Part II: Sulfidation of Coal Char and Synthetic Chars

Introduction

Desulfurization of coal and coal char in hydrogen results in evolution of H_2S. Depending on the process, the H_2S is either entirely or partly removed and recirculated. The work, described in Part II, was undertaken to obtain a better understanding of the interaction between chars and gas mixtures containing H_2S.

A literature survey indicated that no investigations have been made of the sulfidation of carbonaceous materials, including chars, in gas mixtures of H_2 and H_2S such that the sulfur potential was systematically varied.

Experimental

Char from two different sources, prepared under a variety of conditions, was used in this work. The preparation conditions are summarized in Table II.

The preparation of char from Illinois No. 6 coal was described in Part I (Experimental). Char from ash-free filter paper (0.008% ash) was prepared by charring the paper, contained in a high-purity alumina boat, in an atmosphere of dry He at 600 or 900°C for 3 hours. After the paper was charred, the boat was pulled to the cool end of the reaction tube where it slowly cooled. Subsequently, the char was quickly transferred to a desiccator where it was stocked. The chars that were further treated in He at 1250 and 1500°C for 24 and 96 hours, respectively, were taken from this stock.

The sulfidation experiments were done in a vertical furnace with the H_2-H_2S mixture entering at the bottom of the reaction tube. The H_2/H_2S-ratio in the gas was adjusted by using the usual arrangement of capillary flow meters. In most of the experiments a gas flow rate of 30 cm^3(STP)/min was used.

For each sulfidation experiment about 100 mg of char was placed in an alumina tray. In most cases the sulfidizing treatment was one hour, after which the sample was quickly pulled up to the cool top of the reaction tube, while the He was kept flowing. The cooled sample was then transferred to a desiccator. Sulfur in the char was analyzed by the combustion method(1).

In some selected cases about 750 mg of char was sulfidized, and afterwards analyzed for oxygen by the neutron-activation method. The surface areas of the chars used were determined by the BET method.

Results and Discussion

The partially desulfurized coal char (Table II) was sulfidized at 600, 800, and 900°C in H_2-H_2S containing 0 to 100 percent H_2S. The results are given in Figure 14, in which the sulfur content of the char after one hour reaction time is plotted versus the percentage of H_2S in the gas at the experimental temperature, denoted by $(\%H_2S)_T$. Similar results were obtained after sulfidation for 4 hours.

In calculating $(\%H_2S)_T$ from the percentage of H_2S in the ingoing gas (at room temperature), due allowance should be made for the partial dissociation of H_2S at higher temperatures. The equilibrium H_2S percentage of the gas at the reaction temperature was calculated from the available thermodynamic data(2).

The present results may be compared with those obtained by Polansky, et. al.(7) who treated coke in H_2S-N_2 mixtures containing 4.2 and 8.8 percent H_2S. Their results show no pronounced difference in the extent of sulfur absorption at 800 and 900°C.

Of special interest is the absorption of sulfur at 900°C in H_2-H_2S mixtures, containing less than 2 percent H_2S, by previously desulfurized coal char (from Illinois coal). This coal char was produced by desulfurization of a char that originally contained 0.13 percent sulfur as pyrrhotite; this is equivalent to about 0.23 percent iron. Upon sulfidation of this desulfurized coal char, pyrrhotite is expected to form when the sulfur potential is sufficiently high. This is illustrated in Figure 15, where a sudden rise in the amount of sulfur absorbed is observed when $(\%H_2S)_T > 0.3$. This is in good agreement with the value calculated from the thermodynamic data for the iron/pyrrhotite equilibrium(2) at 900°C. The increase in sulfur content at the "break point" in the absorption curve is about 0.20 percent, in good agreement with the estimated amount of iron present in the char.

The sulfur absorption curves, depicted in Figure 14, have the general character of absorption isotherms. However, proper interpretation of these results is hindered by the presence of impurities in the coal char. It was therefore decided to study the sulfidation of essentially impurity-free carbons and synthetic chars.

