible was the weight of the ash.

Volatile Matter. A one gram sample of the material was placed in a porcelain crucible with a tight fitting cover. The crucible was placed in a nichrome triangle over a blast lamp. Over the crucible was placed a 20 gram assay crucible in an inverted position

This inverted crucible had a hole through the bottom which served as a flue for the escaping gases. The sample was then blasted for seven minutes, then removed and cooled. The loss in weight minus the moisture was taken as the volatile matter.

Fixed Carbon. The fixed carbon was obtained by subtracting the moisture, ash and volatile matter from 100.

Table No. 1. Proximate Analysis of Coke

(Magnetic Extract and Non-magnetic Residue)

	Magnetic Extract	Non-magnetic Residue	Coke
Moisture	4.20	4.65	3.30
Volatile Matter	2.06	4.55	3.85
Ash	27.90	9.53	9.90
Fixed Carbon	65.84	81.27	82.93

The ash from the magnetic extract was a deep red in color, while the ashes from the other two were grey in appearance. The analyses of the coke and the nonmagnetic residue were perfectly normal, while the ash of the magnetic residue increased about 18.0%. The fixed carbon decreased about 17.5%.

The proximate analysis shows that the increase of the ash in the case of the magnetic residue was probably due almost entirely to iron in the free state. If there had been any appreciable amount of the sulfide of either iron or carbon, it would have been oxidized and lost in the ash determination and there would have been a larger difference between the gain of iron oxide in the ash in the one case and the loss of fixed carbon in the other. However, this would have been counter-balanced to an appreciable extent as the iron present would take up oxygen from the air and this would cause an increase in weight. The amount of iron in

in the oxide of iron is about 69%, while the percentage of iron in the magnetic oxide varies from 60 to 65 percent. Since the proximate analysis proves nothing definite, a quantitative analysis of the ashes of the magnetic extract and of the coke was made.

Quantitative Analysis of Coke and Magnetic Extract

An analysis of the non-magnetic residue was not made, since this residue resembled the original coke in every respect. The analyses were run according to the methods given in Treadwell and Hall, and in Talbot's Quantitative Analysis.⁽⁹⁾

An analysis of a coke ash should include the following elements: Si, Fe, Al, Ca, Mg, and S. There are other elements present such as Ti, Na, and K, but they generally occur in such small amounts as to be negligible.

The sample of ash was already in a fine state of division, so that grinding was unnecessary. One half gram of the substance to be analyzed was fused in a platinum crucible with about 5 grams of sodium carbonate. The contents of the crucible were dissolved in 150 c. c. of distilled water, with the addition of 20 c. c. of hydrochloric acid. The solution was evaporated to dryness over a steam bath and then dehydrated for four hours in a vacuum oven at 104 degrees Centigrade. This treatment dehydrated the silicate completely. The residue was taken up in 100 c. c. of water with 20 c. c. of hydrochloric acid. The solution was heated until nothing but SiO_2 remained undissolved. The precipitate was filtered upon a quantitative filter paper and washed free of chlorides. The precipitate was ignited in a weighed platinum crucible and weighed. To the ignited precipitate was added 5 c. c. of sulfuric acid, 2 c. c. of water, and 3 c. c. of hydrofluoric acid and the

mixture evaporated until the white fumes of SO_3 were given off. The crucible was again ignited and weighed, and the loss in weight was SiO_2 . The residue in the crucible was iron oxide, and could later be added to the iron precipitate of the sample.

The filtrate from above was treated with 5 c. c. of bromine water to oxidize the iron and then boiled for 10 minutes to get rid of the excess of bromine. To this solution a slight excess of ammonia was added, and the solution boiled again to get rid of the excess of ammonia as the aluminium hydroxide is soluble in an excess. The precipitate was filtered and washed once by decantation and then dissolved from the filter paper with hot dilute hydrochloric acid. The solution was made ammoniacal and the precipitation made again as described above. The precipitate was washed free of chlorides and ignited in a weighed platinum crucible. The ignited precipitate is a mixture of the oxides of iron and aluminium. About 15 times the weight of the ignited oxides was mixed with KHSO_4 and fused at a red heat until SO_3 fumes nearly stop coming off. The fusion is cooled and the mixture is dissolved in distilled water, no acid being necessary. To the clear solution a few c. c. of sulfuric acid are added, and the iron is reduced with pure zinc, and titrated with KMnO_4 . The iron is thus determined and converted into the oxide and reported as such. By subtracting the Fe_2O_3 from the mixture of the oxides, the Al_2O_3 is obtained.

