Title
OXYDESULFURIZATION OF GOAL

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Publication Date
1982-05-01

LBL-14491

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

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(*Ph.D. thesis in part)

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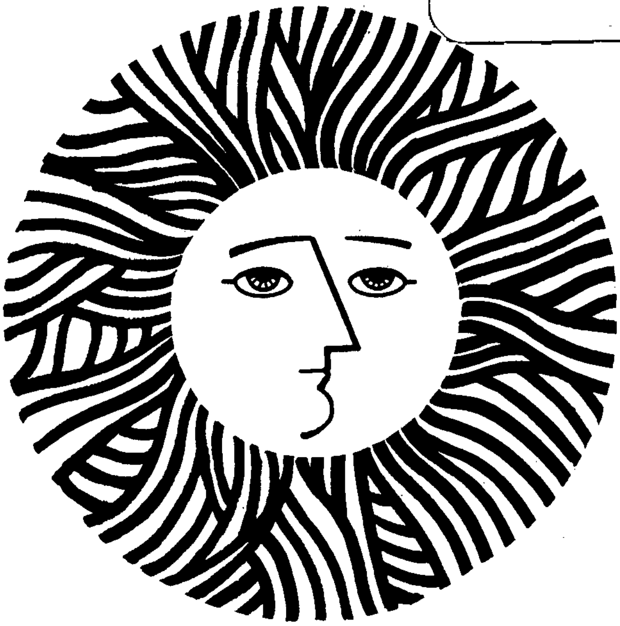

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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OXYDESULFURIZATION OF COAL

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*Ph.D. thesis, in part. See LBL-14216 for section entitled "Homogeneous Hydrogenation of Model-Coal Compounds".

This study was supported by the Assistant Secretary of Fossil Energy, Office of Coal Mining and Preparation of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

ABSTRACT

Pyrite, a principal sulfur-bearing component of high-sulfur coals, reacts with oxygen to form ferric sulfate and sulfuric acid. By using these products as the reaction medium, the use of water is minimized, and the products are recoverable in essentially pure form. The reaction kinetics for oxidation of native pyrite and oxidation of pyrite in coal are compared in the range of 100 to 150°C, and it is concluded that acid iron-sulfate media provide an effective means for inorganic sulfur removal. On the other hand, removal of organic sulfur is difficult to achieve without significantly lowering the heating value of the coal. Therefore the economic use of acidic oxidation is likely to be limited to coals in which pyrite comprises a large part of the total sulfur content.

CONTENTS

I. Introduction

I. INTRODUCTION

A. Potential for Coal Utilization

The increased use of coal is the focus of a national debate over the need for energy and the desire to maintain a healthy environment. With reliable sources of oil and natural gas dwindling, coal is destined to become an increasingly important energy resource, particularly as a fuel in electricity generation.

The United States possess approximately one-third of the world's known economically recoverable coal reserves (S1). Indeed, current estimates indicate that the coal reserves of the U.S. could supplant the use of oil and natural gas for the equivalent of 500 years (C1). Nevertheless, coal production in 1975 was equivalent to only 15.4 quadrillion Btu, a level first achieved in 1918, and today represents only about 18% of our primary energy supply (B1).

A number of ecological problems prevent the full utilization of coal as an energy resource, the most severe being the air pollution from particulate matter, nitrogen oxides, and sulfur oxides produced by combustion in utility boilers. Of these, sulfur dioxide has received the most attention primarily due to the large quantity of emissions, the controversy surrounding its impact, and the great expense involved in SO_2 controls. Coal combustion is now, and is likely to continue to be, the major source of sulfur dioxide emissions in the United States, accounting for more than 58% or 19 million tons in 1972 (P1).

The SO_2 that emerges from the stack of a coal-fired boiler is either removed by impaction in an area close to its source, or transformed into sulfuric acid or some other form of sulfate ion. These sulfates may be transported over a wide area and are removed predominately by rainfall. Such acid rain can damage vegetation and aquatic life, accelerate corrosion of building materials, and even leach toxic materials and destroy nitrogen-fixing bacteria from increasing soil acidity (H1). In addition, one statistical study has shown a direct relationship between atmospheric SO_2 levels and numerous health defects, including chronic respiratory disease, aggravated heart and lung disease, asthma, and children's lower respiratory disease (N1).

Consequently, the Environmental Protection Agency (EPA) has established strict legal standards governing ambient air quality. Under the 1970 amendments to the Clean Air Act, the latest federal standards of performance for new coal-fired power plants call for an upper limit of 1.2 lb SO_2 per million Btu output and for 90% sulfur reduction (or 70% reduction when emissions are less than 0.6 lb SO_2 per million Btu output) (T1). Presently, only a small percentage of the run-of-mine utility coal production in the United States can meet the 1.2 lb SO_2 per million Btu emission limit. The additional requirement of 90% sulfur removal poses an even greater problem and stresses the need for desulfurization technology which will meet both EPA standards and economic feasibility.

B. Forms of Sulfur in Coal

The total amount of sulfur in coal may vary from 0.2 to 10 wt-% but is generally in the range of 1.0 to 4.0 wt-% (D1). Sulfur occurs in both organic and inorganic forms. The ratio of inorganic to organic sulfur ranges from 1:3 to 4:1 but is usually close to 2:1 (A1). Inorganic sulfur therefore comprises the majority of the sulfur in coal.

Inorganic sulfur appears mainly as FeS_2, sulfates, and to a lesser extent, elemental sulfur. FeS_2, the most abundant form of sulfur in coal, may exist as marcasite (orthorhombic crystal lattice) or pyrite (isometric cubic crystal lattice). Marcasite, which is less prevalent than pyrite, may be converted to pyrite on heating. Other infrequently occurring inorganic sulfides include galena (PbS), chalcopyrite ($CaFeS_2$), arsenopyrite (FeAsS), and sphalerite (ZnS). Sulfates, in the form of iron, calcium, and barium salts, are present to a very small extent in freshly mined coal, but increase in concentration with length of exposure of the coal to air due to pyrite oxidation. Elemental sulfur, previously considered to occur in insignificant amounts (G1), is also a product of pyrite autoxidation.

The organic sulfur, which is bound to the hydrocarbon structure of the coal, is classified according to the type of functional group in which it appears. Attar has estimated that thiophenic sulfur constitutes 40-70% of the organic sulfur of bituminous coals, with the remainder existing as aryl, cyclic, and aliphatic sulfides in a ratio of about 3:2:1 (A2).

Both sulfur content and distribution of sulfur forms vary considerably with a coal seam's geographical location. Coal from the western United States tends to be low in total sulfur (less than 1.0 wt-%), with organic sulfur the predominant form. In contrast, Appalachian coals are higher in total sulfur (1.0 to 4.0 wt-%), containing 0.5 to 1.5 wt-% organic sulfur and 0 to 3.0 wt-% pyritic sulfur (M1). Figure 1-1 shows the distribution of sulfur forms found in a survey by Hamersma (H2), and Table 1-1 gives the United States coal reserves by total sulfur content and geographical location estimated by the Electric Power Research Institute (EPRI). Approximately 40% of western coal and 10% of eastern coal could meet the current EPA SO_2 emission standards for existing coal-fired power plants. Total removal of pyrite would allow an additional 30% of eastern coal to meet these standards (E1).

C. Coal Desulfurization Processes

The need to further utilize coal as an energy resource has resulted in the development of a number of methods for reducing the SO_x emissions associated with coal combustion.

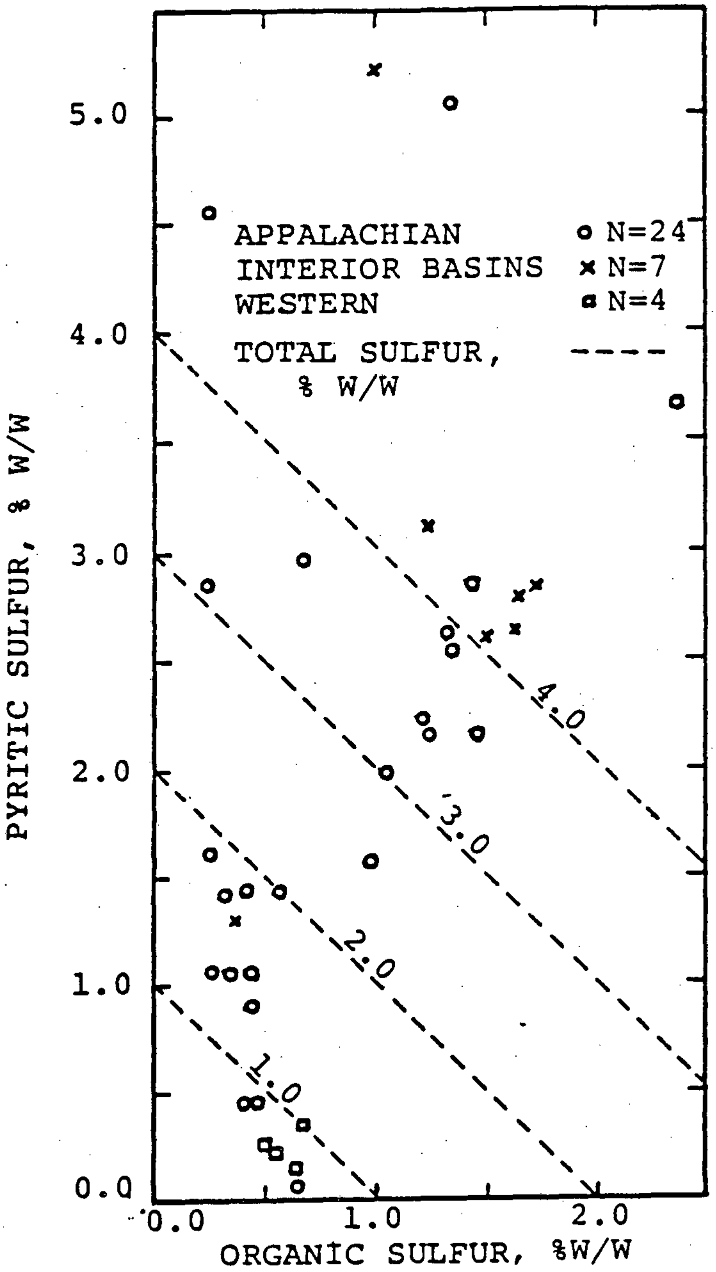

Figure 1-1. Distribution of sulfur forms (dry moisture free basis) in run-of-mine U.S. coals.

Table 1-1. U.S. coal reserve, million net tons[1]

% Sulfur	1.0	1.1-3.0	3.0
East	32,856	55,647	86,553
West	167,325	37,351	6,118
Total	200,181	92,998	92,671

[1] estimated by EPRI

They include removal of sulfur prior to, during, and after combustion. An EPA timetable for the commercial availability of these technologies is given in Table 1-2.

1. Flue-Gas Desulfurization

Post combustion or flue-gas desulfurization (FGD) involves removal of SO_x from stack gases in devices known as scrubbers. In the scrubber, the SO_x-laden flue gas is brought into contact with a liquid which will selectively react with SO_x. Commonly used chemical absorbents include lime, limestone, magnesium oxide, double alkali, sodium carbonate, alkali flyash, and ammonia. In throw-away processes, the absorbent and SO_x react to form a product of little or no market value. Regenerative processes recover the absorbent in a separate unit for reuse in the scrubber, and generally produce a product with some market value such as sulfuric acid or elemental sulfur. Lime-limestone scrubbing, a throw-away process, is presently the dominant technology for flue-gas desulfurization in the United States.

FGD systems are quite expensive requiring considerable amounts of raw materials, energy, water, and manpower. One estimate indicates that a new powerplant's installation of FGD may add 14 percent to investment cost and 18 percent to annualized operating cost if the alternative is no attempt at control of SO_2 emissions (01). Moreover, retrofitting to existing facilities would incur even higher costs. These considerations, combined with the need to control SO_x

Table 1-2. 1976 U.S. EPA survey of coal desulfurization alternatives for the period 1977-1987[1]

Desulfurization Method	Date of Commercial Availability	Potential for Application by 1985, % of Total Power Plant Fuel	Average Total Cost of Power Mills/kwh
Convential Coal-fired Boiler	--	--	31.5
Low-sulfur Coal	Current	less than 50	39.6
Physical Coal Cleaning	Current	less than 14	33.0
Chemical Coal Cleaning	1980	30	36.0
Flue Gas Desulfurization			
Limestone	Current	85	34.7
Lime	Current	85	34.8
Magnesium Oxide	Current	85	34.1
Sodium Sulfite	Current	85	35.5
Aqueous Carbonate	1981	--	34.3
Double Alkali	1981	--	34.3
Citrate	1981	--	34.3
Coal Gasification	1980-85	less than 10	38.7
Coal Liquification	1980-85	0	--
Fluidized Bed Combustion			
Atmospheric	1984-86	0	30.0
Pressurized	mid-1980's	0	35.5

emissions from smaller, non-utility coal combustion processes, have stimulated interest in alternatives to FGD.

2. Fluidized Bed Combustion

One alternative process, fluidized bed combustion, involves immediate removal of SO_x in the furnace. The coal is burned in fluidized bed containing limestone or dolomite which selectively reacts with SO_2 to form a solid or sludge, similar to FGD. Fluidized bed combustion offers some advantages over FGD which can result in lower operating and capital costs. Nevertheless, there is still the need to dispose of large amounts of waste material, effectively shifting the SO_2 problem to a solid-waste problem.

3. Precombustion Desulfurization

Precombustion desulfurization of coal can be divided into three categories: (1) physical separation, (2) conversion of coal to low-sulfur liquid and gaseous fuels (hydrodesulfurization), and (3) chemical desulfurization.

a. Physical Methods

Physical cleaning methods are used to remove pyrite and other ash particles from the organic matter in coal. One of the simplest techniques, gravity separation, makes use of the difference in density of the organic fraction (1.2-1.6 g/cm^3) and the ash fraction (5.0 gm/cm^3), while froth flotation and oil agglomeration take advantage of the hydrophilic nature of pyrite. Other methods include stage crushing and magnetic separation. All of the processes are capable of achieving 70 to 80% pyrite removal, but generally result in sizeable losses of organic matter. Furthermore, physical cleaning methods are totally ineffective in removing organic sulfur, and so have limited applicability.

b. Coal Conversion

Hydrodesulfurization processes can remove both organic and inorganic sulfur as H_2S by hydrogenation of the coal in a solvent at high temperatures and pressures. Hydroprocessing is fairly effective but costly in terms of equipment and hydrogen consumption. Consequently, hydroprocessing is generally reserved for coal liquefaction processes and not as a means of simply providing a sulfur-free boiler fuel.

c. Chemical Methods

Chemical desulfurization processes offer a promising possibility of selectively removing sulfur with low operating costs. Table 1-3 compares five of the most highly developed and well documented processes. All claim more than 90% removal of pyrite and four of the five claim some removal of organic sulfur.

In the KVB process (D2), coal is heated in a fluidized bed reactor in the presence of NO-NO_2-air mixtures. Sulfur is oxidized to SO_2 and sulfates which are subsequently removed in an alkali wash.

Table 1-3

Comparison of Chemical Coal Cleaning Processes

Process	KVB	Battelle	JPL	TRW	PETC
Method	dry oxidation plus caustic leach	caustic leach	oxygen/water leach	acid leach	air/water leach
Reagent	O_2, N_2, NO H_2O, NaOH	NaOH, $Ca(OH)_2$, H_2O, CO_2	Cl_2, H_2O, organic solvent	$Fe_2(SO_4)_3$, H_2O, O_2, naptha	air, H_2O, lime
Pressure (psia)	15-300	350-2500	0-100	15-80	500-1500
Temperature (°C)	40-260	225-350	50-100	90-130	150-200
Retention (hr)	1	1/4-1/2	1/4-2	1/2-10	0-1
% Removal Pyrite	0-90+	0-90+	0-90+	0-90+	0-90+

PAGE 1 of 2

Table 1-3

Comparison of Chemical Coal Cleaning Processes

Process	KVB	Battelle	JPL	TRW	PETC
% Removal Organic Sulfur	0-40	0-70	0-70	0	0-40
Sulfur Product	gypsum	H_2S, elemental sulfur	sulfuric acid	iron sulfates, elemental sulfur	gypsum
% Btu yield	91	79	unavailable	98	94
Add-on Fuel Cost (dry basis), $/annual ton[1]	23	22	unavailable	19	19
clean coal (1976), $/MM Btu[1]	0.98	1.03	unavailable	0.82	0.84

[1] Ref. 02

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The Battelle process (S2) involves heating a slurry of coal in NaOH/Ca$(OH)_2$ solution to relatively high temperatures. The sulfur is converted to Na_2S, which is then reacted with CO_2 and water to form H_2S and Na_2CO_3. The Na_2CO_3 is treated with lime to recover NaOH, and the resulting $CaCO_3$ is converted back to lime by calcining.

The JPL chlorinolysis process (H2) employs a Cl_2/H_2O system to selectively oxide and remove both inorganic and organic sulfur from coal as water-soluble sulfates. It suffers from the disadvantage that large amounts of chlorine are incorporated into the coal and can only be removed by steam stripping at 350°-550°C, and then only incompletely.

The TRW Meyers process (M1) uses a regenerable aqueous ferric sulfate solution to oxide pyritic sulfur to elemental sulfur and sulfates at low temperatures and pressures. The production of elemental sulfur poses a serious drawback since it must be removed in an additional processing step.

The PETC/DOE process (F1) operates at elevated temperature and pressure to convert both inorganic and organic sulfur to sulfuric acid. Although organic sulfur removal up to 40% has been reported, oxidation of the hydrocarbon matrix results in heating value losses of the same magnitude (S3). Furthermore, this process is expected to encounter severe corrosion problems caused by the use of dilute sulfuric acid at high temperature (O2). A similar process developed at the Ledgemont Laboratories (A3) employs oxygen rather than air; oxygen dissolved in basic media has also been investigate by Wheelock and co-workers (T2).

D. Chemistry of Pyrite Oxidation

FeS_2 may be oxidized either by dissolved oxygen or ferric ion. Depending on the conditions, the reaction products will include varying proportions of ferrous sulfate, ferric sulfate, sulfuric acid, and elemental sulfur.