Sulfidation of Synthetic Carbons and Chars

Granulated samples of high-purity electrode graphite and pyrolitic graphite were equilibrated with a 50 percent H_2, 50 percent H_2S mixture at 1000°C for 1.5 hours; there was no detectable sulfur absorption in either form of graphite. In another experiment samples of electrode graphite and pyrite were placed in separate

parts of an evacuated silica capsule and annealed for 20 hours at 650°C. This corresponds to a partial pressure of sulfur vapor of about 0.14 atm, as estimated from the thermodynamic data for the pyrrhotite/pyrite system(2). After this treatment, no sulfur was detected in the graphite.

The present observations are in general agreement with those of Wibaut and van der Kam(8) who found that even at sulfur pressures above atmospheric, no detectable sulfur was absorbed by either diamond powder or Ceylon graphite.

The results obtained for the synthetic chars are given in Figures 16 and 17 for 600 and 900°C, respectively. In most experiments the reaction time was 1 hour; however, some samples were sulfidized for longer times (up to 3 hours). These samples absorbed essentially the same amount of sulfur as those sulfidized for 1 hour. Moreover, it was observed that equilibrium could be reached from both sides. For example, it was found that filter-paper char (prepared at 900°C) which was first sulfidized in a 50 percent H_2, 50 percent H_2S mixture at 600°C to a final sulfur content of $\sim$1 percent could subsequently be partially desulfurized in a 90 percent H_2, 10 percent H_2S mixture to yield a final sulfur content of 0.4 percent. This is essentially the same as the sulfur content after direct sulfidation of the char in the same gas mixture. Similar observations were made at 900°C, indicating that the absorbed sulfur is in equilibrium with the gas and that the process of sulfur uptake is reversible.

The surface areas of the chars (Table II) are indicated in Figures 16 and 17. It is seen that a char with a larger surface area has, in general, a larger capacity for sulfur absorption. The results obtained for coal char are also shown in Figures 16 and 17 for easy comparison. Coal char and filter-paper char (prepared at 600 and 900°C) have about the same surface areas and are seen to absorb similar amounts of sulfur.

The results of x-ray analysis of the various chars used in this investigation were compared in a qualitative way with the data reported by Turkdogan et al.,(9) as shown in Table III together with estimated mean crystallite sizes. It was mentioned before that graphitized electrode graphite, which has a mean crystallite size of 500 A, did not absorb sulfur, whereas the nongraphitized chars did. Thus, it is concluded from these results that the ability of a given char or carbon to absorb sulfur is in the first place determined by its state of crystallinity. In poorly graphitized or nongraphitized carbons, the amount of absorbed sulfur increases with increasing pore surface area.

In view of the strong affinity between sulfur and oxygen, an attempt was made to investigate the effect of oxygen on the sulfur absorption by char. The initial oxygen content of synthetic chars is shown as a function of the surface area in Figure 18. It is seen that the initial oxygen concentration is a strong function of the surface area and hence the temperature at which the char was prepared (Table II).

To study the change in oxygen concentration after sulfidation of the chars, a series of special experiments was conducted; the results are summarized in Table IV. It is interesting to note that the oxygen content after sulfidation was independent, within the analytical error, of the ratio $(p_{H_2S}/p_{H_2})_T$ in the gas. An increase in the sulfidation temperature resulted in a lower oxygen content in the char, particularly if the char had a larger surface area (Figure 18).

In all cases investigated, it was found that the chars with large surface areas contained more oxygen. Because of the interdependence of surface area and oxygen content, it is difficult to separate their effects on the capacity of a given char for sulfur absorption. However, some indication of the influence of oxygen on the sulfur absorption may be obtained from the results shown in Table IV. For instance, the surface areas of filter-paper char prepared at 600 and 900°C were 330 and 272 m^2/g, respectively, a difference of about 20 percent. After sulfidation at 600°C in a gas of high sulfur potential, the oxygen contents of these chars differed by about a factor of two, yet the difference in sulfur absorbed was not more than about 10 percent. These findings indicate that the influence of oxygen on the sulfur absorption is probably secondary.

In this context the work of Hofmann and Ohlerich(10) should be mentioned. They treated sugar charcoal in dry O_2 at about 500°C to obtain a char containing about 10 percent oxygen as surface complexes. Upon sulfidation of this oxygenated char in S_2 at 600°C, they found that the amount of sulfur taken up was equal to that absorbed by a char which was not previously activated in oxygen. Hofmann and Ohlerich concluded, as did Hofmann and Nobbe(11), that the amount of sulfur absorbed by char is dependent only on its surface area.

