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Chemical Desulfurization of Canadian Coal at Elevated Temperatures and Pressures

by

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A thesis submitted to the School of Graduate Studies
in partial fulfillment of the requirements for the
M.A.Sc. degree in
Chemical Engineering

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ABSTRACT

The increased utilization of coal for power generation and process heat together with more stringent enviromental emission control laws have spurred interest in pre-combustion desulfurization. The most promising type of such processes is the chemical cleaning of coal. The Meyers process using aqueous ferric sulfate as a leaching solution is the most highly developed of such processes while many others are still in different stages of development.

In this work, aqueous leaching solutions of 3 M cupric chloride, 1 M cupric sulfate and 0.1 M ferric sulfate were employed to desulfurize the high sulfur content Prince coal from Nova Scotia at elevated temperatures and pressures. Leaching tests of ferric sulfate conducted at 175 °C in a stainless steel (SS316) reactor showed that this solution is corrosive at this temperature.

In 24 hours at 200 °C with minus 35 plus 42 mesh coal samples showed total sulfur removal of 65% using cupric chloride solutions and 36% using cupric sulfate solutions. At 175 °C and 250 psig N_2 pressure, 53% of total sulfur removal was observed using ferric sulfate solution. The rate of total sulfur removal increased with an increase in temperature for all three solutions and longer reaction times did not significantly increase the amount of total sulfur removed due to retardation effects.

The ferric sulfate leaching solution was found to be the most effective in removing ash in coal with removal in the range of 27 to 65%, while solutions of cupric sulfate were only effective in removing 26 to 29% and solutions of cupric chloride were not very effective with low removal rates of 4 to 9%. This ash-removal capability was linked to the increasing presence of sulfuric acid. The reaction with ash could result in the formation of aluminium sulfate which has a retarding effect on the oxidation of pyrites and results in incomplete oxidation of inorganic sulfur as was observed for both ferric sulfate and cupric sulfate solutions.

Coal treated at 200 °C with cupric chloride solution for 24 hours was observed to have lost 1628 Btu/lb of its heating value while treatment with cupric sulfate solutions at 200 °C for one hour only resulted in a loss of 252 Btu/lb. Treatment with 0.1 M ferric sulfate solution at 150 °C and 250 psig O_2 pressure for half an hour showed a small gain in heating value of 70 Btu/lb.

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I. INTRODUCTION

The projected depletion of petroleum and natural gas supplies has resulted in increasing attention being paid to the future increased utilization of coal as a source of energy as well as a feedstock for chemicals. The increased utilization of coal combustion for the generation of electric power and process heat requires the control of pollutants which are potentially harmful to man or enviroment. Although the control of emissions of particulates, nitrogen oxides, and trace elements is receiving attention, most effort has been directed towards the control of emission of sulfur in the form of sulfur-dioxide.

During combustion, the sulfur in coal is converted to enviromentally hazardous, gaseous sulfur oxides. In general, the fate of sulfur dioxide emissions involves photo-oxidation(15) in the atmosphere to form sulfur trioxide which, under humidifying conditions, becomes sulfuric acid or sulfate aerosol which eventually returns to the ground in the form of acid rain. Acid rain, having a pH below 5.6 (which is the pH of normal rain due to the presence of carbonic acid)(18), is now recognized as a worldwide phenomenon correlating with the atmospheric burden(31). Sulfuric acid and acid sulfates can damage vegetation, animal and plant life in lakes, building materials, and soil.

Statistical studies have linked atmospheric sulfur oxides to numerous health defects, including chronic respiratory disease, aggravated heart and lung disease, asthma, and lower respiratory disease of children(56). Recent estimates by Enviroment Canada of sulfur dioxide emissions in North America indicates that about 30.7 million tonnes per year is emitted into the air(17). Of that total, about 25.7 million tonnes come from U.S. sources and the remaining 5 million tonnes are from Canada.

To counter this enviromental problem and to protect public health, more stringent enviromental regulations and flue gas emission control laws have been passed in the United States. The Enviromental Protection Agency (EPA) emission regulations specify 1.2 lb sulfur dioxide per million Btu as the maximum two-hour average emission for existing facilities and no more than 10% (for high-sulfur coals) to 30% (low-sulfur coals) of the sulfur in Run-of-mine coal to escape into the atmosphere. The need to meet these guidelines economically has spurred interest in several potential areas of desulfurization.

The emission of sulfur dioxide from coal combustion may be controlled by one or more of the following:-

1). the use of low sulfur content coal;
2). the conversion of coal into a liquid or gaseous form;
3). the retention of sulfur during combustion;
4). the post-combustion treatment of flue gases;
5). the pre-treatment of coal to remove sulfur;

Reserves of coal which contain sufficiently low concentrations of sulfur to enable sulfur dioxide emission standards to be met when coals are burned are limited and restricted to specific geographical locations. Presently, the expensive costs of coal conversion preclude the use of coal derived liquids or gases for combustion. Processes which retain sulfur during combustion such as fluidized bed combustion (FBC) with limestone as the sulfur retainer are currently being tried and developed(12). The most common method of controlling sulfur dioxide emissions is by the use of flue gas desulfurization (FGD). However, for efficient capture of sulfur dioxide gases, two or more of flue gas scrubbers in series are usually required. Hence, FGD equipment represents a significant portion of the equipment cost of a coal fired power station and this portion increases as the size of the plant decreases making FGD expensive for small industrial boilers(4,39). The remaining option for controlling sulfur dioxide emissions is that of pretreating coal to remove sulfur prior to combustion. Physical or mechanical cleaning of coal by washing and gravity separation is widely employed in the coal industry to remove mineral matter from coal. Such processes are capable of removing 30 to 90% of the pyritic sulfur associated with the mineral matter in coal but can also result in a loss of about 50% of the coal matter. In addition, some coals may have 50% of the total sulfur bound in the organic matrix and this portion cannot be removed by washing processes. In order to decrease the sulfur content of such coals to acceptable levels it is necessary to treat the coal chemically to remove both organic and inorganic sulfur. This is chemical coal cleaning. No such process is, as yet, available commercially although several are under active development. The majority of chemical coal cleaning processes are designed to produce coals with sufficiently low sulfur contents to permit their combustion for power generation without the use of flue gas desulfurization, though some studies have shown that a combination of both coal cleaning and FGD is cheaper than each process being employed individually.

In this study, the Meyers desulfurization process (41) (ferric sulfate leaching) will be employed at elevated temperature and pressures to test its effectiveness in removing pyritic sulfur from the high-sulfur content Prince Coal from Nova Scotia. A second part of this study will employ aqueous solutions of cupric chloride and cupric sulfate (copper salts employed by Stokes (52) to differentiate between pyrite and marcasite) to chemically desulfurize coal and to check whether copper solutions are capable of removing the organic sulfur in coal.

II. LITERATURE SURVEY

The goal of chemical desulfurization processes is to remove the sulfur compounds from the coal whether it is organically bound within the coal matrix or it is present in the inorganic form. To achieve this goal requires an understanding of the nature, properties and types of sulfur in coal. The following sections will include the literature surveys on the structure of coal, forms of sulfur in coal and the reaction chemistry of coal cleaning together with proposed methods of utilizing high-sulfur content coal.

A. Coal and Its Sulfur Compounds

Coal is a highly heterogeneous solid originating from the arrested decay of the remains of plant substance many million of years ago. The precursor of coal was peat, which was formed by bacterial and chemical action on the plant debris. Subsequent actions of heat, pressure and other physical phenomena metamorphosed the peat to various ranks of coal as we know them today. Because of the various degrees of the metamorphic changes during this process, coal is not a uniform substance, and no two coals are ever the same in every respect.

1. Chemical Structure of Coal

Coal can be considered a rock structure containing both macroscopic and microscopic petrographic features(40). The organic matrix of coal consists mainly of carbon, with smaller amounts of hydrogen, oxygen, nitrogen and sulfur. An arbitrary model for the organic matrix of coal proposed by Given(24) is shown in Figure 2-1. This structure was based on spectroscopic and carbon/hydrogen ratio data, as well as a knowledge of the chemical reactions of coal with bromine and oxygen.

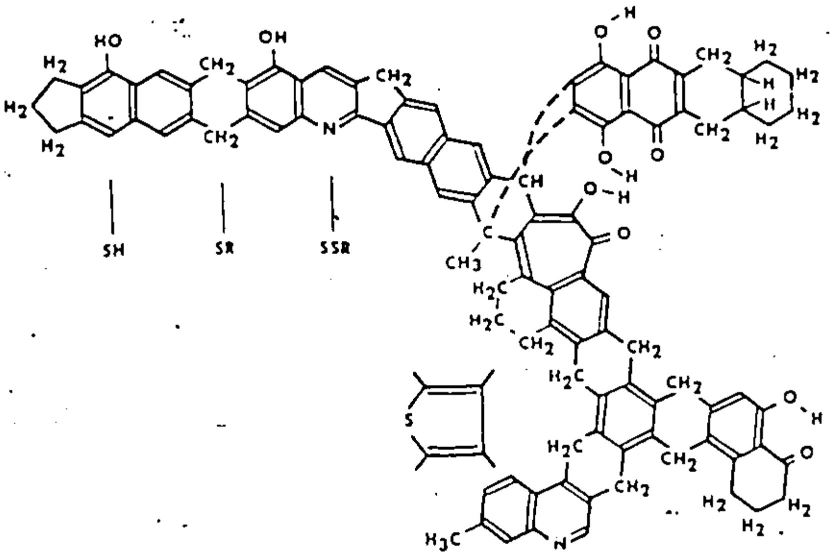


Figure 2-1 Model of Organic Coal Matrix(24)

2. Sulfur In Coal

Sulfur is recognized as one of the major impurities in coal. Its concentration in world coal resources varies between 0.19% and 10%(57), although the range for the world's economically recoverable coal resources is narrower being 0.38% to 5.32%(40).

Sulfur in coal occurs as:

1). Pyritic sulfur;
2). Organic sulfur;
3). Sulfate sulfur;
4). Elemental sulfur;

Pyritic and organic sulfur together account for the large majority of sulfur in coal. Sulfate sulfur occurs chiefly as gypsum ($CaSO_4.2\,H_2O$) and iron sulfate ($FeSO_4$). The amount of sulfate sulfur in coal is generally less than 0.1% and is also soluble in water or acid and is readily removed by washing. The concentration of elemental sulfur in coal is also small, being generally less than 0.2%(27).

2.1 Pyritic Sulfur

The term pyritic sulfur is used to refer to either of the two forms of iron sulfide-FeS_2: pyrite (cubic) and marcasite (orthorhombic). These sulfide forms have the same chemical compositions and thus are difficult to distinguish.

However, in most coals pyrite is usually the more abundant form so that pyrite and marcasite are often collectively referred to as pyrites or iron pyrites. Pyrite in coals can occur in both macroscopic and microscopic forms as(23) :-

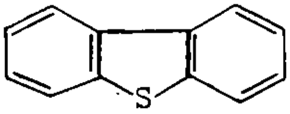
1). Narrow seams or veins up to 150 millimeters thick and up to several hundred millimeters long.
2). Nodules. These consist of framboids which range from a few micrometers to several hundred micrometers in diameter, with most of them being approximately 10 to 20 micrometers in diameter. The framboids consist of assemblies of octahedral crystals.
3). Discrete crystals. These individual pyrite particles may be widely dispersed throughout the coal. They occur mainly between a size range of about 1 to 40 micrometers in diameter, with a major portion of the crystals being between 1 and 2 micrometers in diameter.

The first two types can usually be removed by mechanical cleaning methods, but for the third type the chemical method is necessary because this form of pyrite cannot be completely removed by physical coal cleaning methods as it is uneconomical to grind coal to this order of size and coal matter is rejected along with pyrites.

2.2 Organic Sulfur

The organic sulfur in coal occurs as sulfur bounded within the coal matrix. There exists very little data on the organic sulfur functions in coal. However, it is generally assumed that the organic sulfur can be described by the following classification(46) :

1). Aliphatic or aromatic thiols (mercaptans, thiophenols)
 : R-SH, AR-SH
2) Aliphatic, aromatic or mixed sulfides (thioethers)
 : R-S-R, AR-S-AR, R-S-AR
3). Aliphatic, aromatic or mixed disulfides (bithioethers)
 : R-S-S-R, AR-S-S-AR, R-S-S-AR
4). Heterocyclic compounds of the thiophene type (dibenzothiophene)
 :



Some evidence indicates that the content of thiols is substantially larger in lignites and high volatile bituminous coals than in low volatile coals. The proportion of thiophenic sulfur is also greater in higher ranked coals(3).

In general, organic sulfur is dominant in low-sulfur coal (less than 1.0%) and pyritic sulfur is dominant in high-sulfur coal. Hence, physical coal cleaning is useful in reducing the sulfur content of high-sulfur coals but is less effective when applied to low-sulfur coals.

Table 2-1 gives the sulfur forms of some of the bituminous coals of the world.

TABLE 2-1

Sulfur Forms In Selected Bituminous Coal-Worldwide(40)

Country	Location or mine	Sulfur content. w/w %[1]			Ratio of pyritic to organic sulfur
		Total	Pyritic	Organic	
Australia	Lower Newcastle	0.94	0.15	0.79	0.19
Brazil	Santa Caterina	1.32	0.80	0.53	1.5
Canada	Fernie	0.60	0.03	0.57	0.053
China	Taitung	1.19	0.87	0.32	2.7
Germany	-	1.78	0.92	0.76	1.2
India	Tipong	3.63	1.59	2.04	0.78
Japan	Miike	2.61	0.81	1.80	0.45
Malaysia	Sarawak	5.32	3.97	1.35	2.9
Poland	-	0.81	0.30	0.51	0.59
South Africa	Transvaal	1.39	0.59	0.70	0.84
UK	Derbyshire	2.61	1.55	0.87	1.8
USA	Eagle No. 2	4.29	2.68	1.61	1.7
USSR	Shakhtersky	0.38	0.09	0.29	0.031

[1] Moisture-free basis, pyrite plus sulfate reported as pyrite

3. Other Impurities In Coal

Other impurities in coal are moisture, minerals, and clay. The major minerals present in U.S. bituminous coals are listed in Table 2-2(40).

TABLE 2-2

Minerals Associated with U.S. Bituminous Coals[a]

Group	Species	Formula
Shale	Muscovite	$(K,Na,H_2O\ Ca)_2(Al,Mg,Fe,Ti)_4(Al,Si)_8O_{20}(OH,F)_4$
	Hydromuscobite	
	Illite	
	Bravaisite	
	Montmorillonite	
Kalin	Kaolinite	$Al_2(Si_2O_5)(OH)_4$
	Livesite	
	Metahalloysite	
Sulfide	Pyrite	FeS_2
	Marcasite	
Carbonate	Ankerite	$(Ca,Mg,Fe,Mn)Co_3$
	Ankeritic calcite	
	Ankeritic dolomite	
	Ankeritic chalybite	
Chloride	Sylvine	KCl
	Halite	NaCl

---

a-based on optical microscopy, spectroscopy and analysis of ash content obtained after combustion of the organic coal

B. Chemistry of Coal Desulfurization

1. Chemical Reaction of Pyrites

The chemical reactions of iron pyrite are numerous and so far no solvent which will dissolve significant amounts of iron pyrite without decomposition has been observed. Therefore removal of pyritic sulfur from coal necessitates chemical transformation. Meyers$^{(40)}$ categorizes the reactions of pyrite which are theoretically capable of proceeding at temperatures below the decomposition temperature of coal (approximately 400 °C) as :-

1). A displacement reaction (Eq. 2.1-1)

$$:\!\ddot{\underset{..}{N}}\!: \quad FeS_2 \longrightarrow :\!\ddot{\underset{..}{N}}\!:Fe \quad + \quad S_2^{-2} \qquad (2.1\text{-}1)$$

2). An acid base neutralization (2.1-2)

$$4\,H^{+} + FeS_2 \rightarrow 2H_2S + Fe^{+2} \qquad (2.1\text{-}2)$$

3). An oxidation reaction (2.1-3)

$$O + FeS_2 \rightarrow Fe^{+2} + 2\,S + O^{-2} \qquad (2.1\text{-}3)$$

4). A reduction reaction (Eq. 2.1-4, 2.1-5)

$$FeS_2 + H_2 \rightarrow FeS + H_2S \qquad (2.1\text{-}4)$$

$$FeS + H_2 \rightarrow Fe + H_2S \qquad (2.1\text{-}5)$$

Most of the pyrite reaction reported in the literature are oxidation and reduction reactions. No neutralization reactions are reported and studies on displacement reactions have recently begun.

