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OXYDESULFURIZATION OF COAL PARTICLES

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by

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TABLE OF CONTENTS

	Page
NOTICE.....	i
ABSTRACT.....	iv
LIST OF TABLES.....	v
LIST OF FIGURES.....	vi
NOMENCLATURE.....	vii
1.0 INTRODUCTION.....	1
2.0 BACKGROUND.....	6
3.0 CHEMISTRY.....	10
4.0 KINETIC ANALYSIS.....	13
4.1 Preliminary Analysis.....	14
4.2 Zero Order Kinetics.....	15
4.3 Pseudo-First Order Kinetics.....	16
4.4 Arrhenius Analysis.....	17
5.0 EXPERIMENTAL WORK.....	19
5.1 Apparatus.....	19
5.2 Materials.....	20
5.3 Procedure.....	20
6.0 RESULTS AND DISCUSSION.....	26
6.1 Pyritic Sulfur Reaction.....	27
6.2 Carbon Oxidation.....	29

6.3 Organic Sulfur Reaction.....	32
7.0 CONCLUSIONS.....	35
7.1 Recommendations for Further Investigation...	36
APPENDIX A - Tables 1 through 15.....	37
APPENDIX B - Figures 1 through 19.....	53
APPENDIX C - Computer Programs.....	73
BIBLIOGRAPHY.....	80

Abstract

The kinetics of the pyritic sulfur, organic sulfur and carbon oxidation reactions for the Upper Freeport coal are investigated. Experiments were conducted in a semi-batch reactor to establish the effects of residence time (0-40 mins), temperature (150°C-210°C), partial pressure of oxygen, (100 psig-500 psig), and total pressure (500 psig-1000 psig) on the rates of these reactions. The experimental results indicated that the pyritic sulfur reaction rate is first order with respect to sulfur and a half order with respect to the partial pressure of oxygen. It is independent of the total pressure in the system. Both the carbon oxidation and organic sulfur reactions are zero order with respect to carbon and organic sulfur respectively. The activation energies for all three reactions agree closely with those reported in the literature.

LIST OF TABLES

Table	Title	Page
1	Coal Particle Size Distribution.....	38
2	Summary of Experiments.....	39
3	Experimental Data for Set A.....	40
4	Experimental Data for Set B.....	41
5	Experimental Data for Set C.....	42
6	Experimental Data for Set D.....	43
7	Experimental Data for Set E.....	44
8	Experimental Data for Set F.....	45
9	Experimental Data for Set G.....	46
10	Experimental Data for Set I.....	47
11	Experimental Data for Set J.....	48
12	Experimental Data for Set K.....	49
13	Experimental Data for Set M.....	50
14	Experimental Data for Set N.....	51
15	Weights of Treated Coal Samples.....	52

LIST OF FIGURES

Figure	Title	Page
1	Organic Sulfur Compounds.....	54
2	Sectioned View of Reactor.....	55
3	Schematic Flow Diagram.....	56
4	Percent Pyritic Sulfur Removed vs. Time.....	57
5	First Order Kinetic Plot for Pyrite Reaction..	58
6	Arrhenius Plot for Pyrite Reaction.....	59
7	Percent Pyritic Sulfur Removed vs. Time (Effect of pO_2).....	60
8	First Order Kinetic Plot for Pyrite Reaction (Effect of pO_2).....	61
9	Dependence of Pyritic Sulfur Rate Constant on pO_2	62
10	Percent Carbon Remaining vs. Time.....	63
11	Arrhenius Plot for Carbon Oxidation.....	64
12	Diffusion Controlled Kinetic Plot.....	65
13	Percent Organic Sulfur Remaining vs. Time.....	66
14	Arrhenius Plot for Organic Sulfur Reaction....	67
15	Percent Sulfur Removed vs. Time.....	68
16	Percent Carbon Removed vs. Time.....	69
17	Percent Hydrogen Removed vs. Time.....	70
18	Percent Heating Value Lost vs. Time.....	71
19	Percent Sulfur Removed vs. Time (Effects of pO_2).....	72

NOMENCLATURE

a	Langmuir constant (temperature dependent)
A ₀	Arrhenius frequency factor
C	concentration of reactant
C ₀	initial concentration of reactant
E	activation energy
F	fraction reactant remaining
K	diffusional control rate constant
k	reaction rate constant
pO ₂	partial pressure of oxygen
R	gas constant (8.314 joules/gmole-K)
S	surface area covered by oxygen
T	temperature °(K)
t	time
V	volume of reaction mixture

1.0 INTRODUCTION

The United States is currently facing an energy crisis. This crisis, caused by decreasing oil reserves and increasing prices of oil imports has culminated in a search for alternate sources of energy. Coal is the largest single hydrocarbon source left with the distinct advantage of long term availability. It is also the resource with the highest sulfur and ash content. The United States has over 32% of the world's proven coal reserves, sufficient to last for thirteen centuries at a zero percent growth rate.⁽¹⁾

The barriers which must be overcome before coal can reach its full potential as a source of energy are mainly environmental and hence technological. The major problem facing coal burning power facilities is the production of noxious sulfur oxides (SO_x 's). Current Environmental Protection Agency (EPA) regulations restrict SO_2 emissions for a new facility to 1.2 lbs per million BTU equivalent of coal combusted.⁽²⁾

The sulfur in coal occurs in three forms: pyritic, organic or sulfates. Pyritic sulfur, classified as compounds with the formula FeS_x , represents the bulk of the sulfur in Eastern coals. Organic sulfur is a broad classification containing any sulfur which is chemically bound to the actual

coal matrix. Organic sulfur is the dominant sulfur form in Western coals.⁽³⁾ Sulfates constitute less than a few percent of the total sulfur in most coals.

Presently, control of sulfur oxide emissions is achieved mainly by either stack gas scrubbing or physical coal cleaning techniques. The former process is both expensive and energy intensive.⁽⁴⁾ The latter, although relatively inexpensive and simple to operate, is less effective. In fact, depending on the sulfur composition of the feed coal a plant burning physically pre-cleaned coal may also have to employ flue gas scrubbing in order to meet environmental standards.⁽⁵⁾ A possible alternative to these processes is chemical coal cleaning; i.e., removal of the sulfur by means of a chemical reaction before burning the coal.

There are presently six major chemical coal cleaning methods being developed. A brief summary of these processes is given below and further details can be found elsewhere.⁽⁶⁻¹⁹⁾

(A) Battelle Process^(6,7)

Also known as the Battelle Hydrothermal Coal Process, removes over 90% of the pyritic and up to 70% of the organic sulfur and ultimately converts both to elemental form. The reactants used are $\text{Ca}(\text{OH})_2$, NaOH , CO_2 and water. Reaction times range from 15 to 30 minutes at pressures

between 2.41 and 17.24 MPa and temperatures between 221° and 350°C.

(B) KVB Process (8,9)

The KVB Process, developed by KVB Engineering Inc., also removes over 90% of the pyritic sulfur in addition to up to 40% of the organic sulfur. The reagents employed are NaOH, water, gaseous nitrogen and oxygen. The retention time is one hour at pressures between 0.103 and 2.07 MPa and temperatures between 38° and 260°C.

(C) Ledgemont Process (10,11)

This process, being developed in the Ledgemont Laboratories of the Kennecott Copper Corporation, claims removal of over 90% of the pyritic and up to 20% of the organic sulfur. The reactants are oxygen, water and lime. The residence time varies from 15 minutes to 24 hours at pressures up to 6.89 MPa and temperatures between 10° and 230°C.

(D) Magnex Process (12,13)

The Magnex Process, developed at Hazen Research and funded by Inex Resources, is actually a physical cleaning process with a chemical pre-treatment phase. In this pre-treatment step $\text{Fe}(\text{CO})_5$ is reacted with the pyrite causing it to become more magnetic. Ultimately this pyrite is removed by magnetic separators. By its nature this process is

capable of removing only pyritic sulfur (over 90%). This pre-treatment is conducted at atmospheric pressure and temperatures between 150° and 205°C. The residence time varies between 0.1 and 1 hour.

