

Attempted Removal of Sulfur from Coal and Coke

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The purpose of this paper is to report briefly on some experiments designed to remove inorganic sulfur from coal or to prevent its retention in coke, by chemical means. It may be said at once that although some success was achieved, no method with promise of industrial practicability was found.

A substantial proportion of the sulfur in coals occurs as ferrous disulfide, $\text{Fe}^{+2}\text{S}_2^{2-}$, usually in the mineral form known as pyrite. It is well known that pyrite dissociates to ferrous sulfide and sulfur, the dissociation pressure becoming appreciable at 450-500°. Ferrous sulfide is stable and undergoes little change before 1300-1400°. Various lines of work show that the sulfur released by the pyrite in coal during carbonization becomes fixed in the carbonaceous matter of the coke. Thus Cernic carbonized a series of coals in the presence of finely dispersed synthetic pyrite labelled with S^{35} ; she found that in all cases a more substantial proportion of the radioactivity was retained in the coke than could be accounted for by the ferrous sulfide.

Mazumdar, Lahiri and their co-workers² investigated the reaction of sulfur with coal at 250-350°. Much hydrogen sulfide was released, which they attributed to dehydrogenation of hydroaromatic structures in the organic matrix; others have suggested that in addition dehydrogenation and cross-linking of aromatic nuclei takes place³. If the coal is heated with sulfur at 300-350° and then carbonized, the yield of volatile matter is drastically reduced and the coke has an increased sulfur content². Some known sulfur compounds decompose at 500-600° with formation of hydrogen sulfide or mercaptans⁴; the latter substances, released during coal carbonization, could react elsewhere on the coal surface to give some firmly bound type of sulfur-carbon complex, their sulfur thus remaining in the coke.

It is evident therefore that a number of reactions involving sulfur can take place during coal carbonization, in which both inorganic and organic components play a part. Some of these reactions result in the formation of very stable organically bound sulfur complexes. Hence one possible way to reduce the sulfur content of coke would be to interfere with these reactions at temperatures below 600°, preferably in such a way that relatively stable volatile sulfur compounds are formed. The above ideas guided one of the series of experiments described in this paper: a coal was carbonized at 600° in the presence of various additives, and the sulfur content of the char compared with that of a standard char prepared in the absence of additive.

The other series of experiments was based on the reported solution chemistry of pyrite^{5,6}. Various reagent mixtures are stated to dissolve

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pyrite at temperatures of 20-100°, and it was hoped that one could be found that would remove the disulfide from coal without serious oxidation or other change of the organic substance. It is not clear from the literature what reactions occur in bringing the pyrite into solution. The presumed interpretations of the reactions tested with pyrite in coal are:

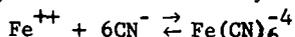
1. Boiling potassium nitrate or chlorate with oxalic acid⁷; the ferrous iron in the presence of the mild oxidizing agent probably gives the very stable ferric oxalate complex, while the sulfur forms potassium sulfite or sulfate.

2. Stannous chloride and hydrochloric acid⁸: the pyrite may be reduced so that ferrous chloride and hydrogen sulfide result.

3. Calcium hypochlorite⁹: the pyrite must be oxidized to ferric sulfate. This reagent has also been used for "sweetening" gasoline, since it removes sulfur from many organic sulfur compounds, including thiophene if the pH is adjusted to weakly alkaline.

4. Aqueous potassium cyanide¹⁰: it is stated¹⁰ that pyrite does not dissolve on treatment with boiling saturated potassium cyanide for 6 hours. However, the following argument⁴ suggests that under the conditions dissolution might take place.