The oxidation of pyrite by ferric sulfate may be represented by the following reactions:

$$FeS_2 + Fe_2(SO_4)_3 \longrightarrow 3FeSO_4 + 2S \qquad (1a)$$

$$FeS_2 + 4Fe_2(SO_4)_3 + 4H_2O \longrightarrow 9FeSO_4 + 4H_2SO_4 + S \qquad (1b)$$

$$FeS_2 + 7Fe_2(SO_4)_3 + 8H_2O \longrightarrow 15FeSO_4 + 8H_2SO_4 \qquad (1c)$$

Similarly the partial oxidation of pyrite by oxygen may result in the formation of elemental sulfur:

$$FeS_2 + 2O_2 \longrightarrow FeSO_4 + S \qquad (1d)$$

If the oxidation proceeds further, ferrous or ferric sulfate and sulfuric acid are produced:

$$2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4 \qquad (1e)$$

$$4FeSO_4 + O_2 + 2H_2SO_4 \longrightarrow 2Fe_2(SO_4)_3 + 2H_2O \qquad (1f)$$

In neutral or basic solutions pyrite may react with oxygen to form ferric oxide:

$$4FeS_2 + 15O_2 + 8H_2O \longrightarrow 2Fe_2O_3 + 8H_2SO_4 \qquad (1g)$$

Once formed, elemental sulfur may be further oxidized either by oxygen or, conceivably, by ferric sulfate:

$$2S + 3O_2 + 2H_2O \longrightarrow 2H_2SO_4 \qquad (1h)$$

$$S + 3Fe_2(SO_4)_3 + 4H_2O \longrightarrow 6FeSO_4 + 4H_2SO_4 \qquad (1i)$$

In an alternate mechanism pyritic sulfur may undergo acid-induced disproportionation to yield ferrous sulfate, elemental sulfur, and hydrogen sulfide:

$$FeS_2 + H_2SO_4 \longrightarrow FeSO_4 + H_2S + S \qquad (1j)$$

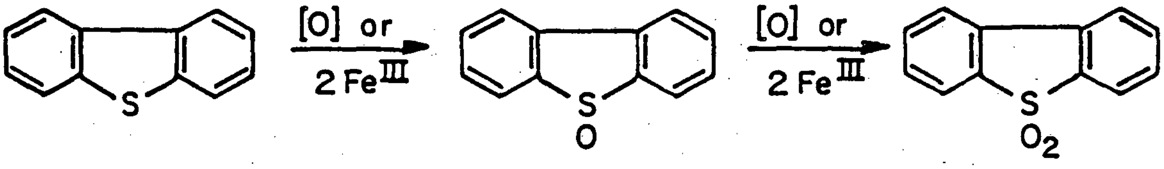
The hydrogen sulfide can then be oxidized by oxygen:

$$2H_2S + O_2 \longrightarrow 2H_2O + S \qquad (1k)$$

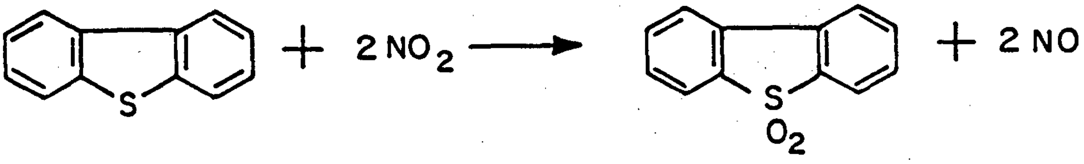
$$H_2S + 2O_2 \longrightarrow H_2SO_4 \qquad (1l)$$

E. <u>Chemistry of Organic Sulfur Oxidation</u>

Oxidation of organic sulfides in coal may convert them to sulfones, sulfoxides, or sulfonic acids. The oxidation of dibenzothiophene (DBT) by oxygen or ferric ion would successively form DBT sulfoxide and DBT sulfone:



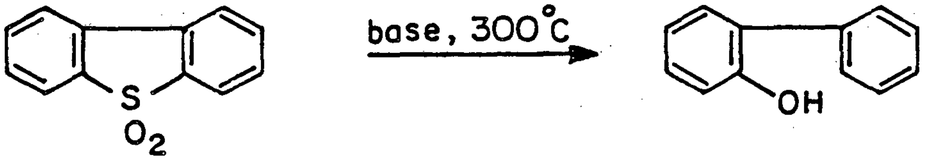
Similarly, NO_2 many be used as an oxidizing agent followed by regeneration:



(1n)

$2NO + O_2 \longrightarrow 2NO_2$ (1o)

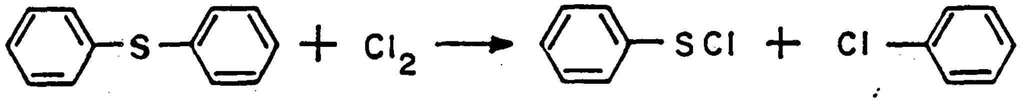
A previous study (F1) on the NO_2 oxidation of dibenzothiophene showed it to be an effective reagent for converting DBT to DBT sulfone. When extended to coal, however, a significant loss of nitrogen oxides was observed, presumably due to nitration of the coal. Hence, the process is not regenerable, requiring continuous addition of NO_2 and only reducing SO_x emissions at the expense of increased NO_x emissions. Elimination of SO_2 from sulfone by hydrolysis replaces the sulfur moiety with oxygen as an alcohol group:



$+ SO_3^{=}$ (1p)

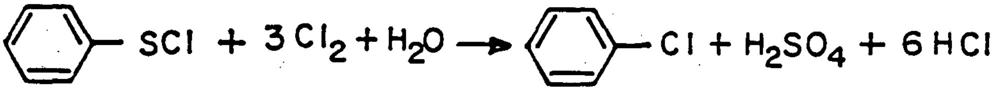
Clary (C2) has investigated the oxidation of a number of sulfur-containing molecules with both oxygen and ferric sulfate. He observed that both diphenyl and di-n-butyl sulfide were susceptible to oxidative attack at 150°C. Nevertheless, heterocyclic sulfur, the major form of sulfur in coal, was found to be totally resistant to oxidation under his conditions, suggesting the limited applicability of this approach. Moreover, the carbon in coal is rapidly converted to CO, CO_2, and humic acids when subjected to an oxidizing environment above 150°C. Subsequent treatment by caustic leach will extract a large percentage of the organic matter, greatly diminishing the heating value of the remaining coal.

Chlorine may also be used to oxidize the organic sulfur in coal. Although it has never been proven effective in removing thiophenic sulfur, it is highly reactive toward sulfides and disulfides. Desulfurization of diphenyl sulfide would begin with cleavage of the carbon-sulfur bond:



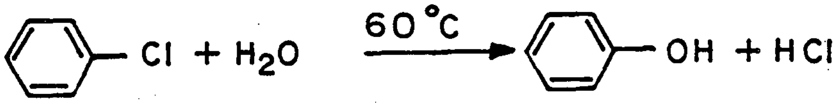
(1q)

Sulfenyl chloride is then oxidized to sulfate:



(1r)

The chlorinated coal is hydrolyzed to produce hydrochloric acid:



(1s)

After hydrolysis the coal is dechlorinated by heating in steam to 350° - 555°C in an attempt to remove the remaining chlorine. Work by Pichan (P2) has shown that chlorination at progressively higher temperatures yields a product that is increasingly difficult to dechlorinate. Indeed, this may be another process which merely replaces the SO_2 emissions problem with another - namely, an HCl emissions problem.

F. Statement of Purpose

The oxidation of pyrite necessarily results in the formation of iron sulfates. Consequently, it is of interest to identify separately the oxidizing function of oxygen and of ferric ion. Previous kinetic studies on pyrite oxidation have been conducted either in iron-salt solutions in the absence of oxygen (K1, M1), or in aqueous solutions using dissolved oxygen with no iron sulfates initially present (W1, M3). In addition, many kinetic studies on coal desulfurization have been performed exclusively with coal; so the intrinsic kinetics of pyrite oxidation have yet to be thoroughly elucidated. An extensive set of experiments utilizing both coal and coal-derived pyrite has been conducted in an acidic iron sulfate medium with the objective of characterizing the role of several key variables with respect to reaction kinetics and product distribution. These variables included sulfuric acid and ferric sulfate concentrations, oxygen partial pressure, temperature, stirring speed, available surface area of bulk pyrite, and particle size for coal. The effect of these variables on loss of coal heating value was also investigated, since some oxidation of carbonaceous matter inevitably occurs.

Emphasis was placed on conditions that would minimize water consumption, facilitate the recovery of H_2SO_4 and either $Fe_2(SO_4)_3$ or Fe_2O_3 as saleable products, and avoid the purchase of any chemicals except oxygen, which could be made on-site. To guide the selection of these conditions, Figure 1-2 was developed to correlate $Fe_2(SO_4)_3$ solubility (in a weight ratio to total H_2SO_4 plus H_2O) as a function of H_2SO_4 content (also as a weight fraction in total H_2SO_4 plus H_2O).

An additional goal was to eliminate the formation of elemental sulfur, which if present must be removed in an additional processing step using either vaporization or solvent extraction. Attainment of this goal was aided by a UV-spectrophotometric method for analyzing elemental sulfur and applicable to both treated and untreated coal (M2).

Under existing EPA regulations, desulfurization processes which remove pyrite alone are of limited applicability. Efficient removal of some or all of the organic sulfur would further extend the viability of chemical desulfurization. Organic sulfur, however, presents a very difficult problem. It is uniformly distributed throughout the coal matrix, and organic sulfur compounds cannot be isolated without changing the organostructure (B3). Consequently, sizable losses in organic matter or heating value or both normally accompany organic sulfur removal. In this study, a number of techniques aimed at organic sulfur removal have been evaluated: oxidation followed by alkali extraction; low-temperature chlorinolysis; NO_2 oxidation; liquid SO_2 extraction; ClO_2 oxidation; and high-temperature oxidation in the $O_2/Fe_2(SO_4)_3/H_2SO_4$ system.

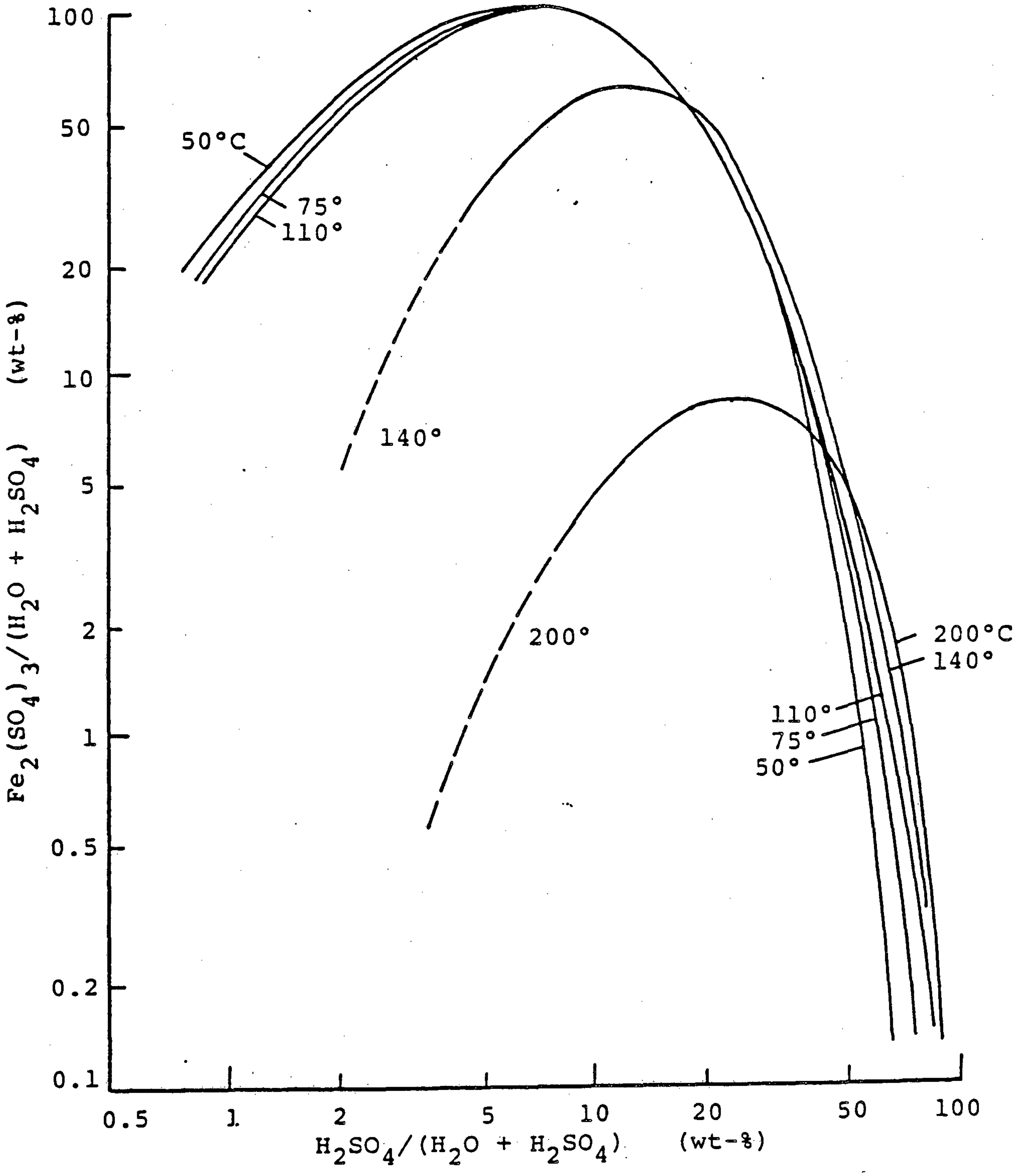


Figure 1-2. Solubility of $Fe_2(SO_4)_3$ in aqueous sulfuric acid (after Posnjak and Merwin, reference P3).

II. EXPERIMENTAL APPARATUS AND PROCEDURE

A. Materials

1. Coal

An Illinois No. 6 bituminous coal was chosen for this investigation. Samples were prepared under conditions that would avoid undue atmospheric oxidation. Large chunks of coal were selected from their original container, and twice passed through a jaw crusher. Subsequent reduction in particle size was accomplished under nitrogen in an airtight glove box. The desired fraction was obtained by alternately sieving the coal and crushing it in a ceramic jar mill, repeating this sequence for very short intervals to prevent excess production of fines. After this size reduction the coal was thoroughly mixed by repeated pouring through a riffler into a one-gallon container and stirring. Still in the glove box under nitrogen, it was then carefully spooned into 32-ounce glass jars fitted with screw caps. The jar tops were sealed with Parafilm and removed from the glove box. The jars were purged with nitrogen and resealed after opening. The relevant properties of the starting coal are given in Table 2-1.

2. Pyrite

The material used in this study was a coal-derived pyrite with the following elemental analysis:

Table 2-1. Analysis of starting coal

Sample	1	2	3
Coal Type	Illinois No. 6	Illinois No. 6	Illinois No.6
Mesh Size; Tyler Screen No.	-20+30	-100+150	-100+150
MF wt-%			
Carbon	65.04	64.82	64.77
Hydrogen	4.56	4.67	4.24
Nitrogen	1.21	1.20	1.18
Sulfur	3.76	3.84	4.19
Oxygen	12.27	11.09	9.19
Ash	13.16	14.38	16.11
Heating Value; Btu/lb, MF	11,565	11,678	11,537
MAF wt-%			
Total Sulfur	4.33	4.49	4.99
Pyritic Sulfur	1.18	1.07	1.39
Sulfate Sulfur	0.44	0.78	--
Elemental Sulfur	0.09	0.09	0.10
Organic Sulfur	2.62	2.55	--
Chlorine	--	0.40	0.41

Fe - 43.2 wt-%, S - 51.0 wt-%, C -3.2 wt-%,
H - 0.2 wt-%, N - 0.08 wt-%

The S to Fe mole ratio of 2.06 is very close to the theoretical value for FeS_2. All experiments were performed with a -60 + 80 mesh fraction of this material. The surface area, determined by the method of Brown (B2), was approximately 140 cm^2/gm.

3. Chemicals

The suppliers and grades of purchased chemicals used in this study are listed in Table 2-2. Water was supplied by an on-site distillation system serving several laboratories.

B. Apparatus

1 Atmospheric-Pressure Experiments

The reactor for runs performed under atmospheric pressure consisted of a 500 ml four-neck round bottom flask, fitted with a variable-speed stirrer, reflux condenser with gas vent, thermometer, and gas sparger. The sparger was made of 1/8" diameter T304 stainless steel tubing; it was closed at the outer end and curved underneath the stirrer for good gas dispersion, with five 0.010" diameter holes located directly below the stirrer. A schematic drawing of the reactor assembly is shown in Figure 2-1.