Some of the filter-paper chars used in this work were analyzed for hydrogen and nitrogen. The results are summarized in Table V, which shows that the major impurities in filter-paper char are oxygen and hydrogen. The oxygen and hydrogen contents decrease with increasing temperature of char preparation, while the nitrogen content remains essentially constant.

The shape of the curves in Figure 19, in which the amount of sulfur in some synthetic chars is shown as a function of $(p_{H_2S}/p_{H_2})_T$, strongly suggests absorptive behavior. Hayward and

Trapnell(12) give examples of typical absorption isotherms and note that chemisorption normally gives rise to isotherms of this general form.

Although a treatment of the present results in terms of idealized absorption isotherms is open to criticism, an attempt will nevertheless be made to treat the results accordingly. It will be shown that such a treatment leads to results which may be considered reasonable.

Assuming that the chemisorbed sulfur forms an ideal monolayer and that each chemisorbed species occupies a single site, application of the ideal Langmuir isotherm gives(12)

$$a = \frac{\theta}{B(1 - \theta)} \qquad 1)$$

where a is the activity of the chemisorbed species, θ the fractional coverage, and B a temperature-dependent parameter containing the heat of chemisorption of sulfur. The fractional coverage $\theta = v/v_m$, where v is the volume of chemisorbed sulfur (STP) per gram of char and v_m the volume giving a complete monolayer of sulfur on the surface of the char. The surface area, S m^2/g, is related to v_m by the following expression:

$$S = \frac{v_m}{22414} NA \cdot 10^{-20} \qquad 2)$$

where N is Avogadro's number and A the cross-sectional area of an absorbed species in A^2. The volume, v, of the chemisorbed sulfur is obtained from the measured sulfur concentration as follows:

$$v = \frac{22414}{3200} (\%S) \qquad 3)$$

Substituting for the sulfur activity $a = (p_{H_2S}/p_{H_2})_T$, $\theta = v/v_m$, and making use of Equations 2 and 3, the following expression is obtained from Equation 1.

$$\frac{1}{(\%S)} (p_{H_2S}/p_{H_2})_T = 1.87 \frac{A}{S} \left[\frac{1}{B} + (p_{H_2S}/p_{H_2})_T\right] \qquad 4)$$

The experimental results plotted in accordance with Equation 4 are given in Figures 20 and 21 for 600 and 900°C, respectively. The slope of each line should be proportional to 1/S; in fact, this is shown to be the case in Figure 22, in which log (slope) is depicted as a linear function of log S with a theoretical slope of -1. From the intercept of this line with the ordinate the value of A,

the cross-sectional area of a chemisorbed species, is calculated to be 17 A^2. This value is to be compared with crosssectional areas ranging from 10 to 50 A^2 as estimated from physical absorption data for a variety of gases(12).

According to Equation 4, the intercepts of the lines in Figures 20 and 21 with the ordinate should be proportional to 1/S. This is shown to be the case in Figure 23, in which log (intercept) is depicted as a function of log S with a theoretical slope of -1. From the intercepts of both lines with the ordinate, together with the previously determined value of A, the temperature-dependent parameter B is obtained. This parameter is proportional to $e^{q/RT}$, where q is the heat of chemisorption of sulfur on char. From the temperature dependence of B, the value of q is estimated to be about -10 kcal/mole, a reasonable value when compared with the heats of chemisorption of other gases on carbon, as listed by Hayward and Trapnell(12).

The foregoing analysis, although of necessity oversimplified, shows that the absorption of sulfur by synthetic chars is most likely mainly governed by chemisorption. It is thus expected that the surface area is an important parameter in determining whether a given char or carbon is able to retain significant quantities of sulfur. This is in agreement with earlier work by Hofmann and Nobbe(11) and by Polansky, et al.(7).

