FE-2449-9

STUDIES IN SUPPORT OF RECIRCULATING BED REACTORS FOR THE PROCESSING OF COAL

TOPICAL REPORT

"THE CHEMISTRY OF SULFUR IN CHAR AND THE IMPLICATIONS FOR HYDROGASIFICATION/HYDRODESULFURIZATION"

by

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prepared for
The U.S. Department of Energy
Division of Energy Technology

Under Contract No. EX-76-C-01-2449

FE-2449-9

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September 1979

Work Performed under Contract No. EX-76-C-01-2449

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This report is the Doctoral Dissertation of Alan Edward Roderick McIver. It was done in partial satisfaction of the requirements for the degree of Doctor of Philosophy at Carnegie-Mellon University.

THE CHEMISTRY OF SULFUR IN CHAR AND THE IMPLICATIONS FOR COAL SULFUR MANAGEMENT IN HYDROGASIFICATION/HYDRODESULFURIZATION

Alan E. McIver

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ABSTRACT

Experimental results, which elucidate the factors which govern the equilibrium distribution of sulfur between organic sulfur in char and gaseous hydrogen sulfide, are presented. These experiments were conducted at between 1200 and 1600°F, for values of the ratio (P_{H_2S}/P_{H_2}) ranging from 1 to 100, atmospheric pressure and for several chars. The rank of the parent coals from which these chars were derived ranged from lignite to anthracite. It is shown that the partial pressure ratio (P_{H_2S}/P_{H_2}) is the pressure-dependent parameter which governs the extent of char sulfidation. It is also shown that the extent of char sulfidation is not uniquely dependent upon char surface area, but decreases with increasing rank of the char, and the rank of the coal from which the char is derived. Char sulfidation is shown to be a reversible process.

The kinetics of char desulfurization are shown to be a function of the physiochemical history of the char -- i.e., char desulfurization is a path-dependent process.

The analogy between the chemistries of oxygen and sulfur in char are explored, and the implications for coal sulfur management are outlined.

ACKNOWLEDGEMENTS

I would like to take this opportunity to express my gratitude to my advisors, Professors Michael Massey, and Thomas Bierl. Their many suggestions are an integral part of this work.

Several other members of the Pittsburgh community have also greatly contributed to this work. Special mention should be made of Walter Robertson, who performed many of the experiments and analyses mentioned here. The ESCA apparatus at the Pittsburgh Energy Technology Center (PETC) was used with the permission and assistance of Dr. Fred Brown, and the experimental work was enthusiastically performed by Leo Makovsky. Harold Chambers, and Dr. Paul Yavorsky, of PETC provided the HYDRANE chars which were employed. George Curran of Consolidation Coal Company graciously performed several char analyses. Dr. Larry Gajdos helped with the editing, and Dr. Bernard Blaustein provided moral support when it was badly needed. Irma Lydon -- dear Irma -- typed the thesis. Lastly, my wife Pamela provided invaluable assistance in editing this document. Their contributions are gratefully acknowledged.

Financial support for this work was provided under the DOE Contract, "Studies in Support of Recirculating Bed Reactors for the Processing of Coal", Contract No. EX-76-C-01-2449.

A.E.M.

DEDICATION

This thesis is dedicated to my mother; small reward for her lifelong struggle, under trying circumstances, on my behalf.

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SYNOPSIS

Most of the coal produced in the United States is used in steam boilers for the generation of electricity(124). The greater portion of it is mined and consumed east of the Mississippi River. However, the sulfur content of eastern coals is generally quite high relative to that of western coals(117,38)(see Figure S.1). Increased environmental awareness and the predominant use of high-sulfur eastern coal in the densely-populated eastern U.S. has led to the enactment of regulations which limit the emission of sulfur dioxide from steam-generating equipment(1,2). These regulations provide incentive for the development of strategies which reduce the emission of sulfur dioxide from steam boilers.

One method of reducing sulfur dioxide emissions involves removing sulfur from coal prior to combustion. This can be accomplished in a variety of physical separation processes, referred to generically as coal beneficiation processes. Over 60% of the coal mined in the United States is cleaned in this way(124). In general, coal beneficiation is a relatively inexpensive way of effecting, in many cases, a substantial reduction in the sulfur (particularly pyritic sulfur) and ash contents of coal. However, it is not able to reduce the sulfur content of most high sulfur eastern coals to the extent that the cleaned coal product meets the above-mentioned sulfur dioxide emission

A second strategy for reducing sulfur dioxide emissions involves removing sulfur dioxide from the products of combustion. This is accomplished

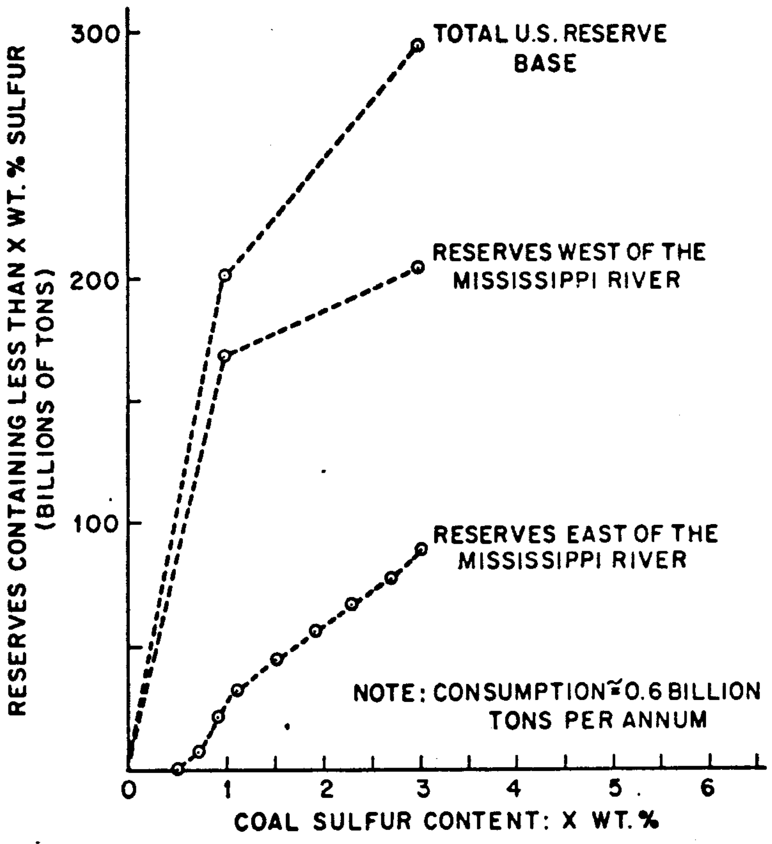

Figure S.1 Coal Reserve Base of the United States by Sulfur Content in so-called flue gas desulfurization (FGD) systems. Many of the coal-fired boilers in the U.S. are currently being retrofitted with FGD scrubbers. These systems are capable of removing most on the order of 90% of the sulfur dioxide in boiler flue gases on a continuous basis. However, FGD is relatively expensive in that capital costs are high and, being an "add-on" strategy, the increased capital costs are not offset by an increase in the efficiency with which electricity is generated from coal.

The limitations of coal beneficiation and FGD provide incentive for the development of alternative coal desulfurization strategies. Pyrolysis conditions occur in several gasification processes -- i.e., steam-oxygen gasification, hydrogasification, etc. At the elevated temperatures encountered in such processes, coal sulfur is distributed between the resultant char and gas phases. The coal hydrogasification pilot-plant data presented in Table S.1 suggests that hydrogenation might be a successful strategy for reducing the sulfur content of the product char.* However, the consensus of opinion in the literature is that coal hydrodesulfurization is not feasible. In the words of Jones(52):

> "From the standpoint of commercial operations, the removal of sulfur from char by simple hydrogen treatment at 1600°F is not practical".

This comment is somewhat premature because, in spite of extensive research in the area, the factors which govern the distribution of sulfur between the char and gas phases are not well understood. This thesis was undertaken

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*Note that these results were obtained in experiments whose primary objective was to establish the feasibility of coal hydrogasification. Little attention was paid to minimizing the sulfur content of the product char in these experiments.

Experiment Number	Pounds Sulfur Dioxide per MM Btu.		Extent of Coal Hydrodesulfurization (c)
	Coal (a)	Char (b)	
HY-1	2.74	0.76	72.3
HY-2	3.51	0.96	72.6
HY-3	3.05	1.49	51.2
HY-4	2.76	1.03	62.7
HY-5	2.76	1.35	51.1
HY-11	3.21	1.00	68.8
HY-12	2.91	1.07	63.2
HY-13	2.62	0.72	72.5
HY-14	6.68	0.90	86.5

Mean = 66.8

Note: (c) = 100[(a)-(b)]/(a)

Table S.1 The Extent of Illinois #6 Bituminous Coal Desulfurization Realized in the HYDRANE Two-Stage Hydrogasifier(55) in an attempt to fill the gap in our knowledge. Research has been conducted to:

- define and structure the uncertainty in the literature,
- experimentally resolve this uncertainty,
- formulate and evaluate models to describe the distribution of sulfur between the char and gas phases, and
- pinpoint remaining areas of uncertainty such that future research proceeds from a well defined basis.

A literature review is presented in Chapter One. It reveals that much is known about the various types of sulfur in coal and char, and their transformations during carbonization. However, little is known about the nature of organic sulfur in coal and char, and the equilibria and kinetics of the reactions which distribute sulfur between the char and gas phases. In other words, this review highlights the uncertainty which surrounds the nature and properties of organic sulfur in char. In addition, it reveals the lack of a cohesive framework on which to base one's understanding of the chemistry of sulfur in char.

To resolve this uncertainty, the factors which govern the distribution of sulfur between organic sulfur in char and hydrogen sulfide in the gas phase have been investigated, using apparatus, techniques and procedures described in Chapter Two. Three sets of apparatus were employed: a horizontal tube furnace, a fluid-bed apparatus, and an ESCA* apparatus.

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*Electron Spectroscopy for Chemical Analysis.

Experiments to test the performance of the horizontal tube furnace revealed that, inter alia, the rate of char sulfidation in this apparatus is diffusion-controlled. Therefore, the horizontal tube furnace was abandoned in favor of fluid-bed apparatus. A so-called history diagram was developed for use in conjunction with this apparatus. The diagram proved invaluable because it provided an unambiguous description of the physiochemical history of char during an experiment. In addition, ESCA calibration procedures, the development of an acid-leaching procedure to minimize the formation of sulfide sulfur in char upon exposure to hydrogen sulfide, and the analytical procedures adopted have been described in detail.

Next, a set of experiments was performed to determine the factors which govern the equilibrium concentration of organic sulfur in char. These experiments are described in Chapter Three. It was observed that the partial pressure ratio (P_{H_2S}/P_{H_2}), rather than the partial pressure of hydrogen sulfide alone, is the concentration parameter which governs the extent of char sulfidation. In a set of experiments to test the validity of Kor's Langmuir Isotherm char sulfidation model, it was noted that the equilibrium concentration of organic sulfur in char is not directly proportional to char surface area. To explain this result, it is hypothesized that sulfur species are chemisorbed at active sites on the char surface. This is called the *active site hypothesis*. It was also noted that:

- a Freundlich Isotherm, rather than the Langmuir or Temkin Isotherms, is the best model to describe char sulfidation data,
- the extent of char sulfidation is strongly dependent upon the rank of the char and the rank of the parent coal from which the char is derived,

- with the partial pressure ratio (P_{H_2S}/P_{H_2}) held constant, the equilibrium concentration of organic sulfur in char increases with increasing sulfidation temperature, and
- the concentrations of moisture and sulfur in char are related.

Experiments to test the reversibility of char sulfidation revealed that, while it is reversible, the kinetics of char desulfurization are extremely slow under the experimental conditions which were employed.

The latter observation prompted an experimental investigation of the factors which affect the kinetics of char hydrodesulfurization. These experiments were performed, with results leading to the conclusion that *char hydrodesulfurization is a path-dependent process.* To explain this result, it is suggested that, upon exposure to elevated temperatures, organic sulfur in char changes into a more stable form. This is called the *transformation hypothesis.* ESCA experiments to establish whether or not such a transformation takes place were inconclusive. However, the results of these experiments did demonstrate that the sulfur species on the surface is not a sulfide, sulfite or sulfate.

An analysis of the char hydrodesulfurization data in the literature is also presented in Chapter Four. An analysis of the data of Zielke, et al(132) showed that, by selectively gasifying a small fraction of the char surface, one can liberate the stable form of organic sulfur from char. This is called the *selective gasification criterion,* and can be used to circumvent the slow desulfurization kinetics of chars which have been severely pretreated.

All of the fluid-bed coal and char desulfurization data in the literature were analysed. It is shown that, provided the selective gasification criterion is satisfied, the rate of removal of organic sulfur from char is probably not kinetically-controlled. However, it is conceded that this might not be true under the rapid-heat up conditions likely to be encountered in actual coal processing equipment.

As is noted in Chapter One, the existing literature lacks a cohesive framework on which to structure one's understanding of the chemistry of sulfur in char. A first step in the development of such a framework is the active site hypothesis. Unfortunately, there is little information in the sulfur literature to substantiate this hypothesis. However, several authors have noted that the chemistries of sulfur and oxygen in char are analogous, and the chemistry of oxygen in char has been extensively investigated. In Chapter Five, the chemistry of oxygen in char, and the analogy between it and the chemistry of sulfur in char are reviewed. This review reveals that there is good reason to believe that oxygen and sulfur in char are chemisorbed at the same active sites on the surface, and that these sites are probably situated at the location of unpaired electrons in the char matrix. The arguments presented in Chapter Five lend credence to the active site hypothesis. In addition, it was noted that, upon adsorption, oxygen undergoes a transformation from a weakly-adsorbed into a more strongly adsorbed species on the surface. This supports the transformation hypothesis. Further, since organic sulfur in char is almost certainly a surface complex, the selective gasification criterion seems reasonable. Consequently, the arguments presented in Chapter Five can be used to explain why:

- the extent of char sulfidation is not a function of char surface area,
- the adsorption isotherm is a function of the rank of the parent coal and the product char,
- the concentrations of moisture and sulfur in char are related,
- the kinetics of char hydrodesulfurization are path-dependent, and
- the extent of char gasification affects the kinetics of char hydrodesulfurization.

In addition, the arguments presented can be used to (a) justify the development of a more general correlation of char sulfidation data, which might allow sulfidation data for a variety of sulfur species to be presented on a single correlation, and (b) explain the effects of sulfidation and pretreatment temperatures upon the adsorption isotherm. Therefore, while some of the arguments presented in Chapter Five remain speculative in nature, they do present a cohesive a framework on which to structure one's knowledge of the chemistry of sulfur in char.

The implications of this research as far as coal sulfur management is concerned are discussed in Chapter Six. There are several factors which govern the distribution of sulfur between char and the gas phase. These factors are reviewed, and are analysed with a view towards maximizing the extent of coal hydrodesulfurization. It is concluded that, provided suitable desulfurization conditions are maintained, the concentration of organic sulfur in char can probably be reduced to environmentally-acceptable levels.

However, the primary limitation of coal hydrodesulfurization lies in its inability to remove inorganic sulfides from the product char. Hence, the potential of coal or char hydrodesulfurization will only be fully realized if strategies for the selective removal of sulfide sulfur from the char can be developed. There are several process strategies which seem capable of attaining this goal.

Finally, the requirements of future research are discussed in Chapter Seven.

CHAPTER ONE

VIEWS FROM THE LITERATURE

Extensive research has been performed on the behaviour of coal sulfur, starting as far back as the early 1800's when Berzelius, Berthollet and Proust observed that elemental sulfur and charcoal, when heated, react to form a "sulfurous carbon"(128,129). Many notable papers have been published in the intervening years. A chronological review of this literature is presented below.

1.1 Literature Review

Much credit for the systematic investigation of the forms of sulfur in coal and char belongs to Powell.

1.1.1 Powell

In the first of several papers on the subject of coal sulfur chemistry, Powell(79) investigated the forms of sulfur in coal using a variety of analytical techniques which he developed.* On the basis of his experimental results, Powell concluded that there are two types of inorganic sulfur (i.e., pyrites and sulfate sulfur), and two types of organic sulfur (i.e., resinic and humus) in coal. While pyrites are present in as-mined coal, he suggested that sulfate sulfur is the result of bacteriologically-assisted oxidation of pyrites. On the basis of

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*The analytical procedures which he developed have subsequently been adopted as a standard ASTM (American Society for the Testing of Materials) procedure (see ASTM #D2492-77).

solubility differences, Powell concluded that organic sulfur in coal occurs in the two forms mentioned previously. Unfortunately, none of the solvents which he employed (i.e., phenol, pyridene, anilene, sodium hydroxide, nitric acid and aqua regia) was able to remove all of the organic sulfur from coal. Hence, the distinction which he draws between the forms of organic sulfur in coal must be treated with skepticism.

In a second paper, Powell(82) studied the changes in the forms of sulfur which take place when coal is coked. These experiments were conducted by inserting a five gram sample of coal into a horizontal tube of fused silica. The silica tube was heated to the desired temperature (i.e., 200-1000°C) and maintained at that temperature for two hours. A stream of carbon dioxide was passed over the coke sample throughout each experiment. The coke was analysed for forms of sulfur, and the amount of sulfur liberated from the coke as hydrogen sulfide and carbon disulfide was measured. Sulfur material balances were satisfied almost exactly in all of the results which he reported. The results of these experiments led Powell to conclude that:

- all of the pyrites decompose completely to form pyrrhotite (FeS_{1+x}), the reaction being complete at 600°C,
- there is complete reduction of the sulfate to sulfides, the reaction being complete at 500°C, and
- complete decomposition of the organic sulfur in coal occurs to form volatile hydrogen sulfide and organic sulfur compounds (in tar), while a major fraction of the organic sulfur in coal is retained in the coke as

> an "organic" sulfur species which displays none of the properties of the organic sulfur in the parent coal.

He also noted that part of the pyrrhotite sulfur disappears, probably to combine with the char matrix. In addition, he noted that the pyrrhotite formed is magnetic.

The above results led Powell to conclude that, upon coking, a major fraction of coal sulfur is retained in the coke as pyrrhotite or as a "carbon-sulfur compound". Powell passed hydrogen rather than carbon dioxide over the coke sample to investigate the effectiveness of hydrogen in removing the latter forms of sulfur from the coke. He concluded that " ... the effect of hydrogen on the removal of sulfur from coke was very noticeable, in most cases the majority of sulfur being removed during a period of hours".

Powell(84) thereafter turned his attention to the nature and properties of the "carbon-sulfur compound". He measured the equilibrium concentration of sulfur in sugar chars which had been exposed to mixtures of hydrogen sulfide in hydrogen at various temperatures (700 and 800°C) in the horizontal tube furnace. The shapes of the adsorption isotherms which he obtained led Powell to conclude that organic sulfur in char is not a compound; instead, it appeared to be " ... adsorbed free sulfur or sulfur compounds, and sulfur in solid solution in the carbon or held on the surface in such a manner that it is impossible to differentiate it from a solution". He noted that, while adsorbed sulfur can be formed in and removed from char quite rapidly, solid-solution sulfur is formed rather slowly, with time constants of the order of days. Subsequent experimental attempts to verify the existence of solid-solution sulfur proved inconclusive.

The above results led Powell to hypothesize that gaseous elemental sulfur, formed as a result of the gas-phase reaction

$$2H_2S \rightleftarrows 2H_2 + S_2 \qquad [1.1]$$

is responsible for the formation of both adsorbed and solid-solution sulfur in char. However, no experimental evidence was presented to support this hypothesis.

In the course of the above investigation, Powell also noted that (a) small quantitites of metallic sulfides other than pyrrhotite -- i.e., calcium and magnezium sulfide -- are also formed in coal chars, and (b) when coke cools, with even limited access to air, oxidation of pyrrhotite occurs according to the reaction:

$$4FeS + 3O_2 \rightarrow 2Fe_2O_3 + 4S \qquad [1.2]$$

1.1.1 Wibaut

In an early paper, Wibaut(126) noted that when amorphous carbon is heated in an atmosphere of sulfur vapour, a "sulfurous carbon" is formed, containing about 2% sulfur, which can be neither extracted with solvents nor separated by heating in a vacuum at 1000°C. These results led him to conclude that the sulfur was "chemically combined" with the carbon.

In a second paper, Wibaut(127) describes experiments in which various carbons (sugar charcoal and Acheson graphite) and distilled flowers of sulfur were mixed and heated in sealed glass tubes at various temperatures (i.e., 300-700°C). After extraction of the product with boiling carbon disulfide (a solvent for elemental sulfur) and toluene (to remove the carbon disulfide), the residue was found to contain up to 25% sulfur. Neither pyridene nor sulfur monochloride were effective in reducing the sulfur content of the residue. However, heating the residue with metallic sodium, potassium hydroxide or sodium hydroxide resulted in a vigorous reaction, and the formation of sodium sulfide, potassium sulfate and sodium sulfate. Wibaut also investigated the behaviour of sulfurous carbons heated in a vacuum to elevated temperatures (500-1000°C), and noted the evolution of elemental sulfur, carbon disulfide and, in some instances, small quantitites of hydrogen sulfide. A significant fraction of the sulfur was liberated as elemental sulfur at temperatures as low as 500°C, whereas both elemental sulfur and carbon disulfide were liberated as the temperature was raised to 1100°C. However, significant concentrations of sulfur were retained in the char residue (2-4%) even after prolonged heating of the residue in vacuum at elevated temperatures (1100°C). In addition, Wibaut demonstrated that graphite fixes much less sulfur (at 600°C) than does the amorphous carbon (prepared from sugar charcoal). He examined the action of hydrogen on the sulfurous carbons and, like Powell, found that hydrogen is effective in removing most (over 90%) of the sulfur in char. He pointed out that an analogy exists in the behaviour of amorphous carbons towards oxygen and sulfur.

In a later paper, Wibaut(128) showed that the amount of sulfur which is "fixed" in char depends upon the properties of the carbon specimens. While sugar char is able to fix large concentrations of sulfur, the amount of sulfur fixed by graphite and diamond is negligible. In a set of experiments using oxygen instead of sulfur, results similar to those mentioned above were obtained. He concluded that " ... only amorphous carbons are able to fix sulfur, while the crystalline modifications do not possess this property". "It seems probable that at least part of the sulfur in these sulfurous carbons is combined to the carbon atoms by valency forces; these valency forces are therefore available in amorphous carbon, but not in diamond or graphite".

1.1.3 Huff

Huff(45) studied the origin of carbon disulfide during the carbonization of coal. In his experiments, various gases and gas mixtures were passed over a coal sample heated to elevated temperatures in a horizontal tube furnace. He noted that, upon carbonization of the coal in carbon dioxide, no measureable quantities of carbon disulfide were formed. However, when the distillation products were passed over a heated sample of by-product coke, significant concentrations of carbon disulfide were formed as a result of a secondary reaction of the sulfur species in the distillation products (hydrogen sulfide and organic sulfur species in tar) with the heated coke. However, subsequent experiments revealed that rapid heating of the coal also resulted in the production of significant quantities of carbon disulfide.

In a second paper, Huff(46) noted the formation of a "carbon-sulfur complex" in coke upon exposure of the coke to hydrogen sulfide. He also mentions the analogy between the chemistries of oxygen and sulfur in coke noted earlier by Wibaut(127).

In a third paper, Huff and Holtz(47) studied the effect of hydrogen sulfide in nitrogen upon sugar chars. These experiments were conducted by passing a mixture of hydrogen sulfide in nitrogen over the sugar chars, which were held in a horizontal tube furnace at the desired temperature

(500-1000°C). The amounts of hydrogen sulfide, carbon disulfide and other gaseous organic sulfur species in the product gases were measured. Their experimental results demonstrated that most of the hydrogen sulfide which was reacted (i.e., 70-90%) appeared in the product gas as carbon disulfide, with the remainder being an unidentified organic sulfur species. They noted that the addition of steam, carbon monoxide or oxygen to the feedgas resulted in a decrease in the amount of carbon disulfide formed. This was accompanied by a corresponding increase in the amount of unidentified organic sulfur species formed, which they believed was carbonyl sulfide (COS). However, when hydrogen was added to the feedgas, the formation of all gaseous organic sulfur species was entirely eliminated.

1.1.4 Snow

Snow(114) reviewed the desulfurization literature. He investigated the desulfurization potential of various gases (nitrogen, hydrogen, carbon dioxide, methane, ethylene, steam, ammonia and water gas) using a fluid-bed apparatus. He noted that, at elevated temperatures (700-900°C), hydrogen is the most effective of all the gases employed in reducing the total sulfur content of Illinois #6 coal.

1.1.5 Mangelsdorf

Mangelsdorf and Broughton(63) studied the desulfurization potential of various gases (carbon monoxide, illuminating gas, steam, hydrogen and blue water gas) on Indiana #5 coal (3.9% total sulfur) in a vertical tube furnace at 600°C. They noted that, at 600°C, blue water gas was the most effective in reducing the sulfur content of char.

1.1.6 Brewer and Ghosh

Brewer and Ghosh(17) passed various gases (ammonia, hydrogen and nitrogen) through a fixed bed of coal (Pittsburgh Seam and Illinois #6 Seam) heated to between 700 and 875°C in a vertical tube furnace, and measured the evolution of sulfur-containing species (hydrogen sulfide, mercaptans, thiophenes, carbon disulfide and carbonyl sulfide), as well as the amount of sulfur retained in the char residue. Sulfur material balances were satisfied to within a few percent. They noted that ammonia is more effective in minimizing the sulfur content of char than is hydrogen or nitrogen. They argued that the enhanced desulfurizing action of ammonia is due to the action of nascent hydrogen on the coke.

In a second paper(30), they performed experiments to (a) determine the desulfurizing effect caused by the addition of inorganic compounds (sodium carbonate, sodium bicarbonate and calcium oxide) to samples of high-sulfur Indian and Illinois #6 coals upon carbonization at 800°C, and (b) establish the optimum temperature, time and rate of heating on the desulfurization when ammonia is passed through a mixture of inorganic salts and the Indian coal mentioned above. They noted that the addition of sodium carbonate resulted in a significantly larger fraction of the coal sulfur being retained in the coke as sodium sulfide.

1.1.7 Consolidation Coal Company Reports

In the first of several important papers and reports on char hydrodesulfurization, Zielke, Curran, Gorin and Goring(132) investigated the kinetics of low-temperature char desulfurization (Pittsburgh Seam coal produced in the Disco Process)* via partial gasification of the char in the low-burnoff range. They performed their experiments using hydrogen as well as hydrogen-steam mixtures in a batch fluid-bed reactor. The char was devolatilized by fluidizing it with nitrogen at 1600°F before admission of the reactant gas. They measured the concentrations of both sulfide sulfur and total sulfur in the char residue. They noted that " ... pure hydrogen is a more effective desulfurization agent at a given percent carbon gasified than hydrogen-steam mixtures". They also noted that " ... the effect of pressure disappears when pure hydrogen is used as a desulfurization agent, and that the sulfur content is a unique function of the percent carbon gasified and is independent of the pressure". They showed that, in pure hydrogen, the gasification of a relatively small percentage of the char results in the liberation of virtually all of the sulfur in the char.

In an unpublished report, Batchelor and Zielke(8) studied the kinetics, and the role of hydrogen sulfide inhibition in char hydrodesulfurization. In their experiments, a batch fluidized bed reactor was employed. They concluded that equilibrium (with respect to hydrogen sulfide in the gas phase and organic sulfur in the char) may be approached relatively easily in deep beds at 1600°F and six atmospheres total pressure.

Batchelor(9) measured the equilibrium concentration of organic and sulfide sulfur in Arkwright char at 1100, 1350 and 1600°F as a function of the concentration of hydrogen sulfide in hydrogen. He presented a graph of the relationship between the equilibrium concentration of total sulfur in char and the partial pressure ratio (i.e., P_{H_2S}/P_{H_2}). He referred to this as the "inhibition isotherm". He noted that char sulfidation is

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*The Disco Process is discussed in detail by Gollmar(32).

reversible. In addition, he noted that his char sulfidation results were similar to those presented by Powell(84).

Batchelor, Gorin and Zielke(12) studied the kinetics of desulfurization of various chars in a batch fluid-bed reactor at 1350 and 1600°F in pure hydrogen. Their experimental results suggested that, in deep beds of char, the rate of char hydrodesulfurization is controlled by equilibrium (i.e., the inhibition isotherm) and material balance rather than kinetic limitations. They also studied the kinetics of char hydrodesulfurization in a continuous fluid-bed reactor at 1100, 1350 and 1600°F and noted that " ... the sulfur in the raw char is more labile in both a thermodynamic and kinetic sense than after thermal treatment for several hours ... undoubtedly transforms the sulfur to a more stable form".

1.1.8 Whelan

Whelan(125) studied carefully prepared samples of British coals, with a microscope. He noted the occurrence of pyrites as (a) minute discrete grains (the sizes of which vary from 0.5 to 40 microns) disseminated throughout the coal, and (b) small concretions, of variable size, but usually between 20 and 100 microns, which frequently show radial structure and sometimes coalesce to form distinct bands parallel to the bedding plane, as well as other veins, and veinlets, etc.

1.1.9 Jacobs and Mircus

Jacobs and Mircus(51) studied the effectiveness of various gases (steam, air and nitrogen) in desulfurizing Illinois #6 coal in a batch fluid-bed reactor at 950°F. They noted that the extent of char desulfurization is a function of particle size. This led them to conclude that mass transfer limitations control the rate of coal desulfurization. They performed experiments in which a mixture of 13% air and 35% steam in nitrogen was used. Results of these experiments showed almost complete removal of pyritic and sulfate sulfur from the char, while the concentration of organic sulfur in the char remained essentially the same as in the parent coal.

1.1.10 Sef

Sef(106) studied the hydrodesulfurization of petroleum coke in a batch fluid-bed reactor at various pressures (1 to 6 atmospheres) and temperatures (450 to 850°C). He demonstrated that the amount of sulfur removed from the char is a function of (a) pressure, (b) particle size, and (c) the amount of carbon gasified. Under suitable experimental conditions he was able to remove practically all of the sulfur from petroleum coke (approximately 95%) while incurring a coke weight loss of the order of 20%.

1.1.11 Polansky

Polansky, Knapp and Kinney(78) studied the sulfidation of high-temperature coke (prepared at 1100°C) using hydrogen sulfide at 800, 900 and 1000°C. They concluded that the concentration of the various forms of sulfur in coke is a function of the "condition" of the coke, the temperature and the partial pressure of hydrogen sulfide.

1.1.12 Cernic-Simic

Cernic-Simic(21) studied the factors which influence the behaviour of coal sulfur during carbonization by passing several gases (steam, hydrogen and ammonia) over coal samples of various rank heated (at 3°C per minute) to the final temperature (500-900°C) in a Koppers tubular electric furnace. She concluded that the rank of the parent coal, the quantity and composition of mineral matter and the quantity of total sulfur in the coal are the principal factors which determine the behaviour of coal sulfur during carbonization and the retention of sulfur in the coke. In particular, she noted that (a) the lower the rank of the parent coal, the greater the proportion of sulfur released during carbonization, and (b) mineral matter in the coke (especially iron and calcium compounds) tends to scavenge volatile sulfur from the gas phase to form sulfides, thereby increasing the proportion of the coal sulfur which is retained in the coke.

1.1.3 Given and Jones

Given and Jones(31) attempted to decrease the proportion of coal sulfur retained in coke during carbonization at 600°C by adding various compounds (e.g., sodium borohydride, ammonium chloride, p-Terphenyl and benzene tetra-carboxylic dianhydride) to coal samples prior to carbonization. They noted that, upon carbonization in the absence of additives, (a) most pyrites decomposes at temperatures of less than 700°C, (b) the sulfur lost by the pyrites is greater than that which is converted into sulfide sulfur, and (c) the proportion of sulfur as organic sulfur increases during carbonization. They also noted that none of the additives employed significantly reduced the proportion of sulfur retained in the coke.

1.1.4 Puri

In the first of several papers on the nature of the carbon sulfur complex, Puri(92) sulfided sugar charcoal by exposing it to hydrogen sulfide or carbon disulfide at 600°C for eight hours. He attempted to desulfurize these materials by passing hydrogen and nitrogen over, or drawing a vacuum on, the sample. In these experiments, the sample was placed in a platinum boat located in a horizontal tube furnace heated to the desired temperature (300-1200°C). He noted that the "Carbon-sulfur complex ....

is highly stable". "It decomposes only on high temperature treatment, up to 1200°C, in vacuum or in a current of nitrogen when the combined sulfur is liberated mostly as H_2S or CS_2 together with small amounts of sulfur vapour". "Heat treatment in a current of hydrogen results in complete elimination of the entire amount of sulfur as H_2S". "Stability of the complex and desorption of combined sulfur as CS_2 indicate strong valency forces operating in the chemisorption of sulfur by char".

Similar results were reported in a second paper(94), in which sugar char was sulfided with elemental sulfur and sulfur dioxide. However, in the case of sulfur dioxide sulfidation, some of the chemisorbed sulfur was recovered as sulfur dioxide when the sample was heated to elevated temperatures in a stream of nitrogen.

In a third paper, Puri(95) studied the catalytic effect of sulfurized charcoals (obtained by treatment with hydrogen sulfide, carbon disulfide, sulfur or sulfur dioxide at 600°C) upon the sodium azide reaction in an attempt to reveal the nature of sulfur groups formed in charcoal upon exposure to the above sulfur species. He noted that the reaction of sodium azide with iodine -- i.e.,

$$2NaN_3 + I_2 \rightarrow 2NaI + 3N_2 \qquad [1.3]$$

is " ... catalysed by sulfide sulfur, soluble as well as insoluble, organic as well as inorganic, as well as thiosulfate and thiol groups but neither by free sulfur nor by sulfur present in ring combination or as sulfite or sulfate structure". He performed several experiments which demonstrated that " ... sulfurized charcoals, obtained by treatment with sulfur, hydrogen sulfide, carbon disulfide or sulfur dioxide at 600°C, catalyse the sodium azide reaction in aqueous solution at ordinary temperatures". These results led Puri to the questionable conclusion that sulfide, hydrosulfide and thioether groups are formed in chars exposed to sulfur, hydrogen sulfide and carbon disulfide at 600°C, while sulfoxide and sulfone groups are formed in chars exposed to sulfur dioxide under the same conditions.

In a fourth paper, Puri(96) used carbonized cane sugar and coconut shells before as well as after degassing at a variety of temperatures (400-1200°C). The amount of combined oxygen in each of the samples was determined by outgassing at 1200°C in a resistance tube furnace, and analysing the gas evolved (CO_2, CO and H_2O). The various char samples were then sulfided by (a) heating a mixture of sample and elemental sulfur for three hours at 600°C, or (b) passing H_2S, CS_2 or SO_2 over the sample for six hours at 600°C in a rotating pyrex glass tube. The treated samples were extracted with carbon disulfide (a solvent for elemental sulfur) to remove any physically-held sulfur in the sample. The amount of bromine fixed by these samples (a measure of the degree of surface unsaturation) was measured for each of the treated char samples. Puri noted that:

- the unsaturated sites, as measured by the bromine value, almost disappear after sulfidation, independent of the sulfurizing agent (S_2, H_2S, CS_2 or SO_2) employed,
- elimination of sulfur (by treatment of the sample with hydrogen at various temperatures) led to the regeneration of an *equivalent* number of unsaturated sites, and
- a significant fraction of the organic sulfur enters into the treated chars by displacing chemisorbed surface oxides.

Puri concluded that the amount of sulfur fixed " ... depends not so much on surface area as on the oxygen and hydrogen contents, and the extent of surface unsaturation .. of charcoal". "There are indications that sulfur is fixed partly by addition at the unsaturated sites and partly by substitution through interaction with certain oxygen groups which come off as CO on high-temperature evacuation".

1.1.15 Mahmoud

Mahmoud, Ayad and Ezz(62) studied the desulfurization of high-sulfur petroleum coke by passing hydrogen (a) over a coke sample in a horizontal tube furnace at various temperatures (500-1000°C) and (b) through a batch fluid-bed of coke at 600-800°C. In the horizontal tube furnace, they noted that the extent of char hydrodesulfurization passes through a maximum at 600°C, and is a function of coke particle size and the gas flowrate. In general, the extent of char desulfurization realized in the horizontal tube furnace was relatively low (a maximum of approximately 50% in three hours at the maximum hydrogen flowrate). The rate of coke desulfurization in the fluid-bed experiments was found to be relatively slow. Substantial desulfurization of the coke was only achieved at very long residence times (approximately 87% desulfurization in 40 hours at 600°C). The coke produced showed improved reactivity towards carbon dioxide (at 950°C) when compared to the reactivity of the untreated coke, and the reactivity of the treated coke decreased with increasing pretreatment temperature (in the range 600-800°C).

1.1.16 Peet

Peet, Simeon and Stott(75) studied the rapid carbonization of three high-sulfur New Zealand coals(a) by injecting a 60x120 mesh sample of coal into a preheated bed of 40-mesh carborundum fluidized with nitrogen or hydrogen at temperatures up to 800°C, and (b) in a disperse-phase reactor.

In the fluid-bed experiments, they noted a linear relationship between the extent of char desulfurization and the loss of weight of the char (both relative to the parent coal), which is of the form

$$\Delta S = a\Delta W + b \qquad [1.4]$$

where ΔS is the percentage reduction in the sulfur concentration of the product char, ΔW is the percentage weight reduction of the product char and a and b are constants. The slope of equation [1.4] was computed to be 1.64 for Wangaloa coal. The extent of desulfurization was shown to be a strong function of the fluid-bed temperature (approximately 76% at 800^{o}C), and was found to increase with increasing fluid-bed temperature. Unfortunately, because the loss in weight of the char could not be measured in the fluid-bed experiments, the loss in weight was calculated from an empirical formula.

In the disperse-phase experiments, a linear relationship like [1.4] was also observed. In addition, an analysis of the product gases from experiments in which nitrogen was employed revealed that no hydrogen sulfide was present in the gas phase. All of the sulfur in the gas phase was found to be in the form of organic sulfur species. They concluded that " ... as far as high-speed carbonization in this type of equipment is concerned, in a nitrogen atmosphere, hydrogen sulfide is not present in significant quantities as an intial product of the decomposition of organic sulfur in coal, but that a fair proportion of the volatilized sulfur is in the form of sulfides capable of reacting with a cadmium chloride solution."

"In a hydrogen atmosphere, an appreciable proportion of the sulfur in the volatile matter and/or char is converted to hydrogen sulfide." "It is probable that this hydrogen sulfide results mainly from the hydrogenation of the char sulfur, but the possibility of vapour-phase reduction of high molecular weight volatile sulfur compounds cannot be discounted."

1.1.17 FMC Corporation Reports

Jones, et al(52) studied the desulfurization of COED (Char Oil Energy Development) chars in a batch fluid-bed reactor fluidized with hydrogen at various temperatures, but primarily at 1600°F. The char was prepared from Illinois #6 (Crown Coal) in the COED PDU (Process Development Unit) at a maximum temperature of 1600°F. The variables investigated were temperature, suppression of gasification by methane addition, hydrogen sulfide concentration and pressure (15-115 psia). The experiments were performed by raising the temperature of the fluid-bed to the desired temperature in a nitrogen atmosphere and then switching over to a hydrogen feed. They concluded that (a) the rate of char desulfurization is essentially constant in the range 1600-1850°F but drops off sharply in the interval 1350 -1600°F, (b) char desulfurization and gasification to form methane are independent reactions, (c) the presence of hydrogen sulfide concentrations of the order of 1.4% are sufficient to severely inhibit char hydrodesulfurization, and (d) the rate of char hydrodesulfurization is independent of particle size. They divided char hydrodesulfurization into three regimes -- i.e., a "flash desulfurization" regime to between 40 and 60% residual sulfur in the char; a slower but still appreciable desulfurization rate to between 10-15% residual sulfur in the char; and a negligible rate of char hydrodesulfurization thereafter. On the basis of models which they developed, they suggested that while "flash desulfurization" corresponds to equilibrium-controlled desulfurization, the second and slower desulfurization regime is the result of Knudsen diffusion in the micropores of the char particles.

In a second paper, Gray, Sacks and Eddinger(36) concluded that the slower desulfurization regime is controlled by either "inherent gas-solid kinetics" or " ... diffusion of hydrogen sulfide through the reacted shell of iron surrounding the FeS". They also assumed that " ... 10% of the sulfur is ... bound in forms which do not react significantly under process conditions". They concluded that while char hydrodesulfurization is practically possible, excessive amounts of hydrogen would be required to reduce the sulfur content to that required of an environmentally-acceptable boiler fuel. This opinion is reiterated in other publications(35), and the economic feasibility of sulfur-acceptor addition desulfurization strategies is explored in a later publication(105).

1.1.18 Vestal, et al

Vestal and Johnson(120) studied the kinetics of coal hydrodesulfurization by passing hydrogen through a fluid bed of coal (ten bituminous coals were employed). The temperature of the fluid bed varied linearly with experimental time. The amount of hydrogen sulfide evolved was analysed in a time-of-flight mass spectrometer. The data gathered were analysed according to Juntgen's method of non-isothermal data analysis. They also obtained kinetic data for several other related reactions -- i.e., the evolution of hydrogen sulfide from pyrites and pyrrhotite, and the kinetics of iron and char sulfidation, as well as the kinetics of sulfidation of various sulfur-acceptor materials such as calcium carbonate and calcium oxide. They concluded that:

- There are two forms of organic sulfur in coal, which they termed Organic I and Organic II. Both of these compounds decompose at relatively moderate temperatures (e.g., 400-500°C).
- Pyrites decomposes to form pyrrhotite which, in turn, decomposes to form elemental iron. These reactions take place in the 450-600°C range of temperatures.
- A third form of organic sulfur, which they refer to as Organic III, is formed in the char upon exposure of the char to hydrogen sulfide. They concluded that " ... single simple reaction does not account for the behaviour of this material".
- As far as the reaction with sulfur-acceptor materials is concerned, " ... the reaction of hydrogen sulfide with these materials (calcium carbonate and calcium oxide) in the temperature range above 500°C is extremely fast so that nearly one half of the sulfur, which might otherwise be evolved in the pyrite and sulfide sulfur peaks, is converted to calcium sulfide and retained in the char".

In a second paper, Yergey, et al(131) presented more detailed experimental results. They attempted to assess the relative importance of the back-reactions with both charcoal and elemental iron by passing a mixture of 1000 ppm. of hydrogen sulfide in helium through beds of charcoal and iron filings. They observed a reaction with the iron filings at approximately 527°C which was essentially complete at 577°C. They also noted the onset of a reaction with charcoal at approximately 577°C. This reaction reduced the concentration of hydrogen sulfide in the feedgas to less than 100 ppm. at 727°C. The behaviour of coal chars was intermediate between the behaviour noted for iron filings and charcoal. On the basis of their results, they concluded that:

- The back reaction of hydrogen sulfide is not important in the evolution of hydrogen sulfide from Organic I and Organic II, and the measured kinetic parameters for these reactions are, therefore, not affected by the back-reactions. The same is true for the measured kinetic parameters for pyrites decomposition.

- The kinetic parameters for pyrrhotite and Organic III decomposition are, however, quite possibly affected by the back-reactions mentioned above and, therefore, the measured kinetic parameters might not be equal to the true values.

They also showed that the rate of sulfidation of iron filings with hydrogen sulfide is mass-transfer controlled at temperatures in excess of approximately 320°C.

1.1.19 Kapur

Kapur, Goel, Murty, and Singh(54) studied the kinetics of ferrous sulfide reduction with hydrogen using a thermogravimetric technique at temperatures which ranged from 650 to 900°C. In these experiments, the weight of a cylindrical pellet of ferrous sulfide,* suspended in a vertical tube furnace through which hydrogen flowed upwards and around the pellet, was measured as a function of time. In analysing their data, they assumed that (a) the process is isothermal, (b) the kinetics of ferrous sulfide reduction are controlled by the rate of reaction at the interface of the unreacted core and the product layer, and (c) the reaction front moves inward at constant velocity. They concluded that the apparent activation energy for ferrous sulfide reduction is 31.6 kcals per gram mole.

1.1.20 Kor

Kor(55) studied the reduction of pyrrhotite in hydrogen at 600, 800 and 900°C. Using a thermogravimetric technique, he concluded that the

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* The cylinders varied in size from 12.83-12.85 mm. in diameter and from 4.14-4.78 mm. in height.

rate of reduction of spherical particles (0.4 to 1.6 cm. diameter) is controlled by counter-current diffusion of hydrogen and hydrogen sulfide in the gas-film boundary layer and in the porous iron layer.

In a second paper, Kor(56) studied the kinetics of hydrodesulfurization of Illinois #6 coal (and coke derived therefrom) using mixtures of various gases (methane, hydrogen and helium), two temperatures (600 and 800°C) and various pressures (1, 5 and 10 atmospheres). The chars were prepared by heating dried coals in hydrogen for three hours at either 600 or 800°C. A thermogravimetric technique was employed to measure the weight loss of the desulfurized sample, and the residue was analysed for total sulfur content by means of a combustion method. He concluded that coal hydrodesulfurization takes place in two stages. In the first stage, rapid desulfurization is accompanied by gasification. It was concluded that the desulfurization and gasification processes are related, and that this relationship is a unique function of temperature. The second stage was found to proceed at a much slower rate. It was concluded that this is due to the slow reduction of pyrrhotite to iron. However, Kor does not attempt to explain why, if the gasification and rapid-rate desulfurization processes are related, the proportion of sulfur liberated is significantly greater than the proportion of carbon which is gasified. In addition, no mention is made of the mass-transfer controlling mechanism which is discussed in the earlier paper(55).

In a third paper, Kor(57) investigated the equilibrium sulfidation of Illinois #6 and filter paper chars at two temperatures (600 and 900°C) and between 2 and 100 percent hydrogen sulfide in hydrogen. The apparatus employed was similar to that described in earlier papers. The filter paper char was prepared by charring ash-free filter paper (0.008% ash) in helium at 600 or 900°C for three hours. These chars were further treated in helium at 1250 and 1500°C for 24 and 96 hours respectively to prepare chars of lower surface area. The measured surface areas* of the three chars prepared in this manner were approximately 300, 30 and 3 m^2 per gram of char. Kor employed a modified form of a Langmuir Isotherm to describe his filter paper char sulfidation data, and noted that " ... the foregoing analysis, although of necessity oversimplified, shows that the adsorption of sulfur by synthetic chars is most likely mainly governed by chemisorption". "It is thus expected that surface area is an important parameter in determining whether (or not) a given char or carbon is able to retain significant quantities of sulfur."

1.1.21 Sinha and Walker

Sinha and Walker(112) studied the desulfurization of coal and char in various atmospheres (i.e., carbon monoxide, air and nitrogen) at between 400 and 600°C. In these experiments, the gas was passed over a boat containing the sample. The boat was positioned within a tube furnace maintained at the desired pretreatment temperature. While the extent of coal desulfurization realized in carbon monoxide was insignificant, substantial reductions (of the order of 50% or greater) were realized when the coals were exposed to air for five minutes at 450°C. Not surprisingly, this desulfurization was accompanied by significant loss in weight of the coal.

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*Measured using the BET (Brunauer, Emmett and Teller) method. The type of gas employed was not specified.

1.1.22 Maa

Maa, Lewis and Hamrin(61) measured inhibition isotherms for Western Kentucky #9 coal at 600 and 870°C. They also measured the extent of char desulfurization and the forms of sulfur in the product char using either pure hydrogen or nitrogen. In these experiments, crushed and sieved (25x140 mesh) coal was introduced into a batch reactor and fluidized with nitrogen. The reactor was then heated to the desired temperature for one hour. The hydrogen or hydrogen sulfide in hydrogen mixture was then passed through the fluid bed, and the concentration of hydrogen sulfide in hydrogen in the product gas was measured using a gas chromatograph. The residue from these experiments was analysed for forms of sulfur using ASTM D2492.

As far as the inhibition isotherm measurements are concerned, they noted that:

- At 600°C, the equilibrium concentration of sulfur in char is independent of the concentration of hydrogen sulfide in hydrogen, and remains constant at 2.6%, while
- At 870°C, the equilibrium concentration of sulfur in char increases for values of the partial pressure ratio $100P_{H_2S}/P_{H_2}$ in excess of unity.

In their desulfurization experiments, they demonstrated that practically all of the sulfur can be removed by treatment of the char with hydrogen at 870°C. In addition, the concentration of sulfur in char decreases as temperature increases. Continuous analysis of the product gases revealed that most of the sulfur had evolved as hydrogen sulfide within ten minutes after the introduction of hydrogen to the fluid-bed.

1.1.23 Block

Block, Sharp and Darlage(15) studied the desulfurization of ten coals in a variety of gases (nitrogen, air, steam and hydrogen) as a function of temperature (300-1000°C) and treatment time (5-60 minutes). To destroy their caking properties, the coals were pretreated by heating in air at 300°C for ten minutes. Weighed samples of the coal were then placed in stainless steel sample boats and exposed to the gas stream in a horizontal tube furnace maintained at the desired temperature. They noted that the extent of coal desulfurization in air at 450°C (the optimum temperature) was primarily the result of pyrites oxidation. At temperatures in excess of 450°C, weight losses due to combustion of the char became excessive. The use of steam at 600°C for 15 minutes produced desulfurization results which were superior to those obtained when air was employed. In this case, the removal of inorganic sulfur was almost complete. However, the concentration of organic sulfur in the char was not significantly changed by the use of steam. In the case of hydrogen, they noted almost complete removal of both organic and inorganic forms of sulfur from the char.

1.1.24 Hamrin

Hamrin and Maa(39) studied the desulfurization of Western Kentucky coal (Kentucky #9) mixed with bottom ash in a batch fluid-bed reactor fluidized with hydrogen at 870°C. The reactor was fluidized with nitrogen and heated to 870°C over a period of 140-180 minutes. Hydrogen flow was then started and maintained for a period of 60-120 minutes. The outlet gas was analysed for hydrogen sulfide every three minutes, using a gas chromatograph. They noted that bottom ash scavenges sulfur from the gas phase, thereby increasing the proportion of sulfur retained in the char. The extent of this scavenging effect was found to be a function of the coal/ash weight ratio.

1.1.25 Belt

Belt and Roder(14) studied the hydrodesulfurization of Pittsburgh hvab bituminous coal in a co-current downflow entrained reactor at various temperatures (1500 to 1900°F), pressures (0-400 psig) and concentrations of hydrogen in nitrogen (0-100%). They noted that the total sulfur content, organic sulfur content and sulfur content per unit of heating value all decreased with increase in temperature, pressure and hydrogen concentration in the entraining gas.

1.1.26 Robinson

Robinson(104) measured inhibition isotherms and the extent of char hydrodesulfurization for a variety of coal chars (West Kentucky, Illinois #6) at two temperatures (805 and 860°C) and three pressures (1, 2.72 and 4.42 atmospheres). The effects of coal washing, acid leaching and particle size were investigated. These experiments were conducted by (a) inserting a weighed sample of char into a vertical tube furnace, (b) fluidizing the char with helium and raising the temperature of the bed to the desired temperature, (c) passing a mixture of hydrogen sulfide in hydrogen through the fluid bed for a selected length of time and (d) allowing the char to cool to ambient temperatures in a helium atmosphere. The char residue was then removed from the furnace and analysed.* The chars employed were prepared by carbonizing coals in a porcelain container under an inert gas at elevated temperatures until tar ceased to be evolved, or by flash pyrolysis in the Garrett Research and Development Company's coal conversion pilot plant. Coals employed were either run-of-mine samples,or samples which had been physically separated by a float-sink preparation. The chars prepared in the procelain container were ground and screened to the desired particle size. The chars were then treated with 0.1-1.0N hydrochloric or sulfuric acid at 80°C for five minutes and then washed free of chloride** or sulfate*** ion. Metals in the char ash were analysed by either emission spectroscopy or atomic adsorption spectroscopy. Robinson concluded, on the basis of his experiments, that:

- o washing or acid leaching of coal or char has a signficant effect upon the inhibition isotherm for the material in question,
- o acid leaching of char results in the almost complete removal of calcium and iron compounds from char,
- o the extent of acid-leached coal hydrodesulfurization is significantly greater than that of run-of-mine coal,
- o the rate of char hydrodesulfurization is relatively rapid compared to the back-reaction of char with hydrogen sulfide,

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*The Eschka method was employed to determine the total sulfur content of the char residue. The analytical method employed to determine the forms of sulfur in the char is not mentioned.

**As determined by the lack of formation of a precipitate upon addition of silver nitrate.

***As determined by the lack of formation of a precipitate upon addition of barium chloride.

- particle size has little effect upon the kinetics of char hydrodesulfurization, and
- the optimum temperature for char hydrodesulfurization is 850°C.

1.2 A Frequent Source of Error in the Literature

There are three forms of sulfur in coal -- i.e., pyrites, organic and sulfate sulfur. During carbonization, pyrites and sulfate sulfur are converted into pyrrhotite. ASTM D2492-77 has been developed as a standard procedure to determine the forms of sulfur in coal. However, because of the change in the forms of sulfur which takes place upon carbonization, ASTM D2492-77 should not be used to determine the forms of sulfur in char. This is because, in dilute hydrochloric acid, pyrrhotite sulfur is liberated as gaseous hydrogen sulfide, and the first step of ASTM D2492-77 involves mixing the sample with dilute hydrochloric acid. Hence, when ASTM D2492-77 is used to determine the forms of sulfur in char, the measured concentration of inorganic sulfur is too low by the amount of pyrrhotite sulfur liberated as hydrogen sulfide.

The total sulfur content, on the other hand, is usually measured by a different technique (i.e., Eschka or a variety of combustion techniques). Hence, this measurement is not affected by the evolution of hydrogen sulfide mentioned above. However, the concentration of organic sulfur in char is computed as the difference between the total and sum of the inorganic sulfur concentrations. Since the latter is too low by the amount of sulfur evolved as hydrogen sulfide, the computed concentration of organic sulfur in the char leads to estimates which are incorrect. The evolution method described by Powell and Thompson(87) can be used in conjunction with ASTM D2492-77 to provide accurate estimates of the forms of sulfur in char.

Because the forms of sulfur analyses are both time consuming and expensive, many authors in the literature have neglected to determine the forms of sulfur in char*. In addition, ASTM D2492-77 was employed in most investigations in which the forms of sulfur in char were measured. The reader should be aware of the errors inherent in the results of such investigations.

1.3 Discussion

Attar(5) has recently reviewed the subject of coal sulfur chemistry from the standpoint of the molecular structure of coal sulfur compounds. He examines the chemistry of these compounds from both kinetic and thermodynamic points of view, and correctly points out that large gaps exist in our understanding of many aspects of coal sulfur chemistry -- e.g., uncertainty surrounds the nature of organic sulfur in both coal and char, reaction paths are not clear, equilibrium information is vague and kinetic information is sketchy.

However, there is another way of thinking about the chemistry of sulfur in coal and char. In this approach, the chemistry is divided into three sections.

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*This is not true in the case of the work done at Consolidation Coal Company (12, 132, 9).

- The fates of sulfur during coal pyrolysis and hydropyrolysis,
- The equilibria which govern the distribution of sulfur between the char and gas phases during the coal pyrolysis and hydropyrolysis, and
- The kinetics of these sulfur distribution reactions.

These subdivisions are discussed in detail in the sections which follow.

1.3.1 The Fates of Sulfur during Coal Pyrolysis and Hydropyrolysis

The fates of sulfur during coal pyrolysis and hydropyrolysis are best summarized graphically. Such a summary is presented in Figure 1.1. Note that as-mined coal contains sulfur in two forms; namely pyrites (FeS_2) and organic sulfur. Pyrite in coal is actually a mixture of pyrite and marcasite. Both possess the same iron/sulfur stoichiometric ratio (i.e., 1:2) but have different crystalline structures. The nature of organic sulfur in coal is uncertain. Powell(79) and Vestal(120) consider it to be the sum of two forms, neither of which has been adequately identified.

While in storage in coal piles, some of the pyrite in coal (generally a relatively small fraction) is converted into sulfate sulfur via bacteriologically-assisted oxidation. There is some uncertainty as to the nature of the sulfate formed as a result of this oxidation reaction. This uncertainty is resolved by the pyrites oxidation models presented by Stumm and Morgan(116). These models reveal that, for kinetic reasons, the iron sulfate encountered in mildly-weathered coals is ferrous sulfate.

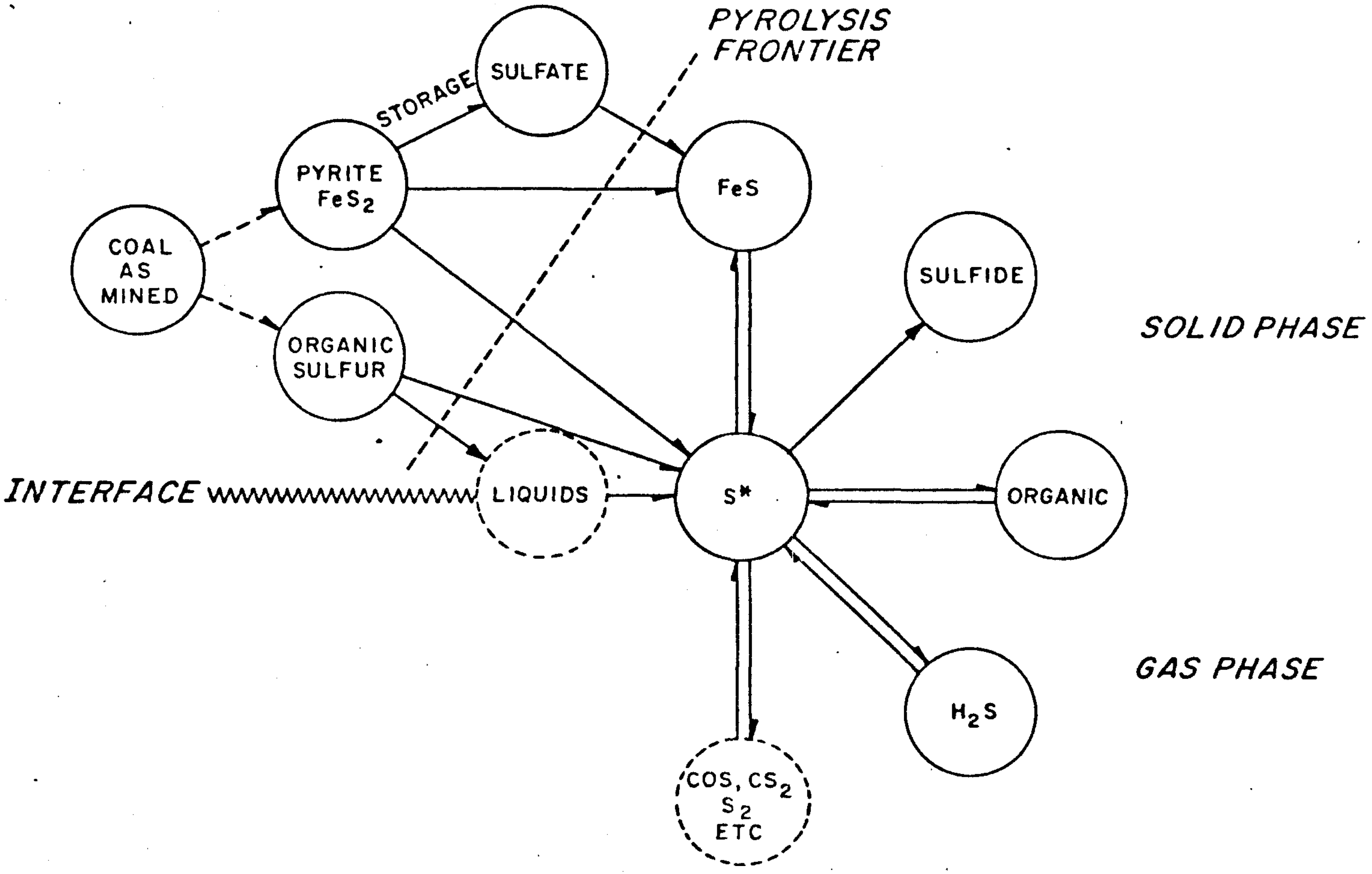


Figure 1.1 The Fates of Sulfur during Coal Pyrolysis and Hydropyrolysis

During pyrolysis, all of the sulfur forms in coal undergo irreversible decomposition reactions. The forms of sulfur in char, which result from these decomposition reactions, are:

1. Pyrrhotite (FeS_{1+x}), which is considered to be a family of iron-sulfur compounds. The equilibrium value of the parameter (x) is a function of temperature and the partial pressure ratio P_{H_2S}/P_{H_2} (118). It is generally quite small and may, for most practical purposes, be neglected.
2. Organic sulfur, the nature of which is not well understood.
3. Metallic sulfides (e.g., CaS, Na_2S) which are formed as a result of sulfidation of mineral constituents inherent in, or added to coal.