2. Oxidation of Iron Pyrite

The sulfur content of iron pyrite can be oxidized to form elemental sulfur (Eq. 2.2-1) or sulfate (Eq. 2.2-2).

$$FeS_2 \rightarrow Fe^{+2} + 2\ S + 2e^- \qquad (2.2\text{-}1)$$

$$FeS_2 + 8\ H_2O \rightarrow Fe^{+2} + 2\ SO_4^{-2} + 16\ H^+ + 14e^- \qquad (2.2\text{-}2)$$

The standard reduction potential of these half-reactions as determined by Biernat and Robins$^{(10)}$ are +0.421 and +0.362 respectively. These reduction potentials are dependent on temperature, pH and concentrations of sulfate and ferrous ion. An example is that at high pH, the SO_4^{-2}/FeS_2 couple can tend toward the H^+/H_2 potential (i.e. 0.00). Oxidants ranging from metal ions (Fe^{+3}, Hg^{+2}, Ag^+) through strong acids (HNO_3 and $HClO_4$) as well as O_2, Cl_2, SO_2 and H_2O_2 have sufficient potential to oxidize iron pyrite according to the standard reduction potentials given in Latimer$^{(30)}$. Table 2-3 summarizes the important ones for our studies.

2.1 Cu^{+2} as Oxidizing Agent

The standard reduction potential of Cu^{+2} is +0.167. At low acidity Cu^{+2} may have the potential to oxidize pyrite. The action of copper salts on mineral pyrite was reported by Stokes$^{(52,53)}$ in 1907. He observed that mineral pyrite is completely converted into ferrous salt and sulfuric acid by

TABLE 2-3

Standard Reduction Potentials in Aqueous Acid Solutions(40)

$H^+ + e^- = 1/2\ H_2$	+0.00
$Cu^{+2} + e^- = Cu^+$	+0.167
$Fe^{+2} + 2\ SO_4^{-2} + 16\ H^+ = FeS_2 + 8\ H_2O$	+0.362
$Fe^{+2} + 2\ S + 2e^- = FeS_2$	+0.421
$1/2\ O_2 + 2\ H^+ + 2e^- = H_2O$	+1.229
$1/2\ Cl_2 + e^- = Cl^-$	+1.34
$Fe^{+3} + e^- = Fe^{+2}$	+0.771
$NO_3^- + 3\ H^+ + 2e^- = HNO_2 + H_2O$	+0.94

aqueous cupric chloride solutions at 200 °C according to (Eq. 2.2-3).

$$FeS_2 + 14\ CuCl_2 + 8\ H_2O \rightarrow 14\ CuCl + FeCl_2 + 2\ H_2SO_4 + 12\ HCl \quad (2.2\text{-}3)$$

In addition, he also observed that the reaction between pyrite and aqueous solutions of cupric sulfate at the same temperature results in the formation of sulfuric acid, but the sulfur is not completely oxidized, a portion remaining in the form of sulfides of copper. The reactions resulting in the formation of cuprous sulfide (Eq. 2.2-4) and cupric sulfide (Eq. 2.2-5) were :

$$5\ FeS_2 + 14\ CuSO_4 + 12\ H_2O \rightarrow 7\ Cu_2S + 5\ FeSO_4 + 12\ H_2SO_4 \quad (2.2\text{-}4)$$

in which 30% of the sulfur is oxidized, or

$$4\ FeS_2 + 7\ CuSO_4 + 4\ H_2O \rightarrow 7\ CuS + 4\ FeSO_4 + 4\ H_2SO_4 \qquad (2.2\text{-}5)$$

in which 12.5% of the sulfur is oxidized. Stokes(54) mentioned that the actual reaction is more complicated since cuprous sulfide (Cu_2S) is attacked by cupric sulfate while cupric sulfide is resistant to this attack. Experiments showed that oxidation percentages were 18.4% and 20.65% for two runs and from these results he concluded that both reactions take place.

Additional reactions could also take place in the cupric sulfate reactions according to Stokes(54) with cupric sulfate($CuSO_4$) and ferrous sulfate($FeSO_4$)(Eq. 2.2-6), pyrite and cupric sulfate (Eq. 2.2-7) and cuprous sulfide and cupric sulfate (Eq. 2.2-8).

$$2\ CuSO_4 + 2\ FeSO_4 \longrightarrow Cu_2SO_4 + Fe_2(SO_4)_3 \qquad (2.2\text{-}6)$$

$$FeS_2 + 14\ CuSO_4 + 8\ H_2O \longrightarrow 7\ Cu_2SO_4 + FeSO_4 + 8\ H_2SO_4 \qquad (2.2\text{-}7)$$

$$Cu_2S + CuSO_4 \longrightarrow CuS + Cu_2SO_4 \qquad (2.2\text{-}8)$$

In all cases, metallic copper can be deposited according to (Eq. 2.2-9).

$$Cu_2SO_4 \longrightarrow Cu + CuSO_4 \qquad (2.2\text{-}9)$$

2.2 Fe^{+3} and O_2 as Oxidizing Agents

In most of the experiments reported to date on the oxidation of pyrite (FeS_2) by ferric ion (Fe^{+3}) or oxygen (O_2), only the following products have been observed : ferrous sulfate ($FeSO_4$), ferric sulfate ($Fe_2(SO_4)_3$), sulfuric acid (H_2SO_4), and elemental sulfur (S). According to Mckay and Halpern(35) reactions of O_2 with FeS_2, S and $FeSO_4$ could involve the following :

$$FeS_2 + 2\ O_2 \longrightarrow FeSO_4 + S \qquad (2.2\text{-}10)$$

$$2\ FeS_2 + 7\ O_2 + 2\ H_2O \longrightarrow 2\ FeSO_4 + 2\ H_2SO_4 \qquad (2.2\text{-}11)$$

$$2\ S + 3\ O_2 + 2\ H_2O \longrightarrow 2\ H_2SO_4 \qquad (2.2\text{-}12)$$

$$8\ FeSO_4 + 2\ O_2 + H_2SO_4 \longrightarrow 4\ Fe_2(SO_4)_3 + 4\ H_2O \qquad (2.2\text{-}13)$$

Experiments performed in the absence of oxygen produced hydrogen sulfide (35) and its presence was attributed to the reaction of (Eq. 2.2-14)

$$FeS_2 + H_2SO_4 \longrightarrow H_2S + FeSO_4 + S \qquad (2.2\text{-}14)$$

The hydrogen sulfide thus produced could then be oxidized by oxygen according to the following reactions :

$$2\ H_2S + O_2 \longrightarrow 2\ H_2O + 2\ S \qquad (2.2\text{-}15)$$

$$H_2S + 2\ O_2 \longrightarrow H_2SO_4 \qquad (2.2\text{-}16)$$

Oxidation reactions by ferric sulfate may occur according to the following equations(35,40) :

$$FeS_2 + 7\ Fe_2(SO_4)_3 + 8\ H_2O \longrightarrow 15\ FeSO_4 + 8\ H_2SO_4 \qquad (2.2\text{-}17)$$

$$FeS_2 + Fe_2(SO_4)_3 \longrightarrow 3\ FeSO_4 + 2\ S \qquad (2.2\text{-}18)$$

$$S + 3\ Fe_2(SO_4)_3 + 4\ H_2O \longrightarrow 6\ FeSO_4 + 4\ H_2SO_4 \qquad (2.2\text{-}19)$$

From the above equations (Eq. 2.2-10, Eq. 2.2-14, Eq. 2.2-15, Eq. 2.2-18) , it can be seen that elemental sulfur can be produced in a number of ways. However, this species is thermodynamically unstable in the oxidizing system under consideration and its presence must be due to chemical kinetic effects(43).

The products from the oxidation of pyrite by O_2 and Fe^{+3} have been controversial. The earliest of such studies performed by Mckay and Halpern(35) employed temperatures between 100 °C to 130 °C, oxygen partial pressures up to 60 psi and sulfuric acid concentration from 0 to 0.15 M. They concluded that elemental sulfur formation was favoured by high acidity and low temperatures (Eq. 2.2-10) and the reverse conditions of low acidity and high temperatures produced mainly sulfuric acid (Eq. 2.2-11) . Recent studies by Mathew and Robins(34) using O_2 at low acidity between 30 to 70 °C to oxidize pyrite did not report elemental sulfur as a reaction product. Similar studies by Majima and Peters(55) with temperatures above 100 °C and higher acidities (pH less than 2) detected fairly large quantities of elemental sulfur (~50%).

Mathews and Robins(33) also studied the oxidation of pyrite with dilute aqueous $Fe_2(SO_4)_3$ solutions at different concentrations of 10^{-4} to 0.12 M and temperatures between 30 to 70 °C and products of ferrous sulfate and sulfuric acid were observed. Similar studies by Meyers(40) with 1 M $Fe_2(SO_4)_3$ solutions at temperatures between 80 to 130 °C and both in the presence and absence of O_2 yield both sulfate and elemental sulfur as products according to the following equation (Eq. 2.2-20):

$$5\ FeS_2 + 23\ Fe_2(SO_4)_3 + 24\ H_2O \rightarrow 51\ FeSO_4 + 24\ H_2SO_4 + 4\ S \quad (2.2\text{-}20)$$

He also stated that elemental sulfur is kinetically stable in acid systems at 110 °C with 150 psi oxygen partial pressure.

McKay and Halpern(35) also stated that the oxidation of pyrite in their studies was due to oxygen only and that the presence of ferric sulfate produced according to Eq. 2.2-13 is too slow to contribute significantly to the oxidation of pyrite. In contrast, Meyers(40) has stated that O_2 does not react with pyrite below 300 °C in aqueous systems, and that Fe^{+3} is the primary reactant even in the presence of large quantities of oxygen. He justified such statements from observations on studies of ferric sulfate between temperatures of 100 to 130 °C which gave the same pyrite oxidation rates and product distribution with or without O_2 provided at up to 85 psi partial pressure. Meyers further claims that generation of Fe^{+3} by Eq. 2.2-13 is faster than the oxidation reactions of FeS_2 by oxygen and that this is the reason for observations of oxidation of pyrite by

O_2 at low temperatures.

Mixon and Vermeulen(43) studied the action of various concentrations of $Fe_2(SO_4)_3$, H_2SO_4 , and O_2 partial pressure on the oxidation of coal pyrite at temperatures up to 150 °C. They concluded that a minimum of 220 psi oxygen partial pressure is necessary for oxygen to be directly involved in the oxidation mechanism. They also observed under conditions of 25% H_2SO_4, 12% $Fe_2(SO_4)_3$ and 420 psi oxygen pressure that at 110 °C elemental sulfur content increases over its feed level and at 120 °C or higher temperatures elemental sulfur content decreases.

3. Removal of Organic Sulfur from Coal by Oxidation

Oxidation with Fe^{+3}/O_2 can potentially convert organic sulfides successively to sulfones, sulfoxides, and sulfonic acids, which may then be hydrolysed in an aqueous system to eliminate sulfur from the organic matrix(43). In this way oxygen would replace the sulfur in an alcohol group. Oxidation of the coal matrix can also occur producing CO, CO_2 and humic acids. These reaction rates increase rapidly above 150 °C. Oxygen addition to the coal matrix for the removal of organic sulfur is an exothermic reaction so that organic sulfur removal by this method means a loss of the coal's heating value. An example of how the sulfur can be removed by this method is as follows(40):

$$R_1 S_x R_2 \xrightarrow{\boxed{O}} R_1SO_3H + R_2SO_3H \xrightarrow[\triangle]{H_2O} R_1OH + R_2OH + 2\ H_2SO_4 \qquad (2.2\text{-}21)$$

C. Methods Proposed For Utilizing High-Sulfur Coals

One of the methods currently employed to minimize sulfur dioxide emissions is to burn only low-sulfur coals. The disadvantage of this practice is that supplies of this grade of coal must be obtained from low-sulfur coal bed areas. Rather than limit the use of coal to low-sulfur types, methods have been proposed and some are still under development for reducing sulfur oxide emissions caused by the burning of high-sulfur coal for fuel. These methods include flue gas desulfurization, fluidized bed combustion and pre-combustion desulfurization processes.

1. Flue Gas Desulfurization

Flue gas desulfurization (FGD) processes are post-combustion emission control methods whereby huge volumes of exhaust gases from coal combustion are chemically scrubbed to remove sulfur oxides. The flue gas desulfurization methods currently being used or developed use limestone, lime, magnesium - oxide, sodium sulfite or basic fly ash in aqueous solutions to capture sulfur oxides with recovered products ranging from calcium sulfite/sulfate sludge or gypsum to sulfuric acid, sulfur dioxide and elemental sulfur.

The above FGD processes are termed wet systems because the flue gases are totally saturated with the capture reactant and the reaction products are collected in a wet phase. There are both non-regenerable and regenerable wet scrubbing processes. Non-regenerable processes are defined as those in which the scrubbing media are disposed of as solid or liquid wastes. In regenerable processes the scrubbing medium is regenerated and reused whilst SO_2 is recovered in a form which may be processed further to sulfuric acid or elemental sulfur. Figure 3-1 shows the flow diagram for this type of regenerable process(43). Such processes require more energy and are more complex than non-regenerable processes. Table 3-1 summarizes the key chemical reactions taking place in three types of of wet flue gas desulfurization process(56).

A disadvantage of the wet FGD process is that during the scrubbing process evaporation of water cools the flue gas to slightly below its dew point. This results in two additional processing steps being required. Mist eliminators are required to remove entrained droplets of scrubbing media and it is also necessary to reheat the flue gas to about 130 °C to prevent condensation, fouling and corrosion in ducts, fans and stacks; to avoid a visible plume; and to improve plume dispersion from the stack(56). Such problems could be overcome by collecting the SO_2 in a dry process. The process is a slight modification of the conventional FGD process where the saturated alkaline contact solution is replaced by a finely atomized spray of alkaline absorbent(44). A controlled amount of liquid is vaporized by the flue gas and the dry reacted product is

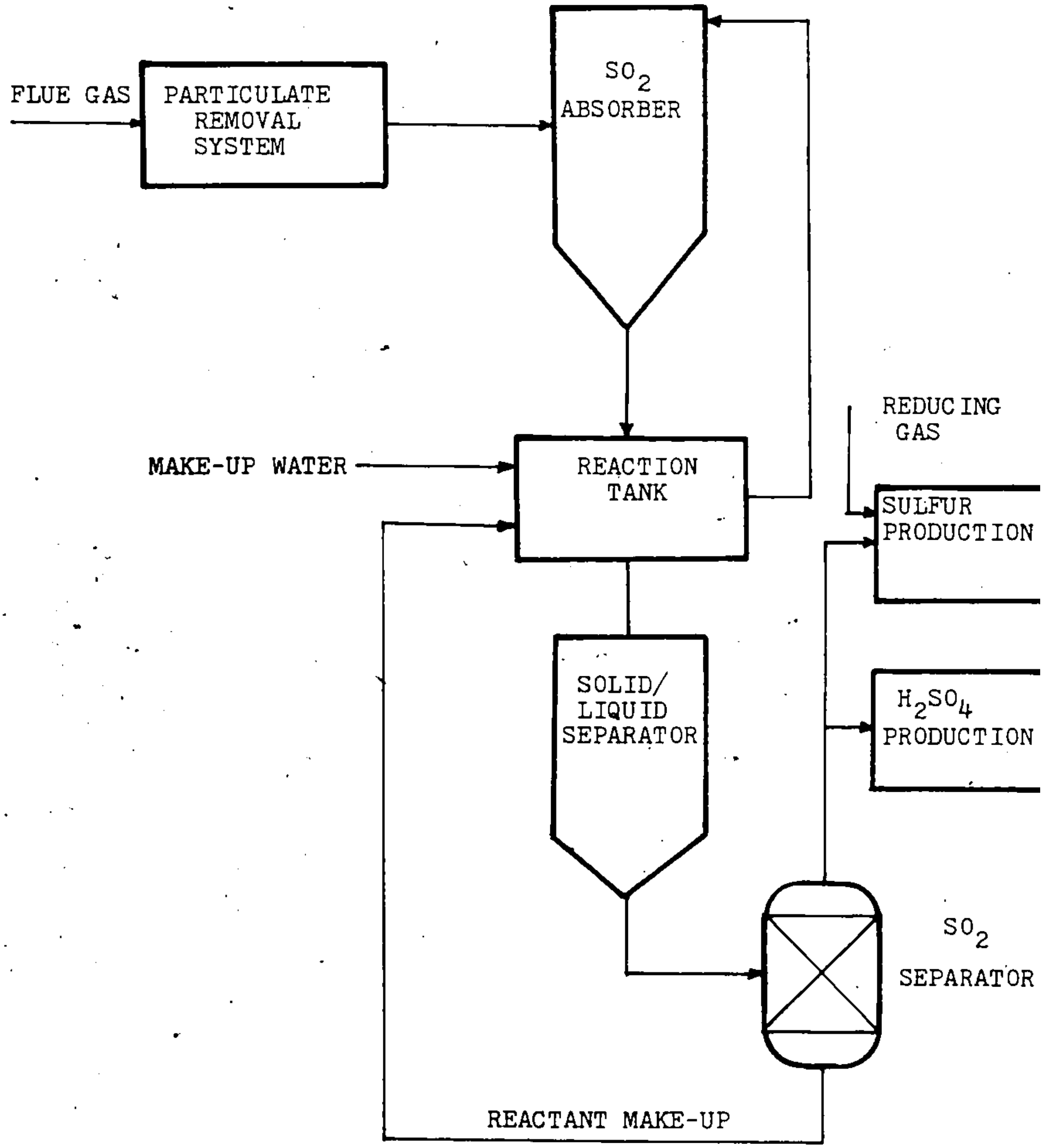


Figure 3-1. Process Flow Diagram For a Wet Regenerable Flue Gas Desulfurization System.(43).