Table 2-2. Sources and purities of chemicals used

Material	Source	Grade	Minimum Purity
Ammonium Chloride	Mallinckrodt	Reagent	99.9
Barium Chloride	Mallinckrodt	Reagent	99.8
Chlorine	Matheson	High Purity	99.5
Cu^o, Copper Shim Stock	--	--	99.0
Cyclohexane	Aldrich	Spectro-photometric	99.0
Eschka's Mixture	J. T. Baker	Reagent	--
Ferric Sulfate	Mallinckrodt	Reagent	99.9
Ferrous Sulfate	Matheson Coleman & Bell	Reagent	99.8
Hydrochloric Acid (37%)	Mallinckrodt	Reagent	99.9
Mercuric Chloride	Allied Chemical	Reagent	99.0
Nitric Acid (70%)	Mallinckrodt	Reagent	99.9
Nitrogen	LBL Supply	--	99.5
Nitrogen Dioxide	LBL Supply	--	99.5
Oxygen	LBL Supply	--	99.5
Phosphoric Acid (85%)	Mallinckrodt	Reagent	--
Potassium Chromate	Mallinckrodt	Reagent	99.9
S^o, Flowers of Sulfur	Mallinckrodt	USP	99.5
Silver Nitrate	Mallinckrodt	Reagent	99.9
Sodium Carbonate	Fisher	ACS Certified	99.5

Table 2-2. Sources and purities of chemicals used

Material	Source	Grade	Minimum Purity
Sodium Chlorate	Mallinckrodt	Reagent	98.0
Sodium Chlorite	Mallinckrodt	Reagent	99.5
Sodium Hydroxide	Mallinckrodt	Reagent	98.0
Stannous Chloride	Mallinckrodt	Reagent	99.9
Sulfur Dioxide	LBL	High Purity	99.9
Sulfuric Acid (96.9%)	Mallinckrodt	Reagent	99.9

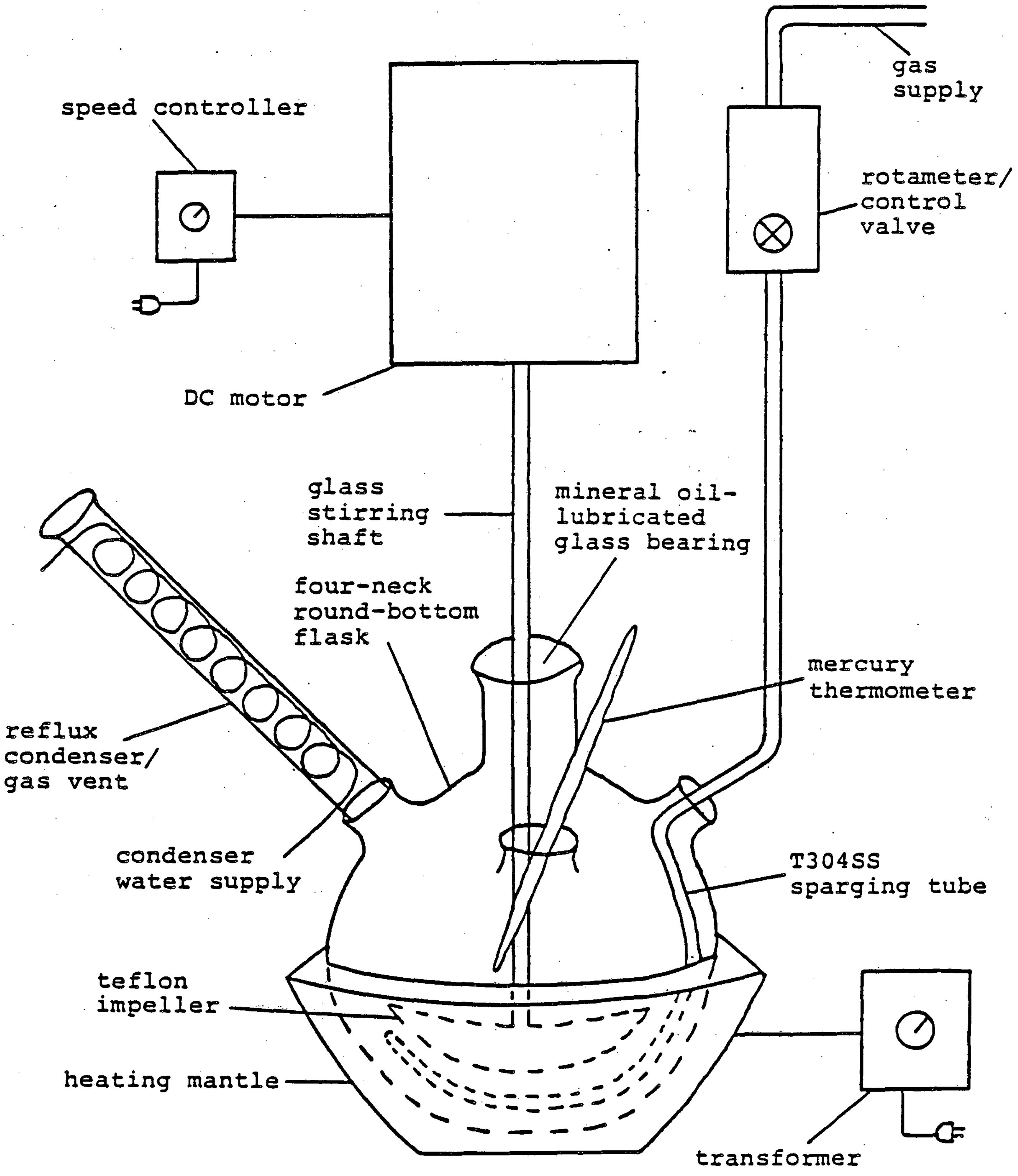


Figure 2-1. Atmospheric-pressure reaction apparatus.

2. High-pressure Experiments

High-pressure reactions were conducted in a 600 ml Parr autoclave constructed of 316 stainless steel and fitted with a Pyrex glass liner (Figure 2-2). The reactor was equipped with a gold-faced inconel rupture disc rated for 1000 psi, a 1000 psig pressure gauge, a needle valve for controlling pressurization, three auxiliary outlet needle valves, a stirrer, a thermocouple (iron-constantan) with 304 stainless steel sheath, and an internal cooling loop. The stirrer was driven by a variable-speed DC motor with speed controller; stirrer rpm was measured with a mechanical tachometer. The pressure gauge was calibrated by setting the autoclave temperature, reading the reactor pressure with the autoclave filled with pure water, and correcting for the deviation from steam pressure due to air in the system. The thermocouple was calibrated against a mercury-filled thermometer from 50° to 200°C, using a heated mineral oil bath. Heat was supplied to the reactor through a 1750-watt quartz-fabric mantle surrounding the vessel body, and cooling water was supplied to the cooling loop through a solenoid valve. Temperature was controlled to within ±3°C of the set-point using a thermocouple-activated proportional controller which regulated both cooling water flow and heat input.

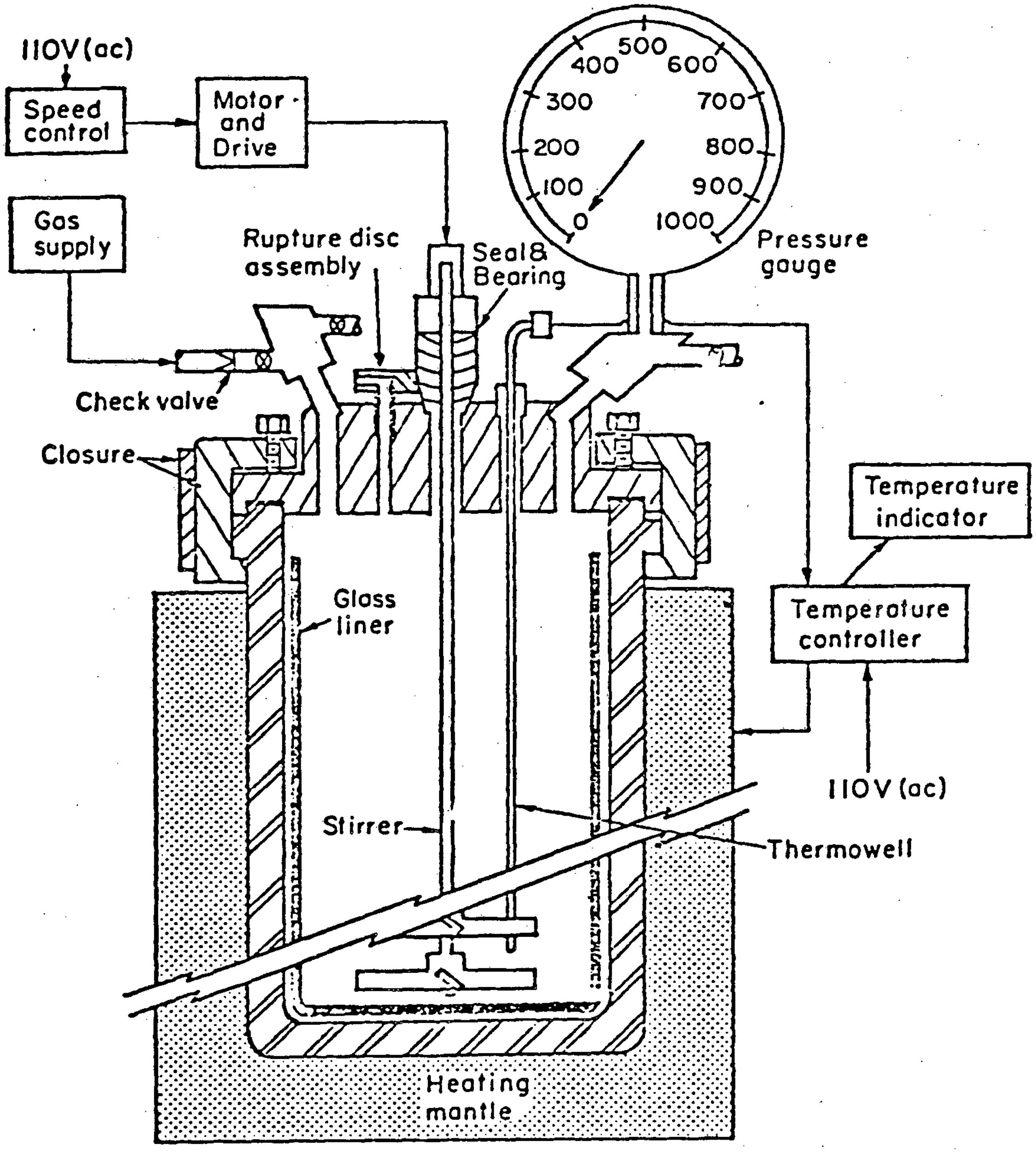


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Figure 2-2. Parr autoclave.

C. Procedure

1. High-Pressure Oxidation

Before each run, the reactor was preheated with boiling water to hasten attainment of the set-point temperature. Gas was then introduced and the total pressure was maintained relatively constant during a run by either adding or venting gas at 5 minute intervals. At the end of a run, the temperature was reduced by a constant internal flow of cooling water and by immersing the reactor body in water. The solids were recovered by vacuum filtration of the slurry through a fine-pore fritted-glass filter; the filtrate being analyzed immediately. The solid product was washed at room temperature with 100 ml 5% sulfuric acid and 200 ml distilled water, transferred to a glass Petri dish, and dried for at least 12 hours at ambient temperature in a vacuum desiccator. Afterwards the dried solids were weighed, and ground to -60 mesh with mortar and pestle for subsequent analysis.

Visually it was observed that 20 grams coal to 110 ml leaching solution gave good contact between gas, solid, and liquid at all stirring speeds used. In runs with pyrite, 100 ml leaching solution was added to 1.05 gm solid (1.00 gm FeS_2).

2. Liquid SO_2 Extraction

Twenty grams of coal were dried under vacuum at 100°C over night to assure that the extraction remained nonaqueous. The dried coal was placed in a 200 mesh stainless steel basket attached to the reactor stirring shaft. SO_2 was condensed by flowing it through 1/4" O.D. stainless steel tubing immersed in a dry ice/acetone bath; 150 ml liquid SO_2 was used in each extraction. The reactor was heated to 150°C with the stirrer and basket assembly slowly rotating. After 1 hour at 150°C, the hot reactor was inverted to drain the coal of SO_2. The pressure was then released so as to flash off the SO_2. The coal was recovered, washed with hot distilled water, and dried before analysis.

3. Cl_2 Treatment

Treatment of 20 grams coal with Cl_2 gas was conducted in an aqueous solution at 75°C. Chlorine was sparged into the reactor at a flow of 0.2 l/min, with vigorous stirring. After 1 hour, the solids were filtered off, washed with distilled water, and transferred with another 110 ml distilled water back to the atmospheric pressure reactor for hydrolysis. This reaction was carried out for 1 hour at 98°C with intermittent additions of NaOH to maintain neutral pH. The final product was collected, washed with distilled water, and prepared for analysis as usual.

4. ClO_2 Treatment

A 1.5M ClO_2 solution was prepared by reaction of 1.60

gm sodium chlorate ($NaClO_3$) with 1.36 gm sodium chlorate ($NaClO_2$) in 3.0M HCl. Twenty milliliters was added dropwise to a slurry containing 20 gm coal and 200 ml 15% H_2SO_4 at 80°C. The reaction was allowed to proceed for 1 hour at atmospheric pressure. At the end of the run the solid product was recovered, washed with distilled water, and prepared for analysis as previously described.

D. Analyses

1. Sulfur Analyses

Sulfur analyses are reported on a moisture- and ash-free (MAF) basis to avoid ambiguities due to variable moisture and ash content in treated coals. Analyses for pyritic, sulfate, and total sulfur, and moisture and ash were performed adhering closely to standard ASTM procedures. Duplicate analyses were regularly used as an internal check, and in all cases ASTM criteria for analytical repeatability were met. Measurement of elemental sulfur was accomplished as described below. Organic sulfur was determined by difference.

Pyritic and sulfate sulfur analyses were performed according to ANSI/ASTM method D2492-77. 500 ml Erlenmeyer flasks (instead of 250 ml) were used in the extractions. Extraction of pyritic sulfur was carried out on the residue from the HCl extraction of sulfate sulfur. As specified in this method, pyritic iron was determined by atomic absorption spectroscopy. Method A, the Eschka method, of ASTM D3177-75 was used to determine total sulfur.

No convenient method presently exists for directly measuring organic sulfur. ANSI/ASTM method D2492-77 prescribes that the sum of pyritic and sulfate sulfur be subtracted from the total sulfur to yield the value for organic sulfur. In this work elemental sulfur was also subtracted from total sulfur.

A technique for direct determination of elemental sulfur content has recently been developed in our laboratory. A detailed description of this technique is presented elsewhere (M2). Briefly, the analytical procedure is as follows:

Coal is prepared by grinding to pass a 60-mesh sieve. A sample of roughly 2 grams is weighed by difference into a cellulose extraction thimble (25 x 100 mm, single thickness). The thimble with coal is placed in an oven set at 103°C and purged with dry nitrogen, this temperature being maintained for 1-1/2 to 2 hours. To extract elemental sulfur, the thimble is inserted into a 100 ml Soxhlet extraction apparatus, set up as shown in Figure 2-3, with spectroquality cyclohexane as the solvent. Heating tape is wrapped around the Soxhlet extractor to keep the solvent close to its boiling point as it contacts the coal, and to help prevent condensation of vapor traveling up the side-arm.

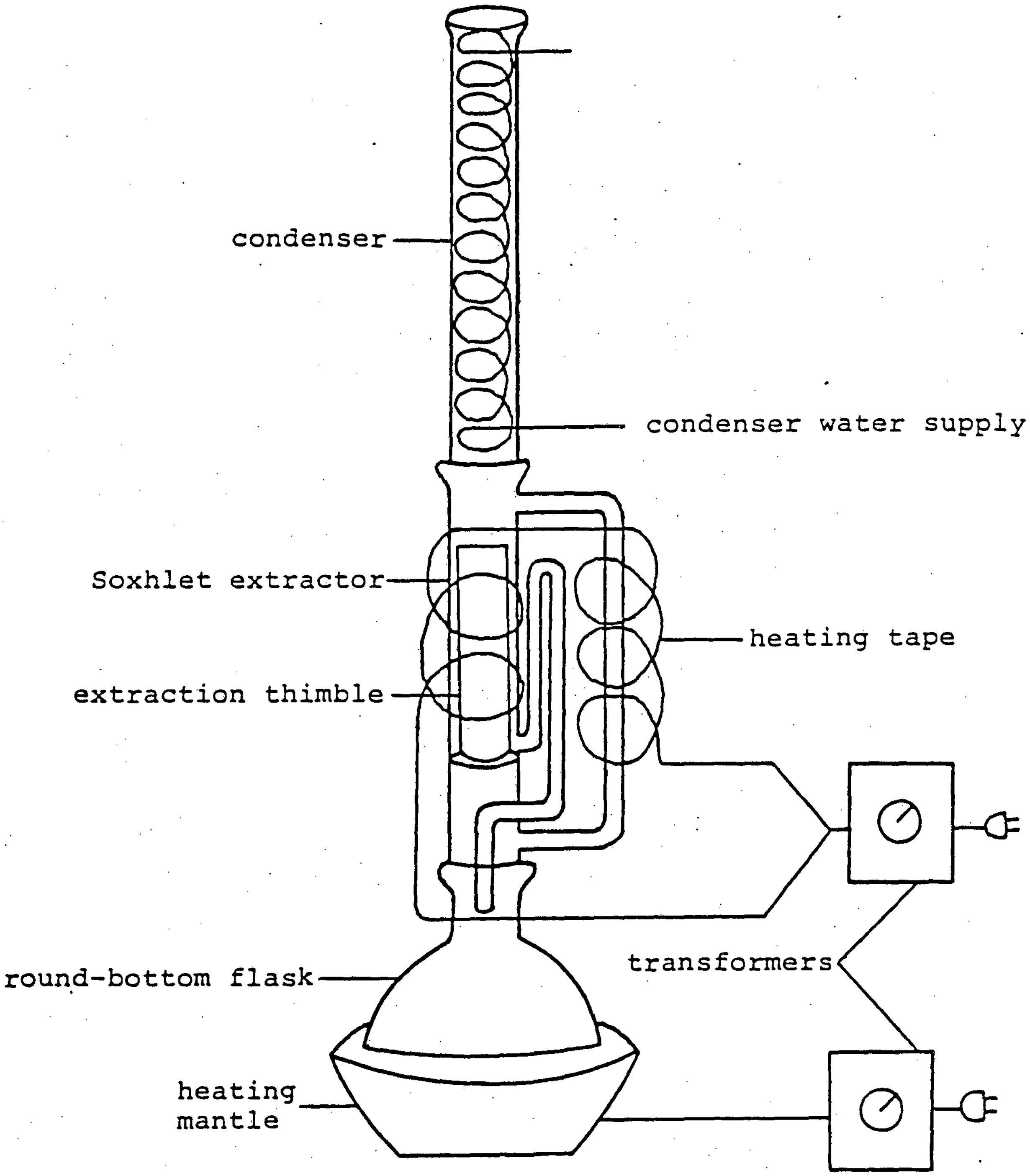

Figure 2-3. Elemental sulfur extraction apparatus.

Initially 85 ml of solvent, in a 100-ml round-bottom flask fitted to the Soxhlet extractor, is brought just to boiling. After 24 hours of extraction, extract is allowed to rise almost to the top level of the siphon tube, and then the heating mantle is removed before it can siphon back into the 100-ml flask. The flask is immediately cooled in a beaker of water, and the contents are quantitatively transferred into a 50-ml volumetric flask, with sufficient washing by cyclohexane to bring the volume to a little less than 50 ml. The 100-ml round-bottom flask is then refilled with fresh cyclohexane to the previous level, and the Soxhlet is set running again. After the next 24 hours of extraction, the second extract is processed in the same manner. After they are cooled to room temperature, each of the two extracts is made up to exactly 50 ml volume with fresh cyclohexane.