It is also worthwhile mentioning that, if char is allowed to cool in the presence of excess air, some pyrrhotite is converted to sulfate sulfur(87).

The pyrolysis frontier mentioned in Figure 1.1 symbolizes the distinction which exists between the reactions of sulfur in coal and char. The reactions which take place during char hydrodesulfurization are, in effect, a subset of the reactions which take place during coal hydrodesulfurization.

Hydrogen sulfide, carbon disulfide, carbonyl sulfide and elemental sulfur are also formed during carbonization. The relative amounts which are produced depend upon the conditions employed. For example:

- o In a hydrogen-rich environment, the concentrations of organic sulfur species (CS_2, COS, S_2) formed are generally quite small because of the relative instability of these species.
- o In an inert atmosphere, measureable concentrations of carbon disulfide are formed, and

- Carbonization of "sulfurous carbons" under vacuum at elevated temperatures leads to the formation of significant amounts of elemental sulfur as well as carbon disulfide.

Some sulfur-containing liquids (tars) are formed during coal pyrolysis. Given sufficient residence time at elevated temperatures, these compounds crack to form char and gas phase species(69).

The mechanisms whereby sulfur is distributed between the char and gas phases are uncertain. For this reason, the reactions presented in Figure 1.1 are shown to pass through an intermediate sulfur species (i.e., S*).

As far as the sulfur distribution reactions between the char and gas phases are concerned, it is generally accepted that:

- Pyrrhotite in the char reacts reversibly with hydrogen in the gas phase to form hydrogen sulfide and elemental iron.
- Organic sulfur in char is the result of a reversible reaction between the char and hydrogen sulfide in the gas phase.
- Metallic sulfides are the result of a reaction between sulfur-acceptors in coal and gaseous sulfur species such as hydrogen sulfide. This reaction is, for all practical purposes, irreversible in a hydrogen-containing environment.

1.3.2 Equilibria which Govern the Distribution of Sulfur between the Char and Gas Phases

An equation to describe the equilibrium constant for the desulfurization of pyrrhotite -- i.e.,

$$FeS(s) + H_2(g) \rightleftarrows Fe(s) + H_2S(g); \; K_p = P_{H_2S}/P_{H_2} \qquad [1.5]$$

has been developed by McIver(66). This equation, which was developed from data presented by Batchelor(9), is presented below.

$$\ell og[K_p] = -[0.3318T + 5458.7]/RT \qquad [1.6]$$

where T is the absolute temperature in degrees Kelvin, and R is the gas constant, in cal./g.mol.°K.

The reaction which leads to the formation of organic sulfur in char has also been discussed by McIver(66). This reaction can be represented as:

$$C(s) + H_2S(g) \rightleftarrows [C\text{-}S](s) + H_2(g) \qquad [1.7]$$

where [C-S](s) is some type of carbon-sulfur complex, the nature of which is still uncertain. On the basis of the equilibrium char sulfidation data presented by Kor(57), McIver developed a model to describe the equilibrium concentration of organic sulfur in char -- i.e.,

$$S = 0.3163\, S_a R / \{R + 1.2392\, T^{0.25} \exp[4562.4T - 1.824 \ell og T + 0.3044]\} \qquad [1.8]$$

where

S = Weight percent sulfur in char (MAF basis)

S_a = Surface area of char; m^2/g

R = Partial pressure ratio $(100P_{H_2S}/P_{H_2})$

P_{H_2S} = Partial pressure of hydrogen sulfide; atm.

P_{H_2} = Partial pressure of hydrogen; atm.

T = Temperature; ^oK

Assuming that the surface area of Batchelor's(9) char was 100 m^2/g., McIver has shown that fairly good agreement was obtained between the results of the model and Batchelor's 1600°F char sulfidation data. However, it was concluded that this model does not accurately describe the adsorption process, and should be regarded as no more than a preliminary attempt to quantitatively define the nature of the adsorption isotherm.

1.3.3 Kinetics of the Sulfur Distribution Reactions

Several authors have investigated the kinetics of char hydrodesulfurization. The results of these investigations are summarized below.

Batchelor and Zielke(8) studied the kinetics of char hydrodesulfurization, and concluded that, under certain conditions (i.e., in deep fluid-beds), their results were equilibrium rather than kinetically-controlled.

As was noted in the literature review, Jones(52) studied the kinetics of COED char hydrodesulfurization. He concluded that char hydrodesulfurization proceeds in two stages:

- o A rapid and equilibrium-controlled "flash" desulfurization, and
- o A slower second stage, in which the rate-controlling mechanism is Knudsen diffusion in the micropores of the char.

These conclusions can be criticised on the grounds that:

(a) the conclusion that the flash desulfurization is equilibrium rather than kinetically-controlled is inadequately substantiated, and

(b) if flash desulfurization is several orders of magnitude more rapid than the second stage, what evidence could lead one to the conclusion that the second stage is diffusion-controlled?

This apparent inconsistency was circumvented in a later paper by Gray, _et al_ (36), who suggested that the rate-controlling mechanism in the second stage is diffusion within pyrrhotite particles (located within the char particles). While it appears to be quite reasonable, no evidence is presented to support this hypothesis.

Kor(56) also studied the kinetics of char hydrodesulfurization. Like Jones(52) and Gray, _et al_ (36), he concluded that char hydrodesulfurizaion takes place in two distinct stages. In the first stage, rapid desulfurization and gasification take place simultaneously. In the second stage, sulfur is removed more slowly, the rate being practically independent of the extent of char gasification. He assumed that the kinetics of the slow second stage can be described by an equation of the form;

$$\delta S/\delta t \quad = \quad -k_s S \qquad [1.9]$$

which, upon integration, yields:

$$\ln(S/S_0) \quad = \quad -k_s t \qquad [1.10]$$

where S is the total sulfur concentration in the char at time t, k_s is a rate constant, and S_0 is the sulfur concentration after 15 minutes of reaction time. However, as has been noted in the literature survey, Kor(55) showed that the kinetics of the reduction of pyrrhotite with hydrogen in the same equipment were mass-transfer controlled. Hence, no firm conclusions can be drawn on the basis of the results presented by Kor.

Yergey, et al(131) noted that the non-isothermal method of kinetic data analysis developed by Juntgen yields good agreement with data obtained by classical methods when applied to the decomposition of magnesium carbonate. Accordingly, Vestal and Johnson(120) and, later, Yergey, et al(131) employed this technique to estimate the kinetic parameters associated with the reactions which occur during coal hydrodesulfurization. They depict coal desulfurization as occurring according to the general reaction:

$$(A_j\text{-}S)_{solid} + H_2(g) \rightleftarrows (A_j)_{solid} + H_2S(g) \qquad [1.11]$$

where A_j-S represents one of a variety of ways in which sulfur is bound in the solid, and A_j represents the pertinent site of this bonding after removal of the sulfur. They employed an expression of the form:

$$-\delta[A_j\text{-}S]/\delta t = k_{oj}\, e^{-E_j/RT}\, [A_j\text{-}S]^{n_j} \qquad [1.12]$$

to describe the rate of reaction [1.11], where $[A_j\text{-}S]$ is the concentration of solid reactant sites of type j, k_{oj} is the pre-exponential factor for the j^{th} reaction, E_j is the activation energy for the j^{th} reaction and n_j is the order of the j^{th} reaction with respect to the sulfur species in question. The technique requires that the temperature of the sample (T) vary linearly with time (t) -- i.e.,

$$\delta T/\delta t \quad = \quad M \qquad [1.13]$$

where M, a constant in any given experiment, ranged between 3 and 100°C per minute. Making several quite reasonable assumptions, integrating equation [1.12] and summing over all j reactions yields an expression for the volume of hydrogen sulfide in the reactor outlet as a function of the parameters k_{oj},E_j and n_j.

In their first paper, Vestal and Johnson(120) assumed that eight reactions occur simultaneously during coal hydrodesulfurization, while in the later paper(131) only seven reactions were assumed. In all fairness it should be noted that the kinetic parameters of three of these reactions (sulfidation of iron filings, charcoal and calcium oxide) can be measured independent of the reactions which occur during coal hydrodesulfurization. However, at least four reactions remain, the kinetic parameters of which must be measured simultaneously. In other words, a twelve-parameter model is employed to describe the evolution of hydrogen sulfide from coal during hydrodesulfurization. The large number of model parameters is, alone, sufficient to make the author somewhat skeptical as to the accuracy and significance of the estimated kinetic parameters. In addition:

- The reported values of the kinetic parameters in the first(120) and second(131) papers are, in several instances, significantly different.
- No attempt was made to establish the effects of pressure, heating rate, surface area, type of coal, concentration and distribution of sulfur forms, thermal history of the char, etc., upon the kinetics of desulfurization of the various sulfur species in coal and char.
- The validity of the model symbolized by [1.12] is subject to the criticism that very little is known about the mechanisms which govern the coal and char desulfurization reations at this stage.

Hence, in the absence of evidence to support the assumptions and hypotheses required in the development of this model, there is little reason to suppose that these are anything other than results of an elegant curve-fitting technique. While the technique, and the approach employed, probably have significant potential, these results are of little immediate practical utility.

On the other hand, these experimental results do lead one to the qualitative conclusion that the desulfurization reactions which take place during coal decomposition are probably more rapid than the char desulfurization reactions:

$$FeS + H_2 \rightleftarrows Fe + H_2S \qquad [1.14]$$

and

$$[C\text{-}S](s) + H_2 \rightleftarrows C(s) + H_2S \qquad [1.15]$$

Robinson's(104) char hydrodesulfurization experiments, in which he demonstrated that the back-reaction in [1.15] is much slower than the rate of char hydrodesulfurization, support this contention.

1.4 Uncertainty in the Literature, and the Focus of Attention on the Nature and Properties of Organic Sulfur in Char

The arguments presented above reveal that, while much is known about the fate of sulfur during coal pyrolysis and hydropyrolysis, uncertainty surrounds many fundamentally-important areas of coal and char sulfur chemistry -- i.e.,

- the nature of organic sulfur in coal and char,
- the mechanisms of the reactions whereby sulfur is distributed between organic sulfur in char and hydrogen sulfide in the gas phase, and
- the factors which affect the equilibria and kinetics of these reactions.

In other words, this review highlights the uncertainty which surrounds the nature and properties of organic sulfur in char. Perhaps more importantly, it reveals the lack of a cohesive framework on which to structure one's understanding of the chemistry of sulfur in char.

In an attempt to resolve the uncertainty surrounding the nature of organic sulfur in char, the factors which govern the distribution of sulfur between organic sulfur in char and hydrogen sulfide in the gas phase have been investigated. The experimental apparatus, and the techniques and procedures employed in this investigation,are described in Chapter Two.

CHAPTER TWO

DESCRIPTION OF THE APPARATUS, AND THE EXPERIMENTAL TECHNIQUES AND PROCEDURES

The experimental apparatus, and the various techniques and procedures employed in this investigation,are described below.

2.1 Apparatus

Three sets of experimental apparatus were employed in this investigation -- i.e., a horizontal tube furnace, a fluid-bed apparatus, and an ESCA apparatus.

2.1.1 Horizontal Tube Furnace

A horizontal tube furnace which is similar to apparatus employed by Powell(79) was initially constructed for use in this investigation. A schematic diagram of the apparatus is presented in Figure 2.1. Not shown in Figure 2.1, the tube furnace is divided into four separate sections. The temperature of each zone is independently controllable. The control element (a thermocouple) is located at the midpoint of each section. A quartz tube (25 mm O.D., 22 mm I.D.) passes through all of the tube furnace sections.

2.1.2 Fluid-bed Apparatus

Schematic diagrams of the fluid-bed apparatus are presented in Figure 2.2, 2.3, and 2.4. The apparatus consists of:

1. A feedgas manifold, which permits one to feed almost any mixture of hydrogen, hydrogen sulfide and helium into the fluid bed. The total gas flowrates in this investigation were typically 0.5 or 1.0 scfh. The concentrations

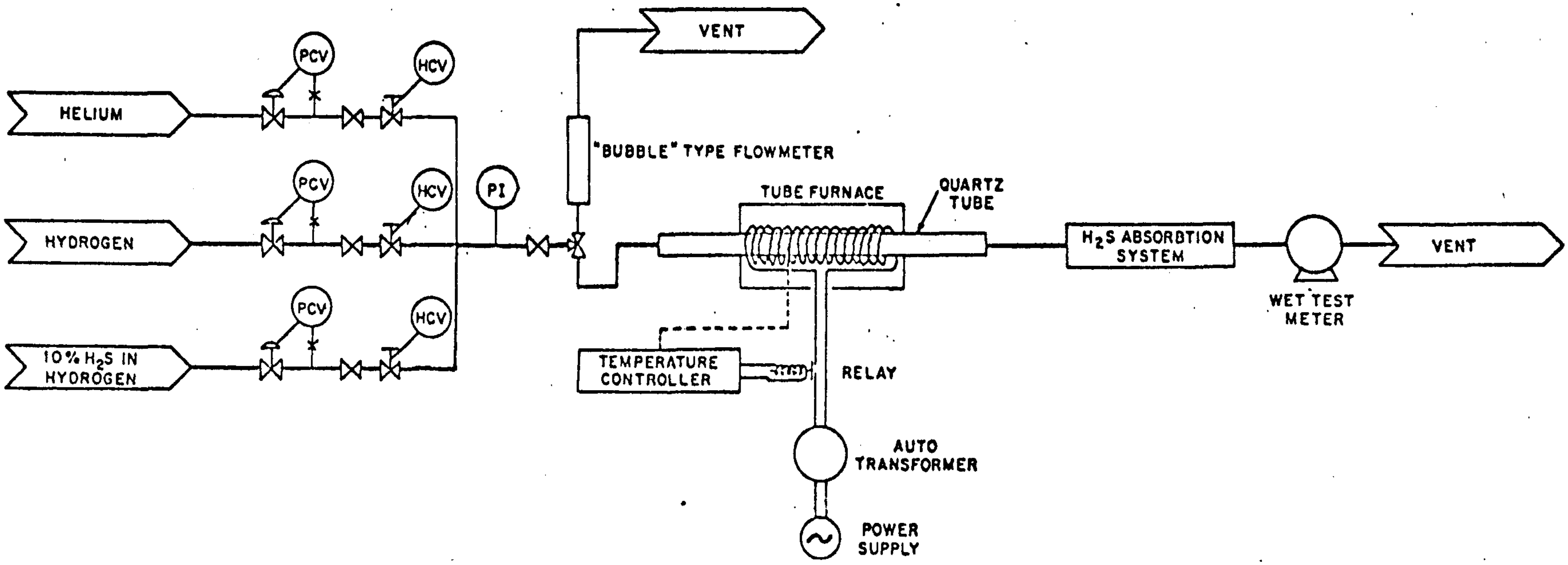


Figure 2.1 Schematic Diagram of the Horizontal Tube Furnace Apparatus

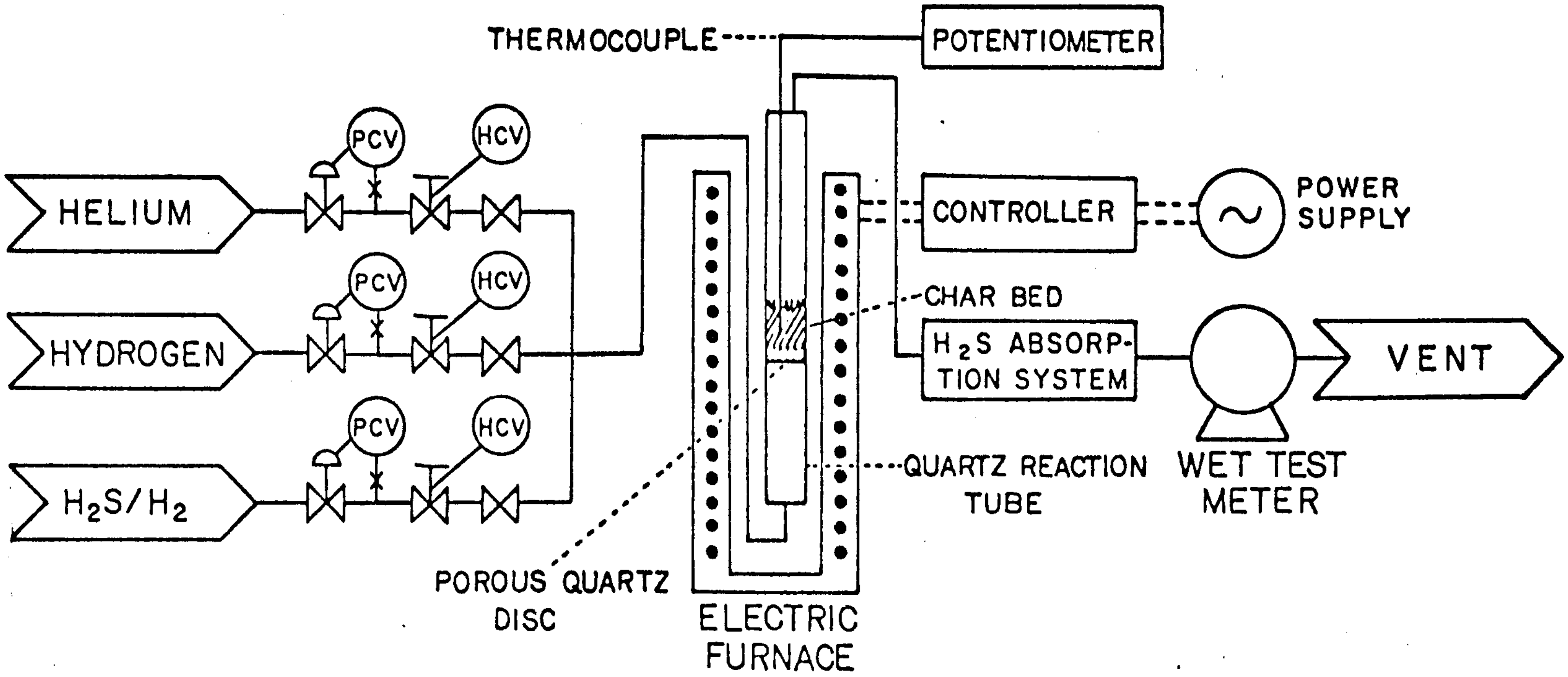
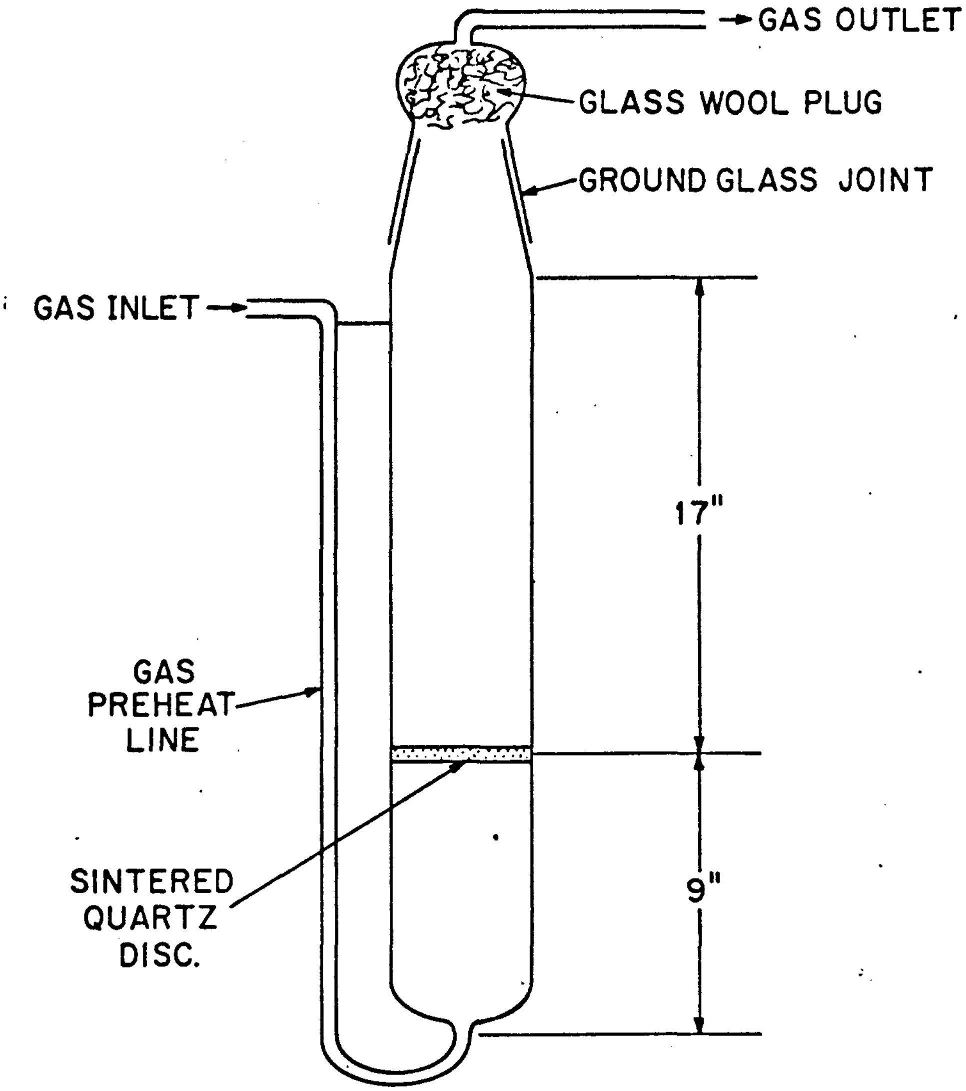


Figure 2.2 Schematic Diagram of the Fluid-Bed Apparatus



QUARTZ FURNACE TUBE
O.D.; 25 MM.-I.D.; 22 MM.

Figure 2.3 Schematic Diagram of the Quartz Furnace Tube

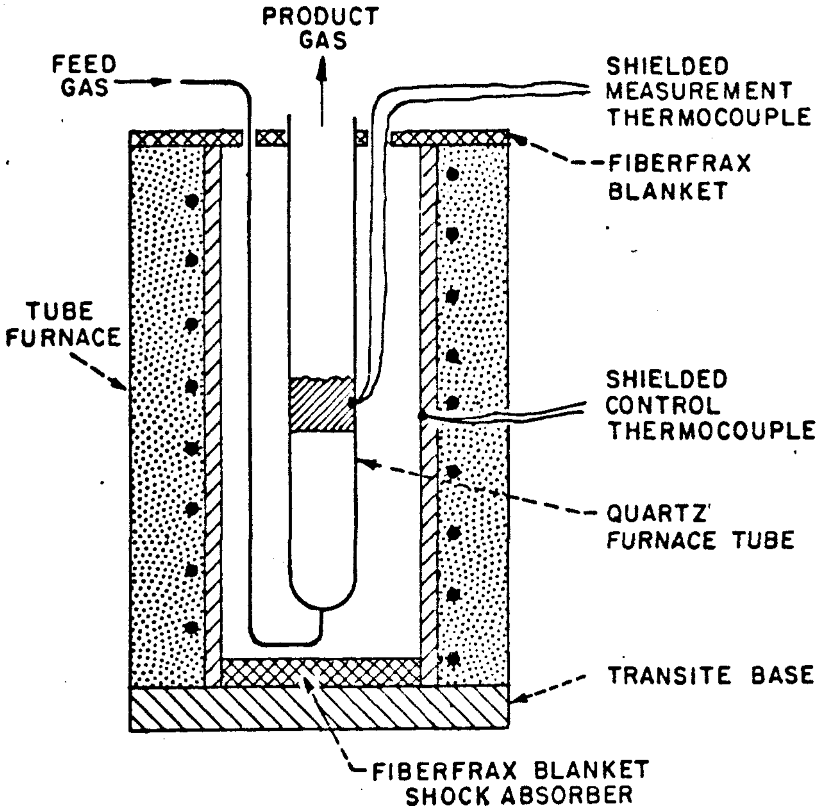


Figure 2.4 Location of the Fluid-Bed Temperature Measurement and Control Thermocouples

of hydrogen sulfide in hydrogen in the feedgas cylinders were chosen so as to permit a wide range of the partial pressure ratio (100 P_{H_2S}/P_{H_2}) to be employed.

2. A vertical tube furnace, insulated at both top and bottom to minimize the effects of natural convection upon the axial temperature profile within the furnace.

3. A quartz furnace tube (see Figure 2.3).

4. A gas scrubbing train, in which hydrogen sulfide is removed from the product gas stream upstream of the product gas metering and vent systems by contacting the product gas with concentrated sodium hydroxide.

5. A product gas metering system, in which the total flowrate of the product gas, minus the hydrogen sulfide, is measured in either a calibrated wet test meter or a bubble flowmeter.

To circumvent problems arising as a result of the non-uniform axial temperature profile within the tube furnace, a shielded chromel alumel thermocouple* was installed on the exterior of the furnace tube opposite the fluid-bed (see Figure 2.4). The temperature measured on this thermocouple (see Figure 2.4) was used to adjust the set point on the temperature controller such that the temperature of the shielded thermocouple was maintained at the desired value ± 10°C.

2.1.3 ESCA Description

ESCA is a sophisticated, though well-established technique capable of providing information regarding the elemental composition, and the oxidation states of elements in surfaces(109,42).

The ESCA apparatus employed in this investigation is a McPhearson ESCA 36 system. It is located at the Pittsburgh Energy Technology Center (PETC), Bruceton, Pennsylvania. This apparatus was used with the permission

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*The thermocouple was shielded by wrapping the junction with FIBERFRAX (Reg. T.M.) insulating blanket to prevent impinging radiation from affecting the accuracy of the temperature measurement.

and assistance of Dr. Fred Brown. The experimental work was performed by Mr. Leo Makovsky.

The processes common to all ESCA systems are summarized in Figure 2.5. Simply stated, the sample (in this case a pulverized char sample spread on the surface of an aluminum plate) is bombarded with a non-destructive beam of X-rays. This ionizing radiation causes ejection of electrons from the sample surface. The electrons pass into a scanning electron monochromator, and a kinetic energy spectrum of the photo-ejected electrons is produced. Suitable calibration of the apparatus, and a knowledge of the energy of the incident X-ray, enable one to compute the binding energy spectrum of the electrons which are ejected from the surface.

The binding energy of an electron is defined as the work required to move the electron from its orbit to infinity. It is a function of the chemical environment of the atom with which the electron is associated. Hence, the binding energy of an electron depends upon (a) the type of element with which the electron is associated, (b) the type of electron, and (c) the valence state of the atom in question. Therefore, a binding energy spectrum for a particular sample provides qualitative (and sometimes quantitative) information regarding the composition, as well as the valence states, of the elements in the sample surface.

Much research has been conducted on the binding energy spectra associated with model sulfur compounds(109). The results of this work are summarized in the valence state correlation chart presented in Figure 2.6. This chart enables one, from the binding energy spectrum of a particular sample, to establish the valence state of sulfur species in the surface.

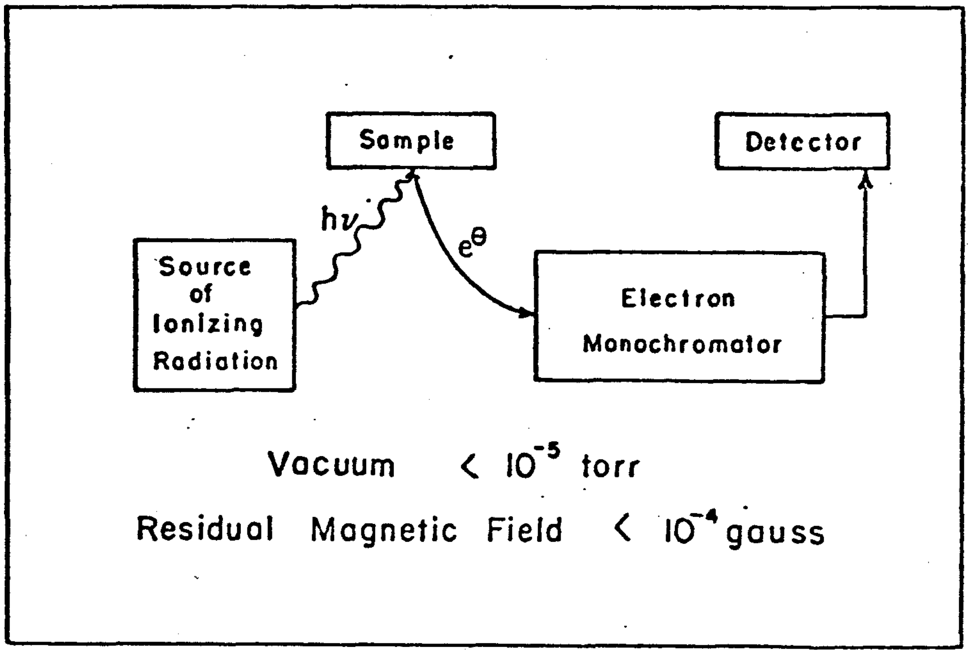

Figure 2.5 Block Diagram showing the Essential Elements of an Electron Spectrometer

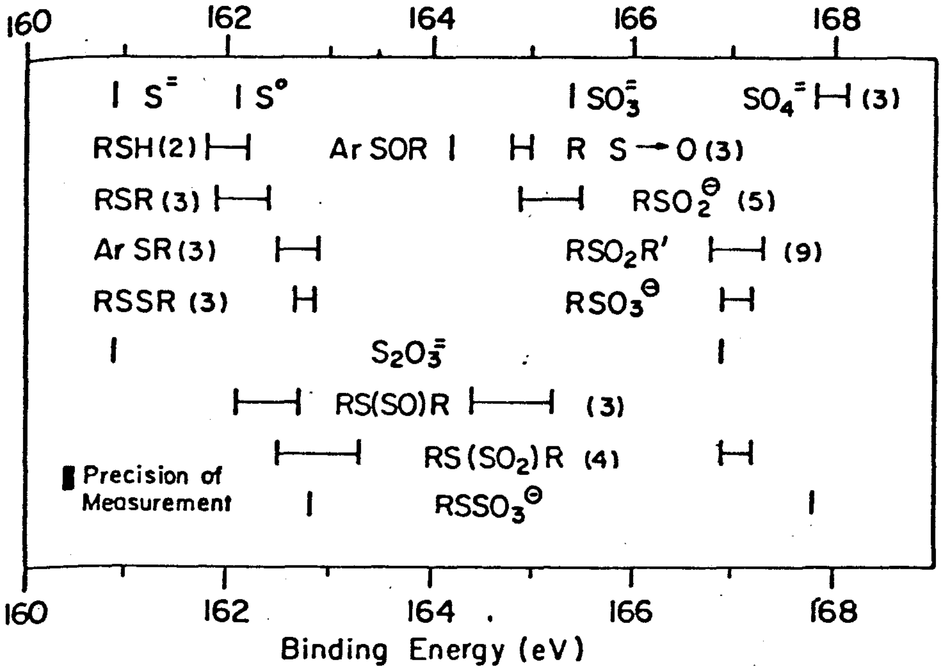

Figure 2.6 Correlation Chart for the Sulfur $2p_3$ Electron Binding Energy

For example, if a sulfur peak were to lie at 160.9 eV, one may assume that the sulfur species is a sulfide ($S^=$). On the other hand, if a sulfur peak were to lie at 168 eV, the sulfur species in question is probably a sulfate ($SO_4^=$).

Many ESCA systems are able to analyze the composition of the material beneath the surface. This is accomplished by bombarding the surface of the sample with ions, in this case argon ions. Ion bombardment (or "sputtering") of the surface peels (perhaps rips is a better word) material from the surface, thereby exposing material beneath the surface for analysis. Therefore, one is in principle able to analyze the composition of the material as a function of depth from the "unsputtered" surface. In practice, calibration of sputtering depth with sputtering time is difficult, particularly in the case of non-homogeneous materials (such as coal char).

The word "surface" has been used rather loosely here. It has been demonstrated that electrons are ejected from atoms which are located some distance into the char matrix(109). It is generally accepted that, for most surfaces, electrons do not emerge from depths greater than 100 angstroms(42). Hence, all of the elements which lie within this distance of the surface will be "seen" in the binding energy spectrum. In other words, as far as ESCA is concerned, all of the material which lies within approximately 100 angstroms of the surface is considered to be part of the surface.

Coal chars are generally quite high surface area materials, with surface areas ranging from approximately 50 -500 m^2/gram. A first-order approximation (assuming the density of the char matrix to be the same as that of graphite -- i.e., 2.26 g/ccs) suggests that the mean distance between surfaces within a char particle ranges from 18-180 A^{o2}. In other words, an ESCA analysis of a char sample provides a bulk analysis of the char (since it "sees" the elements in the bulk as well as on the surface). This has important implications as far as correct interpretation of the analytical results is concerned.

2.2 Experimental Techniques and Procedures

In order to minimize the effects of mass transfer limitations within the char particles, the chars employed in this investigation were ground in a pestle and mortar until all of the material passed through a 200-mesh sieve.

2.2.1 Char Leaching Procedure

After some preliminary experiments to test the efficiency of various char leaching procedures, the following procedure was used to prepare the char samples for use in this investigation.*

1. Prepare two litres of a 0.6N solution of hydrochloric acid in distilled water. Mix the solution with 250 grams of char sample. Heat the mixture to just below boiling point while stirring vigorously, and allow to stand overnight. The following morning, filter the mixture and repeat the procedure.
2. Repeat this procedure five more times using distilled water instead of the dilute solution of hydrochloric acid.
3. Dry the product char overnight at 105°C.

This acid washing procedure was partially successful in reducing the ash concentration in the product char. More importantly, sulfide sulfur

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*The only exception is filter paper char, which was not acid washed.

concentrations in the washed chars employed (prior to exposure to hydrogen sulfide) were negligible -- i.e., less than 0.02% sulfur as sulfide.

2.2.2 Analytical Procedures

Because analyses can be performed quite rapidly in a Leco combustion furnace, the initial analytical plan called for its use in determining the total sulfur concentration of the chars produced in this investigation. A series of experiments was performed to test the accuracy of this analytical procedure. In these experiments, a set of commercially-available sulfur standards was analyzed. These experiments demonstrated our inability to accurately reproduce standard analyses using the Leco apparatus. Hence, attempts to use this apparatus were abandoned in favor of the widely-accepted ASTM procedures.

A summary of the analytical procedures which were adopted is presented in Table 2.1. A set of experiments was performed in which the sulfur standards used to test the Leco apparatus were analysed. These experiments revealed that, while the mean value of the sulfur concentrations compared favorably with the standard concentrations, quite a large degree of scatter was found in the results. Hence, every effort was made to ensure that a representative char sample was used in each analysis. In addition, duplicate analyses were performed whenever possible. The difference between the duplicate analyses presented can be used as a measure of the randomness encountered in the analytical results.

An important point to notice is that analytical procedures for determining the concentration of organic sulfur in char are not available at present. Hence the organic sulfur analyses presented are computed as the difference between the total sulfur concentration and the sum of all inorganic

Type of Analysis	Description of the Analytical Method Employed
Total Sulfur	As specified by ASTM Analysis #D3177-75 alternate A -- Eschka Method
Sulfate, Pyritic and Organic Sulfur	As specified by ASTM Analysis #D2492-77
Moisture	As specified by ASTM Analysis #D3173-73
Ash	As specified by ASTM Analysis #D3174-73
Sulfide Sulfur	The procedure adopted was a slight modification of the method suggested by Powell and Thompson (87). A one gram sample of char is placed in a flask and 25 ml. of a 4.8Nsolution of hydrocloric acid in distilled water is added dropwise. The mixture is heated to the boiling point, and the hydrogen sulfide produced is carried over into an ammoniacal solution of aqueous cadmium chloride, where cadmium sulfide precipitates. This solution is rinsed into a flask, diluted to 250 ml. and neutralized with hydrocloric acid. After addition of a slight excess of hydrochloric acid and a potassium iodide/starch solution, the entire mixture is titrated with a standard solution of potassium iodate (KIO_3).

Table 2.1 <u>Summary of the Analytical Procedures Employed</u>

sulfur forms in the char -- i.e., sulfate, sulfide, or pyrite.

2.2.3 Fluid-Bed Experimental Procedure

A useful tool, called a history diagram, was developed in order to describe the fluid-bed experiments. An example of a history diagram is presented below.

$$\text{START}\ \frac{\text{900°C; 1 Hour}}{\text{0.5 scfh Helium}}\ \frac{\text{1400°F; 1 Hour}}{\text{0.5 scfh He}}\ \frac{\text{1400°F; 1 Hour}}{\begin{array}{l}\text{0.5 scfh; 7.76\%}\\ \text{H}_2\text{S in Hydrogen}\end{array}}\ \frac{\text{1400°F; 20 Mins}}{\text{0.5 scfh; 10\%}}\ \text{ANALYSIS}$$

where a standard cubic foot (scf) of gas is defined as the amount of dry gas contained in one cubic foot at 760 mm. Hg. and 0°C.

The above history diagram describes an experiment in which the following procedure was adopted.

1. Calibrate the metering valves such that the appropriate flow-rate combinations (i.e., 0.5 scfh/helium, 0.5 scfh/7.76% hydrogen sulfide in hydrogen, and 0.5 scfh/10% hydrogen in helium) can be achieved by suitable adjustment of the relevant shutoff and metering valves.

2. Switch on the tube furnace, and allow it to reach a steady-state temperature of 900°C.

3. Place a weighed sample of char into a quartz furnace tube.

4. Insert a clean plug of glass wool into the bulb of the ground glass joint and close the outlet of the quartz tube.

5. Adjust the appropriate metering and shutoff valves such that 0.5 scfh of helium is passed through the fluid-bed.

6. Once the quartz tube has been purged of all air, insert it into the tube furnace. Plug the top of the tube furnace with FIBERFRAX blanket.

7. An hour later, adjust the set point of the temperature controller and allow the tube furnace to cool to a steady-state temperature of 1400°F.

8. After another hour, adjust the appropriate metering and shutoff-valves such that 0.5 scfh of 7.76% hydrogen sulfide in hydrogen passes through the fluid-bed.

9. After another hour, adjust the appropriate metering and shutoff-valves such that 0.5 scfh of 10% hydrogen in helium passes through the fluid-bed.

10. Twenty minutes later, adjust the metering valves such that 0.5 scfh helium passes through the fluid-bed.

11. Terminate the experiment as follows: two minutes after switching to pure helium, extract the quartz tube from the furnace and switch off the helium flowrate. In the process of cooling to ambient temperature, the helium in the furnace tube contracts. In order to compensate for this reduction in volume, open the helium shutoff-valve occasionally so that backflow of sodium hydroxide into the furnace tube is prevented.

12. When the quartz tube has cooled to ambient temperature (below 80°F), open the outlet of the quartz furnace tube carefully to prevent char particles trapped in the glass wool plug from falling back into the char sample. Remove the char sample from the quartz furnace tube, weigh if necessary, and store in a tightly-stoppered glass bottle in a desiccator.

During the course of an experiment, char fines (of the order of 5-10% of the bed material) were elutriated from the fluid bed. The use of the glass wool plug prevented these fines from (a) falling back into the char sample at the end of an experiment, thereby introducing errors into the analytical procedures, and (b) being carried over into the outlet gas.

The development of the history diagram has played an important role in the success of these experiments, because it provides an unambiguous definition of the physiochemical history of the char sample during an experiment. For each of the experiments discussed, a history diagram will be presented below the relevant table of experimental results.

2.2.4 ESCA Procedure and Calibration

The HYDRANE HY-128 bituminous coal char employed in the ESCA studies was thoroughly washed according to the previously mentioned standard procedure. Several samples were then prepared in the fluid-bed apparatus. At the end of preparation, the samples were stored in tightly-stoppered glass sample bottles in a desiccator. When all eight samples had been prepared, they were shipped to PETC for analysis in the ESCA apparatus.

At PETC, the samples were spread onto aluminum sample slides and introduced into the ESCA appratus sample carousel. The system was evacuated to 10^{-7}-10^{-8} torr and maintained at that pressure. A binding energy spectrum for the first sample was obtained. The sample was then "sputtered" (for typically 60 seconds) and a binding energy spectrum for the "cleaned" surface was obtained. This procedure was repeated for the remaining samples in the carousel.

Like most analytical appratus, ESCA systems require calibration.* The calibration of the system at Bruceton was checked by the following experiment:

1. A gold filiament was introduced into the sample carousel in place of the aluminum sample slide.
2. A binding energy spectrum for gold in the region between 70 and 90 eV. was obtained. This spectrum is presented in Figure 2.7.
3. The binding energy for the gold 4f7/2 electron was estimated to be 83.8 eV. from this binding energy spectrum.
4. The published value of the binding energy for the gold 4f7/2 electron (103) is 83.8 eV.

Since the measured and published binding energies for the gold 4f7/2 electron were found to be consistent, the instrument had been accurately calibrated.

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*Because of differences in the "work function" associated with spectrometers, each must be calibrated before use.

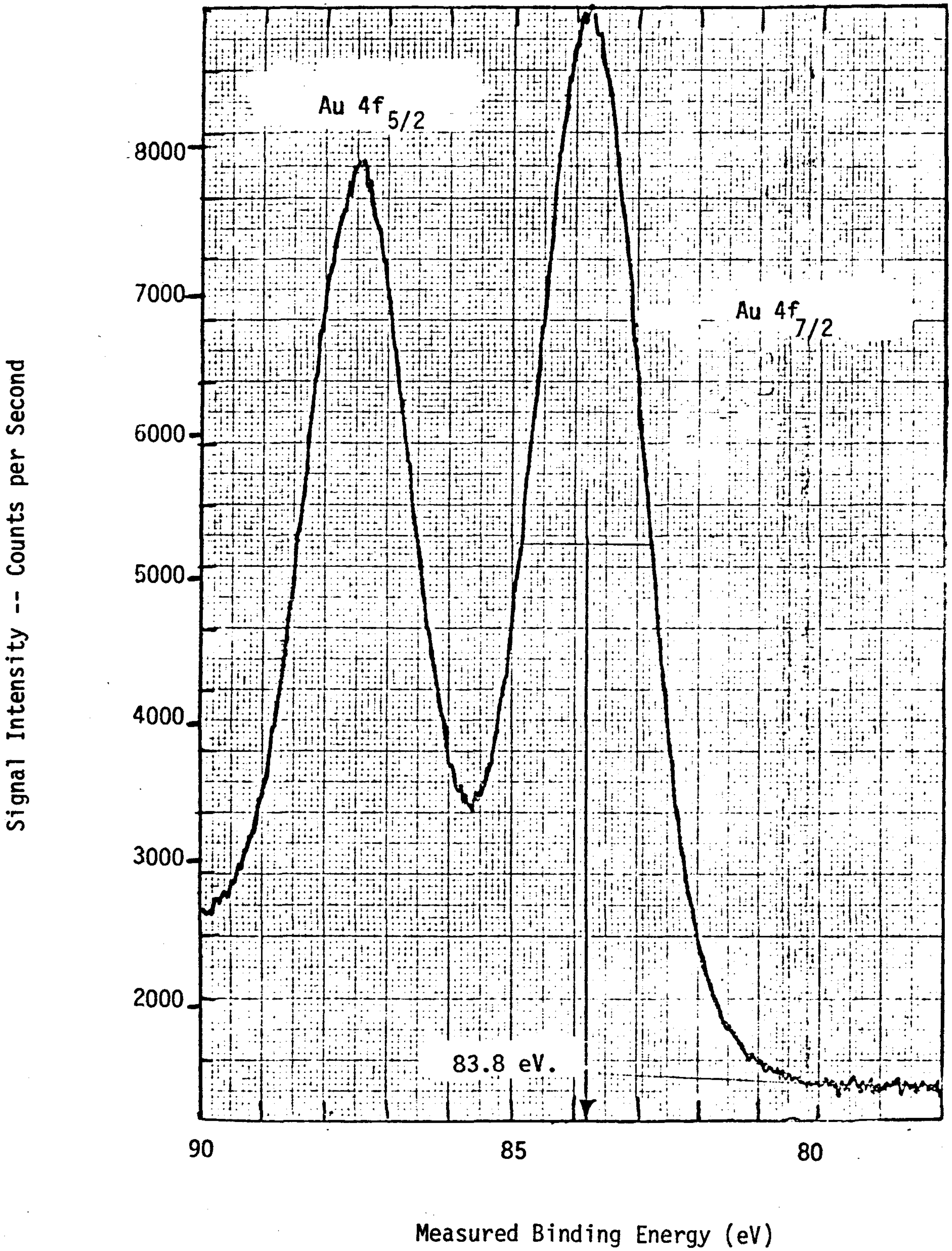

Figure 2.7 Measured Binding Energy Spectrum for Gold Filament

A shift in the binding energy spectrum occurs when different types of samples are studied. Called the sample work function, the magnitude of this shift is characteristic of the sample. It is caused by charging of the sample, and is particularly noticeable in the case of insulators, semiconductors, etc. The sample work function for the chars employed in the ESCA analyses was estimated in the following way:

1. A sample was spread onto the surface of the aluminum sample slide.
2. The slide was introduced into the ESCA sample carousel, and the system was evacuated to 10^{-7}-10^{-8} torr and maintained at that pressure.
3. Gold was evaporated onto the surface of the sample slide (on top of the char sample).
4. The binding energy spectrum for gold in the region between 70 and 90 eV. was obtained, and is presented in Figure 2.8.
5. From this binding energy spectrum, the binding energy of the gold 4f7/2 electron was estimated to be 84.2 eV.
6. The published value(103) of the binding energy of the gold 4f7/2 electron is 83.8 eV.

Hence, the measured value of the binding energy of the gold 4f7/2 electron is 0.4 eV. too high -- i.e., the value of the sample work function is estimated to be 0.4 eV. This value will be used to correct the measured binding energies in order to estimate the true binding energy of the electron in question.

2.3 Analyses of the Chars Employed

While other chars were employed in some of the preliminary experiments described in this thesis, all of the quantitative experiments

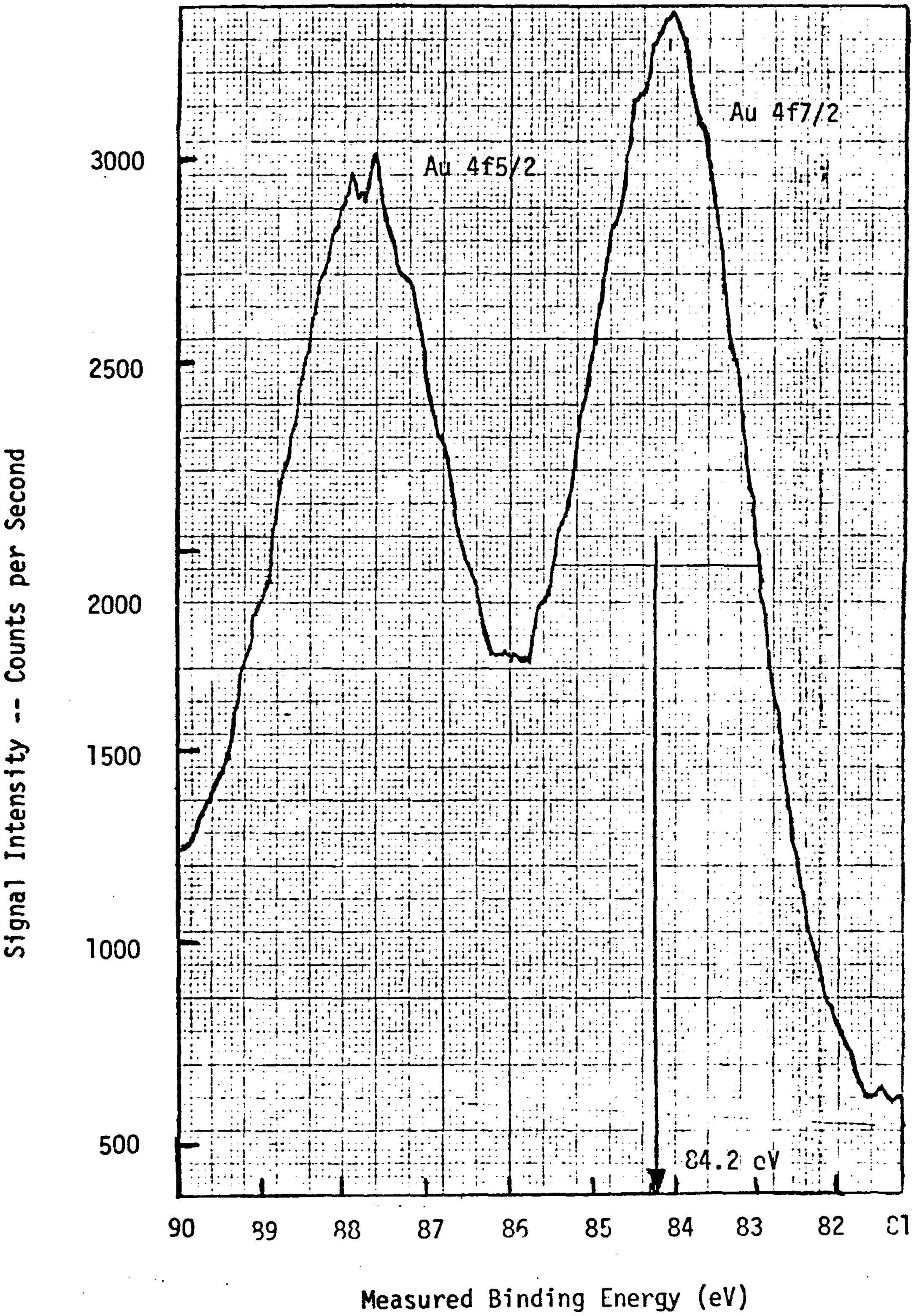

Figure 2.8 Measured Binding Energies for Gold-Coated Char

were performed using five chars -- i.e.,

- HYDRANE - HY-138 North Dakota (Beulah) lignite char
- HYDRANE HY-140 Montana (Rosebud) sub-bituminous char
- HYDRANE HY-128 Illinois #6 (Orient #3) hvc bituminous coal
- Barnebey-Cheney 417 Anthracite-based Activated Charcoal
- Filter Paper Char

The HYDRANE chars employed were all produced in the HYDRANE dilute-phase reactor at PETC at a wall temperature of 900°C, and a total pressure of 69 atmospheres. These chars were supplied by courtesy of Harold F. Chambers and Dr. Paul Yavorsky. The filter paper char was prepared by charring Whatman #40-ashless filter paper in tightly packed sample boats in a horizontal tube furnace (at 900°C in 0.5 scfh helium for three hours). All of the chars (with the exception of filter paper char) were thoroughly acid-washed according to the char leaching procedure described previously. The washed and unwashed chars were analysed at Conoco Coal Development Co., through the courtesy of Mr. George Curran. These analyses, as well as the analyses of the coals as-fed to the HYDRANE reactor (obtained from PETC) are presented in Table 2.2.

2.4 Experiments to Test the Experimental Apparatus and Procedures

Several experiments were performed for the sole purpose of testing the performance of the experimental apparatus and procedures. These experiments are described below.

2.4.1 Development of a Char Leaching Procedure

Chars contain a variety of minerals which, in some instances, are capable of reacting with hydrogen sulfide to form sulfides. The presence of

	HY-138 Lignite		HY-140 Subbituminous		HY-128 Bituminous			BC-417 Anthracite Activated Charcoal		Filter Paper
	Coal	Char	Coal	Char	Coal	Char	Char	Char	Char	Char
	(a)	Washed (d)	(a)	Washed (d)	(a)	Unwashed (b)	Washed (d)	Unwashed (e)	Washed (f)	Unwashed
Proximate Analysis										
Moisture	5.8	--	8.5	--	1.3	--	--	--	--	--
Volatile Matter	39.7	--	38.0	--	35.8	--	--	--	--	--
Fixed Carbon	43.6	--	43.1	--	53.0	--	--	--	--	--
Ash	10.9	--	10.4	--	9.9	--	--	--	--	--
Total	100.0	--	100.0	--	100.0	--	--	--	--	--
Ultimate Analysis (Cl&MF Basis)										
Hydrogen	3.9	1.55	4.0	1.34	4.9	1.56	1.63	1.21	1.26	0.24
Carbon	62.2	82.40	62.7	82.16	71.7	80.00	85.56	82.51	86.90	98.87
Nitrogen	0.9	0.5	0.8	0.62	1.6	1.47	1.48	0.76	0.77	0.04
Oxygen	20.2	6.16	19.7	3.03	10.4	3.08	3.18	3.12	3.32	0.67
Total Sulfur	1.3	1.32	1.4	0.83	1.4	0.92	0.82	0.67	0.62	neg
Ash	11.6	8.08	11.4	12.12	10.0	12.97	7.32	11.73	7.13	0.19
Total	100.1	100.01	100.0	100.1	100.0	99.99	100.00	100.00	100.00	100.01
Sulfide Sulfur	--	neg.	--	neg.	--	0.27	neg	neg	neg	--
Organic Sulfur	--	1.32	--	0.83	--	0.65	0.82	0.67	0.62	--
Chlorine Content (MF Basis)	--	4.82	--	3.16	--	0.04	1.86	0.06	0.25	--
Ash Analysis (SO_3-free Basis)										
Na_2O	--	0.16	--	0.09	--	1.9	0.86	1.4	0.79	--
K_2O	--	0.05	--	0.22	--	2.6	1.3	2.0	1.4	--
CaO	--	40.3	--	19.5	--	2.1	0.93	4.4	0.72	--
MgO	--	13.9	--	9.0	--	1.0	0.56	1.3	0.40	--
Fe_2O_3	--	4.3	--	0.95	--	11.4	1.7	9.9	1.8	--
TiO_2	--	1.1	--	1.85	--	1.5	2.8	1.7	2.6	--
P_2O_5	--	0.22	--	0.07	--	0.19	0.11	0.71	0.28	--
SiO_2	--	28.6	--	59.0	--	56.7	76.7	53.4	69.6	--
Al_2O_3	--	8.9	--	7.9	--	22.1	14.1	24.3	21.9	--
Total	--	97.53	--	98.58	--	99.49	99.06	99.11	99.49	--

Note (a) As-fed to the HYDRANE dilute-phase reactor

(b) Ex the HYDRANE dilute-phase reactor

(c) Operating conditions for the HYDRANE dilute-phase reactor: 69 atm and a wall temperature of 900°C.

(d) Ex HYDRANE dilute-phase reactor, and washed according to the procedure outlined in Section 2.2.1

(e) As-received

(f) Washed according to the procedure outlined in Section 2.2.1

Table 2.2. Analyses of the Chars Employed

sulfides in char (a) complicates the analytical procedures involved, and (b) introduces error into the estimated concentration of organic sulfur in char. Robinson(104) has demonstrated that dilute hydrochloric acid as well as dilute sulfuric acid effect almost complete removal of calcium and iron (the principal sulfide-forming constituents in coal ash) from char. Hence, five sets of char leaching experiments were performed in order to develop an acid-leaching procedure to remove sulfide-forming minerals from char. In these experiments, dilute nitric acid rather than dilute sulfuric acid was used to avoid introducing sulfur into the char. Referred to as experiments A, B, C, D and E, these char leaching procedures are described in detail in Table 2.3. The five types of char employed are described in Table 2.4.

Ash concentrations in the five product chars are presented in Table 2.5. Notice that (a) all the washing procedures employed accomplish a significant reduction in the ash content of the washed char samples, and (b) none of the washing procedures employed is successful in removing all of the ash from the washed char.

In an attempt to understand why none of the washing procedures was effective in removing all the ash from the washed chars, atomic emission spectral analyses for the five unwashed char samples were obtained.* The results of these analyses are presented in Table 2.6. Notice that a

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*These analyses were performed in a 3.4 m, Jarrell-Ash, Ebertmount Emission Spectograph and a Jarrell-Ash 2100 Microphotometer/Comparitor. The char samples were ground and diluted with spectroscopically pure graphite. Weighed amounts of these diluted samples were then analyzed, and the density of the characteristic lines measured with a densitometer for comparison with appropriate standards.

Char Washing Procedure	Description
A	A two-gram portion of each char sample was added to 100 mls. of 0.6N hydrochloric acid and heated, at the boiling point, for one hour. The samples were then filtered and washed with distilled water. This procedure was repeated two more times with fresh hydrochloric acid solution. After washing with hot distilled water, the samples were dried for three hours at 150°C. Finally, one gram of each sample was ashed at 700-750°C for two hours.
B	The same washing procedure as employed in A, except that the hydrochloric acid washing was followed by two washings using 0.6N nitric acid.
C	A three gram portion of sample was added to 100 mls. of 2N hydrochloric acid and heated, at the boiling point, for 0.5 hours. The samples were then filtered and washed with distilled water. This procedure was repeated two more times, and then two more times with 2N nitric acid. The samples were subsequently boiled in distilled water for two hours, filtered, and dried overnight at 150°C. Ashing was then carried out overnight at 700-750°C.
D	A two-gram portion of the sample prepared in C above was boiled in concentrated hydrochloric acid (12N) for one hour. After being filtered, it was boiled three more times in fresh distilled water. Finally, it was filtered, dried overnight at 150°C and ashed overnight at 700-750°C.
E	In a procedure similar to that described in D, the samples were washed in concentrated nitric acid.