(E) TRW Process ^(14,15)

Often called the Myers Process, is the most developed of the chemical coal cleaning techniques. The reagents used are $\text{Fe}_2(\text{SO}_4)_3$, water, oxygen and naphtha at pressures between 0.103 and 0.552 MPa and temperatures between 88° and 135°C. The residence time varies between 30 minutes and 10 hours and results in the removal of over 90% of the pyritic sulfur.

(F) D.O.E. Oxidative Desulfurization Process ^(16,17)

This process, currently being developed at the Pittsburgh Energy Research Center (PERC) is probably covered by patents issued to the Chemical Construction Corporation ⁽¹⁸⁾ and Kennecott Copper Corporation. ⁽¹⁹⁾ The PERC Oxy-desulfurization Process is different from the Kennecott Copper-Ledge-mont Process since air is used rather than pure oxygen. In addition to the air the only other reactants required are lime and water. The process is operated at pressures between 1.52 and 10.34 MPa and temperatures between 150 and 220°C.

5

After a residence time of one hour or less, up to 40% of the organic sulfur and over 90% of the pyritic sulfur is removed.

In an independent economic survey⁽²⁰⁾ it was determined that the most promising of these six are the Ledgemont and D.O.E. processes.

The present work involves a study of the intrinsic kinetics of the Oxidative Desulfurization of coal from the upper seam of the Upper Freeport mine in Kittanning, Pennsylvania using the D.O.E. process.

2.0 BACKGROUND

Up to the present time there has been no investigation into the intrinsic kinetics of the D.O.E. Oxy-desulfurization process. The bulk of the effort, to date, has been concentrated on establishing optimum pressure and temperature ranges and determining the degree of sulfur removal for a series of representative coals. (21,22)

The Kennecott Copper Corporation has performed a kinetic study on the pyrite reaction in their oxygen-water desulfurization process. (23) This study was restricted to temperatures between 80° and 130°C and oxygen pressures between 0.69 and 2.07 MPa. On this basis they proposed a square root relationship between the partial pressure of oxygen and the rate of pyritic sulfur removal and reported an activation energy of 58.62 kJoule per gmole.

The first investigation into the pyrite-oxygen reaction was reported by McKay and Halpern in 1957. (24) In this paper the authors provide a comprehensive description of the basic chemistry of the system along with their study of the reaction kinetics. Based on experiments at temperatures between 100° and 130°C and oxygen partial pressures up to 4 atmospheres (approximately 0.42 MPa) they obtained an activation energy of 55.68 (± 8.4) kJ per gm mole. They also

reported that the rate of pyritic sulfur oxidation was first order with respect to the partial pressure of oxygen and zero order with respect to pyritic sulfur.

Vracar and Vucurovic⁽²⁵⁻²⁷⁾ have studied the oxidation of pyrite in an aqueous system with gaseous oxygen. This investigation was based on the hypothesis that the sulfuric acid produced could be used for alkalining metals from poor quality ores. From their experiments, conducted at temperatures between 50° and 200°C and oxygen partial pressures up to 12 atmospheres (1.21 MPa), they found the oxidation of aqueous pyrite to be an effective method for upgrading metal ores and, more importantly, established a fairly complete kinetic model for pyrite oxidation. They proposed a first order rate dependence on the concentration of pyrite and also a first order dependence on the partial pressure of oxygen up to 6 atmospheres (0.607 MPa). The proportionality for oxygen partial pressure disappears above these conditions. This is explained by an application of the Langmuir equation:

$$S = a * pO_2 \quad (1)$$

According to this relation the surface area covered by oxygen (S) is directly proportional to the oxygen partial pressure (pO_2). Since the oxygen and pyrite must be in

contact for the reaction to occur the rate of reaction is directly related to 'S'. However once the entire surface area of the pyrite particle is covered, any increase in pO_2 does not result in an increased value for 'S' and the expected increase in the rate of reaction. Finally, they calculated an activation energy of 50.97 kJ per gm mole for the pyrite oxidation reaction.

Due to the combination of temperature and oxygen availability in the Oxy-desulfurization process the oxidation of carbon to CO_x 's cannot be prevented. Therefore this work would not be complete without some explanation of the kinetics of these reactions.

Thring and Essenhish⁽²⁸⁾ present an excellent review of the fundamental chemistry and kinetics of solid carbon oxidation. Included in this review are several points of particular significance to the present work:

(A) Gasification of carbon goes to completion in the presence of an excess of oxygen at temperatures between 300° and 4000°K.

(B) The basis of the kinetics of carbon oxidation is the Langmuir isotherm.

(C) At high pressures and at temperatures less than 800°C the reaction is zero order with respect to carbon.

9

Sareen et al.⁽²⁹⁾ have examined the kinetics of the carbon reactions in the Ledge ment oxygen-water coal desulfurization process. In their experiments, conducted at 130°C and 2.07 MPa of oxygen they found carbon dioxide to be the most significant product. This is as would be expected in an excess oxygen environment. The ratio of CO₂ to CO formed was reported to be 22 to 1. They have also established a first order relation between the partial pressure of oxygen and the rate of CO₂ formation at 100° and 130°C; but find the same reaction to have zero order kinetics at 80°C.

A close examination of the findings described above demonstrates that there is by no means complete agreement on the kinetics of the reactions of this system. These differences are probably at least partially due to the wide variability of the temperature and pressure ranges studied. In any case, these works provide an appropriate foundation for the present study.

The objective of this investigation is to develop rate expressions for each of the reactions described above as they occur in the Oxidative Desulfurization of Upper Freeport coal. These expressions will be based on experiments which establish the kinetic effects of the following parameters: temperature, reaction time, partial pressure of oxygen, and total pressure.

3.0 CHEMISTRY

The chemistry of the Oxy-desulfurization process can be represented by three sets of reactions: pyritic sulfur oxidation, solid carbon combustion and organic sulfur removal. A discussion of each of these reactions is given below:

The primary steps in the pyritic sulfur oxidation are: (30)

Because of the dissociative properties of sulfuric acid (H_2SO_4) and ferrous sulfate (FeSO_4), reaction (3) can be more appropriately written as: (31)

Due to the oxidizing atmosphere in the Oxy-desulfurization reactor, most of the ferrous ions (Fe^{+2}) are further oxidized to ferric ions (Fe^{+3}) (32) which can be represented by the following equation:

11

In any case the ferric and ferrous ions are eventually removed as ferric or ferrous sulfates or as iron oxides; predominantly Fe_2O_3 .⁽³³⁾

At temperatures above 140°C the elemental sulfur formed by reaction (2) is further oxidized to sulfuric acid according to the following reaction:

Or to ferrous sulfate and sulfuric acid by:⁽³⁵⁾

On this basis the final products from the pyrite oxidation reactions are sulfuric acid, iron sulfates, and iron oxides.

The oxidation of solid carbon from the coal matrix can be described by the following set of reactions:⁽³⁶⁾

High partial pressures of oxygen do not favor reaction (11) and thus its contribution to the overall carbon oxidation mechanism may be considered negligible.

Since "organic sulfur" is a broad classification for any sulfur atom which is bonded to the organic matrix of the coal it is difficult to outline the possible reaction mechanisms for the organic sulfur reactions. Compounds which fall under the heading of organic sulfur include: mercaptans, sulfides, disulfides, thiophenes, thiols and thiopyrones.⁽³⁷⁾ The basic structures of these compounds are given in Figure 1. Due to the non-homogeneity of coals, it is possible that any given sample may contain one or more of the above compounds at any concentration level.

Friedman et al.⁽³⁸⁾ have provided some insight into the chemistry of organic sulfur removal. They found that although the treatment of coal with compressed air and steam resulted in a 25% decrease in its organic sulfur content; identical treatment of dibenzothiophene (an organic sulfur compound) produced no reaction. For coals containing dibenzothiophene this behavior could be explained as due to the catalytic effect of some other substance or substances present in the coal sample.

4.0 KINETIC ANALYSIS

The kinetic analysis presented in this work is based on standard techniques for a constant volume batch reactor. The following assumptions are made:

(A) The volume of the coal-water slurry remains constant during the reaction time.