To the filtrate from above, NH_4Cl is added, and the solution is made slightly alkaline with NH_4OH and brought to boiling. Ammonium oxalate is added to the solution slowly with stirring and the solution allowed to stand for at least an hour. The precip-

itate was filtered off, washed free of chlorides, and ignited for one half hour. The residue in the crucible was CaO and was reported as such.

The filtrate from above was evaporated until the ammonium salts just began to crystallize out, and enough water was then added to dissolve them. To this solution was added 10 c. c. of sodium ammonium phosphate, and as the precipitate began to form, one third the volume of the solution of NH_4OH was added and the solution allowed to stand for 24 hours. The precipitate was filtered, washed and ignited, and weighed as $\text{Mg}_2\text{P}_2\text{O}_7$. MgO was reported.

According to the ash analyses, the larger part of the magnetic extract is ferric oxide. The results of the analyses are tabulated in the table below.

Table No. 2. Analysis of Ashes

	Magnetic Extract	Coke
Al_2O_3	22.46%	1.44%
Fe_2O_3	77.50%	27.10%
SiO_2	17.08%	42.00%
CaO	.44%	1.01%
MgO	<u>.17%</u>	<u>.32%</u>
Total	98.63%	92.87%

As can be seen from the results, by far the greater portion of the ash of the magnetic extract is composed of ferric oxide. The analysis of the coke ash is normal. The ash analysis did not prove anything definite as to the exact nature of the magnetic mixture. For this reason the iron sulphur ration of the various compounds was desirable, as it might clear up the situation. If the

iron sulphur ratio established corresponded approximately to the iron sulphur ratio of the magnetic sulphide, a great step toward the solution of the problem would be made.

Determination of Iron and Sulphur Ratio.

The sulphur in the magnetic extract, coke and non-magnetic residue was determined according to the method described by Parr.⁽⁸⁾ A .5000 g. sample of the material to be analyzed was exploded in a Parr explosion bomb with a scoop of Na_2O_2 and 1 gram KClO_3 . The fusion was dissolved completely in warm water and the solution acidified with HCl . The solution was then boiled and filtered. About 5 c.c. of bromine water was added to oxidize all of the iron. Then about 10 c.c. of hot BaCl_2 solution was added, and the precipitation allowed to go on for at least 12 hours. The precipitate was filtered, washed, and ignited and weighed as BaSO_4 .

The iron was determined by burning a .5000 gram sample in a nickel crucible with .2000 gram of sugar and a scoop of Na_2O_2 . In every case the fusion was complete. The crucible was covered with a tight fitting cover to prevent the loss of some of the sample during the explosion. A weight of a few ounces held the lid in place during the fusion. The sintered mass in the crucible was dissolved in warm water and then acidified. The solution was made alkaline with ammonia and boiled to coagulate the precipitate of ferric and aluminium hydroxides. The precipitate was filtered and washed by decantation, then dissolved from the paper with dilute sulphuric acid. The iron was then completely reduced with pure zinc, and titrated with KMnO_4 .

Table No. 3. The Iron-Sulphur Ratio of Coke, Magnetic Extract, and Non-magnetic Residue

	Magnetic Extract	Coke	Non-magnetic Residue
Sulphur	1.33	1.44	1.46
Iron	15.50	2.00	2.10

From the results we can see that the sulphur in the magnetic extract decreases about 12% while the iron gains about 13.5%. This would tend to show that there was no magnetic sulphide of iron present, for the sulphur would tend to increase as the iron increased if this were true. If there is any magnetic sulphide present it is in a very small amount as compared with the amount of free iron present. If there was a sulphur-carbon compound present, it was non-magnetic, for the carbon and the sulphur decrease to about the same extent. A knowledge of the amounts of sulphide sulphur and sulphide iron might give more conclusive information. The above iron-sulphur ratios do not correspond to that of pyrrhotite in any case.

Determination of Sulfide Sulphur and Iron Soluble in HCl.