However, the surface area is not the only parameter to be considered. For instance, electrode graphite in the unoxidized state has a surface area of 1 m^2/g(9), approximately the same as filter-paper char prepared at 1500°C (Table II). Yet, no take-up of sulfur by electrode graphite was observed after sulfidation in 50 percent H_2, 50 percent H_2S at 1000°C. The mean crystallite size, together with the X-ray analysis, of electrode graphite(9) shows that its nature is graphitic and therefore more ordered. Blayden and Patrick(13) concluded from their work that so-called disordered carbons with small carbon layers (equivalent to mean crystallite size) and many defects are better able to absorb sulfur than the more crystallite and graphitic carbons. The present findings are consistent with this viewpoint.

Conclusions

In the absence of impurities such as iron, the ability of chars or carbons to absorb significant amounts of sulfur in a sulfidizing gas such as a H_2-H_2S mixture depends on the state of crystallinity of the carbonaceous material. The sulfur absorption decreases with increasing crystallite size. In general, carbons having a mean crystallite size of about 15 Å or less absorb significant amounts of sulfur when treated in H_2-H_2S mixtures. For carbons with a given crystallite size, the higher the pore surface area the higher is the amount of sulfur absorbed.

Sulfur absorption in high-purity chars, obtained from ash-free filter paper, increased with increasing sulfur activity and pore surface area of the char. This is in accord with the Langmuir relation for chemisorption on single sites in an ideal monolayer.

It is concluded from the present experimental results that sulfur is not accommodated in the three-dimensional lattice of the carbon but is chemisorbed on the surface. However, such chemisorption takes place only on the pore walls of nongraphitic (poorly crystalline) carbons, of which chars are good examples.

Acknowledgment

The author wishes to thank J. R. Cauley of this laboratory for his assistance with the experiments.

References

1. "Sampling and Analysis of Coal, Coke, and By-Products," pp. 84-86, Carnegie Steel Corporation, Pittsburgh (Pa), 1929.

2. O. Kubaschewski, E. L. Evans, and C. B. Alcock, "Metallurgical Thermochemistry," 4th ed., Pergamon Press, London, 1967.

3. D. W. van Krevelen, "Coal," Elsevier Publishing Comp, Amsterdam, 1961.

4. J. F. Jones, M. R. Schmidt, M. E. Sacks, Y. C. Chen, and C. A. Gray, Office of Coal Research, R&D Rept. 11, Suppl. to Final Rept., Jan. 9, 1967.

5. J. D. Batchelor, E. Gorin and C. W. Zielke, J. Ind. Eng. Chem., 1960, vol. 52, pp. 161-8.

6. G. J. W. Kor, Met. Trans. 1974, vol. 5, pp. 339-43.

7. T. S. Polansky, E. C. Knapp, and C. R. Kinney, J. Inst. of Fuel, 1961, vol. 34, pp. 245-6.

8. J. P. Wibaut and E. J. van der Kam, Rec. Trav. Chim. Pays-Bas, 1930, vol. 49, pp. 121-37.

9. E. T. Turkdogan, R. G. Olsson, and J. V. Vinters, Carbon, 1970, vol. 8, pp. 545-64.

10. U. Hofmann and G. Ohlerich, Angew. Chemie, 1950, vol. 62, pp. 16-21.

11. U. Hofmann and P. Nobbe, Ber. Deutsche Chem. Ges., 1932 vol. 65, pp. 1821-30.

12. D. O. Hayward and B. M. W. Trapnell, "Chemisorption," 2nd ed., Butterworths, Washington, D. C., 1964.

13. H. E. Blayden and J. W. Patrick, Carbon, 1967, vol. 5, pp. 533-44.

Table II

Source, Conditions of Preparation, Initial Sulfur (S_i) and Oxygen (O_i) Contents and Surface Area (SA) of the Various Chars Studied

Source	Preparation Conditions	Properties of the Char		
		SA, m^2/g	S_i, %	O_i, %
Illinois Coal	5 atm H_2, 800°C for 3 h	400	0.05	-
Ash-free Filter Paper (0.008% ash)	1 atm He, 600°C, 3h	330	0.00	4.0
	1 atm He, 900°C, 3h	272	0.00	1.4
	1 atm He, 600°C, 3h+ 1 atm He, 1250°C, 24h	30	0.00	0.34
	1 atm He, 600°C, 3h+ 1 atm He, 1500°C, 96h	3	0.00	0.14