(B) The reactor is isothermal. This is reasonable since the temperature was controlled within $\pm 3^{\circ}\text{C}$.

(C) Due to the high gas flow rate (34 SCF/hr) the partial pressure of oxygen is constant since oxygen is in excess.

(D) All external mass transfer resistances are negligible. This is reasonable in view of the high stirring speed in the reactor.

(E) Internal diffusion resistances are negligible. This is reasonable since there are no solid products deposited on the pore walls. These resistances are also minimized by the use of finely ground coal samples.

Based on these assumptions, the rate of reaction can be written as: ⁽³⁹⁾

$$\text{Rate} = (1/V) * dN/dt \quad (12)$$

Which can be rewritten as:

$$\text{Rate} = (1/V) * d(C*V)/dt = dC/dt \quad (13)$$

along with the boundary conditions:

$$C = C_0 \text{ at } t = 0 \quad (14)$$

$$C = C \text{ at } t > 0 \quad (15)$$

4.1 Preliminary Analysis

Preliminary data analysis was based on the following equation for an nth order reaction: (40)

$$C^{1-n} - C_0^{1-n} = (n-1)kt \quad (16)$$

Which results from separation and intergration of the basic nth order rate expression:

$$- dC/dt = kC^n \quad (17)$$

Since the initial concentration (C_0) is known as is the concentration (C) at any given time (t) it is possible to calculate a rate constant (k) for each time at a trial order of reaction (n). By calculating the standard deviation (41) in the calculated rate constants for a given data set for a

series of trial orders of reaction it is possible to find the optimum order of reaction for that data set. In other words the order of reaction that results in the smallest standard deviation is the true order of reaction. A copy of the computer program used for the above calculations is provided in Appendix C.

4.2 Zero Order Kinetics

If the reaction rate is independent of the concentration of the reactants, the reaction is said to be zero order.⁽⁴²⁾ For reactions of this type the rate expression is given by:

$$- \frac{dC}{dt} = k \quad (18)$$

Upon integration this yields:

$$C = -kt + C_0 \quad (19)$$

From equation (19) it can be seen that a plot of concentration (C) versus time (t) must produce a straight line to establish a zero order model. Equation (19) also indicates that the absolute value of the slope of this line yields the rate constant (k) and the intercept gives the initial concentration (C₀).

4.3 Pseudo-First Order Kinetics

When a reaction of an order greater than 1 reduces to apparent first order behavior it is explained by pseudo-first order kinetics.⁽⁴³⁾ For examples, consider the reaction:

let the reaction be first order with respect to each reactant; the rate expression is:

$$dc/dt = - k'CB \quad (20)$$

However, if reactant B is in excess, equation (20) can be re-written as:

$$dc/dt = - kC \quad (21)$$

Where the pseudo-first order rate constant (k) is given by:

$$k = k'B \quad (22)$$

Integration of equation (21) gives:

$$\ln (C/Co) = - kt \quad (23)$$

Based on equation (23) a plot of $-\ln (C/Co)$ versus time should yield a straight line for this model to hold. If such

a linear relation holds, equation (23) also indicates that the slope of this line is the pseudo-first order rate constant (k).

4.4 Arrhenius Analysis

The rate of reaction is dependent on both the concentration of the reactant or reactants and the temperature. It has been found that the temperature dependence is well represented by the Arrhenius equation: ⁽⁴⁴⁾

$$k = A_o * \exp (-E/RT) \quad (24)$$

or

$$\ln k = \ln A_o - (E/RT) \quad (25)$$

A plot of $\ln k$ versus $1/T$ ($^{\circ}K$) yields a straight line with a slope of $'-E/R'$ and an intercept of $'A_o'$. Therefore, by using the rate constants for a given reaction calculated at several temperatures (using equation (18) or (23)) the activation energy (E) and the frequency factor (A_o) for that reaction can be determined.

Linear regression analyses were performed on a DEC SYSTEM 1099 computer using BASIC. A listing of the computer program is included in Appendix C. The graphs presented here

were drawn using a Cal-Comp Model 936 Digital Incremental
Plotter.

5.0 EXPERIMENTAL WORK

Experiments were conducted to establish rate expressions for the major reaction systems of the Oxidative Desulfurization process. The parameters investigated include: residence time, temperature, oxygen partial pressure and total pressure. A list of experiments along with the experimental conditions is given in Table 2.

5.1 Apparatus

All experiments were conducted in a two liter stirred autoclave manufactured by the Parr Instrument Company of Moline, (see Figure 2). Due to the corrosive nature of the reaction products (sulfuric acid) a pyrex liner was used to protect the reaction vessel. Temperature control was provided by a Thermoelectric 400 proportional controller.

In order to keep the partial pressure of oxygen constant during the experiment, the reactor was operated in a semi-batch manner (i.e., gas flowing through a batch of liquid). A schematic diagram of the experimental apparatus is given in Figure 3.

5.2 Materials

The coal samples used in this study were from the upper seam of the Upper Freeport mine in Kittanning, Pennsylvania. All the samples were from a single larger sample and can therefore be assumed identical in basic composition. Over 98% of the crushed coal samples passed through a U.S. Standards 100 mesh screen (see Table 1).

The water used in this study was deionized in a column manufactured by Continental Deionized Water Services. Cylinder nitrogen and oxygen were supplied by Air Products Inc. These gases are classified as 'Extra Dry' and therefore have a minimum purity of 99.6%.

5.3 Procedure

The reactor, as mentioned earlier, was operated in a semi-batch manner. The important steps of this procedure are outlined below (for valve nos. refer to Figure 3). During the course of the experimentation the sampling technique was modified. A description of this modified technique is also provided in this chapter.

(A) Half fill the glass liner with water, place in the reactor and bolt on the vessel head. Slowly pressurize

the vessel to experimental pressure using the nitrogen (N_2) regulator and the reactor pressure gauge. Valves M2, 2, 4, 6, 8, and 9 opened.

(B) Set the Back Pressure Regulator (BPR) by increasing the N_2 regulator pressure to approximately 0.35 MPa greater than the experimental pressure and opening the BPR to the point at which the experimental pressure is held in the reactor. Close valve 9.

(C) Set the N_2 flow rate using metering valve M2 and the Wet Test Meter. Record the rotameter reading.

(D) Open valve 1. Set the oxygen (O_2) regulator pressure equal to that on the N_2 regulator. Set the O_2 flow rate using metering valve M1 and the Wet Test Meter. Record the rotameter reading.

(E) Close valves 1, 2, and 8. Depressurize the reactor by opening the BPR.

(F) Disconnect the reactor tubing, remove the reactor head and charge with feed slurry.

(G) Close the N_2 pressure regulator (gauge should read 0). Open valves 2, 8, and 9 to release the line pressure. Reattach the reactor tubing.

(H) Repressurize the reactor as in steps (A) and (B). Check the N_2 flow rate on the rotameter.

(I) Heat the reactor to experimental temperature by setting the temperature controller to experimental temperature plus 22 degrees C.

(J) Begin the reaction by simultaneously opening valve 1 and starting the timer.

(K) At the end of the reaction time, close valve 8 and simultaneously open the BPR to release the pressure from the reactor.

After depressurizing, the reactor was cooled, the coal sample was removed and filtered in a vacuum funnel fitted with a fritted glass filtration disk. After washing with approximately 2 liters of deionized water the sample was dried to a constant weight at 100°C (recorded dried sample weights are listed in Table 15). The above procedure was employed in experimental sets A, C, D, and E.

Since the above mentioned technique was rather cumbersome, an alternate sampling technique was devised for the remaining experiments. This consisted of collecting representative samples from the reactor, at different intervals, during the course of the reaction. Direct sampling from a vessel pressurized at 6.89 MPa causes a violent, and perhaps uncontrollable, surge of sample. This problem was overcome by using a sampling tube with a relatively small volume into

which the sample could be released. The tube was then sealed off from the reactor and its contents collected in a beaker. Because of the small volume of the sampling tube this release was much less violent than that from the reactor itself.