To measure the elemental sulfur content, comparative sulfur-free samples must be prepared from a part of each extract. First two 25-ml volumetric flasks are each loaded with 1.0 mg (±0.3 mg) of pure crystalline sulfur (this may be prepared by heating flowers of sulfur at 103°C for 1 to 2 hours). Then they are separately filled to the mark with 25 ml of the 24- and 48-hour extracts. After dissolution of the sulfur and mixing are complete, these 25-ml samples are treated with copper metal to remove the elemental sulfur quantitatively.

An 0.2-mm thick pure copper sheet, along with graduated cylinders equipped with ground-glass stoppers, is required for this procedure. Strips of copper about 12 x 160-mm are cut out with heavy-duty scissors. A cleaning solution of 50% water and 50% concentrated nitric acid (70%) is used to remove oxide film from the copper surface; each strip is dipped into a test tube filled with cleaning solution for a few seconds, and rinsed first with distilled water and then with acetone. After three successive cleanings, the completely dry strip is slit in two with scissors and inserted into a 5-ml graduated cylinder. Then 4 ml of the sulfur-enriched extract, is pipetted into the cylinder, and the tightly closed cylinder is shaken by hand for 5 minutes. The samples treated in this way are considered sulfur-free, because any further treatment with copper does not change their UV spectrum. Both the 24- and 48-hour extracts are treated in this way, leaving four samples for UV analysis.

On the UV spectrophotometer, the band width is set to 1.0 nm and wavelength is set to 280.0 nm (in principle, readings at two different wavelengths should be taken but such a modification was not made until after this work was completed). Absorbance is then read for both raw and sulfur-free extracts, using UV-transparent quartz cuvettes with 1.0 cm light-path length, and pure cyclohexane as a blank.

If the absorbance of the 24-hour raw extract is greater than 2.0, both it and the 48-hour extract should be diluted by the same amount to reduce the absorbance to a level between 1.5 and 2.0. An identical dilution should then be carried out with the copper-treated extracts. If dilution is carried out, the calculations outlined below should be modified appropriately.

The calculation of elemental sulfur content in the coal is based on Beer's law, $A = \epsilon cb$, where A is the absorbance, ϵ is the extinction coefficient, c is the concentration of light-absorbing species, and b is the light-path length. The quantity of elemental sulfur in solution can be found from the equation,

$$S^{o}(\text{mg}) = (A/\epsilon\ b) \times (\text{ml of solution}),$$

if ϵ is in units of (ml/mg x cm), and b is in units of cm.

The equation for obtaining weight-based parts per million of elemental sulfur in coal follows:

$$\left\{(A_1-A_1^*)/[1-(A_2-A_2^*)/(A_1-A_1^*)]\right\}\cdot V\cdot 10^3 \div [(\epsilon\, b)\cdot W_g],$$

where A_1 = absorbance of 24-hour raw extract

A_1^* = absorbance of copper-treated 24-hour extract

A_2 = absorbance of 48-hour extract

A_2^* = absorbance of copper-treated, sulfur-free 48-hour extract

V = volume of total extract

ϵ = 25.38 (ml/mg · cm), for S^0 in cyclohexane, at a bandwidth of 1.0 nm and wavelength of 280.0 nm

b = 1.0 cm

W_g = weight of coal extracted

This equation is based on the observation that the extraction rate is first order in elemental sulfur content.

2. Moisture Analysis

A 1-gm sample of minus 60 mesh coal was weighed by difference into a pre-dried porcelain capsule, 22 mm in depth and 44 mm in diameter. The capsule was heated in a vacuum oven, with slow purge of dry nitrogen, for a period of one hour, at a temperature in the 104° - 110°C range. The capsule was then cooled in a vacuum desiccator for 1/2 hour and weighed. Percent moisture in the sample was calculated as 100(A-B)/A, where A = grams of moist coal used, and B = grams of dried coal.

3. Ash Analysis

Ash analysis was performed in accordance with the procedure described in ASTM method D3174-73, Note 2, Paragraph a. All values were corrected for the oxidation reaction which occurs during the ashing procedure:

$$2FeS_2 + 11/2\ O_2 \longrightarrow Fe_2O_3 + 4SO_2$$

Corrected ash content was obtained from either of the following equations:

$$(Ash)a = (Ash)w + 5/8 \cdot Sp$$

$$(Ash)b = (Ash)w - 3/8 \cdot SP$$

(Ash)w = weight of ash obtained from ASTM procedure

Sp = weight of pyritic sulfur in coal sample

(Ash)a provides a value that includes pyritic sulfur, for use in calculating and reporting other analytical results on an MAF basis, i.e. relative only to the weight of organic matter in the coal. (Ash)b provides for the iron contained in the pyritic sulfur applicable when sulfur is reported as a separate constituent.

4. Elemental Analysis

Elemental analysis was determined by the College of Chemistry Microanalytical Laboratory. The samples were submitted in sealed 1-gram vials placed inside a bottle containing desiccant. The carbon, nitrogen, and hydrogen tests were performed using a Perkin-Elmer Model 240 CHN Analyzer. Metal analyses were performed by atomic absorption in a

Perkin-Elmer Model 360 Atomic Absorption Spectrophotometer. Oxygen could not be determined directly, and is calculated by difference.

5. Heating Value

The heating values for both treated and untreated coal were estimated from the correlation of Mott and Spooner (M4) and the coal's ultimate analysis. The formula for coals containing less than 11% oxygen is:

$$CV = 144.5X_c + 610X_h - 62.5X_o + 40.5X_s,$$

and for coals containing more than 11% oxygen:

$$CV = 144.5X_c + 610X_h - (65.9 - 0.31X_o)X_o + 40.5X_s.$$

Here X_c, X_h, X_o, and X_s are respectively, the moisture-free weight percentages of carbon, hydrogen, oxygen, and sulfur; CV is the calorific value in Btu/lb, on a moisture-free basis.

6. Analysis of Ferrous and Ferric Iron in Solution

The ferrous and ferric iron concentrations in the reaction medium were measured at the end of each run. Vacuum-filtered leachate was sampled immediately after reaction and quickly cooled. Two equal aliquots (ranging in volume from 0.1 to 1.0 ml, depending upon initial concentration of iron in the leaching solution) were then quantitatively transferred to 500 ml Erlenmeyer flasks, and diluted with 25 ml of 15% HCl. Ferrous iron was measured by titration of one aliquot with 0.05N potassium dichromate, to an endpoint indicated with barium diphenylamine sulfonate. Total iron was measured in the other aliquot by first reducing all the iron with stannous chloride, and then titrating as above (the step-wise procedure of iron analysis is explicitly given in ASTM method D2492, Section 6.2.3.1). Ferric iron was calculated as the difference between total and ferrous iron.

7. Pyrite Analysis

FeS_2 concentration was determined in a manner similar to the ASTM method for pyritic sulfur analysis in coal. After each run with pyrite, the remaining solid was digested in 200 ml 2.1 M nitric acid by refluxing for 2 hours. The solution was then diluted to 250 ml and submitted to the Microanalytical Laboratory for iron analysis by atomic absorption spectroscopy. The amount of pyrite in grams was calculated from the expression:

$$FeS_2 = 4.30 \times 10^5 [Fe]$$

where [Fe] is the reported iron concentration in mg/cc.

III. RESULTS AND DISCUSSION

A. Kinetics of Pyrite Oxidation

A kinetic study of pyrite oxidation in acidic iron sulfate solutions was conducted at 120°C. The experimental data are presented in Table 3-1.

1. Effect of Stirring Speed

The rate of pyrite oxidation was observed to be independent of stirring speed between 400 and 750 rpm, indicating that the reaction rate was not controlled by the transport of oxidant to the pyrite particles. An intermediate setting of 600 rpm was therefore chosen for all subsequent kinetic studies.

2. Effect of Sulfuric Acid Concentration

Since sulfuric acid accumulates during the oxidation of pyrite, it is important to examine its possible effects on the reaction. Several experiments were performed in which the solutions contained initial H_2SO_4 concentrations ranging from 5% to 25%, expressed relative to (H_2O + H_2SO_4) content. No oxygen was present in the system. The initial $Fe_2(SO_4)_3$ concentration held constant at 12%, also expressed relative to (H_2O + H_2SO_4) content; under these conditions varying the H_2SO_4 concentration did not limit the solubility of $Fe_2(SO_4)_3$ at 120°C.

After all runs in which no oxygen was present, upon

Table 3-1. Oxidation of bulk pyrite (120°C)

Run No.	Stirring Speed, rpm	$\frac{H_2SO_4}{H_2O+H_2SO_4}$, wt-%	$\frac{Fe_2(SO_4)_3}{H_2O+H_2SO_4}$, wt-%	O_2 Partial Pressure, Psia	Time, minutes	% Conversion
1	400	25	12	280	30	27.1
2	600	25	12	280	30	27.0
3	750	25	12	280	30	27.0
4	600	5	12	0	60	9.2
5	600	15	12	0	60	9.3
6	600	25	12	0	60	9.3
7	600	25	12	0	15	4.4
8	600	25	12	0	30	6.1
9	600	25	12	0	90	13.1
10	600	25	12	0	120	15.4

PAGE 1 of 3

Table 3-1. Oxidation of bulk pyrite (120°C)

Run No.	Stirring Speed, rpm	$\frac{H_2SO_4}{H_2O+H_2SO_4}$, wt-%	$\frac{Fe_2(SO_4)_3}{H_2O+H_2SO_4}$, wt-%	O_2 Partial Pressure, Psia	Time, minutes	% Conversion
11	600	25	12	0	150	18.0
12	600	25	12	0	180	18.7
13	600	25	12	0	240	26.7
14	600	25	12	280	5	7.3
15	600	25	12	280	15	15.5
16	600	25	12	280	30	27.1
17	600	25	12	280	45	36.8
18	600	25	12	280	60	46.3
19	600	25	12	280	90	62.4
20	600	25	12	360	5	9.8

PAGE 2 of 3

Table 3-1. Oxidation of bulk pyrite (120°C)

Run No.	Stirring Speed, rpm	$\frac{H_2SO_4}{H_2O+H_2SO_4}$, wt-%	$\frac{Fe_2(SO_4)_3}{H_2O+H_2SO_4}$, wt-%	O_2 Partial Pressure, Psia	Time, minutes	% Conversion
21	600	25	12	360	15	19.1
22	600	25	12	360	30	31.6
23	600	25	12	420	5	11.3
24	600	25	12	420	15	21.9
25	600	25	12	420	30	38.0
26	600	0	0	280	15	8.63
27	600	0	0	280	30	15.7
28	600	0	0	280	45	24.6

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opening the reactor a faint H_2S odor was detected. At 120°C H_2S formed by reaction (1j) is apparently oxidized by oxygen but not by $Fe_2(SO_4)_3$.

In any case reaction (1j) must occur only to a small extent, since the fraction of pyrite reacted after 1 hour at 120°C was virtually constant at 0.093 regardless of acid concentration.

3. Effect of Pyrite Surface Area

Heterogeneous reactions involving a solid phase normally proceed at a rate directly proportional to the available surface area. The pyrite feed in all these studies was a particle-size fraction of -60 + 80 mesh; hence, the overall surface area estimated by the method of Brown (B2) was approximately 140 cm^2/gm.

In the absence of oxygen, pyrite disappears so slowly that the total surface area may be assumed constant, thus simplifying the kinetic analysis. When oxygen is present, however, reaction proceeds far enough to cause the pyrite surface area to change over the course of time.

With the assumption that the surface area varies with the 2/3 power of the weight, plotting the instantaneous reaction rate against the total available surface area, as in Figure 3-1, showed a straight line dependence of rate on surface area.

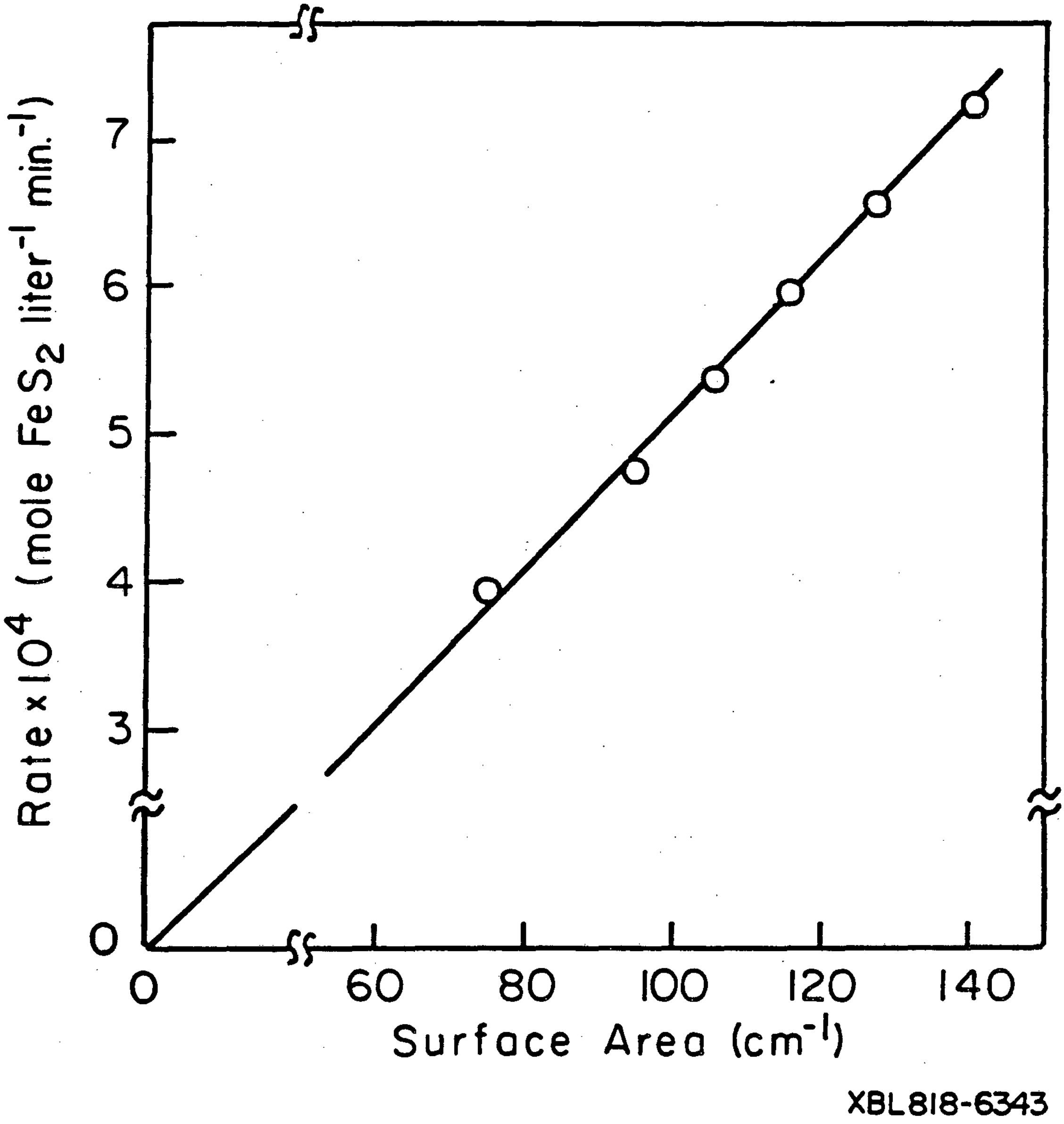

Figure 3-1. Effect of available surace area on rate of pyrite oxidation (12% $Fe_2(SO_4)_3$; 25% H_2SO_4; 280 psi O_2; 120°C).

4. Effect of $Fe_2(SO_4)_3$ Concentration

Consumption and production of $Fe_2(SO_4)_3$ are described by equations (1a-c) and (1f). Time-dependent data were accumulated to determine the effect of $Fe_2(SO_4)_3$ concentration on pyrite oxidation rate, and also to characterize the conditions favoring production of elemental sulfur. These reactions were carried out under nitrogen at 120°C in a treating solution initially containing 12% $Fe_2(SO_4)_3$ (0.68M) and 25% H_2SO_4.

The results are presented graphically in Figure 3-2. While complete oxidation of pyrite by $Fe_2(SO_4)_3$ gives a ratio of Fe^{II} formed to FeS_2 leached of 15, the observed ratio was only about 10, which corresponds to the composite stoichiometric equation:

$$FeS_2 + 4.5\ Fe_2(SO_4) + 4.67\ H_2O \longrightarrow 10\ FeSO_4 + 4.67\ H_2O + 0.83\ S \qquad (3a)$$

This result is a weighted sum of equations (1a) and (1c); hence its coefficients will vary with temperature and other factors.

Kinetic analysis of the pyrite oxidation data, leading to the plot of Figure 3-3, indicates that the rate is first-order in Fe^{III} concentration:

$$-\frac{d[FeS_2]}{dt} = -\frac{1}{9}\frac{d[Fe^{III}]}{dt} = k_1 A [Fe^{III}] \qquad (3b)$$

The constant k_1 was determined to be 1.0×10^{-6} cm^{-2} min^{-1}.