TABLE 3-1

Process Chemistry of Three Types of Flue Gas Desulfurization Systems(56)

Limestone Process:

$CaCO_3 = CaO + CO_2$

$CaO + SO_2 = CaSO_3$

$CaSO_3 + 1/2\ O_2 = CaSO_4$

Dual Alkali Process:

$Na_2SO_3 + SO_2 + H_2O = 2\ NaHSO_3$

$2\ Na_2CO_3 + SO_2 + H_2O = Na_2SO_3 + 2\ NaHCO_3$

$NaHCO_3 + SO_2 = NaHSO_3 + CO_2$

$2\ NaOH + SO_2 = Na_2SO_3 + H_2O$

$Na_2SO_3 + 1/2\ O_2 = Na_2SO_4$

followed by regeneration with slaked lime, $Ca(OH)_2$

$2\ NaHSO_3 + Ca(OH)_2 = Na_2SO_3 + CaSO_3 + 2\ H_2O$

$Na_2SO_4 + Ca(OH)_2 + 2\ H_2O = 2\ NaOH + CaSO_4 \cdot 2H_2O$

Magnesium Oxide Process:

$Mg(OH)_2 + SO_2 = MgSO_3 + H_2O$

$MgSO_3 = MgO + SO_2$

collected downstream in a baghouse. The advantage of this system is claimed to be the removal of both SO_2 and particulate matter in one step with an extra 20 to 30% SO_2 removal capability as a result of the flue gas being physically forced through the alkaline powder being collected on the bags. Figure 3-2 shows a typical dry flue gas desulfurization process. The advantage of dry SO_2 flue gas desulfurization processes over wet scrubbing processes include; a dry product; lower capital costs; lower energy and water requirements; and a more simple design which should be reflected in increased availability and reduced maintainance. Development is still continuing for this system to increase removal efficiencies to that of wet scrubbers.

At its present state of development FGD processes consumes about 10 to 30% of the coal heating value in removing SO_2. Between 70 to 90% of SO_x in flue gases may be removed but at the expense of high capital investment and high operating cost(39). For example, the estimated cost for a plant purchased in 1985 to comply with enviromental regulations will account for up to 46% of the capital cost and 60% of the operating costs. One of the main economic disadvantages posed by FGD process is that the sulfur-removal plant must be designed for peak power loading, when power requirements are less than maximum, part of the capital investment is essentially unused. Extensive research is still being continued to improve the economics of flue gas desulfurization.

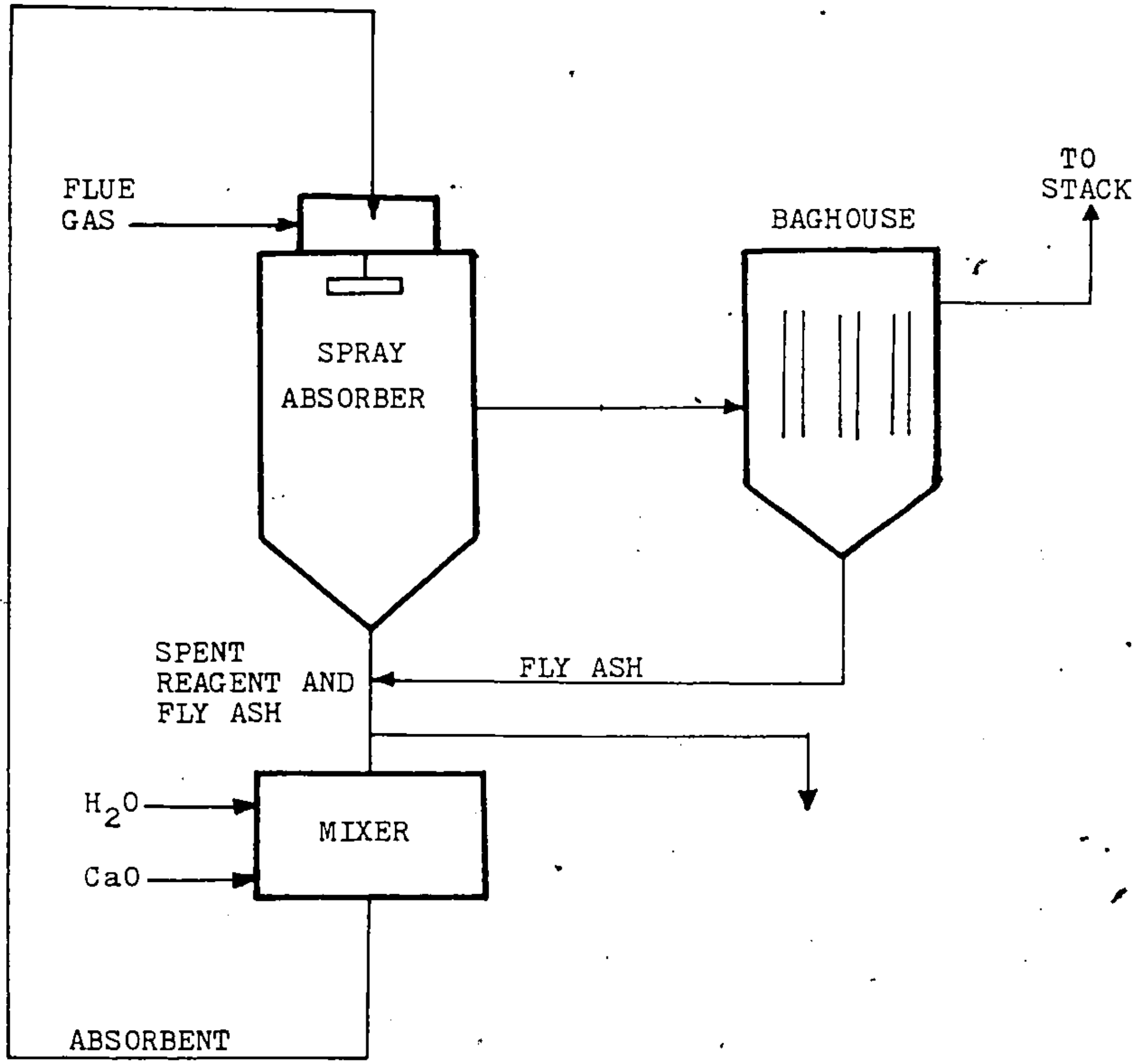


Figure 3-2. Flow Diagram For A Typical Dry Flue Gas Desulfurization Process (44)

2. Fluidized Bed Combustion

In fluidized bed combustion (FBC) processes, combustion of coal takes place in a bed of limestone suspended by air. Sulfur oxides formed from combustion of coal are immediately absorbed by the bed material thus achieving an in-situ desulfurization. As with some of the flue gas desulfurization processes, the chemical reaction for SO_x removal is the calcination of limestone which then reacts with SO_2 and O_2 to give calcium sulfate. Advantages of this method are the high rates of heat transfer to the boiler tubes immersed in the fluidized bed, low combustion temperatures (850-900 ^oC), low NO_x generation, and the ability to meet emission requirements with high-sulfur and low grade coals(12). FBC processes are capable of removing 90% or more of the SO_2 emissions of most coals. However, at the particle sizes required in FBCs, only a small part (about 20%) of the active constituent in the sorbent is available for reaction with SO_2 and high sorbent to sulfur ratios are required. Further development and research are currently continuing in areas of sorbent enhancement techniques and sorbent regeneration to reduce the amount of sorbent required for a given level of SO_2 removal.

3. Pre-Combustion Desulfurization

3.1 Coal Conversion

During the past decade increasing attention has been centered on the removal of sulfur prior to combustion by converting coal into sulfur-free liquid or gaseous fuel. Liquefaction, the conversion of coal into liquid fuels was experimentally performed in 1913 by Berguis. The method involved subjecting coal slurry in an organic solvent with hydrogen gas at high temperatures and pressures. Current liquefaction processes employ the same principle as the original Berguis liquefaction but with different organic solvents and different operating conditions.

A slight modification of the liquefaction process is solvent refined coal (SRC) which is a solid product produced by the treatment of coal in an organic solvent at high temperature and pressure(60). This product which is suitable for use in boilers has up to 60% of the organic sulfur removed by conversion to H_2S and most of the inorganic sulfur removed through H_2S formation and molten state filtration of the solid mineral residue.

The gasification of coal is capable of producing a sulfur-free gaseous fuel or the gases can be converted to a liquid fuel (SALSOL PROCESS). This type of process is also capital-intensive and to be economical it must be carried out on a large scale.

3.2 Coal Cleaning

Coal cleaning methods are the other pre-combustion desulfurization methods. These include both physical and chemical cleaning of coal. Physical cleaning is the least expensive and most highly developed method and is already widely used in the coal industry to remove mineral matter from coal. It involves washing and gravity separation techniques to separate finely ground run-of-mine coal into ash-rich and ash-lean fractions by utilizing the density difference of the organic matter and mineral matter (including pyrite) in coal. Generally the large pyrite particles are removed but the microscopic pyrite particles cannot be removed without lowering the specific gravity of the separating medium, which would result in a significant loss of coal matter (as much as 60%). In addition, as much as 50% of the sulfur in some coals may be associated with the organic portion of the coal matrix and therefore is not removed. Hence physical cleaning of coal alone cannot produce a sulfur-free coal.

The newly emerging technology of pre-combustion desulfurization is the chemical cleaning of coal. None of these proposed processes are presently in commercial use, but are in the stage of bench-scale or pilot-plant scale testing. Table 3-2 summarizes the oxidation-type processes and Table 3-3 lists those processes involving displacement or other types of cleaning processes. These processes claim between 50 to 90%

TABLE 3-2

Summary of Oxidation-type Processes for Chemical Coal Cleaning(27)

Process name	PETC	AMES	LEDGEMONT	ARCO	TRW	JPL
Chemicals used	Air/H_2O lime	O_2 Na_2CO_3	O_2, H_2O, NH_3 lime	O_2, lime Promoter	$Fe_2(SO_4)_3$, O_2 H_2O, lime acetone	Chlorine 1,1,1 tri- chloroethane
Coal size	70-80% 74μm	70-80% 74μm	70-80% 74μm	<595μm	<1.4mm	74-149μm
Temperature(°C)	<150-200	<150	<200	120 343	100-130	60-130
Pressure(MPa)	5.52-6.89	2.07	2.07	2.17, 16.07	0.31-0.61	0.10-0.52
Residence time (hrs)	1	1	1	1, 1	5-8	3/4
% Removal of Pyritic Sulfur	95	80-90	80-90, 65-89	88-98	84-99	71-95 72-95
% Removal of Organic Sulfur	13	20	20	0 23-30	0	46-98
Scale	pilot plant	pilot plant	bench scale	1.2 kg/hr pilot plant	8 ton/day pilot plant	2 kg/hr continuous integrated process

TABLE 3-3

Summary of Displacement and Other Types of Processes for Chemical Coal Cleaning(27)

Process name	KVB	BATELLE	TRW GRAVIMELT	MAGNEX	IGT	G.E. MICROWAVE
Chemicals used	NO_2, NaOH	NaOH, $Ca(OH)_2$ lime, CO_2	NaOH, KOH	Iron penta carbonyl	H_2, iron oxide	NaOH
Coal size	0.6-1.2mm	<297µm	149µm	<1.41mm	<1.41mm	149-150µm
Temperature(°C)	100	250-350	370	-	800	170
Pressure(MPa)	0.10	4.14-17.25	-	0.10	0.10	-
Residence time (secs)	1800-3600	600-1800	1800	39-60	3600	1800-7200
% Removal of Pyritic sulfur	60-100	90-95	90	90	90	57-92
% Removal of Organic sulfur	30-50	20-70	75	50-70	90	0
Scale	50g batch test	10kg/hr continuous	laboratory scale	91kg/hr continuous	.45kg/hr continuous	10 to 500g tests

removal of inorganic sulfur and between 0 to 75% of organic sulfur. The PETC, AMES, LEDGEMONT, ARCO and TRW[a] processes all involve the oxidation of coal sulfur with either oxygen (air for PETC) or ferric ion in aqueous solutions. The major differences between them are the operating conditions used and for the AMES process the neutralization step uses sodium carbonate instead of lime. Also of interest is that the ARCO process uses a promoter to increase oxidation while the LEDGEMONT process uses ammonia to remove some of the organic sulfur. The KVB process uses gaseous NO_2 to oxidize pyrite and some of the organic sulfur in dry coal, with a subsequent hot water wash to remove soluble iron sulfur compounds and reduce trace elements and mineral matter. The spent oxidant, NO, is rapidly reoxidized to NO_2 in the presence of O_2 while the washed coal is treated with a caustic solution for one hour at $93^{\circ}C$ to remove organic sulfur. The BATELLE process uses sodium and calcium hydroxides at relatively high temperatures to convert coal sulfur 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 then treated with lime to recover NaOH, and the resulting $CaCO_3$ is converted back to lime by calcining. The TRW GRAVIMELT process extracts the sulfur from coal (displaces S) by treating with a mixture of 50% potassium hydroxide and 50% sodium hydroxide at 370 $^{\circ}C$ for 3 hours followed by washing with water. Figure 3-3 shows the process flow diagram for the TRW process which uses ferric sulfate as the oxiding agent (41).

Other types of coal cleaning processes include the

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[a] See Appendix I for developers of process

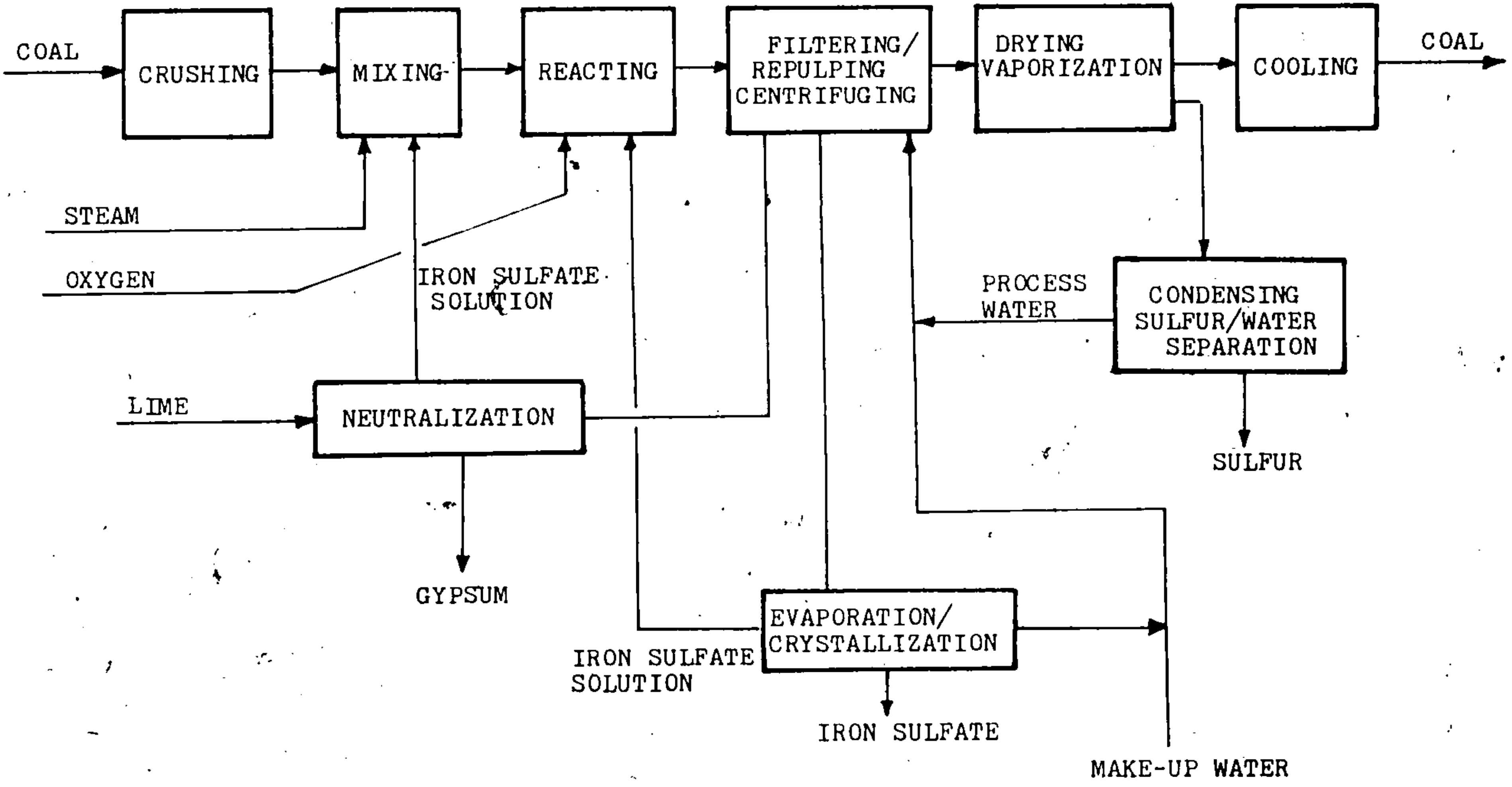

Figure 3-3. Meyers Process Flow Diagram(41)

Magnex, IGT desulfurization and G.E. microwave treating process. In the Magnex process, coal is treated with iron pentacarbonyl to enhance the magnetic susceptibility (pyrite to pyrrhotite-like phase) of pyrite which is subsequently removed by magnetic separation. The IGT flash desulfurization process involves treatment of coal with O_2 at 400 ^oC and a subsequent treatment with H_2 at 800 ^oC to remove sulfur as H_2S in a fluidized bed reactor. The G.E. microwave process involves treatment of pulverized coal with NaOH solution followed by dewatering and irradiation with microwave energy for 30 to 60 seconds under a nitrogen atmosphere to convert both organic and inorganic sulfur to soluble sodium sulfide (Na_2S) and polysulfides (Na_2S_x). The coal is then washed to remove the sulfur compounds and caustic.