Table 2.3 Procedures Employed in the Char Leaching Experiments

Char Number	Company	Description	Approximate Surface Area m^2/gram.	Base Material
1	Barneby-Cheney	BC 417	50-100	Anthracite
2	Calgon	PXC 12x30	287	Coconut
3	Barneby-Cheney	PC	650	Coconut
4	Barneby-Cheney	155	1000-1000	Coconut
5	Barneby-Cheney	GI	1600-1650	Coconut

Table 2.4 Description of the Chars employed in the Char Leaching Experiments

	Type of Char				
Washing Procedure	1	2	3	4	5
Unwashed	11.54	1.75	19.30	3.81	2.37
A	6.69	0.50	12.91	0.43	0.02
B	6.96	4.06	10.74	0.48	0.01
C	8.00	0.82	11.57	2.26	0.08
D	-	-	14.33	-	-
E	-	-	13.70	-	-

Note: All analyses on a weight percent basis.

Table 2.5 Ash Analyses of the Leached Char Samples

	Concentration of Assumed Mineral Form -- Weight %									
Char Number	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	Mn_3O_4	CuO	BaO	Total as Metal oxides	Ash
1	3.9	1.8	0.17	0.13	0.20	0.014	0.007	0.01	6.2	11.54
2	0.30	0.19	0.017	0.067	0.027	0.014	0.002	-	0.62	1.75
3	7.7	4.3	0.38	0.68	0.30	0.04	0.0045	0.01	13.4	19.30
4	0.51	0.025	0.003	0.028	0.088	0.014	0.002	-	0.67	3.81
5	0.28	0.006	-	0.006	0.075	0.014	0.004	-	0.38	2.37

Table 2.6 Atomic Emission Spectra Results for the Unleached Char Samples

significant fraction of the minerals in char are present as oxides of aluminum or silicon, neither of which react with hydrogen sulfide to any appreciable extent. Unfortunately, there is little agreement between the measured ash content of the chars, and the concentration of metal oxides in the char which is computed from the spectral analyses. Hence, one cannot draw any conclusions on the basis of these results.

Because all the washing procedures tested removed roughly the same concentrations of ash from the char samples, a slightly modified version of washing procedure A (see Table 2.3) was adopted as standard procedure in this investigation (see Section 2.2.1). Subsequent analyses revealed that this procedure was effective in eliminating all of the sulfides and sulfate sulfur from the chars prior to exposure to hydrogen sulfide. With two notable exceptions (HYDRANE HY-138 lignite char and HYDRANE HY-140 sub-bituminous char), the standardized procedure also prevented the formation of sulfide sulfur in char after exposure to hydrogen sulfide. These exceptions will be discussed in greater detail in Section 6.1.2

One other fact is worth mentioning in connection with the standardized washing procedure. Robinson(104) noted that his chars, after washing with dilute hydrochloric acid, were " ... washed free from chloride ion as determined by precipitation with silver nitrate ... ". However, in spite of numerous (five) washings of the char with distilled water in the standardized washing procedure, the formation of a precipitate was always noted upon addition of silver nitrate. In other words, the washing procedures employed did not completely rid the samples of chloride ion contamination.

2.4.2 Experiments to Test the Performance of the Horizontal Tube Furnace

2.4.2.1 Measurement of the Axial Temperature Profile

At steady-state, the temperature distribution within a tube furnace is generally a strong function of the axial position within the furnace. Hence, several experiments were performed in which the axial temperatures within the four tube furnace sections were measured. In these experiments, helium was passed through the tube furnace at three scfh, and the axial temperature profile was measured using a thermocouple. These experiments revealed that the axial temperature profile was only uniform (± 10°C) for a small section near the center of each furnace section. Towards each end of the furnace sections, the temperature was 200-300°C lower than that measured at the center of the furnace section. In all subsequent experiments using the horizontal tube furnace, the sample holder was positioned at the point in the furnace where the axial temperature profile was most uniform.

2.4.2.2 Experiments using Ceramic Sample Holders

In an attempt to increase the rate of data acquisition, a set of ceramic holders was machined. These sample holders, which look much like a revolver cylinder, were designed to accommodate six samples simultaneously. Six char samples were loaded, like cartridges, into the cylinder. The samples were prevented from spilling by inserting quartz wool plugs into the end of each cylinder chamber. Unfortunately, it soon became apparent that, because of pressure drop considerations (and, hence, bypassing of the solid by the gas), the use of the ceramic sample holders was impractical. Experiments with these sample holders were therefore abandoned.

2.4.2.3 Experiments to Establish whether or not the Extent of Char Sulfidation is a Function of Time

By definition, equilibrium sulfidation studies require that the extent of sulfidation be independent of the time of exposure of the char to hydrogen sulfide. In order to establish whether or not this requirement is satisfied in the horizontal tube furnace, a set of char sulfidation experiments was conducted. In these experiments, sample boats and lids were employed.* A graphical description and the results of these experiments are presented in Table 2.7. Inspection of the data reveals that the concentration of organic sulfur in the char is a function of (a) the time of exposure of the char to hydrogen sulfide, and (b) the position of the sample within the furnace tube. In addition, the tube Reynolds Number is very low (i.e., approximately 5) at the experimental conditions in question. Hence, the above results suggest that the extent of char sulfidation in the horizontal tube furnace is gas-phase diffusion controlled.

The latter conclusion, as well as the highly non-uniform axial temperature distribution within the furnace, suggested that the horizontal tube furnace was not well suited for use in this experimental program. All experiments using this equipment were therefore abandoned, and the fluid-bed apparatus was constructed as a replacement.

2.4.3 Experiments to Test the Performance of the Fluid-Bed Apparatus.

Preliminary measurements in the vertical tube furnace revealed that, as was the case with the horizontal tube furnace, the axial temperature profile within the vertical tube furnace is highly non-uniform. A transite

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*Notice that this apparatus is similar to the apparatus employed by Powell (79).

Experiment #	X Hours	Weight of Sample in Lid milligrams	Weight of Sample in Boat milligrams	Total Sulfur Concentration - wt%			
				Lid Posn.1	Lid Posn.2	Lid Posn.3	Boat Posn.4
A	2	170	650	0.91	0.83	0.75	0.68
B	4	85	-	1.21	1.08 1.06	-	-

Note: (1) Lid Dimensions; 1.0 cm.x 7.5 cm.
(2) Boat Dimensions; 1.1 cm. x 5 cm.
(3) Filter Paper char prepared by charring at 900°C for 2 hours in 3 SCFH Helium.
(4) Experimental History:

START $\xrightarrow[\text{3SCFH; 5.17\% } H_2S \text{ in Hydrogen}]{1800^\circ F;\ X \text{ Hours}}$ ANALYSIS

(5) Schematic Diagram of the Horizontal Tube Furnace:

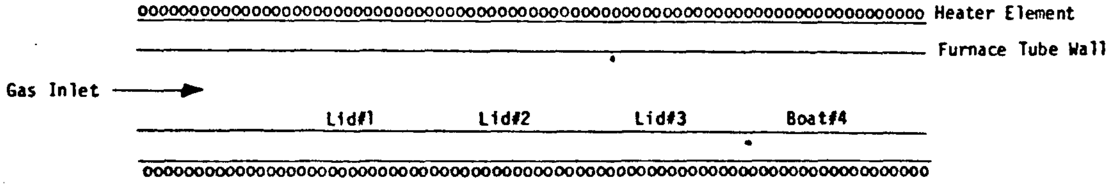

Table 2.7 Results of Experiments to Determine whether or not Char Sulfidation in the Horizontal Tube Furnace is Diffusion-Controlled

base was therefore used to seal the bottom of the furnace. In addition, the top of the furnace was sealed with FIBERFRAX. Both of these modifications resulted in a more uniform axial temperature profile within the tube furnace.

2.4.3.1 Accuracy of the Fluid-Bed Temperature Measurement

To establish whether or not the shielded thermocouple installed on the wall of the quartz furnace tube, external to the fluid bed, provides a reliable measurement of the fluid bed temperature, a shielded thermocouple was introduced into the fluid bed. The furnace was brought up to temperature (1600°F) and, with 0.5 scfh of helium passing through the bed, the temperatures on both thermocouples were measured. These temperatures proved to be identical. Hence, it is concluded that the thermocouple installed on the wall of the quartz furnace tube, external to the fluid bed, provides a reliable measurement of the temperature of the fluid bed. In all subsequent experiments the temperature of the fluid bed was measured using this thermocouple.

2.4.3.2 Measurement of the Time Constants Associated with the Fluid-Bed Apparatus

It is conceivable that, for a variety of reasons (eg., kinetic controls or mass transfer limitations) an equilibrium distribution of sulfur between the char and gas phases is never realized in the fluid-bed apparatus (or, rather, is only realized very slowly). In order to test this hypothesis, a series of char sulfidation experiments was performed, in which various char samples (i.e., HYDRANE-138 lignite char, filter paper chars and coconut-based activated charcoal) were exposed to a mixture of hydrogen sulfide in hydrogen ($100P_{H_2S}/P_{H_2} = 5.45$) for times ranging from

10 minutes to 32 hours at 1600°F. The results of these experiments are presented in Table D.1 as well as in Figure 2.9.

Note that the concentration of organic sulfur in char is not a function of the time of exposure of the char to hydrogen sulfide. Hence, it is concluded that, at 1600°F, the time constants associated with mass transfer in the fluid-bed apparatus are smaller than ten minutes.

A second characteristic time is the time required, after insertion of the quartz furnace tube into the preheated tube furnace, for the temperature of the fluid bed to reach a final steady-state value. Experiments to provide an estimate of this characteristic time were performed by continuously monitoring the temperature of the measurement thermocouple as a function of time. The experiments revealed this time constant to be of the order of 6 minutes.

Some experiments which have been performed require the temperature of the fluid bed to be decreased during the course of an experiment (e.g., from 1832°F to 1400°F). This, in turn, requires that the temperature of the tube furnace be decreased. Ideally, one would prefer to change the latter temperature instantaneously. However, because of the heat capacity of the furnace, and the finite rate of heat transfer from the tube furnace, there is a characteristic time associated with such a change in temperature. A set of experiments was performed to estimate the time required to affect such a change in the furnace temperature. This time was estimated to be approximately 40 minutes. However, when an air jet was introduced via a stainless steel tube into the bottom of the tube furnace, this time was

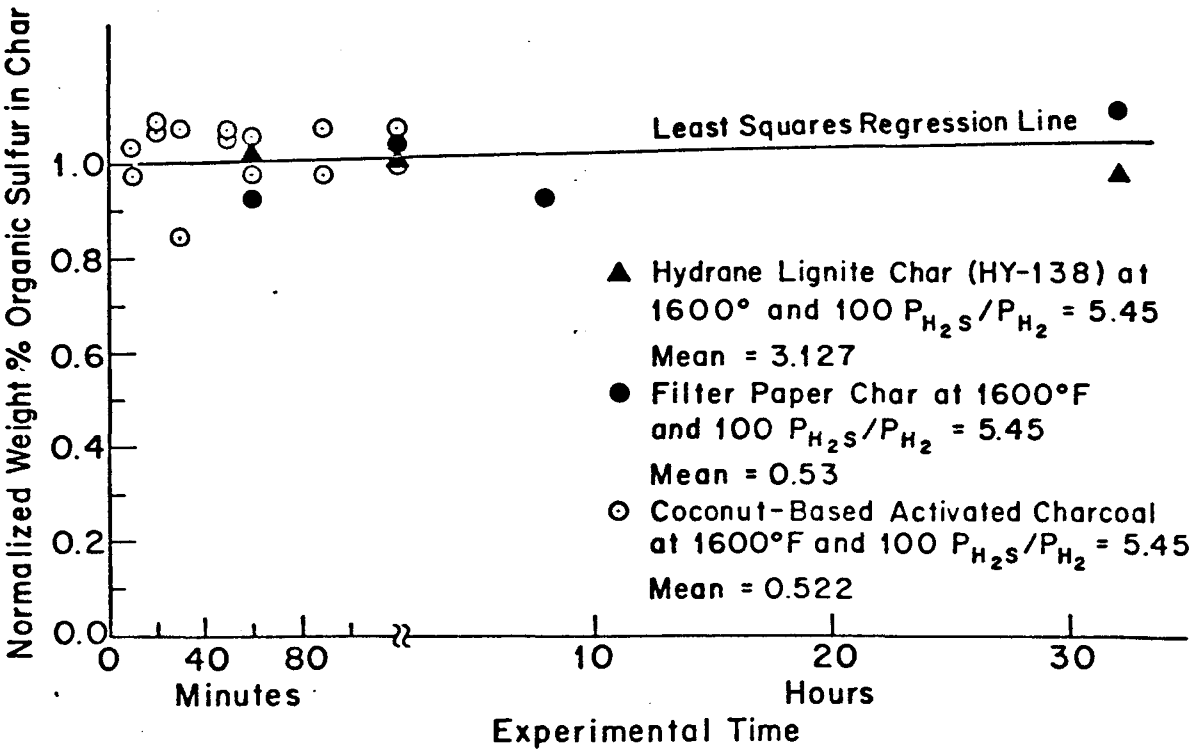

Figure 2.9 Results of Experiments to Establish whether or not the Concentration of Organic Sulfur in Char is a Function of Experimental Time

reduced to approximately 10 minutes. For those experiments in which a rapid decrease in the fluid bed temperature was required, the air jet approach was employed.

The magnitudes of the three characteristic times mentioned above are important because they limit the range of experimental variables which can be explored using the fluid-bed apparatus. For example, the temperature of the tube furnace cannot be reduced from 1632°F to 1200°F in less than say 10 minutes. Perhaps more importantly, the exposure time of the char to hydrogen sulfide should not be less than 10 minutes. The magnitudes of these time constants were taken into account in the design of the fluid-bed experiments mentioned in this thesis.

2.4.3.3 Experiments to Determine Whether or not the Method of Experimental Termination Affects the Experimental Results

Each fluid-bed experiment is terminated by:

1. Switching off the flowrate of the hydrogen sulfide/hydrogen mixture.
2. Passing 0.5 scfh of helium through the fluid-bed for approximately two minutes.
3. Extracting the quartz furnace tube from the tube furnace, and allowing it to cool to ambient temperature, while admitting just enough helium to compensate for the reduction in the gas volume within the tube.
4. Extracting the char sample from the furnace tube and storing it in a tightly-stoppered glass sample bottle in a desiccator.

This method of terminating an experiment could influence its outcome (i.e., it is possible that the helium passing over the char affects a redistribution of sulfur between the char and gas phases in some unknown manner). In order to test this hypothesis, several experiments were performed in which helium, as well as small concentrations of hydrogen in helium were passed through the fluid-bed for five, ten and twenty minutes. The results of these experiments are presented in Table 2.8.

Notice that the concentration of organic sulfur in char is not a function of the length of time for which helium or mixtures of hydrogen in helium are passed over the char. It is concluded that, at 1400°F, the method of experimental termination which has been chosen does not affect the experimental results.

Table 2.8 Results of Experiments to Establish whether or not the Method of Experimental Termination affects the Experimental Results

	Specified				Actual			MF Basis		MAF Basis		MASF Basis		
Expt.#	$\frac{\text{Scf } H_2}{\text{Lb.Char}}$	X% H_2	%He	t min	Sample Collected grams	$\frac{\text{Scfh } H_2}{\text{Hr.}}$	t min	Organic Sulfur %	Ash %	$\frac{\text{Scf } H_2}{\text{LB.MAF Char}}$	Organic Sulfur %	$\frac{\text{Scf } H_2}{\text{Lb.MASF Char}}$	Organic Sulfur (a)	Mean Organic (b)
176	Blank	-	-	-	4.257	0	0	0.895	11.40	0	1.010	0	1.020	1.020
177	Blank	-	-	-	4.235	0	0	0.930	10.56	0	1.040	0	1.051	
178	0	1	99'	5	4.355	0.005	5.0	0.925	10.91	0	1.038	0	1.049	
179	0	0	100	5	4.317	0	5.0	0.920	10.90	0	1.033	0	1.044	
180	0	1	99	10	4.335	0.005	10.0	0.920	9.98	0	1.022	0	1.033	
181	0	0	100	10	4.196	0	10.0	0.850	11.17	0	0.957	0	0.966	
182	0	1	99	20	4.335	0.005	20.0	0.905	10.59	0	1.012	0	1.022	
183	0	0	100	20	4.334	0	20.0	0.865	10.63	0	0.968	0	0.977	

Note: (a) Grams of organic sulfur per 100 grams of moisture, ash and organic sulfur-free char.

(b) This mean value - i.e. 1.020 - is employed in Table to normalize the organic sulfur concentrations.

(c) The sulfide sulfur concentration in the acid-washed HYDRANE [HY-128] Bituminous coal char is negligible

(d) Experimental History:

START $\xrightarrow[\text{0.5 SCFH; He}]{900^{\circ}\text{C; 1 Hour}}$ $\xrightarrow[\text{0.5 SCFH; He}]{1400^{\circ}\text{F; 1 Hour}}$ $\xrightarrow[\text{1 SCFH; 7.76\% } H_2S \text{ in } H_2]{1400^{\circ}\text{F; 1 Hour}}$ BLANK $\xrightarrow[\text{1 SCFH; X\% } H_2 \text{ in Helium}]{1400^{\circ}\text{F; t Minutes}}$ ANALYSIS

(e) Five grams of char sample loaded at the start of each experiment.

CHAPTER THREE

THE EQUILIBRIUM DISTRIBUTION OF SULFUR BETWEEN ORGANIC SULFUR IN CHAR AND HYDROGEN SULFIDE IN THE GAS PHASE

As was noted in the literature review, uncertainty surrounds the factors which govern the equilibrium distribution of sulfur between organic sulfur in char and hydrogen sulfide in the gas phase. The results of experiments conducted to resolve this uncertainty are presented in this chapter.

3.1 Experiments to Determine whether or not the Concentration of Organic Sulfur in Char is a Function of the Partial Pressure of Hydrogen Sulfide

Several authors(84,52,57) have implied that the equilibrium concentration of organic sulfur in char is not a function of the partial pressure of hydrogen sulfide (P_{H_2S}); rather, it appears to be a function of the partial pressure ratio (P_{H_2S}/P_{H_2}). Since this distinction has important process and theoretical implications, and because it has not been experimentally verified, a set of char sulfidation experiments was performed in which the ratio $100P_{H_2S}/P_{H_2}$ was held constant at 5.45, while the sum of the partial pressures of hydrogen and hydrogen sulfide was varied through addition of helium to the feedgas. Results of these experiments are presented in Table D.2 and Figure 3.1.

Notice (see Figure 3.1) that, for hydrogen sulfide partial pressures ranging from 0.0545 to 0.002725 atmospheres*, there is no noticeable variation

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*Note that, since $100P_{H_2S}/P_{H_2} = 5.45$, a direct proportionality exists between the sum of the partial pressures of hydrogen and hydrogen sulfide, and the partial pressure of hydrogen sulfide.

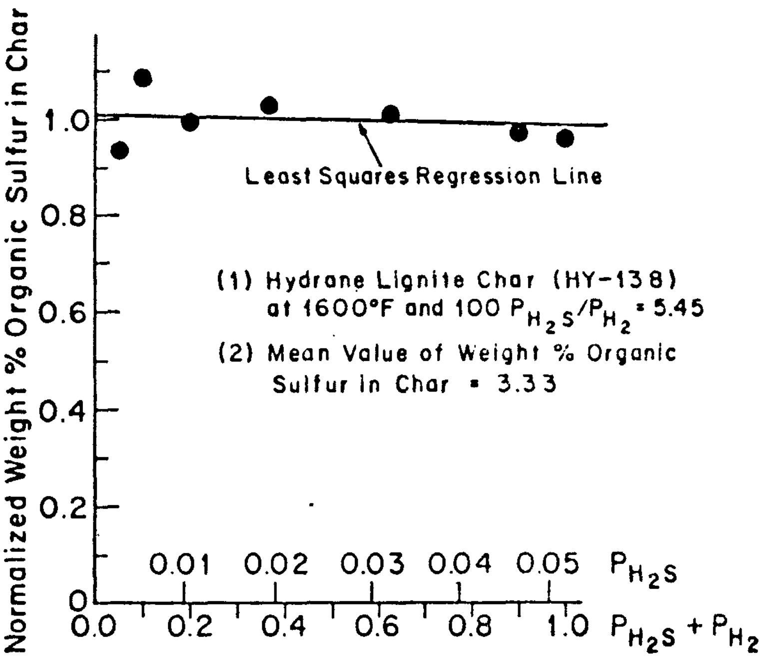

Figure 3.1 Results of Experiments to Establish whether or not the Concentration of Organic Sulfur in Char is a Function of the Partial Pressure of Hydrogen Sulfide

in the concentration of organic sulfur in char. These results suggest that the partial pressure ratio (P_{H_2S}/P_{H_2}) rather than the partial pressure of hydrogen sulfide is the parameter which governs the equilibrium concentration of organic sulfur in char. This will be further substantiated by results presented in Section 3.3.

3.2 Testing Kor's Langmuir Isotherm Char Sulfidation Model

Assuming that the ideal Langmuir Isotherm can be used to describe the adsorption of sulfur in char, Kor(57) developed the following expression;

$$(P_{H_2S}/P_{H_2})/S = 1.87A/S_a[1/B + (P_{H_2S}/P_{H_2})] \qquad [3.1]$$

to describe the equilibrium concentration of organic sulfur in char, where:

P_{H_2S} = partial pressure of hydrogen sulfide; atm

P_{H_2} = partial pressure of hydrogen; atm

S = concentration of organic sulfur in char; wt.%

S_a = surface area of char; m^2/g

A = area per adsorbed sulfur atom; square Angstroms

and B is a dimensionless temperature-dependent parameter. Rearranging equation [3.1] yields:

$$S_a/S = \frac{1.87A[1/B + (P_{H_2S}/P_{H_2})]}{(P_{H_2S}/P_{H_2})} \qquad [3.2]$$

Notice that the right hand side of equation [3.2] is a function of temperature and the partial pressure ratio (P_{H_2S}/P_{H_2}). If (a) Kor's application of the Langmuir Isotherm to char sulfidation data is valid, and (b) the partial pressure ratio and temperature are held constant, the right hand side of [3.2] is constant -- i.e.,

$$S = k_a S_a \qquad [3.3]$$

where k_a is a constant defined by equation [3.2].

3.2.1 Effect of Surface Area upon the Equilibrium Concentration of Organic Sulfur in Char

To establish whether or not equation [3.3] is obeyed, a set of char sulfidation experiments was performed in which the partial pressure ratio (P_{H_2S}/P_{H_2}) and the sulfidation temperature were held constant. At the end of these experiments, the surface areas of the product chars were measured using two methods -- i.e., the nitrogen/BET method at 77°K and the carbon dioxide/Dubinin-Polanyi method at 298°K.* The results of these experiments are presented in Table D.3.

A few words as to why two methods of measuring char surface area were employed are justified at this stage. Use of the nitrogen/BET method at 77°K is widespread, and was in fact employed by Kor(57). However, both Walker and Kini(122) and Marsh and Siemieniewska(64) have concluded that, for molecular sieve-type materials such as coal chars (in which a significant fraction of the total surface area is contained in micropores, the size of which is approximately the same as the adsorbate molecule), carbon dioxide at 298°K provides a more reliable estimate of char surface area than does nitrogen at 77°K. To eliminate any ambiguity

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*In order to calculate the surface area of a char by these two methods, the cross-sectional areas of the nitrogen and carbon dioxide molecules must be known. From the data presented by Walker and Kini(122), these cross-sectional areas were assumed to be 16.2 and 25.3 square Angstroms respectively.

in the interpretation of the data, char surface area was measured using both of the methods mentioned.

The concentration of organic sulfur in char, as a function of char surface area is presented in Figure 3.2. Notice that, if a relationship exists, it is certainly not linear, with an intercept at the origin of the co-ordinates-- i.e., the relationship does not obey equation [3.3]. These results undermine Kor's(57) conclusion that " ... surface area is an important parameter in determining whether or not a given char is able to retain significant quantities of sulfur".

The area-per-adsorbed-atom was estimated from the data presented in Table D.3. The estimated values are presented in Table 3.1. If these values were much lower than those which correspond to monolayer surface coverage one might be led to believe that organic sulfur in char is either the result of a reaction of sulfur species with the char surface or physical adsorption (which permits multilayer surface coverage) rather than chemisorption. However, these estimated values are consistent with or higher than those which correspond to monolayer surface coverage.* Hence, one cannot exclude the possibility that organic sulfur in char is the result of chemisorption of sulfur species in the char.

3.2.2 The Active Site Hypothesis

It seems reasonable to suppose that equation [3.3] is not satisfied because the formation of organic sulfur in char is the result of the chemisorption (rather than physical adsorption) of sulfur species at

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*The values of the area-per-adsorbed-atom presented in Table 3.1 (using the more accurate CO_2/Dubinin-Polanyi Method at 298°K) range between 38 and 227 square Angstroms per atom. This range is consistent with, or higher than the 10-50 square Angstroms per atom mentioned by Hayward and Trapnell(40).

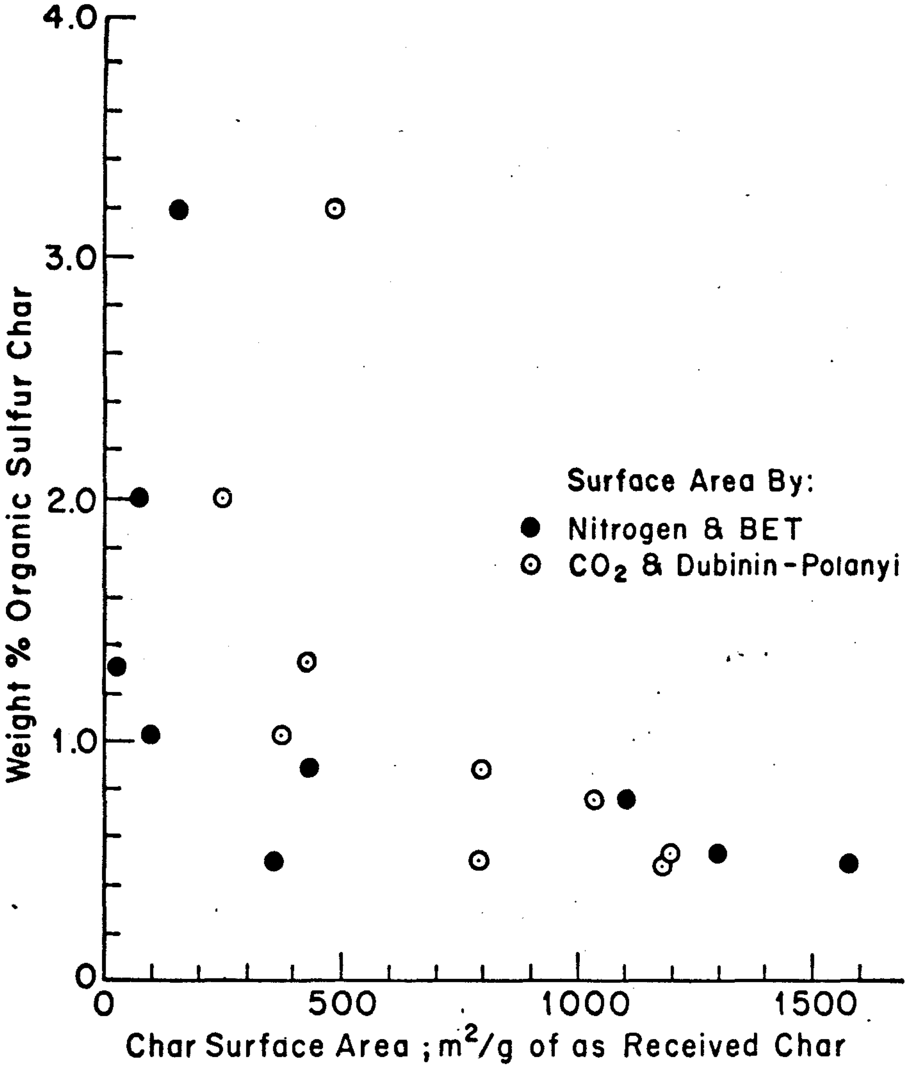

Figure 3.2 Equilibrium Concentration of Organic Sulfur in Char at 1600°F and $100P_{H_2S}/P_{H_2} = 5.45$ versus Char Surface Area

Char Description	Organic Sulfur Content[a]	Surface Area[b] m^2/g.	Surface Area[c] m^2/g.	Area per Adsorbed Atom[d]	Area per Adsorbed Atom[e]
Lignite [HY-138]	6.8	200.3	615	15.7	48.1
Subbituminous [HY-140]	4.2	99.6	298	12.6	37.7
Bituminous [HY-128]	2.5	21.4	498	4.6	105.8
Anthracite-based Activated Charcoal	3.4	110.3	419	17.3	65.5
Filter Paper Char	1.9	370	811	103.5	226.7

Note (a) Grams sulfur per 100 grams MASF Char at 1600°F and $100P_{H_2S}/P_{H_2} = 100$.

(b) Surface Area, by Nitrogen and the B.E.T. Equation, m^2 per gram of MASF char

(c) Surface Area, by CO_2 and the Dubinin-Polyani Equation, m^2 per gram of MASF char

(d) Area per adsorbed sulfur atom, estimated from (a) and (b), A^{o2}

(e) Area per adsorbed sulfur atom, estimated from (a) and (c), A^{o2}

Table 3.1 Calculated Area per Adsorbed Sulfur Atom for Various Chars active sites on the char surface. In other words, it is suggested that the "concentration" of active sites in char, rather than char surface area, governs the extent of char sulfidation. In addition, this hypothesis, hereafter referred to as the *active site hypothesis*, implies that the extent of char sulfidation can be described by one of several ideal adsorption isotherms in the literature. The search for an adequate model to describe char sulfidation data is described below.

3.2.3 Presentation of Filter Paper Char Sulfidation Data according to the Requirements of Various Isotherms

Kor(57) performed several filter paper char sulfidation experiments at 600 and 900°C. In his experiments, the value of the partial pressure ratio ($100P_{H_2S}/P_{H_2}$) ranged from approximately 50 to 6000. However, the range of greatest practical interest extends from approximately 0.1 to 5. In other words, the range in the partial pressure ratio of interest lies well below the range investigated by Kor. In addition, as was mentioned previously, Kor employed an ideal Langmuir Isotherm to describe his sulfidation data. Several other isotherms (Freundlich, Temkin) have also been developed. The assumptions required in the development of these ideal models are outlined in Appendix A. To establish which (if any) of the above mentioned isotherms adequately models char sulfidation data in the partial pressure ratio range of interest, several filter paper char sulfidation experiments were performed at 1600°F. The results of these experiments are presented in Table D.4.

The experimental data are presented according to the requirements of a Langmuir Isotherm (see equation [A.9], Appendix A) in Figure 3.3. Notice that, while the Langmuir Isotherm seems to be a reasonable model of the experimental data for values of the partial pressure ratio

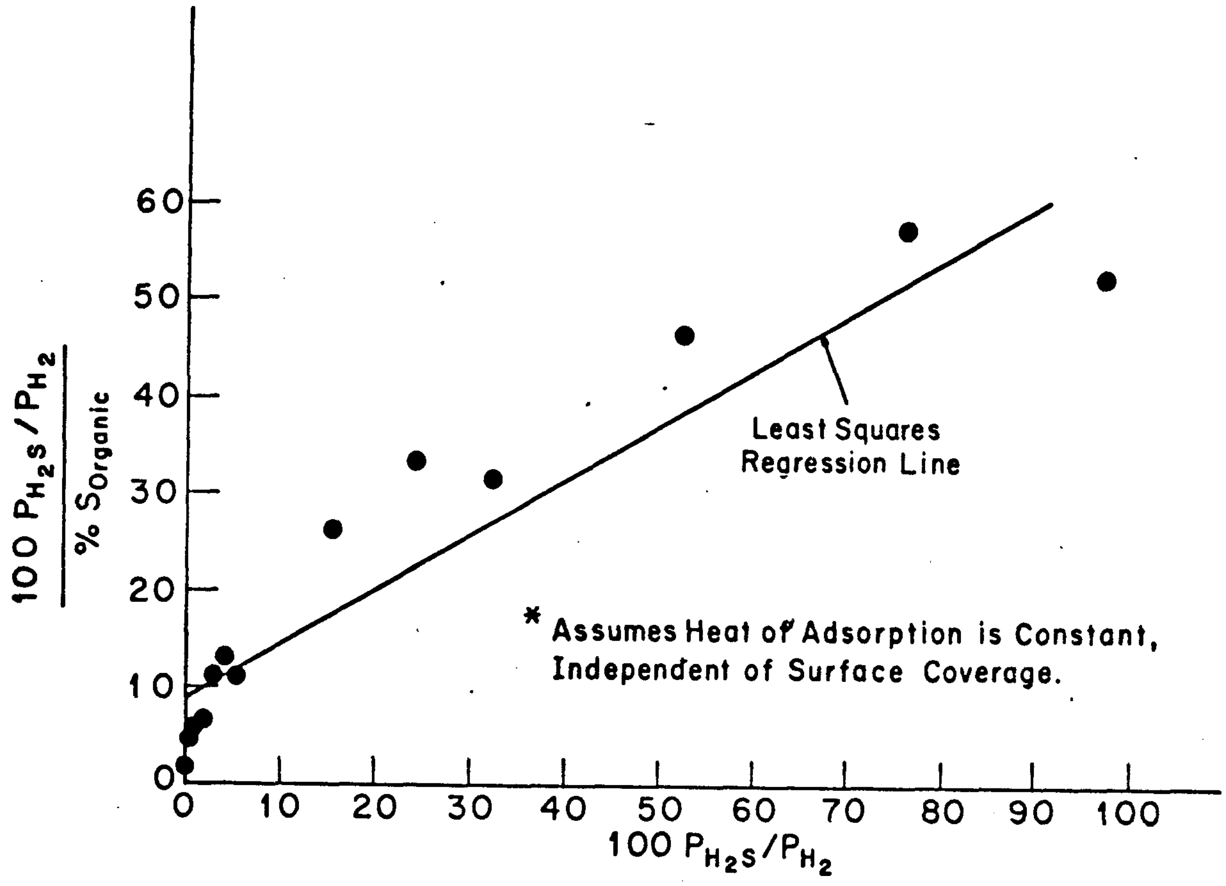

Figure 3.3 Presentation of Filter Paper Char Sulfidation Data at 1600°F according to a Langmuir Isotherm

($100P_{H_2S}/P_{H_2}$) from 5 to 70, appreciable deviation from the least squares regression line occurs at both ends of the range considered. This deviation is particularly noticeable for low values of the partial pressure ratio -- i.e., the range of practical interest. Thus, it is concluded that the Langmuir Isotherm is not an adequate description of char sulfidation data.

The experimental data are presented according to the requirements of a Temkin Isotherm (see equation [A.10] in Appendix A) in Figure 3.4. Notice that, once again, considerable deviation occurs at both extremes of the range in the partial pressure ratio which was investigated.

Powell(84) conducted several sugar char sulfidation experiments at 800°C. His data are presented in Table D.5.* Kor's(57) filter paper char sulfidation data at 600 and 800°C are presented in Table D.6.* The filter paper char sulfidation data presented in Table D.4, as well as Powell's and Kor's data, are presented according to the requirements of a Freundlich Isotherm (see equation [A.13], Appendix A) in Figure 3.5. Notice that:

1. The filter paper char data are accurately represented by a linear regression line for three orders of magnitude variation in the parameter $100P_{H_2S}/P_{H_2}$ -- i.e., from 0.1 to 100.
2. The filter paper char sulfidation data are in reasonable agreement with Kor's filter paper char sulfidation data.
3. There is a noticeable difference between both sets of filter paper char sulfidation data and Powell's sugar char sulfidation data.

Of the three models examined, the Freundlich Isotherm is clearly the best

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*Since tabulated data were not presented, these data were obtained from the graphs presented by Powell and Kor.

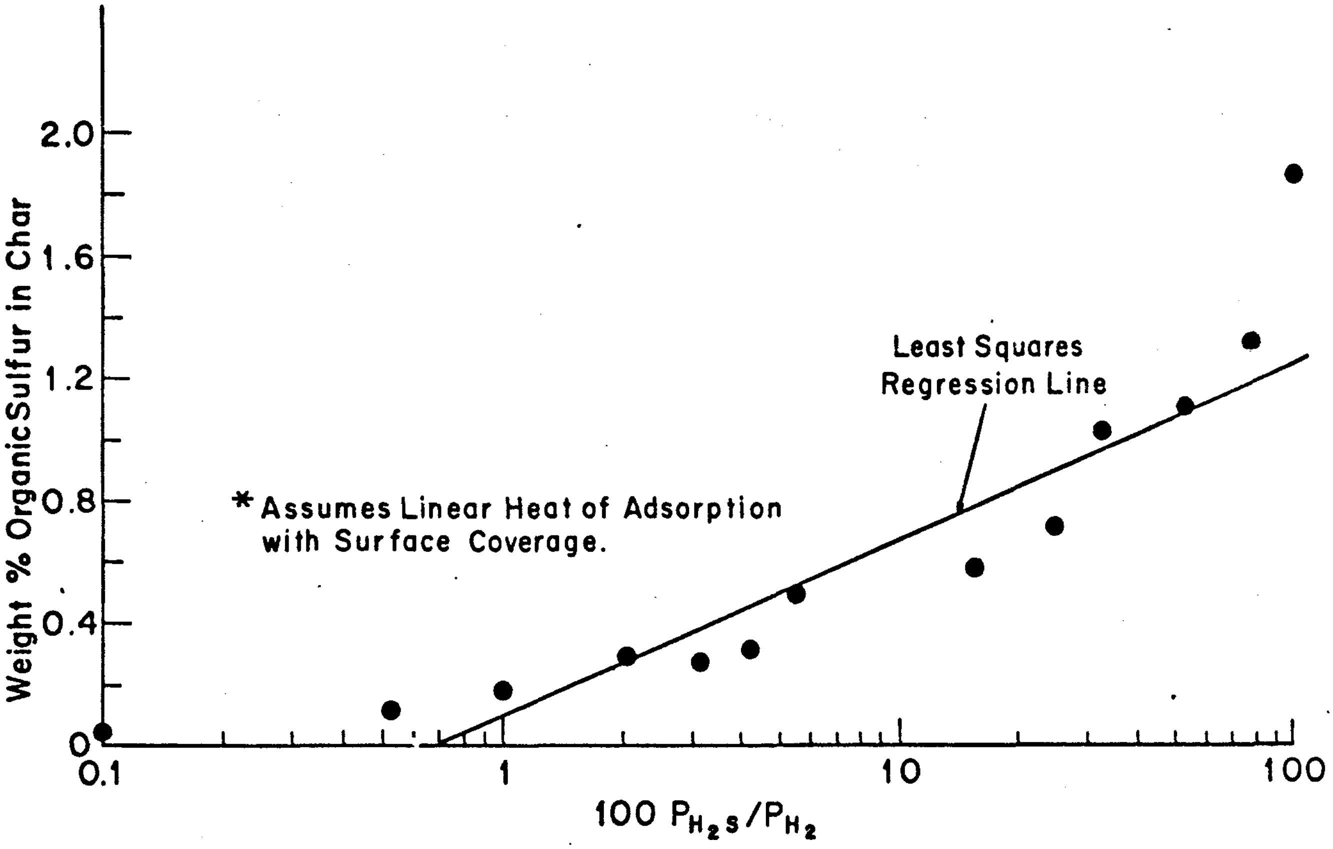

Figure 3.4 Presentation of Filter Paper Char Sulfidation Data at 1600°F according to a Temkin Isotherm

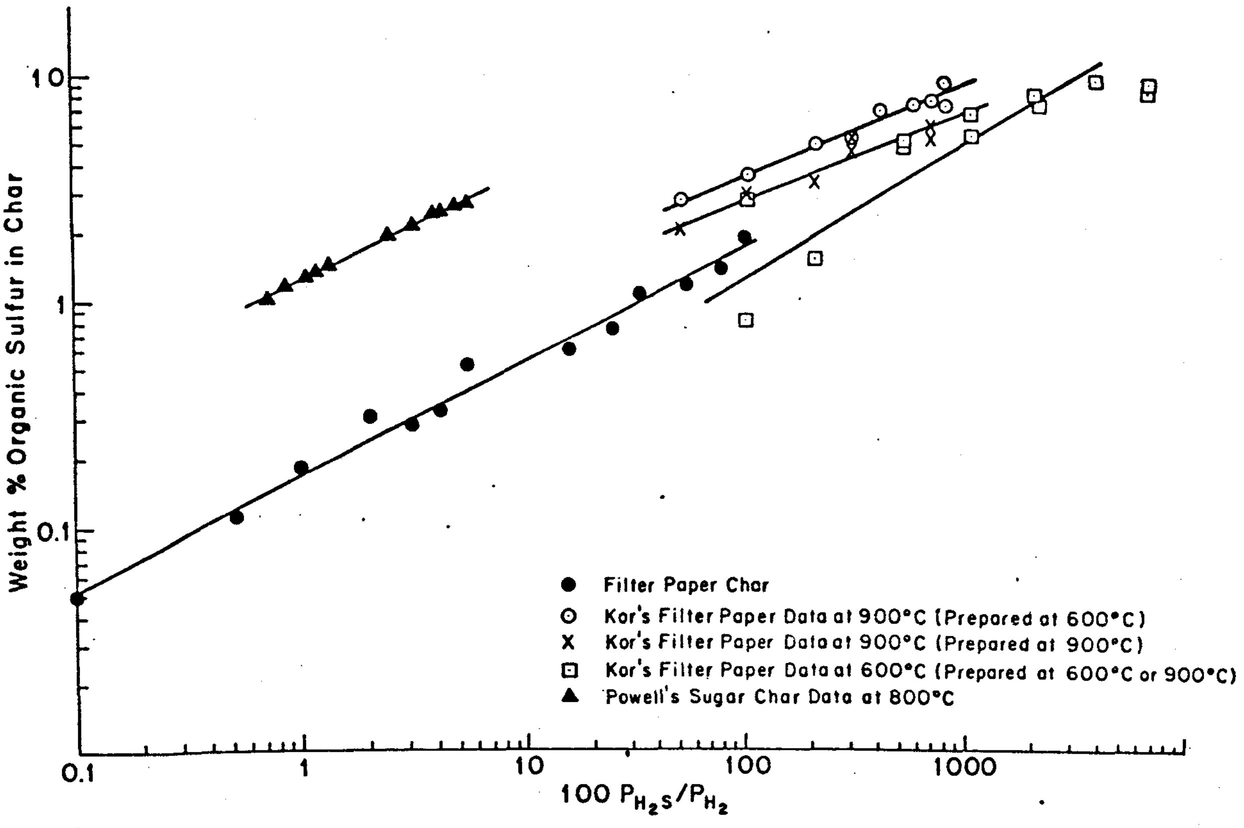

Figure 3.5 Presentation of Filter Paper Char Sulfidation Data at 1600°F according to a Freundlich Isotherm

model with which to describe char sulfidation data. In the development of the Freundlich Isotherm, it is assumed that the heat of adsorption falls logarithmically with increased coverage of active sites in the adsorbent. Further, in the words of Hayward and Trapnell(40): " ... this heat fall is due to surface heterogeneity". Since surface heterogeneity is entirely consistent with the active site hypothesis, the success with which the Freundlich Isotherm describes char sulfidation lends credence to the active site hypothesis.

The noticeable difference between the equilibrium concentration of organic sulfur in the two types of char studied (filter paper and sugar char) suggests that the type of char exerts a profound influence upon the adsorption isotherm. This prompted the investigation which is described below.

3.3 A Parametric Investigation of the Effects of Temperature and the Nature of the Parent Coal upon the Sulfur Adsorption Characteristics of Char

Batchelor's(9) Arkwright Char desulfurization data at 1350 and 1600°F are presented in Figure 3.6 and Table D.7. Note that his data suggest that the concentration of organic sulfur in char *decreases* as temperature *increases*. On the other hand, Kor's filter paper char sulfidation data (see Figure 3.5) lead one to exactly the opposite conclusion.

To resolve this apparent inconsistency in the literature, as well as to establish the effect of the type of char upon the adsorption isotherm, an investigation of the effects of these two parameters upon the adsorption isotherm was conducted. In this investigation five chars of various rank (see Section 2.3) were subjected (in the fluid-bed apparatus) to the experimental history shown below.

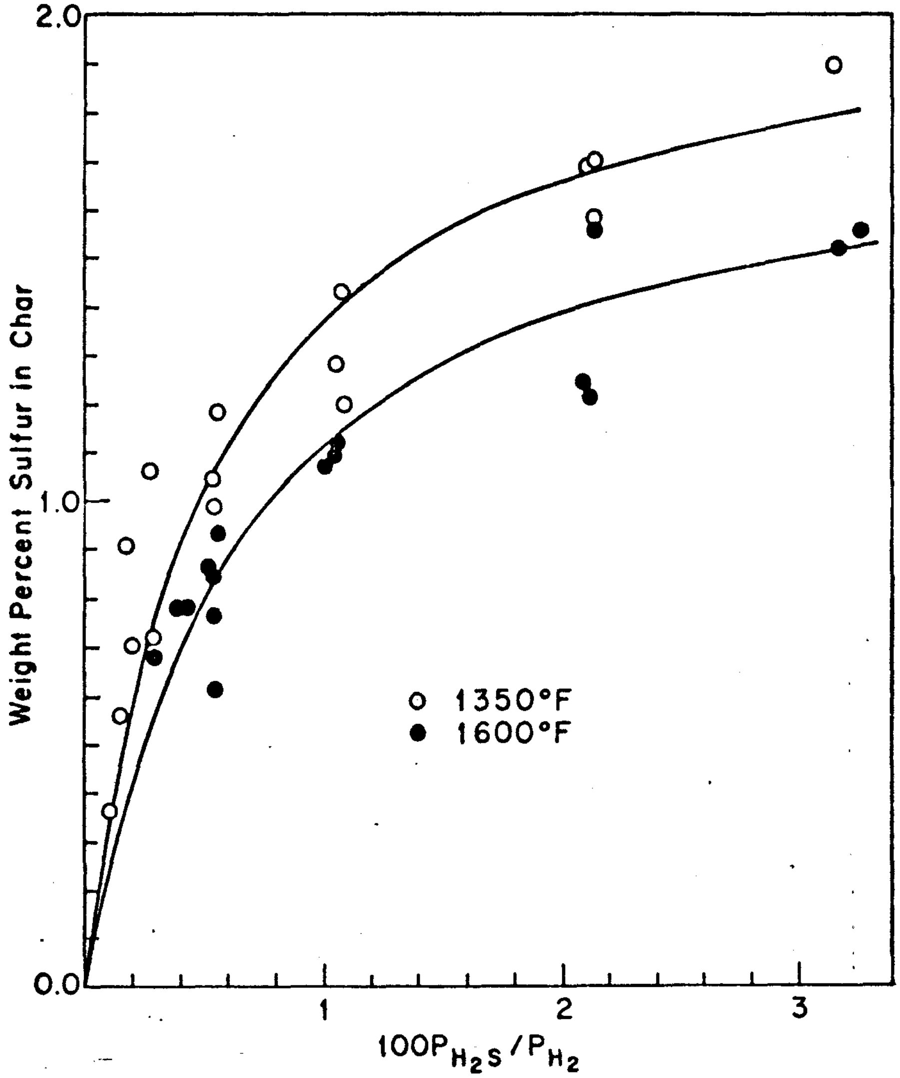

Figure 3.6. Batchelor's(9) 1350 and 1600°F Char Sulfidation Data

START $\dfrac{900^{o}\text{C; 1 Hour}}{\text{0.5 scfh He}}$ $\dfrac{T^{o}\text{F; 1 Hour}}{\text{0.5 scfh He}}$ $\dfrac{T^{o}\text{F; 1 Hour; 1 scfh}}{100P_{H_2S}/P_{H_2}=E}$ ANALYSIS

In the above history diagram, T is either 1200, 1400 or 1600^{o}F, while E ranges from 0.1 to 100. Notice that there are three independent vaiables in this experimental investigation -- i.e., sulfidation temperature (T), the partial pressure ratio (P_{H_2S}/P_{H_2}) and the source of the char. In addition, it should be noted that the pretreatment temperature (900^{o}C) was held constant in this investigation. In other words, *the effect of pretreatment temperature upon the adsorption isotherm was not studied in this investigation.* This must be borne in mind when discussing the results of this investigation, which are presented in Tables D.8, D.9, D.10, D.11 and D.12. These results are discussed below.

3.3.1 Effect of Rank of the Parent Coal

The effect of rank of the parent coal upon the adsorption isotherm at 1600°F is examined in Figure 3.7. Notice that the concentration of organic sulfur in char varies with rank of the parent coal in the following order:

Lignite Char > Sub-bituminous Char > Bituminous Char > Anthracite Char > Filter Paper Char

In other words, the equilibrium concentration of organic sulfur in char *decreases* with increasing rank of the parent coal.

3.3.2 Effect of Temperature

The effect of temperature upon the adsorption isotherm is examined in Figure 3.8 Notice that the concentration of organic sulfur in char *increases* with *increasing* temperature. Hence, these results are consistent

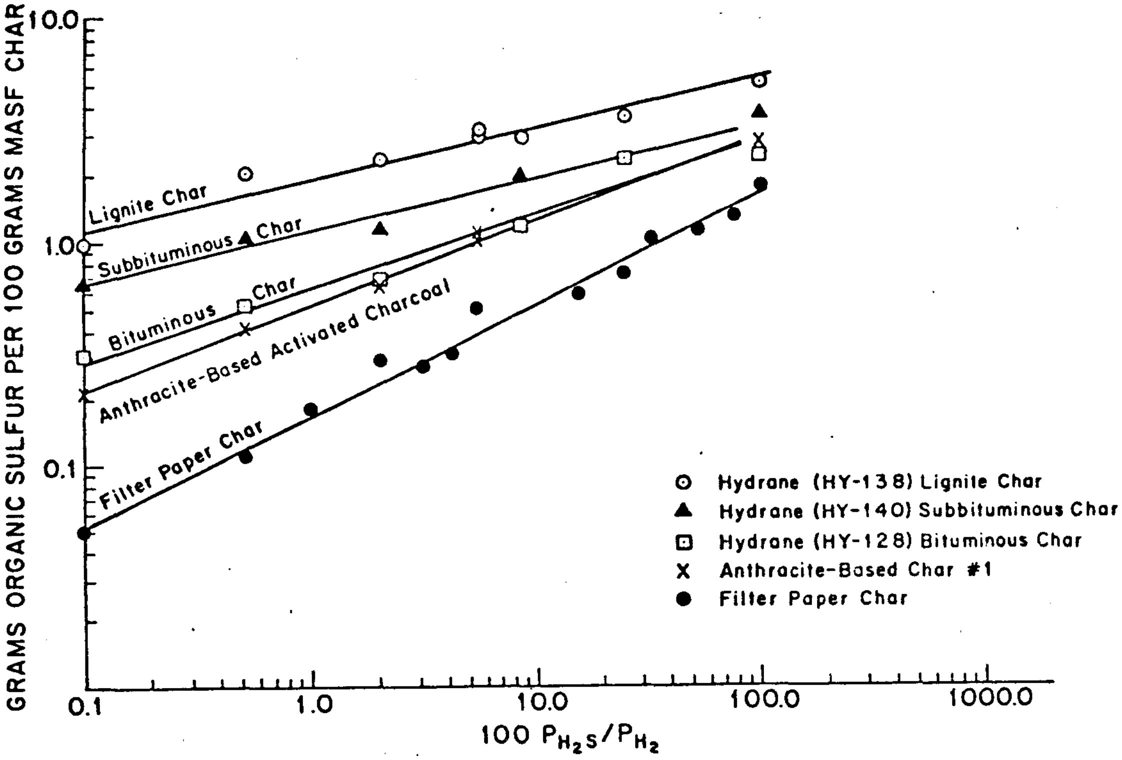

Figure 3.7 Presentation of Sulfidation Data for Various Chars at 1600°F according to a Freundlich Isotherm

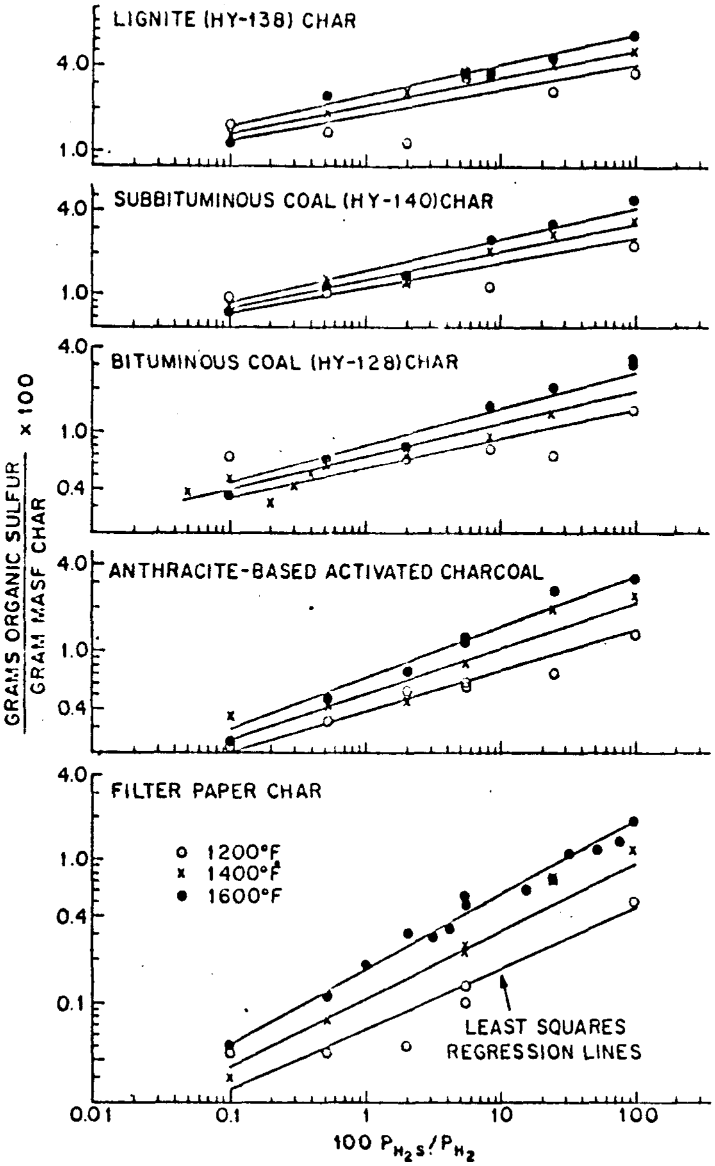

Figure 3.8 The Effect of Temperature upon the Adsorption Isotherm

with the results of Kor(57), and inconsistent with the results of Batchelor(9). The reasons for this apparent inconsistency are discussed in Section 5.3.2. In addition, the effect of temperature upon the adsorption isotherm *decreases* with *decreasing* rank until, at one extreme, in the case of lignite char, the effect of temperature upon the adsorption isotherm is hardly noticeable. Also, the slope of the adsorption isotherm *decreases* with *increasing* rank as well as increasing temperature.

A model for the effect of temperature upon the adsorption isotherm has been developed (see Appendix A). The model and its associated regression constants, are presented in Table 3.2. The results of this model are presented as the least squares regression lines in Figure 3.8. In general, the model describes char sulfidation data fairly well. However, there is quite a large degree of scatter in some of the data. This scatter is particularly noticeable in the case of the lowest temperature (i.e., 1200°F) investigated. The reasons for this scatter, and experiments to improve the data correlation are outlined in Section 7.1.

3.4 Experiments to Determine whether or not Char Properties affect the Sulfur Adsorption Characteristics of Char

Clearly, the rank of the parent coal can only influence the sulfur adsorption characteristics of the char insofar as it affects the properties of the char. In other words, the sulfur adsorption characteristics of char are an intrinsic property of the char itself. A qualitative relationship exists between the rank of the parent coal and the equilibrium concentration of organic sulfur in char because the properties of the parent coal and product char are related. To establish whether or not the above reasoning

Char Description	k_0	a_0 Atm.$^{-1}$	q_m cals. g.mole^{-1}
HYDRANE [HY-138] Lignite Char	4.236	9.972	10299
HYDRANE [HY-140] Subbituminous Char	2.913	2.644	10173
HYDRANE [HY-128] Bituminous Char	1.411	10.672	9061
Anthracite-based Activated Charcoal	1.227	34.037	6460
Filter Paper Char	0.1709	1224.37	4381

Note: Constants to be used in the model:

$$S = k_0 \left\{ a_0' \times 10^{[5.18-9465.9/T]} \times [100 P_{H_2S}/P_{H_2}]^2 \right\}^{RT/2q_m}$$

where S = Organic sulfur content of char; grams organic sulfur per 100 grams of MASF char

k_0 = arbitrary constant; dimensionless

a_0' = arbitrary constant; Atm.$^{-1}$

R = gas constant; cals gmole^{-1} $^{o}K^{-1}$

T = temperature; ^{o}K

q_m = heat of adsorption at zero surface coverage; cals g.mole^{-1}

Table 3.2 Parameters in the Model for the Effect of Temperature upon the Adsorption Isotherm.

is correct, several char samples (15 grams each) were prepared in the fluid-bed apparatus according to the following procedure:

$$\text{START}\ \xrightarrow[\text{0.5 scfh He}]{\text{900°C; 1 Hour}}\ \xrightarrow[\text{0.5 scfh He}]{\text{1400°F; 1 Hour}}\ \xrightarrow[\text{7.0\% H}_2\text{S in Hydrogen}]{\text{1400°F; 1 Hour; 0.5 scfh}}\ \text{ANALYSIS}$$

This experimental history was employed because it represents an "average" condition as far as the adsorption isotherm experiments discussed earlier are concerned. The chars produced in these experiments were analyzed by Huffman Laboratories, Wheat Ridge, Colorado. Their analyses are presented in Tables D.13, D.14, and D.15.

The effect of rank of the product char upon the equilibrium concentration of sulfur in char is examined in Figure 3.9.* These results demonstrate that a relationship between these variables does exist. Further, a linear regression of the data in Figure 3.9 passes close to the point (100,0). Hence, these results are consistent with the results of Wibaut(128), who noted that " ... only amorphous carbons are able to fix sulfur, while the crystalline modifications of carbon (graphite and diamond) do not possess this property". Similar behaviour for graphite has been noted by Kor(56).

3.5 Relationship between the Moisture and Sulfur Concentrations in Char

At the end of each of the experiments described above, the char samples were quickly transferred to tightly-stoppered glass sample bottles and stored in a desiccator. When all of the experiments had been completed, the samples were shipped to Huffman Laboratories for analysis. The analyses

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*The weight percent carbon in MAF char (the abcissa in Figure 3.9) data are obtained from Table D.15. The grams of total sulfur per 100 grams of MASF char (the ordinate in Figure 3.9) data are obtained from Table D.13.