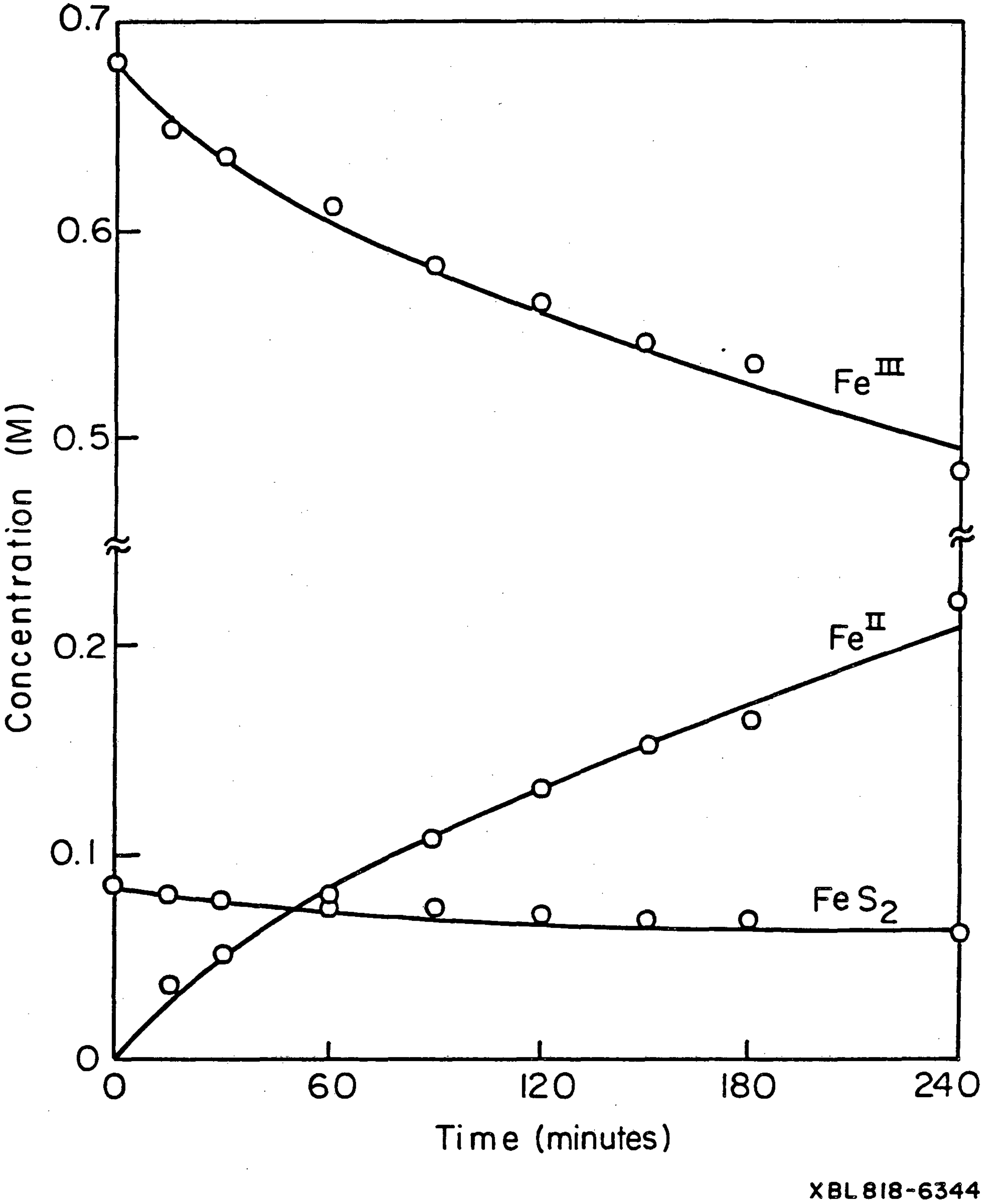

Figure 3-2. Oxidation of pyrite by $Fe_2(SO_4)_3$ (25% H_2SO_4; 120°C).

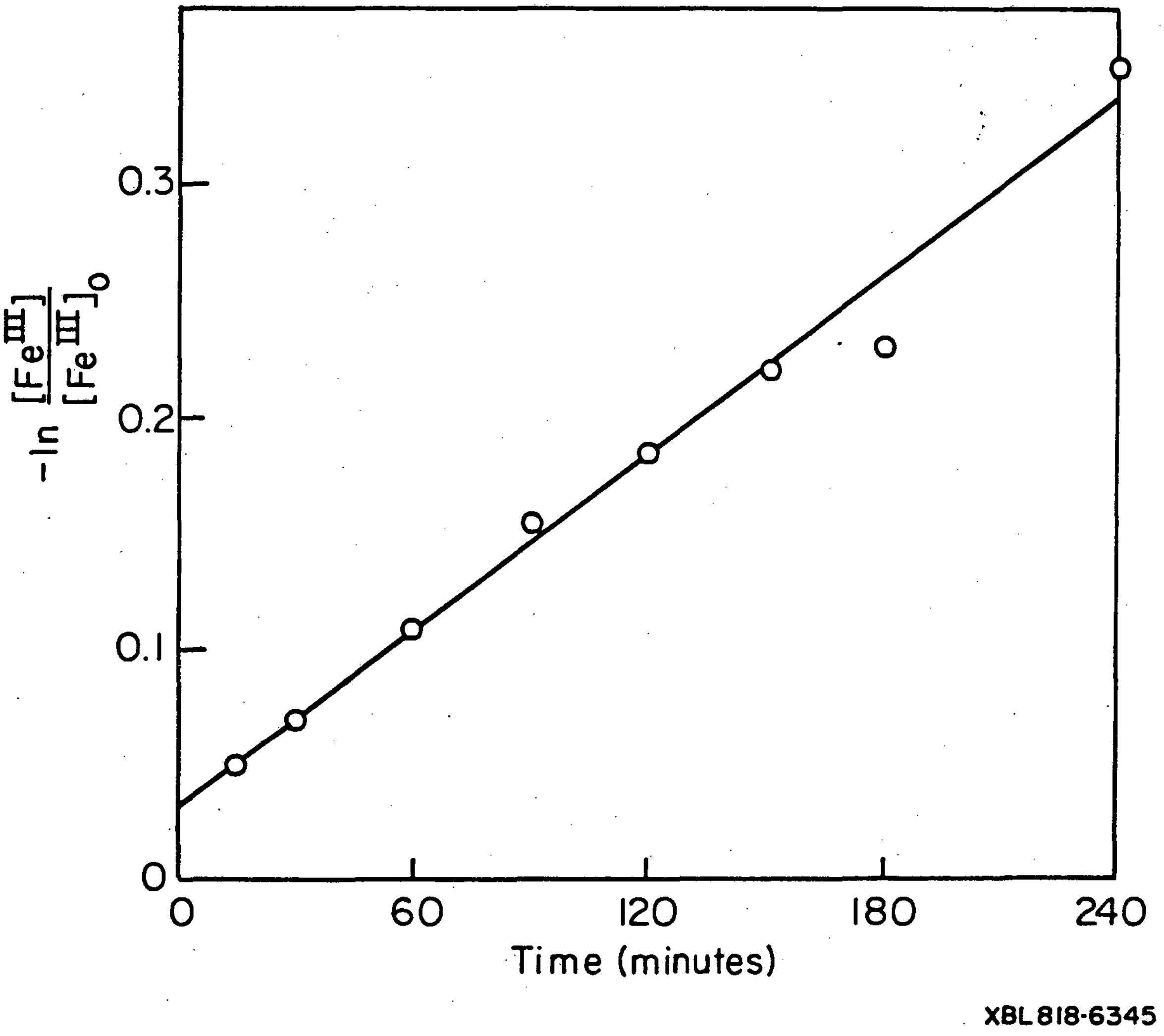

Figure 3-3. First-order plot for oxidation of pyrite by $Fe_2(SO_4)_3$ (25% H_2SO_4; 120°C).

Although other investigators (K1, M1) have implicated Fe^{II} as an effective variable in the kinetics, our results offer no support for that claim.

5. Effect of Oxygen Partial Pressure

The role of oxygen in pyrite oxidation has been a point of controversy. Meyers (M1) has suggested that, in iron sulfate solutions, the oxygen serves only to maintain the iron in its highest oxidation state, and does not directly oxidize pyrite. He thus assumed that oxidation of FeS_2 by ferric sulfate was the rate-limiting step, and that the ratio of ferric ion to total iron was the controlling factor. This assumption was repeated but not proved by King and Perlmutter (K1). Use of such a ratio is difficult to explain theoretically and is incorrect if our observation of the relative inertness of ferrous ion is accurate.

Figure 3-4 shows the rate plots for a series of experiments conducted at 120°C under oxygen partial pressures of 280, 360, and 420 psi, in treating solution initially containing 12% $Fe_2(SO_4)_3$ and 25% H_2SO_4. By beginning with an excess of ferric sulfate, the ferric ion concentration was maintained above 90% of the total iron in solution. In reactions performed under N_2, the ferric ion concentration fell below 80% of the total iron, but only after more than 3 hours of reaction.

Comparing the two cases, the rate of pyrite oxidation

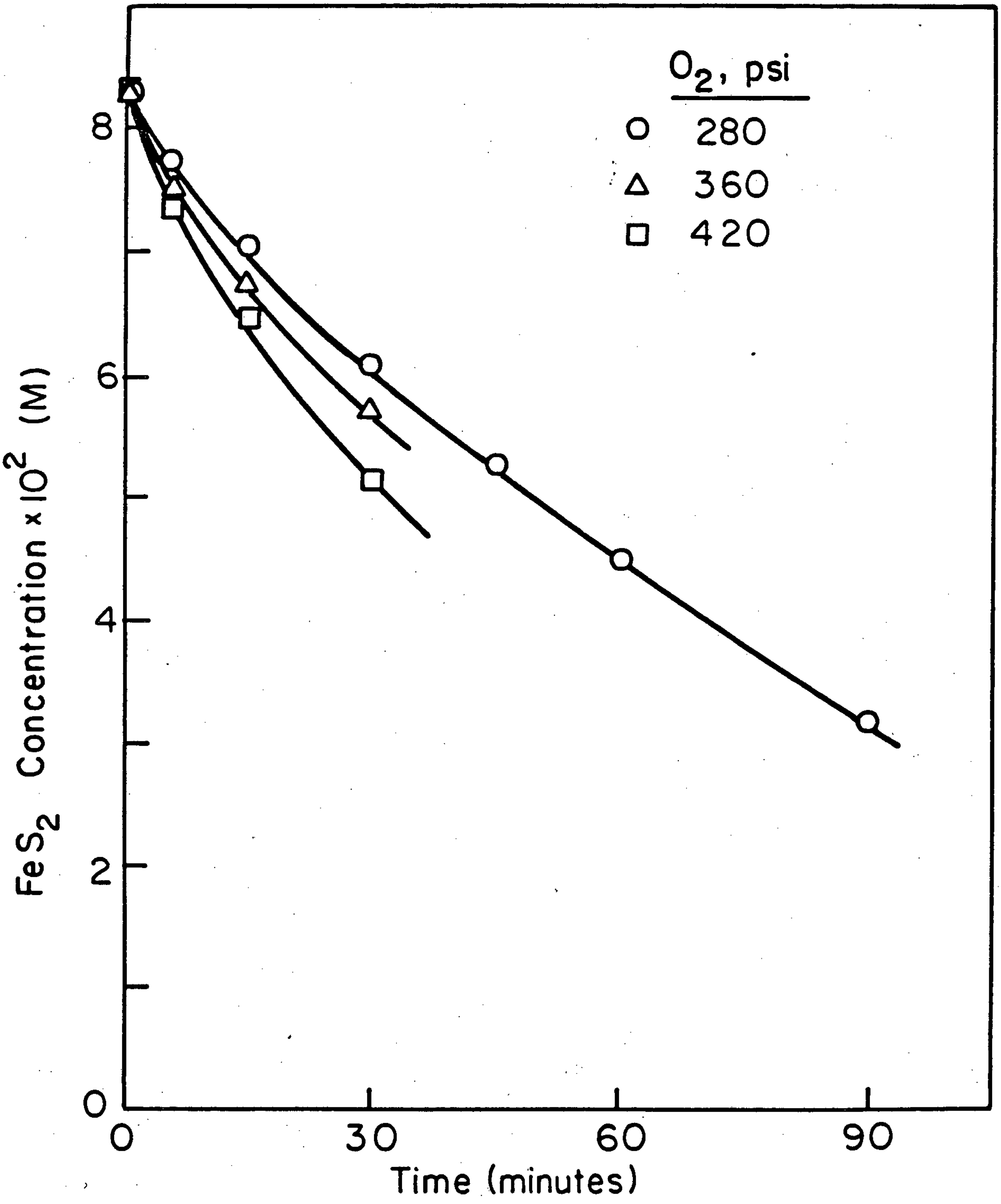

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Figure 3-4. Autoxidation of pyrite (12% $Fe_2(SO_4)_3$; 25% $H_2(SO_4)_3$; 120°C).

is approximately 7 times faster under 280 psi of O_2 than when no O_2 is present. Therefore oxygen must be oxidizing pyrite directly, with ferric sulfate playing a secondary role. Indeed this conclusion agrees with the previously reported finding (M3) that autoxidation of pyrite is much faster than that of ferrous ion.

The results in Figure 3-5 indicate that the rate of pyrite oxidation is linearly dependent on oxygen partial pressure with a rate constant k_2 of 1.7×10^{-8} M cm^{-2} psi^{-1} min^{-1}. This is consistent with work by McKay and Halpern (M3), but differs from the one-half-order dependence reported by Warren (W1) and by Slagle and Shah (S3).

Thus it appears that pyrite oxidation proceeds by two parallel pathways, and that the complete rate can be represented by the sum of the two corresponding expressions:

$$-\frac{d[FeS_2]}{dt} = 1.0 \times 10^{-6} A [Fe^{III}] + 1.7 \times 10^{-8} A P_{O_2} \qquad (3c)$$

The rate of pyrite oxidation by oxygen in water at 120°C and 280 psi O_2, shown by Figure 3-6, is approximately 25% slower than in the $Fe_2(SO_4)_3/H_2SO_4$ solution, even though the oxygen solubility should be greater. This effect is too large to be due to additional oxidation by ferric sulfate. A possible explanation is that in the nearly neutral solution an insoluble solid crust forms around the pyrite particle as it reacts, introducing an additional resistance --

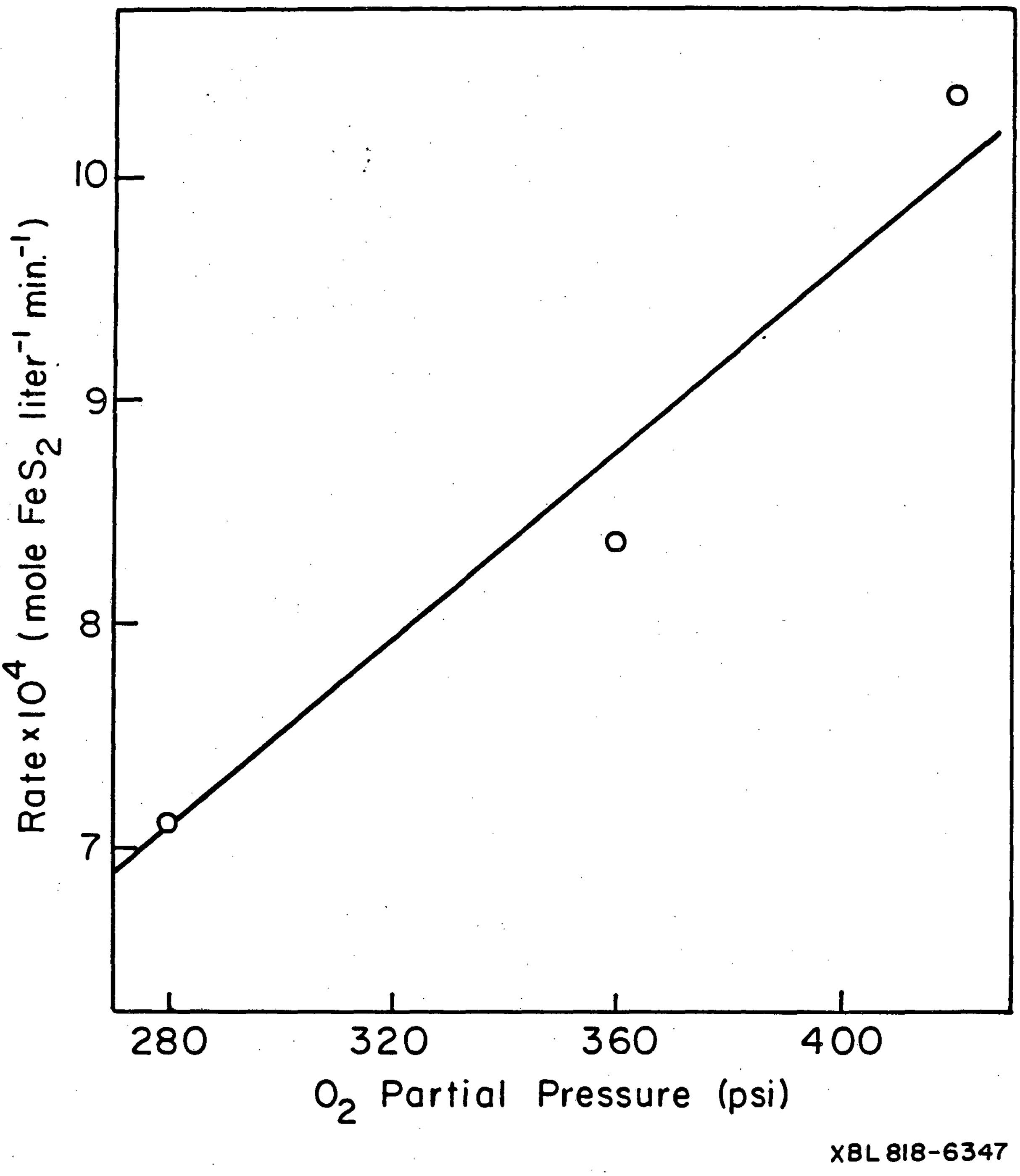

Figure 3-5. Dependence of pyrite oxidation rate on O_2 partial pressure (12% $Fe_2(SO_4)_3$; 25% H_2SO_4; 120°C).