Research and development are still continuing for coal cleaning processes but some of these are being terminated (PETC, LEDGEMONT) due to the lack of funding(27).

In summary, the literature survey indicates that only the inorganic sulfur in coal is well defined. The organic sulfur is not well understood. A knowledge of the types of sulfur in coal is important in our studies because chemical desulfurization of coal requires a chemical reaction between the sulfur-group and the desulfurizing chemical. The types of impurities must also be known as reaction might occur with the desulfurizing chemical thus not only competing for the reagent but also contaminate the coal with unwanted by-products. The reaction chemistry of the copper solutions with the coal's inorganic sulfur indicates that precipitates of CuCl, Cu_2S and CuS are produced. These precipitates must be removed as they contaminate the coal. The literature survey on the reaction chemistry of ferric sulfate and O_2 treatment of coal has been the most widely studied chemical desulfurizing system. Controversy still exists as to whether O_2 reacts directly with the coal's sulfur at low temperatures or in the system Fe^{+3} is formed which then causes the desulfurization. The reaction chemistry also shows that both elemental sulfur and sulfuric acid can be produced. Though some controversy still exists as to whether the elemental sulfur is stable within the oxidizing system. It is important to identify the products as additional steps would have to be used to remove by-products. Finally there are many proposed processes of coal desulfurization. The most highly developed one is flue gas desulfurization which is now practiced commercially though it is expensive. Chemical cleaning of coal is the most promising alternative to flue gas desulfurization. At present no commercial coal cleaning (chemical) process exists. A chemical is yet to be found that would remove both organic and inorganic sulfur without too much damage to the coal matrix.

III. DESULFURIZATION EXPERIMENTS

A. Coal Preparation

The bituminous coal used in this work was Prince coal from Nova Scotia which has a high sulfur content. Samples for reactions were prepared under conditions chosen to avoid undue exposure to the atmosphere. Samples of coal were taken from their original, non-airtight containers and ground to smaller sizes. The ground samples were then screened to obtain the desired particle size range in a Model RX-24 portable sieve shaker. The desired coal size was then carefully spooned into labeled, large containers with screw caps and thoroughly mixed. This processing was continued until enough coal was collected for experimentation. The jars were placed into a dessicator and only removed when required for analysis or desulfurization experiments.

B. Chemicals

The suppliers and grades of purchased chemicals used in this study for the desulfurization experiments are listed in Table 4-1 and those for coal analysis in Table 4-2. The water used for desulfurization experiments and coal analysis was distilled water.

TABLE 4-1

Sources and Purities of Chemicals Used for Desulfurization Experiments

Chemical	Source	Grade	Minimum Purity(%)
$CuCl_2$	Fisher	-	-
$CuSO_4$,anhydrous 98%	B.D.H	-	99.9
$Fe_2(SO_4)_3$ n-hydrate	J.T. Baker	Baker Analysed Reagent	99.9
H_2SO_4(96.1%)	J.T. Baker	Baker Analysed Reagent	99.9
HCl(37%)	J.T. Baker	Baker Analysed Reagent	99.9
N_2(dry)	Liquid Carbonic Canada	-	-
O_2(dry)	-	-	-
Toluene	J.T. Baker	Baker Analysed Reagent	100.0

TABLE 4-2

Sources and Purities of Chemicals Used for Coal Analyses

Chemical	Source	Grade	Minimum Purity(%)
H_2O_2(30%)	J.T. Baker	Baker Analysed Reagent	99.9
2-Propanol	J.T. Baker	-	-
$BaClO_4$, anhydrous	J.T. Baker	-	-
NH_4OH(29.4%)	J.T. Baker	Baker Analysed Reagent	99.9
Perchloric Acid(70%)	G.F.S	Reagent ACS	99.9
New Methylene Blue	J.T. Baker	'Baker' TM	
Thorin	J.T. Baker	-	-
Dowex 50w-x8 H^+,20-50 Mesh	J.T. Baker	Baker Analysed	-
Phenothalien	J.T. Baker	Baker Analysed Reagent	-
NaOH	Fisher Scientific Company	-	-
H_2SO_4(96.1%)	J.T. Baker	Baker Analysed Reagent	-

C. Coal Analysis

The analytical methods mentioned below were applied in the same way to both untreated and treated coal. Inorganic, organic and total sulfur analyses were performed by the author. Total sulfur was determined by the Modified Oxygen-flask method(1) (MOF). Organic sulfur was determined by the method used by Block et al.(11) with the Leco sulfur determination method replaced by the MOF method. The inorganic sulfur was determined as the difference between the total sulfur and the organic sulfur. Duplicate analyses were performed periodically for cupric chloride and cupric sulfate runs. The ultimate and ash analyses for some runs were supplied by the EMR Laboratory (Runs #14C, #12CS, #49 and those in Table 4-3, Table 4-4).

Sulfur analyses are reported on a moisture and ash-free basis (MAF) to avoid undue differences in the results due to variable ash contents in treated coals. The weight of the organic matter was assumed to change very slightly during a run and all percentage total removal of sulfur was based only on MAF data.

The heating values of raw coal, Run#14C, Run#12CS, and Run#49 were determined from the correlations of Mott and Spooner(45) and the coals ultimate analyses. The formulas for coals containing less than 11% oxygen is :

TABLE 4-3

C,H,N,S,ASH and O analyses for Untreated Coal Samples

Sample No.	1	2
Coal	Prince Coal	Prince Coal
Carbon	65.91	67.33
Hydrogen	4.19	4.41
Nitrogen	1.30	0.95
Sulfur	4.29	4.94
Oxygen	8.16	7.52
Ash	16.15	14.85

TABLE 4-4

Ash Analysis of Raw Prince Coal[a]

Component	Percentage
SiO_2	36.10
Al_2O_3	23.16
Fe_2O_3	33.31
TiO_2	0.72
P_2O_5	0.29
CaO	1.09
MgO	0.84
SO_3	1.48
Na_2O	0.41
K_2O	2.13
BaO	-
SrO	0.05
Mn_3O_4	-
LOF	0.31

a-analysis supplied by EMR laboratory

$$Q = 144.5 X_c + 610 X_h - 62.5 X_o + 40.5 X_s \quad (4.1\text{-}1)$$

and for coals containing more than 11% oxygen:

$$Q = 144.5 X_c + 610 X_h - (65.9 - 0.31 X_o) X_o + 40.5 X_s \quad (4.1\text{-}2)$$

Here X_c, X_h, X_o, and X_s are moisture-free weight percentages of carbon, hydrogen, oxygen and sulfur respectively. Q is the calorific value in Btu/lb on a moisture-free basis. Mechanical losses of material were not accounted for in the calculation of the heating values of treated coals.

D. Experimental Procedures

1. Cupric chloride and Cupric sulfate Experiments

The reactors for these runs consisted of 30 ml capacity glass tubes of 2-cm diameter with tapered tops. Temperature was monitored with a thermocouple connected to a portable thermolyne pyrometer and immersed into a 30 ml reactor tube containing oil. Reactor tubes were placed in a divided metal box constructed of iron mesh and heated in a closed furnace. Temperature control was manual with desired temperature settings obtained with the help of a prepared curve of temperature rise versus time (Figure 4-1).

Conditions under which these experiments were performed are listed in Table 4-5 and Table 4-6 for cupric chloride and

TABLE 4-5

Cupric Chloride Experiments (Coal Sample #2)

Experimental No.	Order[a]	Temperature (°C)	Time (hr)
21C	12	150	3
1C	1	150	3
20C	11	150	12
8C	3	150	12
17C	8	150	24
6C	2	150	24
18C	9	175	3
19C	10	175	12
16C	7	175	24
15C	6	200	1
12C	4	200	2
22C	13	200	3
25C	14	200	12
14C	5	200	24

a - order in which the experiments were performed

TABLE 4-6

Cupric Sulfate Experiments (Coal Sample #2)

Experimental No.	Order[a]	Temperature (°C)	Time (hr)
21CS	11	150	3
20CS	10	150	12
17CS	7	150	24
18CS	8	175	3
19CS	9	175	12
16CS	6	175	24
15CS	5	200	1
12CS	1	200	2
13CS	3	200	2
22CS	12	200	3
11CS	1	200	3
25CS	13	200	12
14CS	4	200	24

a-order in which the experiments were performed

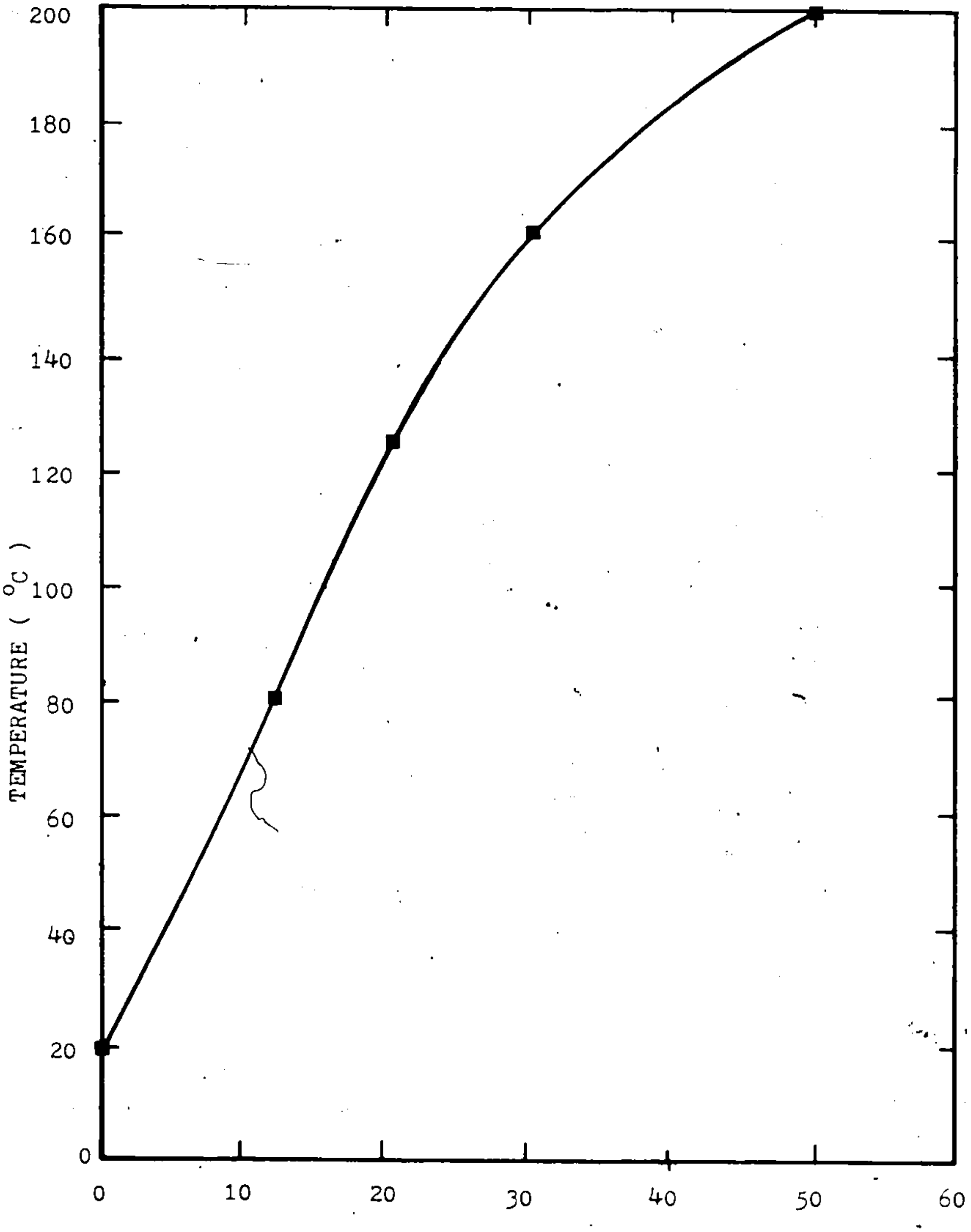

Figure 4-1 Temperature Rise Characteristics for Cupric Chloride and Cupric Sulfate Experiments (no reactor tubes)

cupric sulfate respectively. Two grams of coal was introduced into the glass reactor tubes through a glass funnel. Twenty milliliters of either 3M cupric chloride or 1M cupric sulfate solution was then poured into the tubes. Reactor tubes were then sealed with a hot flame, placed into the compartments of the metal box and heated to the desired reaction temperature. After 1, 2, 3, 12 or 24 hours reaction, the mixture was filtered. The cupric chloride reaction product was washed with 20 ml concentrated hydrochloric acid to remove the precipitated cuprous chloride and then washed 4 times with 100 ml of distilled water, each wash being followed by vacuum filtering. The solids were then vacuum drained until dry enough to be transferred by spatula to a crucible and then dried in an oven at 100 °C for one hour. The dried solids were then ground using a ceramic mortar and pestle. Samples so prepared, ready for analysis, were stored inside a dessicator in labeled (15 × 45) millimeter glass vials with screw caps. The procedure for cupric sulfate was similar to that of cupric chloride except that reaction mixture was washed with hot sulfuric acid, dried for one hour at 100 °C, then refluxed with 200 ml toluene for one hour at 110 °C to remove any elemental sulfur formed from reaction of sulfuric acid with cupric sulfide according to the following equation (Eq. 4.1-3)

$$CuS + 2\,H_2SO_4 \;=\; S + CuSO_4 + 2\,H_2O + SO_2 \qquad (4.1\text{-}3)$$

Coal was dried at 150 °C, prepared and stored in the same way as that done for cupric chloride.

2. Ferric Sulfate Experiments

The ferric sulfate leaching experiments were carried out in a 3-liter cylindrical stainless steel (SS316) reactor shown in Figure 4-2. The reactor was equipped with a porous plate, a needle valve for controlling reaction pressure, two auxillary valves for controlling gas, liquid and coal feed, one auxillary outlet valve, a stainless steel (SS316) gas sparger, a pump for liquid circulation and a thermocouple (iron constantan) with a stainless steel sheath (SS316). The thermocouple was calibrated against a mercury-filled therometer from 0 to 175 °C using a heated mineral oil bath. This calibration curve is shown in Figure 4-3. Heat was supplied to the reactor through a fabric mantle surrounding the vessel body and along the recirculation lines. Temperature was controlled to within ±3 °C of the set-point using a proportioning controller activated by the thermocouple.

The conditions under which the ferric sulfate experimental runs were performed are shown in Table 4-7. The substantial heating-pressurizing and cooling-depressurizing periods were carefully controlled to be of similar duration for each experiment to allow meaningful comparision of the effects of different reaction conditions on desulfurization rates.