The solubility of pyrite in water is said⁹ to be 4×10^{-5} gm mol./l., so that the solubility product would be 1.6×10^{-9} and the concentration of Fe^{++} in equilibrium with the solid 4×10^{-5} gm. ion/l. However, recent unpublished work¹² suggests that the figures are considerably too high, but that in view of the instability of the S_2^{-2} ion its concentration could be suppressed and that of Fe^{++} materially increased by removing oxygen from the system. Now if a suitable ligand were added to the suspension, such that Fe^{++} is strongly complexed and its concentration in equilibrium with the complex reduced below that calculated from the solubility product of pyrite, the pyrite should in principle go into solution. One of the most stable complexes formed by Fe^{++} is the ferrocyanide:



for which the stability constant at 25° is 10^{24} . Simple calculation shows that if pyrite dissolved in 5N cyanide solution until the ferrocyanide concentration became 0.1 N, the equilibrium concentration of Fe^{++} would be 6×10^{-30} gm. ion/l. Even if the solubility product of pyrite is considerably less than 1.6×10^{-9} , it should still dissolve in cyanide solution. Equilibria should be more favorable at room temperature than 100°. Some experiments on the treatment of coal with cyanide solution have been made:

Results

The coal used in this study was a high-volatile A bituminous coal from Champion Mine of the Pittsburgh seam. Relevant analytical data are given below:

<u>Proximate Analysis</u> :	Volatile matter	35.85%	Ash	11.35%
	Fixed carbon	52.8%	Moisture	1.19%
<u>Ultimate Analysis</u>	(d.m.m.f., Parr's basis) 83.4%C, 5.7%H, 1.6%N, 0.6%S, 8.6% O (by diff.)			

Sulfur Distribution:

total	2.46%,	pyritic 1.95%,	organic 0.49%,	sulfatic 0.02%
% of total sulfur:	79%	20%	1%	

A. Change in Sulfur Distribution on Carbonization

A 30 gm. sample of coal (65 x 150 mesh) was placed in a sample holder and lowered into a furnace already preheated to the desired temperature; a flow of nitrogen (1 litre/min.) passed upwards through the furnace. The sample was left in the furnace for one hour after it reached temperature equilibrium, and then cooled in nitrogen. The char was then analysed for the total sulfur and the various inorganic forms of sulfur by standard A.S.T.M. procedures;¹³ the organic sulfur is determined by difference. Data were obtained for a series of temperatures from 200-700°. The results are plotted in Figs. 1 and 2, where the sulfur distribution is shown as percentages of the total sulfur in the char and as percentages of the total sulfur in the raw coal respectively; the latter curve includes the proportion of sulfur lost in volatile products (obtained by difference).

It should be noticed that even by 200-300° there appears to be some gain of organic sulfur and loss of pyrite even though no ferrous sulfide could be detected. Possibly the organic material reduces pyrite, forming unstable sulfur-containing groups which subsequently are lost as volatile matter. The points for organic sulfur could be made to lie on a curve having a maximum at 200-250° and a minimum at about 400°, which would support the above suggestion, but the number of points available hardly justifies the drawing of more complex curves than those shown in the figures.

It is clear that by 600-700° most of the pyrite has decomposed, that the sulfur lost by the pyrite is much more than equivalent to the amount of sulfide formed, and that the proportion of organic sulfur in the char has considerably increased.

B. Carbonization in the Presence of Additives

For these experiments, the same apparatus and methods were used as above. For each experiment, 27 gms. of coal and 3 gms. additive were mixed by hand for 30-60 minutes; the mix was apparently dry even when the additive was liquid, owing to adsorption. Two rates of heating were used, 5.5-5.8°/min., and 80-90°/min.; conditions during carbonization were static, that is, no nitrogen flow was used. In the first case the sample was held at the maximum temperature (600°) for 15 minutes, and in the second for 60 minutes. The product, after cooling in nitrogen, was finely ground and analysed for total sulfur by the Eschka method.

Twenty seven substances were tested as additives, of which all but three were organic. They included various alcohols and sugars, which would give water and possibly olefins on pyrolysis; several high polymers, which should give on pyrolysis monomers capable of picking up sulfur; and some aromatic and aliphatic oxygen compounds that might take up sulfur to give a stable but volatile heterocyclic compound. Carbonization in the presence of most of these substances gave a char containing less sulfur than if no additive had been used, but the effect was small. It was appreciable for the four substances listed in Table I. It has been reported¹⁴ that powdered pyrite is slowly decomposed by ammonium chloride, a sublimate of ammonium sulfide being formed; at 335°, 7% sulfur is lost in 25 minutes.