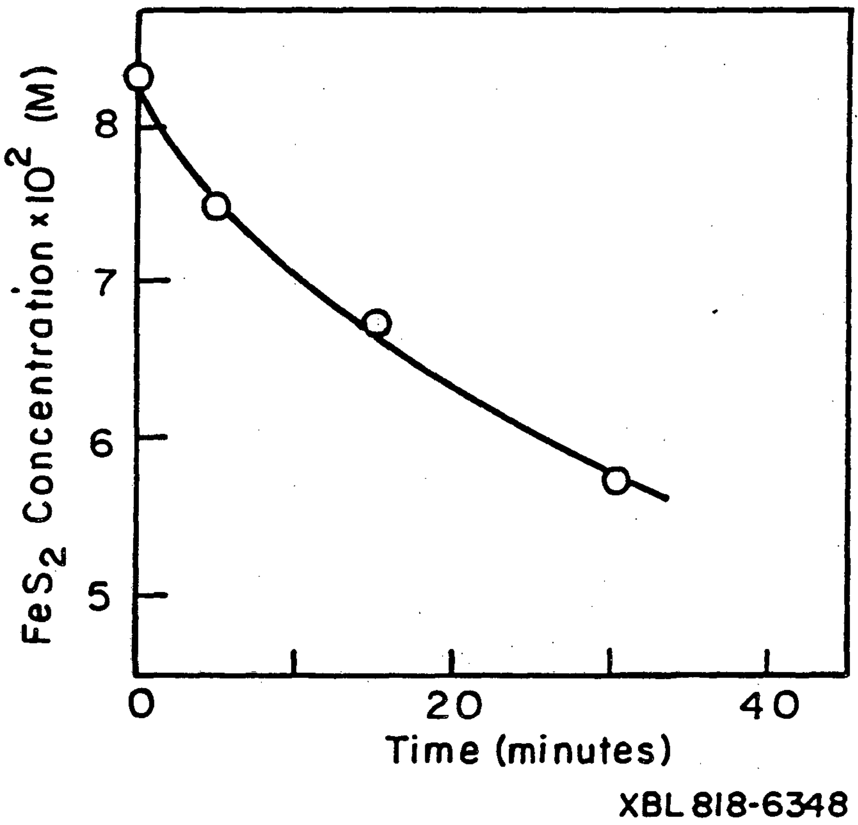

Figure 3-6. Rate of pyrite oxidation in water (280 psi O_2; 120°C).

diffusion of oxidant to the surface of unreacted material; such a crust has been observed in the autoxidation of pyrite in aqueous sodium bicarbonate, and identified as Fe_2O_3 (T2), suggesting reaction (1g). By contrast, in the $Fe_2(SO_4)_3/H_2SO_4$ solution, the reaction product is immediately dissolved which leaves the unreacted pyrite fully exposed.

B. Oxidation of Pyrite in Coal

An extensive set of experiments has been performed to evaluate the effects of stirring speed, particle size, sulfuric acid and iron sulfate concentrations, oxygen partial pressure, and temperature on pyrite leaching from coal. The results are given in Table 3-2.

1. Effect of Stirring Speed

As with bulk pyrite, stirring speed has little effect on reaction rate. Under 280 psi O_2 at 120°C for 1 hour, with a treating solution initially containing 25% H_2SO_4 and 12% $Fe_2(SO_4)_3$, no change in conversion was observed above 600 rpm. This speed was therefore adopted for all subsequent experiments.

2. Effect of Particle Size

Particle size distribution of the coal appears to be critically important in pyrite removal. At 150°C and 280 psi O_2, in 12% $Fe_2(SO_4)_3$ / 25% H_2SO_4 solution, a -100 + 150m

Table 3-2. Pyrite leaching from coal

Run No.	Coal Sample	$\frac{H_2SO_4}{H_2O+H_2SO_4}$, wt-%	$\frac{Fe_2(SO_4)_3}{H_2O+H_2SO_4}$, wt-%	O_2 Partial Pressure, Psia	Temperature °C	Time, minutes	% Pyrite Removed
29*	2	25	12	280	120	60	60
30	2	25	12	280	120	60	63
31**	2	25	12	280	120	60	63
32	1	25	12	280	150	60	63
33	2	25	12	280	150	60	76
34	2	25	12	280	120	10	24
35	2	25	12	280	120	20	44
36	2	25	12	280	120	30	49
37	2	25	12	280	120	40	59
38	2	25	12	280	120	50	59

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Table 3-2. Pyrite leaching from coal

Run No.	Coal Sample	$\frac{H_2SO_4}{H_2O+H_2SO_4}$, wt-%	$\frac{Fe_2(SO_4)_3}{H_2O+H_2SO_4}$, wt-%	O_2 Partial Pressure, Psia	Temperature °C	Time, minutes	% Pyrite Removed
39	2	25	12	420	200	60	78
40	3	5	12	420	150	60	76
41	3	25	12	420	150	60	84
42	3	5	12	420	130	60	80
43	3	15	12	420	130	60	80
44	3	25	12	420	130	60	75
45	2	0	0	280	120	10	31
46	3	15	24	420	130	60	75
47	2	25	12	0	120	10	22
48	1	25	12	150	150	60	43

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Table 3-2. Pyrite leaching from coal

Run No.	Coal Sample	$\frac{H_2SO_4}{H_2O+H_2SO_4}$, wt-%	$\frac{Fe_2(SO_4)_3}{H_2O+H_2SO_4}$, wt-%	O_2 Partial Pressure, Psia	Temperature °C	Time, minutes	% Pyrite Removed
49	1	25	12	200	150	60	56
50	3	25	12	280	150	60	76
51	3	25	12	420	100	60	62
52	3	25	12	420	110	60	67
53	3	25	12	420	120	60	70
54	3	25	12	420	140	60	80

Stirring Speed = 600 rpm

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fraction (sample 2) showed 76% pyrite conversion after 1 hour while a -20 + 30m fraction showed only 56% conversion. Particle size effects would probably be greater at shorter residence times since exposed pyrite is rapidly oxidized. Data taken from runs made with the -100 + 150m sample are presented in Figure 3-7. These runs were carried out in the same treating solution and at the 280 O_2 pressure, but at 120°C. Little improvement in pyrite removal is accomplished after about 40 minutes, -59% conversion compared with 63% for 1 hour. The remaining pyritic sulfur is extremely difficult to remove, even under extreme conditions; treatment for 1 hour at 200°C and 420 psi O_2 improves the conversion to 78% (sample 2 represents a heavily weathered coal, containing approximately 0.8% sulfate sulfur, thereby reducing the percentage conversion compared to freshly mined coal).

Whereas pyrite conversion levels off with time, the loss in heating value of the coal, as shown in Figure 3-8, proceeds at a constant rate, dependent upon particle size. As can be seen from Figure 3-9, an excessive loss of heating value (relative to pyrite removal) occurs in the latter stages of reaction, and provides a strong incentive for minimizing the residence time. Thus, decreasing the particle size is clearly advantageous for pyrite oxidation. The effect seems to represent a higher exposure of pyrite surfaces and a shortened diffusion path. Fine grinding, however, is costly, and results in a coal that may be both less stable and more difficult to transport. These factors must

Table 3-3. Heating Value Loss

Run No.	Coal Sample	Time, minutes	Pyrite Removed, %	Heating Value Loss, %
34	2	10	24	2.0
35	2	20	44	4.7
36	2	30	49	6.2
37	2	40	59	8.6
38	2	50	59	10.2
30	2	60	63	12.2
32	1 (-20+30m)	60	56	9.1
45	2	10	31	2.9
47	2	10	22	5.8

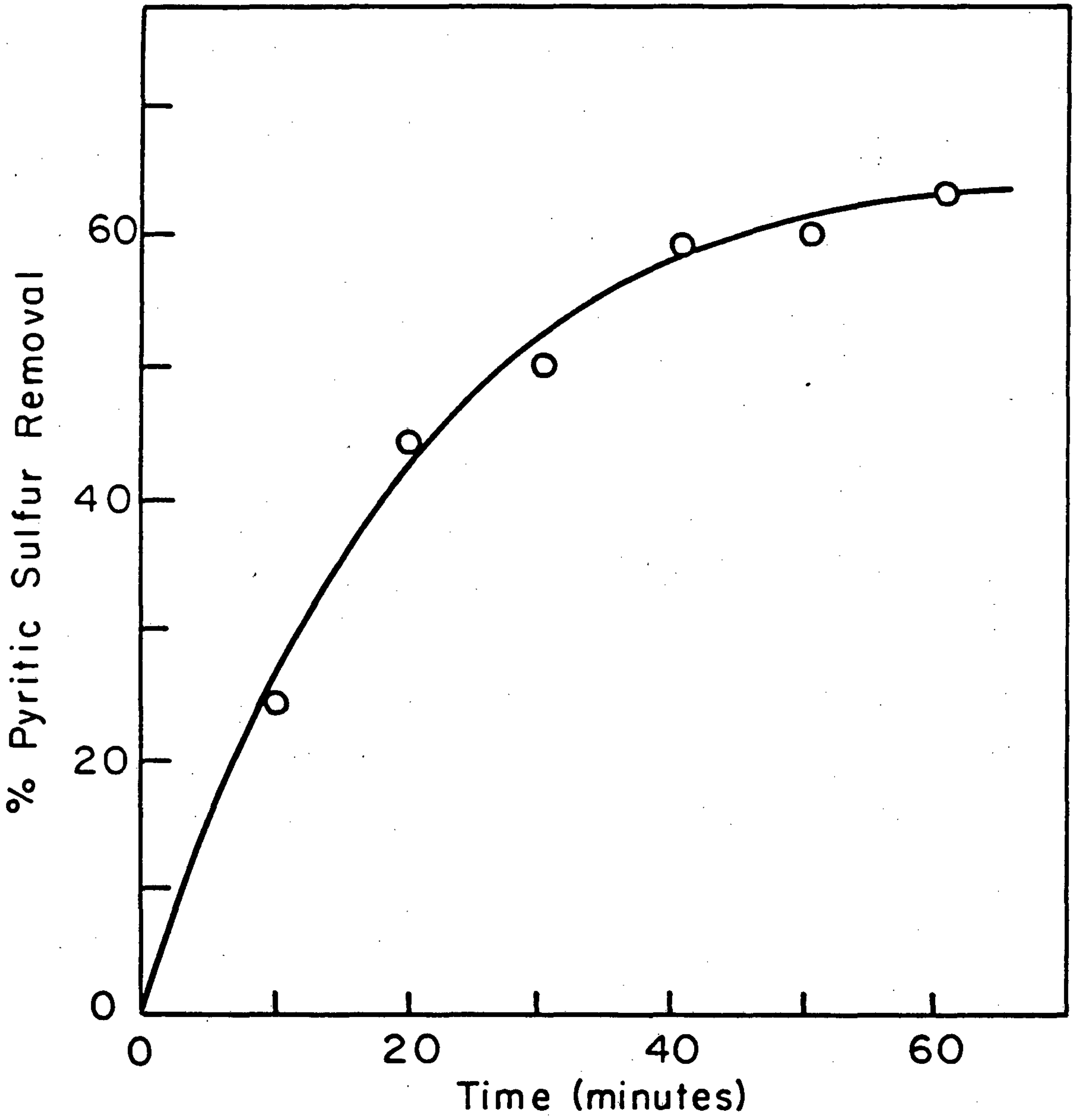

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Figure 3-7. Rate of pyrite removal; (sample 2 coal; 12% $Fe_2(SO_4)_3$; 25% H_2SO_4; 280 psi O_2; 120°C).

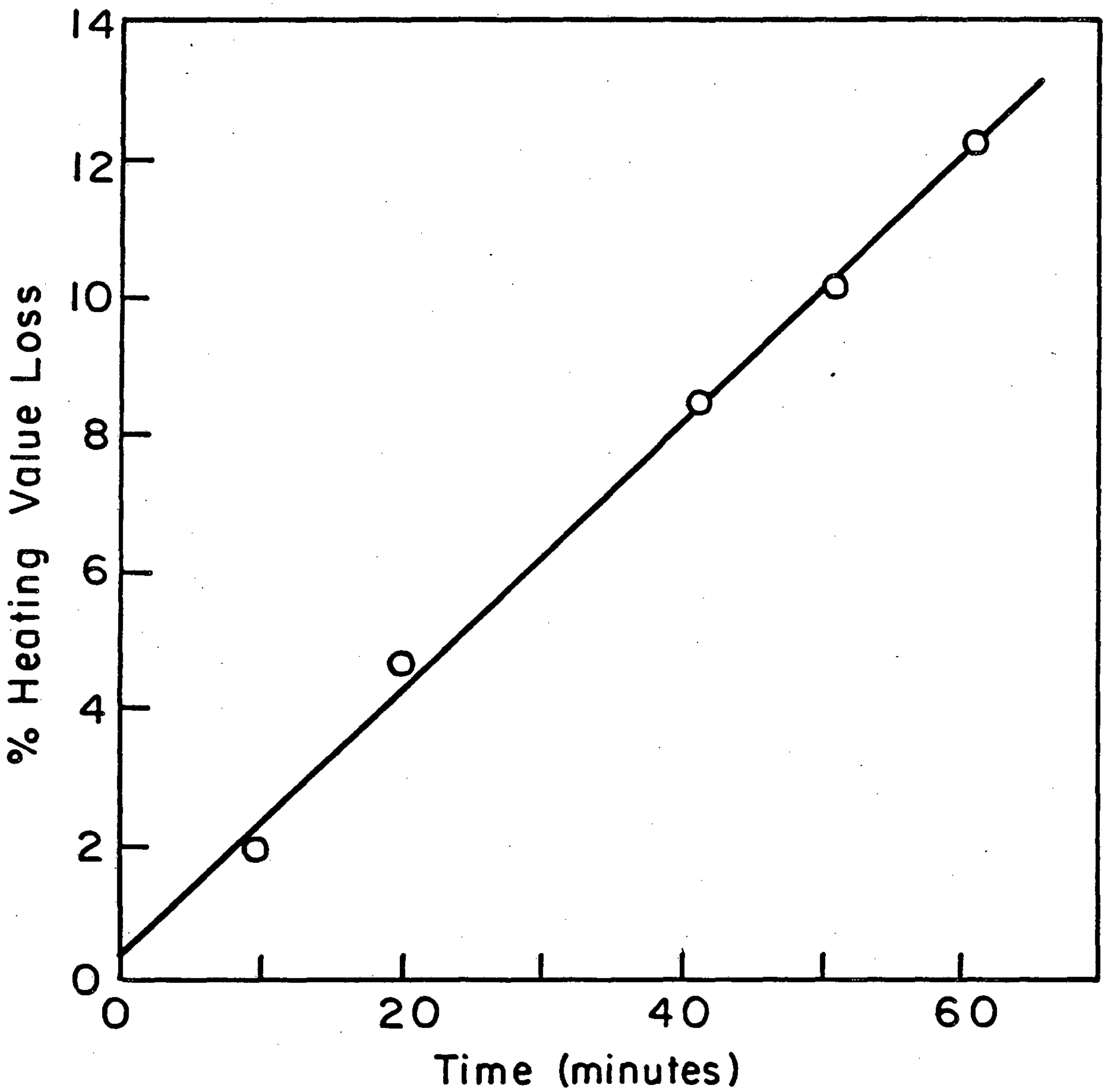

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Figure 3-8. Rate of heating value loss (sample 2 coal; 12% $Fe_2(SO_4)_3$; 25% H_2SO_4; 280 psi O_2; 120°C).

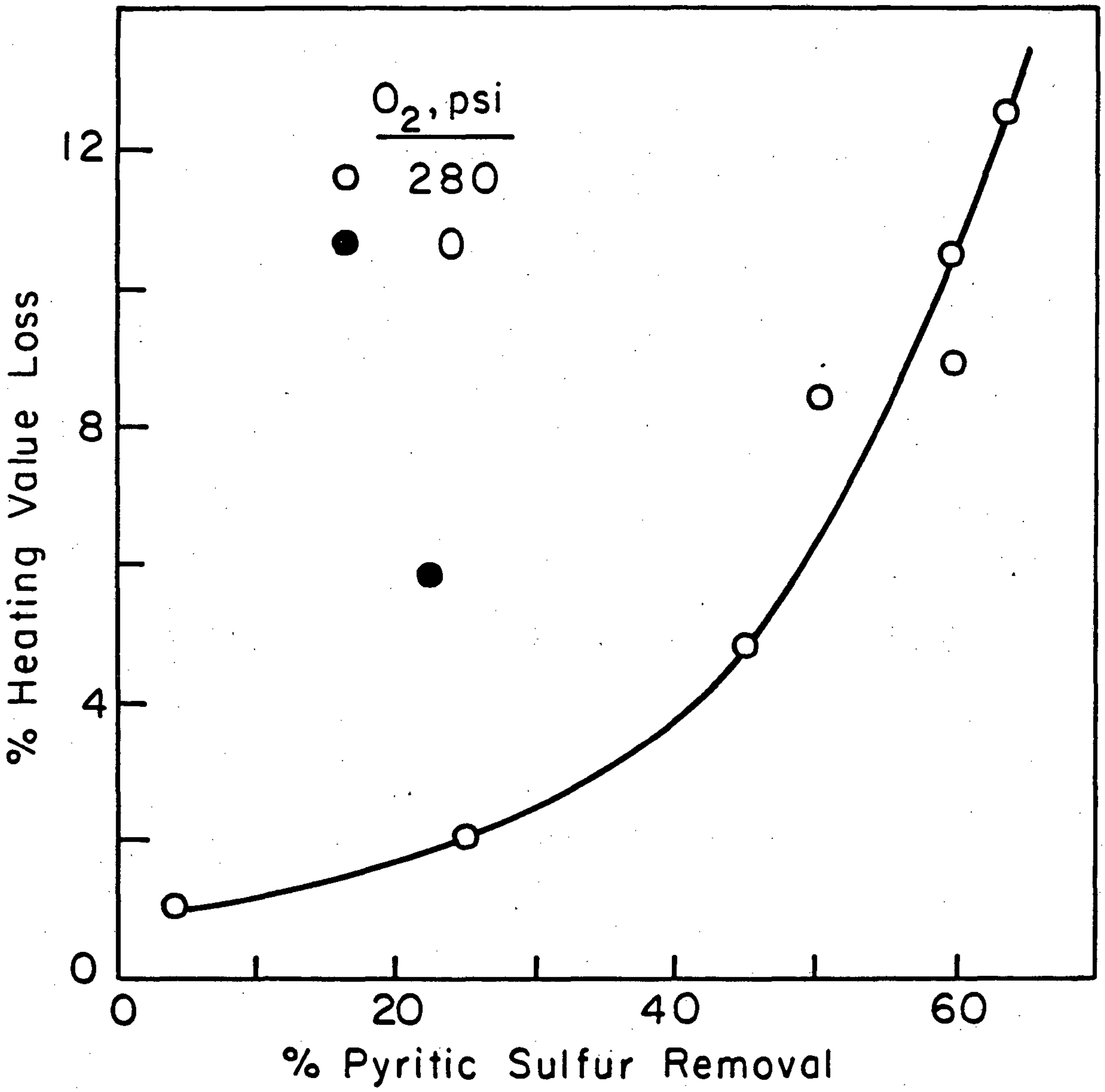

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Figure 3-9. Dependence of heating value loss on pyrite removal (sample 2 coal; 12% $Fe_2(SO_4)_3$; 25% H_2SO_4; 120°C).

be balanced against reduced losses in heating value.