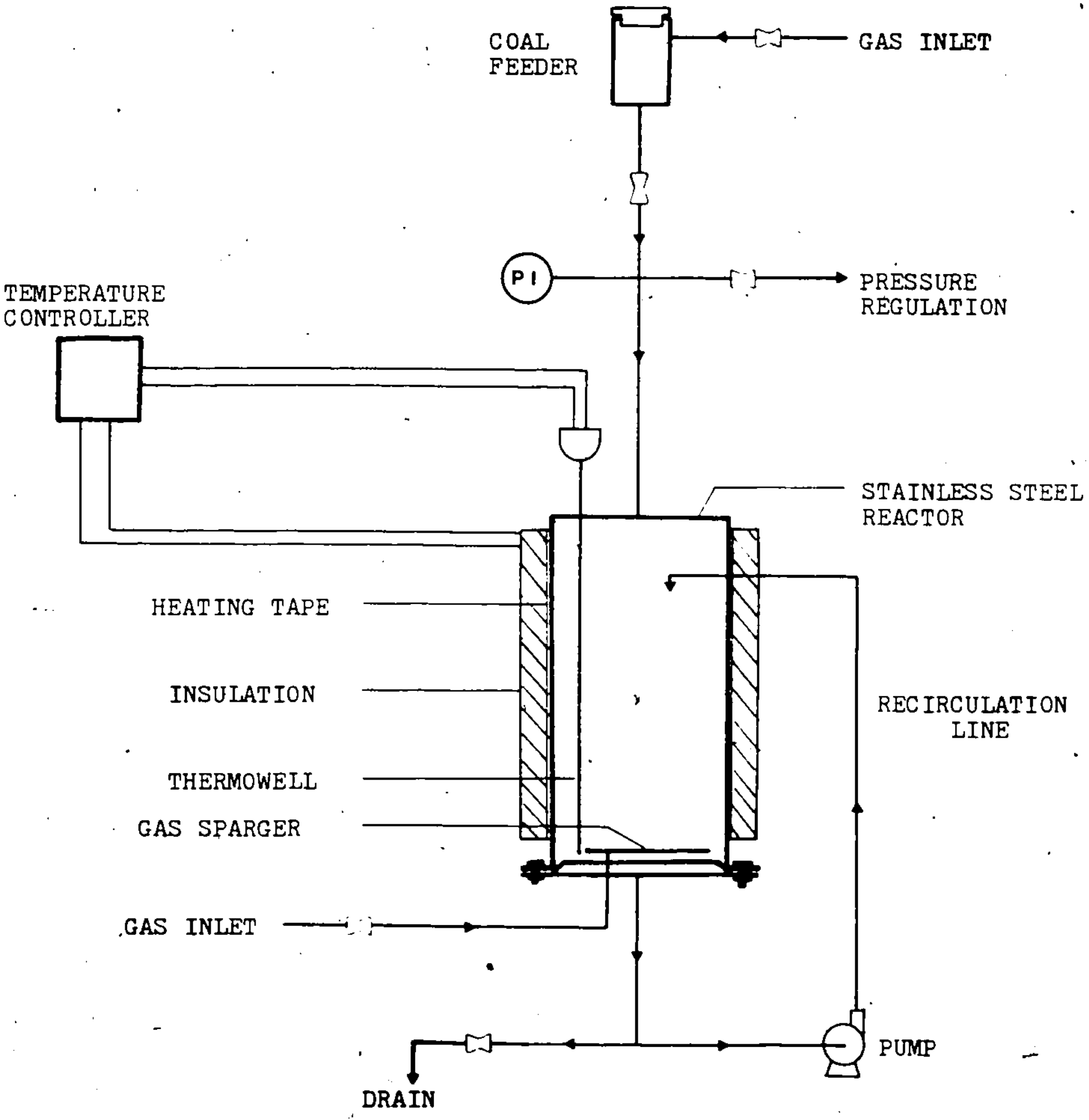

Figure 4-2. Apparatus for Ferric Sulfate Experiments.

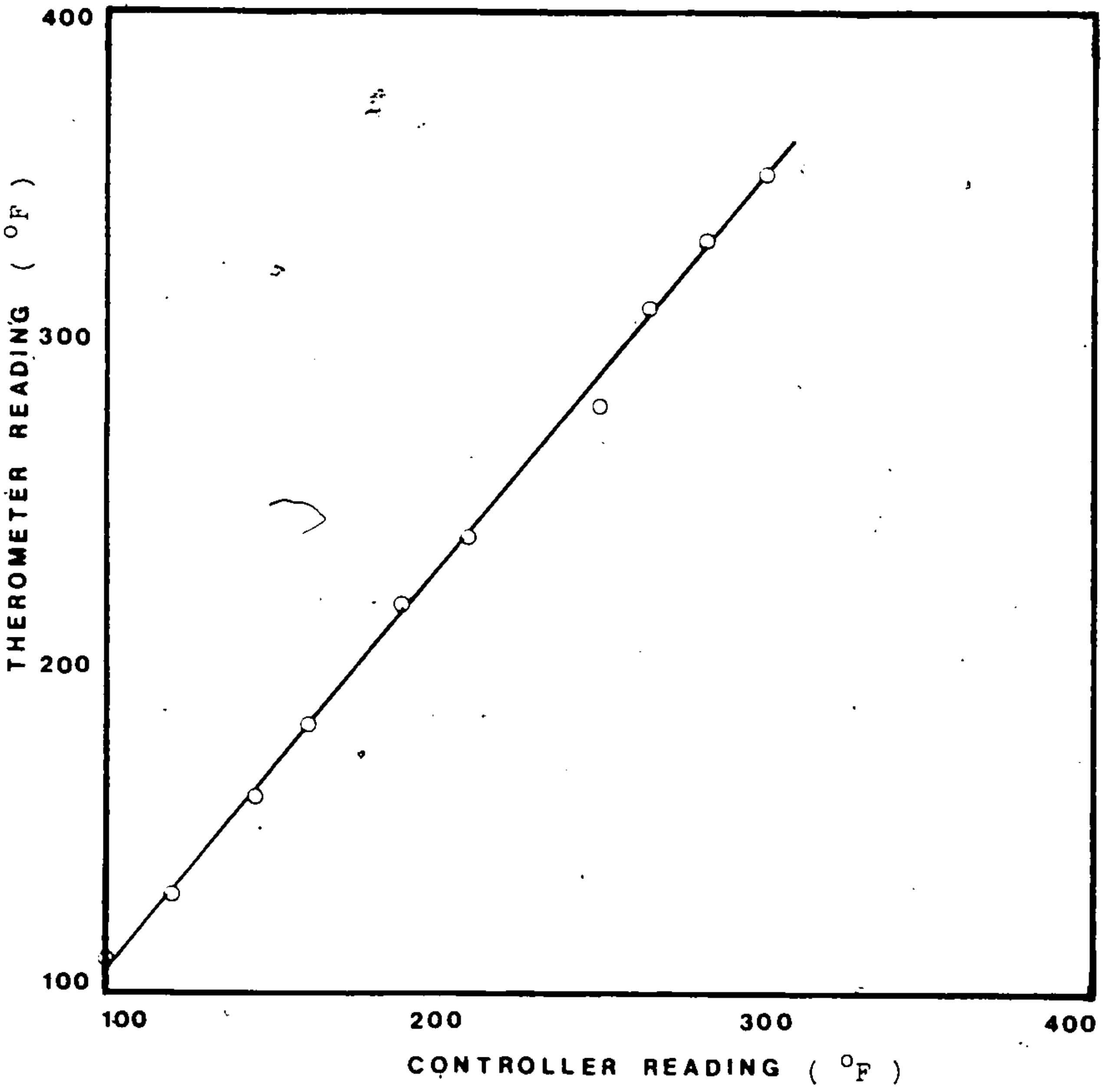

Figure 4-3 Calibration Curve of Temperature Controller for Ferric Sulfate Desulfurization Experiments

TABLE 4-7

Ferric Sulfate Experiments (Coal Sample #1)

Experimental No.	Order[a]	Temperature (°C)	Time (hr)
36	12	100	½
34	10	100	1
35	11	100	1½
33	9	100	3
44	15	100	½
43	14	100	1
45	16	100	1½
42	13	100	3
26	4	150	½
21	1	150	1
25	3	150	1½
24	2	150	3
30	8	175	½
28	6	175	1
29	7	175	1½
27	5	175	3

a-order in which the experiments were performed

Before each run the reactor was flushed with nitrogen gas except for the run with oxygen in which case the reactor was flushed with oxygen. Two liters of aqueous 0.1 M $Fe_2(SO_4)_3$ solution was loaded and the reactor was pressurized to 200 psig (1.4 MPa) total pressure with nitrogen or oxygen gas. The reactor was heated to the desired temperature and coal was loaded under pressure of nitrogen (oxygen) gas until a total pressure of 250 psig (1.7 MPa) was attained. A relatively constant total pressure was maintained during a run by either venting excess pressure through the gas outlet or adding nitrogen (oxygen) gas. After completion of the reaction, the spent liquid was rapidly drained out through the auxillary outlet valve and the bottom of the reactor was immersed into cooling water. The solid products from the reactor were carefully recovered, washed with hot dilute hydrochloric acid, dried and then extracted with toluene to remove elemental sulfur. The product was dried and prepared for analysis using the same procedures as that for cupric chloride runs.

Table 4-8 shows the sulfur and ash contents of the two coal samples used in the experiments together with the mesh size of coal used and the number of experiments carried out for each of the leaching solutions.

TABLE 4-8

Sulfur and Ash Analysis of Raw Coals

Sample No.	1	2
Coal Type	Prince Coal	Prince Coal
Mesh Size; Tyler Screen No.	minus 35 plus 42	minus 35 plus 42
Total Sulfur[a]	5.12	5.80
Organic Sulfur	1.65	1.86
Inorganic Sulfur	3.47	3.94
Ash	16.15	14.85
Runs Made		
Cupric Sulfate	-	13
Cupric Chloride	-	14
Ferric Sulfate	18	-

a- moisture and ash-free basis

IV. RESULTS AND DISCUSSION

A. SULFUR REMOVAL

The total sulfur remaining (as weight percentage) on the solid coal products as a result of the desulfurization experiments described in Table 4-5, Table 4-6 and Table 4-7 and the percentage of total sulfur removal relative to the total sulfur in raw coal for $CuCl_2$, $CuSO_4$, and $Fe_2(SO_4)_3/N_2$ treatment are shown in Table 5-1, Table 5-2 and Table 5-3 respectively. The total, organic and inorganic sulfur form analysis for several treated coals and the percentage removal of each type with respect to the sulfur present in the raw coal are presented in Table 5-4.

1. Experiments with Cupric Chloride Solutions

The experiments listed in Table 4-5 were run at 150 to 200 °C and varying times between 1 to 24 hours to determine conditions at which cupric chloride solutions are effective in removing pyritic sulfur. And secondly to determine whether organic sulfur can be removed in the presence of cupric salts in aqueous media either as a result of a catalytic effect on the elimination of organic sulfur from the coal matrix or the conversion of the organic sulfur to a soluble removable form as observed by Krzymien(29). A 3 M aqueous solution was used for these experiments which provided about 100% reactants in excess of that required stoichiometrically based on the total sulfur being pyritic sulfur.

The results of the treatment of raw coal with aqueous 3 M cupric chloride solutions is summarized in Table 5-1. The results indicate that the largest amount of total sulfur removal occured at 200 °C with the removal percentages varying from 49% in 1 hour to 65% in 24 hours. The latter percentage is close to the total amount of inorganic sulfur present in the raw coal sample #2 shown in Table 4-4, thus indicating almost complete removal of inorganic sulfur assuming no organic sulfur is removed. This would be in agreement with the work of Stokes(53) who observed that heating mineral pyrite at 200 °C for 5 hours decomposed the sulfur in iron pyrite to sulfuric acid. The retardation of the reaction after the first hour of reaction at 200 °C is attributed to the rapid depletion of iron pyrites, the precipitation of cuprous chloride (large white crystals) and the absence of agitation thus making it difficult for the unspent leach solution to come into contact with the remaining iron pyrites. The change in pH from between 2 to 3 (original solution) to less than 0.01 (for spent solution) in all cases could also be responsible for the retardation of the reaction, as at high acidity the foward reaction is unfavourable.

Organic sulfur analyses for Run #22C and Run #16C are shown in Table 5-4 which shows a +4.0% organic sulfur removal

TABLE 5-1

Experimental Results of Chemical Desulfurization of Prince Coal with 3M Cupric Chloride Solutions Based on Total Sulfur Analysis

Experimental No.	Temperature (°C)	Time (hr)	Total Sulfur Remaining (%)[a]
21C	150	3	3.89
1C	150	3	3.94
20C	150	12	4.10
8C	150	12	3.89
17C	150	24	3.89
6C	150	24	3.79
18C	175	3	3.58
19C	175	12	3.38
16C	175	24	2.97
15C	200	1	2.41
12C	200	2	2.30
22C	200	3	2.20
25C	200	12	1.96
14C	200	24	1.84

a-see Appendix II for analytical methods used for the former and a 5.0% organic sulfur increase for the latter. These removal percentages are too small and variable (increase and decrease in organic sulfur) for any positive conclusion to be drawn. Also contributing to the above problem is that during the analysis for organic sulfur, the inorganic sulfur must first be extracted with nitric acid which is also capable of removing organic sulfur even though the adopted treating condition of 25% by volume nitric acid for 24 hours at room temperature is supposed to minimize this effect. According to our method of organic sulfur analysis (Appendix-II) this would result in a small apparent decrease in organic sulfur. The IEA (International Energy Agency)(27) publication on the chemical desulfurization of coal mentioned that organic sulfur determination by electron microprobe X-ray analysis (EPM) resulted in values which are up to 30% lower than those indicated by the standard chemical method (ASTM D2492-77) of analysis. This observation was believed to be due to the encapsulation of discrete pyrite particles during the acid leaching step so that residual inorganic sulfur is credited to organic sulfur. In our case this would be observed as an increase in organic sulfur. Further complicating the above problem is that the analytical methods for sulfur determination were not designed for chemically treated coals and additional chemical by-products created and retained on the coal as a result of chemical desulfurization may cause the analytical method to give an incorrect sulfur content reading. This was observed in our studies when the ion exchange step (to remove interfering metal ions) was omitted, the analytical method gave an apparent zero sulfur content which was attributed to the presence of cuprous chloride (incomplete removal) on the coal. Fritz and Yamamura(20) showed that errors in the sulfur detection method can be caused by the presence of ions such as chloride, nitrate, fluoride and phosphate. The complete removal of sulfur (both organic and inorganic) from Prince coal as observed by Krzymien(29) was not obtained in our studies which further points to the possible interfering effects of chemical by-products (CuCl) with the sulfur analysis. The removal of CuCl or its effect on the analysis was not discussed by the author. Further experiments are needed to clarify this point together with a special emphasis on the measurement of organic sulfur with the different proposed techniques to screen out any effects due to the presence of chemical by-products.

The effects of time and temperature on the total amount of sulfur removed is shown in Figure 5-1 and Figure 5-2 @ respectively. Figure 5-1 shows that increases in time after the initial 3 hours of treatment do not result in large increases in the total amount of sulfur removed. This was attributed to the depletion of pyrites, precipitation of cuprous chloride, absence of agitation and an increase in acidity (large change in pH) plus slower oxidation rates at temperatures of 150 °C and 175 °C could be the reason why complete inorganic sulfur removal cannot be achieved at these temperatures. Figure 5-2 shows that an increase in temperature

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@ - see Appendix III for fitting procedure

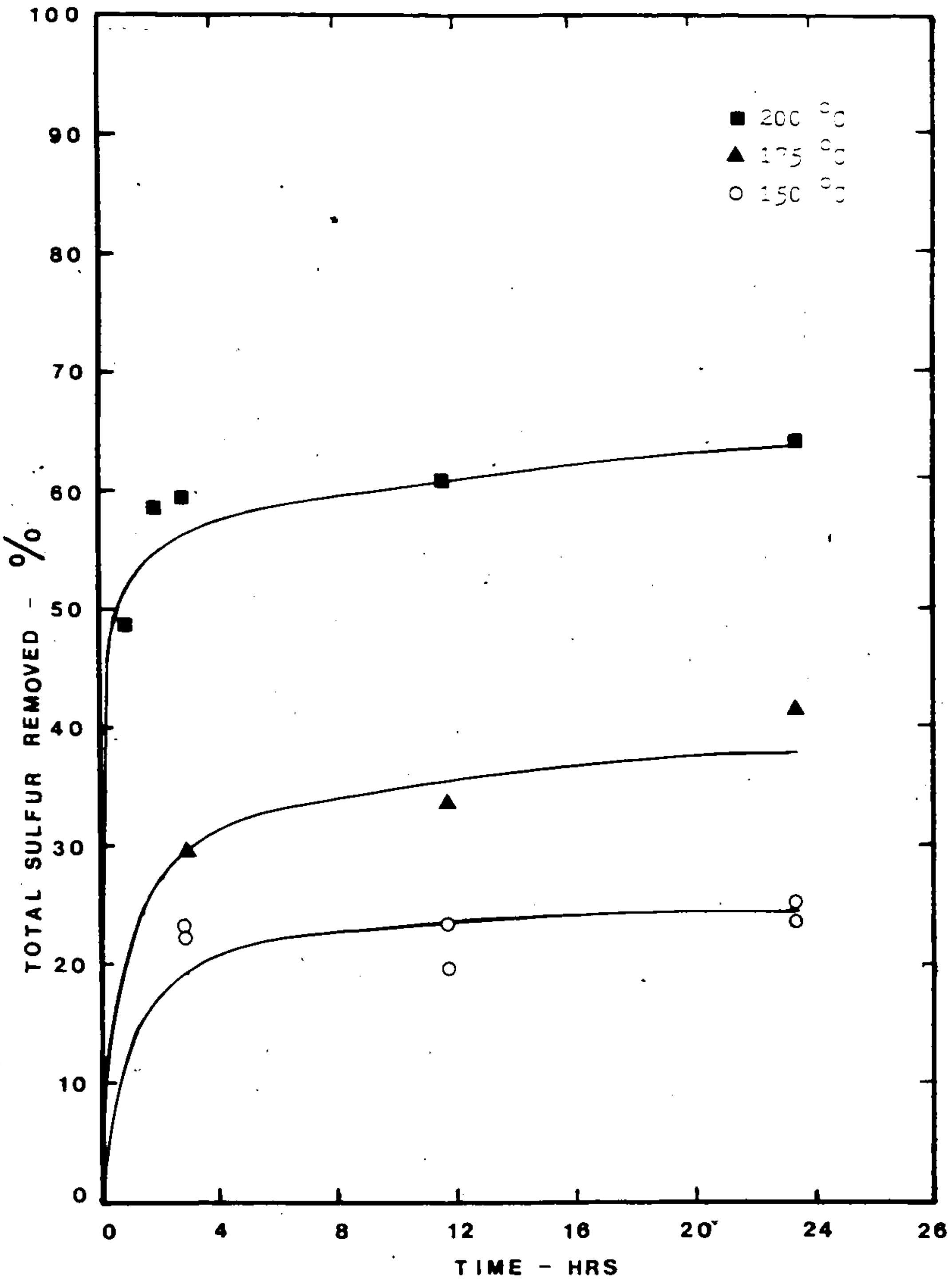

Figure 5-1 . Effect of Time on Total Sulfur Removed at Various Temperatures for Prince coal Treated with 3 M $CuCl_2$ Solutions