TABLE I

Carbonization of Pittsburgh Seam Coal at 600° in the Presence
of Additives (10% concentration)

<u>Additive</u>	<u>Heating rate</u> °/min.	<u>% loss in</u> <u>wt. at 600°</u>	<u>% S in</u> <u>Char</u>	<u>S in coke</u> <u>S in coal</u> ^x 100
None	92.2	28.5	2.11	61.3
	5.6	23.8	2.22	68.8
Benzene-1,2,4,5-tetra- carboxylic dianhydride	80.0	21.5	1.60	51.0
	5.6	16.2	1.42	48.4
p. diphenyl-benzene (Santowax P)	77.5	29.7	2.03	58.0
	5.4	23.6	1.57	48.8
Sodium borohydride, NaBH ₄	72.5	10.0	1.64	60.0
	5.63	6.72	1.47	55.7
Ammonium chloride	72.5	23.0	1.68	52.3
	5.6	21.4	1.32	42.2

It will be noticed that sulfur removal was more effective at the lower rate of heating. With the diphenylbenzene and the borohydride, hard cokes were obtained. Ammonium chloride yielded a very soft coke. The dianhydride gave a soft granular product, and the plastic zone appeared to have been destroyed or greatly reduced. At 5% concentration of additive the use of ammonium chloride showed some reduction of sulfur (1.87 and 1.93% S in the char at 70.5 and 65.6°/min. heating rate respectively); the other substances had little effect.

C. Treatment with Aqueous Solutions

1. Potassium Cyanide. 200 ML of 10% cyanide solution (approx. 1.5N) were allowed to percolate through 30 gm. coal in a column. The coal was (a) 65 x 150 mesh, and (b) -200 mesh, and percolation took 105 minutes and 36 hours respectively. No attempt was made to remove oxygen from the system. The product was washed with 200 ml. water, dried at 110° and carbonized as before. The total sulfur contents of the char were (a) 2.44, (b) 2.00%.
2. Potassium Cyanide and Potassium Nitrate. 15 Gm. coal (65 x 150 mesh) was refluxed gently for 6 hours in a solution of 0.15 mole each of cyanide and nitrate in 250 ml. water. The filtered, washed and dried coal contained 1.90% S (compared with 2.46% in the untreated coal).
3. Potassium Nitrate and Oxalic Acid. A suspension of 15 gm. coal in 250 ml. of a solution of 0.01 mole oxalic acid and 0.02 mole nitrate was left at room temperature for 24 hours, and then refluxed for 8 hours. The sulfur content of the product was 1.94%.
4. Stannous Chloride and Hydrochloric Acid. The treatment was as in #3 (0.01 mole each SnCl₂ and HCl). The sulfur content of the product was 2.35%.
5. Calcium Hypochlorite. A solution of 10 gm. hypochlorite in 190 ml. of water, adjusted to pH8 by addition of acetic acid, was allowed to percolate through 30 gm. 65 x 150 mesh coal (this took 3 hours). The ash content of the product was 13.3% (untreated coal, 11.35%) and the sulfur content 2.13%

D. Discussion and Conclusions

The preliminary experiments on sulfur distribution confirmed that

sulfur from pyrite becomes fixed in the organic matter of the char on carbonization, and that any interference with this process must take place at 350-500° if it is to reduce the sulfur content of the char. Carbonization in the presence of certain additives did cause a marked removal of sulfur, though probably not as much as would be desirable in industrial practice. Under the conditions used, the amount of additive needed was relatively large and would be costly in practice; in two cases weak cokes were obtained. In addition, the use of ammonium chloride would give rise to serious corrosion problems. However, the principle that sulfur fixation can be interfered with and reduced in extent is confirmed. For effective action it is no doubt necessary that the additive should volatilize and penetrate the coal particles (if the latter are as big as 65 x 150 mesh) or diffuse readily through the fused mass. If very finely divided coal could be charred in a fluidized bed up to 500-600° as a pretreatment in a fluidizing gas containing a fair partial pressure of ammonia, hydrogen, or possibly moist carbon dioxide, it is likely that the sulfur content of the char could be greatly reduced.