Table III

Qualitative Comparison of the Crystallinity of Filter-Paper Chars Used in This Work With the Crystallinity and Mean Crystallite Size of Some Carbons Investigated by Turkdogan, et al.[9)]

Type of Char and Preparation Temp., °C	Crystallinity from Turkdogan's Work	
	Qualitative Comparison From X-ray Analysis	Mean Crystallite Size, Å
Filter paper (600)	Between coconut charcoal and "vitreous" carbon	~10 - ~16
Filter paper (900)		
Filter paper (1250)	Approaching vitreous carbon	~16
Filter paper (1500)	Same as vitreous carbon	~16

Table IV

Oxygen and Sulfur Contents of Filter-Paper Chars After Sulfidation at 600 and 900°C for 1 Hr in Gases of Various Sulfur Potential

Sulfidation Temperature, °C	Preparation Temperature, °C	O_i, %	$\left(\frac{PH_2S}{pH_2}\right)_T$	Sulfidized Char % O	Sulfidized Char % S
600	600	4.0	0.05	1.7	0.80
			61.5	1.6	9.50
	900	1.4	0.05	0.8	0.20
			61.5	0.8	8.40
	1250	0.34	0.05	0.2	0.03
	1500	0.14	0.05	0.1	0.02
			61.5	0.1	0.05
900	600	4.0	0.05	0.7	0.90
			7.6	0.6	7.50
	900	1.4	0.05	0.9	0.40
			7.6	0.6	5.80
	1500	0.14	0.05	0.1	0.01
			7.6	0.1	0.25

* O_i = initial oxygen content of the char.

Table V

Chemical Analysis of Filter-Paper Char in Relation to Preparation Temperature

Char-Preparation Temperature, °C	Composition, weight percent			
	Carbon	Oxygen	Hydrogen	Nitrogen
600	93.9	4.0	1.9	0.02
900	97.0	1.4	0.6	0.06
1250	99.6	0.34	0.2	0.04