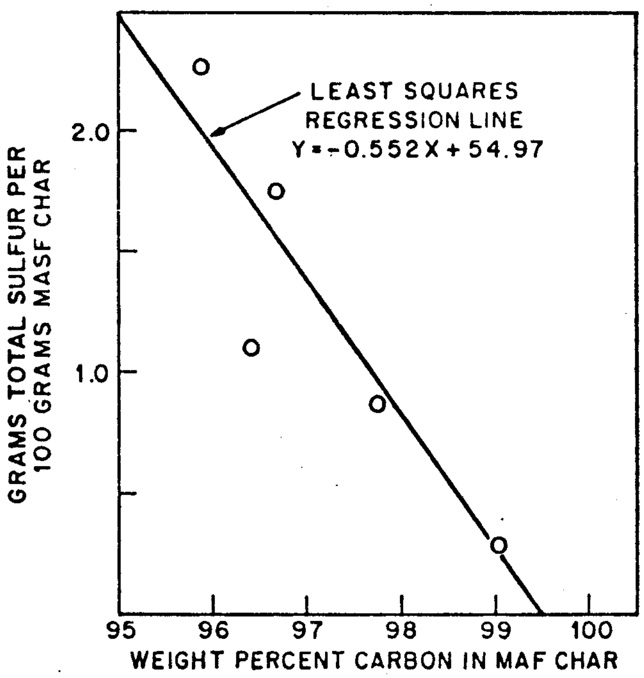

Figure 3.9 The Relationship between the Rank of the Product Char and the Concentration of Organic Sulfur

performed in Colorado (see Table D.13) revealed that the chars contained a significant concentration of moisture. Undoubtedly moisture was adsorbed by the char during sample preparation and analysis. Therefore, the conditions under which moisture adsorption took place are uncertain. Nevertheless, a noticeable relationship (see Figure 3.10) exists between the moisture and total sulfur concentrations in char.

While the reason for the above observation is not entirely clear, several investigators(3,4,26,65,77,97) have observed a similar relationship for oxygen-covered surfaces. Walker and Janov(123) conducted a series of water-adsorption measurements on Graphon (a graphitized carbon black) as a function of temperature (20, 10, 1 and -3.3°C), the partial pressure ratio (P/P_0)*, and the fraction of the Graphon surface covered with oxygen-carbon surface complex. Amongst other things, they noted that:

- It is a well-established fact that, while well-cleaned carbon surfaces are essentially hydrophobic, the presence of oxygen complexes on some part of the surface renders the surface hydrophilic.
- The extent of water adsorption is proportional to that fraction of the surface covered by chemisorbed oxygen.
- Adsorption of water would be expected to be localized at lattice sites containing oxygen, as a result of hydrogen bonding, and
- Removal of the oxygen complex sharply decreases water adsorption.

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*P is the measured partial pressure of water vapour above the char sample, while P_0 is the saturation vapour pressure at the temperature in question.

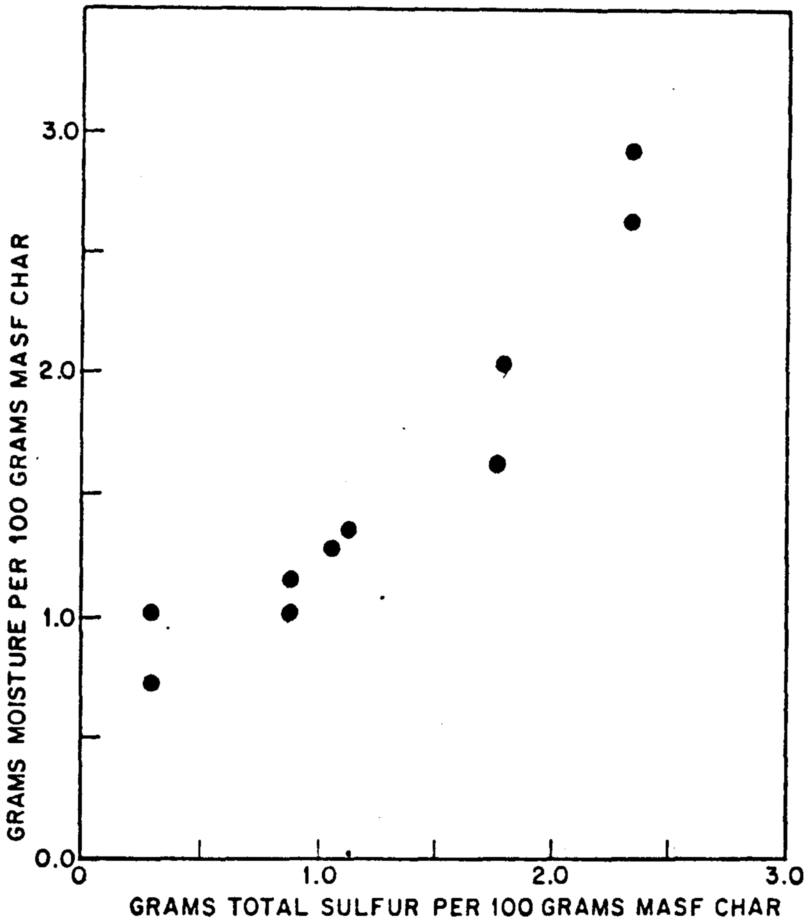

Figure 3.10 The Relationship between the Concentrations of Moisture and Total Sulfur in Char

The analogy between carbon-oxygen and carbon-sulfur complexes will be discussed in Section 5.2. Assuming, for the moment, that such an analogy exists, the above observations suggest that the relationship noted in Figure 3.10 is probably the result of moisture adsorption at sulfur-covered active sites on the char surface. Experiments of the type conducted by Walker and Janov(123) should be conducted with sulfur-covered chars to establish whether or not the latter statement is correct. In the absence of such experimental data, the hypothesis that moisture adsorption takes place at sulfur-covered active sites in the char is a plausible explanation for the relationship noted in Figure 3.10.

3.6 An Experimental Attempt to Verify the Existence of a Relationship between the Hydrogen and Sulfur Adsorption Characteristics of Char

Dr. P. Walker, of Pennsylvania State University, State College, Pennsylvania, suggested that the extent of hydrogen adsorption could be used as a measure of the concentration of active sites in char. In order to test this hypothesis, the hydrogen and sulfur adsorption characteristics of various chars were examined at 1600°F.

In adsorption measurements, the method of sample preparation is important. In these experiments, the following preparation procedure was adopted:

1. The filter paper char sample was prepared by charring the filter paper (Whatman 40 ashless - i.e., 0.01% ash) for three (3) hours in the horizontal tube furnace in a stream of helium, the flowrate of which was 0.5 scfh. This sample had been stored for some time and, hence, was dried for 24 hours at 110°C prior to use in these experiments.

2. The lignite and anthracite-based activated charcoal samples were prepared according to the experimental history

$$\text{START}\ \frac{\text{900°C; 1 Hour}}{\text{0.5 scfh Helium}} \qquad \frac{\text{1600°F; 1 Hour}}{\text{0.5 scfh Helium}}\ \text{ANALYSIS}$$

   in the fluid-bed apparatus.

The hydrogen adsorption characteristics of these chars were then measured in a conventional BET apparatus. A quartz adsorption cell was specially constructed for these experiments because of the elevated temperatures of the adsorption measurements -- i.e., 1600°F. Each sample was weighed in the container. A quartz wool plug was inserted above the sample and the container was then sealed. The sample was degassed under high vacuum while slowly raising the temperature to 1600°F. This degassing was continued for several hours and was considered complete when a constant high vacuum -- i.e., 10^{-6} mm. Hg. - was achieved. The free space volume was then determined using helium at 1600°F. Following pumpdown to high vacuum, the hydrogen adsorption measurements were conducted in a manner similar to that of a conventional BET determination.

The results of these experiments are presented in Table 3.3. Also presented are estimates of the amount of sulfur adsorbed by these chars (at 1600°F and $100P_{H_2S}/P_{H_2} = 5.45$). These estimates were obtained from the adsorption isotherms presented in Tables D.8, D.11, and D.12. The surface areas presented in Table 3.3 are the same as those presented in Table D.3.

The data presented in Table 3.3 reveal that there does seem to to be a relationship between the sulfur concentrations and the amount of hydrogen adsorbed. However, the reason for this relationship is not readily apparent.

Table 3.3 Comparison between the Amounts of Hydrogen and Sulfur Adsorbed on Various Chars at 1600°F

		Surface Areas				Hydrogen Adsorption				Sulfur Adsorption		
Expt#	Char Description	Surface area (a)	Surface area (b)	Surface area (c)	Surface area (d)	Pressure (e)	H_{2ads} (f)	H_{2ads} (g)	H_{2ads} (h)	Organic Sulfur (i)	S_{2ads} (j)	S_{2ads} (k)
258	HYDRANE	158	200.3	485	615	235.2	244.6	1.55	0.50	4.06	3.17	1.03
	[HY-138]					494.4	260.7	1.65	0.54			
	Lignite					734.7	257.7	1.63	0.53			
257	Anthracite-based	99	110.3	376	419	233.0	135.4	1.37	0.36	1.15	1.63	0.43
						497.8	152.2	1.54	0.40			
	Activated					744.8	154.5	1.56	0.41			
	Charcoal											
10	Filter	359	370	788	811	235.7	165.3	0.46	0.21	0.507	0.21	0.10
	Paper					497.5	197.7	0.55	0.25			
	Char					742.2	221.2	0.62	0.28			

Note: (a) Surface area, by Nitrogen and B.E.T. method, m^2 per gram of as-received char
(b) Surface area, by Nitrogen and B.E.T. method, m^2 per gram of MASF char
(c) Surface area, by Carbon Dioxide and Dubinin-Polyani equation, m^2 per gram of as-received char
(d) Surface area, by Carbon Dioxide and Dubinin-Polyani equation, m^2 per gram of MASF char
(e) Hydrogen pressure, mm Hg.
(f) Hydrogen adsorbed, micromoles per gram of as-received char
(g) Hydrogen adsorbed, micromoles per m^2 of char, using the Nitrogen surface area - i.e. (a)
(h) Hydrogen adsorbed, micromoles per m^2 of char, using the Carbon Dioxide surface area - i.e.(c)
(i) Organic sulfur content of char at 1600°F and $100P_{H_2S}/P_{H_2}=100$, grams per 100 grams of MASF char
(j) Sulfur - i.e.S_2 - adsorbed, micromoles per m^2 of char, using the N_2 surface area - i.e.(b)
(k) Sulfur - i.e.S_2 - adsorbed, micromoles per m^2 of char, using the Carbon Dioxide surface area - i.e.(d)

3.7 Testing the Reversibility of Char Sulfidation

Batchelor(9) concluded that char sulfidation is a reversible process. Since a lack of reversibility would have important practical and theoretical implications, it was decided to test Batchelor's conclusions. Accordingly, a set of experiments was performed using HYDRANE HY-128 bituminous char. In these experiments, the chars were first exposed to a relatively high concentration of hydrogen sulfide in hydrogen $(100H_{H_2S}/P_{H_2} = 100)$ for one hour at 1600°F. The chars were then exposed to lower concentrations of hydrogen sulfide in hydrogen -- i.e.,

$$(100P_{H_2S}/P_{H_2}) = Z;\ Z = 0.1,\ 0.52,\ 1.97,\ 7.5, \text{ and } 24.6$$

for varying periods of time -- i.e., 1, 4 and 8 hours. The results of these experiments are presented in Table D.16 and Figure 3.11. The results of a linear regression of the 1600°F sulfidation data in Table D.10 (i.e., the adsorption isotherm) are also presented in Figure 3.11.

Notice that all of the experimental data points lie well above the adsorption isotherm. However, the extent of this deviation is clearly a function of the exposure time (1, 4 or 8 hours). The data generated at an exposure time of 8 hours lie quite close to the adsorption isotherm. It seems reasonable to conclude that char sulfidation is a reversible process. However, the kinetics of char desulfurization (at the experimental conditions which were employed) are so slow that the equilibrium condition is only regained after very long times of exposure of the char to the lower concentration of hydrogen sulfide in hydrogen.

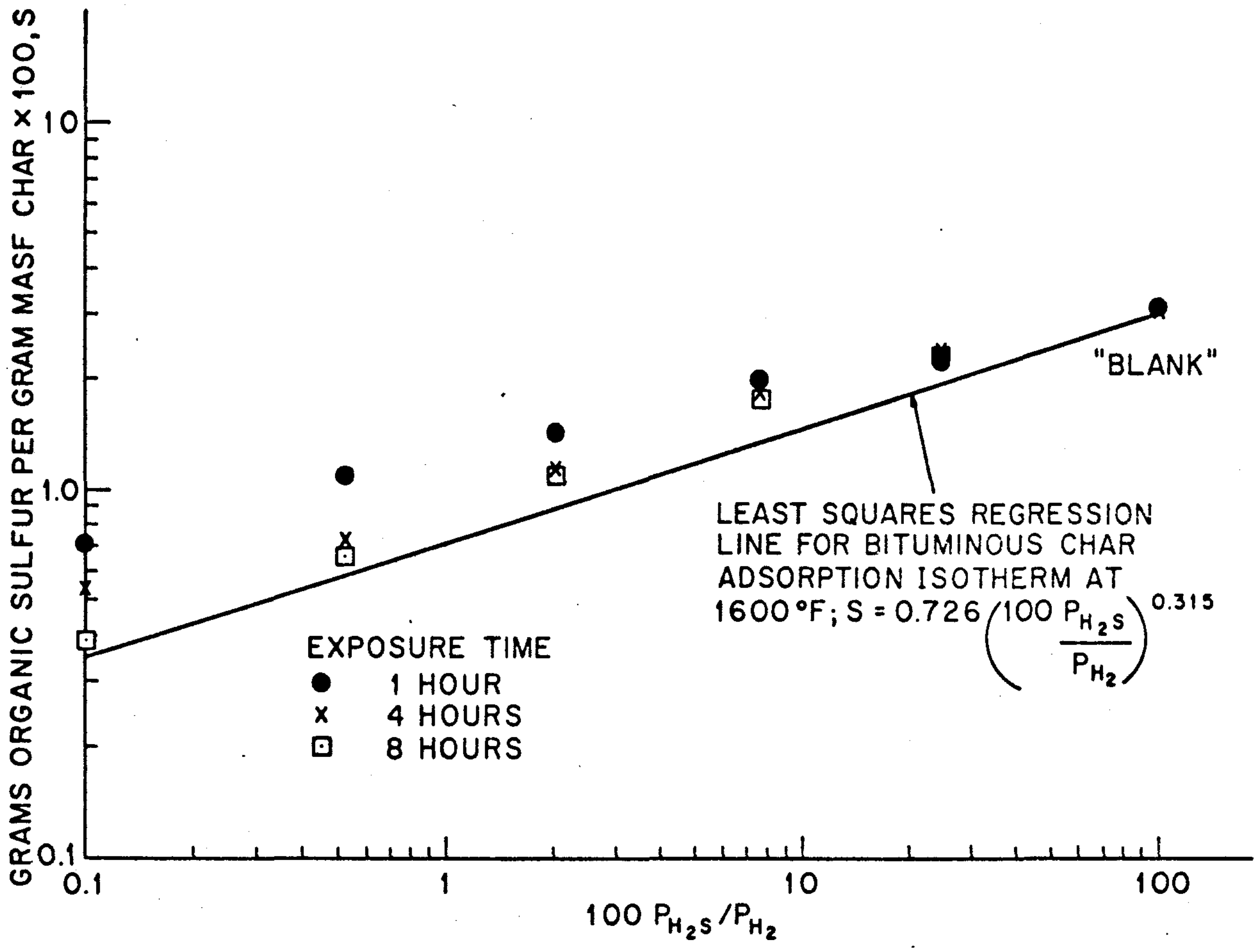

Figure 3.11 Results of Experiments to Establish whether or not Char Sulfidation is Reversible

3.8 Summary and Conclusions

It is suggested that organic sulfur in char is formed as a result of the chemisorption of sulfur species at active sites on the char surface. Consistent with this hypothesis, the experimental results presented in this chapter have revealed that:

1. The equilibrium concentration of organic sulfur is not a function of the partial pressure of hydrogen sulfide. Instead, the governing parameter is the partial pressure ratio (P_{H_2S}/P_{H_2}).
2. There is no readily apparent relationship between the equilibrium concentration of organic sulfur in char and char surface area. This conclusion is inconsistent with Kor's observations. Nevertheless, it is consistent with the active site hypothesis in that the variable of significance as far as sulfur adsorption is concerned is the specific concentration of active sites in the char rather than the specific surface area.
3. Of the three adsorption isotherms tested (i.e., Langmuir, Temkin and Freundlich), the Freundlich Isotherm is the best model with which to describe char sulfidation data.
4. There is a definite relationship between the rank of the parent coal and the sulfur adsorption characteristics of the product char. The concentration of organic sulfur in char varies with rank of the parent coal in the following order:

   Lignite Char > Sub-bituminous Char > Bituminous Char > Anthracite Char

   i.e., the concentration of organic sulfur in char *increases* with *decreasing* rank of the parent coal.
5. Consistent with the results of Kor(57), the equilibrium concentration of organic sulfur in char *increases* with *increasing* temperature. The effect of temperature upon the adsorption isotherm is most noticeable in the case of high-rank coal chars but becomes progressively less noticeable until, at the opposite end of the rank spectrum, the effect of temperature upon the adsorption isotherm is hardly noticeable. In addition, the slope of the adsorption isotherm *increases* with *increasing* temperature.

6. A relationship exists between the char rank and the equilibrium concentration of organic sulfur in char. This relationship suggests that the concentration of organic sulfur in char *decreases* with *increasing* rank of the char. This result is consistent with Wibaut's(129) observation that: " ... only amorphous carbons are able to fix sulfur, while the crystalline modifications of carbon (graphite and diamond) do not possess this property".

7. A relationship exists between the concentration of organic sulfur in char, and the concentration of moisture adsorbed by the char at ambient conditions. This observation is consistent with observations in the literature regarding the relationship between the moisture and oxygen concentrations in char.

8. There is no readily-apparent relationship between the hydrogen and sulfur adsorption characteristics of the chars examined in this investigation.

9. Char sulfidation is a reversible process. However, the kinetics of char hydrodesulfurization are so slow (at least for the experimental conditions employed in this investigation) that the equilibrium condition is not regained even after exposure of the char to lower concentrations of hydrogen sulfide for periods of as long as eight hours.

The latter conclusion serves as an introduction to Chapter Four, where the factors which affect the kinetics of char hydrodesulfurization are discussed.

CHAPTER FOUR

KINETICS OF CHAR HYDRODESULFURIZATION

The experiments mentioned in Section 3.7 suggest that, while char sulfidation is reversible, the kinetics of char hydrodesulfurization are extremely slow. In other words, these results suggest that char hydrodesulfurization is kinetically-controlled. Both Kor(56) and Jones(52) have employed kinetic models to describe their char hydrodesulfurization data. On the other hand, Batchelor(9) suggested that his deep-bed results could be described using a pseudo-equilibrium model. This will hereafter be referred to as Batchelor's *pseudo-equilibrium hypothesis*.

These different interpretations reveal that uncertainty surrounds the correct interpretation of char desulfurization data.

In an attempt to resolve this uncertainty, a series of char hydrodesulfurization experiments was performed using the fluid-bed apparatus. To assist in the analysis of the data from these experiments, an ideal model of the fluid-bed reactor has been developed (see Appendix B). In the development of this model, it is assumed that:

(a) The adsorption isotherms discussed earlier can be used to describe the equilibria which govern the reaction.

$$C(s) + H_2S(g) \rightleftarrows [C\text{-}S](s) + H_2(g) \qquad [4.1]$$

where

C(s) is the char matrix, and
[C-s](s) is a carbon-sulfur species in the char.

(b) The char hydrodesulfurization reactions are so rapid that a pseudo-equilibrium distribution of sulfur is maintained between the char and gas phases at all stages of the experiment in question, and

(c) The batch fluid-bed reactor behaves as an ideal CSTR* with respect to both the char and gas phases.

This model, hereafter referred to as the *Equilibrium Model,* is a tool which can be used to "measure" the rate of char hydrodesulfurization in the experiments described below.

4.1 Investigation of the Kinetics of Lignite Char Hydrodesulfurization

In the first set of char hydrodesulfurization experiments, the kinetics of lignite char (HYDRANE HY-138) hydrodesulfurization at 1400°F were examined. In an attempt to separate the effects of (a) desulfurization time and (b) the volume of hydrogen passed through the fluid-bed (per lb. of MASF char) on the experimental results, these experiments were divided into two subsets:

1. A subset of experiments in which pure hydrogen was passed through the fluid-bed (which contained W_1 grams of MASF char) at a flowrate of Q_1 scfh for t_1 hours. The total volume of hydrogen passed through the fluid bed (per g. of MASF char in the bed) is V_1 where

$$V_1 = Q_1 t_1 / W_1 \qquad [4.2]$$

2. A subset of experiments in which a gaseous mixture of 10% hydrogen in helium was passed through the fluid bed (which contained W_2 grams of MASF char) at a flowrate of Q_2 scfh for t_2 hours. The total volume of hydrogen passed through the fluid bed, per gram of MASF char in the bed, is V_2 where

$$V_2 = 0.1 Q_2 t_2 / W_2 \qquad [4.3]$$

---

* Continuous Stirred Tank Reactor.

Combining equations [4.2] and [4.3] yields:

$$t_2/t_1 = 10V_2W_2Q_1/(V_1W_1Q_2) \tag{4.4}$$

The independent variables in these subsets (V, W, and Q) were chosen such that, for a pair of experiments (one from each of the subsets)

$$V_1 \approx V_2 \tag{4.5}$$

$$W_1 \approx W_2 \tag{4.6}$$

$$Q_1 \approx Q_2 \tag{4.7}$$

Combining equations [4.4], [4.5], [4.6], and [4.7] yields:

$$t_2 \approx 10t_1 \tag{4.8}$$

In other words, the hydrodesulfurization time differs by an order of magnitude in the subsets.

The results of these experiments are presented in Table D.17, as well as in Figure 4.1. Also presented in Figure 4.1 are the results of the Equilibrium Model at 1400°F (See Appendix B Case One). Notice that:

1. The extents of char hydrodesulfurization realized in the two subsets are indistinguishable, and
2. The extent of char hydrodesulfurization realized in both of these experimental subsets is substantially less than that which is predicted on the basis of the equilibrium model.

These observations appear to be inconsistent. The nature of this inconsistency is demonstrated by the following argument. The latter observation leads one to the conclusion that the rate of char hydrodesulfurization in these experiments is kinetically controlled. The experimental results should be

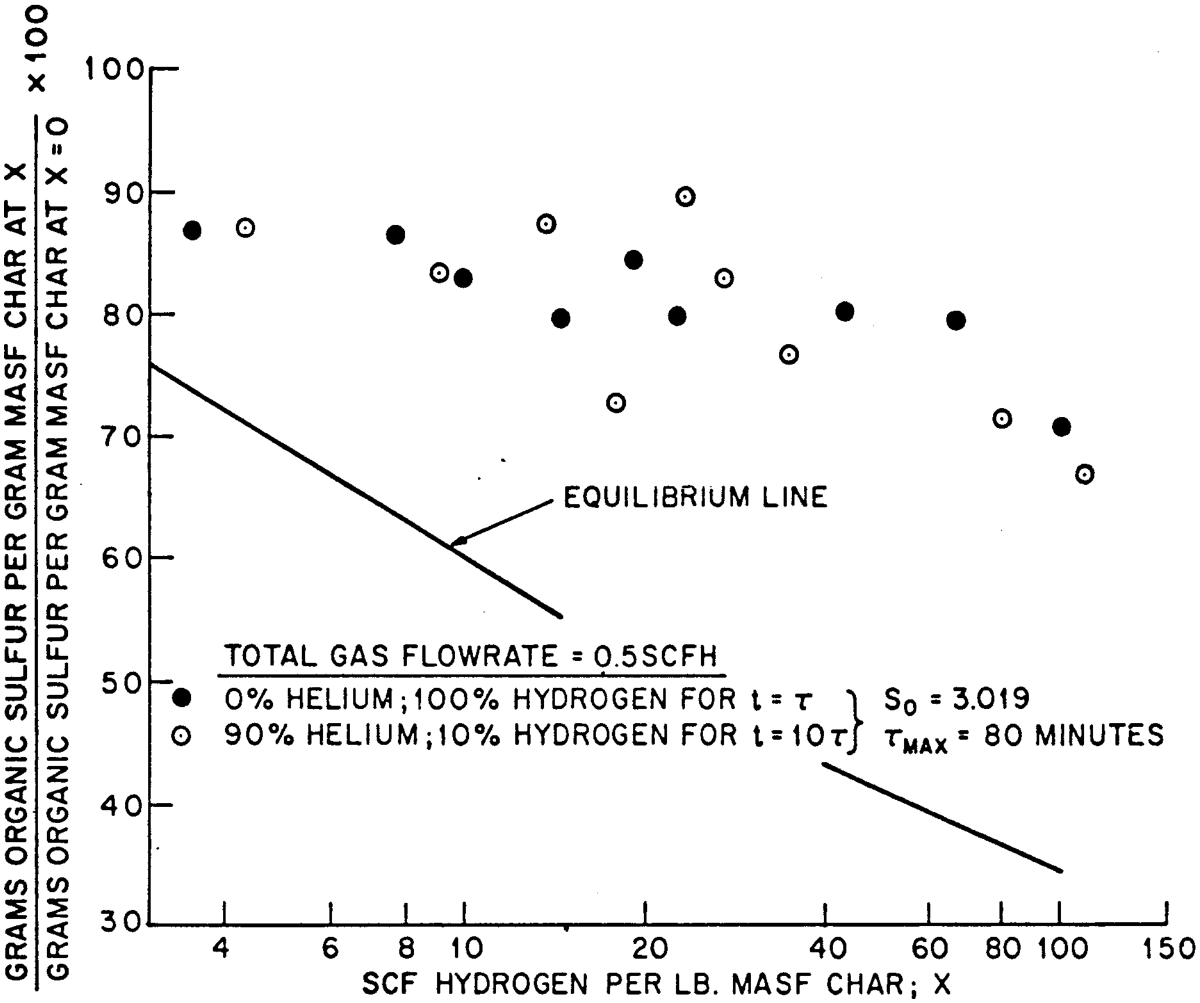

Figure 4.1 Hydrodesulfurization Data for HYDRANE HY-138 Lignite Char at 1400°F

a function of the desulfurization time. The latter hypothesis is, however, inconsistent with the former observation -- i.e., there is no noticeable effect of hydrodesulfurization time upon the above mentioned experimental results.

4.2 Investigation of the Kinetics of Bituminous Char Hydrodesulfurization

To clarify the inconsistency in the above results, a second set of char hydrodesulfurization experiments, using HYDRANE HY-128 bituminous coal char, was performed in the fluid-bed apparatus at 1400°F. These experiments are, in all respects, identical to the experiments in which lignite chars were employed. The results of these experiments are presented in Table D.18, as well as in Figure 4.2. Also presented in Figure 4.2 are the results of the Equilibrium Model for bituminous coal char at 1400°F (see Appendix B Case Two). Notice, in Figure 4.2 that:

1. Once again, the extent of char hydrodesulfurization realized in these experiments is substantially less than that which is predicted on the basis of the equilibrium model.
2. In contrast to the lignite char desulfurization experiments discussed previously, there is a noticeable difference between the two subsets of experimental results. More specifically, note that *less* char desulfurization is realized at *longer* desulfurization times.

The latter observation provided the clue for which we had been searching. There are two possible explanations for the above observations; the kinetics of char hydrodesulfurization are a function of the hydrogen partial pressure, or increased residence time of organic sulfur in the char has a deleterious effect upon the kinetics of char hydrodesulfurization.

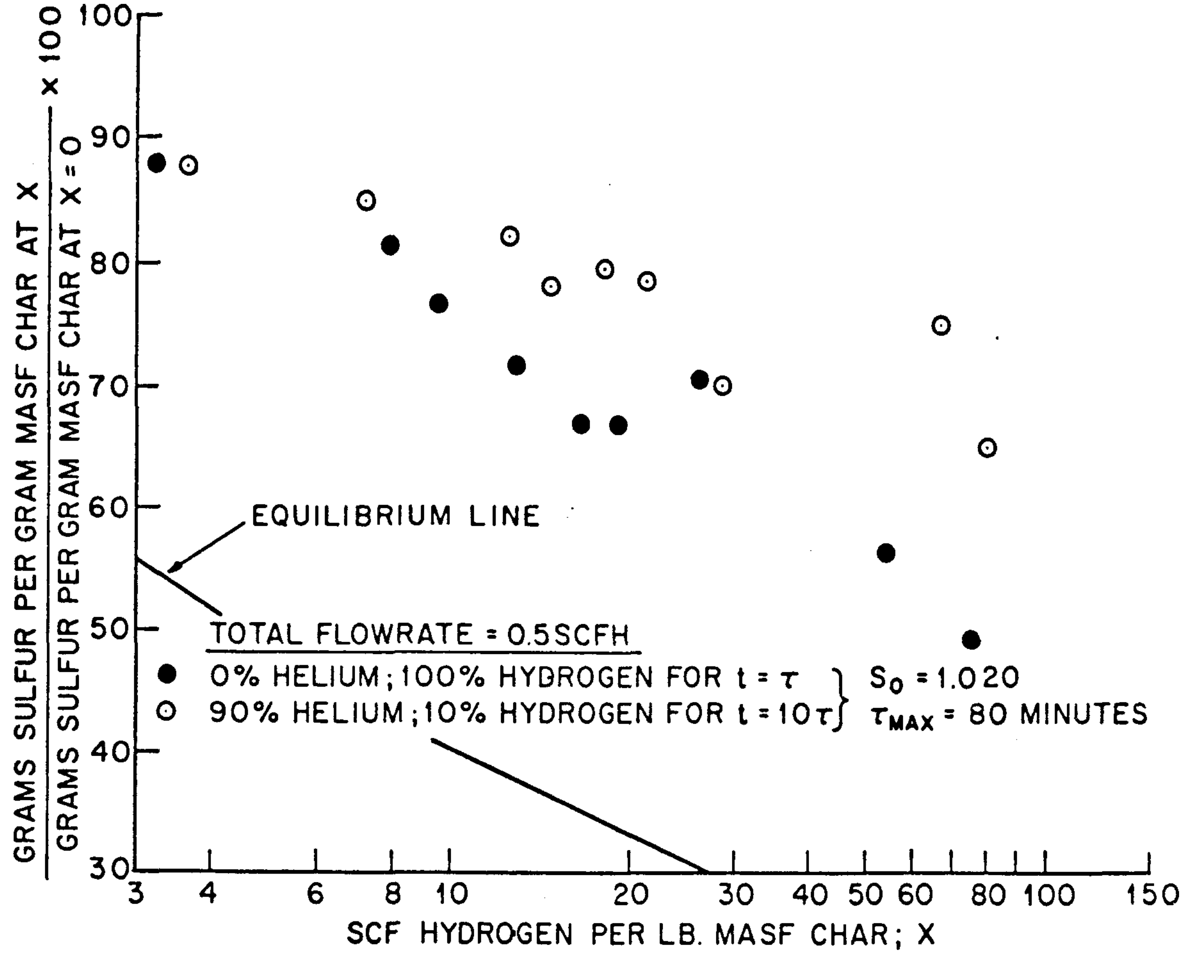

Figure 4.2 Hydrodesulfurization Data for HYDRANE HY-128 Bituminous Char at 1400°F

4.3 The Effect of the Residence Time of Organic Sulfur in Char upon the Kinetics of Char Hydrodesulfurization

In attempting to separate the effects of these two variables upon the kinetics of char hydrodesulfurization, a third set of bituminous coal (HYDRANE HY-128) char hydrodesulfurization experiments was performed in the fluid-bed apparatus at 1400°F. This set of experiments was divided into two subsets. In both of these subsets, the hydrogen partial pressure, hydrogen flowrate, and desulfurization time (for a pair of experiments, one from each of the subsets) were held constant. However, the time of exposure of the char to hydrogen sulfide (T) in the two subsets was different -- i.e., 1 hour and 10 minutes respectively. The results of these experiments are presented in Table D.19, and Figure 4.3.

Notice that the extent of desulfurization realized at the shorter exposure time (T = 10 minutes) is *greater* than that realized at the longer exposure time (T = 1 hour). These results demonstrate that the extent of char hydrodesulfurization is dependent upon the physiochemical history of the char -- i.e., *char hydrodesulfurization is a path-dependent process.* The latter conclusion is consistent with Batchelor's(12) observation that " ... the sulfur in raw char is more labile in both a thermodynamic and kinetic sense than after thermal treatment for several hours". "Thermal treatment of the char for several hours ... undoubtedly transforms the sulfur into a more stable form".

Unfortunately, the thermal history of the char is also a variable in the above subsets of experiments. Separate experiments will be required to resolve which of the two variables (decreased time of exposure of the

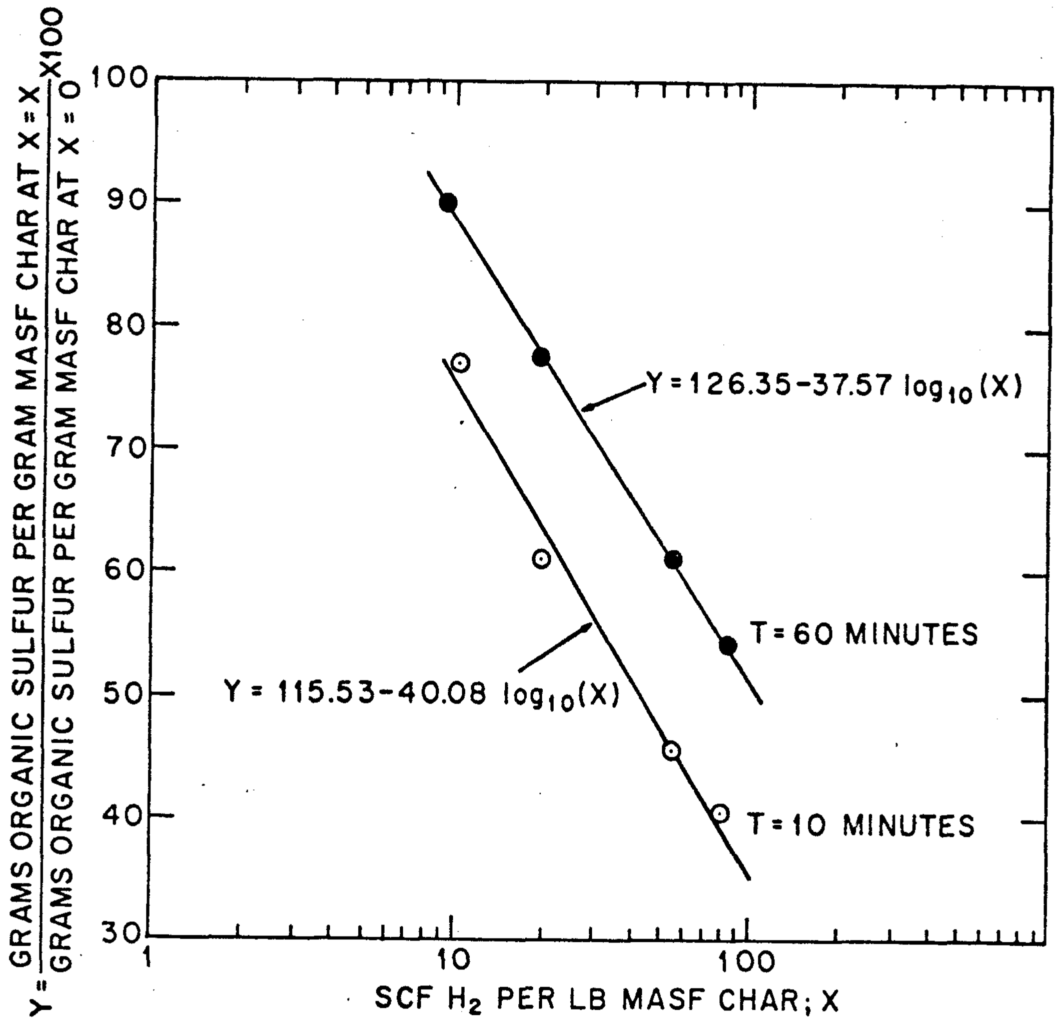

Figure 4.3 Results of Experiments to Establish whether or not the Residence Time of Organic Sulfur in Char affects the Kinetics of Char Hydrodesulfurization

char to hydrogen sulfide or changing thermal history of the char) is responsible for the observed path-dependent nature of char hydrodesulfurization.

4.4 The Transformation Hypothesis

Initially, Powell's solid-solution sulfur hypothesis(84) seemed to provide a plausible explanation for the observed path-dependent nature of char hydrodesulfurization. However, this hypothesis is inconsistent with the observation that the concentration of organic sulfur in char is not a function of the time of exposure of the char to hydrogen sulfide,* and the fact that the extent of char hydrodesulfurization is *lower at longer* desulfurization times (see Section 4.2).

An alternative explanation for the path-dependent nature of char hydrodesulfurization is that exposure of the adsorbed sulfur species on the char surface to elevated temperatures results in a transformation of the adsorbate into a more stable form. This is called the *transformation hypothesis*. Unfortunately, there is little information in the sulfur literature to support this hypothesis. However, there are data in the oxygen literature which, by analogy, can be used in its defense. This data is presented in Chapter Five. Nevertheless, additional experiments are required to establish the validity of this hypothesis.

4.5 ESCA Experiments to Determine the Nature and Properties of Organic Sulfur in Char

In an attempt to establish whether or not a transformation in the

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*Powell's solid-solution sulfur hypothesis suggests that a solid-solution of elemental sulfur is slowly formed in chars upon exposure of the char to hydrogen sulfide. This suggests that a slow increase in the concentration of organic sulfur should be observed in char with increased time of exposure of the char to hydrogen sulfide. However, in experiments in which chars were exposed to hydrogen sulfide for as long as 32 hours, no such increase was observed (see Section 2.4.3.2).

adsorbed sulfur species takes place, a bituminous coal char (HYDRANE HY-128) was prepared under a variety of conditions for analysis in the ESCA system at PETC. A description of the char preparation conditions employed is presented in Table 4.1. Notice that:

1. The only variable in experiments 1 through 4 is the time of exposure of the char to hydrogen sulfide (t_3; $t_3 = 0$, 10, 30 and 90 minutes respectively). A comparison of the ESCA results for experiments 2,3 and 4 should therefore reveal whether or not the time of exposure of the char to hydrogen sulfide affects the nature of organic sulfur in char.

2. In experiment number 6, the exposure time (t_3 = 10 minutes) is the same as it is in experiment number 2. However, the characteristic char pretreatment times (t_1; t_2 = 10 minutes) are both lower than the corresponding values for experiment number 2 (t_1 = 60 minutes, t_2 = 110 minutes). Thus, experiment number 6 was designed to establish whether or not the thermal history of the char (and not exposure time) affects the formation of organic sulfur in char. Once again, experiment number 5 is a background sample with which to compare the results of experiment number 6.

3. In experiments 7 and 8, the pretreatment temperature (T_1 = 1400°F) was reduced from the 1632°F employed in experiments 5 and 6. The experiments are, in all other respects, identical. Hence, experiment number 8 is designed to establish whether or not pretreatment temperature affects the formation of organic sulfur in char.

Binding energy spectra for all eight unsputtered char samples are presented in Figures 4.4, 4.5, and C.1 through C.6. Binding energy spectra for the sputtered samples* are presented in Figures C.7 through C.12.

In all of the binding energy spectra, a peak occurs at a binding energy of approximately 153 eV. Published binding energies in the literature suggest that this is a silicon 2s electron peak. To establish whether or not this peak is due to the presence of silicon in the sample,

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*Samples were sputtered for 60 seconds.

Experiment #	T_1 °F	T_2 °F	t_1 Mins	t_2 Mins	t_3 Mins	Description
1	1632	1400	60	120	-	Background
2	1632	1400	60	110	10	
3	1632	1400	60	90	30	
4	1632	1400	60	30	90	
5	1632	1400	10	20	-	Background
6	1632	1400	10	10	10	
7	1400	1400	10	20	-	Background
8	1400	1400	10	10	10	

Where the variables T_1, T_2, t_1, t_2 and t_3 are defined by the history description:

$$\text{START} \xrightarrow[1.0\ \text{Scfh}\ H_2]{T_1{}^\circ F;\ t_1\ \text{Minutes}} \xrightarrow[1.0\ \text{Scfh}\ H_2]{T_2{}^\circ F;\ t_2\ \text{Minutes}} \xrightarrow[100P_{H_2S}/P_{H_2} = 7.5]{T_2{}^\circ F;\ t_3\ \text{Minutes};\ 0.5\ \text{SCFH}} \text{ANALYSIS}$$

Table 4.1 Char Preparation Conditions employed in the ESCA Experiments

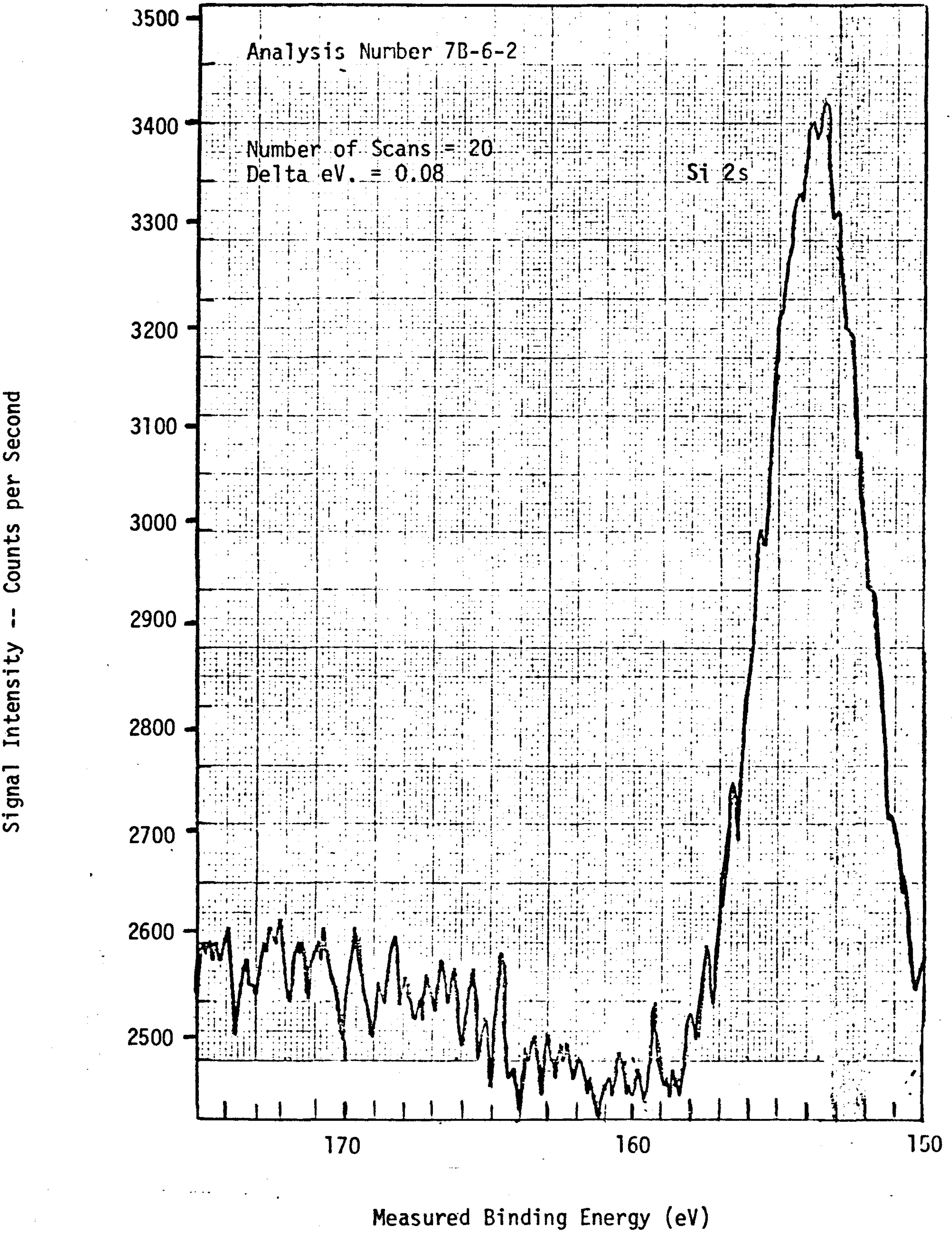

Figure 4.4 Measured Binding Energy for Sample #1 (Unsputtered).

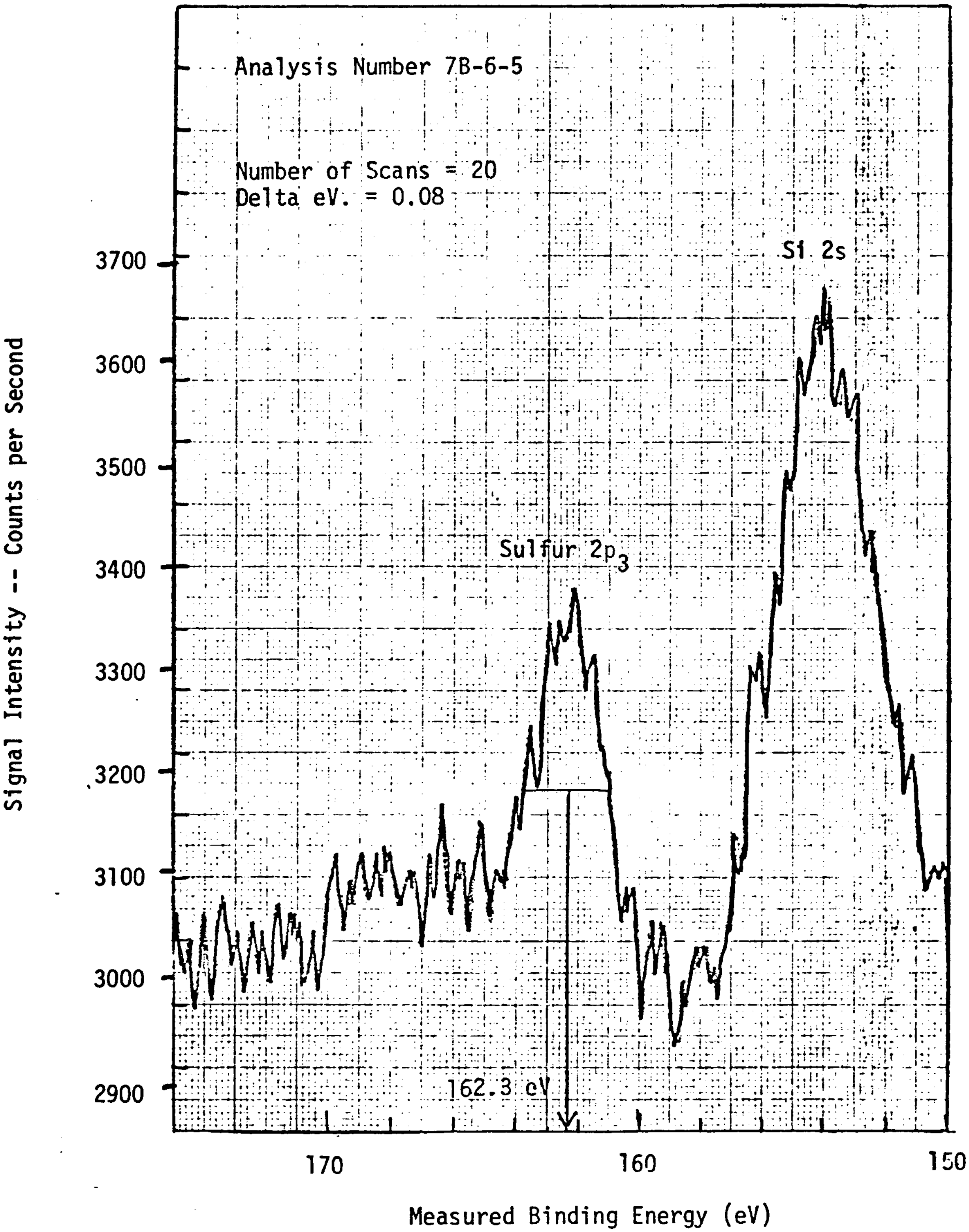

Figure 4.5 Measured Binding Energies for Sample #2 (Unsputtered).

a binding energy spectrum for char #1 was obtained in the region of 153 and 103 eV. The latter spectrum was measured because the most intense silicon peak (silicon $2p_3$) lies at approximately 103 eV. These two spectra are presented in Figures 4.6 and 4.7. Notice in Figure 4.7, that a peak is indeed found at approximately 102 eV. The latter spectra provide strong support for the hypothesis that the peak which lies at approximately 153 eV. is a silicon 2s electron peak. As a further check, the relative areas of these two peaks were measured. The ratio of these two areas is 1.3 -- i.e.,

$$\frac{\text{Area of silicon } 2p_3 \text{ Peak}}{\text{Area of silicon 2s Peak}} = 1.3 \qquad [4.9]$$

This value is quite close to the value of 1.5 presented in the literature(103). There is little doubt that the peak which lies at approximately 153 eV. is a silicon 2s electron peak.

A second peak occurs in the binding energy spectra for those char samples which were exposed to hydrogen sulfide (i.e., samples 2, 3, 4, 6, and 8). This peak is present for both unsputtered *and sputtered char samples*. However, with one possible exception,* this peak is not observed in the background samples (samples 1, 5, and 7). In addition, this peak lies within the range of binding energies which one would expect for a sulfur $2p_3$ electron (i.e., 160-170 eV. - see Figure 2.6). There is little doubt that the observed peak is a sulfur electron peak. Estimated values of the binding

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* There is a small peak in the binding energy spectrum for sample #7 (see Figure C.5).

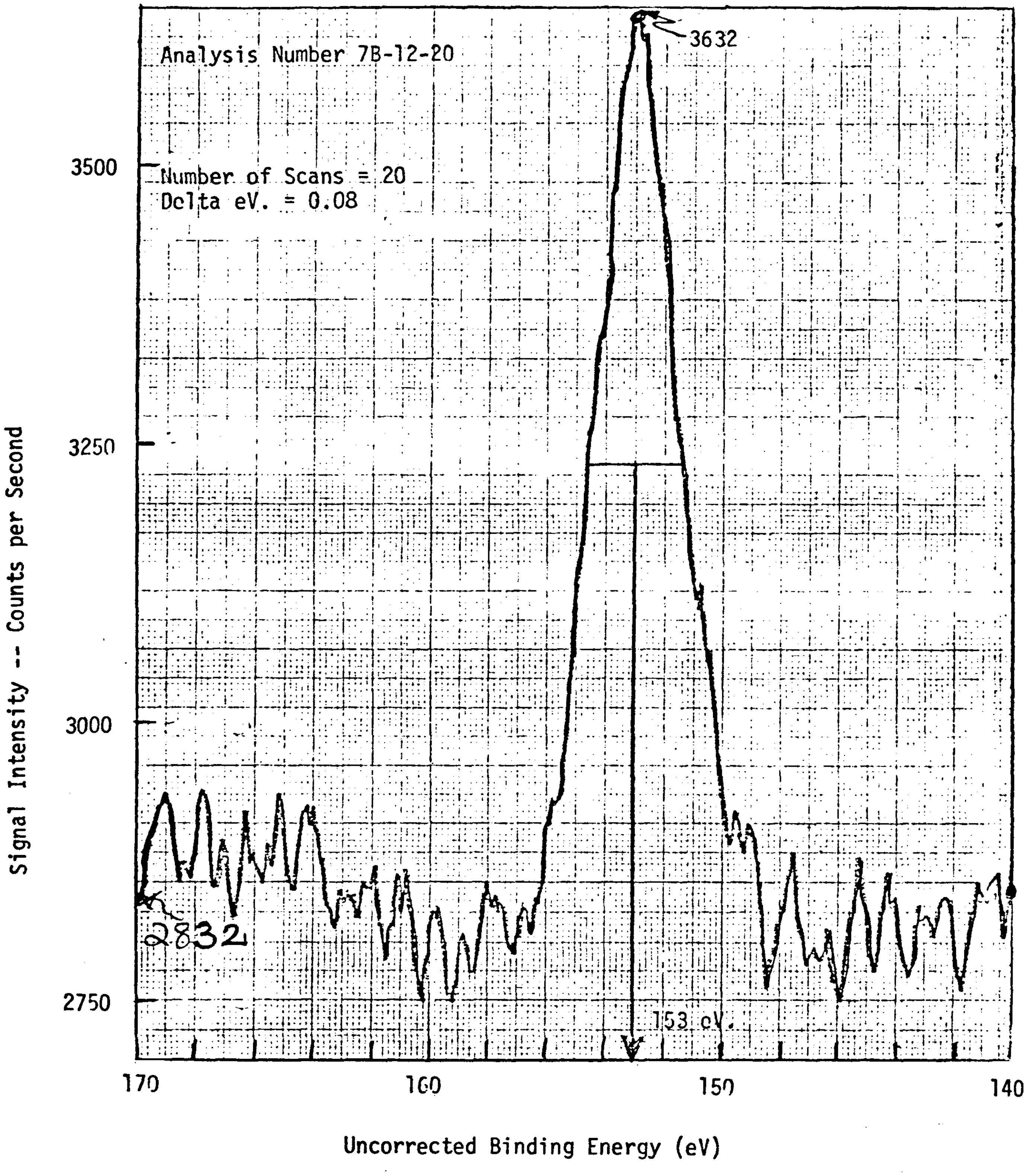

Figure 4.6 Measured Binding Energy Spectrum for the Silicon 2s Electron for Sample #1

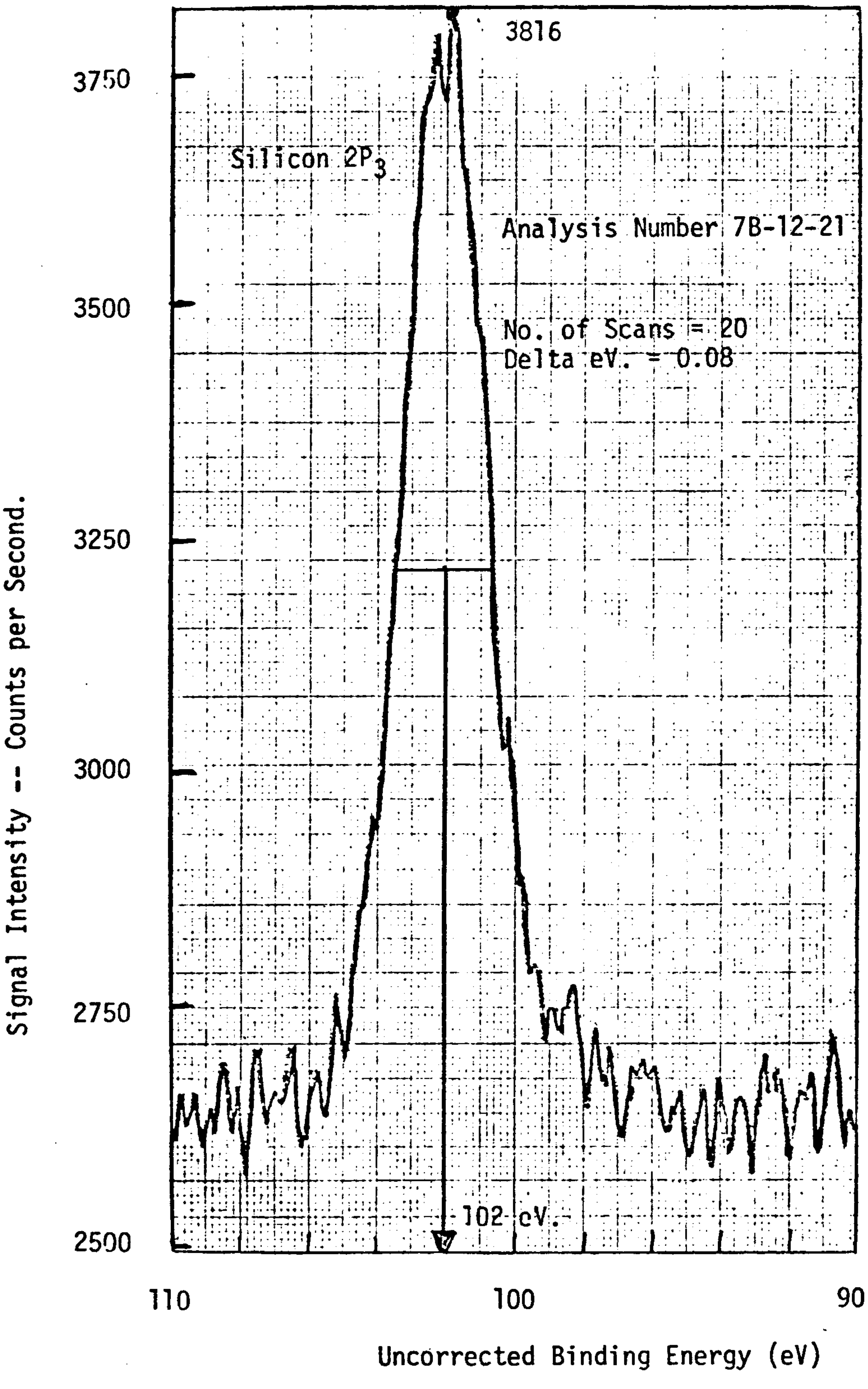

Figure 4.7 Measured Binding Energy Spectrum for the Silicon $2p_3$ Electron for Sample #1

energy for this peak are tabulated in Table 4.2. Notice that the mean value of the binding energy for this peak is 162.4 eV. Correcting for the work function of the char sample (0.4 eV. - see Section 2.2.4), the true binding energy of this peak is 162.0 eV. Ratcliffe sulfided chars with sulfur dioxide(98). An ESCA analysis of his chars revealed a sulfur peak at approximately the same binding energy as that noted above(99). Thus, the above results are consistent with the results of Ratcliffe*.

The true binding energy of the sulfur peak (i.e., 162.0 eV.) is close to the value of 162.2 eV. for zero-valent sulfur noted in the valence correlation chart for the sulfur $2p_3$ electron presented in Figure 2.6. This might lead one to suspect that organic sulfur in char is chemisorbed elemental sulfur. Unfortunately, the binding energy correlation chart in Figure 2.6 reveals that a number of sulfur species other than elemental sulfur (e.g., R-SH, R-S-R, R-S-S-R, Ar-S-R, and probably Ar-SH, AR-S-R, and Ar-S-S-R as well) also have binding energies of approximately 162.0 eV. Thus, the nature of the sulfur species on the surface remains uncertain. In addition, suppose a transformation did take place between two sulfur species on the surface. One would be unable to observe such a transformation using ESCA, because the shift in the binding energy associated with such a transformation would be imperceptible. Consequently, the ESCA experiments did not realize their objective -- i.e., to establish whether or not a transformation of the sulfur species on the surface takes place.

On the other hand, there are two significant conclusions which

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* Note that the binding energy of the sulfur $2p_3$ electron in char is the same, independent of whether hydrogen sulfide or sulfur dioxide is responsible for char sulfidation.

Sample Number	Measured Binding Energy (eV)
Unsputtered	
1	---
2	162.3
3	163.2
4	162.5
5	---
6	162.4
7	---
8	162.3
Sputtered	
1	---
2	162.4
3	---
4	162.2
5	---
6	162.0
7	---
8	162.2
Mean	162.4

Table 4.2 Measured Binding Energies for the Sulfur $2p_3$ Electron

can be drawn from these results -- i.e.,

1. The "chemical environment" of all sulfur atoms on the surface is similar, since only one sulfur $2p_3$ binding energy peak is observed. Surface species such as Ar-S-S can justifiably be excluded from further consideration.
2. The sulfur species on the surface is almost certainly not a sulfide, sulfite or sulfate (i.e., $S^=$, $SO_3^=$ or $SO_4^=$).