None of the treatment with aqueous solutions was particularly effective. However, it is striking that the cyanide treatment had no effect on 65 x 150 mesh coal with a contact time of 1 3/4 hours, but an appreciable one on -200 mesh coal in 36 hours. Of the other treatments, potassium nitrate/cyanide and potassium nitrate/oxalic acid had an appreciable effect even on the coarser coal size.

There seems little doubt that the primary difficulty in all the sulfur removal processes tested is in getting adequate contact between the reagent and the finely dispersed pyrite grains. It seems probable that with a more sophisticated appreciation of pyrite chemistry much of the pyrite could be removed from a coal with an aqueous solution of a suitable complexing agent, provided finely pulverized coal can be used.

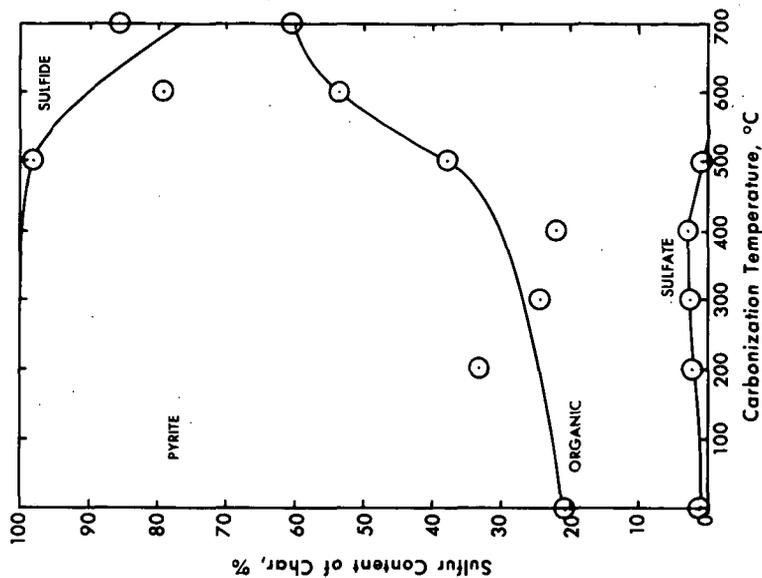
Acknowledgement

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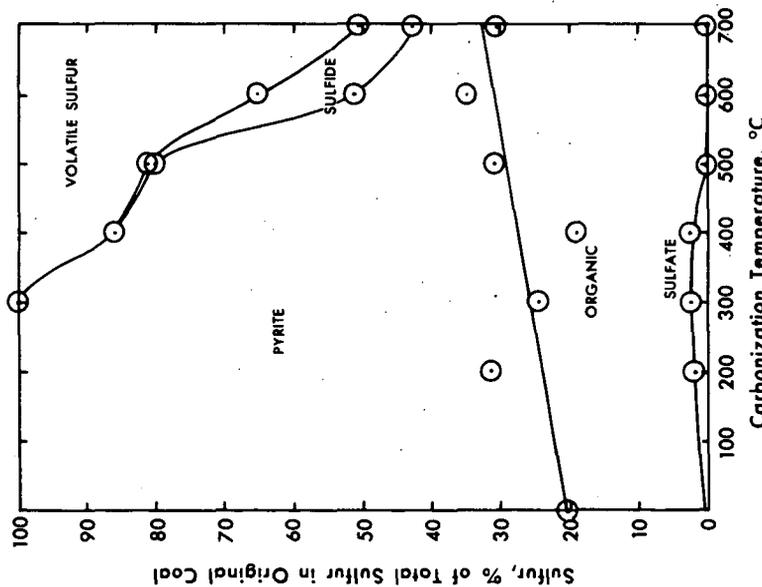
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DISTRIBUTION OF FORMS OF SULFUR IN PITTSBURGH SEAM COAL AND CHARS, EXPRESSED AS FRACTIONS OF TOTAL SULFUR IN SAMPLE ANALYSED

Figure 2



DISTRIBUTION OF FORMS OF SULFUR IN PITTSBURGH SEAM COAL AND CHARS, BASED ON TOTAL SULFUR IN UNHEATED COAL

Figure 1