The sampling tube consists of a 28 centimeter section of 3/8 inch O.D. (.035 wall) stainless tubing with a valve at one end and a fitting for connection to the liquid sampling valve of the reactor at the other. The volume of this tube is approximately 15 cc. Sample sizes were usually smaller, however; since a portion of this volume becomes filled with compressed gases when sampling. The samples collected using the above technique were small enough to insure validity of the constant volume reactor assumption.

This sampling technique was used in experimental sets B and F through N. The steps involved in the modified sampling procedure are given below.

(A) Follow steps (A) through (J) as described in the earlier procedure.

(B) Attach the sampling tube to the liquid sampling valve on the reactor head (sampling tube valve closed).

(C) Twenty seconds prior to the end of the reaction time close the gas inlet valve (see Figure 2).

(D) Open the liquid sampling valve completely to fill the sampling tube.

(E) As soon as the sampling valve is completely opened begin opening the gas inlet valve and closing the liquid sampling valve simultaneously.

(F) Once the sampling valve is completely closed, open the valve at the end of the sampling tube to release the sample into a beaker.

(G) Filter and wash the sample as described previously.

5.4 Sample Analysis

All samples were analyzed by the Coal Analysis Laboratory of the U.S. Bureau of Mines. Initially, all samples were analyzed for Sulfur forms, carbon, hydrogen and heating value. However, due to the small samples (less than 1.5 grams) collected using the modified sampling technique (set B and sets F through N) these samples could not always be tested for all of these components.

In the sulfur forms analysis the total sulfur was determined by the Eschka method; a technique based on the amount of SO_2 produced on combustion of the coal sample in the presence of pure oxygen. The concentration of pyrite and sulfates was

determined by Atomic absorption. The organic sulfur content was calculated by subtracting the sulfates and pyritic sulfur from the total sulfur.

Carbon and hydrogen concentrations were established by the standard 'carbon train' method. In this procedure a known weight of sample is oxidized, producing CO_2 and H_2O which are collected and weighed to determine the carbon and hydrogen content of the sample. Heating values were determined by combustion of the samples in an oxygen bomb calorimeter.

Error in the chemical analysis was kept within ASTM standards. Less than 1% for sulfur forms, carbon and hydrogen and less than 50 BTU for the Heating value determination.

6.0 RESULTS AND DISCUSSION

The non-homogeneity of coal prevents the postulation of a concrete mechanism for the reactions occurring during the Oxy-desulfurization process. It is possible, however, to establish overall kinetic expressions for the important reaction systems. These reaction systems, categorized according to the classification of the reactant, are given below.

- (A) pyritic sulfur reaction
- (B) carbon oxidation
- (C) organic sulfur reaction

Results from the kinetic analysis of each of these systems will be discussed separately. The experimental data on which these findings are based, are listed in tables 3 through 14.

Several of the experiments conducted in this work, although not directly applicable to the kinetic study, were necessary to support the assumptions on which this study was based. The findings from each of these experiments are described below.

In experiments F and G the concentration of the coal slurry was varied. In experiment F the normal coal concentration was doubled (.22 g coal/ml water) and in experiment G this concentration was halved (.05 g coal/ml water). These

variations in the slurry concentration produced no significant change in the rate per unit volume of the reactions being studied; thus confirming that the reaction rate was not physically controlled (i.e., by gas absorption or diffusion).

Experiments M and N were conducted to determine if any reaction was occurring during the time in which the reactor was being heated to experimental temperature. The data from these runs indicated that although some reaction may have occurred; it was insignificant and can be neglected.

6.1 Pyritic Sulfur Reaction

Since the majority of the sulfur in Upper Freeport coal is pyritic (61%); the establishment of a kinetic model for the pyritic sulfur reaction was the major objective of this study.

Figure 4 illustrates the degree of pyritic sulfur/^{removal} for temperatures between 150° and 210°C. Similar experiments were attempted at 230°C (Set D) but adequate temperature control could not be achieved due to rapid temperature increases at the start of the reaction. The temperature excursions at this operating temperature were probably the result of a combination of rapid pyrite reaction and carbon oxidation.

Statistical optimization (using equation 16) of the data in Figure 4 indicates the orders of reaction to be 1.6, 1.4, and 1.3 for 150, 190 and 210 C respectively. It was found that first order kinetics produce a reasonable fit for data at all temperatures and therefore was chosen as the general model for this system. The first order kinetic plots at different temperatures are shown in Figure 5. The rate constants were calculated by linear regression analysis of these data. (45)

An Arrhenius plot based on the rate constants from Figure 5 gives an activation energy of 46.68 (± 1.3) kJ/gm-mole for the pyrite reaction (Figure 6). This value compares favorably with those calculated by McKay and Halpern (55.7 ± 8.4 kJ/mole, (46) Vracar and Vucurovic (47) (50.97 kJ/gm mole) and Sareen et al. (48) (58.62 kJ/mole). The intercept of this plot yields a frequency factor (A_0) of $4.508 \times 10^4 \text{ min}^{-1}$. Therefore, an expression for the rate constant (k) at an oxygen partial pressure of 1.72 MPa and a total pressure of 6.89 MPa can be written as:

$$k = 4.508 * 10^4 * \exp (-46,683/RT) \quad (26)$$

The rate of pyrite oxidation was found to be independent of total pressure, at a constant partial pressure of

29

oxygen, for pressures between 3.4 and 6.89 MPa. However, the pyrite reaction did exhibit a dependence on the partial pressure of oxygen. This relationship was established for oxygen partial pressures of 0.689, 1.72 and 3.44 MPa at a total pressure of 6.89 MPa. The effect of oxygen partial pressure on pyrite removal is shown in Figure 7. The first order kinetic plots for these data are shown in Figure 8. The overall dependence on the oxygen partial pressure was established based on the relation:

$$k = pO_2^n \quad (27)$$

From the above equation a plot of $-\ln k$ versus $\ln pO_2$ will have a slope of '-n'. A plot of this type is given in Figure 9. Linear regression analysis of these data yields a slope of $-.495$. Thus, the overall rate expression for the pyritic sulfur reaction can be written as:

$$\text{Rate} = 1.109 * 10^4 * \exp (-46,683/RT) * C_s * pO_2^{.495} \quad (28)$$

(pO_2 in atmospheres)

6.2 Carbon Oxidation

Large carbon losses resulting during the chemical cleaning of the coal could make the Oxy-desulfurization process

economically unattractive. Therefore, the kinetics of the carbon oxidation in this system is of great importance.

Carbon losses were found to be insignificant below 190°C; but above this temperature the losses became significant enough to warrant further study. A plot of the percentage carbon remaining versus reaction time is shown in Figure 10. From this plot it can be seen that at each temperature the reaction demonstrates zero order kinetics for an initial period of reaction time; i.e., the rate of reaction is independent of carbon concentration. This is consistent with the model for solid carbon oxidation reported by Thring and Essenhish⁽⁴⁹⁾ for temperatures less than 800 C. Based on the zero order rate constants, from Figure 10, an Arrhenius plot was constructed (Figure 11). The activation energy for the carbon oxidation reaction derived from this curve is 85.24 kJ/mole. This value is well within the range of values given by Thring and Essenhish (73.3 to 184.2 kJ/mole)⁽⁵⁰⁾ and reasonably close to that reported by Sareen et al.⁽⁵¹⁾ (73.86 kJ/mole). Based on the Arrhenius plot in Figure 11 an expression for the rate constant for the carbon oxidation reaction can be written as:

$$k = 8.815 * 10^8 * \exp (-85,235/RT) \quad (29)$$

For longer reaction times (outside the initial zero order regime) the rate of reaction shows a marked decrease (see Figure 10). This decreased reaction rate can be explained by an intraphase diffusional resistance, i.e., an ash barrier or a break down of the pore structure, which causes the diffusion of the oxygen into the coal particle to be the controlling mechanism.