3. Effect of Sulfuric Acid Concentration

The effect of sulfuric acid concentration was studied in several runs with sample 3 coal and 12% concentration of $Fe_2(SO_4)_3$. The results are presented in Table 3-4. At 150°C and 420 psi O_2, 25% acid yield 84% conversion, and 5% acid yielded 76% conversion after 1 hour. At 130°C and 420 psi, 25% acid gave 75% conversion, while 15% acid and 5%acid both gave 80% conversion. Thus, similar to the oxidation of bulk pyrite, the conversion of pyrite in coal seems to be essentially independent of sulfuric acid concentration between 5 and 25 weight percent.

Reaction proceeds somewhat more rapidly in water than in the $Fe_2(SO_4)_3$ / H_2SO_4 solution. At 120°C and 280 psi, 31% conversion is achieved after 10 minutes in water as compared with 24% conversion in 12% $Fe_2(SO_4)_3$ and 25% H_2SO_4. Thus the leaching of pyrite from coal differs from the reaction of bulk pyrite, which is oxidized more rapidly in the $Fe_2(SO_4)_3$ / H_2SO_4 medium.

4. Effect of Ferric Sulfate Concentration

The effect of changing ferric sulfate concentration at a constant sulfuric acid concentration of 15% was evaluated with sample 3 coal at 130°C and 420 psi. After 1 hour at 12% $Fe_2(SO_4)_3$, the conversion was 80%, while at 24% $Fe_2(SO_4)_3$ the conversion was 75%. Considering that reaction

Table 3-4. Effect of acid strength on pyrite removal

$\frac{H_2SO_4}{H_2O+H_2SO_4}$, wt-%	Temperature, °C	Pyrite Removed, %
5	150	76
25	150	84
5	130	80
15	130	80
25	130	75

12% $Fe_2(SO_4)$; 420 psi O_2; 1 hr; Sample 3 coal in water gives a slightly higher oxidation rate, these results suggest a mildly adverse dependence of pyrite conversion on ferric sulfate concentration.

In leaching pyrite from coal with iron sulfates, much of the ferric sulfate is reduced by organic matter in the coal rather than by pyrite. Ferrous sulfate then competes with pyrite for molecular oxygen. In one run in the absence of oxygen, over 6 times as much ferric ion was reduced by organic matter as by pyrite. Figure 3-9 illustrates the disproportionate loss in heating value under those conditions. In any case, it is important to realize that in studies of pyrite oxidation in coal by iron salts, runs which simply monitor the disappearance of ferric ion are without value for determining the reaction kinetics.

Nevertheless, iron sulfates apparently play a beneficial role in reducing the metal corrosion by sulfuric acid. We did not detect appreciable pitting of our reactor internals, made of 316 stainless steel, in the $Fe_2(SO_4)_3$ / H_2SO_4 system below 150°C. Without dissolved iron present, 25% sulfuric acid was quite corrosive, and very dilute sulfuric acid even more so. At 120°C and 280 psi O_2, the autoxidation of pyrite in a neutral aqueous medium by molecular oxygen yielded only two detectable products, H_2SO_4 and Fe_2O_3, and proved to be the most corrosive. In addition, production of Fe_2O_3 increases the ash content of the coal according to equation (1g).

5. Effect of O_2 Partial Pressure

The effect of increasing oxygen partial pressure is shown in Table 3-5. Runs made with -20 + 30 mesh coal indicate a first-order dependence of removal on oxygen partial pressure, analogous to the results obtained for bulk pyrite. The effect of oxygen partial pressure is not as noticeable after 1 hour's reaction with finely ground coal (sample 3); 280 psi gave a conversion of 76% at 150°C, while 420 psi gave 84% conversion.

Oxygen is also important in preventing the formation of elemental sulfur. At 120°C, an oxygen partial pressure of 280 psi results in an 11% reduction of the initial elemental sulfur content of the coal. An increase to 420 psi, however, gives a 34% removal of elemental sulfur after 1 hour. Below 200 psi a net increase in the elemental sulfur content of the coal might be anticipated at 120°C.

6. Effect of Temperature

The effect of temperature on pyrite removal is given in Figure 3-10. Five runs with sample 3 coal at 420 psi O_2, in treatment by 12% $Fe_2(SO_4)_3$ / 25% H_2SO_4, demonstrate the advantage of moderate temperature increase. At temperatures of 100°, 110°, 120°, 130°, and 140°C, the respective pyrite conversions were 62, 67, 70, 75 and 80%.

Temperature, like oxygen partial pressure, plays a crucial role in the fate of elemental sulfur. At 100° or 110°C

Table 3-5. Effect of oxygen partial pressure on pyrite removal

Coal Sample	O_2 Partial Pressure, psia	Pyrite Removed, %
1	150	21
1	200	43
1	280	56
3	280	76
3	420	84

12% $Fe_2(SO_4)_3$; 25% H_2SO_4; 150°C; 1 hr

Table 3-6. Elemental Sulfur Removal

Run No.	O_2 Partial Pressure, psia	Temperature, °C	Pyrite Removed, %	Elemental Sulfur Removed, %
32	280	120	63	11
53	420	120	70	34
51	420	100	62	-46
52	420	110	67	-3.3
46	420	130	75	50
54	420	140	80	78
41	420	150	84	86

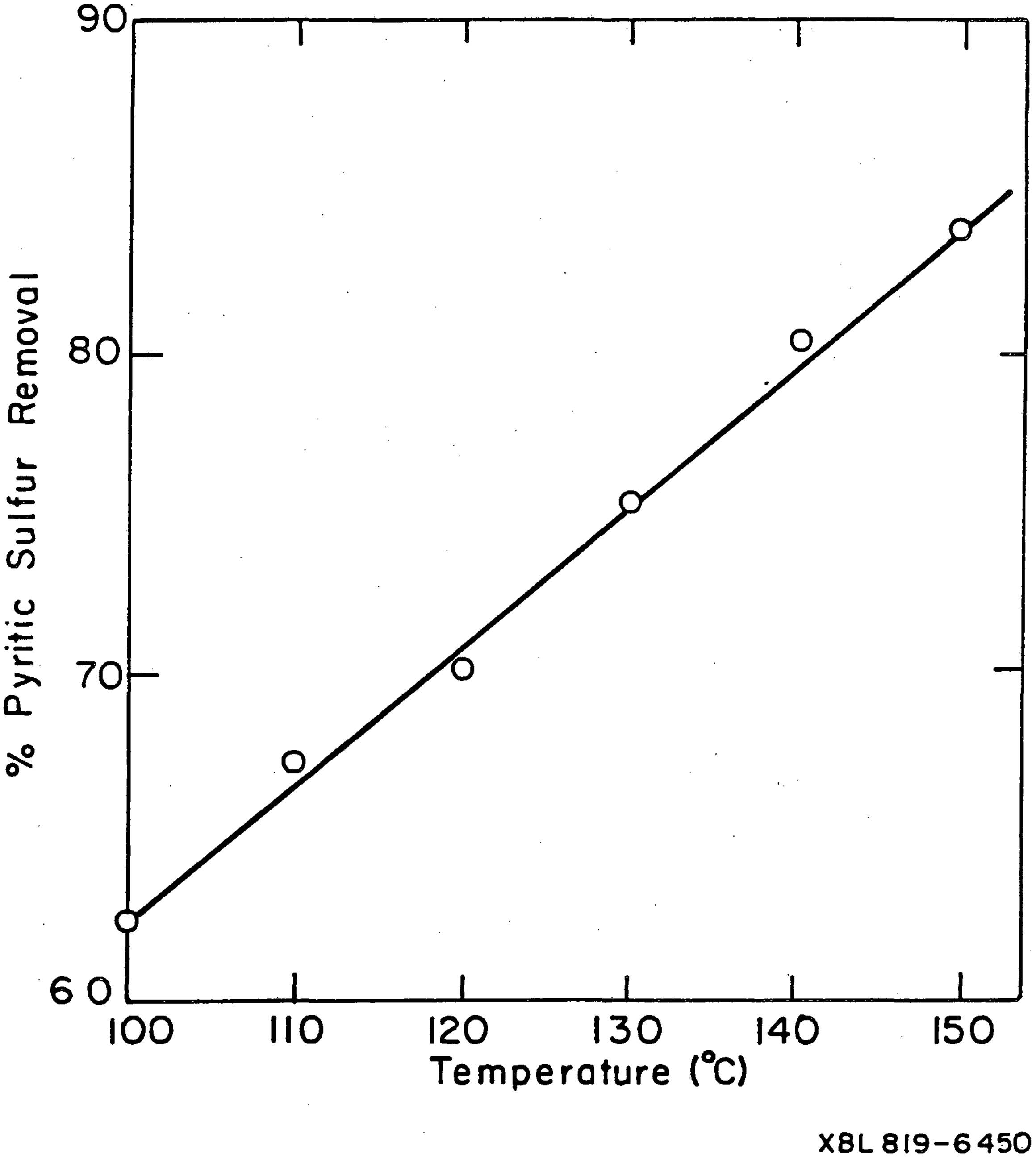

Figure 3-10. Effect of temperature on pyrite removal (sample 3 coal; 12% $Fe_2(SO_4)_3$; 25% H_2SO_4; 420 psi O_2; 1 hr).

the elemental sulfur content increases above its feed level - generally between 0.09 and 0.13% - even at 420 psi O_2. The balance point occurs near 120°, providing the oxygen partial pressure is sufficiently high, i.e. greater than about 200 psi. At 130° and 420 psi O_2, reductions of between 50% and 95% are found and the need to remove elemental sulfur in an additional step is eliminated. These results are presented graphically in Figure 3-11.

C. Removal of Organic Sulfur from Coal

The removal of organic sulfur from coal without destruction of the hydrocarbon matrix would significantly improve the effectiveness of coal desulfurization technology. This study is aimed at evaluating several existing techniques and exploring some new ones. The various treatments and their effect on pyritic and organic sulfur removal and heating value loss to the coal are summarized in Table 3-7.

1. NaOH Treatment

One run was performed to investigate a two-step desulfurization scheme involving oxidation followed by treatment with 10% NaOH. Coal was initially subjected to 280 psi O_2 for 1 hour at 150°C in 12% $Fe_2(SO_4)_3$ and 25% H_2SO_4. The resulting coal was then contacted for 1 hour with 10% NaOH at 200°C. Analysis of the solid product showed a minor increase in pyritic sulfur removal (83% compared to 75%

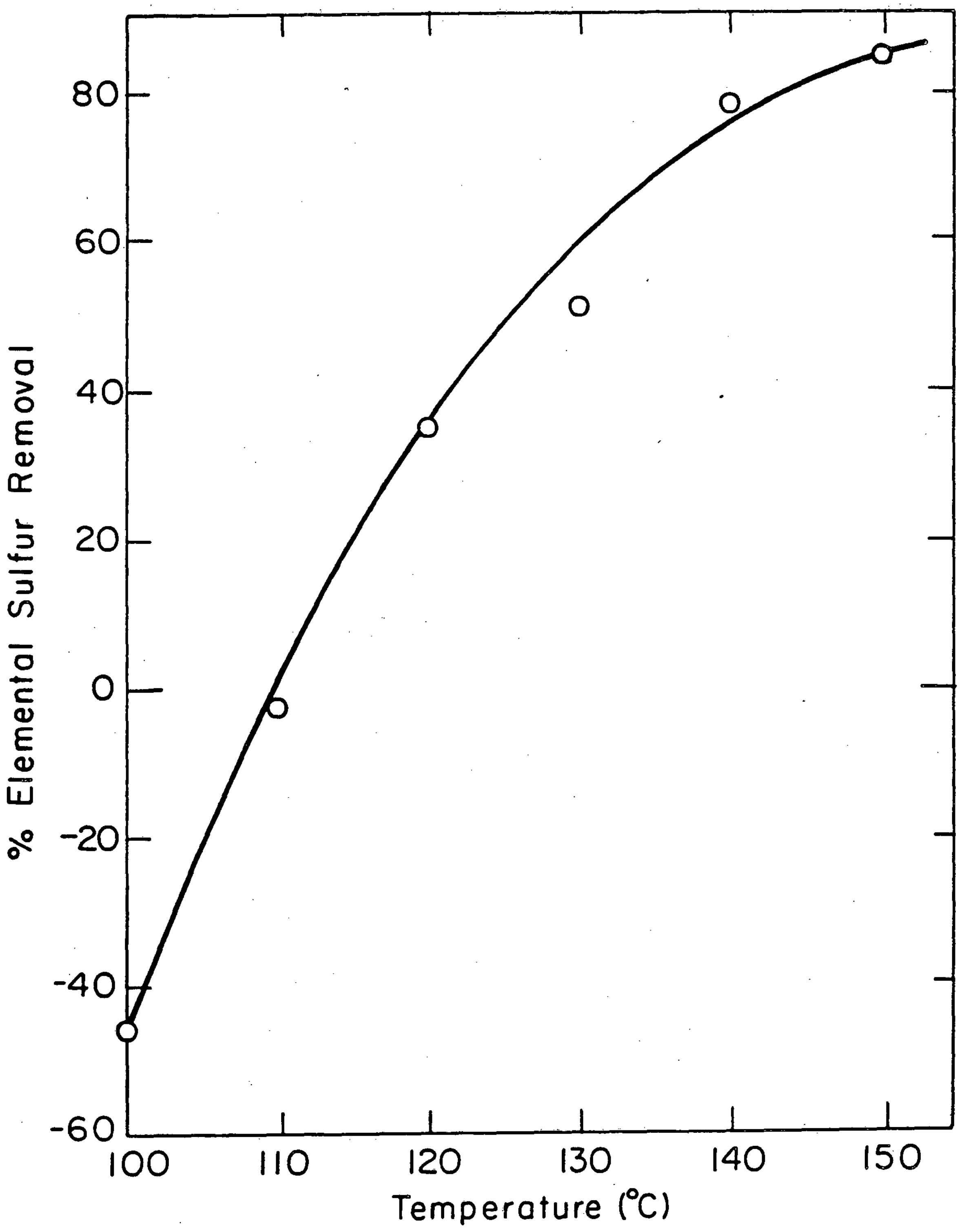

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Figure 3-11. Effect of temperature on elemental sulfur removal (sample 3 coal; 12% $Fe_2(SO_4)_3$; 25% H_2SO_4; 420 psi O_2; 1 hr).

Table 3-7. Removal of organic sulfur from coal (sample 2)

Treatment	Description	% Pyritic Sulfur Removal	% Organic Sulfur Removal	% Heating Value Loss
NaOH Extraction*	(1) 1 hr; 150°C; 280 psi O_2 12% $Fe_2(SO_4)_3$; 25% H_2SO_4 (2) 1 hr; 200°C; 10% NaOH	83	43	44
Low-Temperature* Chlorinolysis	(1) 1 hr; 75°C; $Cl_2(g)$ (2) 1 hr; 98°C, H_2O	--	60	--
NO_2 Oxidation	1/2 hr; 120°C; 12% $Fe_2(SO_4)_3$; 25% H_2SO_4	40	<1	--
NO_2 Oxidation	1/2 hr; 120°C; H_2O	40	<1	--
Liquid SO_2 Extraction	(1) 1 hr; 120°C; 420 psi O_2 12% $Fe_2(SO_4)_3$; 25% H_2SO_4 (2) 1 hr; 150°; SO_2 (l)	65	26	8

Table 3-7. Removal of organic sulfur from coal (sample 2)

Treatment	Description	% Pyritic Sulfur Removal	% Organic Sulfur Removal	% Heating Value Loss
Liquid SO_2 Extraction	(1) 1 hr; 150°C; 420 psi; O_2 12% $Fe_2(SO_4)_3$; 25% H_2SO_4 (2) 1 hr; 150°C; SO_2 (1)	72	-59	11
Liquid SO_2 Extraction	(1) 1 hr; 120°C; 420 psi; O_2 12% $Fe_2(SO_4)_3$; 25% H_2SO_4 (2) 1 hr; 150°C; SO_2 (1) (3) 1 hr MEK extraction	70	-2	10
Liquid SO_2 Extraction	1 hr; 150°C, SO_2 (1)	<1	-61	2
ClO_2 Treatment	1 hr; 80°C; 15% H_2SO_4; 1.5 M ClO_2	40	<1	--
High-Temperature Oxidation	1 hr; 200°C; 420 psi, O_2; 12% $Fe_2(SO_4)_3$; 25% $H_2SO_4^*$	78	38	30

* Sample 3 Coal

prior to NaOH treatment) and a modest 9% reduction in the organic sulfur content. 38% of the coal's organic matter was lost in this run, probably as humic acids extracted into the basic solution; thus, when calculating percentage sulfur removal on a material-fed, material-recovered basis, 43% of the organic sulfur and 90% of the pyritic sulfur were removed, with 65% removal of total sulfur. The loss in organic material, however, is much too great for this approach to have any practical application.

2. Low-Temperature Chlorinolysis

Coal was reacted with Cl_2 gas in aqueous solution for one hour at 75°C and then treated with water at 98°C for one hour, the latter step intended to hydrolyze carbon-chlorine bonds according to equation (1s). This procedure resulted in a greater extent of organic sulfur removal (60%) than any of the other methods tested. Unfortunately, massive amounts of chlorine were incorporated into the remaining coal - 10.2% (MAF) compared with 0.4% (MAF) in the starting coal. Chlorination of the coal presents a serious drawback since dechlorination is a difficult and energy-intensive process requiring temperatures up to 450°C, is only partially effective (T2), and tends toward large losses of organic material.

3. NO_2 Oxidation

Two runs were conducted under 50 psi NO_2. In one case the treating solution contained 12% $Fe_2(SO_4)_3$ and 25% H_2SO_4; in the other, only water was present. Both reactions were heated at 120°C for 30 minutes.

Significant removal of organic sulfur was not detected in either run, although some nitration of the coal did occur. The nitrogen content was increased by 36% (MAF) in the $Fe_2(SO_4)_3$ / H_2SO_4 medium; in water the increase was considerably greater - 140% (MAF), possibly due to formation of nitric acid. Both runs resulted in 40% removal of pyritic sulfur. This compares with 50% removal under similar conditions but with 280 psi O_2.