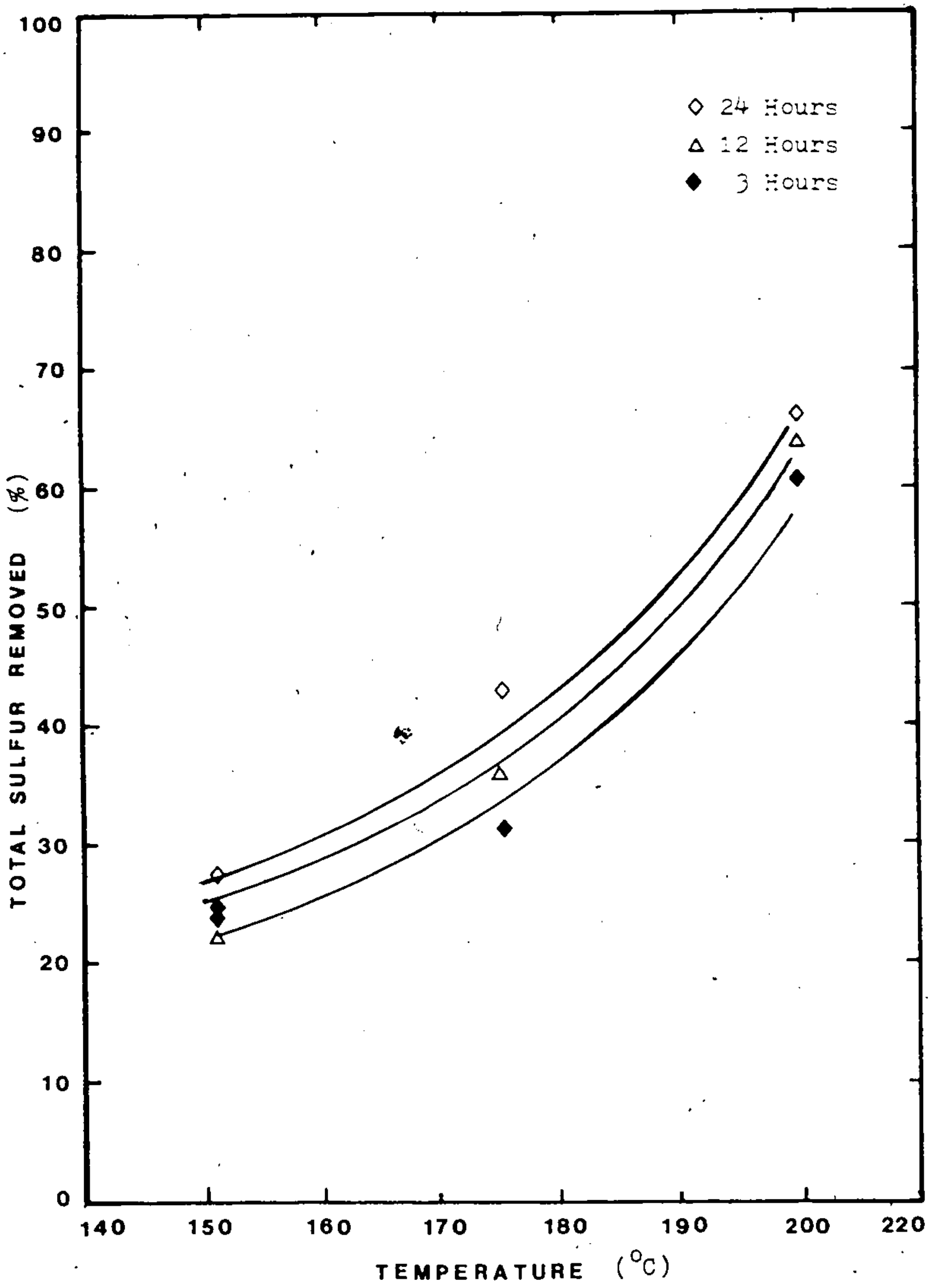

Figure 5-2 Effect of Temperature on Total Sulfur Removed at Various Times for Prince coal Treated with 3 M $CuCl_2$ Solutions

increases the total amount of sulfur removed and the largest amount of sulfur removal occurs when the temperature is increased from 175 °C to 200 °C than from 150 °C to 175 °C. It shows that temperature is the most important of the two variables and that time is the least important as the differences between the three curves (3,12, 24 hours) are small. This can also be seen from Figure 5-1 which shows that the largest amount of sulfur removal occurs in the first 3 hours of reaction at all temperatures.

In summary, all the results from the leaching experiments with cupric chloride solutions indicate that to remove sulfur (inorganic) efficiently, high reaction temperatures (200 °C) and short reaction times are desirable and that these solutions in aqueous media do not affect the organic sulfur in coal at the experimental conditions used in our studies.

2. Experiments with Cupric Sulfate Solutions

The experiments listed in Table 4-6 were run at 150 °C to 200 °C at various times between 1 to 24 hours for the same reasons as those given for cupric chloride, namely to test the effectiveness of aqueous cupric sulfate solutions for sulfur removal and to compare the amount of sulfur removed by the two copper solutions. Another benefit of these experiments was that if the sulfur removal rates of the two solutions were similar then the preferred solution to be used would be cupric sulfate as it is less corrosive than cupric chloride. A 1 M cupric sulfate solution was used which again was approximately 100% in excess of that required stoichiometrically (total sulfur considered as being FeS_2).

The results of treating the raw Prince coal with aqueous cupric sulfate solutions are summarized in Table 5-2. The results indicate very low removal rates compared to that of cupric chloride treatment. The maximum amount of sulfur removal occured at 200 °C as expected (can be deduced from the results of $CuCl_2$ treatment) but the amount removed is only 36% of the total, which is 45% less than that for cupric chloride under the same conditions. Table 5-4 shows the organic sulfur analyses for Run #14CS and Run #16CS and which indicates an apparent increase in organic sulfur of 51% and 58% for the two runs and this is the main reason for the low removal rates observed. One of the possible reasons for the apparent increase in organic sulfur could be due to the retention of cuprous sulfide (Cu_2S, produced according to Eq. 2.2-4) and cupric sulfide (CuS, produced according to Eq. 2.2-5) which are the products of unoxidized iron pyrite. The copper sulfides might not have been removed by washing with H_2SO_4 according to Eq. 5.2-1 and Eq. 5.2-2;

$$CuS + 2\,H_2SO_4 \longrightarrow S + CuSO_4 + 2\,H_2O + SO_2 \qquad (5.2\text{-}1)$$

$$Cu_2S + 2\,H_2SO_4 \longrightarrow CuS + CuSO_4 + 2\,H_2O + SO_2 \qquad (5.2\text{-}2)$$

TABLE 5-2

Experimental Results of Chemical Desulfurization of Prince Coal with 1M Cupric Sulfate Solutions based on Total Sulfur Analysis

Experimental No.	Temperature (°C)	Time (hr)	Total Sulfur Remaining (%) [a]
21CS	150	3	4.06
20CS	150	12	4.11
17CS	150	24	3.85
18CS	175	3	3.80
19CS	175	12	3.74
16CS	175	24	3.64
15CS	200	1	4.16
12CS	200	2	3.90
22CS	200	3	3.69
11CS	200	3	3.59
25CS	200	12	3.54
14CS	200	24	3.33

a-see Appendix II for analytical methods used

According to Mellors(48) some varities of crystalline sulfide of Cu_2S are not attacked by either dilute or concentrated acid. Calculations of the sulfur produced as Cu_2S stoichiometrically (Eq. 2.2-4) plus the initial amount of organic sulfur present in the raw coal do yield total sulfur values which are larger than the observed sulfur values. Hence for the calculated and observed values to coincide would require that most of the CuS be removed together with a slight loss of Cu_2S. In our case this is possible as the CuS precipitate (fine grey-black powder) can be removed by simple washing because of the large density difference between the coal particles and the CuS precipitate. The above explanations together with CuS not being oxidized by the nitric acid pre-treatment before organic sulfur analysis would result in observed organic sulfur values being higher than in the original coal. The residual sulfur being credited to organic sulfur. The other possibility could be the actual formation of organic sulfur due to the catalytic presence of either $CuSO_4$ or Cu-metal(5). The Cu-metal was observed in the reaction product and could have been produced according to Eq. 2.2-9 as a result of the formation of cuprous sulfate (Cu_2SO_4) from Eq. 2.2-6. Eq. 2.2-7 and Eq. 2.2-8.

The above shows that it is difficult to obtain conclusive results as to whether the organic sulfur is removed and it is due mainly to conventional analysis being applied to treated coals which has its sulfur transformed into a form which is not present in raw coal and which cannot be distinguished by the analytical method. More experiments are required to screen out the effects of chemical by-products together with the use of different organic sulfur determination techniques.

The effect of time and temperature on the total sulfur removed is shown in Figure 5-3 and Figure 5-4@ respectively. Both show that time and temperature do not have a large effect as that observed for $CuCl_2$ treatment. This is due mainly to the apparent increase in organic sulfur effect observed. As in the $CuCl_2$ runs, retardation of reaction occured after the first 3 hours of reaction. Again this is attributable to depletion of pyrites, absence of agitation, precipitation of CuS (Cu_2S) and increase in acidity (pH of spent solution less than 0.01).

In summary, the results indicate that $CuSO_4$ in aqueous media under the conditions tested could not remove the sulfur in the coal effectively due to many side reactions occuring together with the difficulty in separating the by-products from the coal. No conclusion could be drawn from the organic sulfur analyses as to whether organic sulfur is removed by $CuSO_4$ solutions.

Complete removal of sulfur using $CuSO_4$ solutions as observed by Krzymien was not obtained in our experiments.

@-see Appendix for treatment of experimental results

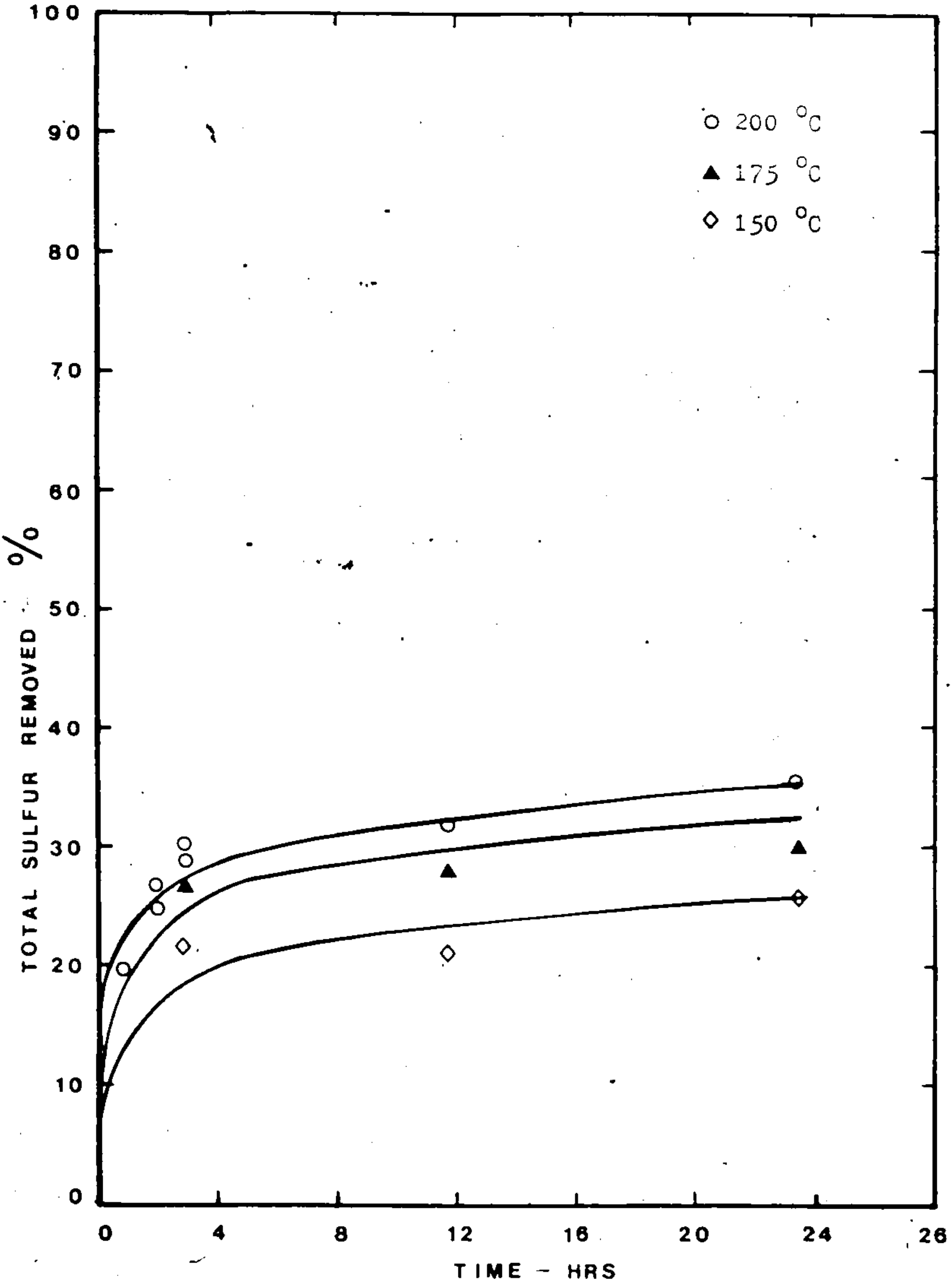

Figure 5-3 Effect of Time on Total Sulfur Removed at Various Temperatures for Prince Coal Treated with 1 M $CuSO_4$ Solutions