The diffusion controlled reaction hypothesis was supported by application of an intraphase diffusional control model developed by Weisz and Goodman⁽⁵²⁾ for oxidation of carbonaceous substances in porous catalyst particles. This model is given below:

$$\frac{1}{2}(1-F)^{2/3} - \frac{1}{3}(1-F) = Kt \quad (30)$$

where:

$$F = C/C_0 \quad (31)$$

For this model to be valid a plot of $(\frac{1}{2}(1-F)^{2/3} - \frac{1}{3}(1-F))$ versus time must yield a straight line. These plots are shown in Figure 12. The linear relations shown in this figure demonstrate the applicability of the diffusional control model to the carbon oxidation system for larger reaction times. The slopes of the lines in this figure represent rate

constants in the diffusional controlled period (K).

Comparison of Figures 4 and 10 indicates that the starting point of the diffusional control regime corresponds closely to the time at which the pyritic sulfur reaches completion (i.e., 98% conversion). This supports the hypothesis that a break down of the pore structure could occur in the coal particles as a result of the removal of structurally significant pyrite crystals.

6.3 Organic Sulfur Reaction

Because of the wide variability in the data pertaining to the organic sulfur reaction it is difficult to establish an accurate kinetic model for this reaction. The variation in this data is probably a result of the inherently low organic sulfur content (0.76%) of Upper Freeport coal. Which is compounded by the fact that there is, as yet, no reliable chemical analysis for organic sulfur compounds. In fact, the organic sulfur contents reported in this work were found by subtracting the percentage sulfates and pyritic sulfur from the total sulfur content of the coal sample.

Figure 13 illustrates the degree of organic sulfur removal as a function of reaction time for temperatures between

150° and 210°C. These data indicate that the organic sulfur removal is insignificant below 190°C.

Primarily based on statistical optimization of these data a zero order model is postulated. The rate constants (k's) shown in Figure 13 represent linear regression slopes based on this model. An Arrhenius plot was also constructed for this system and is shown in Figure 14. This plot yields an activation energy of 78.66 kJ/gm mole and a frequency factor of 1.26×10^7 g sulfur/g cola-min. Therefore, the rate constant can be written as:

$$k = 1.26 \times 10^6 \cdot \exp (-78,653/RT) \quad (32)$$

In addition to the kinetic models, the data also illustrates several interesting trends from the process development point of view. Figure 15 demonstrates the effect of temperature on the overall removal of sulfur. According to Myers⁽⁵³⁾ an Eastern coal containing 0.8% or less total sulfur meets the federal pollution standards. This sulfur content, which corresponds to a 60% sulfur removal on Figure 15, can be attained rapidly for every temperature studied especially for the run at 210°C; where the reaction time required is of the order of a few minutes.

Figures 16, 17, and 18 illustrate the degree of removal of carbon and hydrogen and the percentage of the original heating value lost. This data, as expected, indicates that the loss in heating value is directly related to the removal of carbon and hydrogen. This loss is insignificant for the experiments at 150°C and moderate for the 190°C experiments; however, at 210°C the heating value losses become significant. Comparison of Figures 15 and 17 illustrates that the increased heating value losses between experiments at 210°C and 190°C are not accompanied by comparable increase in sulfur removal. These data indicate that the optimum operating temperature for this process at a total pressure of 6.89 MPa and a partial pressure of oxygen of 1.72 MPa lies below 210°C.

Figure 19 demonstrates the effect of oxygen partial pressure on sulfur removal. It may be mentioned here that although an increase in oxygen partial pressure results in increased sulfur removal; an increase in the total pressure at a constant oxygen partial pressure has no effect.

7.0 CONCLUSIONS

The information gained from this investigation illustrates that the Oxidative Desulfurization process is an attractive method for removing sulfur from Upper Freeport coal. In fact, for temperatures between 150° and 210°C the coal samples were treated to within federal pollution standards in less than 40 minutes of reaction time. The degree of sulfur removal was found to be independent of total pressure at a constant partial pressure of oxygen.

The pyritic sulfur reaction is rapid and exhibits both a temperature and oxygen partial pressure dependence. This reaction is well represented by a first order rate expression, having an activation energy of 46.68 kJ/mole and a square root correlation to the partial pressure of oxygen.

Loss of heating value due to carbon oxidation during the desulfurization process could pose a serious problem. The carbon oxidation reaction demonstrates a strong temperature dependence, the measured activation energy is 85.24 kJ/mole, however; and therefore this problem can be overcome by operating at a low temperature. The kinetic mechanism of the carbon reaction can be divided into two segments: an initial zero order regime and a somewhat slower, possibly diffusion

controlled regime.

Due to scatter in the experimental data only a tentative kinetic model was developed for the organic sulfur reaction. The data was found to support strongly a zero order kinetic model and an activation energy of 78.66 kJ/mole was obtained.

7.1 Recommendations for Further Investigation

(A) Conduct a similar study using a coal with a high organic sulfur content and a low pyritic sulfur content; e.g. Indiana No. 5.

(B) Conduct a similar study using a coal with a comparable organic and pyritic sulfur content; e.g. Illinois No. 6.

(C) Study the intraphase diffusion effects by testing both larger and smaller coal particles.

APPENDIX A
TABLES 1 THROUGH 15

Table 1: Coal Particle Size Distribution

Percentage of Particles	Between (Mesh size)		Between (microns)	
0.2	---	+40	>370	---
0.3	40	60	250	370
0.9	60	100	149	250
18.0	100	200	74	149
58.4	200	325	44	74
22.2	325	---	---	44

Table 2: Summary of Experiments

Set	Temp. (C)	Press. (MPa)	PO ₂ (MPa) (g coal/ml H ₂ O)	Conc. (g coal/ml H ₂ O)	Stirrer (r.p.m.)	Reaction times (minutes)
A	150	6.89	1.72/250	0.1	1000	5,10,15,20,40
B	190	6.89	3.44/500	0.1	1000	3,5,10,15,20
C	210	6.89	1.72	0.1	1000	5,10,15,20,40
D	230	6.89	1.72	0.1	1000	5,10
E	190	6.89	1.72	0.1	1000	5,10,15,20,40
F	150	6.89	1.72	0.22	1000	40
G	190	6.89	1.72	0.05	1000	40
I	190	6.89	0.69/100	0.1	1000	5,16,25
J	190	3.44/500	1.72	0.1	1000	5,10,15
K	190	5.17/750	1.72	0.1	1000	5,10,15
M	230	6.89	0.0	0.1	1000	40
N	160	6.89	0.0	0.1	1000	40

 DATA FOR SET :

A.

TEMPERATURE : 150 DEGREES C
 PRESSURE : 1000 PSI
 % OXYGEN : 25
 CONCENTRATION: 0.1 GRAMS COAL PER ML WATER

PERCENTAGES OF TOTAL SAMPLE WEIGHT

(MOISTURE AND ASH FREE BASIS)
 (HEATING VALUES IN [BTU/LB])

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE	CARBON	HYDROGEN	HEATING VALUE
0	2	1.19	0.76	0.07	88.1	4.7	15436
5	1.2	0.37	0.78	0.04	87.3	4.8	15199
10	1.3	0.6	0.67	0.03	87.9	4.8	15269
15	1	0.18	0.75	0.05	87.1	4.7	15032
20	0.9	0.12	0.75	0.05	87.3	4.7	15103
40	0.8	0.04	0.76	0.01	87.4	4.7	15022

PERCENTAGES OF ORIGINAL REMOVED

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE	CARBON	HYDROGEN	HEATING VALUE
5	40	68.9076	-2.63158	42.8571	0.908059	-2.12766	1.55537
10	35	49.5798	11.8421	57.1429	0.227015	-2.12766	1.08189
15	50	84.874	1.31579	28.5714	1.13507	0	2.61726
20	55	89.916	1.31579	28.5714	0.908059	0	2.15729
40	60	96.6387	0	85.7143	0.794551	0	2.68204

Table 3: Experimental Data for Set A

 DATA FOR SET :

B

TEMPERATURE : 190 DEGREES C
 PRESSURE : 1000 PSI
 % OXYGEN : 50
 CONCENTRATION: 0.1 GRAMS COAL PER ML WATER

PERCENTAGES OF TOTAL SAMPLE WEIGHT

(MOISTURE AND ASH FREE BASIS)