4. Liquid SO_2 Extraction

Removal of up to 40% of the organic sulfur in coal by liquid SO_2 extraction has been recently reported (B4). An independent but very similar investigation was conducted by the author, yielding ambiguous results and creating doubt about the previous study.

In an initial run, coal was first subjected to oxidation in 12% $Fe_2(SO_4)_3$ / 25% H_2SO_4 at 120°C and 420 psi O_2 for 1 hour. The resulting coal was then extracted with liquid SO_2 according to the procedure described in Chapter II. Subsequent analysis showed a 26% removal of organic sulfur with a concommitant 8% loss in heating value. Numerous attempts to repeat this result, however, were failures. In all subsequent experiments an apparent increase in the organic sulfur content of the coal was observed. Since standard ASTM methods for sulfur analysis were used throughout this study, the "organic" sulfur amounts to non-pyritic sulfur which is not extracted by 4.8N HCl.

Liquid SO_2 behaves as a mild Lewis acid, and donor-acceptor reactions with aromatic, amine, and oxygen containing functional groups are probably responsible for SO_2 incorporation as adducts. Increases of 60% in the non-HCl-extractable sulfur were not uncommon and indicate the stability of the SO_2 complex. In one experiment, liquid SO_2 treatment was followed by a 1 hour Soxhlet extraction with methyl ethyl ketone, to no beneficial result. Furthermore, analysis of the extracted material showed a sulfur content essentially the same as the starting coal, demonstrating that liquid SO_2 does not act to extract sulfur-containing molecules preferentially.

It is the author's opinion that a sizable fraction of the organic sulfur removal reported by Burrow and Glavincevski (B4) occurs after SO_2 extraction during a sequential wash including 3.8M nitric acid. In the ASTM method for pyrite analysis in coal, treatment with 2.1M nitric acid results in substantial oxidation and extraction of organic matter. Therefore, it seems likely that their technique is very similar to NaOH treatment, and only gives significant removal of organic sulfur when calculated on a material-fed, material-recovered basis. Such an approach is of little benefit in reducing SO_2 emissions, relative to the coal's calorific value.

5. ClO_2 Treatment

Chlorine dioxide (ClO_2) is a strong oxidizing agent commonly used in water treatment. Its potential for oxidative desulfurization was evaluated by addition of a 1.5M solution to a coal slurried in 15% H_2SO_4 at 80°C. Appreciable removal of organic sulfur was not detected, and only a modest 40% removal of pyritic sulfur was observed. A tenfold increase in the chlorine content of the coal from 0.4% (MAF) to 4.0% (MAF) eliminated ClO_2 treatment from further consideration.

6. High-Temperature Oxidation

One run was made in which coal was reacted in 12% $Fe_2(SO_4)_3$ / 25% H_2SO_4 at 420 psi O_2 and 200°C for 1 hour. 38% removal of organic sulfur was accomplished but at the expense of a 30% loss in the heating value of the coal. Other investigations have reported similar results for high-temperature oxidation in nearly neutral media (S3). The extreme conditions necessary to remove organic sulfur oxidatively seem necessarily to result in commensurate losses in the heating value due to oxidation of organic matter. Metal corrosion also becomes a serious problem at elevated temperatures.

IV. CONCLUSIONS

A. Pyrite Oxidation

Contrary to previous claims (M1), dissolved oxygen, like ferric ion, is capable of direct interaction with pyrite. At 120°C, 280 psi O_2, and in 12% $Fe_2(SO_4)_3$ / 25% H_2SO_4, pyrite autoxidation proceeds at a rate approximately 7 times greater than oxidation by ferric ion. The complete rate law is given by the sum of the two corresponding expressions:

$$-\frac{d[FeS_2]}{dt} = k_1 A [Fe^{III}] + k_2 A P_{O_2}$$

where $k_1 = 1.0 \times 10^{-6}$ cm^{-2} min^{-1} and $k_2 = 1.7 \times 10^{-8}$M cm^{-2} psi^{-1} min^{-1}. Ferrous iron has no effect on the kinetics; reaction (1f) simply determines the ratio of Fe^{II} to Fe^{III} in solution. Sulfuric acid plays a beneficial role in solubilizing the products of pyrite oxidation but does not significantly alter the product distribution. Elemental sulfur is formed according to reaction (3a) at 120°C but is consumed under 280 psi O_2 via reaction (1h).

Removal of pyrite from coal is extremely sensitive to particle size, the exposed pyrite being readily oxidized. Oxidation of more deeply imbedded pyrite is probably mass-transfer limited and requires much longer residence times. Heating value loss occurs at a constant rate over time and provides incentive for minimizing residence time. Sulfuric acid concentration between 5 and 25 weight percent has no observable effect on pyrite conversion. Iron sulfates have a mildly adverse effect with Fe^{III} oxidizing organic matter at a greater rate than pyrite and Fe^{II} competing with FeS_2 for oxygen. Metal corrosion by sulfuric acid is apparently abated, however, in the presence of iron salts.

The fate of elemental sulfur is primarily determined by temperature and oxygen partial pressure. A temperature in excess of 115°C is necessary to avoid elemental sulfur production even at high O_2 partial pressure. As the temperature is increased a net reduction in elemental sulfur content can be achieved provided the O_2 partial pressure is maintained above 200 psi.

On the basis of our results, we believe that 90+% removal of pyrite from high-sulfur bituminous coal could be accomplished by using the following treating conditions:

- 125°C - 140°C
- 400 psi O_2
- minus 100 mesh coal
- 30 to 40 minutes residence time
- 25% H_2SO_4 and 10-15% $Fe_2(SO_4)_3$, both expressed relative to (H_2O + H_2SO_4 content)
- 30-40 volume % solids loading of the reactor.

Coal essential free of inorganic sulfur would be provided, along with sulfuric acid and ferric sulfate as marketable by-products.

B. Projected Desulfurization Plant Layout

The objectives of minimizing the consumption of water and purchased chemicals, and of producing marketable by-products rather than disposable wastes, can be embodied in a conceptual design utilizing the experimental data reported here. A proposed process layout is shown in Figures 4-1A and 4-1B.

Coal preparation would involve conventional crushing and grinding, probably to minus 100 mesh, with size separation and recycling as necessary. Hydraulic classification of the sized fractions would be used to separate low-, medium-, and high-density materials. Only medium-density material (i.e. with specific gravity of 1.3 to 1.6) would be subjected to chemical cleaning, the low-density material being adequately low in sulfur content and the high-density material being considered unusable.

The prepared feed is blended into recycle acid, in a 1:2 volume ratio, passes through a slurry pump, and is fed in series to a bank of autoclaves (at 140°C and 450 psig). Each autoclave is fed with 95% oxygen prepared by pressure-swing absorption through molecular sieves, and provides 10 minutes holding-time. The off-gases, withdrawn at 60% oxygen and containing CO_2 as the main impurity, may be partly recycled after adsorptive purification, or entirely purged

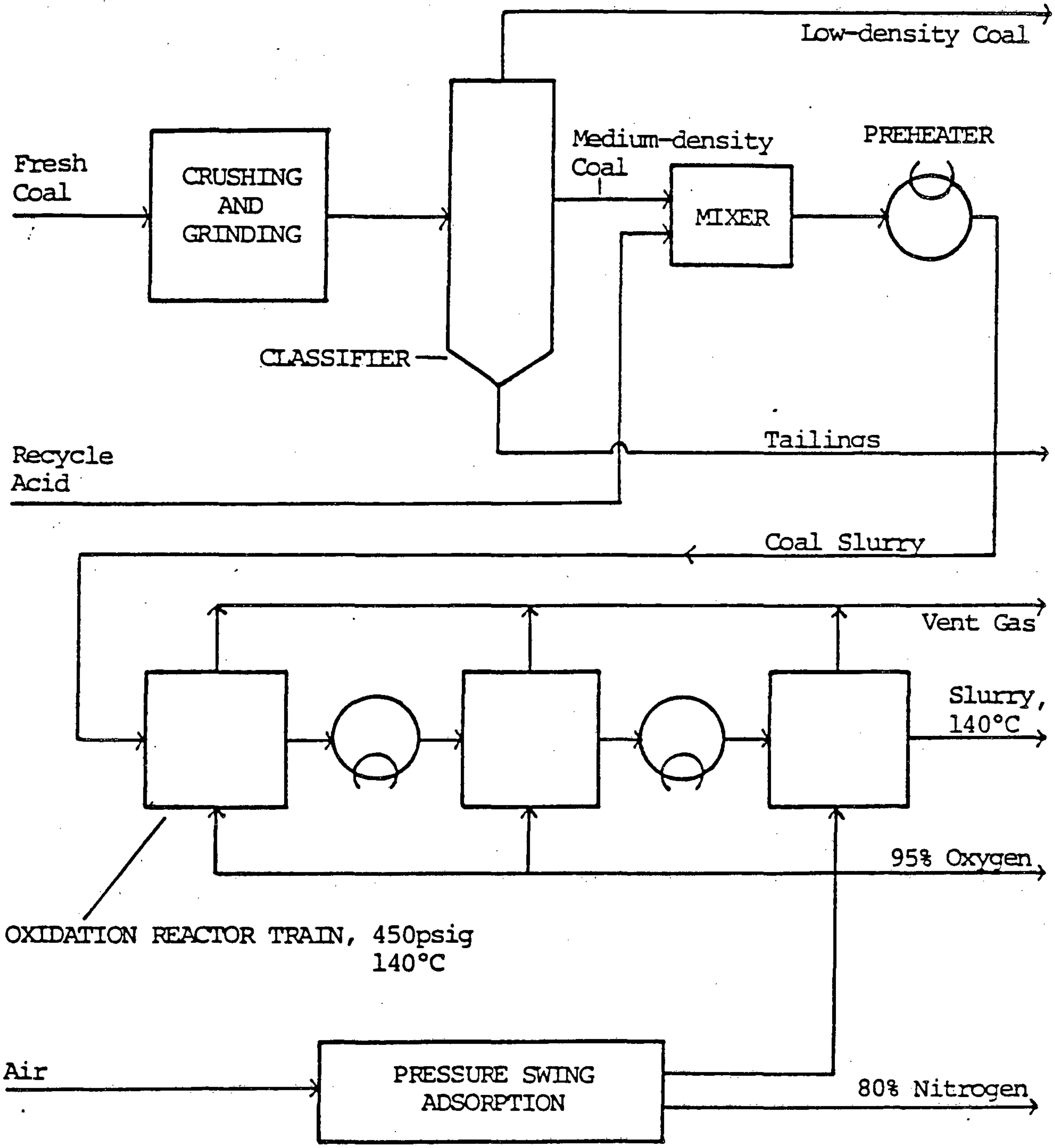

Figure 4-1.A. UCB coal desulfurization process flow diagram; desulfurization section.

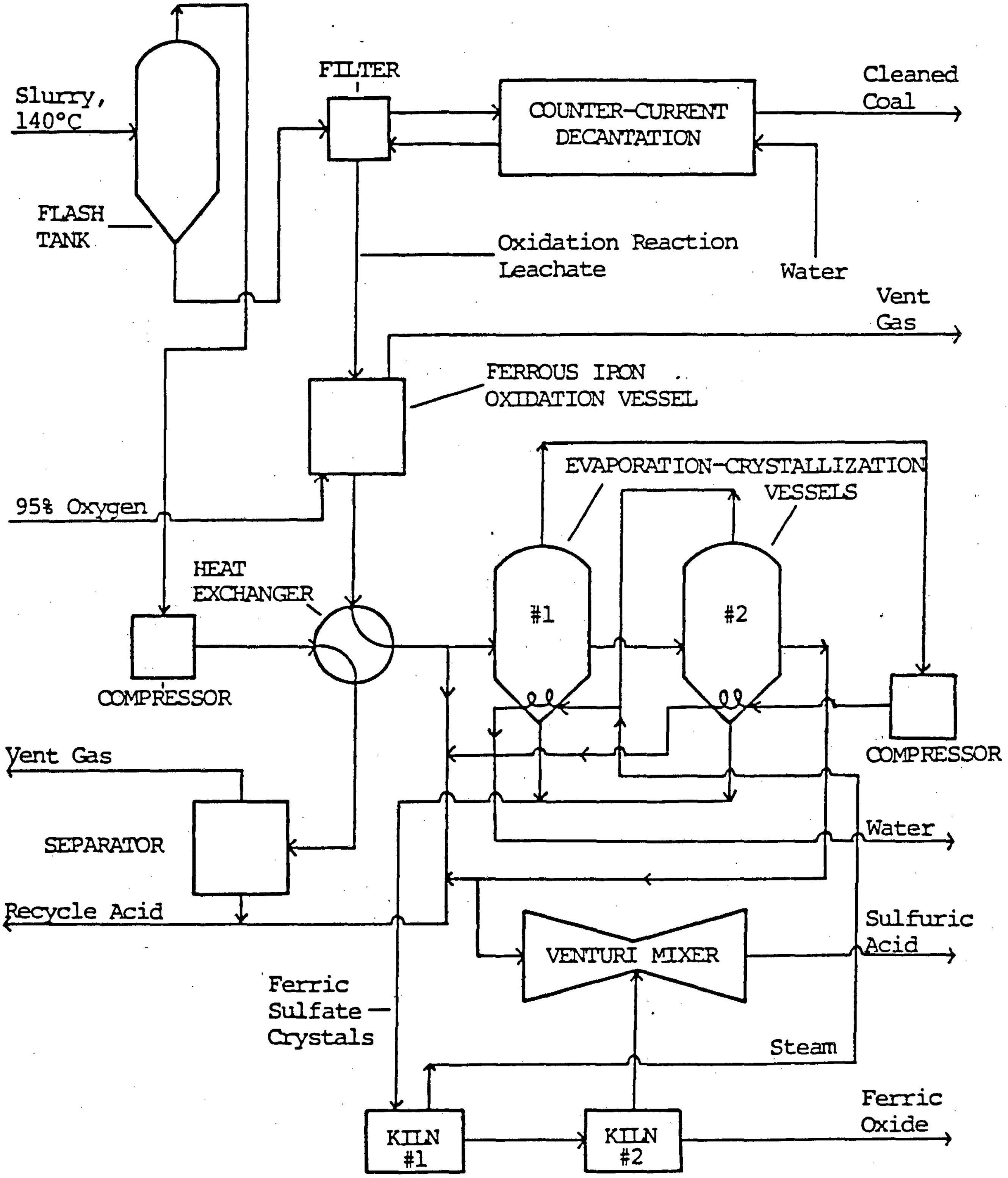

Figure 4-1.B. UCB coal desulfurization process flow diagram; recovery section.

through a vent-gas disposal system.

The treated slurry then enters a flash tank where its pressure is reduced to atmospheric, and from there passes to a washing rotary filter where coal is separated from the acid. The coal is washed with minimum amounts of water, by counter-current decantation, and the water is returned to the process. The leachate is treated with oxygen to convert all ferrous iron to the ferric form. This step could possibly be eliminated by recycling trace catalysts (e.g. Cu^{2+} or Mn^{2+}) in the leaching solution, to maintain a high concentration of Fe^{3+} during oxidative desulfurization; alternatively, a constant amount of Fe^{2+} could be allowed to build up in the leaching solution, with excess being removed in the evaporation-crystallization step.

If acid fed to the reactors contains 25% H_2SO_4 and 15% $Fe_2(SO_4)_3$, the product liquor from the ferrous iron oxidation vessel will contain about 26% and 18%, respectively. After degassing, about 82% of the acid will be recycled. The other 18% will go to double-effect evaporation and crystallization, actuated by vapor compression of steam from the first effect. The acid strength leaving the first effect will be 38%, the temperature in that effect about 120°C, and the iron sulfate about 22%. The second effect, at 150°C, will discharge 66% acid with 2% of ferric sulfate. About 78% of this product acid will be returned to the recycle acid stream, diluted with condensate and with wash liquor from the decantation to restore it to feed composition.

Ferric sulfate crystallized from the evaporators will be washed, drained dry, and fed to two kilns in series. The first, at 150°C, will discharge chemically bound water, the off-gases being cooled to condense out water and then conveyed to vent-gas disposal. The second kiln, at 520°C, will discharge gaseous sulfur trioxide and solid ferric oxide in marketable form. The ferric oxide is likely to contain minerals leached by acid from the coal; if higher-purity product is desired, the crude ferric sulfate can be recrystallized before feeding to the kilns.

The relatively small stream of 66% acid diverted from the process after evaporation passes first to a chilling crystallizer which lowers its temperature to 50°C and reduces its ferric sulfate content to 0.2%. It then enters a venturi-mixer unit which is fed with sulfur trioxide produced from the ferric sulfate, so as to bring the acid product to a concentration level of 90% or greater.

C. Removal of Organic Sulfur from Coal

Organic sulfur removal poses a much more difficult problem. Low-temperature chlorinolysis is a fairly effective technique but results in massive chlorination of the coal. Dechlorination requires extremely severe conditions and has yet to be proven totally effective. Oxidation followed by NaOH extraction results in a sizable loss of organic matter as humic acids are extracted into the basic solution. The organic sulfur content of the remaining solid is only slightly less than the starting coal. Removal of organic sulfur by liquid SO_2 extraction as reported by Burrow and Glavincevski (B4) is believed to be an artifact of their experimental procedure, namely, a nitric acid wash. It seems unlikely that actual removal of sulfur compounds from the coal's organostructure can be accomplished without bond cleavage.

Oxidative methods, while effective for removing pyrite, are not very successful in removing organic sulfur. NO_2 treatment suffers from the additional drawback of nitrating the coal. Similarly, ClO_2 treatment results in chlorination of the coal. Oxidation at 200°C in the O_2 / $Fe_2(SO_4)_3$ / H_2SO_4 system gives 38% removal of organic sulfur but considerable oxidation of organic matter also occurs, resulting in a 30% loss in heating value.

In summary, chemical removal of inorganic sulfur prior to combustion offers a realistic alternative to more expensive technologies in reducing SO_x emissions. Removal of organic sulfur, on the other hand, requires more complicated and expensive processes that, as yet, have proven only partially effective. Moreover, detrimental changes in the structure of the coal often result, further reducing their applicability. Perhaps, what is most needed is legislation that intelligently considers both economic and technological feasibility when establishing environmental standards.

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