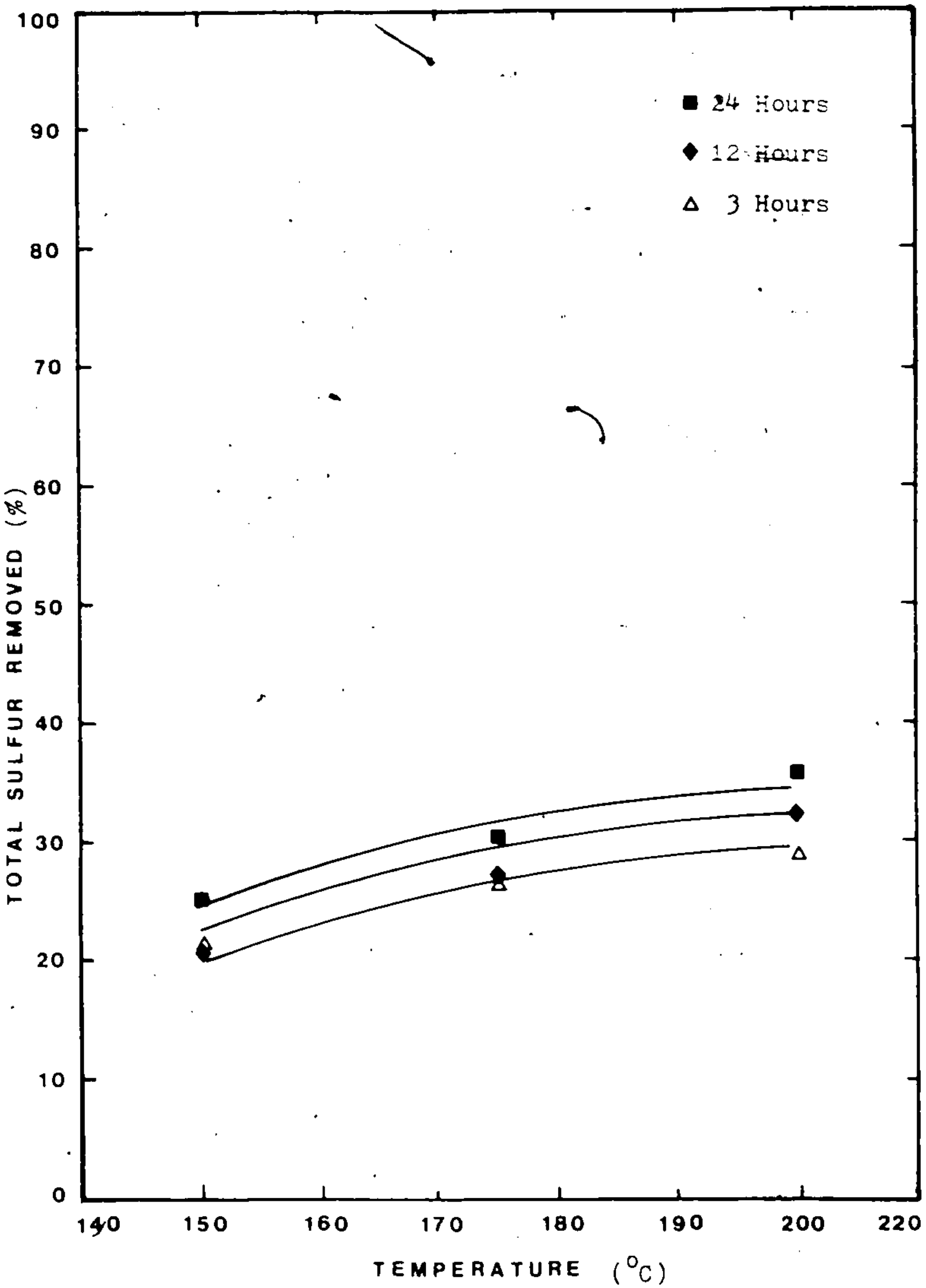

Figure 5-4 Effect of Temperature on Total Sulfur Removed at Various Times for Prince coal Treated with 1 M $CuSO_4$ Solutions

3. Experiments With Ferric Sulfate

The experiments listed in Table 4-7 were run at 250 psig N_2 and at 100 to 175 °C for varying times of ½ to 3 hours. These runs were to be repeated using oxygen (gas) pressure to investigate whether or not oxygen had an effect on the desulfurization at these conditions. Unfortunately only one run (#49) using oxygen pressure was performed since additional runs could not be carried out because of sealing problems encountered due to corrosion of the sealing surfaces of the stainless steel reactor by previous runs. Run #33, 34, 35 and 36 were done ~~under~~ a nitrogen pressure of 150 psig to ensure that nitrogen did not take part in the reaction. The similarities in the amount of total sulfur removed compared with those performed under 250 psig (1.7MPa) N_2 pressure indicate that nitrogen did not indeed take part in the reaction.

The results for these leaching experiments are summarized in Table 5-3 and shown as a function of time in Figure 5-5. It can be seen that passivation of pyrite occurred at 100 °C and 150 °C. The passivation at 175 °C is not as prominent as that at lower temperatures though it prevented the oxidation of inorganic sulfur from proceeding to completion. The passivation effect as a result of ferric sulfate leaching ~~was also~~ observed by Betancourt and Hancock(8) and Yurovskii(57). Yurovskii linked this passivation effect to the formation of iron sulfates from the leaching experiments and the subsequent adsorption of these on the FeS_2 particle surface. To illustrate this point, the desulfurization was carried

TABLE 5-3

Experimental Results of Chemical Desulfurization of Prince Coal with 0.1M Ferric Sulfate Solutions Based on Total Sulfur Analysis

Experimental No.	Temperature (°C)	Time (hr)	Total Sulfur Remaining (%) [a]
36 [b]	100	½	3.35
34	100	1	3.23
35	100	1½	3.29
33	100	3	3.30
44	100	½	3.36
43	100	1	3.29
45	100	1½	3.50
42	100	3	2.87
26	150	½	3.28
21	150	1	3.08
25	150	1½	3.63
24	150	3	2.91
30	175	½	3.40
28	175	1	2.82
29	175	1½	2.45
27	175	3	2.40

a-see Appendix II for analytical methods used

b-run under a nitrogen pressure of 150 psig

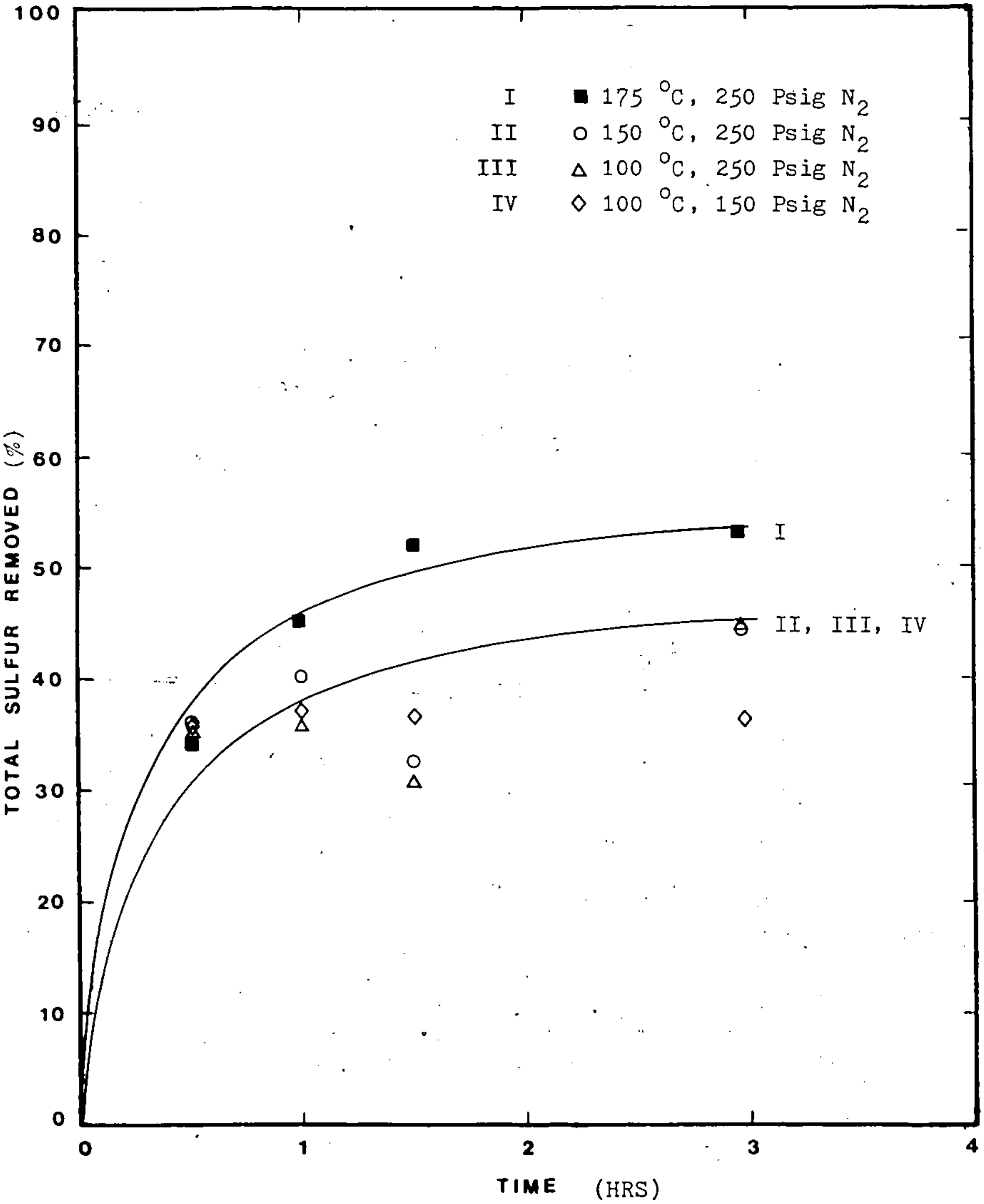

Figure 5-5 Effect of Time on Total Sulfur Removed at Various Temperatures for Prince Coal Treated with 0.1 M Ferric Sulfate Solutions

TABLE 5-5

Organic, Inorganic and Total Sulfur Analyses for Treated Samples

Leaching Solution	Temperature (^{o}C)	Time (hr)	% Sulfur Removed		
			Total	Inorganic	Organic
$CuCl_2$	200	3	60	91	+4
$CuCl_2$	175	24	52	83	-5
$CuSO_4$	200	24	36	88	-58
$CuSO_4$	175	24	30	75	-51
$Fe_2(SO_4)_3$ /O_2	150	0.5	47	71	+6
$Fe_2(SO_4)_3$ /N_2	150	0.5	41	68	-5

a – + indicates a decrease and - an increase in organic sulfur content out in stages. That is, for a 4-hour run, the desulfurization would be performed in four 1-hour reaction periods, with each period followed by washing with water. It was observed that more pyrites (FeS_2) could be removed in four 1-hour stages than in a single 4-hour treatment in which case retardation of the reaction was observed. Betancourt and Hancock(8) obtained over 90% pyrite removal for some coals by treating in two stages. Formation of a film of elemental sulfur on the surface of the pyrite particle was observed by Yurovskii(57) and was thought to be responsible for the passivation. Another aspect of the retardation effect was proposed by Yurovskii(57) as being caused by the ash in coal. He observed that desulfurization of coal decreases with an increase in ash content of the coal. Using a fluoride complex to dimineralize the coal or more specifically to remove the alumino-silicate parts of the high ash content coal , a significant increase in desulfurization was obtained upon treatment with ferric sulfate solutions. Further investigations revealed that the retarding effects can be caused by adding SiO_2 and Al_2O_3 to the coal. It was found that Al_2O_3 has the largest effect on the retardation of the reaction and this was attributed to the formation of $Al_2(SO_4)_3$ which is known to be adsorped fairly intensively by various compounds having a large surface area. The adsorption of aluminum sulfate is thought to be detrimental to desulfurization by the formation of a protective film over the pyrite particles thus obstructing the diffusion of the oxidizing solution. It is also hardly soluble thus increasing the sulfur content of residual coal and thereby compensating and sometimes exceeding the reduction of sulfur effected by ferric sulfate. The ash analysis of untreated Prince coal is shown in Table 4-4 indicating 36.1% SiO_2 and 23.16% Al_2O_3 which together constitutes about 59% of the total ash and 8% of the coal. This Al_2O_3 could be one of the reasons why the oxidation of inorganic sulfur does not proceed to completion, in addition to the adsorption of iron sulfate and elemental sulfur adsorption on the coal.

The maximum amount of sulfur removal by ferric sulfate leaching occured at 175 °C and 250 psig N_2. This amounts to 53% of the total sulfur and assuming no organic sulfur removal corresponds to 83% pyritic sulfur removal. This could probably be increased to over 90% by treating in stages. Figure 5-5 shows that an increase in temperature from 100 to 150 °C does not change the total amount of sulfur removed but increasing the reaction temperature to 175 °C does result in an increase in the total amount of sulfur removed.

The result of the one run under 250 psig oxygen at 150 °C for ½ hour is shown in Table 5-4 as Run #49. The total amount of sulfur removed was 47% compared with 41% total sulfur removal under nitrogen pressure (#50). This shows that the addition of O_2 might have an effect of increasing the pyrite oxidation rate as observed by Mixon et al.$^{(43)}$ who specified that a minimum of 220 psia O_2 pressure is required for oxygen to have an effect.

The total amount of sulfur removed in Run #50 (41%) was larger than that of Run #26 under the same treating conditions. This was attributed to better liquid/solid contact in Run #50 due to the continuous flow of nitrogen through the reactor providing an agitating effect.

The organic sulfur analysis for Run #49 and Run #50 is shown in Table 5-4. The former indicates a net removal of +6.0% of organic sulfur which shows that a slight oxidation of organic sulfur by oxygen could have occured. An increase of 5% in organic sulfur content for Run #50 shows that ferric sulfate leaching alone does not have an effect on the organic sulfur as reported by previous investigators(8,40,43).

In summary, increasing the reaction temperature from 150 °C to 175 °C increases the amount of sulfur removed; an increase in reaction time does not have a large effect on sulfur removal due to passivation effects; oxygen addition improves oxidation rates and has a small effect on organic sulfur at 150 °C; and retardation of the reaction is linked to the adsorption of aluminum sulfate, elemental sulfur and iron sulfate on the coal surface.

B. Ash Removal

The ultimate analysis shown in Table 5-6 and the ash analysis shown in Table 5-5 for coals treated with cupric chloride solutions indicate that only 4 to 9% of the ash in raw coal is removed.

TABLE 5-5

Ash Analyses for Original and Treated Coals

Leaching Solution	Temperature (°C)	Time (hr)	% Ash[a]	% Ash Removed
Raw Coal	—	—	16.53 ± 0.54[b]	—
$CuCl_2$	200	3	15.43	6.65
$CuCl_2$	175	24	15.92	3.69
$CuCl_2$	150	24	15.09	8.71
$CuSO_4$	200	3	11.70	31.30
$CuSO_4$	175	24	12.16	26.44
$CuSO_4$	150	24	12.15	26.50
$Fe_2(SO_4)_3$ /N_2	150	0.5	7.95	51.91
$Fe_2(SO_4)3$ /O_2	150	0.5	5.93	64.13

a – see Appendix II for analytical method used

b – standard deviation

TABLE 5-6

Ultimate Analysis of Original and Treated Coal Samples MF-WT%[a] (c)

Leaching Solution	Raw Coal	$CuCl_2$[1]	$CuSO_4$[2]	$Fe_2(SO_4)_3/O_2$[3]
Carbon	67.33	65.95	67.69	72.72
Hydrogen	4.41	2.94	4.10	4.02
Sulfur	4.94	1.88	3.79	2.60
Nitrogen	0.95	1.08	1.13	1.14
Ash	14.85	13.87	14.67	5.78
Oxygen[b]	7.52	14.38	8.62	13.74

a - moisture-free weight percent

b - oxygen by difference

c - analysed by EMR Laboratory

1 - treated at 200 °C for 24 hours

2 - treated at 200 °C for 2 hours

3 - treated at 150 °C for ½ hour

This low reactivity with ash suggests that the chloride portion of the leaching solution does not react appreciably with the ash and the oxidation of the inorganic sulfur can proceed to completion without interference from chemical by-products. This was observed for Run #14C in which most of the inorganic sulfur was removed. Meyers(40) also reported that complete oxidation of FeS_2 was obtained using ferric chloride solutions.

The ash analysis shown in Table 5-5 and the ultimate analysis shown in Table 5-6 for coal treated with cupric sulfate solutions (22CS, 17CS, 16CS, 12CS) indicate a larger percentage of the ash, between 26 to 29% of the total is removed. This higher reactivity with ash suggests that the sulfate portion of the leaching solution is more reactive with the ash components. The final result being the formation of aluminum and other sulfates which retard the reaction thus preventing the complete oxidation of pyrite. This results in lower oxidation rates compared to cupric or ferric chloride solutions.

The ash removal for ferric sulfate leaching is very high ranging from 26 to 65% as shown in Table 5-5 and Table 5-6. This ash removal ability could be linked to the presence of sulfuric acid which is known to aid in dimineralization. From Eq. 2.2-3, Eq. 2.2-4, and Eq. 2.2-5, sulfuric acid is produced to a smaller extent by the cupric chloride reaction and to a larger extent by the cupric sulfate reactions while 4% by volume of 1M H_2SO_4 had to be added to the leaching solutions of ferric sulfate to prevent hydrolysis and precipitation. The apparent result is that an increase in sulfuric acid content in the leaching solutions results in an increase in ash removal. An attempt was made to correlate the retardation of the reaction with the amount of ash removed at 150 °C and 175 °C. A comparison of the total sulfur and ash removed is shown in Table 5-7. At 175 °C, an increase in ash removal does coincide with a decrease in reaction rate but at 150 °C variable results were obtained. This further re-enforces the suggestion that it is not the amount of ash removed but the type of components (SiO_2,Al_2O_3) in the ash being reacted that is responsible for the retarding effects.

C. Heating Value Recovery

Ultimate analyses were obtained for raw and treated coals (Run #14C, Run #12CS and Run #49). The formulas of Mott and Spooner(45) were used to calculate heats of combustion, enabling the determination of heating value losses as a result of chemical treatment of coal. The analyses are summarized in Table 5-6 and the corresponding heating values are summarized in Table 5-8.