A few words of caution about the latter conclusion are justified. Careful inspection of the binding energy spectra for samples 2, 3, 4, 6, and 8 (see Figures 4.4 and C.1 through C.6) suggests that a second sulfur $2p_3$ peak may occur in the 165-168eV. region of the binding energy spectrum. This would suggest the presence of small amounts of $SO_3^=$ or $SO_4^=$ type sulfur in the char. Unfortunately, any discussion about the possible existence of such a sulfur form would be speculative in nature because of the noise level in all of the binding energy spectra, and the possible contamination of the char sample with oxygen when the samples were transferred from the fluid-bed apparatus to the ESCA apparatus. These words of caution notwithstanding, the latter conclusion undermines Puri's(95) conclusion that sulfide sulfur is formed in char upon exposure to hydrogen sulfide at 600°C.

4.6 Effect of Carbon Conversion; The Selective Gasification Criteria

Kor(56) has noted that the extent of char desulfurization is a function of the extent of char gasification. However, he did not attempt to explain why the extent of desulfurization is substantially greater (by a factor of five or six) than the corresponding extent of gasification.

On the other hand, Zielke, et al(132) reached almost exactly the opposite conclusion in noting that: " ... the two reactions (char hydrodesulfurization and hydrogasification) are independent, however, such that desulfurization can be achieved even when methanization is suppressed". Zielke's data are analysed below in an attempt to resolve this apparent inconsistency in the literature.

The char used in their experiments was derived from a Pittsburgh Seam coal prepared by low-temperature (1100°F) carbonization in the Disco Process.* The chars were subsequently devolatilized under rather severe conditions -- i.e., one hour in a 1.5 inch reactor fluidized with nitrogen at 1600°F -- prior to admission of the reactant gas. The chars were then desulfurized at 1600°F using either pure hydrogen, or hydrogen-steam mixtures. The superficial gas velocity was held constant in these experiments (at 0.44 feet per second), while the independent variables -- i.e., pressure, char sample weight and run time -- varied between 1-6 atmospheres, 10-220 grams, and 17-1435 minutes respectively. The results of the experiments are presented in Table D.20.

The extent of char desulfurization in hydrogen and hydrogen-steam mixtures is presented, as a function of the volume of hydrogen passed through the fluid-bed, in Figure 4.8. In this figure, the hydrogen-steam data are presented as closed circles, while the pure hydrogen data are presented as open circles. Notice that the extent of char hydrodesulfurization realized in steam-hydrogen mixtures is significantly greater than that realized

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*A description of the Disco Process is presented by Wilson(130)

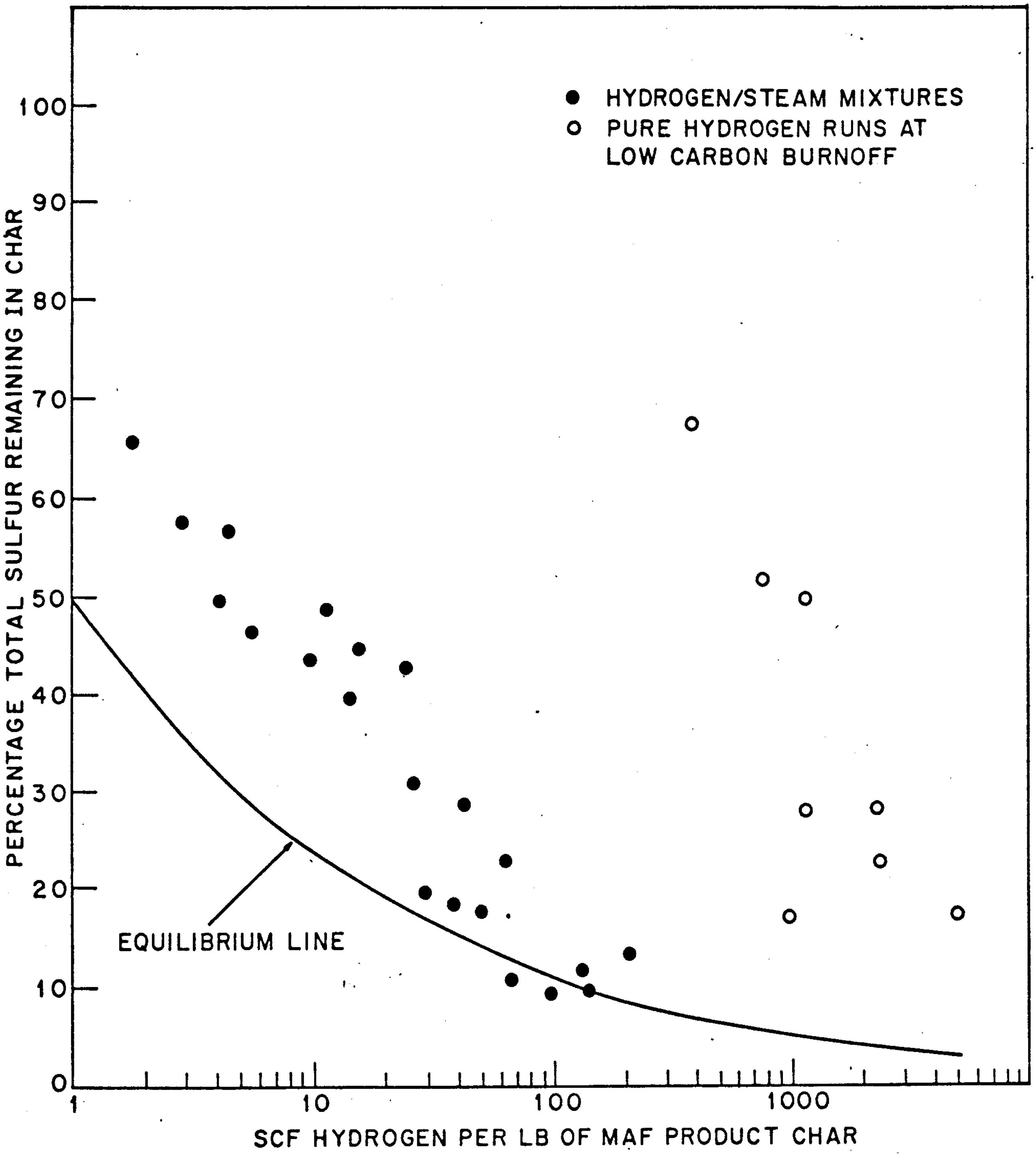

Figure 4.8 Consolidation Coal Company's Disco Char Hydrodesulfurization Results at 1600°F in Hydrogen and Hydrogen/Steam Mixtures

in pure hydrogen (or, conversely, less hydrogen is required to affect the same extent of char hydrodesulfurization). This observation suggests that hydrogen-steam mixtures are more effective than pure hydrogen as far as hydrodesulfurization is concerned. However, there is a second variable in these experiments -- i.e., the extent of char gasification. The extent of char gasification varied between 10 and 20% in the steam-hydrogen mixtures, whereas it varied between 0 and 10% in the pure hydrogen experiments. In order to establish the effect of carbon gasification upon the extent of char hydrodesulfurization, the results of the pure hydrogen experiments are discussed in greater detail below.

In the pure hydrogen runs, the extent of char gasification was varied by changing the pressure (1, 1.5, and 6 atmospheres) and the hydrogenation time (100-1435 minutes). However, the volume of hydrogen employed in all of these experiments was essentially "infinite" as far as any equilibrium limitations upon the extent of char hydrodesulfurization are concerned. Hence, the only variable of significance in the pure hydrogen experiments is the extent of carbon conversion. The extent of char desulfurization, as a function of the extent of char gasification, is presented in Figure 4.9. Notice that a definite relationship exists between the extents of char desulfurization and gasification. However, this is only true for relatively low carbon conversions. Above approximately 8% gasification, the extent of char desulfurization becomes constant (at approximately 20% of the sulfur content of the feed char) and independent of the extent of char gasification. An inspection of Zielke, et al's(132)

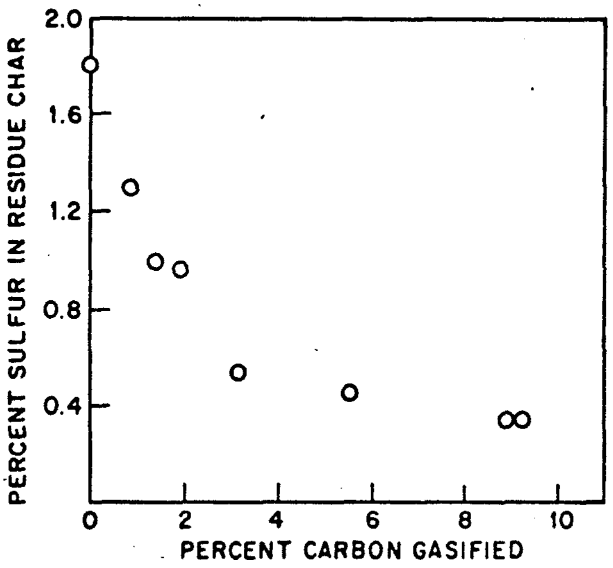

Figure 4.9 The Effect of Char Gasification upon the Extent of Char Hydrodesulfurization

data reveals that a significant fraction of the residual sulfur in the product char was sulfide sulfur.

The above results can be explained as follows: According to the active-site hypothesis, organic sulfur in char is a sulfur species which is chemisorbed at active sites on the char surface. For relatively high surface area materials such as coal chars (100-500 m^2/gram), char conversions of the order of 5% correspond to the removal of 1-2 monolayers of carbon from the char surface. Hence, selective gasification results in a liberation of the chemisorbed sulfur on the surface, thereby circumventing the slow desulfurization kinetics associated with the stable form of sulfur in char. This will be referred to hereafter as the *selective gasification criterion.*

Notice that these results are consistent with the active site hypothesis. In addition, these results explain why several investigators -- i.e., Zielke, et al(132), and Kor(56) -- have observed a relationship between the extents of char desulfurization and gasification.

The above results led to speculation that, provided the selective gasification criterion is satisfied, the kinetics of char hydrodesulfurization are probably equilibrium and material balance rather than kinetically-controlled. To test this hypothesis, all of the fluid-bed char desulfurization data in the literature were analysed. The results of this analysis are presented below.

4.7 Analysis of the Batch Fluid-Bed Hydrodesulfurization Data in the Literature

There are three sets of well-documented fluid-bed desulfurization data in the literature -- i.e.,

1. Zielke, *et al's*(132) Disco char hydrodesulfurization data at 1600°F.
2. Jones'(52) COED char hydrodesulfurization data at 1600°F.
3. Hiteshue's(43) Pittsburgh Seam coal and char hydrodesulfurization data at 800°C.

Unfortunately, the product chars were analysed for forms of sulfur in only one of the above mentioned investigations -- i.e., that of Zielke, *et al*.(132) The three sets of experimental data are, perforce, analyzed below on the basis of reductions in the total, rather than organic sulfur content of the chars.

4.7.1 Consolidation Coal Company's Disco Char Hydrodesulfurization Data at 1600°F

A description of the experimental apparatus and techniques employed by Zielke *et al*(132) has been presented in Section 4.6. The results of their experiments are presented in Table D.20 and Figure 4.8. Also presented in Figure 4.8 are the results of the Equilibrium Model (see Appendix B Case Three). In their steam-hydrogen experiments, the mass of feed char varied between 22 and 219 grams -- i.e., an order of magnitude variation in the mass of feed char employed. Since the hydrogen-steam data presented in Figure 4.8 seem to be reasonably consistent, it seems unlikely that bed depth significantly affects the extent of char hydrodesulfurization realized in Zielke's experiments. In addition, pressure varied between one and six atmospheres. For the same reasons as those mentioned above, pressure does not seem to significantly affect Zielke's results. Hence, it seems reasonable to assume that the extent of char hydrodesulfurization in Zielke's steam-hydrogen experiments is probably equilibrium and material balance rather than kinetically-controlled. The fact that significant deviations (i.e., 15-20%) from the Equilibrium Model occur is, however, not consistent with this hypothesis.

4.7.2 FMC Corporation's COED Char Hydrodesulfurization Data

Jones'(52) batch fluid-bed COED char hydrodesulfurization experiments were performed in a 0.824 inch I.D. fluid-bed. The COED chars employed in these experiments were exposed to temperatures of 1600°F in the COED Process Development Unit for unspecified lengths of time. In his experiments, a weighed sample of char was introduced into the fluid-bed, the bed was fluidized with nitrogen and heated to the desired steady-state temperature. When this temperature was reached, the feedgas was changed from nitrogen to hydrogen. At the end of the experiment, the reactor was dismantled and the char weighed and analysed for weight percent sulfur. The results of Jones' experiments are presented in Table D.4, as well as Figure 4.10. Also presented in Figure 4.10 are the results of the Equilibrium Model (see Appendix B Case 4).

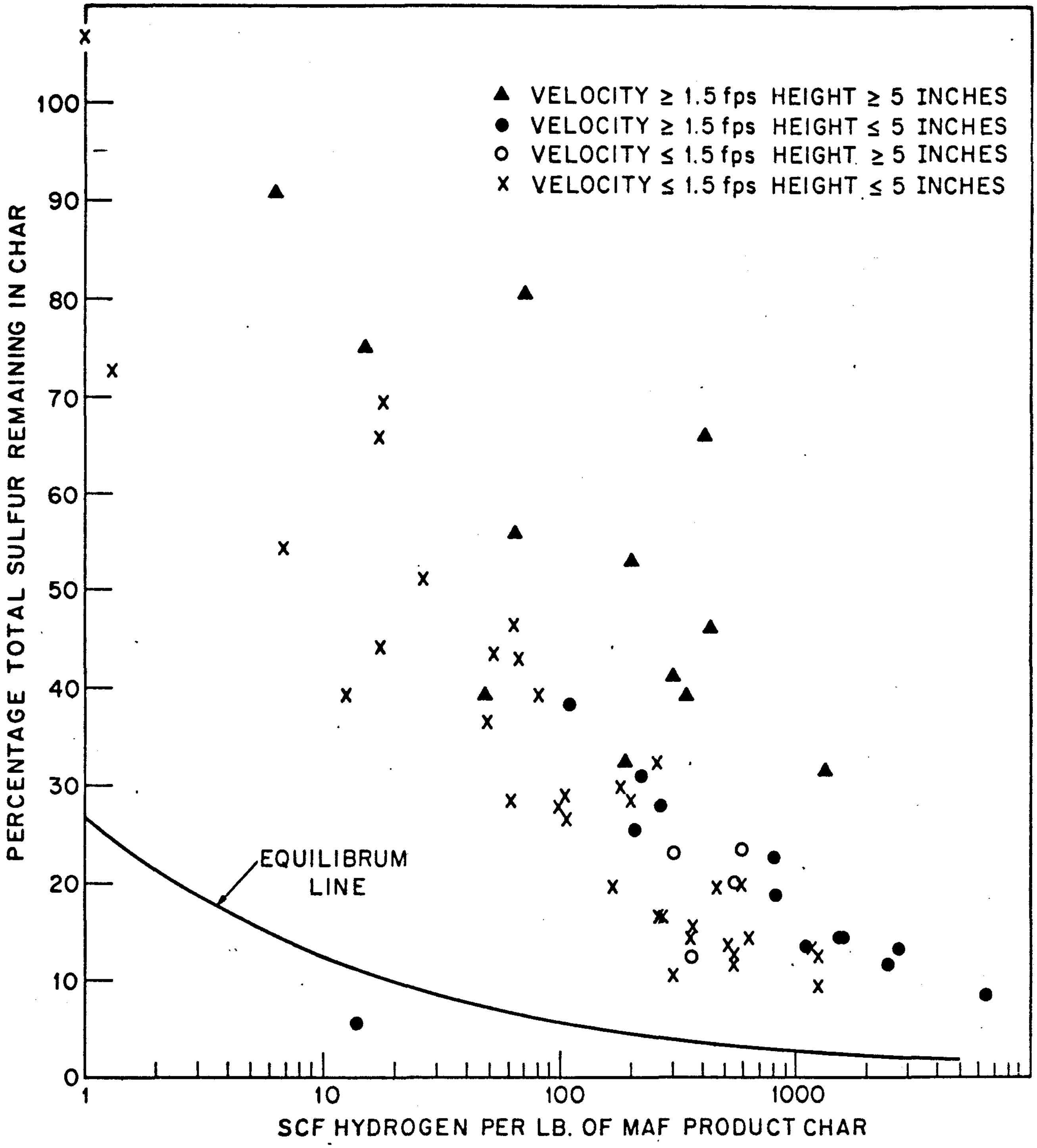

Figure 4.10 FMC Corporation's COED Char Hydrodesulfurization Results at 1600°F

In contrast to Zielke's steam-hydrogen data presented previously, Jones' data presented in Figure 4.10 exhibit a considerable degree of scatter. Jones assumed that this scatter was the result of kinetic limitations upon the rate of char hydrodesulfurization. Gray, et al(36) later modified this explanation, suggesting that the extent of char desulfurization in these experiments is controlled by the rate of desulfurization of sulfide sulfur. However, there is another equally plausible explanation for this scatter in the data. This is discussed below.

The data presented in Figure 4.10 have been arbitrarily divided into four groups according to the following criteria:

Velocity $\geq$ 1.5 fps and Bed Depth $\geq$ 5 inches
Velocity $\geq$ 1.5 fps and Bed Depth < 5 inches
Velocity < 1.5 fps and Bed Depth $\geq$ 5 inches
Velocity < 1.5 fps and Bed Depth < 5 inches

Notice that most of the scatter occurs in association with experiments in which both the bed depth and superficial gas velocity were large -- i.e., greater than 5 inches and 1.5 feet per second respectively. Since such conditions are conducive to the formation of bubbles and slugs in fluid-beds, a plausible explanation for the scatter is that excessive bypassing of the solid by the gas occurred in Jones' high velocity - high-bed depth experiments.

The mean value of the extent of gasification (see Table D.21) is 9.7% -- i.e., substantially greater than the 5% required to satisfy the selective gasification criterion mentioned in Section 4.6. Nevertheless, eleven of the data in Table D.21 fall below this limit. These data are not included in the data presented in Figure 4.11. In addition, none of the

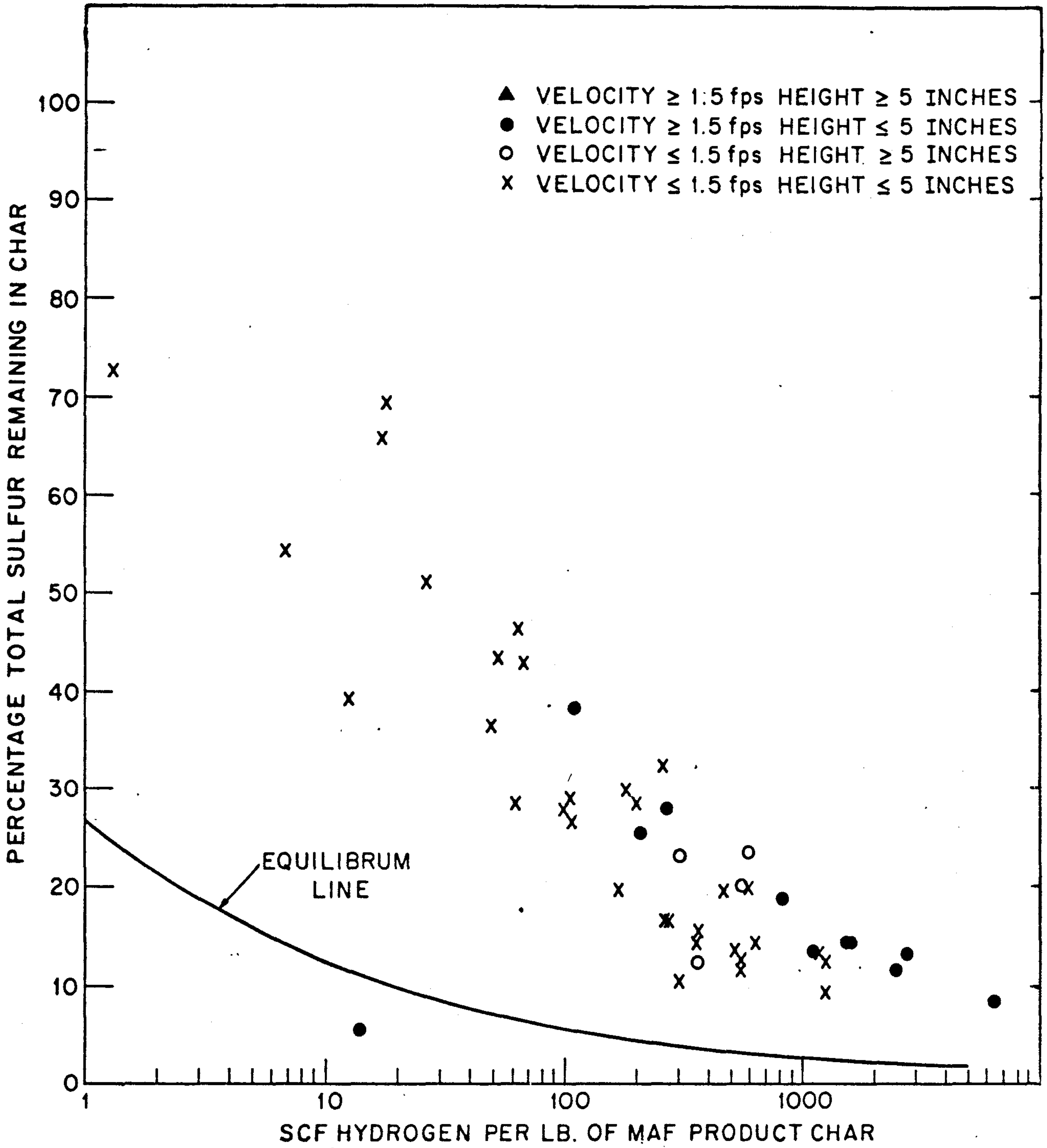

Figure 4.11 Selected Results from FMC Corporation's COED Char Hydrodesulfurization Data

high-velocity high-bed-depth data are presented in Figure 4.11. Notice the marked improvement in the correlation presented in Figure 4.11 when compared with the correlation presented in Figure 4.10.

4.7.3 Hiteshue's Coal and Char Hydrodesulfurization Data

Hiteshue(43) performed coal and char hydrogasification studies in a so-called "hot rod" reactor at 800°C and pressures from 250 to 1000 psig. The coal used in these studies was a Pittsburgh hvab seam coal. The char employed was prepared from this coal by heating it in a continuous stream of helium at 600°C for two hours. The reactor was an electrically-heated length of 5/16" I.D. stainless steel tubing. The experimental procedure which was employed is as follows: Firstly, a porous stainless steel disc was pressed into the tube, an eight gram sample (of coal or char) was placed in the reactor, and a second porous disc was pressed into the tube above the sample. Hydrogen was passed through the reactor at the desired pressure and, once a constant flowrate had been established, the reactor was rapidly heated (in approximately one minute) to 800°C. The reactor was held at this temperature for the desired run time (0-30 minutes), after which it was rapidly cooled to room temperature by spraying it with water. The flow of hydrogen was maintained during the cooling period. At the end of an experiment, the product char was extracted from the reactor and analysed for total sulfur. These analyses, in addition to the analyses of the feed char, are presented in Tables D.22, and D.23, as well as in Figure 4.12. Also presented in Figure 4.12 are the results of the Equilibrium Model (see Appendix B Cases Five and Six).

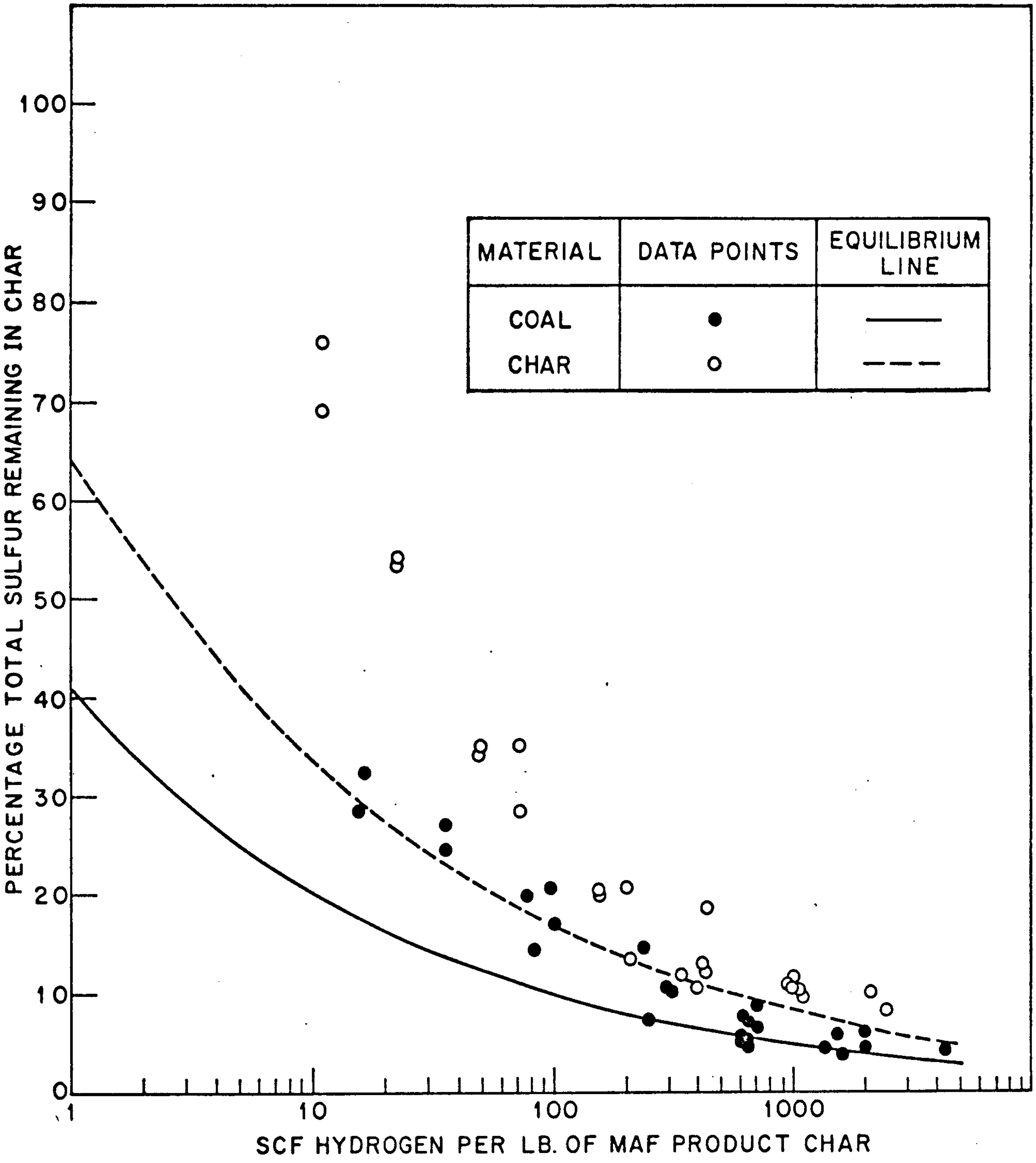

Figure 4.12 Hiteshue's Bituminous Coal and Char Hydrodesulfurization Results at $800^{\circ}C$

4.7.4 Selected Coal and Char Hydrodesulfurization Data

With some exceptions, the data of Zielke, et al (132), Jones (52), and Hiteshue (43) are presented in Figure 4.13. The data excluded, and the reasons for their exclusion, are summarized below:

1. Data from experiments in which char conversions of less than 5% occurred. These data were excluded because they do not satisfy the selective gasification criterion mentioned in Section 4.6. The data excluded on this basis are from experiment numbers:

   34, 41, 42, 43, 44, 45, 46, 69, 70 and 80 in Table D.21

   S-28, S-29, S-30, S-34, and S-35 in Table D.20

   583, 590, 582, and 588 in Table D.22

2. Jones' high-velocity, high-bed-depth data. The data excluded on this basis are from experiment numbers:

   30, 33, 36, 40, 44, 46, 48, 60, 69, 71, 72, and 73 in Table D.21.

Note that only 29 of a total of 144 data points -- i.e., 20.1% -- have been excluded on the basis of the criteria mentioned above. Also presented in Figure 4.13 is the so-called equilibrium envelope. This envelope encompasses the range in the extent of char desulfurization anticipated on the basis of the Equilibrium Model presented in Appendix B Cases 3, 4, 5, and 6.

An examination of Figure 4.13 reveals that considerable differences exist between the results of the Equilibrium Model and the experimental data. In general, the experimental results lie above the envelope predicted by the Equilibrium Model. There are several possible reasons for this discrepancy:

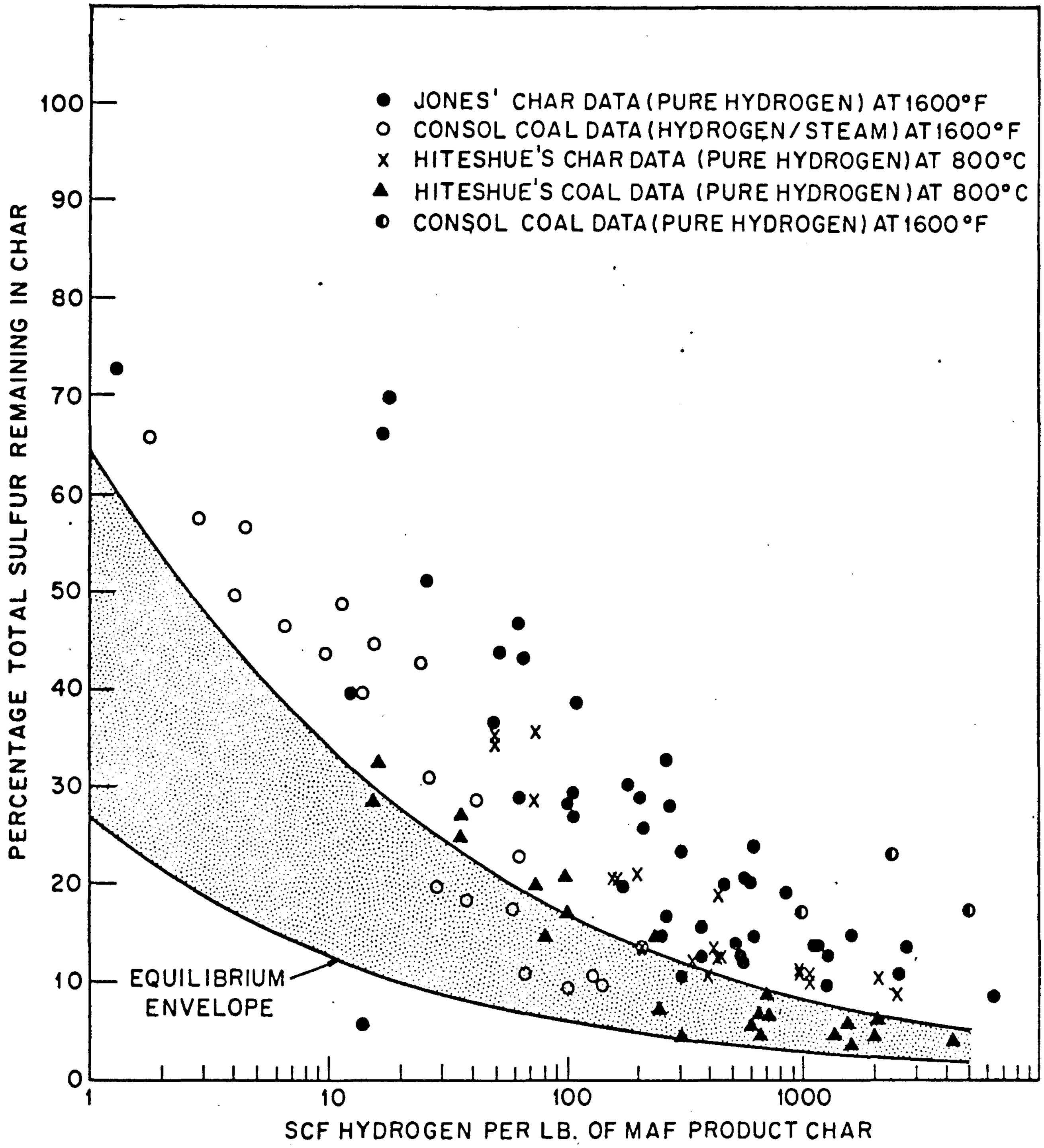

Figure 4.13 Selected Batch Fluid-Bed Coal and Char Hydrodesulfurization Results

1. The rate of char hydrodesulfurization in these experiments is kinetically-controlled, or

2. The rate of char and coal hydrodesulfurization is material balance and equilibrium-controlled, but

   - the model of the fluidized bed apparatus developed in Appendix B is an inadequate description of the experimental reactors employed in Zielke, et al, Jones', and Hiteshue's experimental investigations,

   - the adsorption isotherm developed in Appendix A does not accurately describe the equilibrium distribution of sulfur between the char and gas phases. There are several reasons why this could be true -- e.g., the experimental histories of the chars employed in the adsorption isotherm experiments are different, or

   - the presence of iron sulfides (as well as other inorganic sulfides such as calcium sulfide) in the chars adversely affects the experimentally-observed extent of char desulfurization. The 10-20% difference between the experimental and predicted results could quite conceivably be explained on this basis.

Clearly one is not able to resolve which of the above mentioned factors (if any) is responsible for the difference between the observed and predicted extent of char and coal desulfurization. Resolution of this uncertainty must await the availability of more suitable experimental data.

Nevertheless, in view of the very broad range of experimental conditions which were employed (see Table 4.3), the consistency in the coal and char desulfurization results from three different sources is somewhat surprising. This observation leads the author to the speculative conclusion that, provided the selective gasification criterion is satisfied, there is no reason to believe that the removal of organic sulfur from char in batch fluid-bed reactors is kinetically-controlled. This conclusion if, of course, consistent with Batchelor's(9) pseudo-equilibrium hypothesis. In addition,

Variable	Hiteshue-Coal	Zielke-Char	Hiteshue-Char	Jones-Char	Range
Total Sulfur Concentration in Feed Coal or Char	2.2	1.92-2.35	1.3	2.77-5.52	1.3-5.5
Char Residence Time-Minutes	1-31.0	17.0-1435.0	1-31.0	2.0-360.0	1-1435.0
Total Pressure -- Atmospheres	18-69.	1.0-6.9	18-69.	1.0-7.8	1-69.0
Temperature -- °C	800	871	800	871	800-871
Superficial Gas Residence Time Seconds	2.2[a]	0.09-1.55	2.2	0.07-8.4	0.07-8.4
Superficial Gas Velocity Feet per Second	1.2	0.44	1.2	0.019-2.23	0.019-2.2
Sample Size -- Grams	8	9.33-211.7	8	45.-100	8-211
Char Conversion	30.9-69.8	0.36-23.0	0-44.0	0-47.4	0-69.8
Reactor Diameter -- Inches	5/16	1.5	5/16	0.824[b]	0.31-1.5

Note: (a) Estimated from the reactor length (32 inches) and the superficial gas velocity (1.2 fps).

(b) The inside diameter of a 3/4 inch, schedule 40 stainless steel pipe.

Table 4.3 Conditions Employed in the Batch Fluid-Bed Desulfurization Experiments the above results demonstrate that a suitable choice of hydrodesulfurization conditions can lead to almost complete removal of sulfur from char. Hence, these results are consistent with many such observations in the literature.

4.8 Summary and Conclusions

Experiments have been performed to resolve the uncertainty which surrounds the kinetics of char hydrodesulfurization. These experiments have revealed that *char hydrodesulfurization is a path-dependent process. A* tentative explanation for this path-dependent behaviour is that prolonged exposure of organic sulfur in char to elevated temperatures results in a transformation of the sulfur species on the surface into a more stable form. This is called the *transformation hypothesis*. Results of ESCA experiments, designed to reveal whether or not such a transformation takes place, were inconclusive. However, the ESCA experiments did reveal that (a) the sulfur species on the surface is **not** a sulfide, sulfite or sulfate, and (b) the "chemical environment" of all sulfur atoms on the surface is similar.

An analysis of the batch fluid-bed coal and char hydrodesulfurization data in the literature has revealed that the hydrodesulfurization kinetics of chars which have been pretreated at elevated temperatures for prolonged periods of time can be enhanced by selective gasification of a relatively small fraction of the char during hydrodesulfurization. This is called the *selective gasification criterion*, and is significant because (a) it is consistent with the active site hypothesis, (b) it reveals the reason for the relationship between the extents of char gasification and desulfurization noted by various authors, and (c) it provides a strategy to circumvent practical problems associated with the slow desulfurization kinetics of chars which have been severely pretreated. In addition, it is tentatively concluded that, provided the selective gasification criterion is satisfied, there is no reason to believe that the rate of removal of organic sulfur from char in batch-fluid beds is kinetically-controlled. The latter conclusion is consistent with Batchelor's pseudo-equilibrium hypothesis. Finally, these results demonstrate that a suitable choice of hydrodesulfurization conditions can lead to almost complete removal of organic sulfur from char.

CHAPTER FIVE

SYNTHESIS

As was noted in Chapter One, the existing literature lacks a cohesive framework on which to structure one's understanding of the chemistry of sulfur in char. The active site hypothesis is a first step in the development of such a framework. Unfortunately, there is little information in the literature to substantiate this hypothesis. However, it has been noted(46,127) that the chemistries of oxygen and sulfur in char are analogous. In addition, the chemistry of oxygen in char has been extensively investigated(24,88,89,91,113,115). The chemistry of oxygen, and the analogy between it and the chemistry of sulfur in char are reviewed in this chapter. It will be shown that the use of this analogy enables one to integrate much of what is known about the chemistry of sulfur in char into a cohesive and consistent framework.

5.1 Review of the Chemistry of Oxygen in Carbonaceous Materials

It has long been known that oxygen reacts with carbon to form a "carbon-oxygen complex". Rheade and Wheeler(100) were first to notice that: " ... carbon, at all temperatures up to 900°C and probably above that temperature, has the power of pertinaciously retaining oxygen". "This oxygen cannot be removed by exhaustion alone, but only by increasing the temperature of the carbon during exhaustion". "When quickly released in this manner it appears, not as oxygen, but as carbon monoxide and carbon dioxide". They thought that, during combustion " ... each oxygen molecule that comes into collision with the carbon becomes 'fixed' insofar as it is rendered incapable of further progress by the attraction of several carbon molecules". Similar observations were made by Langmuir(60), who noted that " ... a plausible guess as to (the constitution of the carbon-oxygen complex) is that it consists of oxygen atoms chemically combined with carbon atoms which form the surface of the filament".

5.1.1 The Mechanism of Carbon Oxidation

A review of the literature regarding the mechanism of carbon oxidation has been presented by Von Fredersdorff and Elliott(121). They noted that " ... the general conclusion is that the mechanism of oxidation must involve preferential attack of the carbon lattice at specific areas or active sites, also termed reactive centers". They suggested that the mechanism of carbon oxidation may be represented by:

$$C_f + O_2 \rightleftarrows [C\text{-}O] + O(ads) \qquad [5.1]$$

$$C_f + O(ads) \rightleftarrows [C\text{-}O] \qquad [5.2]$$

$$[C\text{-}O] \rightleftarrows CO + nC_f \qquad [5.3]$$

and

$$C_f \rightleftarrows C(inactive) \qquad [5.4]$$

where C_f denotes an active site on the carbon surface capable of reaction, [C-O] represents chemisorbed atomic oxygen, CO is gaseous carbon monoxide, O(ads) is a free radical of oxygen and C(inactive) is an active site which is rendered inactive as a result of thermal annealing. Similar mechanisms were suggested for the gasification of carbon with carbon dioxide -- i.e.,

$$C_f + CO_2 \rightleftarrows [C\text{-}O] + CO \qquad [5.5]$$

and steam -- i.e.,

$$C_f + H_2O \rightleftarrows [C\text{-}O] + H_2 \qquad [5.6]$$

Both of the above oxygen-exchange reactions are accompanied by the carbon-oxygen complex desorption reaction:

$$[C\text{-}O] \rightleftarrows CO \qquad [5.7]$$

The total concentration of active sites (C_t) is equal to the sum of all the unoccupied (C_f) and occupied sites ([C-O]) -- i.e.,

$$C_t = C_f + [C\text{-}O] \qquad [5.8]$$

Von Fredersdorff and Elliott(121) have shown that, assuming C_t is constant -- i.e.,

$$C_t = K \qquad [5.9]$$

the above mechanisms for oxygen, steam and carbon dioxide can be reduced to:

- o Langmuir-type adsorption isotherms for the adsorbate in question, and
- o Rate expressions for char gasification such as

$$r_{CO_2} = kP_{CO_2}/\{1 + aP_{CO} + bP_{CO_2}\} \qquad [5.10]$$

where r_{CO_2} is the rate of char gasification in carbon dioxide, P_{CO_2} is the partial pressure of carbon dioxide, P_{CO} is the partial pressure of carbon monoxide, and k, a and b are constants. The latter approach has been adopted by Ergun(27) in the analysis of his carbon dioxide gasification data.

Like Ergun, Grabke(33,34) assumed that carbon dioxide gasification proceeds according to the reactions:

$$CO_2 \quad + \quad C \quad \underset{k_1'}{\overset{k_1}{\rightleftarrows}} \quad [C\text{-}O] \quad + \quad CO \qquad [5.5]$$

and

$$[C\text{-}O] \quad \underset{k_2'}{\overset{k_2}{\rightleftarrows}} \quad CO \qquad [5.7]$$

He noted that, under the experimental conditions which he employed, the rate of the reverse reaction in [5.7] is negligible. In two separate experiments, he directly measured the rates of the forward reactions in [5.5] and [5.7]*. The results of his experiments revealed that the rates of the forward and reverse reactions in [5.5] are approximately two orders of magnitude greater than the rate of the forward reaction in [5.7]. In other words, the rate of the forward reaction in [5.7] controls the rate of char gasification, while reaction [5.5] is at pseudo-equilibrium under the experimental conditions which he employed. Hence:

$$v_1 \quad \simeq \quad v_1' \quad \gg \quad v_2 \qquad [5.11]$$

where v_1, v_1' and v_2 are the reaction rates of the forward and reverse reactions in [5.5] and v_2 is the reaction rate of the forward reaction in [5.7].

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* Noting that, at steady-state, the rate of the forward reaction in [5.7] -- i.e., v_2 -- is one half the rate of formation of carbon monoxide, Grabke measured v_2 by measuring the rate of formation of carbon monoxide. The rate of the forward reaction in [5.5] was measured using a radioactive tracer technique.

5.1.2 A Model for the Equilibrium Concentration of Oxygen in Char

The reader should note that, because of reaction [5.7], char oxidation is a dynamic process. Hence, the equilibrium concentration of oxygen in char cannot be measured using the techniques employed in Chapter Three (i.e., measurement of the concentration of sulfur in char at the equilibrium condition). Instead, an expression for the equilibrium concentration of oxygen in char must be inferred from kinetic measurements like those presented by Grabke(34). This aim is pursued below.

In analysing his data, Grabke noted that his kinetic data were *not consistent with the Langmuir-type adsorption isotherm employed by Ergun(27).* To circumvent this inconsistency, he assumed that:

$$v_1 = k_1(a_o)\, P_{CO_2} \qquad [5.12]$$

and

$$v_1' = k_1'(a_o)\, P_{CO} \qquad [5.13]$$

where $k_1(a_o)$ and $k_1'(a_o)$ are rate coefficients which are functions of the activity of oxygen (a_o) on the surface. Notice that $k_1(a_o)$ can be computed from measured values of v_1 and P_{CO_2}. An analysis of his experimental data revealed that, for a thirty-fold variation in the partial pressure ratio (P_{CO_2}/P_{CO}), $k_1(a_o)$ can be described by an equation of the form:

$$k_1(a_o) = z_1[P_{CO_2}/P_{CO}]^{-m} \quad ; m \geq 0 \qquad [5.14]$$

where z_1 is the rate constant associated with the forward reaction in equation [5.5]. *Grabke was unable to explain this result.*

However, if one allows that the chemistries of oxygen and sulfur in char are analogous, a plausible explanation for the relationship noted in [5.14] emerges. Assuming that (a) the equilibrium concentration of oxygen in char can be described by a Freundlich Isotherm, and (b) the rate of the reverse reaction in [5.5] is proportional to the concentration of surface oxide in the char:

$$k_1'(a_0) = xz_1'[P_{CO_2}/P_{CO}]^y \quad ; y \leq 1 \qquad [5.15]$$

where z_1' is the rate constant of the reverse reaction in [5.5] and x and y are parameters which characterize the adsorption isotherm. Combining equations [5.11], [5.12], [5.13] and [5.15] yields:

$$k_1(a_0) = xz_1'[P_{CO_2}/P_{CO}]^{-(1-y)} \quad ; (1-y) \geq 0 \qquad [5.16]$$

Notice that equation [5.16] is functionally-identical to equation [5.14] Hence, it seems reasonable to conclude that the *equilibrium concentration of oxygen in char is better described by a Freundlich rather than a Langmuir Isotherm.*

5.1.3 The Kinetics of Char Oxidation and Gasification

The preceding discussions reveal that, while carbon dioxide gasification proceeds via the formation of a carbon-oxygen complex, the rate-controlling mechanism involves desorption of the complex according to reaction [5.7]. Von Fredersdorff and Elliott(121) suggest that, in addition to carbon dioxide gasification, combustion and steam gasification also proceed via the formation of a carbon-oxygen complex. For example, in the case of steam gasification:

$$H_2O + C \rightleftarrows [C\text{-}O] + H_2 \qquad [5.6]$$

Notice that a combination of reactions [5.5] and [5.6] yields the Water Gas Shift Reaction:

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad [5.17]$$

where the equilibrium constant (K_w) for this reaction is given by:

$$K_W = P_{CO_2}P_{H_2}/\{P_{CO}P_{H_2O}\} \qquad [5.18]$$

Grabke(34) reasoned that, if the rate-controlling mechanisms in steam and carbon dioxide gasification are the same (i.e., the same carbon-oxygen complex is formed in both cases), the rates of gasification in steam and carbon dioxide should be the same when:

$$P_{CO_2}/P_{CO} = K_W P_{H_2O}/P_{H_2} \qquad [5.19]$$

i.e., when the concentrations of the carbon-oxygen complex in the CO_2/CO and H_2O/H_2 systems are identical. Grabke has experimentally verified that this is true. Hence, it seems that *combustion, carbon dioxide gasification, steam gasification and the Water Gas Shift reaction all proceed via the formation of the same carbon-oxygen surface complex. In addition, the kinetics of combustion, and steam and carbon dioxide gasification are probably all controlled by the rate of desorption of this complex.* Consequently, a good grasp of the nature and properties of the carbon-oxygen complex is essential if the chemistry of oxygen in char is to be properly understood.

5.1.4 Concentration of Unpaired Electrons in Char and the Active Site Hypothesis

The development of Electron Spin Resonance Spectroscopy (ESR) has enhanced our understanding of the nature of the carbon-oxygen complex. ESR is an extremely sensitive and direct technique for studying the concentration of unpaired electrons (free radicals) in gases, liquids and solids. This technique has been used to study the concentration of unpaired electrons in various types of carbonaceous materials -- i.e., graphite, sugar chars and activated carbons(6,18,19,41,48,49,73,111,119). These studies have revealed that, upon carbonization, a large number of unpaired electrons is "trapped" in carbonaceous materials. The consensus of opinion in the literature is that these unpaired electrons arise as a result of bond breakage around condensed carbon rings, and at dislocations and other imperfections in the crystalline lattice. Exposure to temperatures in excess of 600°C leads to changes in the crystalline structure and, hence, to a decrease in the concentration of unpaired electrons.

The concentration of unpaired electrons is of interest in this investigation because it gives rise to paramagnetism. In addition, exposure of chars to paramagnetic gases or solutions of paramagnetic salts leads to a substantial decrease in the concentration of unpaired electrons in char(49). In other words, these results suggest that paramagnetic gases (e.g., oxygen) are adsorbed at active sites (i.e., the location of unpaired electrons) in the char matrix. Unfortunately, this hypothesis has not been adequately tested (i.e., a 1:1 correspondence between the number of oxygen atoms adsorbed and the decrease in the number of unpaired electrons in char has not been demonstrated). However, the results of Puri(90,93,96) lend credence to this hypothesis. He used a "bromine value"* as his index of the degree of surface unsaturation, and concluded that "... oxygen and bromine are fixed at the same unsaturated sites, and that the amount of unsaturation in a charcoal is a definite quantity".(90) Further, Puri(96) suggested that "... the unpaired spin centers are associated with unsaturated sites as measured by the bromine value.

While additional experiments are required to demonstrate the link between the concentration of unpaired electrons on char and Puri's bromine value, it seems reasonable to conclude that *oxygen is chemisorbed at active sites in char, and that these active sites are situated at the location of unpaired electrons in the char matrix*. However, there is reason to believe that there is more than one form of organically-bound oxygen in char. This possibility is discussed below.

5.1.5 The Forms of Organically-bound Oxygen in Char.

In investigating the nature of the carbon-oxygen complex, Puri(91) suggested that "... oxygen complexes with carbon are capable of evolving carbon dioxide (CO_2-complex) and carbon monoxide (CO-complex) ...". Thus, Puri subscribed to the hypothesis that there are two forms of oxygen in char. The results of Ingram's ESR experiments(6,48,49) strongly support this hypothesis. The first form is viewed as a purely physical interaction with the surface.

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* The amount of bromine adsorbed on char from an aqueous solution of bromine.

The second consists of an actual pairing, or strong localization of the unpaired electrons in the char by the incoming unpaired electrons in oxygen. However, Ingram has noted that, if left for a long time at room temperature, an irreversible change in the former species takes place to form the latter. In support of these observations, Selwood(107) noted that, while molecular oxygen is paramagnetic, "combined oxygen" is diamagnetic. He reviewed the results of several investigators who exploited this difference in magnetic susceptibility to measure the relative concentrations of physically and chemisorbed oxygen species on char surfaces. Using a modified Guoy-balance technique, Juza(53) observed a progressive decrease in the concentration of physically-adsorbed oxygen with increases in temperature and residence time of the adsorbate on the char surface. Hence, it seems that, upon exposure to oxygen, *a weakly-bonded oxygen species is formed on char surfaces which gradually changes into a more stable surface oxide.* Unfortunately, a more detailed description of the oxygen species on the surface is not available at present.

Having reviewed the chemistry of oxygen in carbonaceous materials in some detail, the next step is to illustrate the analogy between the chemistries of oxygen and sulfur in char. This is pursued in Section 5.2.

5.2 The Analogy between the Chemistries of Oxygen and Sulfur in Char.

The chemistries of oxygen and sulfur in char are analagous in that sulfur and oxygen are members of the same group of elements in the periodic table (Group VI). In addition, molecular oxygen and sulfur are unusual in that both are paramagnetic -- i.e., both possess unpaired electrons(121). However, there are several analogies between the chemistries of oxygen and sulfur in char of a more specific nature. These analogies are outlined in the subsections which follow below.

5.2.1 The Active Site Hypothesis

Puri(96) sulfided two high-temperature chars (1200°C-outgassed charcoal and sugar charcoal) with sulfur and hydrogen sulfide. The resulting chars were subsequently exposed to hydrogen at various temperatures. This procedure resulted in the partial removal of sulfur from the char, the extent being a function of the hydrogen treatment temperature. Using, as in the case of oxygen, the bromine value as his index of the degree of surface unsaturation, he showed that: "... with the elimination of sulfur, an *equivalent* number of unsaturated sites are generated". Hence, it seems that sulfur, like oxygen, and bromine are fixed at the same unsaturated sites. Therefore, it seems reasonable to assume that *oxygen and sulfur are adsorbed at the same active sites in char, and that these sites are situated at the location of unpaired electrons in the char matrix*. ESR experiments, in which sulfur rather than oxygen is adsorbed, should be performed to establish whether or not the concentration of unpaired electrons in char and the amount of sulfur adsorbed are related.

5.2.2 The Nature of the Adsorption Isotherm.

The analysis presented in Section 3.2.3 has shown that the

Freundlich Isotherm is the best model to describe char sulfidation data. In addition, the analysis of Grabke's kinetic data (see Section 5.1.2) has shown that the Freundlich Isotherm also accurately describes the equilibrium concentration of oxygen in char. Consequently, the chemistries of oxygen and sulfur in char are analogous in that the same model can be used to describe the equilibrium concentration of the adsorbate in char.

5.2.3 The Transformation Hypothesis

The arguments presented in Section 5.1.5 suggest that, upon exposure to oxygen, a weakly-bonded oxygen species is formed in char which gradually changes into a more stable surface oxide. On the other hand, it was suggested in Section 4.4 that the reason for the path-dependent nature of char hydrodesulfurization is that a similar transformation in the carbon-sulfur complex takes place. Unfortunately, ESCA experiments to establish whether or not such a transformation takes place (see Section 4.5) were unsuccessful.

5.2.4 Moisture Adsorption

The moisture adsorption characteristics of char has been the subject of several investigations in the literature(3,4,26,65,77,97,113,123). The consensus of opinion is that moisture adsorption takes place at the location of carbon-oxygen species on the char surface. In other words, the equilibrium concentrations of moisture and oxygen in char are related. In view of the analogies between the chemistries of oxygen and sulfur in char, it is not too surprising that a similar relationship has been observed between the concentrations of moisture and sulfur in char (see Figure 3.10).

5.2.5 The Mechanisms of Char Oxidation and Sulfidation.

The discussion in Section 5.1.3 leads one to the conclusion that char combustion, and steam or carbon dioxide gasification all proceed via the formation of the same carbon-oxygen surface species. These oxygen-exchange reactions can be represented as:

$$O_2 + C \rightleftarrows 2[C\text{-}O] \quad ; [C\text{-}O]_e = \Psi[P_{O_2}] \qquad [5.20]$$

$$CO_2 + C \rightleftarrows [C\text{-}O] + CO \quad ; [C\text{-}O]_e = \Psi[P_{CO_2}/P_{CO}] \qquad [5.5]$$

and

$$H_2O + C \rightleftarrows [C\text{-}O] + H_2 \quad ; [C\text{-}O]_e = \Psi[P_{H_2O}/P_{H_2}] \qquad [5.6]$$

where $[C\text{-}O]_e$ represents the equilibrium concentration of oxygen in char and Ψ represents a general functional dependance (probably a Freundlich Isotherm). Notice the similarity between the above reactions and the overall reaction employed to describe char sulfidation -- i.e.,

$$H_2S + C \rightleftarrows [C\text{-}S] + H_2 \quad ; [C\text{-}S]_e = \Psi[P_{H_2S}/P_{H_2}] \qquad [5.21]$$

where $[C\text{-}S]_e$ represents the equilibrium concentration of organic sulfur in char. It seems reasonable to anticipate that an analogous set of char sulfidation reactions may exist -- i.e.,

$$S_2 + C \rightleftarrows 2[C\text{-}S] \quad ; [C\text{-}S]_e = \Psi[P_{S_2}] \qquad [5.22]$$

$$CS_2 + C \rightleftarrows [C\text{-}S] + CS \quad ; [C\text{-}S]_e = \Psi[P_{CS_2}/P_{CS}] \qquad [5.23]$$

and

$$COS + C \rightleftarrows [C\text{-}S] + CO \quad ; [C\text{-}S]_e = \Psi[P_{COS}/P_{CS}] \qquad [5.24]$$

The existence of such reactions would explain why several authors -- e.g., Wibaut(126,127,128,129), Huff(44,46,47) and Puri(92,94,95,96) have observed that sulfur species other than hydrogen sulfide react to form, or are produced via the formation of, a carbon-sulfur complex.

The experiments of Ratcliffe(99) are of interest in this regard. In his experiments, lignite chars were sulfided with sulfur dioxide, hydrogen sulfide, carbon disulfide or elemental sulfur. The chars were subsequently analysed in an ESCA apparatus similar to that mentioned in Section 2.1.3. Binding energy spectra for these chars revealed a sulfur $2p_3$ electron peak at the same binding energy in all cases. This led Ratcliffe to conclude that the same carbon-sulfur complex is formed, irrespective of the sulfur species responsible for char sulfidation. Ratcliffe also concluded that the carbon-sulfur complex in char is not a sulfide. Hence, these results, and the results discussed in Section 4.5, are not consistent with Puri's (95) conclusion that sulfide sulfur is formed in chars upon exposure to hydrogen sulfide. In addition, these results are not consistent with Puri's conclusion that sulfoxide and sulfone groups are formed in char upon exposure to sulfur dioxide. Instead, the above results, and the analogy between the chemistries of sulfur and oxygen in char lead one to conclude that the same carbon-sulfur complex is formed in char, irrespective of the sulfur species responsible for char sulfidation.

5.3 Implications of the Analogy

While many of the arguments presented thus far remain unproven, the extent of the analogy between the chemistries of oxygen and sulfur in char lends credence to the active site and transformation hypotheses. In addition, since organic sulfur in char is almost certainly a surface species, there is little reason to doubt the validity of the selective gasification criterion. Furthermore, a clearer understanding of the observed relationship between the concentrations of moisture and sulfur in char (see Section 3.5) emerges from the discussion presented in Section 5.2.4. However, there are several other implications worthy of mention.

5.3.1 A General Correlation of Char Sulfidation Data

The above arguments, as well as the observation (see Section 3.1) that the equilibrium concentration of organic sulfur in char is a function of the partial pressure ratio (P_{H_2S}/P_{H_2}), might lead one to suspect that the mechanism of char sulfidation involves adsorption of elemental sulfur on the char. Such a mechanism was first suggested by Powell$^{(84)}$. He hypothesized that gaseous elemental sulfur, formed as a result of the reaction:

$$2H_2S \rightleftarrows 2H_2 + S_2 \qquad [5.25]$$

is responsible for the formation of organic sulfur in char via the reaction:

$$S_2(g) \rightleftarrows 2[C\text{-}S] \qquad [5.26]$$

However, there are several equally plausible char sulfidation mechanisms which lead to a dependance of the adsorption isotherm upon the partial pressure ratio (P_{H_2S}/P_{H_2}). For example, Wibaut(127) suggested that, because the equilibrium gas phase concentration of elemental sulfur is very small in the H_2/H_2S system at the temperatures in question (i.e., 10^{-8} to 10^{-10} atmospheres), a more plausible char sulfidation mechanism is:

$$H_2S \quad + \quad C \quad \rightleftarrows \quad [C\text{-}S] \quad + \quad H_2 \qquad [5.21]$$

Unfortunately, the author is not aware of information which could be used to establish which (if any) of the above mechanisms is responsible for char sulfidation. Consequently, the mechanism of, and the adsorbate responsible for,char sulfidation remain uncertain.

