THE ACTION OF ORGANIC SULPHUR IN COAL DURING THE COKING PROCESS.—By A. L. McCALLUM, B. Sc., Halifax.

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I was led to undertake this investigation by the conflicting statements of the authorities as to the action of organic sulphur during the coking process. Some say that the whole of the organic sulphur remains in the coke, others that part is volatilized, and still others that all the organic sulphur is driven off in the coking process. It is barely possible that all these statements are true of different coals, but I wanted, if possible, to find out what was the case with a typical Nova Scotia coking coal.

It occurred to me that if I could get a series of samples with a decreasing amount of inorganic sulphur and an increasing amount of organic, I would be able to get some data on the above subject, by determining the amount of inorganic and organic sulphur, and at the same time the amounts of volatile and fixed sulphur in the various samples.

It might be well at this point to say a few words as to the manner in which sulphur occurs in coal. To the best of our knowledge sulphur occurs in three forms in coal:—(1) as sulphates; (2) as iron pyrites; (3) as organic sulphur.

The coal used in this investigation was practically free from sulphates so that we have the two latter forms only to deal with.

The action of iron pyrites when subjected to heat without access of air is well known. There is a loss of one atom of sulphur according to the equation $Fe\,S_2 = Fe\,S + S$. The coke oven presents ample time and the necessary conditions for this reaction to be complete.

Not knowing in what state of combination the organic sulphur occurs in coal, it is impossible to say what effect the heat of the coke oven will have. It was, as previously stated, in an attempt to throw some light on this question, that the investigation was undertaken.

Now to return to our coal samples. The only way to obtain such a series of samples as previously mentioned, viz.: with decreasing inorganic and increasing organic sulphur was to fractionate the coal on the basis of specific gravity, that is separate it into several fractions of gradually decreasing specific gravity. The means used to accomplish this were solutions of calcium chloride of varying specific gravities. The coal used was crushed to pass through $\frac{1}{12}$ inch mesh screen and was then placed in a vessel containing a solution of calcium chloride of slightly higher specific gravity than that of the coal.

For instance, the raw coal was found to have a specific gravity of 1.323. For this a calcium chloride solution of 1.35 specific gravity was used. This separated the coal into two fractions having the following specific gravities: the lighter material 1.275, and the heavier 1.731.

Part of this lighter or floating fraction was reserved for analysis and the remainder was treated with a calcium chloride solution of lower specific gravity. This procedure was kept up until, at a specific gravity of 1.24, there was no floating fraction.

Between these two extremes I obtained five fractions of the following respective specific gravities:

No. 1	1.323
No. 2	1.275
No. 3	1.261
No. 4	1.253
No. 5	1.243

The proximate analyses of these samples are as follows:—

TABLE I.

No.	Volatile matter.	Fixed carbon.	Ash.	Sulphur.	Sulphur in coke.
1	35.10	59.74	5.16	2.06	1.80
2	35.92	61.57	2.51	1.29	1.17
3	36.10	62.27	1.63	1.09	.85
4	37.47	61.50	1.03	.95	.78
5	37.75	61.35	.90	.88	.68

The only method at present available for the determination of the organic sulphur in coal is by difference, and there is one inherent source of error which, however, I think is not material. The method referred to is as follows:—The percentage of iron is determined. Then this iron is combined with the necessary amount of sulphur to form iron pyrites ($Fe S_2$). This amount of sulphur is deducted from the total amount in the coal and the balance is called organic sulphur.

The error referred to in this method is due to the fact that it is almost certain that there is some iron present as silicate in the "stone and shale" which are always present in the coal. But as the percentage of iron in the "stone and shale" rarely exceeds 3 per cent. and the percentage of stone and shale in the coal under consideration rarely exceeds 5 per cent. of the coal by weight, it will readily be seen that any error introduced will be exceedingly small.

Applying this method to the samples under consideration, we obtain the figures given in Table II.

TABLE II.

No.	Organic sulphur.	Inorganic sulphur.
1	37.86%	62.14%
2	56.59%	43.41%
3	71.56%	28.44%
4	83.16%	16.84%
5	85.23%	14.77%

We have thus clearly obtained a series of samples with gradually decreasing inorganic and increasing organic sulphurs.

There is also another way in which the total sulphur may be distributed, viz.: as volatile and fixed sulphur; meaning of course, that sulphur which escapes during the coking process and that which remains in the coke.

The method used in obtaining this information is to first determine the total sulphur in the coal and then the total sulphur in the coke produced from that particular coal. From this it is easy to calculate the amount of sulphur volatilized.

Table III gives the figures thus obtained.

TABLE III.

No.	Volatile sulphur.	Fixed sulphur.
1	33.49%	66.51%
2	42.64%	57.36%
3	50.46%	49.54%
4	49.47%	50.46%
5	52.27%	47.73%

There is not the same regularity as shown in Table II, but there seems to be an increase in the amount of volatile sulphur in those samples having a high percentage of organic sulphur.

Now if the only sulphur volatilized was the one atom of sulphur in pyrites according to the above mentioned squation, we can calculate what the percentage of volatile sulphur should be; because the sulphur called inorganic is assumed to be present as iron pyrites. So that if we take half the inorganic sulphur it should correspond with the percentage of volatile sulphur if the above supposition is true, and also if there is no organic sulphur volatilized.

The result of this calculation is given in Table IV.

TABLE IV.

No.	One half the Inorganic sulphur.	Volatile sulphur.	Difference.
1.......	31.07	33.49	2.42
2.......	21.70	42.64	20.94
3.......	14.22	50.46	36.24
4.......	8.42	49.47	41.05
5.......	7.38	52.27	44.89

This would seem to indicate that when the inorganic sulphur was in excess the above supposition is approximately true, but that it does not hold at all when the organic is in excess. It seems rather strange why this should be so unless it is due to mass action.

I think we are perfectly justified in concluding that in the coking process a very considerable part of the organic sulphur is volatilized.