Since pyrrhotite is soluble in HCl, .5000 gram samples were treated with dilute HCl until no more H_2S gas was evolved. The insoluble residue was then filtered and washed, and the remaining sulphur determined by the explosion method as explained above. The difference between the total sulphur and the sulphur just determined was taken as the sulphide sulphur.

The filtrate from above was made ammoniacal, and the precipitate filtered and washed. The precipitate was then dissolved with dilute sulphuric acid and the iron determined by titration with $KMnO_4$ as described.

The results are shown in the following table:

Table No. 4. Iron and Sulphide Sulphur Ratios of
Magnetic Extract, Coke, and Non-magnetic Residue.

	Magnetic Extract	Coke	Non-magnetic Residue.
Iron soluble in dilute HCl	14.6%	1.55%	1.51%
Sulphide Sulphur	.70%	.48%	.53%

The ratio for the iron and sulphur in coke and non-magnetic residue is approximately 3 to 1. If it were the pyrrhotite, the ratio would be about 2 to 1. If there is a sulphide of iron present it is not the magnetic sulphide or it would appear in the magnetic extract. There is no iron sulphur compound known with a ratio corresponding to the iron sulphur ratio of the magnetic extract.

However there is an increase of sulphide sulphur in the case of the magnetic extract. This increase is probably due to the fact that free iron when dissolved in an acid liberates nascent hydrogen and this in turn will take out some of the sulphur which is in the coke in another form, as H_2S . In order to prove this fact enough pure iron wire was added to a sample of the coke to make its iron content equal to that of the magnetic extract, and the analysis for the sulphide sulphur was run on this sample. The result was that the sulphide sulphur liberated by the excess iron brought the total sulphide sulphur up to that of the magnetic extract. However there is .50% of sulphide sulphur that should be accounted for in the non-magnetic residue and the coke. It is evident that there is not an appreciable amount of the magnetic sulphide of iron present in the coke, as the analyses of the coke and the non-magnetic residue show practically the same iron sulphur ratio and farther the small increase of sulphide sulphur in the

magnetic extract can be accounted for by assuming that it is due to the fact that the hydrogen liberated by the free iron in the acid solution has the ability to take some of the sulphur which is in another form out of the coke in the form of H_2S .

To prove these facts more definitely, a synthetic coke was made, and a series of experiments completed with it.

Synthetic Coke.

A synthetic coke was prepared by heating together at a temperature of about 700 degrees Centigrade a mixture of sugar carbon and sulphur. The above temperature was used as it approximates the temperature at which the low temperature coking takes place.

The coke was pulverized in a mortar so that no iron would get into the mixture. A strong magnet was run through the finely divided coke and no particles adhered to the magnet. This practically eliminates the possibility of a carbon sulphur compound being formed at this temperature with magnetic properties.

The coke was analyzed for total sulphur and sulphide sulphur by the usual methods, and the following results obtained:

Table No. 5. Iron and Sulphide Sulphur Ratio of Synthetic Coke.

Total Sulphur	3.00%
Sulphide Sulphur	.09%

The sulphide sulphur is considerable lower than in the case of the other samples that were analyzed. Enough pure iron wire was added to the sample to bring its iron content up to that of the magnetic extract. The sulphide sulphur increased to only .16%. The difference between the sulphide sulphur in the synthetic coke and that of the other samples which were analyzed may be attributed

to the sulphides of iron, but not the magnetic sulphide, as the sulphide sulphur did not increase enough in the magnetic extract to warrant that conclusion.

IV. General Summary.

1. There was no magnetic carbon sulphur compound formed at the temperature of the coking oven.
2. Iron pyrites is almost completely dissociated into free iron and sulphur. The free iron remains in the coke as such and the sulphur goes into the gas or remains in the coke or tar in some other form.
3. That the greater part of the magnetic material in the magnetic extract is free iron.
4. There is quite likely some pyrites in the coke, but its iron sulphur ratio is considerably lower than that of pyrrhotite. The pyrites in this coke is non-magnetic.
5. If a scheme of analyses for the determination of the sulphides in the presence of iron, and the sulphur as retained by the coke were worked out, a great deal as to the exact nature of the iron and sulphur combinations in the coke would be learned.
6. With the aid of empirical cokes made at different temperatures, possibly a temperature could be found at which the magnetic sulphide of iron would be formed and in this way the control of its formation effected. A carbon sulphur compound might also be obtained, even by the addition of some other element.

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