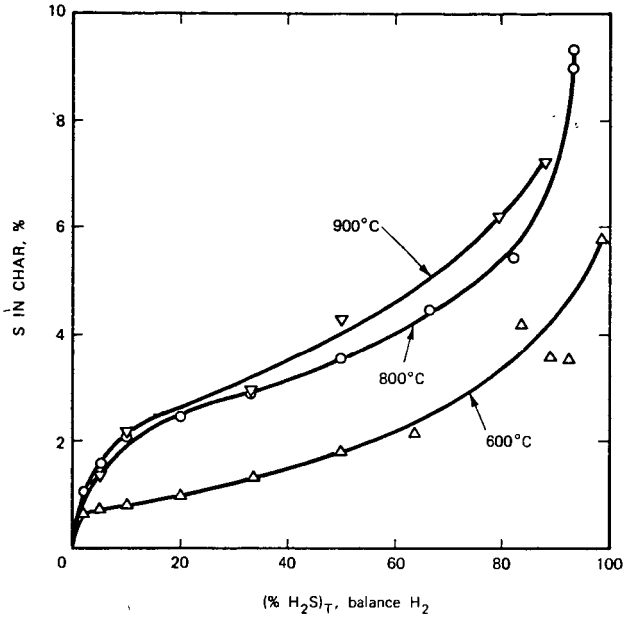

Figure 14. SULFIDATION OF PREVIOUSLY DESULFURIZED CHAR FROM ILLINOIS NO. 6 COAL AT INDICATED TEMPERATURES

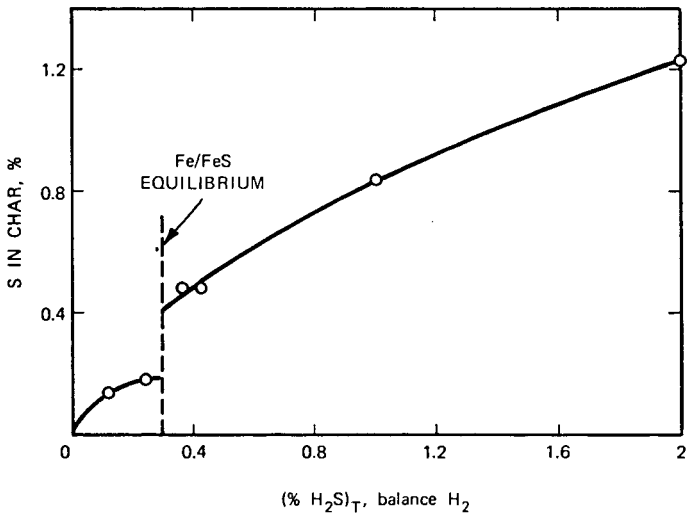

Figure 15. SULFIDATION OF PREVIOUSLY DESULFURIZED CHAR AT 900°C IN H_2-H_2S MIXTURES FOR LOW PERCENTAGES OF H_2S

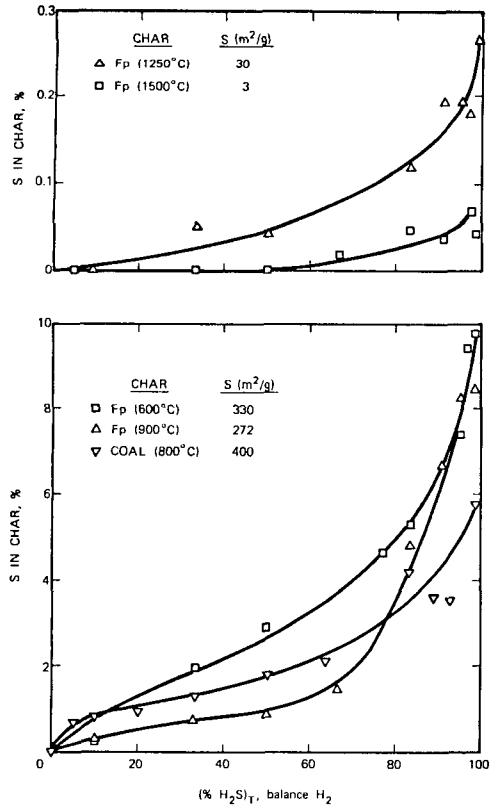

Figure 16. SULFIDATION AT 600°C IN H_2-H_2S MIXTURES OF VARIOUS CHARS, HAVING INDICATED PORE SURFACE AREA (S)

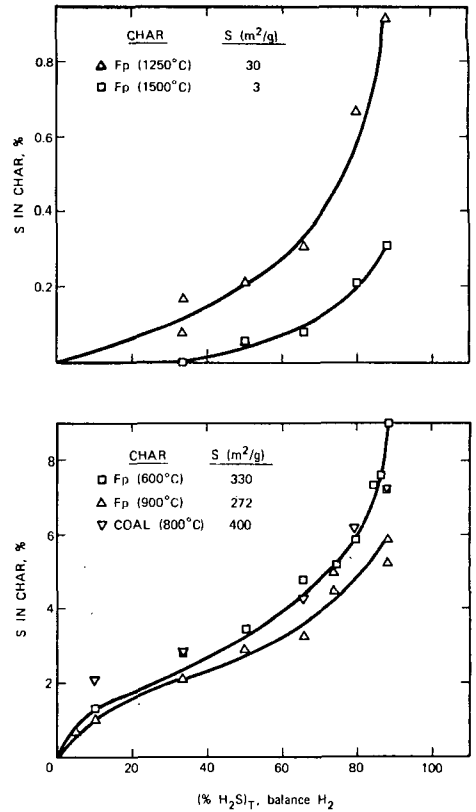

Figure 17. SULFIDATION AT 900°C IN H_2-H_2S MIXTURES OF VARIOUS CHARS, HAVING INDICATED PORE SURFACE AREA (S)