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE
0	2	1.19	0.76	0.07
3	1	0.34	0.68	0.02
5	0.9	0.1	0.74	0.04
10	0.7	0.06	0.63	0.05
15	0.8	0.02	0.8	0.01
20	0.75	0.02	0.64	0.09

PERCENTAGES OF ORIGINAL REMOVED

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE
3	50	71.4286	10.5263	71.4286
5	55.	91.5966	2.63158	42.8571
10	65.	94.958	17.1053	28.5714
15	60	98.3193	-5.26316	85.7143
20	62.5	98.3193	15.7895	-28.5714

Table 4: Experimental Data for Set B

 DATA FOR SET :

C

TEMPERATURE : 210 DEGREES C
 PRESSURE : 1000 PSI
 % OXYGEN : 25
 CONCENTRATION: 0.1 GRAMS COAL PER ML WATER

PERCENTAGES OF TOTAL SAMPLE WEIGHT

(MOISTURE AND ASH FREE BASIS)
 (HEATING VALUES IN [BTU/LB])

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE	CARBON	HYDROGEN	HEATING VALUE
0	2	1.19	0.76	0.07	88.1	4.7	15436
5	0.8	0.08	0.68	0.06	85.1	4.5	14632
10	0.7	0.02	0.64	0.03	82.7	4	13879
15	0.7	0.02	0.64	0.05	81.5	3.9	13489
20	0.7	0.02	0.64	0.05	82.4	4	13925
40	0.6	0.02	0.56	0.06	78.7	3.5	12804

PERCENTAGES OF ORIGINAL REMOVED

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE	CARBON	HYDROGEN	HEATING VALUE
5	60	93.2773	10.5263	14.2857	3.40522	4.25532	5.2066
10	65.	98.3193	15.7895	57.1429	6.1294	14.8936	10.0868
15	65.	98.3193	15.7895	28.5714	7.49149	17.0213	12.6134
20	65.	98.3193	15.7895	28.5714	6.46992	14.8936	9.78881
40	70	98.3193	26.3158	14.2857	10.6697	25.5319	17.051

Table 5: Experimental Data for Set C

 DATA FOR SET :

D

TEMPERATURE : 230 DEGREES C
 PRESSURE : 1000 PSI
 % OXYGEN : 25
 CONCENTRATION: 0.1 GRAMS COAL PER ML WATER

PERCENTAGES OF TOTAL SAMPLE WEIGHT

(MOISTURE AND ASH FREE BASIS)
 (HEATING VALUES IN BTU/LB)

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE	CARBON	HYDROGEN	HEATING VALUE
0	2	1.19	0.76	0.07	88.1	4.7	15436
5	0.8	0.1	0.69	0.06	84.2	4.1	14089
10	0.7	0.03	0.61	0.04	79.3	3.5	12962

PERCENTAGES OF ORIGINAL REMOVED

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE	CARBON	HYDROGEN	HEATING VALUE
5	60	91.5966	9.21053	14.2857	4.42679	12.766	8.72635
10	65.	97.479	19.7368	42.8571	9.98865	25.5319	16.0275

Table 6: Experimental Data for Set D

 DATA FOR SET :

F

TEMPERATURE : 150 DEGREES C
 PRESSURE : 1000 PSI
 % OXYGEN : 25
 CONCENTRATION: 0.219512 GRAMS COAL PER ML WATER

PERCENTAGES OF TOTAL SAMPLE WEIGHT

(MOISTURE AND ASH FREE BASIS)
 (HEATING VALUES IN [BTU/LB])

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE	CARBON	HYDROGEN	HEATING VALUE
0	2	1.19	0.76	0.07	88.1	4.7	15436
40	1	0.03	0.89	0.07	87.3	4.7	15003

PERCENTAGES OF ORIGINAL REMOVED

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE	CARBON	HYDROGEN	HEATING VALUE
40	50	97.479	-17.1053	0	0.908059	0	2.80513

Table 8: Experimental Data for Set F

 DATA FOR SET :

G

TEMPERATURE : 150 DEGREES C
 PRESSURE : 1000 PSI
 % OXYGEN : 25
 CONCENTRATION: 4.76190E-2 GRAMS COAL PER ML WATER

PERCENTAGES OF TOTAL SAMPLE WEIGHT

(MOISTURE AND ASH FREE BASIS)
 (HEATING VALUES IN [BTU/LB])

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE	CARBON	HYDROGEN	HEATING VALUE
0	2	1.19	0.76	0.07	88.1	4.7	15436
40	0.7	0.02	0.64	0.05	82.5	4.2	13873

PERCENTAGES OF ORIGINAL REMOVED

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE	CARBON	HYDROGEN	HEATING VALUE
40	65.	98.3193	15.7895	28.5714	6.35641	10.6383	10.1257

Table 9: Experimental Data for Set G

 DATA FOR SET :

I.

TEMPERATURE : 190 DEGREES C
 PRESSURE : 1000 PSI
 % OXYGEN : 10
 CONCENTRATION: 0.1 GRAMS COAL PER ML WATER

PERCENTAGES OF TOTAL SAMPLE WEIGHT

(MOISTURE AND ASH FREE BASIS)

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE
0	2	1.19	0.76	0.07
5	1	0.15	0.8	0.01
16	1	0.08	0.94	0.01
25	0.9	0.04	0.75	0.07

PERCENTAGES OF ORIGINAL REMOVED

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE
5	50	87.395	-5.26316	85.7143
16	50	93.2773	-23.6842	85.7143
25	55.	96.6387	1.31579	0

Table 10: Experimental Data for Set I

 DATA FOR SET :

J

TEMPERATURE : 190 DEGREES C
 PRESSURE : 500 PSI
 Z OXYGEN : 50
 CONCENTRATION: 0.1 GRAMS COAL PER ML WATER

PERCENTAGES OF TOTAL SAMPLE WEIGHT

(MOISTURE AND ASH FREE BASIS)

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE
0	2	1.19	0.76	0.07
5	1.6	0.21	1.38	0.04
10	1	0.09	0.82	0.05
15	0.8	0.03	0.63	0.08

PERCENTAGES OF ORIGINAL REMOVED

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE
5	20.	82.3529	-81.5789	42.8571
10	50	92.437	-7.89474	28.5714
15	60	97.479	17.1053	-14.2857

Table 11: Experimental Data for Set J

 DATA FOR SET :

K

TEMPERATURE : 190 DEGREES C
 PRESSURE : 750 PSI
 % OXYGEN : 33.33
 CONCENTRATION: 0.1 GRAMS COAL PER ML WATER

PERCENTAGES OF TOTAL SAMPLE WEIGHT

(MOISTURE AND ASH FREE BASIS)

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE
0	2	1.19	0.76	0.07
5	1	0.16	0.76	0.04
10	--	0.08	--	0.02
15	0.8	0.03	0.7	0.07

PERCENTAGES OF ORIGINAL REMOVED

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE
5	50	86.5546	0	42.8571
10	--	93.2773	--	71.4286
15	60	97.479	7.89474	0

Table 12: Experimental Data for Set K

 DATA FOR SET :

M

TEMPERATURE : 230 DEGREES C
 PRESSURE : 1000 PSI
 % OXYGEN : 0
 CONCENTRATION: 0.1 GRAMS COAL PER ML WATER

PERCENTAGES OF TOTAL SAMPLE WEIGHT

(MOISTURE AND ASH FREE BASIS)
 (HEATING VALUES IN [BTU/LB])

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE	CARBON	HYDROGEN	HEATING VALUE
0	2	1.19	0.76	0.07	88.1	4.7	15436
40	1.7	1.04	0.65	0	87.9	4.8	15380

PERCENTAGES OF ORIGINAL REMOVED

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE	CARBON	HYDROGEN	HEATING VALUE
40	15.	12.605	14.4737	100	0.227015	-2.12766	0.362788

Table 13: Experimental Data for Set M

 DATA FOR SET :

N

TEMPERATURE : 160 DEGREES C
 PRESSURE : 1000 PSI
 % OXYGEN : 0
 CONCENTRATION: 0.1 GRAMS COAL PER ML WATER

PERCENTAGES OF TOTAL SAMPLE WEIGHT

(MOISTURE AND ASH FREE BASIS)
 (HEATING VALUES IN [BTU/LB])

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE	CARBON	HYDROGEN	HEATING VALUE
0	2	1.19	0.76	0.07	88.1	4.7	15436
40	1.8	1.18	0.59	0	88.2	4.8	15442

PERCENTAGES OF ORIGINAL REMOVED

TIME [MINS.]	SULFUR	PYRITIC SULFUR	ORGANIC SULFUR	SULFATE	CARBON	HYDROGEN	HEATING VALUE
40	10.	0.840335	22.3684	100	-0.113508	-2.12766	-3.88702E-2

Table 14: Experimental Data for Set N

*
Table 15: Weights of Treated Coal Samples

Set	Reaction time (min.)	Sample Weight (grams)
A	5	88.2
A	20	86.9
C	5	89.7
C	10	90.1
C	15	90.8
C	20	90.8
C	40	90.3
D	5	89.7
D	10	90.8
E	5	89.3
E	10	89.4
E	20	90.4
E	40	90.7

*
Original weight was 90.0 grams in all cases

APPENDIX B
FIGURES 1 THROUGH 19

Figure 1: Organic Sulfur Compounds.