Nevertheless, *since the equilibrium concentration of organic sulfur in char is governed by thermodynamic rather than mechanistic criteria, one can think of elemental sulfur as being the adsorbate even though this might not be strictly correct from a mechanistic standpoint.* In addition, the thermodynamic requirements of the reaction:

$$2H_2S \quad \rightleftarrows \quad 2H_2 \quad + \quad S_2 \; ; \; K_{p_{25}} = P_{S_2}P_{H_2}^2/P_{H_2S}^2 \qquad [5.25]$$

yield

$$P_{S_2} \quad = \quad K_{p_{25}}[P_{H_2S}/P_{H_2}]^2 \qquad [5.26]$$

where $K_{p_{25}}$ is the equilibrium constant for reaction [5.25]. Hence, one can replace the partial pressure ratio (P_{H_2S}/P_{H_2}) with P_{S_2} in a correlation of char sulfidation data. However, one must resist the temptation to draw mechanistic conclusions from the use of such a correlation.

P_{S_2} has (thus far) not been employed as the correlation parameter because the concentration of elemental sulfur is not easily measured in the H_2/H_2S system. Hence, the use of P_{S_2} as the correlation parameter demands that one calculate, from measured values of P_{H_2S} and P_{H_2}, the partial pressure of elemental sulfur via equation [5.26]. This unavoidably introduces an additional parameter ($K_{p_{25}}$) into the data correlation.

On the other hand, there is a potentially significant advantage associated with the use of P_{S_2} as the correlation parameter. At equilibrium, the activity of sulfur on the surface and the partial pressure of gaseous elemental sulfur are related -- i.e.,

$$P_{S_2} \quad = \quad \phi(a_{[C-S]}) \qquad [5.27]$$

where $a_{[C-S]}$ represents the activity of sulfur on the surface, and ϕ represents a general functional dependence. Futhermore, the gas phase concentrations of sulfur species other than hydrogen sulfide must satisfy the thermodynamic requirements of reactions similar to that of [5.25] -- e.g.,

$$CS_2 \rightleftarrows C + S_2 \; ; \; K_{p_{28}} = P_{S_2}/P_{CS_2} \qquad [5.28]$$

$$2COS \rightleftarrows 2CO + S_2 \; ; \; K_{p_{29}} = P_{S_2}[P_{CO}/P_{COS}]^2 \qquad [5.29]$$

and

$$2SO_2 \rightleftarrows 2O_2 + S_2 \; ; \; K_{p_{30}} = P_{S_2}[P_{O_2}/P_{SO_2}]^2 \qquad [5.30]$$

where K_{p_i}; i=28,29,30, is the equilibrium constant for reaction [5.i]. Combining equations [5.26], [5.27], [5.28], [5.29] and [5.30] yields:

$$\phi(a_{[C-S]}) = P_{S_2} = K_{p_{25}}[P_{H_2S}/P_{H_2}]^2 = K_{p_{28}}P_{CS_2} = K_{p_{29}}[P_{COS}/P_{CO}]^2 = K_{p_{30}}[P_{SO_2}/P_{O_2}]^2 \quad [5.31]$$

In other words, one should be able to correlate char sulfidation data for a variety of sulfur species on a single isotherm in which P_{S_2} is used as the correlation parameter. Such a compression of data would be useful from a practical point of view.

Curran(22), who first suggested the latter approach, has presented the author with some unpublished char sulfidation data which can be used to test the latter hypothesis. A few words about the generation of this data are justified at this stage. Two sets of experiments were performed -- i.e., (a) a set of experiments in which a mixture of hydrogen, hydrogen sulfide and helium was passed through a bed of char at 1880°F, and (b) a single experiment in which a mixture of six mole percent sulfur dioxide in nitrogen was used. The char employed in these experiments was derived from a Pittsburgh Seam coal, carbonized in the low-temperature Disco process and subsequently partially gasified in steam at 1700°F. The chars were pretreated in the fluid-bed reactor by fluidizing with hydrogen for thirty minutes prior to admission of the reactant gas. The results of these experiments are presented in Table D.24 and Figure 5.1. Also presented in Figure 5.1 are (a) the results of Batchelor's Arkwright char sulfidation experiments at 1600°F (see Table D.7) and (b) the HYDRANE HY-128

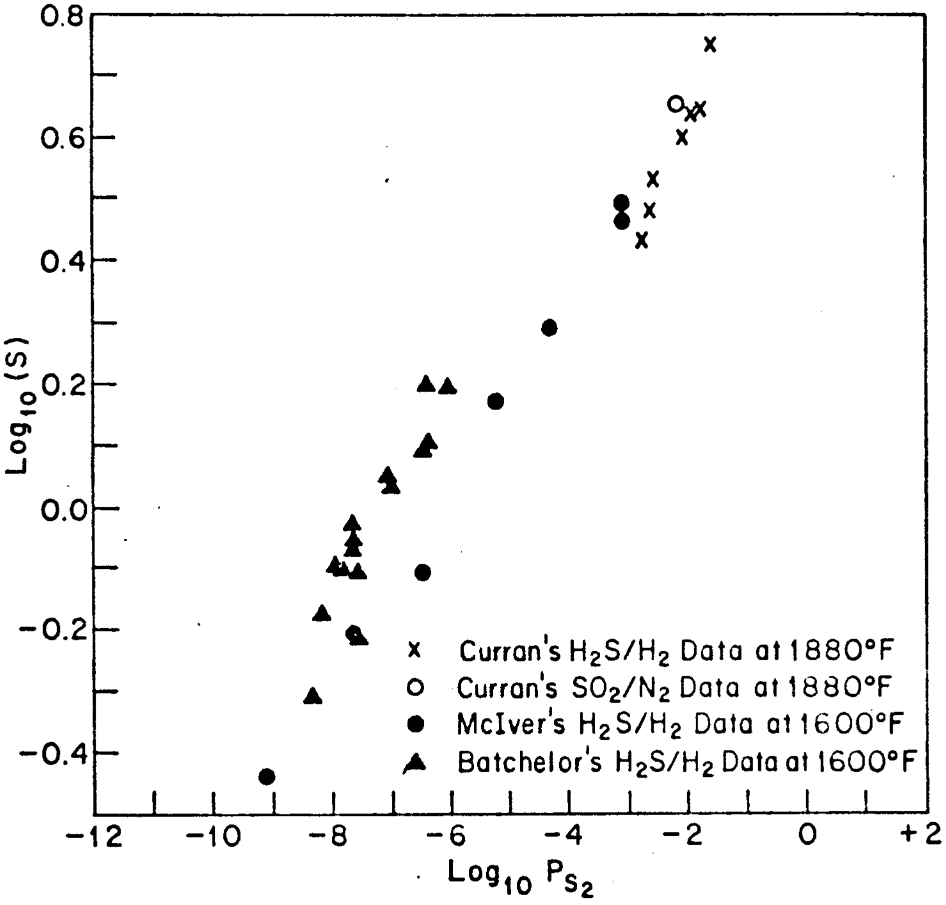

Figure 5.1 An Alternative Correlation of Char Sulfidation Data

char sulfidation results at 1600°F (see Table D.7). Notice that:

- Curran's hydrogen sulfide and sulfur dioxide sulfidation data are consistent, and
- while some scatter exists in the data, the results of three separate investigations of the equilibrium sulfidation characteristics of bituminous coal char are consistent over a very wide range (eight orders of magnitude) in the partial pressure of elemental sulfur.

Unfortunately, only one data for sulfur dioxide (see Table D.24 or Figure 5.1) is presently available to support this alternative method of correlating char sulfidation data. Nevertheless, the preceding arguments do suggest that further investigation of this type of data correlation is potentially rewarding.

5.3.2 The Effect of Temperature upon the Adsorption Isotherm

The fraction of active sites on the char surface which are occupied by sulfur (Θ) is defined by the following equation:

$$\Theta = S/k_o \qquad [A.4]$$

where S = concentration of organic sulfur in char, and

k_o = "concentration" of active sites in char.

Rearranging yields:

$$S = k_o \Theta \qquad [5.32]$$

Notice that S is the product of k_o and Θ. The relevance of this will become apparent later.

Ingram(49) performed ESR experiments which are of interest here. He noted that, upon carbonization in the absence of oxygen, the concentration of unpaired electrons in carbonaceous materials (active sites) in carbonaceous materials passes through a maximum at 500-600°C, and decreases thereafter. In other words, the concentration of active sites in char (k_o) is a function of the maximum pretreatment temperature (T_p) -- i.e.,

$$k_o = \xi(T_p) \qquad [5.33]$$

where ξ represents a general functional dependence. In addition, Ingram's(49) results imply that:

$$[\delta \ln(\xi)/\delta T_p] \leq 0 \qquad [5.34]$$

The latter expression will be used later. It is important to bear in mind that k_o and, hence, S are functions of T_p. Θ is also a temperature-dependent parameter. However, Θ is a function of the sulfidation temperature (T_s) -- i.e.,

$$\Theta = \Xi(T_s) \qquad [5.35]$$

5.3.2.1 Sulfidation Temperature

In the experiments mentioned in Section 3.3, the pretreatment temperature (T_p) was held constant at 900°C (1632°F), while the sulfidation temperature (T_s) varied between 1200 and 1600°F. These experiments revealed that the equilibrium concentration of organic sulfur in char *increases* as temperature *increases*. However, for most adsorption equilibria, the equilibrium concentration of adsorbate on the surface *decreases* as temperature *increases*(40). In retrospect, an entirely plausible explanation for this apparent inconsistency has emerged. A Freundlich Isotherm, of the form:

$$\Theta = [a_o P]^{RT_s/\alpha q_m} \quad ; a_o P \leq 1 \qquad [5.36]$$

has been used (see Appendix A and Section 3.2.3) to describe char sulfidation data, where:

P = partial pressure of the adsorbate in question,
a_o = reciprocal of P at $\Theta = 1$,
R = universal gas constant; 1.987 cal./g.mol.^oK.
q_m = heat of adsorption at $\Theta = 0$; cal./g.mol.

and α is a constant which depends upon the nature of the adsorption process. If the adsorbate is dissociatively adsorbed, α is equal to two, whereas if the process is non-dissociative, it is equal to unity. Combining [5.32] and [5.36] yields:

$$S = k_o[a_oP]^{RT_s/\alpha q_m} \quad ; a_oP \leq 1 \qquad [5.37]$$

Differentiating yields:

$$[\delta \ln(S)/\delta T_s]_P = \ln(a_oP)R/\alpha q_m \qquad [5.38]$$

Since $a_oP \leq 1$

$$[\delta \ln(S)/\delta T_s]_P \leq 0 \qquad [5.39]$$

Consequently, [5.36] predicts that, at constant P, S should decrease with increasing T_s. This is consistent with that which is normally observed$^{(40)}$. However, this is not consistent with the experimental results mentioned in Section 3.3.

In these experiments, the partial pressure ratio (P_{H_2S}/P_{H_2}) rather than P was held constant. To develop a relationship between S and the partial pressure ratio, one must, once again, address the question of the nature of the adsorbate in the H_2S/H_2 system. As was noted previously, one can think of elemental sulfur as being the adsorbate even though this is not necessarily correct from a mechanistic standpoint. Hence:

$$P = P_{S_2} \qquad [5.40]$$

At equilibrium, the gas phase concentration of elemental sulfur is given by [5.26]. Substituting [5.26] and [5.40] into [5.36] yields:

$$S = k_o\{a_o K_{p_{25}} [P_{H_2S}/P_{H_2}]^2\}^{RT_s/\alpha q_m} \qquad [5.41]$$

Values of $K_{p_{25}}$ are obtained from [A.23] and are presented below:

Temperature(^oF)	Equilibrium Constant(atm.)
1200	$8.24.10^{-6}$
1600	$9.10.10^{-4}$

Upon substitution into equation [5.26], these values reveal that the partial pressure of the adsorbate (P) increases, at constant P_{H_2S}/P_{H_2}, by two orders of magnitude in the 1200-1600^oF temperature interval. Because of this large change, [5.41] predicts that S increases with increasing temperature -- i.e.,

$$[\delta \ln(S)/\delta T_s]_{P_{H_2S}/P_{H_2}} \geq 0 \qquad [5.42]$$

Thus, a clearer understanding emerges for the apparently inconsistent behaviour of sulfur adsorption with temperature. The reason is that, in the experiments mentioned in Section 3.3, the partial pressure ratio (P_{H_2S}/P_{H_2}) rather than the partial pressure of the adsorbate (P) was held constant. Bearing this distinction in mind, the results presented in Section 3.3

are entirely consistent with that which is encountered in most adsorption equilibria.

5.3.2.2 Pretreatment Temperature

In the above analysis, it was assumed that, since T_p was held constant, k_0 was constant. However, Batchelor(9) performed a set of char sulfidation experiments in which both the pretreatment and sulfidation temperatures were variables. His experimental results are analysed below to establish the effect of pretreatment temperature upon the adsorption isotherm.

In Batchelor's experiments, a Vycor (Reg. T.M.) reactor was heated, a ten gram sample of Arkwright low-temperature bituminous coal char was added and fluidized with nitrogen. After approximately ten minutes (the time required to reach a final steady-state temperature of 1100,1350 or 1600°F), the char was fluidized with a mixture of hydrogen sulfide in hydrogen (between 0.11 and 3.15 mole % H_2S in H_2) at a superficial gas velocity of 0.44 feet per second. Char sulfidation was continued for between two and four hours, after which the sample was extracted from the reactor and analysed for total and sulfide sulfur. The results of Batchelor's experiments are presented in Figure 3.6.

Notice, firstly, that the pretreatment temperature was not held constant in Batchelor's experiments. Here the pretreatment and sulfidation temperatures were the same -- i.e.,

$$T_s = T_p \qquad [5.43]$$

The equilibrium concentration of organic sulfur in char (S) decreases as temperature increases in Batchelor's experiments (see Figure 3.6)

-- i.e.,

$$[\delta \ln(S)/\delta T]_{P_{H_2S}/P_{H_2}} \leq 0 \qquad [5.44]$$

where, since the sulfidation and pretreatment temperatures are the same, the subscript on T has been dropped. This is opposite to the trend noted in [5.42], and the reason is as follows; differentiating equation [5.32] yields:

$$[\delta \ln(S)/\delta T]_{P_{H_2S}/P_{H_2}} = [\delta \ln(k_o)/\delta T] + [\delta \ln(\Theta)/\delta T]_{P_{H_2S}/P_{H_2}} \qquad [5.45]$$

$$= [\delta \ln(k_o)/\delta T] + [\delta\{\ln(a_o K_{p_{25}} [P_{H_2S}/P_{H_2}]^2) RT/\alpha q_m\}/\delta T]_{P_{H_2S}/P_{H_2}} \qquad [5.46]$$

The first (k_o) term on the right hand side of [5.46] is (from [5.34]) less than zero. The second (Θ) term is (from [5.42]) greater than zero. Consequently, the fact that the equilibrium concentration of organic sulfur in char decreases with increasing temperature in Batchelor's experiments is a *reflection of the struggle between the two temperature-dependent terms* on the right hand side of [5.45] *to dominate the temperature-dependent behaviour of S.*

Some of Kor's(57) experimental results can be used to support the preceding arguments. The following table was constructed from the data presented in Table D.6.

	T_p		
T_s	600	900	$(\Delta S/\Delta T_p)_{T_s;P_{H_2S}/P_{H_2}}$
600	2.8	0.8	-2.0/300
900	3.5	2.9	-0.6/300
$(\Delta S/\Delta T_s)_{T_p;P_{H_2S}/P_{H_2}}$	+0.7/300	+2.1/300	

Kor's(57) Filter Paper Char Sulfidation Data at $100P_{H_2S}/P_{H_2}=100$

Notice that:

- Consistent with [5.42], $(\Delta S/\Delta T_s)_{T_p;P_{H_2S}/P_{H_2}} \geq 0$
- Consistent with [5.44], $(\Delta S/\Delta T_p)_{T_s;P_{H_2S}/P_{H_2}} \leq 0$

In other words, these results are consistent with the preceding arguments. Perhaps more importantly, they clearly illustrate the effects of sulfidation and pretreatment temperatures upon the equilibrium concentration of organic sulfur in char. Notice that, in order to minimize the equilibrium concentration of organic sulfur in char, one would prefer to *maximize the pretreatment temperature, and minimize the sulfidation temperature*. The latter observation has important practical implications, which are discussed in Section 6.2. However, it is worthwhile mentioning that the effects of the sulfidation and pretreatment temperatures upon the adsorption isotherm explains why several authors(61,104) have observed that the extent of char hydrodesulfurization is maximized at a particular temperature.

The preceding arguments are important for several reasons: (a) they are consistent with the results of Kor(57), (b) they resolve the apparent inconsistency between the results of Batchelor(9) and the experimental results mentioned in Section 3.3, (c) they demonstrate that the effect of temperature upon the adsorption isotherm is not inconsistent with that which is normally observed(40), (d) they support the active site hypothesis, (e) they offer an explanation as to why several authors have observed that the extent of char hydrodesulfurization is maximized at a particular temperature, and (f) they clearly illustrate the effects of sulfidation and pretreatment temperatures upon the adsorption isotherm.

5.4 Summary and Conclusions

The chemistry of oxygen, and the analogy between the chemistries of oxygen and sulfur in carbonaceous materials have been reviewed in this chapter. It is suggested that oxygen and sulfur are adsorbed at active sites on the char surface, and that these are probably situtated at the location of unpaired electrons in the char matrix. Hence, the arguments presented in this chapter lend credence to the active site hypothesis. In addition, it was noted that, upon adsorption, oxygen changes from a weakly into a more strongly adsorbed species on the surface. Therefore, the above arguments support the transformation hypothesis. Further, since organic sulfur in char is almost certainly a surface complex, there is little reason to doubt the validity of the selective gasification criterion. Consequently, the arguments presented in this chapter can be used to explain why:

- the extent of char sulfidation is not dependant upon char surface area,
- the adsorption isotherm is a function of the rank of the parent coal and the product char,
- the concentrations of moisture and sulfur in char are related,
- the kinetics of char hydrodesulfurization are path-dependent, and
- the extent of char gasification significantly affects the kinetics of char hydrodesulfurization.

In addition, the arguments presented in this chapter can be used to (a) justify the development of a more general correlation of char sulfidation data, which might allow data for a variety of sulfur species to be presented on a single correlation, and (b) explain the effects of sulfidation and pretreatment temperatures upon the adsorption isotherm. The latter explanation is important because it explains the apparent inconsistency noted in Section 3.3.2.

Consequently, while some of the arguments presented in this chapter remain speculative in nature, these arguments do provide a cohesive and consistent framework on which to structure one's knowledge of the chemistry of sulfur in char.

CHAPTER SIX

IMPLICATIONS FOR COAL SULFUR MANAGEMENT

In Chapters One through Four, the factors which govern the distribution of sulfur between the char and gas phases have been investigated. It is the objective of this chapter to outline some practical implications of the results of these investigations.

6.1 Review of Factors which Govern the Distribution of Sulfur between the Char and Gas Phases

During coal pyrolysis, sulfur is distributed between the sulfur species in char (pyrrhotite, sulfided-acceptors and organic sulfur) and hydrogen sulfide in the gas phase. Factors which affect this distribution are:

6.1.1 The Concentration of Pyrites and Sulfur-Acceptors in Coal

Above 500°C, pyrites decomposes to form pyrrhotite via the overall reaction$^{(79)}$:

$$FeS_2 + H_2 \rightarrow FeS + H_2S \qquad [5.1]$$

This reaction is, for all practical purposes, irreversible. However, pyrrhotite further decomposes according to the reaction:

$$FeS + H_2 \rightleftarrows Fe + H_2S \; ; \; K_p = P_{H_2S}/P_{H_2} \qquad [5.2]$$

The equilibrium constant (K_p) for reaction [5.2] is estimated from equation [1.5]. These values are presented, as a function of temperature, below:

Temperature(^{o}C;^{o}F)	Equilibrium Constant
700; 1291	0.00102
800; 1471	0.00187
900; 1632	0.00309
1000; 1832	0.00473

Notice that the values of the partial pressure ratio (P_{H_2S}/P_{H_2}) required for the reduction of pyrrhotite to elemental iron are quite low. As was noted by Jones(52), these values are so low that pyrrhotite will not, for most practical purposes, be reduced to elemental iron. Consequently, a significant fraction of pyritic sulfur in coal will be retained in char as pyrrhotite.

Sulfur-acceptors (e.g., CaO, $CaCO_3$) react, upon exposure to hydrogen sulfide, to form sulfided acceptors via reactions such as:

$$MO + H_2S \rightarrow MS + H_2O \qquad [5.3]$$

and

$$MCO_3 + H_2S \rightarrow MS + H_2O + CO_2 \qquad [5.4]$$

where M represents a general sulfur acceptor. In hydrogen-containing environments, these reactions are, for all practical purposes, irreversible. In addition, Yergey _et al_(131) have demonstrated that these reactions are rapid at the elevated temperatures (i.e., 600-1000^{o}C) in question. Consequently, sulfur will be retained in the char as sulfided-acceptor.

Hence, the concentration of pyrites and sulfur-acceptors in the material to be desulfurized strongly affects the distribution of sulfur between the resultant char and gas phases. These arguments are consistent with the results of Robinson(104) who noted that removal of pyrites and sulfur-acceptors from the coal prior to hydrodesulfurization significantly reduces the concentration of total sulfur retained in the product char.

6.1.2 Type of Coal

The type of coal affects the concentration of sulfur retained in char in two ways. Firstly, the rank of the parent coal significantly affects the adsorption isotherm and, hence, the equilibrium concentration of organic sulfur in char. Secondly, significant concentrations of sulfide sulfur (other than that due to pyrrhotite or sulfided-acceptor) are formed in low-rank coal chars upon exposure to hydrogen sulfide. An inspection of the data in Tables D.8 and D.9 reveals that, despite the thorough acid-leaching procedures which were adopted (see Section 2.2.1), both the lignite and subbituminous chars contained significant concentrations of sulfide sulfur after exposure to hydrogen sulfide. However the measured concentrations of sulfide sulfur in the higher rank chars which were employed (see Tables D.10 and D.11) were negligible. While the reason for the formation of sulfide sulfur in low-rank chars is not well understood, a plausible explanation is that, because of the known ion-exchange properties of low-rank coals(74), adsorbed sulfur acceptors react to form sulfides upon exposure to hydrogen sulfide.

6.1.3 Sulfidation Temperature

For most adsorption equilibria, the concentration of the adsorbate decreases as temperature increases. As is shown in Section 5.3.2, this is observed in the H_2S/H_2 system when the partial pressure of the "effective" adsorbate (i.e., P_{S_2}) is held constant. However, when the partial pressure ratio (P_{H_2S}/P_{H_2}) is held constant, the equilibrium concentration of organic sulfur in char increases as temperature increases. This effect is significant because it allows one to cool an equilibrium mixture of char and hydrogen sulfide in hydrogen in, for example, heat exchangers, without incurring an increase in the concentration of organic sulfur in the char.

6.1.4 Char Thermochemical History

Thermochemical history is a generic title which embraces all of the history-dependent factors which affect the distribution of sulfur between the char and gas phases. Two such factors have been identified in this investigation:

- o the pretreatment temperature. It was noted in Section 5.3.3 that the concentration of unpaired electrons (active sites) in char is a function of the maximum temperature to which the char is exposed during pretreatment.
- o upon exposure to elevated temperatures, organic sulfur in char changes into a more stable form. This is called the transformation hypothesis.

The former affects the equilibrium concentration of organic sulfur in char, while the latter affects the kinetics of char hydrodesulfurization.

The abovementioned factors suggest a variety of strategies which could be adopted to minimize the concentration of sulfur in char. These strategies are discussed in Section 6.2

6.2 Ways to Maximize the Extent of Coal Desulfurization; Implications for Coal Hydrodesulfurization

Let the extent of desulfurization (E) be defined by the equation:

$$E = [S_{Feed} - S_{Prod}]/S_{Feed} = 1 - S_{Prod}/S_{Feed} \qquad [5.5]$$

where S_{Feed} = concentration of total sulfur in the feed material, and

S_{Prod} = concentration of total sulfur in the product char.

The preceding discussions suggest that E will be maximized if:

- the concentrations of pyrites and sulfur-acceptors in the feed is minimized,
- high-rank coals or coal chars are employed, and
- the "right" char thermochemical history is employed. On the one hand, maximizing the pretreatment temperature would minimize the concentration of active sites in char (k_o). On the other hand, the fraction of active sites on the surface which are covered (Θ) increases as the sulfidation temperature increases. Since the equilibrium concentration of organic sulfur in char is the product of these two factors -- i.e.,

$$S = k_o \Theta \qquad [5.6]$$

a tradeoff between these competing factors is required to minimize the equilibrium concentration of organic sulfur in char.

In addition, one would prefer to avoid severe char pretreatment prior to desulfurization. However, if this is unavoidable, selective gasification of a small fraction of the char should enable one to circumvent problems associated with the slow kinetics of desulfurization of stable froms of organic sulfur in char. The latter comments are of interest as far as stagewise counter-current contacting equipment is concerned.

There is another factor which affects the extent of desulfurization (E) -- i.e., the sulfur content of the feed (S_{Feed}). Notice that, firstly, only the concentration of organic sulfur in the product is affected by the gas phase concentration of hydrogen sulfide*. Secondly, the equilibrium concentration of organic sulfur in char is relatively insensitive to changes in the partial pressure ratio (P_{H_2S}/P_{H_2}).** While an increase in S_{Feed} results in a significant increase in the partial pressure ratio, the equilibrium

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* The concentrations of pyrrhotite and sulfided-sulfur acceptors are, for most practical purposes, not a function of the partial pressure ratio (P_{H_2S}/P_{H_2}) -- see Section 6.1.1.

** Notice that the equilibrium concentration of organic sulfur in char is related to the partial pressure ratio by an expression of the form:

$$S = a[P_{H_2S}/P_{H_2}]^b \qquad [5.7]$$

The exponent (b) in the above equation is generally quite small (e.g., between 0.19 and 0.25 for the six case studies mentioned in Appendix B). Hence, the equilibrium concentration of organic sulfur in char is relatively insensitive to large changes in the partial pressure ratio.

concentration of organic sulfur in char and, hence, S_{Prod}, is not significantly affected by such an increase. In other words, the extent of char desulfurization should be highest when high sulfur coals are employed. A example of this is provided by experiment HY-14 in Table S.1. Notice that the extent of desulfurization realized in this experiment is noticeably higher than that realized in the other experiments mentioned.

The above discussions suggest that, provided suitable desulfurization conditions are maintained, the concentration of organic sulfur in char can be reduced to acceptably low levels*. However, coal hydrodesulfurization is limited in its ability to remove inorganic sulfides from the char. Hence, the potential of coal hydrodesulfurization is contingent upon the development of alternative strategies which selectively remove inorganic sulfides from char. Such strategies are discussed below.

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* Assuming that the equilibrium isotherm data for bituminous coals are representative of the organic sulfur concentrations which can be realized in actual practise (see Figure 3.8), the concentration of organic sulfur in char should fall in the 0.3-0.6 wt% sulfur range. These values are lower than the value of 0.9 wt% which corresponds to the 1.2 lbs SO_2/MM Btu. limit which is widely quoted throughout the literature(1,2)

6.3 Strategies for the Removal of Inorganic Sulfides from Char

Several coal desulfurization strategies have been widely discussed in the literature -- i.e. flue gas desulfurization, coal beneficiation, addition and regeneration of sulfur-acceptors, coal hydrodesulfurization, etc. A discussion of the relative merits of these strategies is beyond the scope of this thesis. However, it is worthwhile noting that the consensus of opinion in the literature is that coal or char hydrodesulfurization is practically infeasible. For example, Jones(52) noted that: "From the standpoint of commercial operations, the removal of sulfur from char by simple treatment with hydrogen at 1600°F is not practical". "Prohibitively large quantities of hydrogen would be required since the mole fraction of (hydrogen sulfide) in the gas in equilibrium with ferrous sulfide ... is about three parts per thousand". "The removal of hydrogen sulfide from a recycled hydrogen stream by conventional means would also be impractical since large volumes of hydrogen would have to be cooled to near-room temperature, scrubbed and reheated". In other words, Jones has:

- correctly noted that a major limitation on the feasibility of hydrodesulfurization lies in its inability to remove inorganic sulfides from char, and
- assumed that strategies for the removal of inorganic sulfides from char do not exist.

However, there are several techniques which have potential for minimizing the concentration of inorganic sulfides in char.

6.3.1 Coal Leaching and Beneficiation

One means of minimizing the formation of inorganic sulfides in char is to remove the sulfide-forming inorganic constitutent in coal prior to hydrodesulfurization. Several strategies to accomplish this objective have been investigated or adopted -- i.e.,

- Coal Beneficiation. Approximately 60% of the coal mined in the United States is cleaned in a variety of coal beneficiation processes(124). In general, coal beneficiation results in a substantial reduction in both the pyrites and ash contents of the cleaned coal product. Unfortunately, coal beneficiation is limited in its ability to remove all of the inorganic constituents in coal capable of reacting to form sulfides. In addition, an appreciable fraction of the as-mined coal is discarded as refuse from the cleaning plant(20).
- Chemical Methods. A variety of low-temperature sulfur removal processes, in which coal is leached with various chemicals, have been investigated. These processes have been reviewed by Myers(67).
- Magnetic Removal of Pyrites. Magnetic separation has been proposed as a method of removing pyrites from coal. The primary disadvantage of this method is that the magnetic susceptibility of pyrites is rather low.

In general, all of these methods are limited by cost, the extent to which pyrites or sulfur-acceptors can be liberated from the coal, or the amount of coal discarded as refuse.

6.3.2 Post-Hydrodesulfurization Sulfides Removal

An alternative strategy, which has received little attention in the literature, is to remove inorganic sulfides from the char *after* hydrodesulfurization. There are three strategies which fall into this category -- i.e., sulfide oxidation, regeneration and magnetic separation.

Reactions [5.8] and [5.9] can be used to describe the reactions which occur during sulfide oxidation:

$$FeS + (1+\gamma/2)O_2 \rightarrow FeO_\gamma + SO_2 \qquad [5.8]$$

and

$$CaS + 3/2O_2 \rightarrow CaO + SO_2 \qquad [5.9]$$

While the chemistry of these reactions is not well understood, reaction [5.8] has long been used in the regeneration of iron oxide boxes(32) at temperatures as low as 100°F. In support of these arguments, Jacobs and Mircus(51) observed almost complete removal of both sulfate and pyritic sulfur from coal fluidized with a mixture of 13% air and 35% steam in nitrogen at 950°F. Similar observations were made by Sinha and Walker(112) and Block _et al_(15). On the other hand, Jones(52) noted that side reactions to form sulfates accompany reaction [5.9]. Such reactions would lead to the incomplete liberation of sulfide sulfur from char.

Another strategy, sulfide regeneration, can be represented by the reaction:

$$CaS + CO_2 + H_2O \rightarrow CaCO_3 + H_2S \qquad [5.10]$$

Jones(52) has noted that this reaction proceeds rapidly at temperatures as low as 800°F, and the resulting product gas may contain up to 20% hydrogen sulfide. Notice that, in both sulfide oxidation and regeneration, the temperatures are low enough to avoid significant gasification of the char matrix. Hence, these strategies seem capable of removing sulfide sulfur from char without significantly affecting the char yield. However, there is some uncertainty as to whether or not the sulfur dioxide and hydrogen sulfide, produced via reactions [5.8], [5.9] and [5.10] will react with the char matrix, thereby reincorporating the liberated sulfide sulfur as organic sulfur in the char.

Powell(82) was the first to notice that pyrrhotite in char is magnetic. Unlike pyrites, which has a relatively low magnetic susceptibility, pyrrhotite is ferrimagnetic(13,16,101). Hence, a third strategy for the removal of inorganic sulfur from char -- i.e., magnetic separation -- is seen to have significant potential. Unfortunately, most experimental efforts have centered around attempts to remove pyrites from coal. However, the obvious advantages of pyrrhotite rather than pyrites removal suggests that this strategy demands more careful attention.

6.4 Post Hydrodesulfurization Sulfur-Acceptor Addition.

One other strategy seems worthy of mention here. In most sulfur-acceptor addition desulfurization strategies, the sulfur-acceptor is introduced into, or passes through a reaction zone where pyrolysis and hydropyrolysis conditions occur. Since the addition of sulfur-acceptor in such a zone absorbs the gaseous hydrogen sulfide which is evolved, this strategy has the advantage of producing an effluent gas which is essentially sulfur-free. However, this strategy does not take advantage of the desulfurization which takes place in conjunction with coal pyrolysis and hydropyrolysis. Consequently, the sulfur-acceptor requirements of such a strategy are higher than is necessary.

A minor process modification, which does not suffer from the latter disadvantage, involves transferring the hydrodesulfurized char to a second reaction zone, where the sulfur-acceptors are added. In the latter strategy, only the residual sulfur in the char (primarily pyrrhotite sulfur) is absorbed by the acceptor. Consequently, the amount of acceptor which must be added is reduced. An order of magnitude estimate of this reduction ranges from between 40-70% of the sulfur-acceptor requirements of the more conventional sulfur-acceptor addition strategy mentioned above. The magnitude of this reduction would be, for reasons mentioned in Sections 6.1 and 6.2, most noticeable for coals in which a major fraction of the coal sulfur is present as organic sulfur.

6.5 Summary and Conclusions

The discussions in this chapter suggest that, provided suitable desulfurization conditions are maintained, coal or char hydrodesulfurization can probably reduce the concentration of organic sulfur in the product char to acceptably low levels. However, the primary limitation of coal hydrodesulfurization lies in its inability to remove inorganic sulfides from the char. Hence, the potential of hydrodesulfurization will only be fully realized when strategies for the selective removal of sulfide sulfur from char are developed. However, there are several strategies which seem capable of selective removal of these sulfides from the char.

CHAPTER SEVEN

FUTURE RESEARCH

While much has been learned about the chemistry of sulfur in char, some areas of uncertainty remain. These are discussed in this chapter.

7.1 Scatter in the Adsorption Isotherm Data

Mr. George Curran(22) has correctly pointed out that a significant degree of scatter exists in the adsorption isotherm data which are presented in Tables D.8, D.9, D.10, D.11 and D.12 and Figure 3.8. In retrospect, a plausible explanation for the inconsistency in this data has emerged. In the adsorption isotherm experiments mentioned above, the following fluid-bed experimental procedure was adopted:

$$\text{START} \xrightarrow[\text{0.5 scfh He}]{900^{o}\text{C; 1 Hour}} \xrightarrow[\text{0.5 scfh He}]{T^{o}\text{F; 1 Hour}} \xrightarrow[100P_{H_2S}/P_{H_2}=E]{T^{o}\text{F; 1 Hour; 1 scfh}} \text{ANALYSIS}$$

where T is either 1200, 1400 or 1600^{o}F and E ranges from 0.1 to 100. Notice that this experimental procedure involves "severe pretreatment" of the char -- i.e., exposure of organic sulfur in the char to 900^{o}C temperatures for one hour in helium. As was noted in Chapter Four, such conditions are conducive to the formation of stable forms of organic sulfur in the char. Thus, if desulfurization of the char is required to attain the equilibrium condition, this desulfurization would only proceed very slowly. Therefore, the measured values of the concentration of organic sulfur in char are probably too high in those experiments in which desulfurization of the char is required to attain the equilibrium condition. In other words:

$$[C\text{-}S]_{Initial} > [C\text{-}S]_{Measured} \Rightarrow [C\text{-}S]_{Measured} > [C\text{-}S]_{Equilibrium} \quad [6.1]$$

where $[C\text{-}S]_{Initial}$ is the concentration of organic sulfur in the feed char, $[C\text{-}S]_{Measured}$ is the measured concentration of organic sulfur in the product char, and $[C\text{-}S]_{Equilibrium}$ is the concentration of organic sulfur in the product char at the equilibrium condition.

Values of $[C\text{-}S]_{Initial}$ were obtained from the char analyses presented in Table 2.2, and are presented in Table 7.1. These values were compared with the values of $[C\text{-}S]_{Measured}$ which are presented in Tables D.8, D.9, D.10, D.11 and D.12 to establish which of the adsorption isotherm experiments mentioned in these tables satisfy the criterion imposed by equation [6.1]. The experiments which satisfy this criterion are also mentioned in Table 7.1. Notice that a significant number of the adsorption isotherm experiments -- i.e., 32 or 28.3% of a total of 113 experiments -- satisfy the criterion imposed by equation [6.1].

These experiments should be repeated if the abovementioned inconsistency in the adsorption isotherm data is to be eliminated. In the repeat experiments, procedures will have to be adopted to

Char	$[C-S]^{(a)}$ Initial	Experiments for which the Results are Suspect
HYDRANE HY-138 Lignite Char	1.46	166,144,124,125
HYDRANE HY-140 Subbituminous Char	0.95	163,126,127
HYDRANE HY-128 Bituminous Char	0.89	136,168,150,174,164,171,128 170,172,173,98,142,129,99,143
Barnebey-Cheney 417 Anthracite-based Activated Charcoal	0.67	137,169,151,36,43,130,94,146 131,95
Filter Paper Char	0.00	

Note: (a) MASF Basis

Table 7.1. Equilibrium Char Sulfidation Experiments for which the Results are Suspect

avoid problems which arise as a result of the formation of stable forms of organic sulfur in char. Such problems can be circumvented by using hydrogen rather than helium during char pretreatment --i.e., the following procedure could be adopted in the repeat experiments:

$$\text{START} \xrightarrow[\text{0.5 scfh } H_2]{900^{\circ}\text{C; 1 Hour}} \xrightarrow[\text{0.5 scfh } H_2]{T^{\circ}\text{F; 1 Hour}} \xrightarrow[100P_{H_2S}/P_{H_2} = E]{T^{\circ}\text{F; 1 Hour; 1 scfh}} \text{ANALYSIS}$$

Such a procedure was employed in the preparation of HYDRANE HY-128 bituminous char for analysis in the ESCA experiments (see Section 4.5). Subsequent ESCA analyses of the chars from the "blank" experiments revealed that these chars did not contain significant concentrations of sulfur (see Figures 4.4, C.3, C.7 and C.11). Hence, the use of the above experimental procedure should circumvent problems associated with the formation of stable forms of organic sulfur in char and, therefore, should provide more reliable char sulfidation data than was generated via the experiments mentioned in Table 7.1.

7.2 Effect of Pretreatment Temperature upon the Extent of Char Sulfidation

In the char sulfidation experiments mentioned in Section 3.3, the pretreatment temperature was held constant at 900°C. In other words, the effect of pretreatment temperature upon the adsorption isotherm was not investigated. However, the arguments presented in Section 5.3.3 reveal that the effect of pretreatment temperature upon the adsorption isotherm is probably significant. Since a practical hydrodesulfurization strategy would probably be conducted at temperatures other than 900°C, the effect of pretreatment temperature upon the adsorption isotherm would have to be thoroughly investigated before the adsorption isotherm data presented in Section 3.3 would be of significant practical utility.

7.3 Relationship between the Concentrations of Moisture and Sulfur in Char

It has been noted (see Sections 3.6 and 5.2.4) that a relationship exists between the concentrations of moisture and sulfur in char. It is hypothesized that this relationship is the result of titration of sulfur species on the surface by water molecules. If correct, such an observation would have important implications. For example, it would provide experimental support for the active site hypothesis, and the analogy between the chemistries of sulfur and oxygen in char. Experiments similar to those performed by Walker and Janov(123), who employed oxygen-covered chars, should be conducted using sulfur-covered chars to establish whether or not the above hypothesis is correct.

7.4 Resolution of the Uncertainty Surrounding the Mechanism of Char Sulfidation

It was noted in Section 5.3.1 that the mechanism of char sulfidation remains uncertain. While it is anticipated that the mechanisms of char oxidation and sulfidation are probably analogous, this hypothesis is unproven. Experiments should be conducted to establish whether or not elemental sulfur is the sulfur species responsible for char sulfidation. Experiments similar to those performed by Grabke(33,34) might enable one to resolve this uncertainty.

7.5 Development of a More General Correlation of Char Sulfidation Data

Several authors have noted that a number of sulfur species other than hydrogen sulfide react with char to form carbon-sulfur complexes. It is suggested in Section 5.3.1 that it might be possible to present char sulfidation data for all such species on a single correlation, in which the partial pressure of elemental sulfur (P_{S_2}) is employed as the correlation parameter. Unfortunately, only one datum for sulfur dioxide (see Table D.24) is presently available to support this alternative method of correlation. Nevertheless, the compression of sulfidation data for such a variety of sulfur species would be very useful from a practical point of view. Additional experiments similar to those described in Section 3.3 should be performed in which sulfur species other than hydrogen sulfide are employed to sulfide the char. Such experiments should enable one to evaluate the relative merits of this alternative correlation method.

7.6 Electron Spin Resonance and Magnetic Susceptibility Measurements

Electron Spin Resonance (ESR) and magnetic susceptibility measurements are sensitive and direct ways of measuring changes in the magnetic properties of carbonaceous materials as a function of, for example, temperature or the adsorption of various gases. Ingram(49) has shown that such measurements can be obtained at the severe experimental conditions of interest as far as char sulfur chemistry is concerned. Hence, these techniques could be used to:

- investigate factors which affect the concentration of unpaired electrons in char,
- establish whether or not there exists a 1:1 relationship between the decrease in the number of unpaired electrons in char and the amount of sulfur or oxygen chemisorbed on the char surface,
- establish whether or not there is a relationship between the concentration of unpaired electrons in char and the reactivity of the char towards, for example, sulfur or oxygen, and
- quantitatively investigate changes in the magnetic properties of chars which have been exposed to sulfur or oxygen -- i.e., test the validity of the transformation hypothesis.

Such investigations might (a) provide strong support for the active site hypothesis, (b) lead to the development of an easily-measureable index of char and coal reactivity, and (c) lead to an enhanced understanding of the path-dependent nature of char hydrodesulfurization.

The author is not aware of any other experimental techiques capable of generating such fundamentally-important information about the nature and properties of organic sulfur in char.

7.7 Factors which Affect the Feasibility of Coal and Char Hydrodesulfurization

Uncertainty surrounds four factors which affect the feasibility of coal and char hydrodesulfurization. These factors are discussed in the following subsections.

7.7.1 The Path-Dependent Nature of Char Hydrodesulfurization

The experiments described in Section 4.3 revealed that char hydrodesulfurization is a path-dependent process. Unfortunately, there were two variables in those experiments -- i.e., the thermal history of the char and the time of exposure of the char to hydrogen sulfide. Since the experimental results cannot be used to separate the effects of these variables upon the kinetics of char hydrodesulfurization, the underlying reason for the path-dependent nature of char hydrodesulfurization remains uncertain. However, the arguments presented in Section 5.5.3 support the transformation hypothesis. Hence, while it is anticipated that increased time of exposure of the char to hydrogen sulfide is responsible for the path-dependent char hydrodesulfurization kinetics noted, this hypothesis needs to be tested. An example of an experimental procedure which could be used to test this hypothesis is as follows:

START	900°C; 1 Hour	1400°F;(X-T)Mins	1400°F;T Mins;1 scfh	1400°F;Z Mins	ANALYSIS
	0.5 scfh H_2	0.5 scfh H_2	$100P_{H_2S}/P_{H_2}=E$	0.5 scfh H_2	

where $X > T$

and X,E and Z are constants, while T is an experimental variable.

7.7.2 Effect of Carbon Gasification

In attempting to explain Zielke's(132) experimental results (see Section 4.6), it was suggested that selective gasification of char surfaces results in the liberation of stable forms of organic sulfur from the surface. This in turn leads to enhanced kinetics of char hydrodesulfurization. However, there is at least one other explanation for Zielke's results. Selective gasification could lead to an increase in the size of the pores in char particles. The enhanced rates of mass-transfer resulting from such an increase in pore size could be responsible for the enhanced kinetics of char hydrodesulfurization observed by Zielke. This alternative interpretation of his results needs to be thoroughly checked.

7.7.3 Feasibility of Coal Hydrodesulfurization.

The analysis of the batch fluid-bed coal and char hydrodesulfurization data in the literature (see Section 4.7) suggests that, provided the selective gasification criterion is satisfied, the kinetics of coal and char hydrodesulfurization are probably controlled by equilibrium and material balance criteria rather than kinetic limitations. However, the rate of heating in these experiments was rather low. The kinetics of coal and char hydrodesulfurization under the rapid-heatup, "flash" desulfurization conditions likely to be encountered in actual practise should be investigated. The results of such experiments may enable one to relate much of the theory which has been developed in this thesis to the more stringent conditions likely to be encountered in actual coal processing equipment.

7.7.4 Feasibility of Post-Hydrodesulfurization Sulfides Removal

As was noted in Section 6.2, the feasibility of coal hydrodesulfurization is contingent upon the development of strategies which minimize the formation or removal of sulfide sulfur from the product char exiting a hydrodesulfurization process. Several strategies seem capable of attaining this goal without significantly affecting the char yield (see Section 6.3). In particular, however, three post-hydrodesulfurization sulfides removal strategies (i.e., sulfide oxidation, regeneration or magnetic separation) have significant potential. Unfortunately, most experimental investigations of these strategies have been conducted using coal rather than char. However, there is good reason to believe that these strategies would be better applied to char rather than coal hydrodesulfurization. This is certainly true in the case of magnetic separation because, whereas the magnetic susceptibility of pyrites in coal is relatively low, pyrrhotite in char is ferrimagnetic. In addition, since the oxidation and regeneration strategies are conducted at temperatures at which coal starts to devolatilize, desulfurization was accompanied by excessive weight loss when coal was employed(51,112). However, since the chars which exit a coal hydrodesulfurization process will have been exposed to elevated temperatures, a corresponding weight loss should not be observed when the oxidation and regeneration strategies are applied to char desulfurization. Hence these two strategies seem capable of selective removal of sulfide sulfur from char without incurring a significant reduction in the char yield[*]. Thus, an experimental investigation of these three sulfide removal strategies is potentially very rewarding.

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[*] Note that the temperatures required in the oxidation and regeneration strategies (i.e., 300-500°C) are not high enough to result in significant gasification of the char with either oxygen, steam or carbon dioxide.

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APPENDIX A

MODELS FOR THE EQUILIBRIUM CONCENTRATION OF ORGANIC SULFUR IN CHAR

In developing a model to describe the equilibrium concentration of organic sulfur in char, three ideal models (i.e., the Langmuir, Temkin and Freundlich Isotherms) have been tested in Chapter Three. It is the objective of this appendix to outline the development of these models.

Model Development

Adsorption isotherms can be divided into five categories -- i.e., Types I through V(40). Types II through V describe the formation of multilayers, condensation of liquid in capillaries, etc. Hence they are used to describe physical adsorption. Type I adsorption isotherms, on the other hand, are limited to sub-monolayer surface coverage. Since chemisorption is similarly limited, it is usually described by Type I isotherms.

The active site hypothesis implies that organic sulfur in char is formed as a result of *chemisorption* of sulfur species at active sites in char. Hence, only Type I isotherms will be considered in this appendix. There are three such isotherms -- i.e., the Langmuir, Temkin and Freundlich Isotherms. They differ in the assumptions required in their development. In the case of the Langmuir Isotherm, it is assumed that the heat of adsorption is constant and independent of the extent of surface coverage. This leads to an equation of the form:

$$\Theta \quad = \quad (aP)^{1/\alpha}/\{1 + (aP)^{1/\alpha}\} \qquad [A.1]$$

where Θ = fractional coverage of active sites on the surface

P = partial pressure of the adsorbate; atm.

a = temperature-dependent parameter; atm.$^{-1}$

and α is a constant which depends upon the mechanism of adsorption. If the adsorption process is non-dissociative, α is equal to unity. However, if the adsorbate molecule dissociates upon adsorption, it is equal to 2.

If it is assumed that the heat of adsorption varies linearly with fractional coverage of active sites on the surface, the Temkin Isotherm results -- i.e.,

$$\Theta = \ln(A_o P) RT/\alpha' q_m \qquad [A.2]$$

where T = absolute temperature; ^oK

R = universal gas constant; 1.987 cal./g.mol.^oK

q_m = heat of adsorption at $\Theta = 1$

A_o is a temperature-dependent parameter and α' is a constant.

If it is assumed that the heat of adsorption varies logarithmically with fractional coverage of the active sites on the surface, the Freundlich Isotherm results -- i.e.,

$$\Theta = [a_o P]^{RT/\alpha q_m} \quad ; \; a_o P \leq 1 \qquad [A.3]$$

where a_o is the reciprocal of the partial pressure of the adsorbate at $\Theta = 1$.

From the active site hypothesis, the fractional coverage of the active sites on the surface (Θ) is defined by the equation;

$$\Theta = S/k_o \qquad [A.4]$$

where S is the equilibrium concentration of organic sulfur in char, and k_o is the "concentration" of active sites in char.

A question arises as to the nature of the adsorbate responsible for the formation of organic sulfur in char. Powell(84) postulated that elemental sulfur (i.e., S_2) is responsible. However, as is noted in Chapter Five, the mechanism of char sulfidation is uncertain. Nevertheless, since the equilibrium concentration of organic sulfur in char is governed by thermodynamic rather than mechanistic criteria, one can think of elemental sulfur as being the adsorbate even though this is not necessarily correct from a mechanistic standpoint. Hence:

$$P = P_{S_2} \qquad [A.5]$$

In addition, the thermodynamics of the reaction:

$$2H_2S \rightleftarrows 2H_2 + S_2 \qquad [A.6]$$

require that

$$P_{S_2} = K_p[P_{H_2S}/P_{H_2}]^2 \qquad [A.7]$$

where P_{S_2} = partial pressure of hydrogen sulfide; atm.

K_p = equilibrium constant for reaction [A.6]; atm.

and P_{H_2} = partial pressure of hydrogen; atm.

Langmuir Isotherm Model

Combining equations [A.1], [A.4], [A.5] and [A.7] yields

$$S = k_o(aK_pR_p^2)^{1/\alpha}/\{1 + (aK_pR_p^2)^{1/\alpha}\} \qquad [A.8]$$

where R_p is the partial pressure ratio (P_{H_2}/P_{H_2}). McIver(66) has shown that equation [A.8] best describes char sulfidation data with α set equal to 2. Substituting this value into equation [A.8] and rearranging yields:

$$(P_{H_2S}/P_{H_2})/S \quad = \quad k_1(P_{H_2S}/P_{H_2}) + k_2 \qquad [A.9]$$

where $k_1 = 1/k_0$

$k_2 = 1/\{k_0(aK_p)^{0.5}\}$

This form of the Langmuir Isotherm was employed in Figure 3.3 to test the applicability of the Langmuir Isotherm to char sulfidation.

Temkin Isotherm Model

Combining equations [A.2], [A.4], [A.5] and [A.7] yields

$$S \quad = \quad k_3 \ln(P_{H_2S}/P_{H_2}) + k_4 \ln(A_o K_p) \qquad [A.10]$$

where $k_3 = 2k_oRT/\alpha' q_m$

and $k_4 = k_oRT/\alpha' q_m$

This form of the Temkin Isotherm was employed in Figure 3.4 to test the applicability of the Temkin Isotherm to char sulfidation.

Freundlich Isotherm Model

Combining equations [A.3], [A.4], [A.5], and [A.7] yields

$$S \quad = \quad k_o[a'_o K_p(100P_{H_2S}/P_{H_2})^2]^{RT/\alpha q_m} \qquad [A.11]$$

where $a'_o = a_o/10000$ [A.12]

Taking logarithms yields:

$$\ell og(S) = k_5\ \ell og(100P_{H_2S}/P_{H_2}) + k_6 \qquad [A.13]$$

where $k_5 = 2RT/\alpha q_m$

and $k_6 = \ell og(k_o) + RT/\alpha q_m\ \ell og(a_o' K_p)$

This form of the Freundlich Isotherm was employed in Figure 3.5 to test the applicability of the Freundlich Isotherm to char sulfidation.

Estimation of Parameters in the Freundlich Isotherm Model

Using a general expression for the equilibrium constant (K_p) of the form:

$$\ell og[K_p] = z_1 + z_2/T \qquad [A.14]$$

where z_1 and z_2 are constants, and substituting into equation [A.11] yields:

$$S = k_o[a_o'\ 10^{(z_1 + z_2/T)}(100P_{H_2S}/P_{H_2})^2]^{RT/\alpha q_m} \qquad [A.15]$$

Taking logarithms yields:

$$\ell og[S] = k_7 + k_8 T + k_9 T\ \ell og[100P_{H_2S}/P_{H_2}] \qquad [A.16]$$

where $k_7 = \ell og[k_o] + Rz_2/\alpha q_m$ [A.17]

$k_8 = [z_1 + \ell og(a_o')]R/\alpha q_m$ [A.18]

and $k_9 = 2R/\alpha q_m$ [A.19]

The three constants, k_7, k_8 and k_9 in equation [A.16] can be obtained from a linear regression of the char sulfidation data presented in Tables D.8, D.9, D.10, D.11 and D.12. Once these values have been determined, they can be substituted into equations [A.17], [A.18] and [A.19] in order to compute the constants k_o, a_o, z_1, z_2, α and q_m. Because there are six unknowns in these three equations, they are indeterminate. Hence, an *arbitrary* choice of the three variables z_1, z_2 and α will not affect the accuracy with which the experimental data are modelled. However, the computed values of k_o, a_o and q_m are affected by this choice. More specifically;

$$q_m = k_9\,\alpha/2R \qquad [A.20]$$

$$\ell og(a_o') = k_8 k_9\,\alpha^2/2R - z_1 \qquad [A.21]$$

and

$$\ell og(k_o) = k_7 - 2R^2 z_2/\alpha^2 k_9 \qquad [A.22]$$

Kor(53) has supplied an equation for K_p -- i.e.,

$$\ell og[K_p] = 5.18 - 9465.9/T \qquad [A.23]$$

Note that this equation is similar to others presented in the literature(59). Hence, assuming that $S_2(g)$ is the adsorbate responsible for the formation of organic sulfur in char;

$$z_1 = 5.18 \qquad [A.24]$$

and $$z_2 = -9465.9 \qquad [A.25]$$

Using equations [A.24] and [A.25], and assuming that elemental sulfur is dissociatively adsorbed on the char surface (i.e., $\alpha = 2$), the values of k_o, a_o and q_m can be computed from the values of k_7, k_8 and k_9 obtained from the linear regression of the experimental data. These computed values are presented in Table 3.2, and should be employed in conjunction with the model

$$S = k_o[a_o' 10^{(5.18-9465.9/T)}(100P_{H_2S}/P_{H_2})^2]^{RT/2q_m} \qquad [A.26]$$

to describe the equilibrium concentration of organic sulfur in char. The experimental data, and the results of the model are compared in Figure 3.8.

Significance of the Model Parameters

Two assumptions have been made in the development of the model represented by equation [A.26] -- i.e.,

- elemental sulfur is the adsorbate which, alone, is responsible for the formation of organic sulfur in char, and
- elemental sulfur is dissociatively adsorbed on the char surface.

However, since the value of α can only assume the values of 1 (in the case of non-dissociative adsorption) or 2 (in the case of dissociative adsorption), the value of the parameter q_m is, from equation [A.20], either correct or too low by a factor of 2. However, in both these cases, q_m retains the significance of being an index (measure) of the heat of adsorption. The same cannot be said of the parameters a_o and k_o. If the former assumption is correct, the computed values of a_o and k_o correspond to the reciprocal of the partial pressure of the adsorbate (P_{S_2}) when the surface is saturated (i.e., $\Theta = 1$), and the "concentration" of active sites in the char respectively. However, if the former assumption is not valid, these parameters are entirely dependent upon the choice of z_1 and z_2 (see equations [A.24] and [A.25]) and, hence, have no fundamental significance. Thus the significance of the parameters a_o, k_o and, to a lesser extent, q_m are dependent upon the validity of the two assumptions mentioned above.

Summary and Conclusions

Using an ideal Freundlich Isotherm as a basis, a model for the equilibrium adsorption of sulfur on char has been developed. This model is of the form:

$$S = k_o[a_o' 10^{(5.18 - 9465.9/T)}(100P_{H_2S}/P_{H_2})^2]^{RT/2q_m} \quad [A.26]$$

where the parameters k_o, a_o and q_m are a function of the nature of the char employed. Estimated values of these parameters for the five chars employed in this investigation are presented in Table 3.2. This model seems to provide an adequate description of char sulfidation data for very large variations (three orders of magnitude) in the partial pressure ratio (P_{H_2S}/P_{H_2}). In addition, the model correctly predicts an increase in the concentration of organic sulfur in char with increases in temperature. Furthermore, all of the assumptions required in the development of the ideal

Freundlich Isotherm (i.e., Type I adsorption, variation in the heat of adsorption with surface coverage, etc.) are consistent with the active site hypothesis. Unfortunately, the assumption that elemental sulfur is the adsorbate responsible for the formation of organic sulfur in char is one assumption that cannot, at this stage, be substantiated. If this assumption is valid, the parameters k_o, a_o' and q_m have theoretical significance.

APPENDIX B

BATCH FLUID-BED EQUILIBRIUM HYDRODESULFURIZATION MODEL

The Batch Fluid-bed Equilibrium Model is a model of a batch fluid-bed hydrodesulfurization reactor. In the development of this model, it is assumed that:

- only one form of sulfur -- i.e., organic sulfur -- is present in the char,
- the adsorption isotherms presented in Chapter Three and analysed in Appendix A can be used to describe the equilibria which govern the reaction:

$$H_2S + C \rightleftarrows [C\text{-}S] + H_2 \qquad [B.1]$$

  where [C-S] is an adsorbed sulfur species on the char surface,

- the char hydrodesulfurization reactions are so rapid that a pseudo-equilibrium distribution of sulfur is maintained between the char and gas phases at all stages of the desulfurization experiment in question, and
- the batch fluid-bed reactor behaves as an ideal CSTR with respect to both the char and gas phases.

A transient material balance over such a reactor yields:

$$W/100\ \delta S/\delta t = -QP_{H_2S}\ z_1 z_2/(Pz_3) \qquad [B.2]$$

where W = mass of char in the fluid-bed; grams of MASF char.

S = concentration of organic sulfur in char; grams per 100 grams of MASF char.

t = time; hours.

Q = flowrate of hydrogen entering the reactor; scfh (at 0^oC and 760 mm. Hg.)

P_{H_2S} = partial pressure of hydrogen sulfide; atm.

P = sum of the partial pressures of hydrogen and hydrogen sulfide exiting the reactor; atm.

z_1 = conversion factor from lbs. to grams; 453.6 g./lb_m.

z_2 = grams sulfur per g. mol. of hydrogen sulfide; 32 g./g.mol.

z_3 = conversion factor from scf to lb. mol; 359 scf/lb. mol.

From Appendix A, the equilibrium distribution of sulfur between the char and gas phases can be described by an equation of the form:

$$S = b[P_{H_2S}/P_{H_2}]^a \qquad [B.3]$$

where P_{H_2} = partial pressure of hydrogen in the gas stream exiting the reactor; atm.