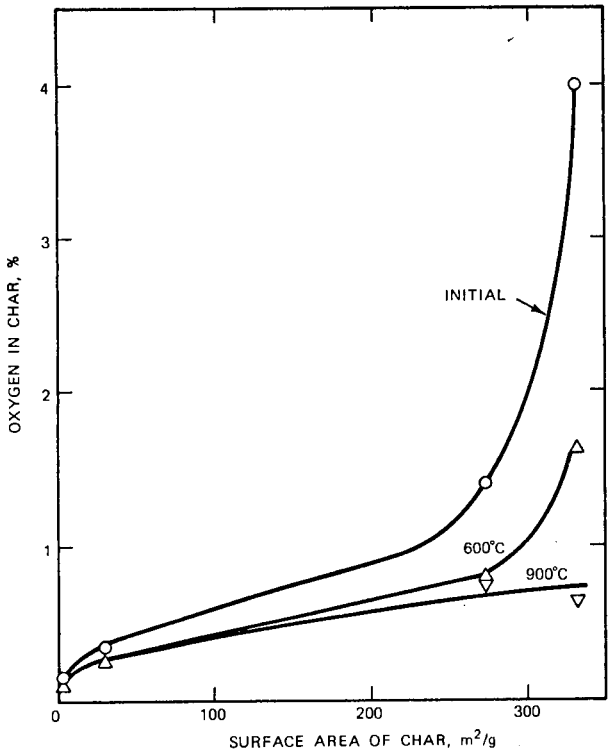

Figure 18. OXYGEN CONCENTRATION IN SYNTHETIC CHARS AS A FUNCTION OF SURFACE AREA: INITIAL, AND AFTER SULFIDATION AT 600 AND 900°C