Mercapatan

Sulfide

Disulfide

Thiol

Thiophene

Thiopyrone

Figure 2: Sectioned view of reactor

Sectioned View of No. 4442 Bomb, 2000 ml.

REACTOR IN HEATING JACKET

Figure 4: % Pyritic Sulfur removed vs. time

Figure 5: First order kinetic plot for pyrite reaction

Figure 6: Arrhenius plot for pyrite reaction

Figure 7: % Pyritic sulfur removed vs. time
(effect of pO_2)

Figure 8: First order Kinetic plot for pyrite reaction (effect of $p\text{O}_2$)

Figure 9: Dependence of pyritic sulfur rate constant on pO_2 .

Figure 10: % Carbon remaining vs. time

Figure 11: Arrhenius Plot for carbon oxidation

Figure 12: Diffusion Controlled Kinetic Plot

Figure 13: % Organic Sulfur Remaining vs. time

Figure 14: Arrhenius Plot for Organic Sulfur Reaction

Figure 15: % Sulfur Removed vs. time

Figure 16: % Carbon Removed vs. time

Figure 17: % Hydrogen Removed vs. time

Figure 18: % Heating Value Lost vs. time

Figure 19: % Sulfur Removed vs. time
(effects of pO_2)

```

00010  REM
00020  REM
00030  REM      THIS PROGRAM FINDS THE OPTIMUM ORDER OF REACTION
00040  REM      BASED ON THE EQUATION:
00050  REM
00060  REM      CA**Q-CA0**Q=P*K*T      (EQ. 29 P. 51 LEVENSPIEL)
00070  REM
00080  REM      K = RATE CONSTANT
00090  REM      CA = CONC. AT TIME T
00100  REM      CA0 = CONC. AT TIME ZERO
00110  REM      P = N - 1
00120  REM      Q = 1 - N
00130  REM      N = ORDER OF REACTION
00140  REM
00150  REM
00160  REM      WRITTEN BY: DAVID J. SLAGLE
00170  REM
00180  REM
00190  DIM C(50),K(50),T(50)
00200  MARGIN 132
00210  PRINT "INPUT SET CODE:"
00220  INPUT A$
00230  PRINT "INPUT COMPONENT ON WHICH OPTIMIZATION IS BASED E.G. PYRITIC SULFUR"
00240  INPUT B$
00250  PRINT "INPUT INITIAL TRIAL ORDER, FINAL TRIAL ORDER, AND STEP SIZE"
00260  INPUT V1,V2,V3
00270  PRINT
00280  PRINT "INPUT INITIAL CONC. (A0)"
00290  INPUT A0
00300  PRINT
00310  PRINT "INPUT NUMBER OF POINTS NOT COUNTING THE POINT AT ZERO TIME (M)"
00320  INPUT M
00330  PRINT
00340  PRINT "INPUT TIME, CONC. STARTING WITH THE POINT AFTER ZERO TIME [T(I), C(I)]"
00350  PRINT
00360  FOR I=1 TO M
00370  INPUT T(I),C(I)
00380  NEXT I
00390  T(0)=0
00400  C(0)=A0
00410  PRINT
00420  PRINT
00430  PRINT TAB(19); "STATISTICAL OPTIMIZATION FOR SET "A$
00440  PRINT TAB(19); "(BASED ON "B$,")"
00450  PRINT
00460  PRINT TAB(30); "INPUT DATA"
00470  PRINT TAB(30); "-----"
00480  PRINT TAB(27); "TIME"; TAB(40); "CONC."
00490  PRINT
00500  FOR U = 0 TO M
00510  PRINT TAB(27); T(U); TAB(39); C(U)
00520  NEXT U
00530  PRINT
00540  PRINT
00550  PRINT TAB(8); "ORDER OF REACTION"; TAB(30); "RATE CONSTANT"; TAB(46); "STAND. DEV."
00560  PRINT TAB(8); "-----"; TAB(30); "-----"; TAB(46); "-----"
00570  G=100000
00580  FOR N= V1 TO V2 STEP V3
00590  S=0
00600  S2=0
00610  Q=1-N
00620  P=N-1
00630  IF N=1 THEN B30
00640  FOR J=1 TO M
00650  K(J)=(C(J)**Q-A0**Q)/(T(J)*P)

```

```
00660 S=K(J)+S
00670 NEXT J
00680 A1=S/M
00690 FOR R= 1 TO M
00700 Z=K(R)-A1
00710 Z2=Z*Z
00720 S2=S2+Z2
00730 NEXT R
00740 S3=S2/(M-1)
00750 D=SQRT(S3)
00760 PRINT
00770 PRINT TAB(13);N;TAB(31);A1;TAB(46);D
00780 IF D<G THEN 800
00790 GO TO 830
00800 G=D
00810 O9=N
00820 K9=A1
00830 NEXT N
00840 PRINT
00850 PRINT
00860 PRINT*THE SMALLEST STANDARD DEVIATION IS:*,G
00870 PRINT
00880 PRINT*THEREFORE THE OPTIMIZED ORDER OF REACTION IS:*,O9
00890 PRINT
00900 PRINT*WHICH HAS AN AVERAGE K VALUE OF:*,K9
00910 STOP
00920 END
```

```

00010 REM
00020 REM
00030 REM *****
00040 REM
00050 REM A PLOT AND LINEAR REGRESSION PROGRAM
00060 REM BY: DAVID J. SLATLE
00070 REM
00080 REM *****
00090 REM
00100 REM
00110 MARGIN 132
00120 DIMENSION X(50),Y(6),Z(6),C1(50),C9(50),D9(50),T(50),P1(50)
00130 PRINT*READ IN X-AXIS LABEL ON LINE 2250.*
00140 PRINT
00150 PRINT*READ IN Y VALUE LABEL ON LINE 2260.*
00160 PRINT
00170 PRINT*TO PLOT A FUNC. OF Y VS. X INSERT THE FUNC. AT LINE 700.*
00180 PRINT* E.G. TO PLOT 5*Y VS. X INSERT:*
00190 PRINT* 700 D9(L)=5*D9(L)*
00200 PRINT
00210 PRINT*READ IN Y-AXIS LABEL AT LINE 2270.*
00220 PRINT
00230 PRINT*READ IN DATA: X,Y. BEGINNING AT LINE 2280.*
00240 PRINT
00250 PRINT*TO INPUT DATA (INSTEAD OF READING IT IN) CHANGE LINE 650*
00260 PRINT* I.E. CHANGE 650/READ/INPUT/*
00270 PRINT
00280 REM
00290 REM X4 = INITIAL X VALUE, Y4 = INITIAL Y VALUE
00300 REM
00310 REM X2= DELTA X, Y2= DELTA Y, N= # OF POINTS
00320 REM
00330 REM X7 = MAXIMUM X, Y7 = MAXIMUM Y
00340 PRINT*INPUT SET CODE:*
00350 INPUT D$
00360 PRINT* FOR REVERSIBLE REACTIONS INPUT EQUILIBRIUM CONCENTRATION*
00361 PRINT* OTHERWISE INPUT ZERO.*
00362 INPUT Q7
00370 REM
00380 PRINT*INPUT INITIAL X AND Y. MAXIMUM X AND Y. NO. OF POINTS.*
00390 PRINT*BE SURE TO SEPARATE THE NOS. WITH COMMAS.*
00400 PRINT*TURN TO THE BEGINING OF THE NEXT PAGE BEFORE HITTING RETURN.*
00410 PRINT
00420 INPUT X4,Y4,X7,Y7,N
00430 REM
00440 X2=(X7-X4)/50.
00450 Y2=(Y7-Y4)/50.
00460 Y3=10*Y2
00470 X3=10*X2
00480 READ A$
00490 READ B$
00500 READ C$
00510 S1=0
00520 S2=0
00530 Q1=0
00540 Q2=0
00550 Q3=0
00560 Z9=0
00570 C7=0
00580 J6=0
00590 N6=54-N
00600 FOR K=0 TO 5
00610 Y(K)=(Y3*K)+Y4
00620 Z(K)=(X3*K)+X4