Substituting [B.3] into [B.2] and rearranging yields:

$$W/100\ \delta S/\delta t = -Qz_1z_2[S/b]^{1/a}\ [P_{H_2}/P]/z_3 \qquad [B.4]$$

Note that, since the partial pressure ratio (P_{H_2S}/P_{H_2}) is generally quite small (i.e., of the order of 0.05 or less):

$$P_{H_2}/P \simeq 1 \qquad [B.5]$$

Substituting [B.5] into [B.4] and rearranging yields:

$$\int S^{-1/a}\,\delta S \quad = \quad -100z_1z_2/(b^{1/a}Wz_3)\int \delta t \qquad [B.6]$$

or $$S^{1-\alpha}/(1-\alpha) \quad = \quad -100z_1z_2b^{-\alpha}t/(Wz_3) \quad + \quad k \qquad [B.7]$$

where $$\alpha \quad = \quad 1/a \qquad [B.8]$$

and k is an arbitrary constant.

<u>Boundary Condition</u>; when $t = 0$, $S = S(0)$ [B.9]

Hence $$k \quad = \quad S(0)^{1-\alpha}/(1-\alpha) \qquad [B.10]$$

Substituting equation [B.10] into [B.7] yields:

$$S(t)/S(0) \quad = \quad [1-100z_1z_2b^{-\alpha}t(1-\alpha)S(0)^{\alpha-1}/(Wz_3)]^{1/(1-\alpha)} \qquad [B.11]$$

Note that the total volume of hydrogen passed through the fluid bed in time t per lb. of MASF char -- i.e., G -- is given by:

$$G \quad = \quad z_1Qt/W \qquad [B.12]$$

Substituting [B.12] into [B.11] yields:

$$S(t)/S(0) \quad = \quad [1-100z_2(1-\alpha)S(0)^{\alpha-1}Gz_3^{-1}b^{-\alpha}]^{1/(1-\alpha)} \qquad [B.13]$$

Equation [B.13] can be employed to describe one limit (i.e., the limit imposed by the assumptions mentioned at the beginning of this appendix) on the kinetics of hydrodesulfurization. However, to use this equation,the parameters α, b and S(0) must be available. These constants are a function of the type of char employed, the temperature at which the desulfurization experiment is conducted and the sulfur content of the feed char. Hence, these constants are dependent upon the experimental conditions employed. In the case studies presented below, the values of α and b will be obtained from the adsorption isotherm correlations developed in Appendix A. The value of S(0) is of course unique to the experiment in question.

CASE STUDIES

<u>Case One</u>; <u>A model for the Lignite Char Hydrodesulfurization Experiments Presented in Section 4.1</u>

The lignite char hydrodesulfurization experiments were conducted at 1400°F. Therefore, from [A.22] and Table 3.2:

$$S \quad = \quad 5.351[P_{H_2S}/P_{H_2}]^{0.1994} \qquad [B.14]$$

Hence $\quad a \quad = \quad 0.1994$

α = 5.015

b = 5.351

and, from Table D.17;

S(0) = 3.019

Substituting into equation [B.13] yields:

$$S(t)/S(0) = [1 + 0.6722G]^{-0.2491} \qquad [B.15]$$

Case Two: A Model for the Bituminous Coal Char Hydrodesulfurization Experiments Presented in Section 4.2

The bituminous coal char hydrodesulfurization experiments presented in Chapter Four were conducted at 1400°F. Hence, from [A.22] and Table 3.2:

$$S = 1.854[P_{H_2S}/P_{H_2}]^{0.2266} \qquad [B.16]$$

Hence a = 0.2266

α = 4.413

b = 1.854

and, from Table D.18;

S(0) = 1.02

Substituting into equation [B.13] yields:

$$S(t)/S(0) = [1 + 2.136G]^{-0.293} \qquad [B.17]$$

Case Three: A Model for the Steam-Hydrogen Char Desulfurization Data of Zielke et al

Zielke et al's(132) Disco char hydrodesulfurization experiments were conducted at 1600^0F. Hence, from equation [A.22] and Table 3.2:

$$S = 2.469[P_{H_2S}/P_{H_2}]^{0.2510} \qquad [B.18]$$

Hence
$a = 0.2510$
$\alpha = 3.984$
$b = 2.469$

In addition, from Table D.20:

$$S(0) = 2.159$$

Substituting into equation [B.13] yields:

$$S(t)/S(0) = [1 + 7.218G]^{-0.335} \qquad [B.19]$$

Case Four: A Model for Jones' COED Char Hydrodesulfurization Data

Jones'(52) COED char hydrodesulfurization experiments were performed at 1600^0F. Hence, from [A.22] and Table 3.2:

$$S = 2.467[P_{H_2S}/P_{H_2}]^{0.250} \qquad [B.20]$$

Hence: $a = 0.250$

$\alpha = 4.000$

$b = 2.467$

and, from Table D.21:

$S(0) = 4.185$

Substituting into equation [B.13] yields:

$$S(t)/S(0) = [1 + 52.94G]^{-0.333} \qquad [B.21]$$

Case Five: A Model for Hiteshue's Bituminous Coal Char Hydrodesulfurization Experiments

Hiteshue's(43) bituminous coal char hydrodesulfurization experiments were conducted at 800°C. Hence, from [A.22] and Table 3.2:

$$S = 2.054[P_{H_2S}/P_{H_2}]^{0.236} \qquad [B.22]$$

Hence $a = 0.236$

$\alpha = 4.237$

and $b = 2.054$

From Table D.22:

$S(0) = 1.3$

Substituting into equation [B.13] yields:

$$S(t)/S(0) = [1 + 3.20G]^{-0.309} \qquad [B.23]$$

Case Six: A Model for Hiteshue's Bituminous Coal Hydrodesulfurization Data

In this case, the constants a, α and b are the same as in Case Five (because the parent material -- i.e., bituminous coal -- and the temperature were the same in both cases). However, the sulfur content of the feed was different -- i.e.,

$$S(0) = 2.2$$

Substituting this value into [B.13] yields:

$$S(t)/S(0) = [1 + 17.63G]^{-0.308} \qquad [B.24]$$

The six models presented above are presented in Figures 4.1, 4.2, 4.8, 4.10, 4.11, 4.12 and 4.13.

APPENDIX C

FIGURES

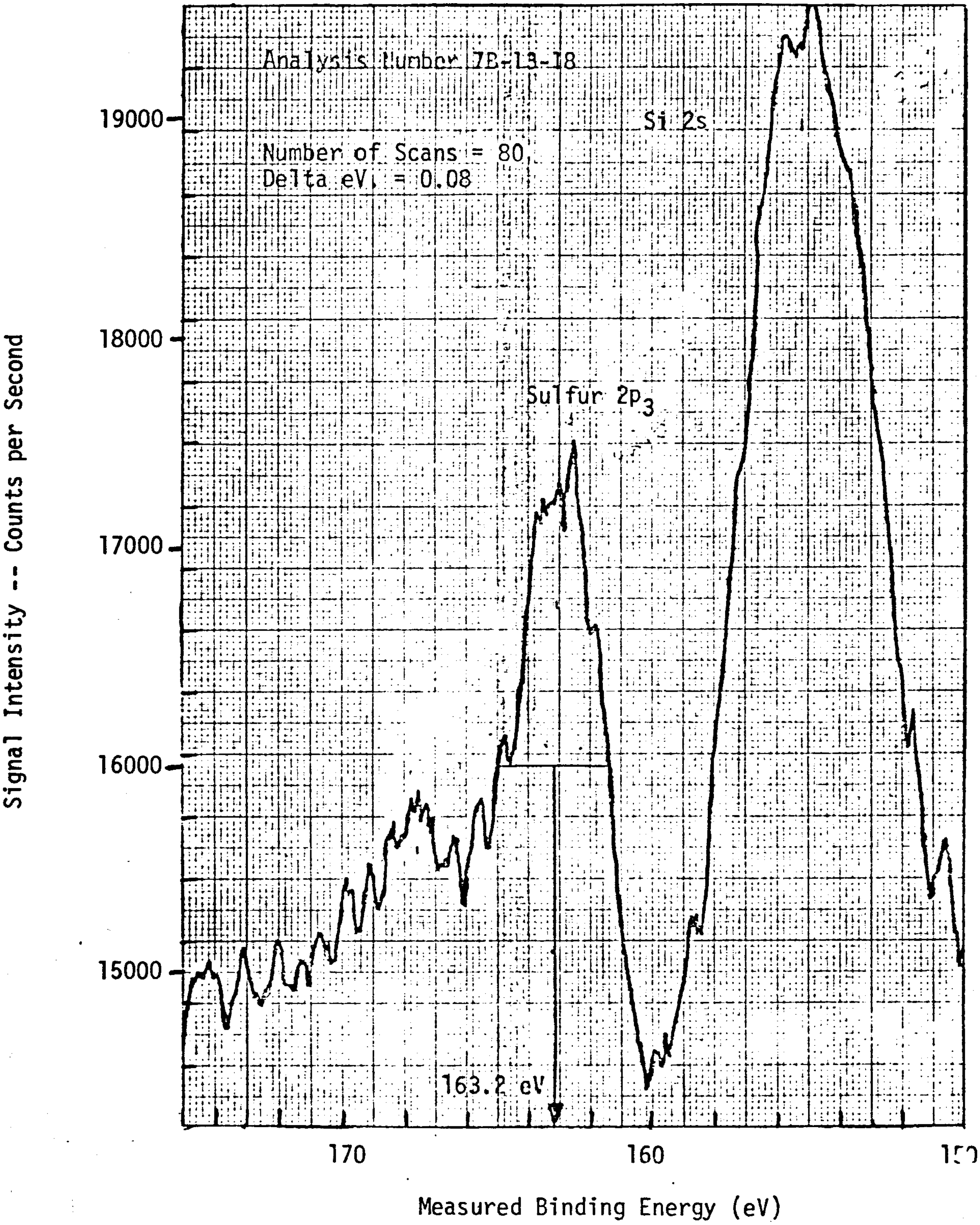

Figure C.1 Measured Binding Energy Spectrum for Sample #3 (Unsputtered)

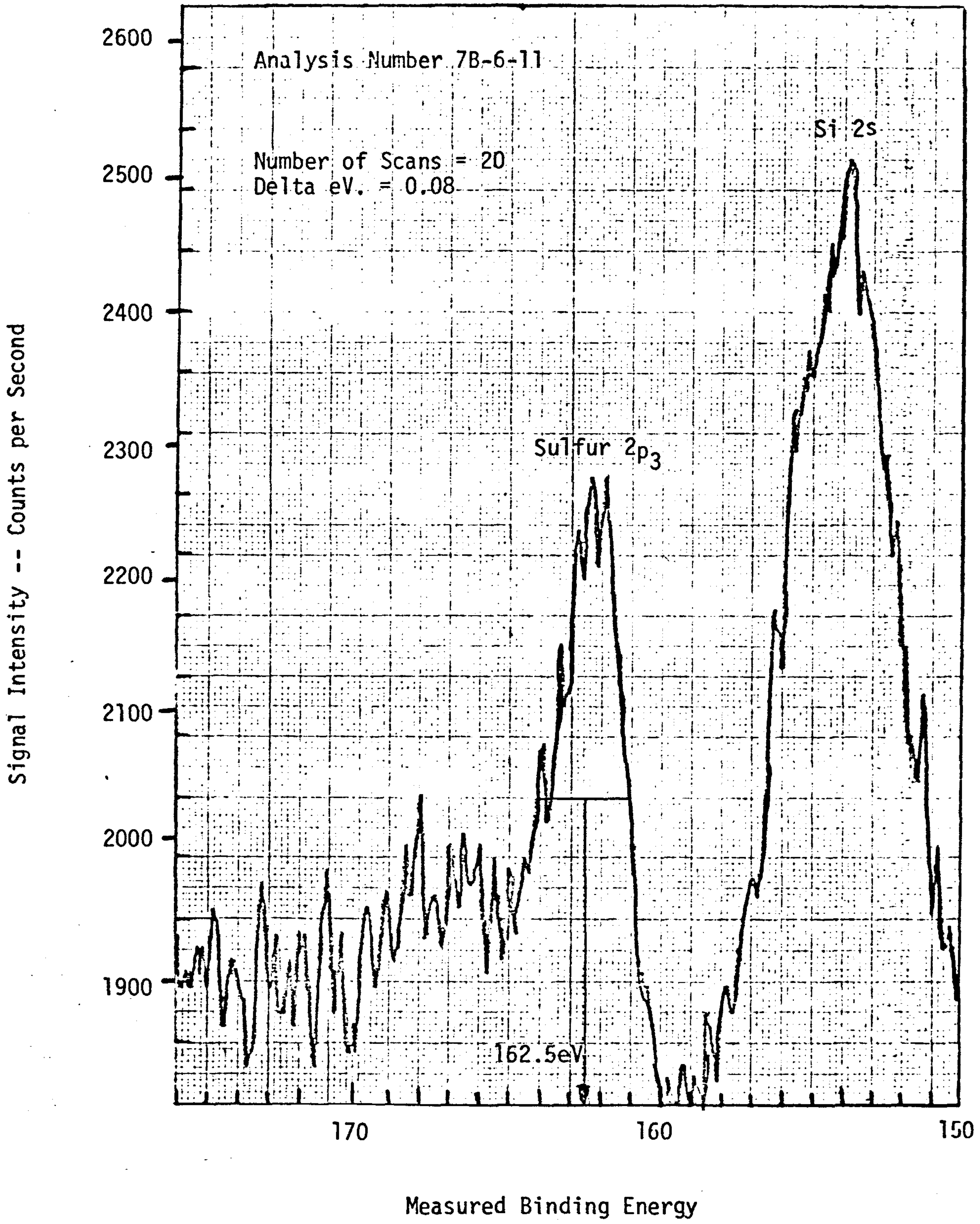

Figure C.2 Measured Binding Energy Spectrum for Sample #4 (Unsputtered)

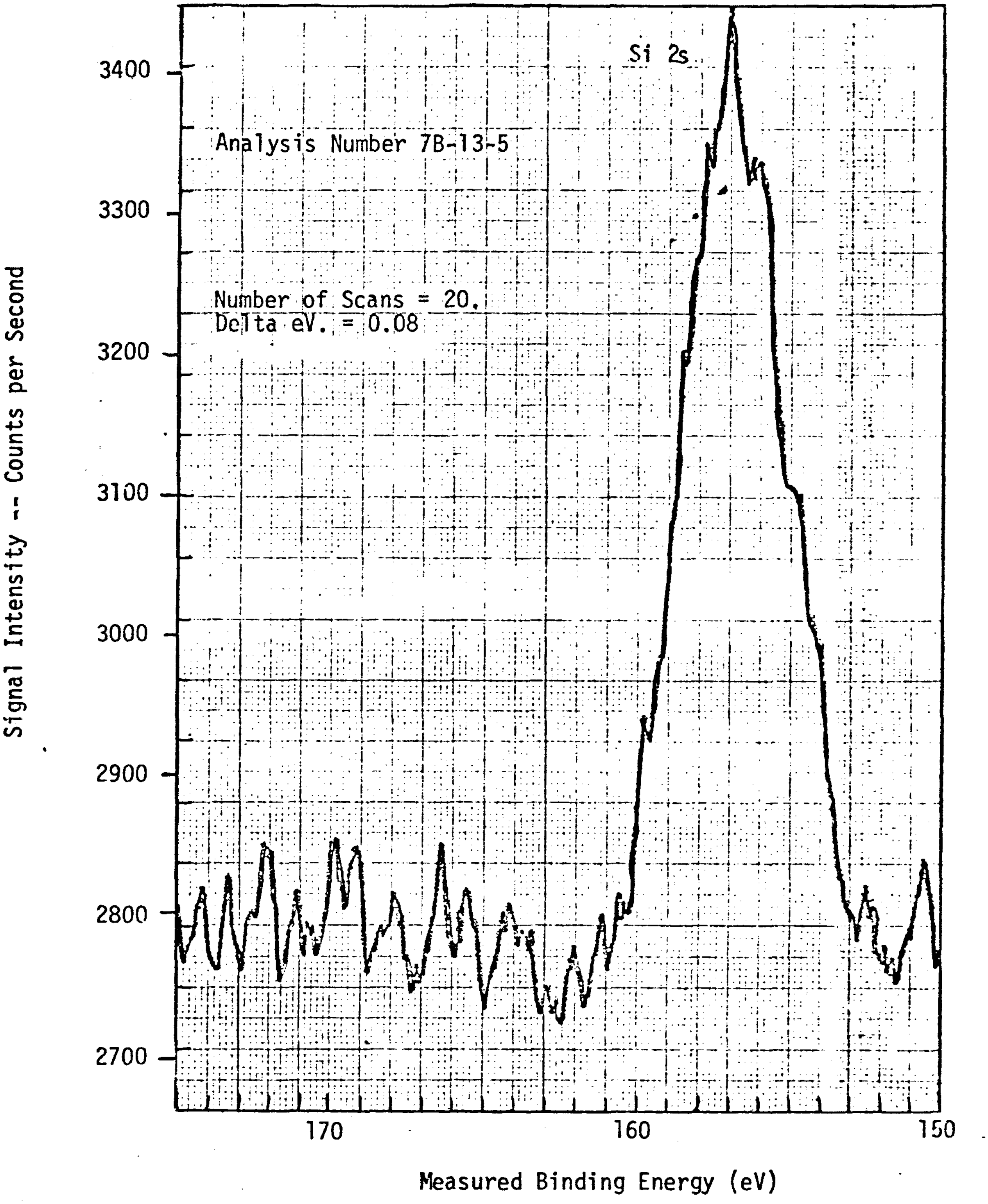

Figure C.3 Measured Binding Energy Spectrum for Sample #5 (Unsputtered)

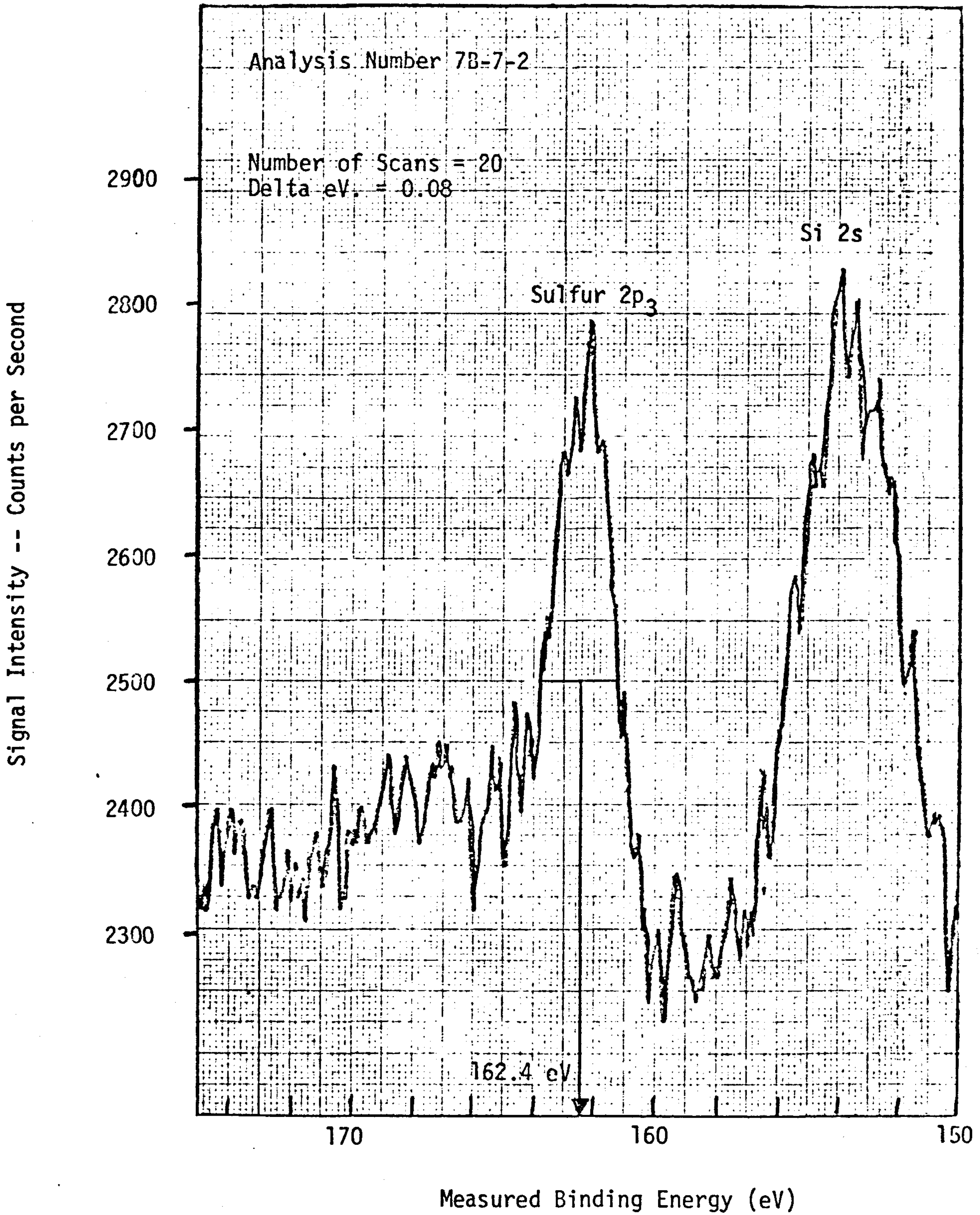

Figure C.4 Measured Binding Energy Spectrum for Sample #6 (Unsputtered).

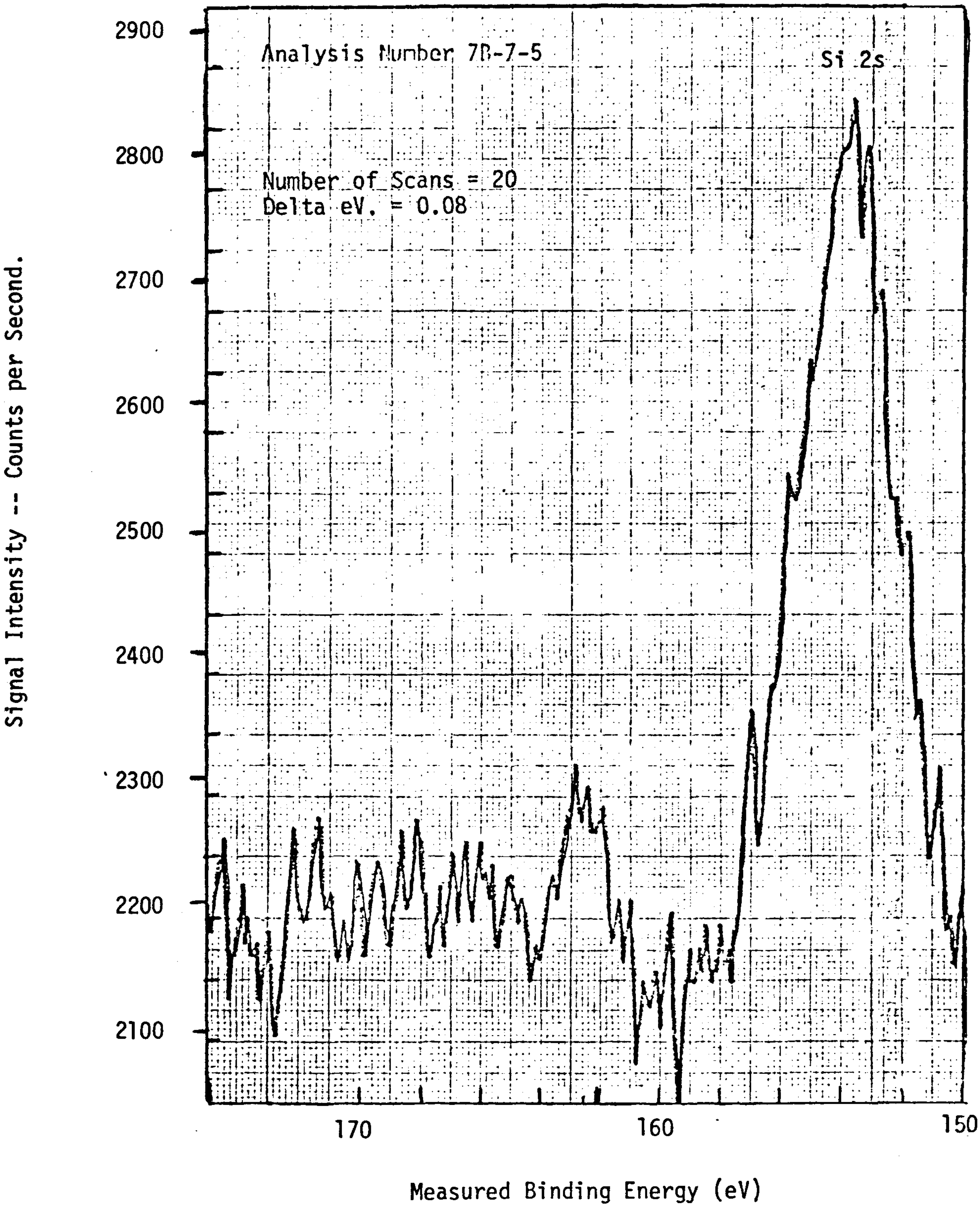

Figure C.5 Measured Binding Energy Spectrum for Sample #7 (Unsputtered).

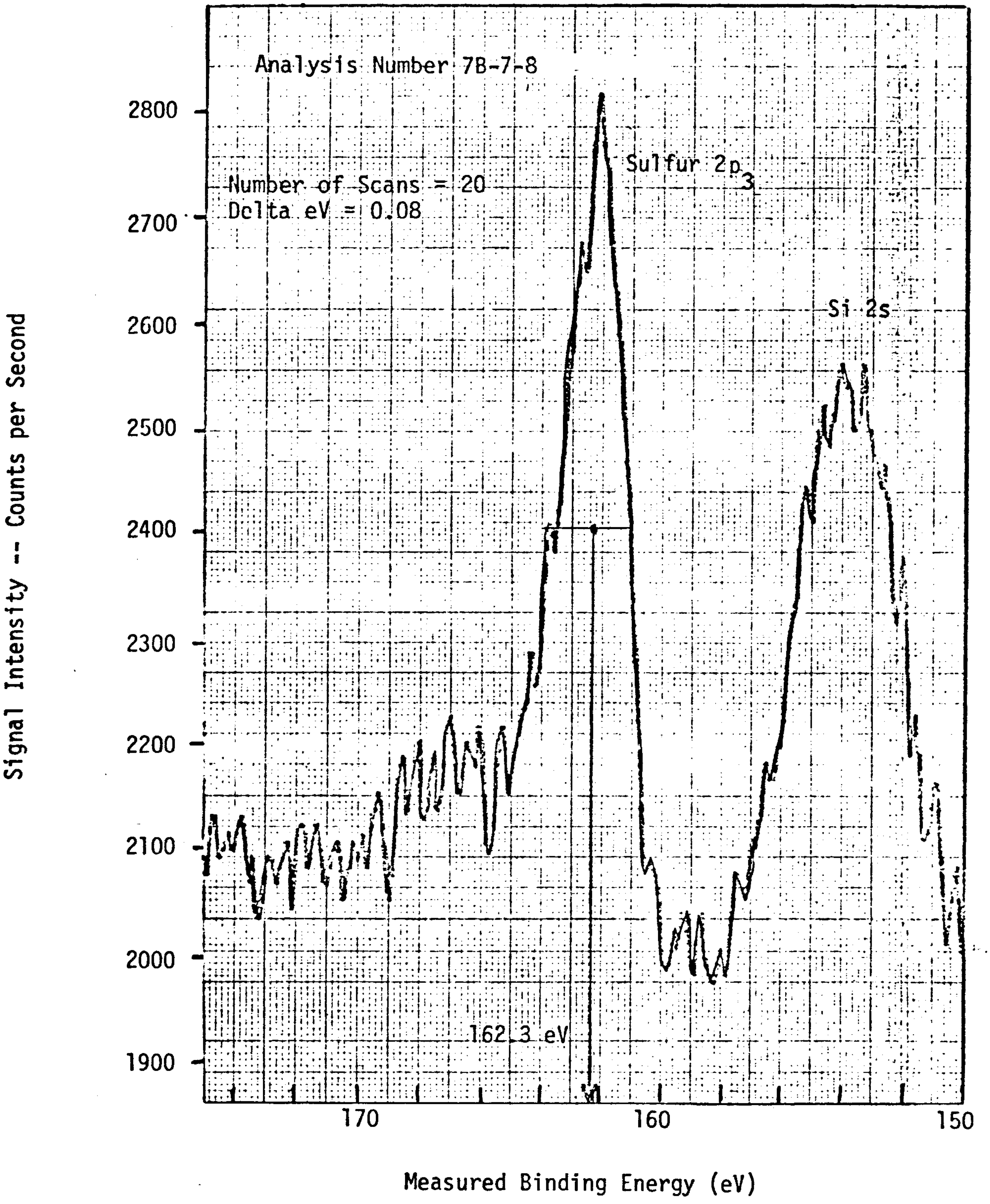

Figure C.6 Measured Binding Energy Spectrum for Sample #8 (Unsputtered)

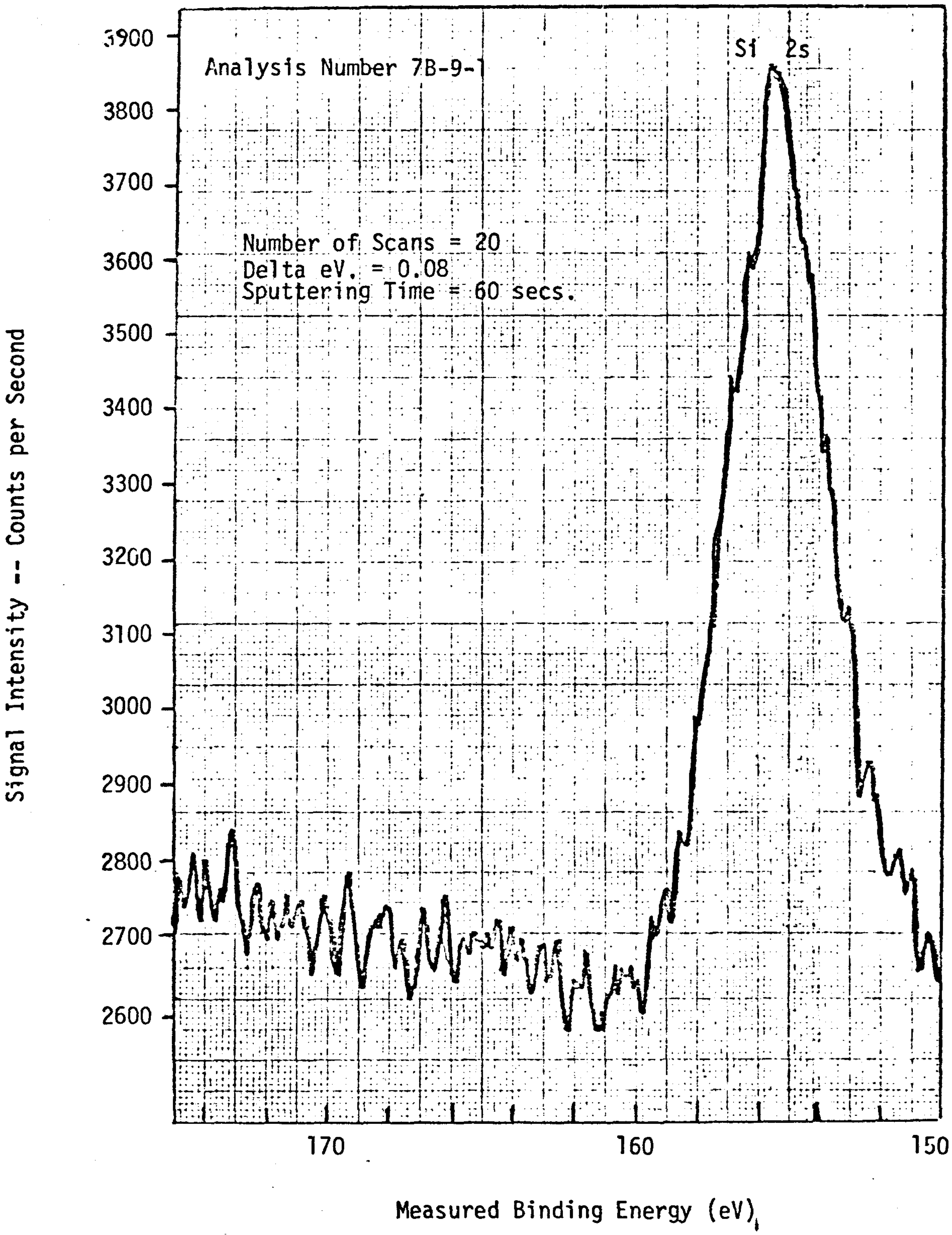

Figure C.7 Measured Binding Energy Spectrum for Sample #1 (Sputtered).

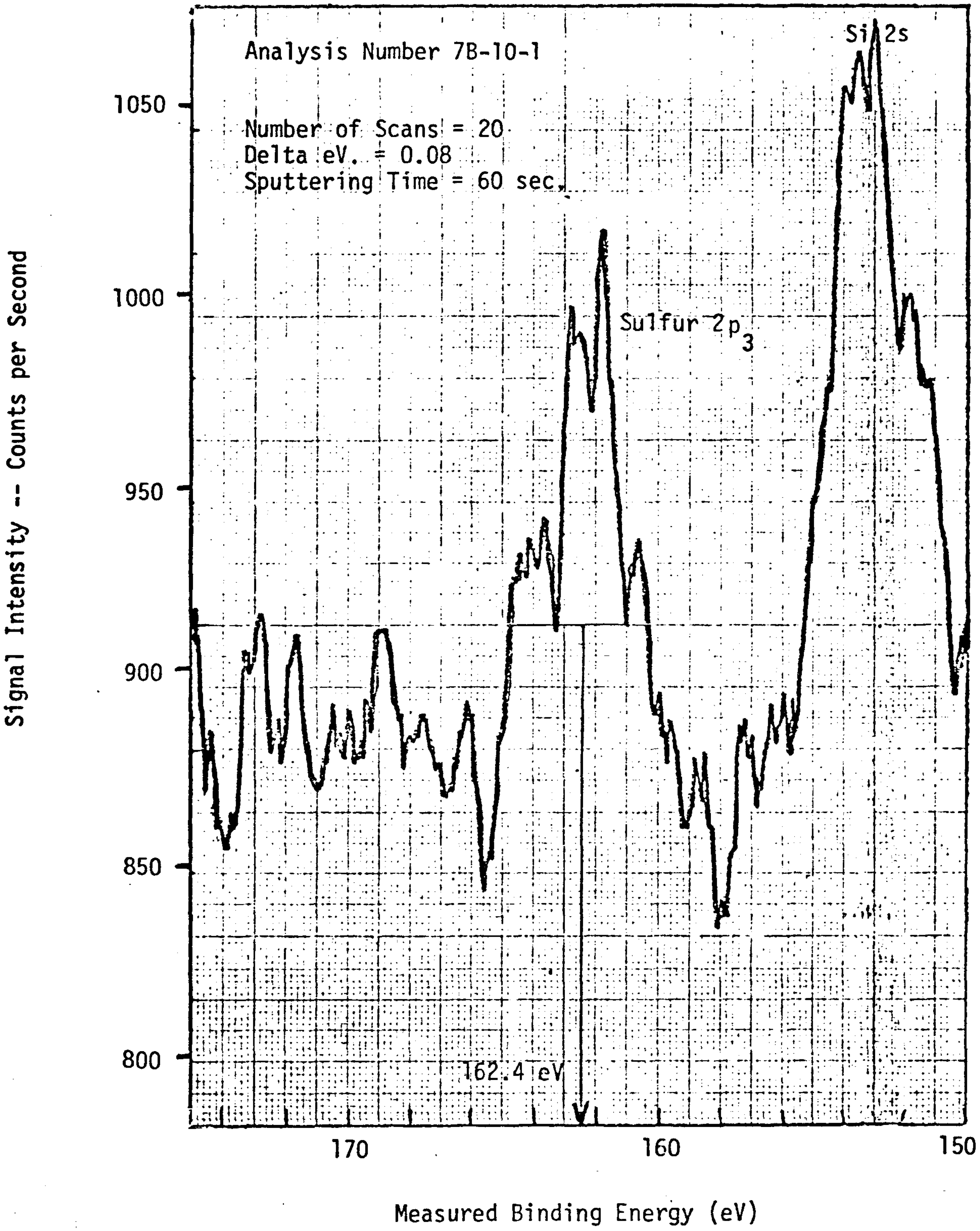

Figure C.8 Measured Binding Energy Spectrum for Sample #2 (Sputtered).

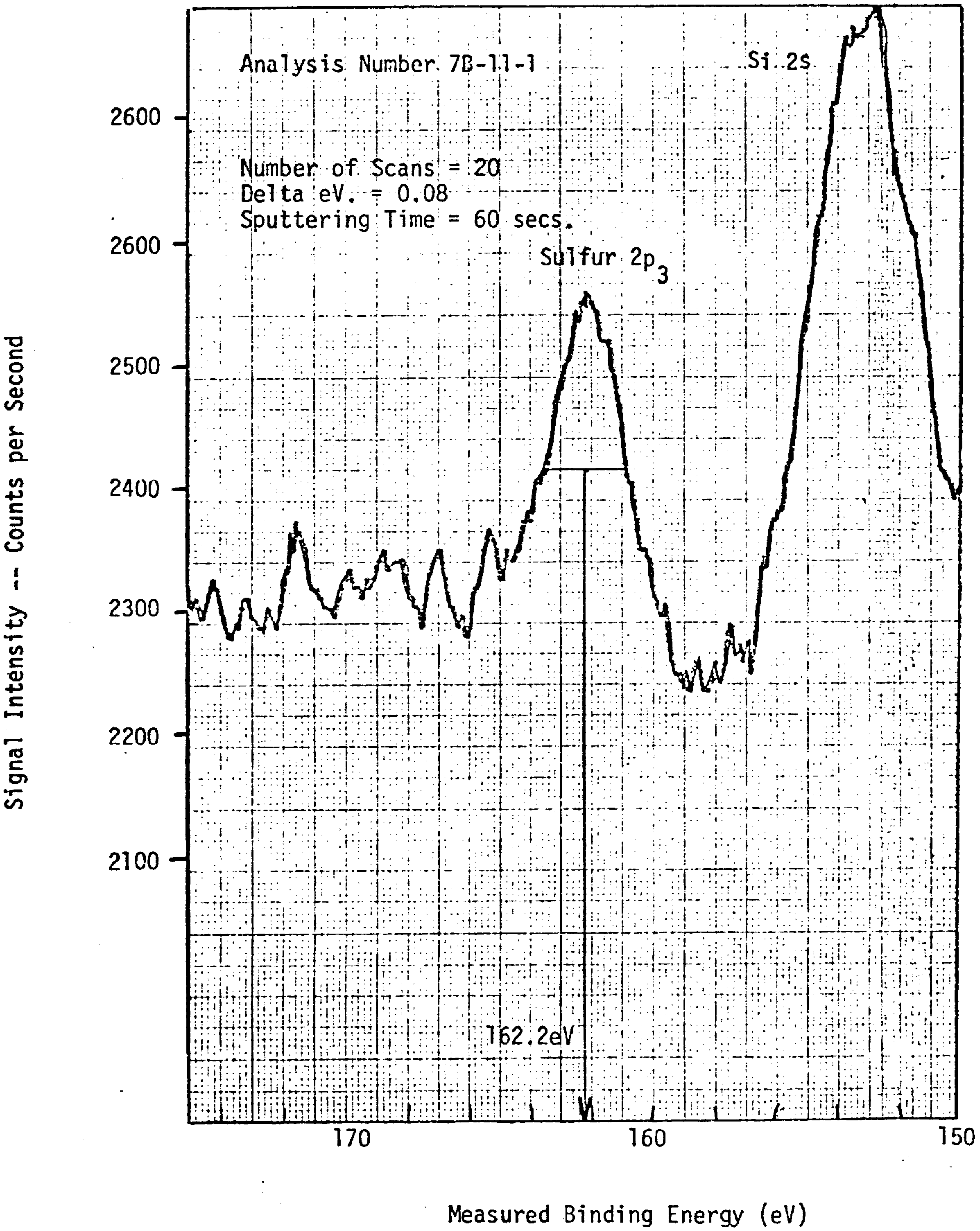

Figure C.9 Measured Binding Energy Spectrum for Sample #4 (Sputtered).

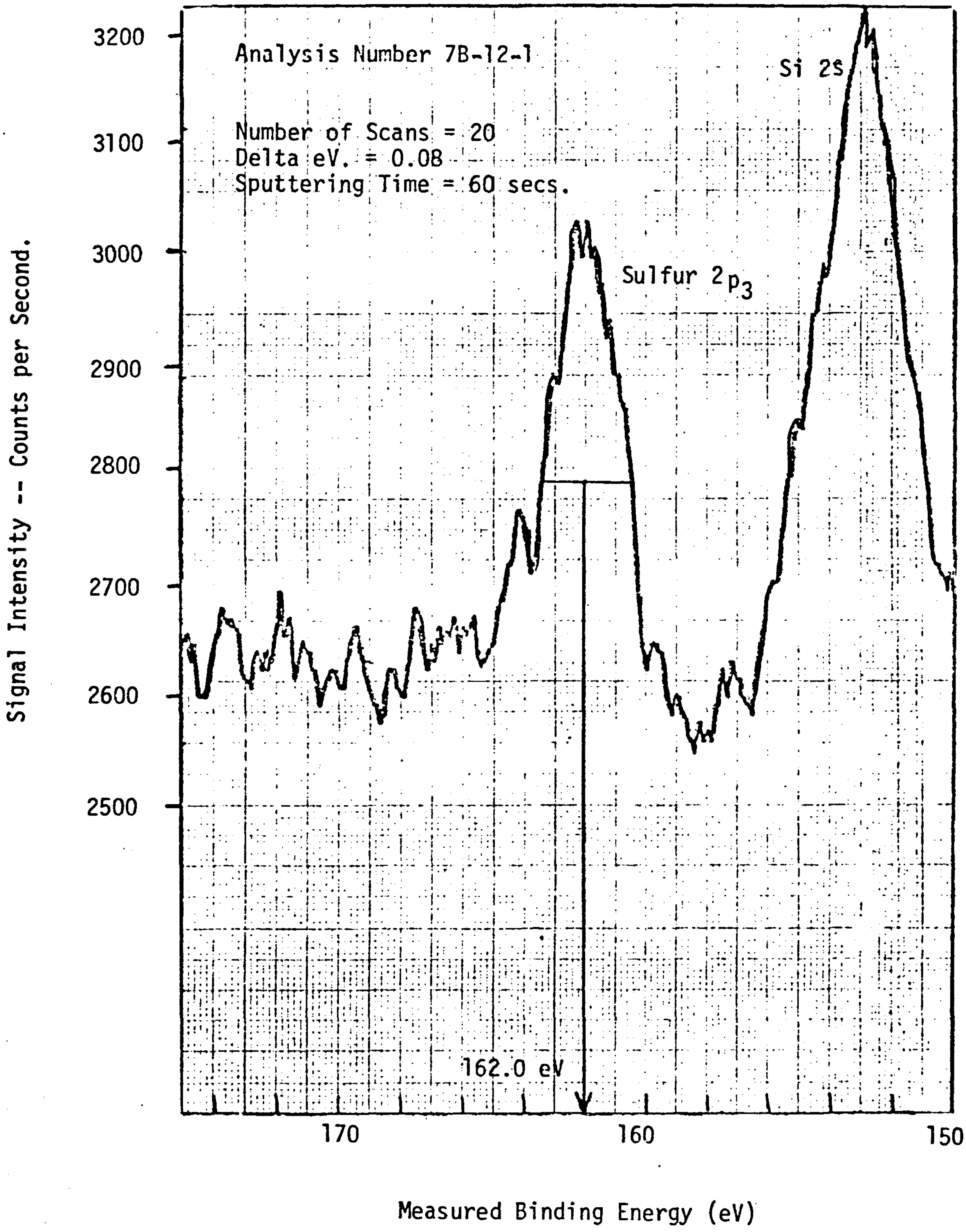

Figure C.10 Measured Binding Energy Spectrum for Sample #6 (Sputtered).

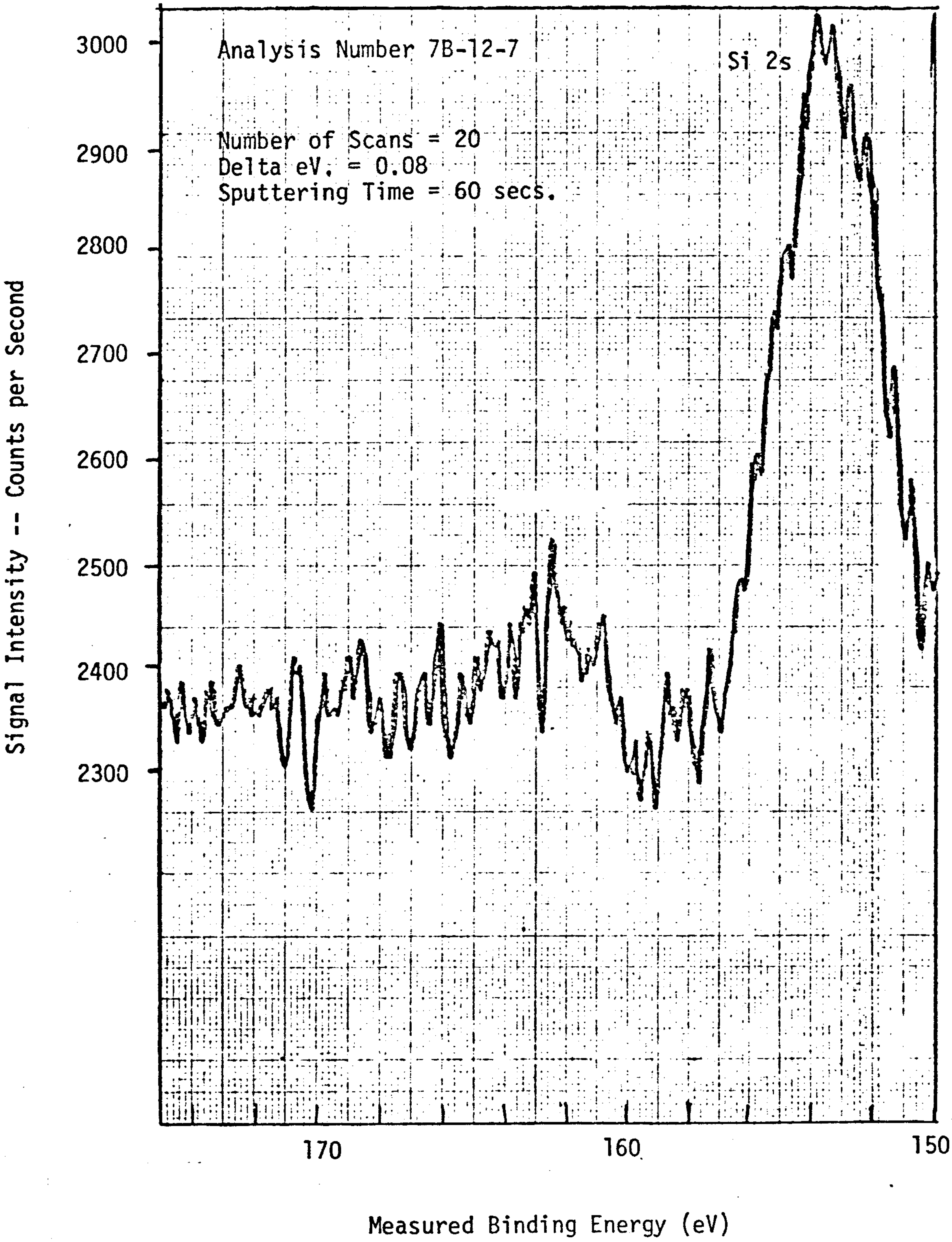

Figure C.11 Measured Binding Energy Spectrum for Sample #7 (Sputtered).

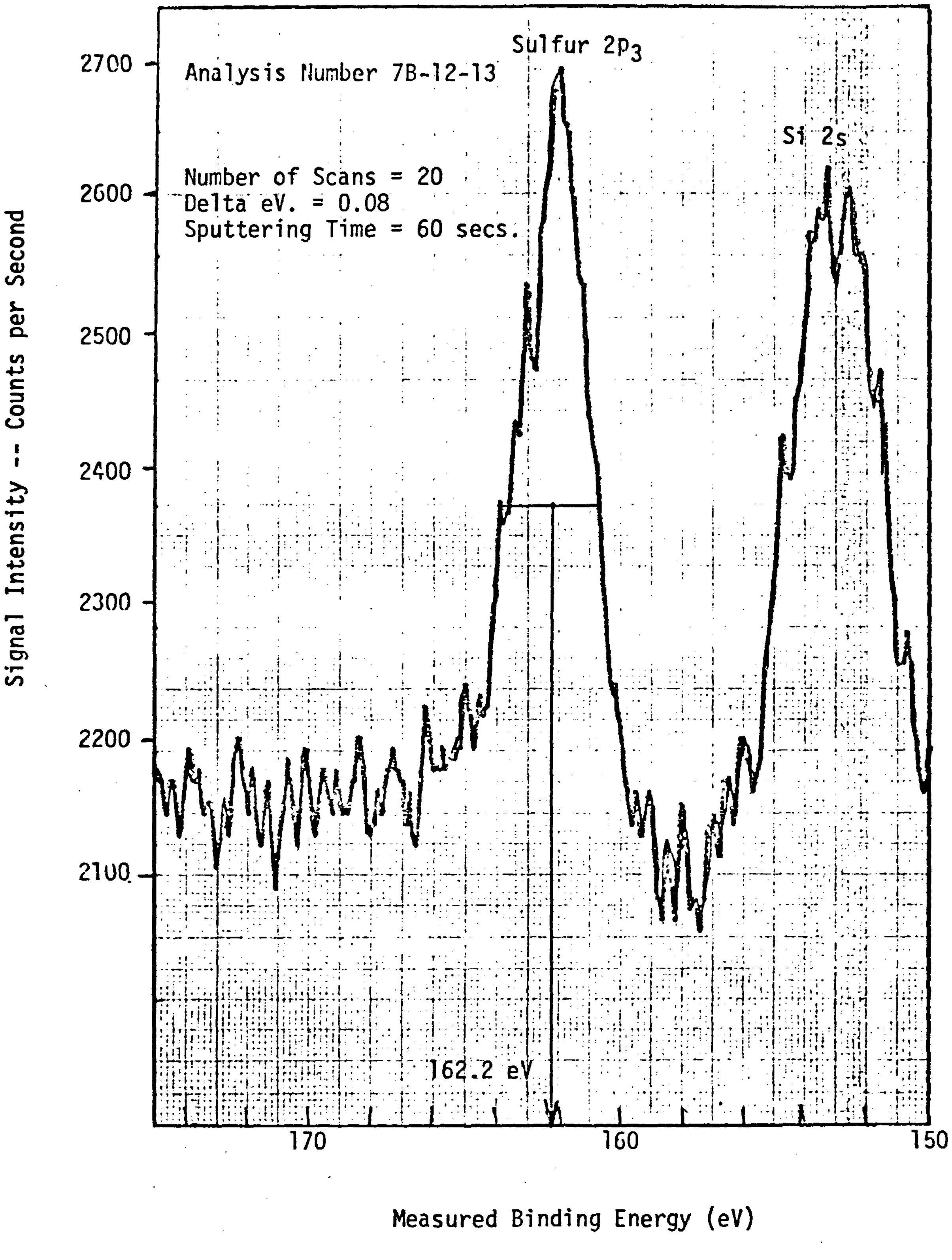

Figure C.12 Measured Binding Energy Spectrum for Sample #8 (Sputtered).

APPENDIX D

TABLES

Experiment #	Char Type	X Hours	Total Sulfur wt%	Sulfide Sulfur wt%	Organic Sulfur wt%	Mean	Normalized Organic Sulfur %
10	Filter Paper	1	0.49	Negligible	0.49	0.53	92.5
11	"	2	0.55	"	0.55		103.8
82	"	8	0.49	"	0.49		92.5
84	"	32	0.59	"	0.59		111.3
29	HYDRANE Lignite [HY-138]	1	3.87	0.67	3.20	3.127	102.3
27		2	4.00	0.79	3.11		99.5
86	"	32	4.09 4.24	1.13 1.06	3.07		98.2
1A	Coconut-based Activated Charcoal [Char#3]	10/60	0.29 0.51 0.54	Negligible	0.447	0.522	85.6
5		20/60	0.57 0.56	"	0.565		108.2
2	"	30/60	0.44 0.56 0.56	"	0.52		99.6
6	"	45/60	0.56 0.55	"	0.555		106.3
3	"	1	0.55 0.51		0.530		101.5
7	"	90/60	0.56 0.51	"	0.535		102.5
4	"	2	0.52 0.56	"	0.54		103.4

Table D.1 Results of Experiments to Establish whether or not the Time of Exposure to Hydrogen Sulfide affects the Amount of Sulfur Adsorbed

Experiment #	Partial Pressure of Helium; B Atm.	Partial Pressure of $H_2 + H_2S$ Atm.	Total Sulfur wt%	Sulfide Sulfur wt%	Organic Sulfur wt%
29	0.0	1.0	3.87	0.67	3.20(96.1)[a]
88	0.1	0.9	3.89 3.86	0.66 0.60	3.24(97.2)
89	0.37	0.63	3.99 3.95	0.60 0.63	3.36(100.8)
90	0.63	0.37	4.08 4.09	0.59 0.74	3.43(102.9)
92	0.80	0.20	4.34 4.33	1.00 1.03	3.32(99.6)
91	0.90	0.10	4.51 4.52	0.91 0.87	3.63(108.9)
93	0.95	0.05	4.44 4.39	1.29 1.33	3.11(93.3)

Note: (a) Figures in parenthesis are normalized to 100% of the mean value - i.e., 3.33

(b) Experimental History:

START — 900°C, 1 Hour / 0.5SCFH Helium — 1600°F; 1 Hour / 0.5SCFH Helium — 1600°F; 1 Hour; 1 SCFH / B Atm. Helium; remainder is a mixture of 5.17% H_2S in Hydrogen — ANALYSIS

Table D.2 Results of Experiments to Establish whether or not the Concentration of Organic Sulfur in Char is a Function of the Partial Pressure of Hydrogen Sulfide

Char Description	Expt #	%Ash (a)	%Moisture (b)	Organic Sulfur (c)	Surface Area (d)	Surface Area (e)	Surface Area (f)	Surface Area (g)
HYDRANE [HY-138] Lignite Char	29	14.27	3.64	4.06	158	200.3	485	615
HYDRANE [HY-140] Subbituminous Char	107	14.74	2.72	2.14(h)	80.5	99.6	241	298
HYDRANE [HY-128] Bituminous Char	105	11.92	1.73	1.19(h)	18.3	21.4	425	498
Char # 1; Anthracite based Activated Charcoal	9	7.69	1.56	1.15	99.	110.3	376	419
Char # 2	20	0.90	2.44	0.92	433.	452.	795	830
Char # 3	3	2.37	1.70	0.56	1303	1366	1198	1256
Char # 4	21	3.16	1.80	0.80	1212	1285	1069	1134
Char # 5	24	0.49	1.04	0.49	1580	1619	1179	1208
Filter Paper Char	10	0.61	1.77	0.507	359	370	788	811

Note (a) % Ash - on an as-received basis
(b) % Moisture - on an as-received basis
(c) Organic sulfur content, in grams of organic sulfur per 100 grams of MASF Char, at 1600°F and $100P_{H_2S}/P_{H_2} = 5.45$
(d) Surface area, by the Nitrogen and B.E.T. equation method, m^2 per gram of as-received char
(e) Surface area, by the Nitrogen and B.E.T. equation method, m^2 per gram of MASF char
(f) Surface area, by the Carbon Dioxide and Dubinin-Polyani equation method, m^2 per gram of as-received char
(g) Surface area, by the Carbon Dioxide and Dubinin-Polyani equation method, m^2 per gram of MASF char.
(h) Estimated from adsorption isotherms
(i) Experimental History:

START 900°C; 1 Hour — 0.5 SCFH Helium → 1600°F; 1 Hour — 0.5 SCFH Helium → 1600°F; 1 Hour — 1 SCFH; 5.17% H_2S in Hydrogen → ANALYSIS

Table D.3 Results of Experiments to Establish whether or not the Equilibrium Concentration of Organic Sulfur in Char is a Function of Surface Area.

Experiment %	$100P_{H_2S}/P_{H_2}$ [X]	Total[(a)] Sulfur %	Sulfide[(a)] Sulfur %	Organic[(a)] Sulfur %;[S]	$\frac{100P_{H_2S}}{[S]xP_{H_2}}$
72	0.0988	0.05	Negligible	0.05	1.98
71	0.523	0.11	"	0.11	4.75
75	1.01	0.18	"	0.18	5.61
69	2.03	0.30	"	0.30	6.77
76	3.09	0.28	"	0.28	11.04
70	4.16	0.32	"	0.32	13.00
10	5.45	0.49	"	0.49	11.12
78	15.45	0.59	"	0.59	26.19
79	24.32	0.73	"	0.73	33.32
74	32.54	1.04	"	1.04	31.29
81	52.64	1.13	"	1.13	46.58
80	76.41	1.33	"	1.33	57.45
73	97.63	1.86	"	1.86	52.49

Note: (a) Total, sulfide and Organic sulfur contents on an as-received basis

(b) Experimental History:

START	900°C; 1 Hour 0.5Scfh Helium	1600°F; 1 Hour 0.5 Scfh Helium	1600°F; 1 Hour 1Scfh; $100P_{H_2S}/P_{H_2}$=X	ANALYSIS

(c) Filter Paper Chars prepared by charring raw filter paper at 900°C for 3 hours in a horizontal tube furnace at 3 SCFH Helium.

Table D.4 Filter Paper Char Sulfidation Data at 1600°F

$P_{S_2} \times 10^{10}$ (a) Atm.	$100P_{H_2S}/P_{H_2}$ (b)	Total Sulfur (c) Wt. %
90	0.707	1.0
130	0.850	1.13
200	1.054	1.25
250	1.179	1.32
310	1.312	1.41
1090	2.461	1.89
1710	3.082	2.10
2590	3.793	2.34
3000	4.082	2.40
4000	4.714	2.54
5140	5.344	2.65

Note: (a) Since tabulated data were not presented, these data were estimated from the graphical data presented by Powell.

(b) Calculated using the formula (presented by Powell):

$$100P_{H_2S}/P_{H_2} = 100 \times \sqrt{P_{S_2}/K_p}$$

where K_p, the equilibrium constant for the reaction $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$ is equal to 1.8×10^{-4} at 800°C.

(c) Since the sulfide sulfur concentration in sugar chars is probably insignificant, it seems reasonable to assume that the organic sulfur concentration is equal to the total sulfur concentration.

(d) The conditions of char preparation were not specified by Powell.