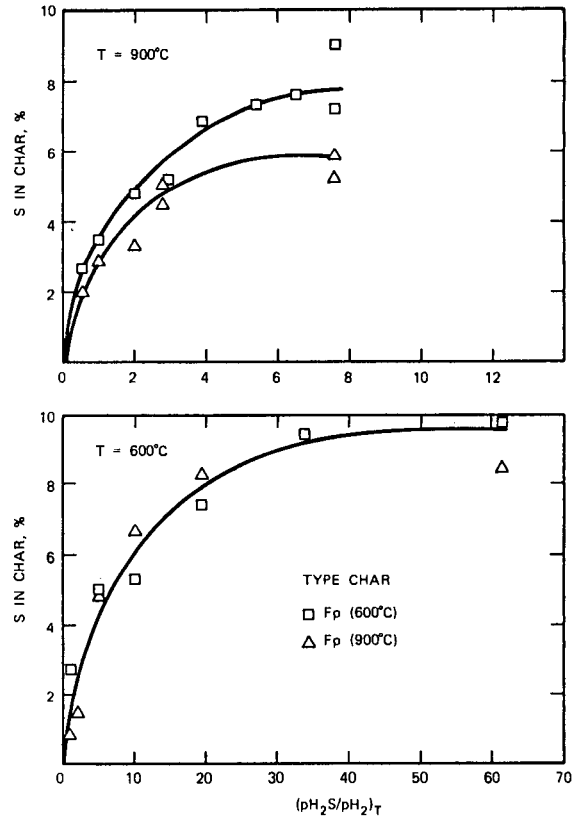

Figure 19. SULFIDATION OF VARIOUS CHARS AT 600 AND 900°C, SHOWING CURVES TYPICAL FOR CHEMISORPTION

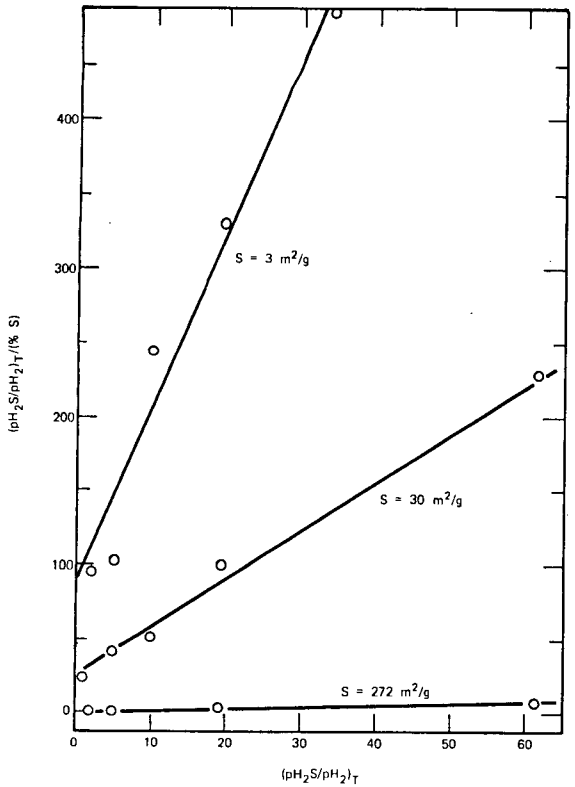

Figure 20. LANGMUIR ISOTHERMS SHOWING SULFUR CHEMISORPTION AT 600°C ON CHARS HAVING INDICATED SURFACE AREAS

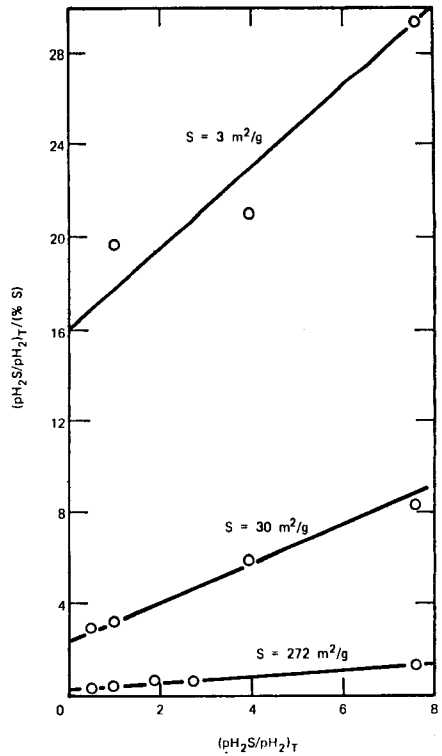

Figure 21. LANGMUIR ISOTHERMS SHOWING SULFUR CHEMISORPTION AT 900°C ON CHARS HAVING INDICATED SURFACE AREAS

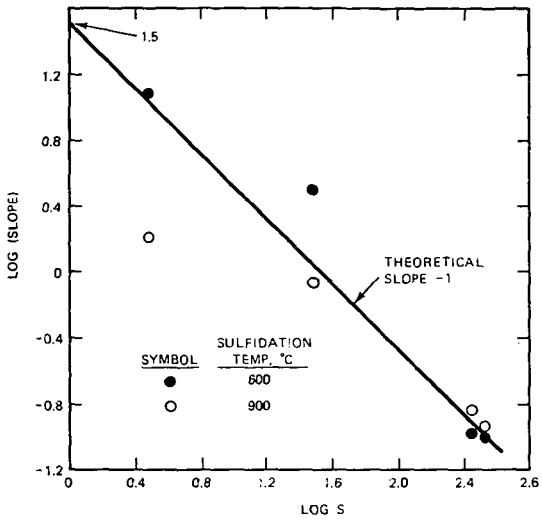

Figure 22. SLOPE OF CHEMISORPTION ISOTHERMS AT 600 AND 900°C AS A FUNCTION OF THE SURFACE AREA OF THE CHAR

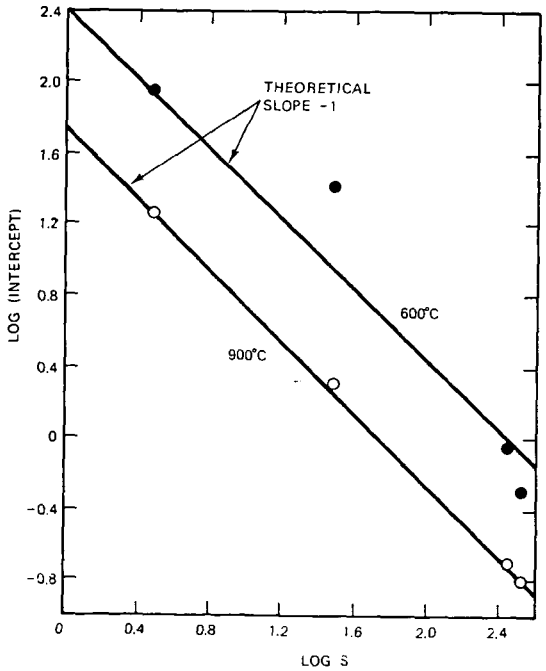

Figure 23. INTERCEPT OF CHEMISORPTION ISOTHERMS WITH ORDINATE AS A FUNCTION OF SURFACE AREA OF THE CHAR, SULFIDIZED AT INDICATED TEMPERATURES