```

```

00630 NEXT K
00640 FOR L=1 TO N
00650 INPUT C9(L),D9(L)
00660 C1(L)=D9(L)
00670 T(L)=C9(L)
00680 REM
00690 REM PUT FUNC. OF D9(L) HERE EG. D9(L)=LOG(D9(L))
00700 D9(L)=-LOG(D9(L))
00710 F1(L)=D9(L)
00720 NEXT L
00730 FOR L= 0 TO 50
00740 X(L)=-1
00750 NEXT L
00760 FOR I=1 TO N
00770 C=C9(I)
00780 D=D9(I)
00790 C=C-X4
00800 D=D-Y4
00810 A=C/X2
00820 E=D/Y2
00830 X(A)=B
00840 NEXT I
00850 IF X(0)>=0 THEN 870
00860 GO TO 890
00870 C6=INT(X(0))
00880 C7=10
00890 PRINT
00900 PRINT TAB(33);"PLOT OF DATA FROM SET",D6
00910 PRINT
00920 PRINT TAB(31);C6; " --->"
00930 PRINT
00940 PRINT TAB(11);Y(0)TAB(21);Y(1)TAB(31);Y(2)TAB(41);Y(3)TAB(51);Y(4)TAB(61);Y(5)
00950 IF C7>0 THEN 970
00960 PRINT TAB(12);"+-----+-----+-----+-----+----->"
00965 GO TO 1140
00970 FOR J=0 TO 50
00980 J6=J6+1
00990 IF J=C6 THEN 1070
01000 IF J=0 THEN 1040
01010 IF J6 =10 THEN 1040
01020 PRINT TAB(J+12);"-";
01030 GO TO 1120
01040 PRINT TAB(J+12);"+";
01050 J6=0
01060 GO TO 1120
01070 PRINT TAB(J+12);"*";
01080 IF J6=10 THEN 1110
01090 IF C6=0 THEN 1110
01100 GO TO 1120
01110 J6=0
01120 NEXT J
01130 PRINT TAB(63);"----->"
01140 J1=0
01150 Z1=1
01160 FOR J=1 TO 50
01170 J1=J1+1
01180 IF X(J)=0 THEN 1300
01190 IF X(J)=-1 THEN 1270
01200 IF J1=10 THEN 1230
01210 PRINT TAB(12);":":TAB(X(J)+12);"*"
01220 GO TO 1400
01230 PRINT TAB(5);Z(Z1);TAB(12);"+":TAB(X(J)+12);"*"
01240 Z1=Z1+1
01250 J1=0
01260 GO TO 1400
01270 IF J1=10 THEN 1370
-----

```

```

01280 PRINT TAB(12);"I"
01290 GO TO 1400
01300 IF J1=10 THEN 1330
01310 PRINT TAB(12);"K"
01320 GO TO 1400
01330 PRINT TAB(5);Z(Z1)TAB(12);"K"
01340 Z1=Z1+1
01350 J1=0
01360 GO TO 1400
01370 PRINT TAB(5);Z(Z1)TAB(12);"K"
01380 Z1=Z1+1
01390 J1=0
01400 NEXT J
01410 PRINT TAB(12);"I"
01420 PRINT TAB(12);"I"
01430 PRINT TAB(12);"V"
01440 PRINT
01450 PRINT
01460 PRINT
01470 PRINT
01480 PRINT
01490 PRINT
01500 PRINT
01510 PRINT TAB(22);"DATA USED IN ABOVE PLOT"
01520 PRINT TAB(22);"-----"
01530 PRINT
01540 IF Z9 > 0 THEN 1630
01550 PRINT TAB(12);"NO."TAB(23);A$;TAB(40);B$;TAB(53);C$
01560 FOR H1=1 TO N
01570 PRINT
01580 PRINT TAB(11);H1TAB(23);T(H1)TAB(40);C1(H1)TAB(52);P1(H1)
01590 NEXT H1
01600 PRINT
01610 PRINT
01620 GO TO 1810
01630 PRINT TAB(20);"NO."TAB(32);A$;TAB(44);C$
01640 FOR J9=1 TO N
01650 PRINT
01660 PRINT TAB(20);J9TAB(32);C9(J9)TAB(44);D9(J9)
01670 NEXT J9
01680 PRINT
01690 PRINT
01700 PRINT
01710 PRINT TAB(26);"LINEAR REGRESSION DATA"
01720 PRINT TAB(26);"-----"
01730 PRINT
01740 PRINT
01750 PRINT
01760 PRINT TAB(19);"(DEVIATION WITHIN 95% CONFIDENCE LIMIT)"
01770 PRINT
01780 PRINT TAB(14);"INTERCEPT=";B8;TAB(24);"SLOPE=";B1"/-";B2
01790 PRINT
01800 PRINT TAB(14);"AVG. X=";A1TAB(42);"AVG. Y=";A2"/-";B9
01810 Z9=Z9+1
01820 IF Z9>=2 THEN 9999
01830 REM
01840 REM LINEAR REGRESSION CALCULATIONS
01850 REM
01851 REM
01852 REM
01853 REM
01854 REM
01855 REM
01856 REM
01857 REM
01858 REM

```

BASED ON THE TECHNIQUE DESCRIBED IN:
 PLANT DESIGN AND ECONOMICS
 FOR CHEMICAL ENGINEERS
 SECOND EDITION
 M.S. PETERS AND K.D. TIMMERHAUS
 PP. 695-700

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01859 REM
01860 FOR M= 1 TO N
01870 S1=S1+T(M)
01880 S2=S2+F1(M)
01890 Q1=Q1+(T(M)*T(M))
01900 Q2=Q2+(F1(M)*F1(M))
01910 Q3=Q3+(T(M)*F1(M))
01920 NEXT M
01930 A1=S1/N
01940 A2=S2/N
01950 R5=Q2-(S2*S2/N)
01960 R3=Q3-(S1*S2/N)
01970 R1=Q1-(S1*S1/N)
01980 B1=R3/R1
01990 B8=A2-(B1*A1)
02000 REM
02010 REM          95% CONFIDENCE LIMIT CALCULATIONS
02020 REM
02030 R3=.33333*(R5-(B1*R3))
02040 R4=R3/R1
02050 B2=3.18*(SQRT(R4))
02060 R5=R3/N
02070 B9=3.18*(SQRT(R5))
02080 REM
02090 REM          TO PLOT REGRESSION DATA
02100 REM
02110 FOR P=1 TO N
02120 D9(P)=(B1*C9(P))+B8
02130 NEXT P
02140 C9(N+1)=X4
02150 D9(N+1)=(B1*X4)+B8
02160 N=N+1
02170 FOR M=1 TO N6
02180 PRINT
02190 NEXT M
02200 PRINT
02210 PRINT TAB(33);"LINEAR REGRESSION PLOT"
02220 PRINT TAB(33);"-----"
02230 PRINT
02240 GO TO 730
02250 DATA INV. TEMP.
02260 DATA K
02270 DATA NEGATIVE LN K
09998 STOP
09999 END

```

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