Table D.5 Powell's Sugar Char Sulfidation Data at 800°C

Sulfidation Temperature °C	Preparation Temperature °C	$100P_{H_2S}/P_{H_2}$	Total Sulfur [(a)]
900	600	50	2.7
900	600	100	3.5
900	600	200	4.8
900	600	290	5.1
900	600	390	6.8
900	600	550	7.3
900	600	660	7.6
900	600	760	7.2
900	600	760	9.1
900	900	50	2.0
900	900	100	2.9
900	900	200	3.3
900	900	290	5.1
900	900	290	4.5
900	900	760	5.1
900	900	760	5.8
600	600	100	2.8
600	600	500	5.0
600	600	1000	5.2
600	600	2000	7.3
600	600	3600	9.5
600	600	6200	9.8
600	900	100	0.8
600	900	200	5.0
600	900	500	5.2
600	900	1000	7.3
600	900	1900	9.5
600	900	6200	9.8

Note: (a) Units are grams of sulfur per 100 grams of as-received char. Since the sulfide sulfur concentration in Filter Paper char is insignificant, the organic sulfur content is equal to the total sulfur concentration.

(b) These data are estimated from the graphs presented by Kor

Table D.6. Kor's(57) Filter Paper Char Sulfidation Data at 600 and 900°C

Experiment	%H_2S in H_2	$100P_{H_2S}/P_{H_2}$	%Sulfur(MAF)	g. Sulfur / 100 g MAF char	$Log_{10}[S]$	$Log_{10}[P_{S_2}]$ (a)	Temperature ^{o}F
74	0.11	0.11	0.36	0.36	-0.44	-10.16	1350
75	0.15	0.15	0.52	0.52	-0.28	- 9.89	1350
86	0.17	0.17	0.91	0.92	-0.04	- 9.78	1350
73	0.20	0.20	0.70	0.70	-0.15	- 9.64	1350
79	0.26	0.26	0.72	0.73	-0.14	- 9.41	1350
70	0.27	0.27	1.06	1.07	0.03	- 9.38	1350
68	0.53	0.53	1.04	1.05	0.02	- 8.79	1350
69	0.54	0.54	1.18	1.19	0.08	- 8.77	1350
78	0.53	0.53	0.98	0.99	0.00	- 8.79	1350
67	1.06	1.07	1.20	1.21	0.08	- 8.18	1350
71	1.05	1.06	1.43	1.45	0.16	- 8.19	1350
77	1.03	1.04	1.28	1.30	0.11	- 8.20	3150
66	2.05	2.09	1.69	1.72	0.24	- 7.60	1350
72	2.07	2.11	1.70	1.73	0.24	- 7.59	1350
76	2.07	2.11	1.58	1.61	0.21	- 7.59	1350
85	3.04	3.13	1.90	1.94	0.29	- 7.25	1350
37	0.24	0.24	0.49	0.49	-0.31	- 8.33	1600
38	0.29	0.29	0.68	0.68	-0.17	- 8.17	1600
46	0.38	0.38	0.78	0.79	-0.10	- 7.93	1600
39	0.42	0.42	0.78	0.79	-0.10	- 7.84	1600
33	0.54	0.54	0.76	0.77	-0.11	- 7.63	1600
34	0.54	0.54	0.61	0.61	-0.21	- 7.63	1600
35	0.51	0.51	0.86	0.87	-0.06	- 7.68	1600
40	0.54	0.54	0.93	0.94	-0.03	- 7.63	1600
41	0.52	0.52	0.85	0.86	-0.07	- 7.66	1600
42	0.54	0.54	0.76	0.77	-0.11	- 7.63	1600
48	0.53	0.53	0.76	0.77	-0.11	- 7.64	1600
30	1.00	1.01	1.07	1.08	0.03	- 7.01	1600
31	1.03	1.04	1.09	1.10	0.04	- 7.06	1600
47	1.05	1.06	1.12	1.13	0.05	- 7.04	1600
32	2.07	2.11	1.21	1.22	0.09	- 6.44	1600
43	2.05	2.09	1.24	1.26	0.10	- 6.45	1600
58	2.09	2.14	1.56	1.58	0.20	- 6.43	1600
36	3.07	3.17	1.52	1.54	0.19	- 6.09	1600
59	3.15	3.25	1.56	1.58	0.20	- 6.07	1600

Note: (a) Calculated from Equation [A.23], Appendix A

Table D.7 Batchelor's Char Sulfidation Data at 1350 and 1600^{O}F

			Moisture-free Basis				MASF Basis	MAF Basis
Expt. #	Temperature °F T	$100P_{H_2S}/P_{H_2}$ E	Total Sulfur %	Sulfide Sulfur %	Mean Organic Sulfur %	Ash %	Organic Sulfur (a)	Organic Sulfur %
134	1200	0.1	1.50 1.52	0.22 0.26	1.27	14.91*	1.516	1.493
166	1200	0.52	1.47 1.47	0.34 0.31	1.145	13.45	1.341	1.323
144	1200	1.97	2.46 2.49	0.46 0.51	0.990	14.91*	1.177	1.163
35	1200	5.45	2.97 2.98	0.13 0.23	2.795	14.91*	3.397	3.285
42	1200	5.45	3.05 3.15	0.29 0.35	2.780	14.91*	2.377	3.267
162	1200	24.6	2.57 2.63	0.33 0.41	2.230	14.17	2.667	2.598
120	1200	97.6	3.57 3.59	0.56 0.58	3.010	14.91*	3.667	3.537
124	1400	0.1	1.43 1.43	0.32 0.27	1.135	14.91*	1.352	1.334
96	1400	0.52	2.23	0.66 0.68	1.560	15.28	1.876	1.841
138	1400	1.97	2.80 2.81	0.66 0.91	2.135	16.57	2.626	2.559
40	1400	5.45	3.57 3.56	0.59*	2.975	14.91*	3.623	3.496
44	1400	5.45	3.49 3.50	0.59*	2.905	14.91*	3.535	3.414
108	1400	8.41	2.81 3.50 3.54	0.64 0.61	2.910	14.91*	3.541	3.420
152	1400	24.6	3.91 3.92	0.51 0.59	3.365	14.05	4.075	3.915
116	1400	97.6	4.69 4.60	0.54 0.44	4.155	14.91*	5.078	4.833
125	1600	0.1	1.59 1.64	0.63 0.67	0.965	14.91*	1.147	1.134
97	1600	0.52	3.08	1.03	2.050	14.91*	2.468	2.409
139	1600	1.97	3.21 3.26	0.85 1.22	2.200	14.91*	2.654	2.585
29	1600	5.45	3.88 3.86	0.85	3.020	14.91*	3.680	3.549
27	1600	5.45	4.00 4.00	0.79	3.210	14.91*	3.920	3.772
109	1600	8.41	4.01 4.02	1.04 1.04	2.975	14.91*	3.623	3.496
153	1600	24.6	4.54 4.67	0.85 0.95	3.705	14.91*	4.552	4.354
117	1600	97.6	6.19 6.22	0.76	5.370	15.96	6.826	6.390

Note: (a) Grams of organic sulfur per 100 grams of MASF Char
(b) The * implies that these data were assumed equal to the mean value of the data in the same column
(c) Experimental History

$$\text{START} \xrightarrow[\text{0.5 SCFH He}]{900^{\circ}\text{C; 1 Hour}} \xrightarrow[\text{0.5 SCFH He}]{T^{\circ}\text{F; 1 Hour}} \xrightarrow[100P_{H_2S}/P_{H_2}=E]{T^{\circ}\text{F; 1 Hour; 1 SCFH}} \text{ANALYSIS}$$

Table D.8 HYDRANE HY-138 Lignite Char Adsorption Isotherm Data

			Moisture-free Basis				MASF Basis	MAF Basis
Expt. #	Temperature °F T	$100P_{H_2S}/P_{H_2}$ E	Total Sulfur %	Sulfide Sulfur %	Mean Organic Sulfur %	Ash %	Organic Sulfur (a)	Organic Sulfur %
135	1200	0.1	0.89 0.83	0.04	0.82	14.69	0.970	0.961
167	1200	0.52	0.93 1.05	0.13	0.86	14.47	1.15	1.005
145	1200	1.97	1.31 1.08	0.13	1.065	14.42	1.260	1.244
175	1200	8.41	0.86 1.36	0.15	0.960	15.01	1.143	1.13
163	1200	24.6	0.56 0.57	0.10	0.465	15.66	0.554	0.551
121	1200	97.6	2.07 2.06	0.18	1.885	14.77*	2.262	2.212
126	1400	0.1	0.80 0.81	0.08	01725	14.32	0.853	0.846
100	1400	0.52	1.24	0.15	1.09	14.57	1.292	1.276
140	1400	1.97	1.27 1.14	0.15	1.055	15.71	1.268	1.252
104	1400	8.41	1.83 1.84	0.15 0.15	1.685	15.27	2.029	1.989
154	1400	24.6	2.50 2.32	0.14	2.270	13.99	2.711	2.639
112	1400	97.6	3.03 3.04	0.17	2.865	14.97	3.486	3.369
127	1600	0.1	0.82 0.80	0.15	0.66	15.45	0.787	0.781
101	1600	0.52	1.30 1.22	0.26	1.00	15.41	1.196	1.182
141	1600	1.97	1.28 1.49	0.23	1.155	13.62	1.355	1.337
105	1600	8.41	2.20 2.20	0.17 0.22	2.005	14.77*	2.409	2.352
155	1600	24.6	2.87 2.88	0.22	2.655	13.99	3.185	3.087
113	1600	97.6	4.18 4.18	0.25	3.930	14.72	4.831	4.608

Note: (a) Grams of organic sulfur per 100 grams of MASF Char
(b) The * implies that these data were assumed equal to the mean value of the other data presented in the same column
(c) Experimental History:

START $\frac{900^{\circ}\text{C; 1 Hour}}{\text{0.5 SCFH He}}$ $\frac{T^{\circ}\text{F; 1 Hour}}{\text{0.5 SCFH He}}$ $\frac{T^{\circ}\text{F; 1 Hour; 1 SCFH}}{100P_{H_2S}/P_{H_2} = E}$ ANALYSIS

Table D.9 HYDRANE HY-140 Subbituminous Char Adsorption Isotherm Data

			Moisture-free Basis				MASF Basis	MAF Basis
Expt. #	Temperature °F T	$100P_{H_2S}/P_{H_2}$ E	Total Sulfur %	Sulfide Sulfur %	Mean Organic Sulfur %	Ash %	Organic Sulfur (a)	Organic Sulfur %
136	1200	0.1	0.56 0.61	Negligible	0.585	12.01*	0.669	0.665
168	1200	0.52	0.45 0.64	"	0.530	11.44	0.602	0.598
150	1200	1.97	0.68 0.43	"	0.555	11.55	0.631	0.627
174	1200	8.41	0.67 0.62	"	0.645	12.17	0.739	0.734
164	1200	24.6	0.57 0.60	"	0.585	11.80	0.668	0.663
122	1200	97.6	1.20 1.20	"	1.20	12.17	1.385	1.366
171	1400	0.05	0.34 0.33	"	0.335	12.24	0.383	0.382
120	1400	0.1	0.41 0.40	"	0.405	11.81	0.461	0.459
170	1400	0.2	0.23 0.31	"	0.270	12.12	0.308	0.307
172	1400	0.3	0.36 0.36	"	0.360	12.97	0.416	0.414
173	1400	0.4	0.43 0.45	"	0.44	12.06	0.503	0.500
98	1400	0.52	0.51	"	0.51	11.67	0.580	0.577
142	1400	1.97	0.58 0.57	"	0.575	12.21	0.659	0.655
106	1400	8.41	0.87 0.71	"	0.790	12.29	0.909	0.901
156	1400	24.6	0.99 1.39	"	1.19	11.60	1.295	1.278
114	1400	97.6	1.81 1.82	"	1.815	11.35	2.090	2.047
129	1600	0.1	0.31 0.32	"	0.315	12.12	0.359	0.358
99	1600	0.52	0.53	"	0.53	13.54	0.617	0.613
143	1600	1.97	0.68 0.69	"	0.685	11.67	0.782	0.776
107	1600	8.41	1.29 0.99 1.32	"	1.305	12.01*	1.505	1.483
157	1600	24.6	2.44 0.99	"	1.715	11.67	2.012	1.942
115	1600	97.6	2.55 2.53		2.54	11.73	2.963	2.878
237	1600	97.6	2.87	"	2.85	8.44	3.213	3.113

Note: (a) Grams of organic sulfur per 100 grams of MASF Char.
(b) The * implies that these data were assumed equal to the mean value of the other data in the same column
(c) Experimental History:

START $\xrightarrow[\text{0.5 SCFH He}]{900^{\circ}\text{C; 1 Hour}}$ $\xrightarrow[\text{0.5 SCFH He}]{T^{\circ}\text{F; 1 Hour}}$ $\xrightarrow[100P_{H_2S}/P_{H_2}=E]{T^{\circ}\text{F; 1 Hour; 1 SCFH}}$ ANALYSIS

Table . HYDRANE HY-128 Bituminous Coal Char Adsorption Isotherm Data

Table D.10. HYDRANE HY-128 Bituminous Char Adsorption Isotherm Data

			Moisture-free Basis				MASF Basis	MAF Basis
Expt. #	Temperature °F T	$100P_{H_2S}/P_{H_2}$ E	Total Sulfur %	Sulfide Sulfur %	Mean Organic Sulfur %	Ash %	Organic Sulfur (a)	Organic Sulfur %
137	1200	0.1	0.21 0.20	Negligible	0.205	7.68	0.222	0.222
169	1200	0.52	0.21 0.39	"	0.30	7.62	0.326	0.325
151	1200	1.97	0.47 0.52	"	0.495	7.32	0.537	0.534
36	1200	5.45	0.54 0.55	"	0.545	8.69	0.601	0.597
43	1200	5.45	0.53 0.53	"	0.53	7.89	0.578	0.575
165	1200	24.6	0.67 0.61	"	0.64	7.69	0.698	0.693
123	1200	97.6	1.18 1.18	"	1.18	7.67	1.295	1.278
130	1400	0.1	0.33 0.33	"	0.33	7.80	0.359	0.358
94	1400	0.52	0.39	"	0.39	7.83	0.425	0.423
146	1400	1.97	0.40 0.40	"	0.40	9.66	0.445	0.443
47	1400	5.45	0.76 0.75	"	0.755	7.55	0.824	0.817
39	1400	5.45	0.74 0.77	"	0.755	8.14	0.829	0.822
160	1400	24.6	1.71 1.65	"	1.68	11.88	1.943	1.906
110	1400	97.6	2.17	"	2.17	7.44	2.400	2.344
131	1600	0.1	0.20 0.23	"	0.215	8.62	0.236	0.235
95	1600	0.52	0.42	"	0.42	7.81	0.458	0.456
147	1600	1.97	0.65 0.64	"	0.645	10.86	0.729	0.724
9	1600	5.45	1.00 1.06	"	1.03	8.06	1.133	1.120
12	1600	5.45	1.11 1.12	"	1.115	7.75	1.224	1.209
161	1600	24.6	2.33 2.38	"	2.355	7.46	2.611	2.545
111	1600	97.6	2.95 2.96	"	2.955	3.80	3.169	3.072

Note: (a) Grams of sulfur per 100 grams of MASF Char
(b) The * implies that these data were assumed equal to the mean value of the other data in the same column
(c) Experimental History:

START $\frac{900^{\circ}C;\ 1\ Hour}{0.5\ SCFH\ He}$ $\frac{T^{\circ}F;\ 1\ Hour}{0.5\ SCFH\ He}$ $\frac{T^{\circ}F;\ 1\ Hour;\ 1\ SCFH}{100P_{H_2S}/P_{H_2} = E}$ ANALYSIS

Table D.11 Barnebey Cheney 417 Anthracite-based Activated Charcoal Adsorption Isotherm Data

			Moisture-free Basis				MASF Basis	MAF Basis
Expt. #	Temperature °F T	$100P_{H_2S}/P_{H_2}$ E	Total Sulfur %	Sulfide Sulfur %	Mean Organic Sulfur %	Ash %	Organic Sulfur (a)	Organic Sulfur %
133	1200	0.1	0.04 0.05	Negligible	0.045	0.61*	0.045	0.045
103	1200	0.52	0.05 0.04	"	0.045	0.61*	0.045	0.045
149	1200	1.97	0.05 0.05	"	0.05	0.61*	0.05	0.05
30	1200	5.45	0.09 0.11	"	0.10	0.37	0.100	0.10
45	1200	5.45	0.12 0.14	"	0.13	0.33	0.130	0.13
159	1200	24.6	0.77 0.77	"	0.77	0.61*	0.781	0.775
119	1200	97.6	0.50 0.49	"	0.495	0.61*	0.500	0.498
132	1400	0.1	0.03 0.03	"	0.03	0.61*	0.030	0.030
102	1400	0.52	0.08 0.07	"	0.075	0.61*	0.075	0.075
148	1400	1.97	0.72 0.71	"	0.715	0.61*	0.724	0.719
37	1400	5.45	0.23 0.22	"	0.225	1.83	0.230	0.229
38	1400	5.45	0.24 0.25	"	0.245	1.76	0.250	0.249
158	1400	24.6	0.72 0.71	"	0.715	0.61*	0.724	0.719
118	1400	97.6	1.12 1.13	"	1.125	0.61*	1.145	1.132
72	1600	0.1	0.05	"	0.05	0.61*	0.050	0.050
71	1600	0.52	0.11	"	0.11	0.02	0.110	0.110
75	1600	1.01	0.18	"	0.18	0.61*	0.181	0.181
69	1600	2.03	0.30	"	0.30	0.31	0.302	0.301
76	1600	3.09	0.29	"	0.28	0.61*	0.283	0.282
70	1600	4.16	0.32	"	0.32	0.06	0.321	0.320
10	1600	5.45	0.44 0.48	"	0.46	0.61*	0.465	0.463
11	1600	5.45	0.53 0.56	"	0.545	0.23	0.549	0.546
78	1600	15.45	0.59	"	0.59	0.61*	0.498	0.594
79	1600	24.32	0.73	"	0.73	0.61	0.739	0.734
74	1600	32.54	1.04		1.04	0.61	1.097	1.046
81	1600	52.64	1.13	"	1.13	0.61	1.150	1.137
80	1600	76.41	1.33		1.33	0.61	1.351	1.333
73	1600	97.63	1.86	"	1.86	0.61	1.807	1.871

Note: (a) Grams of sulfur per 100 grams of MASF Char
(b) The * implies that these data were assumed equal to the mean value of the other data in the same column
(c) Experimental History;

START $\xrightarrow[0.5\ \text{SCFH He}]{900^{\circ}\text{C; 1 Hour}}$ $\xrightarrow[0.5\ \text{SCFH He}]{T^{\circ}\text{F; 1 Hour}}$ $\xrightarrow[100P_{H_2S}/P_{H_2} = E]{T^{\circ}\text{F; 1 Hour; 1 SCFH}}$ ANALYSIS

Table D.12 Filter Paper Char Adsorption Isotherm Data.

Table D.13 Char Analyses

Experiment Number	222		223		224		225		226		Calculation Procedure
Carbon	82.61	82.38	82.04	82.01	87.34	87.45	90.12	89.75	97.70	97.60	A
Hydrogen(c)	0.78	0.87	0.73	0.80	0.63	0.71	0.73	0.51	0.49	0.42	B
Nitrogen	0.58	0.61	0.60	0.59	1.52	1.50	0.53	0.81	0.19	0.22	C
Oxygen(c)	2.38	2.71	1.62	1.41	1.28	1.30	0.95	0.93	0.68	0.55	D
Total Sulfur	1.96	1.97	1.49	1.48	0.96	1.01	0.80	0.81	0.29	0.28	E
Ash	11.48	11.67	13.46	13.48	7.35	7.06	7.38	7.38	0.10	0.12	F
Total	99.79	100.12	99.94	99.77	99.08	99.03	100.51	100.19	99.45	99.19	G
Moisture	2.45	2.27	1.70	1.35	1.15	1.22	1.06	0.92	1.00	0.71	H
Grams Total Sulfur per 100 grams MASF Char	2.34	2.34	1.79	1.77	1.07	1.12	0.88	0.89	0.30	0.29	I = 100E/[A+B+C+D-H]
Grams Moisture per 100 grams MASF Char	2.92	2.62	2.04	1.62	1.28	1.36	1.16	1.01	1.02	0.72	J = 100H/[A+B+C+D-H]

Note: (a) All analyses are on an as-received basis.
(b) Oxygen determined directly by high-temperature (1300°C) carbonization in a stream of nitrogen
(c) Analyses include hydrogen or oxygen in moisture

			Moisture-free Basis						
Experiment Number	Char Description	Moisture (b)	Carbon	Hydrogen	Oxygen	Nitrogen	Total Sulfur	Ash	Total
222	HYDRANE HY-138	2.45	84.68	0.51	0.20	0.59	2.00	11.76	99.99
	Lignite Char	2.27	84.29	0.63	0.71	0.62	2.01	11.94	
223	HYDRANE HY-140	1.70	83.45	0.54	0.11	0.61	1.51	13.69	99.84
	Subbituminous Char	1.35	83.13	0.65	0.21	0.59	1.50	13.66	
224	HYDRANE HY-128	1.15	88.35	0.50	0.26	1.53	0.97	7.45	99.06
	Bituminous Char	1.22	88.53	0.58	0.27	1.51	1.02	7.14	
225	Anthracite-based(c)	1.06	91.08	0.61	0.10	0.53	0.80	7.45	100.37
	Activated Charcoal	0.92	90.58	0.41	0.11	0.81	0.81	7.44	
226	Filter Paper	1.00	98.68	0.38	0.10	0.19	0.29	0.10	99.55
	Char	0.71	98.29	0.34	0.10	0.22	0.28	0.12	

Note: (a) All analyses in weight percent
(b) As-Received Basis
(c) Barnebey-Cheney 417

Table D.14 Analyses of Chars on a Moisture-Free Basis

		Moisture & Ash-Free Basis					
Experiment Number	Char Description	Carbon	Hydrogen	Oxygen	Nitrogen	Total Sulfur	Total
222	HYDRANE HY-138 Lignite Char	95.86	0,65	0,52	0,69	2,28	100.00
223	HYDRANE HY-140 Subbituminous Char	96,67	0,70	0,19	0,69	1,75	100.00
224	HYDRANE HY-128 Bituminous Char	96,38	0,59	0,28	1,66	1,09	100.00
225	Barnebey Cheney 417 Anthracite-based Char	97,74	0,55	0,12	0,73	0,86	100,00
226	Filter Paper Char	99,05	0.36	0,10	0,21	0,28	100,00

Note: (a) All analyses in weight percent,

Table D.15 Analyses of Char on a Moisture and Ash-free Basis

Expt.#	X Hours	Z	MF Basis Total Sulfur (a)	MF Basis % Ash (b)	MASF Basis Organic Sulfur (c)
237	Blank	Blank	2.83 2.87	8.44	3.213
115	Blank	Blank	2.55 2.53	11.73	2.963
241	1	24.6	2.00 1.99	8.33	2.225
231	1	7.5	1.74 1.80	8.69	1.977
229	1	1.97	1.26 1.26	9.77	1.416
233	1	0.52	0.96 1.01	8.24	1.085
234	1	0.1	0.64 0.65	8.00	0.706
243	4	24.6	2.14 2.13	8.60	2.392
228	4	7.5	1.59 1.59	10.81	1.815
230	4	1.97	0.98 1.05	8.71	1.124
235	4	0.52	0.66 0.66	8.44	0.726
232	4	0.1	0.51 0.47	8.85	0.540
242	8	24.6	2.08 2.08	8.36	2.322
240	8	7.5	1.60 1.60	8.70	1.784
239	8	1.97	0.99 --	9.27	1.103
238	8	0.52	0.60 0.60	8.83	0.662
236	8	0.1	0.34 0.36	8.97	0.386

Note: (a) Weight% total sulfur in MF char. The sulfide sulfur content of HY-128 char is, in all cases, negligible.

(b) Weight% ash in MF char

(c) Grams of organic sulfur per 100 grams of MASF Char

(d) Experimental History:

$$\text{START} \xrightarrow[\text{0.5 SCFH He}]{900^{\circ}\text{C; 1 Hour}} \xrightarrow[\text{0.5 SCFH He}]{1600^{\circ}\text{F; 1 Hour}} \xrightarrow[100P_{H_2S}/P_{H_2}=97.6 \text{; 0.5 SCFH}]{1600^{\circ}\text{F; 1 Hour}} \text{BLANK} \xrightarrow[100P_{H_2S}/P_{H_2}=Z \text{; 0.5 SCFH}]{1600^{\circ}\text{F; X Hours}} \text{ANALYSIS}$$

(5) HYDRANE [HY-128] Bituminous chars employed in all experiments

Table D.16 Results of Experiments to Establish whether or not Char Sulfidation is Reversible

Table D.17 Results of Fluid-bed Char Hydrodesulfurization Experiments at 1400°F using HYDRANE HY-138 Lignite Char

	Specified				Actual			Moisture-Free Basis				MAF Basis		MASF Basis		
Expt.#	Scf H_2 / Lb.Char	X% H_2 in He	%He	t Min	Sample Collected grams	Scfh H_2	t Min	Total Sulfur % Mean	Sulfide Sulfur %	Organic Sulfur %	Ash %	Scf H_2 / Lb.MAF Char	Organic Sulfur (a)	Scf H_2 / Lb.MASF Char (b)	Organic Sulfur (c)	Normalized %
202	-	-	-	-	3.861	-	-	3.07	0.60	2.47	14.65	0	2.894	0.	2.980	100
203	-	-	-	-	3.926	-	-	3.105	0.57	2.535	14.55	0	2.967	0.	3.058	
204	2.5	100	0	3.3	3.838	0.457	3.3	2.815	0.64	2.175	14.68	3.48	2.549	3.571	2.616	86.7
205	5.0	100	0	6.6	3.798	0.486	6.6	2.74	0.58	2.160	14.93	7.51	2.539	7.706	2.605	86.3
206	7.5	100	0	9.9	4.012	0.5	9.0	2.69	0.58	2.110	13.33	9.78	2.435	10.024	2.496	82.7
207	10.0	100	0	13.0	4.136	0.5	13.0	2.625	0.63	1.995	15.03	13.98	2.348	14.316	2.404	79.6
208	12.5	100	0	16.5	3.892	0.495	16.5	2.670	0.56	2.110	14.95	18.65	2.481	19.124	2.544	84.3
209	15.0	100	0	19.8	3.967	0.5	20.0	2.605	0.60	2.005	14.74	22.35	2.352	22.888	2.409	79.8
219	20.0	100	0	26.5	3.792	0.497	36.0	2.540	0.54	2.000	15.37	42.15	2.363	43.170	2.420	80.2
220	40.0	100	0	52.9	3.717	0.497	54.0	2.460	0.50	1.960	16.10	65.07	2.336	66.626	2.392	79.2
221	60.0	100	0	79.4	3.619	0.499	79.0	2.335	0.56	1.775	15.11	97.01	2.091	99.082	2.136	70.8
210	2.5	10	90	33.0	3.890	0.056	33.0	2.810	0.63	2.180	14.69	4.21	2.555	4.320	2.622	86.8
211	5.0	10	90	66.0	3.714	0.056	66.0	2.635	0.55	2.085	15.11	8.86	2.456	9.083	2.518	83.4
212	7.5	10	90	99.0	3.762	0.056	101.	2.775	0.60	2.175	15.33	13.42	2.569	13.774	2.637	87.3
213	10.0	10	90	132.	3.780	0.056	132.	2.485	0.67	1.815	15.53	17.50	2.149	17.884	2.196	72.7
214	12.5	10	90	165.	3.668	0.056	165.	2.920	0.70	2.220	15.68	22.59	2.633	23.201	2.704	89.6
215	15.0	10	90	198.	3.721	0.056	198.	2.645	0.57	2.075	15.02	26.51	2.442	27.174	2.503	82.9
216	20.0	10	90	264.	3.705	0.056	255.	2.505	0.58	1.925	14.99	34.28	2.264	35.074	2.316	76.7
217	40.0	10	90	529.	3.510	0.056	549.	2.340	0.55	1.790	15.11	78.01	2.109	79.691	2.154	71.3
218	60.0	10	90	739.	3.596	0.056	770.	2.265	0.56	1.705	15.19	106.89	2.010	109.083	2.051	67.9

Note: (a) Wt%
(b) Scf Hydrogen per Lb. of moisture, ash and organic sulfur-free char.
(c) Grams of organic sulfur per 100 grams of moisture, ash and organic sulfur-free char
(d) Experimental History:

START — 900°C, 1 Hour / 0.5SCFH; Helium — 1400°F; 1 Hour / 0.5 SCFH; Helium — 1400°F; 1 Hour / 1 SCFH; 7.76% H_2S in H_2 — BLANK — 1400°F; t Minutes / 1 SCFH; X% H_2 in Helium — ANALYSIS

Table D.18 Results of Fluid-bed Char Hydrodesulfurization Experiments at 1400°F using HYDRANE HY-128 Bituminous Char

	Specified				Actual			MF Basis		MAF Basis		MASF Basis		
Expt.#	Scf H_2 / Lb.Char	X% H_2	%He	t min	Sample Collected grams	Scfh H_2 / Hr.	t mins	Organic Sulfur % Mean	Ash %	Scf H_2 / Lb. MAF Char	Organic Sulfur %	Scf H_2 / Lb.MASF Char	Organic Sulfur (a)	Normalized Organic Sulfur (b)
184	2.5	100	0	3.3	4.324	0.5	3.3	0.790	11.05	3.243	0.888	3.272	0.896	87.8
186	5.0	100	0	6.61	4.409	0.491	8.5	0.735	10.60	8.004	0.822	8.070	0.829	81.3
188	7.5	100	0	9.92	4.349	0.5	9.9	0.695	10.33	9.596	0.775	9.671	0.781	76.6
190	10.0	100	0	13.23	4.037	0.469	13.1	0.645	10.96	12.922	0.724	13.016	0.729	71.5
192	12.5	100	0	16.53	4.272	0.505	16.5	0.605	10.51	16.477	0.676	16.589	0.681	66.8
200	15.0	100	0	19.84	4.278	0.495	20.0	0.600	10.91	19.367	0.673	19.498	0.678	66.5
201	20.0	100	0	26.46	2.815	0.515	17.0	0.640	10.40	26.242	0.714	26.431	0.719	70.5
199	40.0	100	0	52.91	4.076	0.504	52.0	0.505	11.06	54.655	0.568	54.967	0.571	56.0
198	60.0	100	0	79.36	4.286	0.487	79.0	0.440	10.81	76.087	0.493	76.464	0.495	48.5
185	2.5	10	90	33.07	4.2	0.055	33.0	0.790	10.82	3.663	0.886	3.696	0.894	87.6
187	5.0	10	90	66.14	4.288	0.055	67.0	0.765	10.94	7.275	0.859	7.338	0.866	84.9
189	7.5	10	90	99.21	3.692	0.055	99.0	0.735	11.36	12.579	0.829	12.684	0.836	82.0
191	10.0	10	90	132.28	4.169	0.055	132.0	0.705	10.63	14.731	0.789	14.848	0.795	77.9
193	12.5	10	90	165.34	4.202	0.055	165.0	0.720	10.36	18.214	0.803	18.361	0.810	79.4
194	15.0	10	90	198.41	4.302	0.055	198.0	0.710	10.46	21.373	0.793	21.544	0.799	78.3
195	20.0	10	90	264.55	4.291	0.055	265.0	0.630	10.74	28.769	0.706	28.974	0.711	69.7
197	40.0	10	90	529.10	3.709	0.055	529.0	0.670	11.84	67.269	0.760	67.784	0.766	75.1
196	60.0	10	90	739.65	4.295	0.055	744.0	0.580	10.63	80.594	0.649	81.120	0.653	64.0

Note: (a) Grams of organic sulfur per 100 grams of Moisture, ash and organic sulfur-free char.
(b) The mean value of the organic sulfur concentration is 1.020 grams of organic sulfur per 100 grams of MASF char.
(c) Experimental History:

$$\text{START}\xrightarrow[\text{0.5 SCFH; He}]{\text{990°C; 1 Hour}}\xrightarrow[\text{0.5 SCFH; He}]{\text{1400°F; 1 Hour}}\xrightarrow[\text{1 SCFH; 7.76\% } H_2S \text{ in } H_2]{\text{1400°F; 1 Hour}}\text{BLANK}\xrightarrow[\text{1 SCFH; X\% } H_2 \text{ in Helium}]{\text{1400°F; t Minutes}}\text{ANALYSIS}$$

(d)The sulfide sulfur concentration in the acid-washed HYDRANE [HY-128] Biuminous coal char is negligible.

Table D.19 Results of Experiments to Establish whether or not the Time of Exposure to Hydrogen Sulfide affects the Kinetics of Char Hydrodesulfurization

	Specified					Actual			MF Basis				Results		
Expt.#	Gas G	Scf H_2 / Lb.Char	X% H_2	T Min	t Min	Sample Collected	t Min	Scf H_2 / Hr.	%Ash	%Total Sulfur	%Sulfide Sulfur	%Organic Sulfur	Scf H_2 / Lb.MASF Char	Organic Sulfur (a)	Normalized Organic Sulfur
265	H_2	0.0	---	60	---	4.186	----	0.500	8.84	.82,.81	Neglig.	0.815	0.0	0.902	100.0
267	H_2	7.5	100	60	6.9	3.029	6.9	0.500	8.43	.74,.73	"	0.735	9.47	0.810	89.8
270	H_2	15.0	100	60	13.9	2.937	13.9	0.500	8.69	.62,.65	"	0.635	19.72	0.700	77.6
275	H_2	40.0	100	60	37.0	3.018	37.0	0.500	14.70	.46,.47	"	0.465	54.6	0.548	60.8
278	H_2	60.0	100	60	55.6	2.900	55.6	0.500	14.54	.41,.42	"	0.415	85.2	0.488	54.1
273	H_2	0.0	---	10	----	3.020	----	0.500	14.45	.91,.89	"	0.900	0.0	1.063	100.0
274	H_2	7.5	100	10	6.9	2.990	6.9	0.500	14.30	.70,.69	"	0.695	10.25	0.818	77.0
276	H_2	15.0	100	10	13.9	3.156	13.9	0.500	14.63	.55,.55	"	0.550	19.6	0.648	61.0
277	H_2	40.0	100	10	37.0	3.054	37.0	0.500	14.30	.40,.43	"	0.415	53.7	0.486	45.7
279	H_2	60.0	100	10	55.6	3.307	55.6	0.500	14.23	.36,.37	"	0.365	81.0	0.428	40.3

Note: (a) Grams of organic sulfur per 100 grams of MASF char.

(b) Experimental History:

$$\text{START} \xrightarrow[\text{Gas G; T Mins}]{900^{o}\text{C; 0.5 Scfh}} \xrightarrow[\text{Gas G; T Mins}]{1400^{o}\text{F; 0.5 Scfh}} \xrightarrow[\text{T Mins; 7.76\% } H_2S \text{ in Hydrogen}]{1400^{o}\text{F; 0.5 Scfh}} \text{BLANK} \xrightarrow[\text{t Mins; X\% } H_2 \text{ in Helium}]{1400^{o}\text{F; 0.5 Scfh}} \text{ANALYSIS}$$

Table D.20 Consolidation Coal Company's Disco Char Hydro-desulfurization Results at 1600°F

Expt.#	Pressure Atm	$\%H_2$ in Feedgas (a)	t Min.	Sample Size grams MAF Char;(b)	Scf H_2 Lb. MAF Char (i)	S(0) % (c)	S(t) % (c)	Carbon Burnoff (h)	$\%S_{rem}$ (g)	Red Depth Inches (e)	Gas Residence Time (f)
S-19	1	10	24	21.32	4.5	2.13	1.37	12.1	56.5	0.83	0.16
S-20	1	10	30	41.77	2.9	2.13	1.39	12.3	57.3	1.62	0.31
S-21	1	10	39	84.36	1.8	2.13	1.60	12.2	65.9	3.27	0.62
S-22	6	25	17	41.56	24.5	2.10	1.00	10.9	42.4	1.61	0.30
S-23	6	25	22	84.61	15.5	2.12	1.07	11.9	44.5	3.28	0.62
S-24	6	25	25	130.12	11.5	2.12	1.17	11.7	48.7	5.04	0.96
S-2	1	10	48	21.56	9.8	2.29	1.24	19.8	43.4	0.84	0.16
S-1	1	10	63	42.16	6.6	2.30	1.34	20.8	46.2	1.64	0.31
S-3	1	10	80	85.28	4.1	2.29	1.42	19.8	49.7	3.31	0.63
S-7	1	25	81	21.50	41.8	2.30	0.83	21.0	28.5	0.84	0.16
S-8	1	25	93	40.87	25.9	2.35	0.94	23.0	30.8	1.59	0.30
S-9	1	25	109	85.03	14.1	2.29	1.14	20.5	39.6	3.30	0.63
S-4	1	50	197	21.57	204.5	2.32	0.39	21.6	13.2	0.84	0.16
S-5	1	50	231	40.23	130.6	2.35	0.35	22.8	11.5	1.56	0.30
S-6	1	50	242	85.11	62.6	2.29	0.65	20.2	22.7	3.30	0.63
S-13	6	25	38	41.89	59.4	2.29	0.49	19.7	17.2	1.63	0.31
S-14	6	25	48	84.63	37.5	2.29	0.52	20.2	18.1	3.29	0.62
S-15	6	25	57	130.6	28.8	2.29	0.56	20.0	19.6	5.07	0.96
S-10	6	50	90	85.09	139.8	2.29	0.28	20.3	9.7	3.30	0.63
S-11	6	50	96	129.7	97.4	2.29	0.26	19.9	9.1	5.03	0.95
S-12	6	50	107	211.65	66.6	2.29	0.31	20.1	10.8	8.21	1.55
S-28	1	100	100	9.40	376.4	1.92	1.30	0.85	67.1	0.49	0.09
S-29	1	100	200	9.41	756.6	1.92	1.00	1.35	51.4	0.49	0.09
S-30	1	100	300	9.40	1141.	1.92	0.97	1.80	49.6	0.49	0.09
S-34	6	100	50	9.38	1159.	1.92	0.55	3.17	27.7	0.49	0.09
S-32	6	100	100	9.41	2367.	1.92	0.46	5.50	22.7	0.49	0.09
S-31	6	100	200	9.41	4913.	1.92	0.36	8.90	17.1	0.49	0.09
49A	1.5	100	1435	86.32	964.	1.92	0.36	9.21	17.1	4.47	0.85
S-35	6.9	87	100	9.33	2267.	1.92	0.54	0.36	28.0	0.48	0.09

Note: (a) With the exception of Run No. S-35, in which the gas mixture consists of 87% H_2 and 13% CH_4, the remeinder of the gas is steam
(b) Estimated, assuming an ash concentration of 3.4% in the moisture-free char
(c) Wt% total sulfur in the feed and product chars respectively, on a moisture-free basis
(d) All these experiments were conducted in a 1.5 inch batch fluidized bed reactor, at a superficial gas velocity of 0.44 fps
(e) Estimated from a knowledge of the weight of feed char, and the fact that 10 grams of feed char occupies 0.5 inches of bed height
(f) Estimated from (5) and the superficial gas velocity of 0.44 fps - i.e., see (4); seconds
(g) Percentage sulfur remaining - i.e., S(t)x100x[1-(8)/100]/S(0)
(i) Scf hydrogen (1 Atm; 0°C) per lb. of MAF product char.

				As Rec'd Basis			MAF Basis				MAF Basis							
Expt.#	Press atm	t min	Scf H_2/Hr. (m)	Feed Char gram	%Moist in Feed	%S in Feed (a)	Feed Char gram (1)	%S in Feed (b)	Prod Char gram (c)	%S in Prod. (d)	Prod Char gram (e)	%S in Prod (f)	$\%S_{rem}$ (g)	Scf H_2/Lb. (h)	Gas Velocity fps (i)	Bed Height inches (k)	Gas Residence Time (j)	Char Conv. (n)
1	7.82	60	3.88	10.	9.2	2.31	7.42	2.77	7.5	0.28	5.84	0.360	10.2	301.	0.16	3.8	2.00	21.3
12	7.82	120	4.06	10.	9.2	2.31	7.42	2.77	7.8	0.52	6.14	0.661	19.8	600.	0.166	3.8	1.9	17.3
13	4.42	60	4.02	10.	9.2	2.31	7.42	2.77	8.6	0.77	6.94	0.954	32.2	263.	0.293	3.8	1.1	6.5
14	7.82	240	12.3	100.	3.7	3.19	79.7	3.825	77.4	0.48	60.8	0.611	12.1	367.	0.086	6.5	6.3	23.7
16	7.82	180	28.0	100.	3.7	3.19	79.7	3.825	80.0	0.90	63.4	1.136	23.6	601.	0.196	6.5	2.8	20.5
21	1.02	180	14.7	100.	3.7	2.85	79.7	3.417	82.3	0.76	65.7	0.952	23.0	305.	0.106	6.5	5.1	17.6
24	7.82	360	13.7	100.	3.7	2.85	79.7	3.417	82.7	0.66	66.1	0.826	20.1	564.	0.097	6.5	5.6	17.1
25	1.02	30	1.68	5.	5.37	3.04	3.902	3.645	4.4	0.86	3.57	1.060	26.6	107.	0.537	1.9	0.30	8.5
26	4.08	30	7.21	5.18	5.37	3.04	4.042	3.645	4.43	0.65	3.57	0.807	19.5	458.	0.564	2.0	0.29	11.7
27	1.02	15	2.03	5.04	5.37	3.04	3.933	3.645	4.532	0.90	3.695	1.104	28.5	62.3	0.65	1.9	0.25	6.1
28	4.08	30	24.1	4.90	5.37	3.04	3.823	3.645	4.30	0.46	3.487	0.567	14.2	1568.	1.89	1.8	0.08	8.8
29	1.02	15	6.96	5.11	5.37	3.04	3.987	3.645	4.59	0.80	3.742	0.981	25.2	211.	2.23	1.9	0.07	6.1
30	4.08	30	21.7	20.11	5.37	3.04	15.692	3.645	17.86	1.26	14.522	1.550	39.3	339.	1.70	7.6	0.37	7.5
31	4.08	15	5.64	5.40	5.37	3.04	4.214	3.645	4.67	0.64	3.774	0.792	19.4	170.	0.443	2.1	0.39	10.4
32	1.02	45	1.81	5.67	5.37	3.04	4.424	3.645	4.93	0.54	2.329	1.143	16.5	264.	0.581	2.1	0.31	47.4
33	4.08	15	24.1	20.12	5.37	3.04	15.739	3.645	17.87	1.05	14.522	1.292	32.7	188.	1.88	8.2	0.37	7.7
34	4.08	15	27.0	5.00	5.37	3.04	3.902	3.645	4.63	0.69	3.800	0.841	22.5	806.	2.12	1.9	0.08	2.6
35	1.02	45	5.9	5.275	5.37	3.04	4.116	3.645	4.736	0.43	3.860	0.528	13.6	520.	1.89	2.0	0.09	6.2
36	1.02	15	6.42	20.69	5.37	3.04	16.144	3.645	18.66	1.24	15.225	1.520	39.3	47.8	2.06	7.9	0.32	5.7
37	4.08	45	6.15	5.19	5.37	3.04	4.047	3.645	4.636	0.37	3.775	0.454	11.7	554.	0.483	2.0	0.34	6.7
38	1.02	90	5.75	5.17	5.37	3.04	4.034	3.645	4.40	0.45	3.542	0.559	13.4	1104.	1.84	2.0	0.09	12.2
39	4.08	45	27.2	5.22	5.37	3.04	4.073	3.645	4.527	0.37	3.660	0.458	11.3	2528.	2.16	2.0	0.08	10.1
40	1.02	90	6.18	19.34	5.37	3.04	15.093	3.645	17.268	1.31	14.057	1.609	41.1	299.	1.98	7.3	0.31	6.9
41	1.02	90	1.56	5.27	5.37	3.04	4.112	3.645	4.99	0.50	4.115	0.606	16.6	257.	0.498	2.0	0.33	-0.1
42	1.02	5	1.73	5.15	7.84	3.47	3.890	4.161	4.619	1.55	3.764	1.902	44.2	17.4	0.553	1.9	0.29	3.2
43	4.08	5	7.68	4.94	7.84	3.47	3.732	4.161	4.387	1.40	3.567	1.722	39.6	80.4	0.604	1.9	0.26	4.4
44	1.02	5	6.00	20.07	7.84	3.47	15.165	4.161	18.245	2.60	14.913	3.181	75.1	15.2	1.92	7.6	0.33	1.7
45	4.08	5	21.6	5.06	7.84	3.47	3.823	4.161	4.477	1.10	3.637	1.354	30.9	225.	1.70	1.9	0.09	4.9
46	4.08	5	25.1	20.30	7.84	3.47	15.337	4.161	18.38	1.94	15.011	2.375	55.9	63.2	1.97	7.7	0.33	2.1
47	4.08	30	24.7	5.144	7.31	3.91	3.914	4.688	4.393	0.60	3.539	0.745	14.4	1583.	1.94	2.0	0.08	9.6
48	4.08	30	25.5	21.673	7.31	3.91	16.491	4.688	18.218	2.80	14.620	3.489	66.0	406.	2.00	8.2	0.34	11.3
49	4.08	15	25.5	5.102	7.31	3.91	3.882	4.688	4.281	0.80	3.434	0.997	18.8	842.	2.00	1.9	0.08	11.5
50	4.08	5	25.5	5.162	7.31	3.91	3.928	4.688	4.429	1.16	3.572	1.438	27.9	270.	2.00	2.0	0.08	9.1
51	4.08	45	26.2	5.026	7.31	3.91	3.824	4.688	4.101	0.57	3.267	0.716	13.1	2728.	2.05	1.9	0.08	14.6
52	4.08	90	25.7	4.532	7.31	3.91	3.448	4.688	3.499	0.38	2.747	0.484	8.2	6366.	2.02	1.7	0.07	20.3
53	2.04	5	6.48	4.607	7.31	3.91	3.505	4.688	3.100	1.53	2.335	2.031	28.8	105.	1.02	1.8	0.14	33.4
54	2.04	15	6.43	5.166	7.31	3.91	3.931	4.688	4.446	1.17	3.588	1.450	28.2	203.	1.07	1.9	0.15	8.7
55	2.04	15	6.37	5.697	7.31	3.91	4.335	4.688	4.924	1.23	3.978	1.523	29.8	182.	0.998	2.2	0.18	8.2
56	2.04	30	5.70	5.205	7.31	3.91	3.960	4.688	4.594	0.60	3.640	0.742	14.5	355.	0.895	2.0	0.18	8.1
57	2.04	30	6.34	5.634	7.31	3.91	4.287	4.688	4.867	0.63	3.932	0.780	15.2	366.	0.998	2.1	0.18	8.3
58	2.04	45	6.37	5.062	7.31	3.91	3.852	4.688	4.315	0.60	3.475	0.745	14.3	624.	1.00	1.9	0.16	9.8
59	2.04	45	6.47	5.978	7.31	3.91	4.549	4.688	5.026	0.53	4.034	0.660	12.5	546.	1.01	2.2	0.19	11.3
60	4.08	90	26.3	19.643	7.50	3.92	14.909	4.700	16.688	1.32	13.427	1.641	31.4	1332.	2.07	7.4	0.30	9.9
61	1.02	2	1.68	5.107	7.50	3.92	3.876	4.700	4.553	2.17	3.705	2.667	54.2	6.9	0.539	1.9	0.30	4.4
62	1.02	2	6.37	4.989	7.50	3.92	3.787	4.700	4.357	2.07	3.529	2.556	5.7	13.9	2.03	1.9	0.08	6.8
63	4.08	2	6.24	5.071	7.50	3.92	3.808	4.700	4.432	2.06	3.590	2.543	51.0	26.3	0.489	1.9	0.33	5.7
64	1.02	5	1.66	4.911	6.97	3.55	3.753	4.257	4.326	2.57	3.511	3.167	69.6	17.9	0.530	1.9	0.29	6.4
65	1.02	15	1.69	5.130	6.97	3.55	3.921	4.257	4.535	1.60	3.683	1.970	43.5	52.0	0.525	1.9	0.31	6.1
66	1.02	5	1.60	5.30	5.86	4.22	4.110	5.060	4.42	3.10	3.540	3.871	65.9	17.1	0.511	2.0	0.32	13.9
67	1.02	15	1.76	4.965	5.86	4.22	3.850	5.060	3.939	2.27	3.155	2.863	46.4	63.3	0.564	1.9	0.28	18.1
68	4.08	2	25.8	5.064	7.50	3.92	3.844	4.700	4.394	1.57	3.553	1.942	38.2	110.	2.02	1.9	0.08	7.6
69	4.08	5	25.4	18.349	7.50	3.92	13.927	4.700	16.749	3.14	13.703	3.838	80.4	70.1	2.00	7.0	0.29	1.6
70	1.02	2	6.36	20.373	7.50	3.92	15.463	4.700	18.683	3.53	15.301	4.310	90.7	6.3	2.04	7.7	0.32	1.0
71	2.04	5	6.40	5.043	7.50	3.92	3.828	4.700	4.470	1.73	3.633	2.129	43.0	66.6	1.00	1.9	0.16	5.1
72	4.08	15	25.6	21.228	7.50	3.92	16.112	4.700	18.687	2.15	15.153	2.651	53.0	192.	2.04	8.0	0.33	6.0
73	4.08	30	25.4	19.134	7.50	3.92	14.523	4.700	16.547	1.90	13.371	2.351	46.0	431.	1.99	7.3	0.30	7.9
74	4.08	90	6.37	5.127	7.50	3.92	3.891	4.700	4.299	0.40	3.440	0.500	9.4	1260.	0.499	2.0	0.33	11.6
75	2.04	90	6.43	5.334	7.52	3.63	4.047	4.353	4.082	0.50	3.797	0.617	13.3	1152.	1.01	2.0	0.18	6.2
76	2.04	90	6.29	5.245	7.52	3.63	3.980	4.353	4.368	0.50	3.497	0.625	12.7	1224.	0.985	2.0	0.17	12.1
77	1.02	5	1.63	6.914	7.52	3.63	5.246	4.353	6.088	1.47	4.940	1.812	39.2	12.5	0.552	2.5	0.38	5.8
78	1.02	15	1.64	5.327	6.83	3.47	4.079	4.161	4.743	1.30	3.859	1.598	36.3	48.2	0.525	2.0	0.32	5.4
79	1.02	30	1.60	5.208	6.83	3.47	3.988	4.161	4.491	1.03	3.626	1.276	27.9	100.	0.512	2.0	0.32	9.1
80	1.02	10	0.07	5.148	7.74	3.42	3.895	4.101	4.689	2.25	3.834	4.425	106.8	1.4	0.0225	2.0	7.2	1.6
81	1.02	10	0.06	5.157	7.57	4.60	3.911	5.516	4.320	3.63	3.464	4.527	72.7	1.3	0.0193	2.0	8.4	11.4

Note:
(a) Moisture-free basis
(b) Estimated, assuming 16.6% ash in as-received feed char
(c) As-received basis
(d) Moisture-free basis
(e) Estimated from an ash balance on the feed and product Chars
(f) Estimated from an ash balance on the feed and product chars
(g) Percentage sulfur in product char - i.e., (6)x(5)x100/[(2)x(12)]
(h) Scf hydrogen per lb. of MAF product char
(i) Superficial gas velocity; fps
(j) Superficial gas Residence time - i.e., (11)/[(9)x12]
(1) Estimated, assuming 16.6% ash in as-received feed char.
(m) Basis for Scf not noted.
(n) MAF Basis

Table D.21 FMC Corporation's COED Char Hydrodesulfurization Data at 1600°F.

Expt.#	Feed Material	Pressure Atm.	t Min. (a)	Hydrogen Flowrate (b)	% Conv. (c)	S(0) % (d)	S(t) % (e)	$\frac{\text{Scf } H_2}{\text{Lb.MAF Char}}$ (i)	%S_{rem} (h)
583	char	18.0	1	10	0.0	1.3	0.9	11.1	69.2
590	char	18.0	1	10	1.2	1.3	1.0	11.2	76.0
605	char	18.0	6	10	7.5	1.3	0.4	71.9	28.5
621	char	18.0	6	10	8.7	1.3	0.5	72.8	35.2
601	char	18.0	16	10	13.2	1.3	0.2	204.	13.4
620	char	18.0	16	10	10.4	1.3	0.3	198.	20.7
629	char	18.0	31	10	20.1	1.3	0.2	430.	12.3
630	char	18.0	31	10	20.5	1.3	0.2	432.	12.2
582	char	35.0	1	20	1.0	1.3	0.7	22.4	53.3
588	char	35.0	1	20	0.0	1.3	0.7	22.2	53.8
606	char	35.0	6	20	12.9	1.3	0.3	153.	20.1
619	char	35.0	6	20	13.2	1.3	0.3	153.	20.1
602	char	35.0	16	20	15.8	1.3	0.2	421.	13.0
618	char	35.0	16	20	18.8	1.3	0.3	437.	18.8
628	char	35.0	31	20	28.4	1.3	0.2	939.	11.0
631	char	35.0	31	20	30.4	1.3	0.2	987.	10.7
636	char	35.0	31	20	28.4	1.3	0.2	959.	11.0
580	char	69.0	1	40	11.1	1.3	0.5	49.9	34.2
587	char	69.0	1	40	9.4	1.3	0.5	48.9	34.9
607	char	69.0	6	40	22.4	1.3	0.2	343.	12.0
622	char	69.0	6	40	32.6	1.3	0.2	394.	10,4
604	char	69.0	16	40	32.1	1.3	0.2	1044.	10.5
623	char	69.0	16	40	34.2	1.3	0.2	1078.	10.1
632	char	69.0	31	40	44.0	1.3	0.2	2453.	8.6
640	char	69.0	31	40	34.4	1.3	0.2	2094.	10.1

Note:
(a) Total solids residence time, including the one minute heatup time.
(b) Hydrogen flowrate, in Scf per hour.(Basis for Scf not noted)
(c) Wt% conversion of char to gas, on an MAF basis
(d) Sulfur content of feed char, wt% on an MAF basis
(e) Sulfur content of the product char, wt% on an ash-free basis. Since the moisture content of the chars is generally small, this also corresponds to the sulfur content on an MAF basis
(f) The superficial gas velocity in all of these experiments was nominally 1.2 fps
(g) The mass of char loaded in all of these experiments was nominally 8 grams (as-received basis)
(h) Percentage sulfur remaining - i.e., S(t)x100x[1-(c)/100]/S(0)
(i) Scf per lb. MAF product char.

Table D.22. Results of Hiteshue's Coal Hydrodesulfurization Experiments at 800°C

Expt.#	Feed Material	Pressure Atm	t Min (a)	Hydrogen Flowrate (b)	% Conv (g)	S(0) % (c)	S(t) % (d)	Scf/Lb. MAF Char (i)	%S_{rem} (h)
575	Coal	18.0	1	10	30.9	2.2	0.9	15.3	28.3
585	"	18.0	1	10	35.5	2.2	1.1	16.4	32.3
595	"	18.0	6	10	37.5	2.2	0.6	101.	17.1
615	"	18.0	6	10	35.2	2.2	0.7	97.7	20.6
597	"	18.0	16	10	42.6	2.2	0.4	294.	10.6
613	"	18.0	16	10	44.4	2.2	0.4	304.	10.1
627	"	18.0	31	10	50.0	2.2	0.2	654.	4.6
635	"	18.0	31	10	47.2	2.2	0.3	619.	7.2
584	"	35.0	1	20	40.4	2.2	1.0	35.4	27.1
591	"	35.0	1	20	40.2	2.2	0.9	35.3	24.5
600	"	35.0	6	20	45.8	2.2	0.6	234.	14.8
610	"	35.0	6	20	48.1	2.2	0.3	245.	7.1
599	"	35.0	16	20	52.8	2.2	0.3	715.	6.4
612	"	35.0	16	20	51.8	2.2	0.4	700.	8.8
625	"	35.0	31	20	51.8	2.2	0.2	1356.	4.4
634	"	35.0	31	20	56.8	2.2	0.3	1514.	5.9
574	"	69.0	1	40	45.5	2.2	0.8	77.4	19.8
586	"	69.0	1	40	47.6	2.2	0.6	80.5	14.3
576	"	69.0	6	40	58.1	2.2	0.3	604.	5.7
598	"	69.0	6	40	61.0	2.2	0.4	649.	7.1
614	"	69.0	6	40	58.9	2.2	0.3	616.	5.6
616	"	69.0	6	40	60.3	2.2	0.3	638.	5.4
596	"	69.0	16	40	66.4	2.2	0.4	2009.	6.1
608	"	69.0	16	40	65.6	2.2	0.3	1962.	4.7
624	"	69.0	16	40	57.8	2.2	0.2	1600.	3.8
633	"	69.0	31	40	69.8	2.2	0.3	4331.	4.1

Note: (a) Total solids residence time, including one minute heatup time
(b) Hydrogen flowrate, in Scf per hour (Basis for Scf not noted)
(c) Sulfur content of raw coal, wt% on an MAF basis
(d) Sulfur content of product char, wt% on an ash-free basis. Since the moisture content of the product char is negligible, this also corresponds to the sulfur concentration on an MAF basis
(e) The mass of coal loaded in all of these experiments was 8 grams (as received basis)
(f) The superficial gas velocity in all of these experiments was approximately 1.2 fps
(g) Wt% conversion of coal to gas, on an MAF basis
(h) Percentage sulfur remaining in product char - i.e., (d)x100x[1-(g)/100]/(c)
(i) Scf per lb. MAF product char.

Table D.23. Results of Hiteshue's Char Hydrodesulfurization Experiments at 800°C

Table D.24. Curran's Unpublished Char Sulfidation Data at 1880°F

Type of Gas	Temperature °F	$100P_{H_2S}/P_{H_2}$	$P_{S_2} \times 10^3$ atm(a)	% Sulfur [S]	$\text{Log}_{10}[S]$	$\text{Log}_{10}[P_{S_2}]$
H_2S/H_2	1880	185	27.1	5.58	0.75	-1.56
"	1880	153	18.5	4.33	0.64	-1.73
"	1880	128	12.9	4.36	0.64	-1.89
"	1880	108	9.23	3.94	0.60	-2.03
"	1880	59.8	2.83	3.37	0.53	-2.54
"	1880	55.4	2.43	3.04	0.48	-2.61
"	1880	47.3	1.77	2.69	0.43	-2.75
SO_2/N_2 6%:94%	1880	--	6.7	4.44	0.65	-2.17

Note: (a) Calculated from equation [A.23]

Table D.25. HYDRANE HY-128 Char Sulfidation Experimental Data

Experiment No.	Temperature	$100P_{H_2S}/P_{H_2}$	%Sulfur (MAF)	$\mathrm{Log}_{10}[P_{S_2}]$ (a)	$\mathrm{Log}_{10}[S]$
129	1600	0.1	0.36	-9.09	-0.44
99	1600	0.52	0.61	-7.66	-0.21
143	1600	1.97	0.78	-6.50	-0.11
107	1600	8.41	1.48	-5.24	0.17
157	1600	24.6	1.94	-4.31	0.29
115	1600	97.6	2.87	-3.11	0.46
237	1600	97.6	3.11	-3.11	0.49

Note: (a) Calculated from Equation [A.23], Appendix A.