In Run #14C, coal was treated for 24 hours at 200 °C with aqueous 3 M cupric chloride solution. The carbon content decreased by 3%, hydrogen by 34%, nitrogen increased by 13% and oxygen increased by 88%. The large changes in hydrogen and oxygen do indicate some changes in organic matrix and with the large addition of oxygen (exothermic reaction, loss of heat) together

TABLE 5-7

Comparison of Total Sulfur and Ash Removed at 175 °C and 150 °C For Ferric Sulfate Treatment

Temperature (°C)	Time (hr)	Total Sulfur Removed (%)	Ash Removed (%)
150	½	36	44
150	1	40	35
150	1½	30	28
150	3	44	38
175	½	34	44
175	1	45	45
175	1½	52	47
175	3	53	67

TABLE 5-8

Heating Values for Raw and Treated Coals from Experiments 14C, 12CS, 49[1]

Coal	Heat Content (Btu/lb), MF[2]	Overall Heat Content Loss from Reaction; %[3]
Raw Coal Sample #2	12,149	-
Treated Coal		
Run #14C	10,521	13.40
Run #12CS	11,897	2.07
Run #49	12,219	-0.58

1 – calculated from formulas of Mott and Spooner, see Section III.C

2 – moisture-free basis

3 – loss of solids during treatment not considered

with a loss of carbon and hydrogen should result in a loss of heating value. This loss amounts to 1628 Btu/lb for Run #14C.

In Run #12CS, coal was treated for 1 hour at 200 °C with aqueous 1 M cupric sulfate solution. The carbon content was not significantly altered (+0.34%), hydrogen loss was only 8%, nitrogen increased by 19% and oxygen increased by 14%. The small changes in hydrogen, oxygen and carbon content for the treated coal indicate that the coal matrix is not largely altered and hence the heating value change should be small. The calculated heating value loss for this run was only 252 Btu/lb.

In Run #49, coal was subjected to oxygen pressure of 250 psig and a temperature of 150 °C in the presence of 0.1 M ferric sulfate solution. Carbon content was observed to decrease by 2%, hydrogen decreased by 18%, nitrogen increased by 9% and oxygen increased by 65%. A gain in heating value of 70 Btu/lb was observed for this run.

D. Corrosion and Related Problems

The ferric sulfate desulfurization experiments were performed in a stainless steel (SS316) reactor. Severe corrosion was encountered at 175 °C where the leaching solution became brown in colour. At 150 °C and lower temperatures no severe corrosion was observed and the stains left by the previous corrosive runs were re-dissolved in the leaching solution at these temperatures. The first thermocouples (iron-constantan) used were destroyed by corrosion even before the reaction temperature was attained. This problem was solved by using a thermowell constructed out of the same stainless steel (SS316) material as the reactor.

Severe precipitation of solids occurred when high concentration of 1.0 M and 0.5 M $Fe_2(SO_4)_3$ solutions were used. This precipitation was minimized by using a 0.1 M $Fe_2(SO_4)_3$ solution with the addition of 80 ml 1 M H_2SO_4. Small amounts of yellow precipitate still continued to form on the wall of the reactor. Smallest amount of precipitation was obtained at 100 °C and at 175°C the precipitate became brown in colour and occurred in fairly large quantity especially at longer reaction times. The precipitate was removed from the solid reaction product by washing with 1 M HCl.

V. CONCLUSIONS

The following conclusions were deduced from the analyses performed on Prince coal which was treated with aqueous solutions of cupric chloride, cupric sulfate and ferric sulfate:

1. At 200°C, a 3 M cupric chloride solution was found to be very effective in removing the inorganic sulfur in coal. A maximum of 65% of the original sulfur in coal was removed.

2. A 1 M cupric sulfate solution was not as effective as a 3 M cupric chloride solution in removing the sulfur in coal. The largest amount of sulfur removed was only 36% at 200 °C.

3. At 175 °C, a 0.1 M ferric sulfate solution was more effective than either cupric chloride or cupric sulfate in removing the sulfur with a maximum removal of 53% compared to 30% for $CuCl_2$ and 27% for $CuSO_4$.

4. The amount of sulfur removed increased markedly with an increase in temperature upon treatment with cupric chloride solution. Increases in temperature resulted in only small increases in the amount of sulfur removed upon treatment with either ferric sulfate or cupric sulfate.

5. Longer reaction times did not result in large increases in the amount of sulfur removed upon treatment with the three solutions.

6. Ferric sulfate solution was the most effective in removing the ash in coal with removal between 27-65%. Cupric sulfate solution was moderately effective in removing only 26-29% of the ash. Cupric chloride solutions was the least effective in removing the ash with observed removal between 4 to 9%.

7. Treatment of coal with cupric chloride and ferric sulfate solutions did not have a large effect on the organic sulfur in coal while treatment with cupric chloride solution resulted in large apparent increases in organic sulfur.

8. Analyses of three treated samples indicated that about 13% of the coal's heating value was loss upon treatment with cupric chloride solution and about 2% upon treatment with cupric sulfate solution. The coal's heating value remained relatively unchanged upon treatment with ferric sulfate solution.

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APPENDIX I

LIST OF DEVELOPERS OF CHEMICAL DESULFURIZATION PROCESSES(27)

The following table lists the chemical desulfurization processes and their developers mentioned in the coal cleaning section in the literature survey.

Process Name	Developer
PETC oxydesulfurization process	Pittsburg Energy Technology Center
Ames wet oxidation process	Ames Laboratory, Iowa State University
Ledgemont oxygen leaching process	Hydrocarbon Research Inc.
ARCO promoted oxydesulfurization process	Atlantic Richfield Company
TRW Meyers process	TRW Systems and Energy
JPL chlorinolysis process	California Institute of Technology
KVB process	Research Cottrell Inc.
Batelle hydrothermal coal process	Batelle Columbus Laboratories
TRW gravimelt process	TRW
General Electric microwave treatment process	General Electric Company
Magnex process	Nedlog Technology Group
IGT hydrodesulphurization process	Institute of Gas Technology

APPENDIX II

Methods of Coal Analysis used in our Laboratory

1. Total Sulfur Analysis

Method: Modified-oxygen Flask Method using Thorin as the indicator (1.2).

Apparatus: 2L Erlenmeyer flask, chromel A wire combustion grate, Perkin-elmer AD-2Z autobalance and Manostat Digi-Pet.

Remarks: The pH finish (3) to the modified oxygen-flask method was found to be inadequate for both copper salts and ferric sulfate solutions treated coal. The former treatment gave the same sulfur values for all samples due to some interference presently unknown. The sulfur values for ferric sulfate treatment were 10% higher.

Ion exchange using DOWEX was not absolutely necessary for ferric sulfate runs though it enabled the ease of end point detection during titration. Ion exchange was absolutely necessary for the coal treated by copper solutions as end point was apparently reached when the thorin indicator was added.

2. Organic Sulfur Analysis

Method: Similar to the one used by Block et al. (8)

A 50 mg sample of coal is put into 10 ml of 25% by volume nitric acid for 24 hours, washed, dried and analysed for total sulfur using MOF. This was considered to be organic sulfur.

3. Inorganic Sulfur Analysis

Method: Inorganic sulfur was obtained by subtracting the organic sulfur from total sulfur.

4. Ash Analysis

Method: Considered to be the ash remaining after combustion. An oven dried tared quartz crucible of appropriate size is hung in a wire holder below the grate to prevent loss of ash. After combustion the grate of known tare, and crucible still containing ash is removed and weighed.

APPENDIX III

CURVE FITTING OF EXPERIMENTAL DATA

A treatment of the experimental results of $CuCl_2$ and $CuSO_4$ treatment appears in the following pages. The experimental data was fitted to an exponential-type equation using a computer subroutine (Rosenbrock Minimization). Before the fitted model is tested for model inadequacy using the R-Test and residual plots, Barlett's test is employed to confirm that variances from repeated runs could be pooled.

Experimental Data of Cupric Chloride and Cupric Sulfate fitted to the following equation:

$$\% S = 100\exp\left(B(\theta)\right)^{C}$$

where $\% S$ = percentage sulfur remaining on coal
θ = time (hr)
C = constant
$B = f(T) = B_o + B_1 T + B_2 T^2$ (T in °C)

Procedure: Rosenbrock Minimization (Computer Subroutine)

A. Cupric Chloride Experiments

$B_o = 5.0230$
$B_1 = 6.4286 \times 10^{-2}$
$B_2 = 2.1464 \times 10^{-4}$
$C = 0.10$

1. Barlett's Test for Pooling of Variances

$\Lambda = 3.3902$

at $\alpha = 0.05$ $\chi^2 = 5.991$

$\Lambda < \chi^2$ pooling of variances ok

2. R-Test

$R = 0.3868$

at 0.05 level F-value = 8.79

R F-value Suggest that any inadequacy in the fitted model is not significantly larger (at the 0.05 significance level) than experimental error.

3. Residual Plots

Figure III-1 and Figure III-2 does not show any evidence of systematic behaviour in the residuals, suggesting that the fitted model provides an adequate representation of the data.

B. Cupric Sulfate Experiments

$B_o = 1.1193$

$B_1 = 1.3892 \times 10^{-2}$

$B_2 = 3.4469 \times 10^{-5}$

$C = 0.13$

1. Barlett's Test for Pooling of Variances

$$\Lambda = 0$$

at $\alpha = 0.05$ $\chi^2 = 3.841$

$\Lambda < \chi^2$ pooling of variances ok

2. R-Test

$$R = 0.2$$

at 0.05 level F-value = 19.40

R F-value Suggest that any inadequacy in the fitted model is not significantly larger (at the 0.05 significance level) than experimental error.

3. Residual Plots

Figure III-3 and Figure III-4 does not show any evidence of systematic behaviour in the residuals, suggesting that fitted model provides an adequate representation of the data.

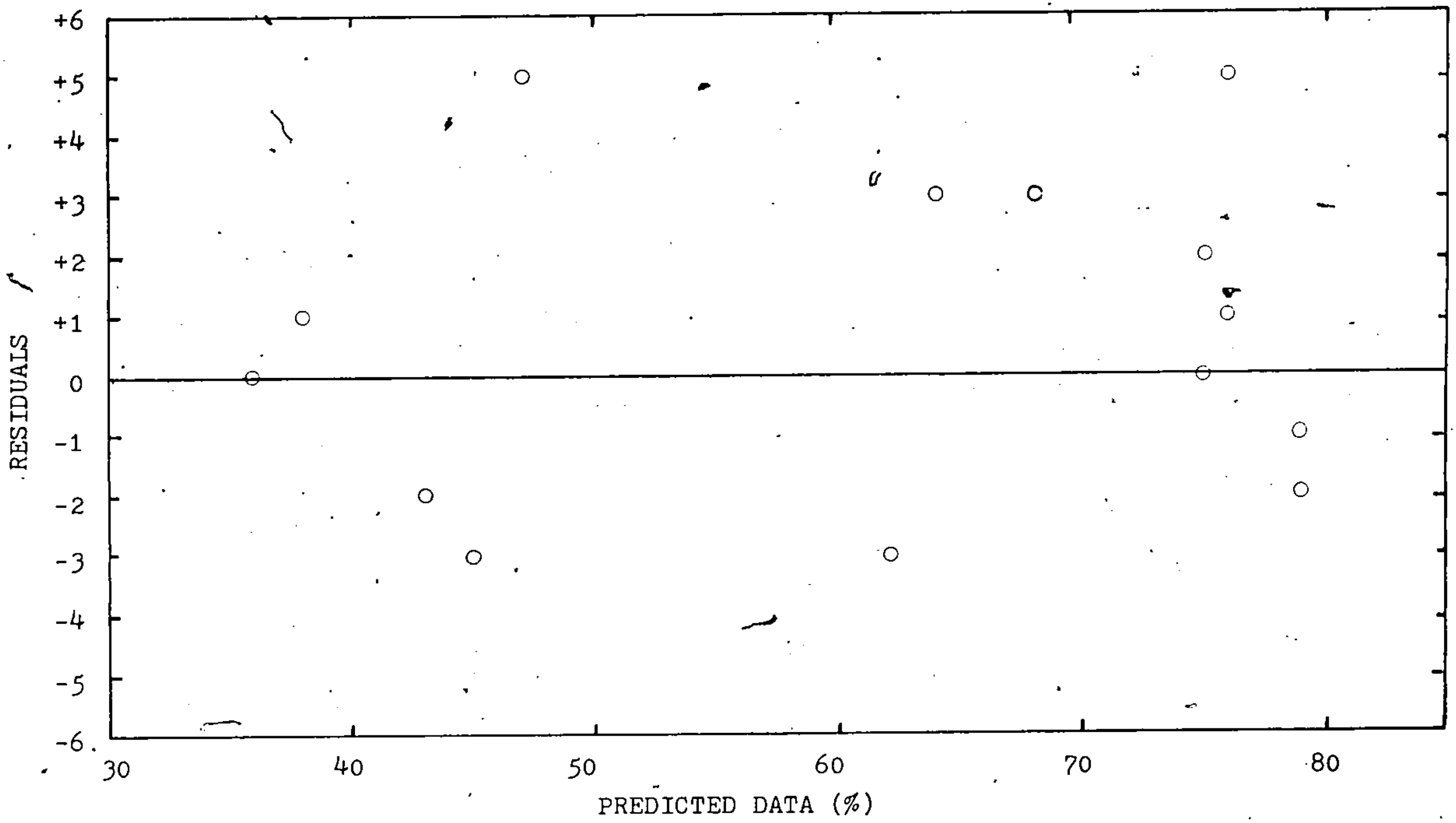

Figure III-1 Residual Plot for Cupric Chloride Desulfurization Data

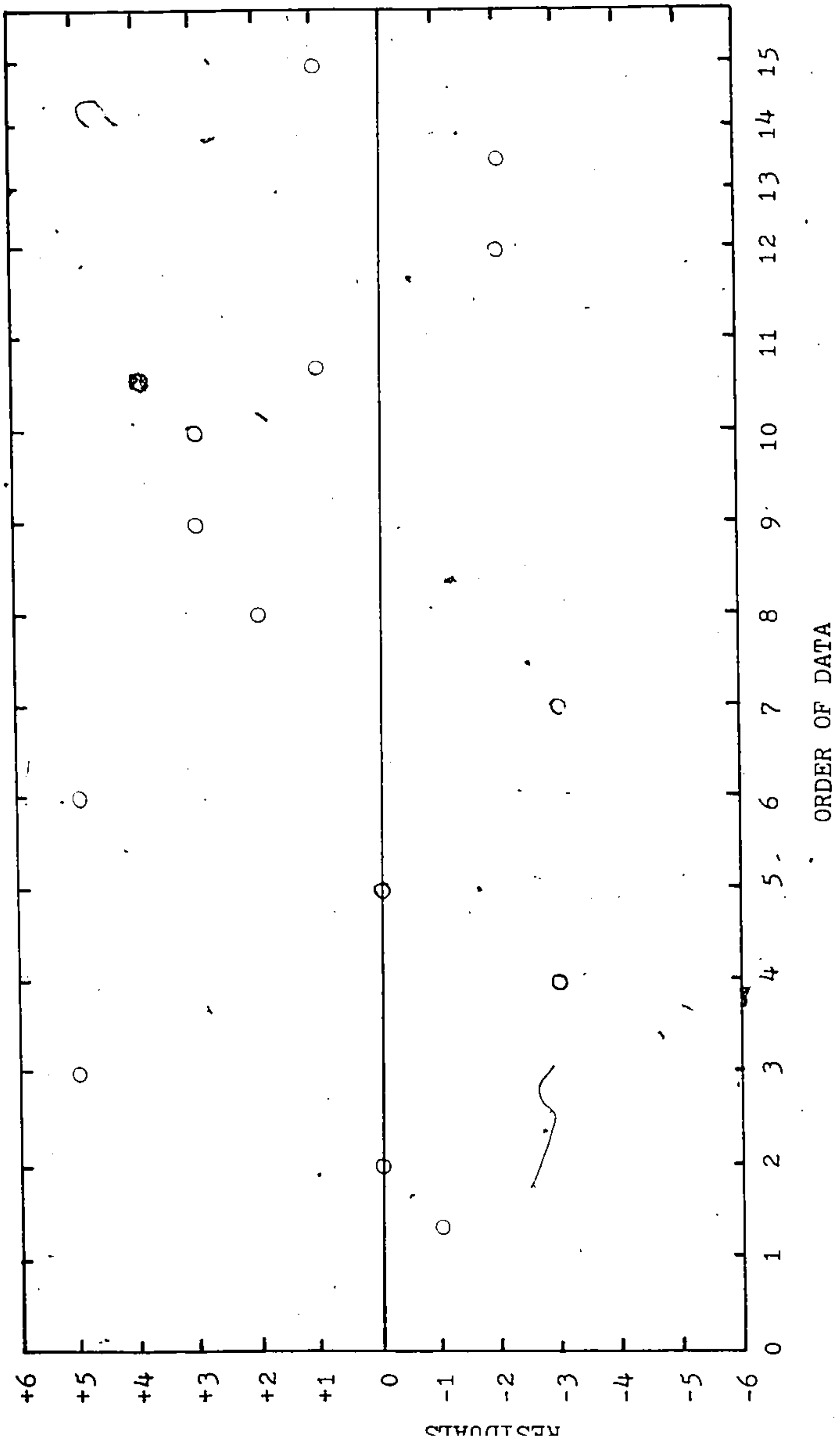

Figure III-2 Residual Plot for Cupric Chloride Desulfurization Data

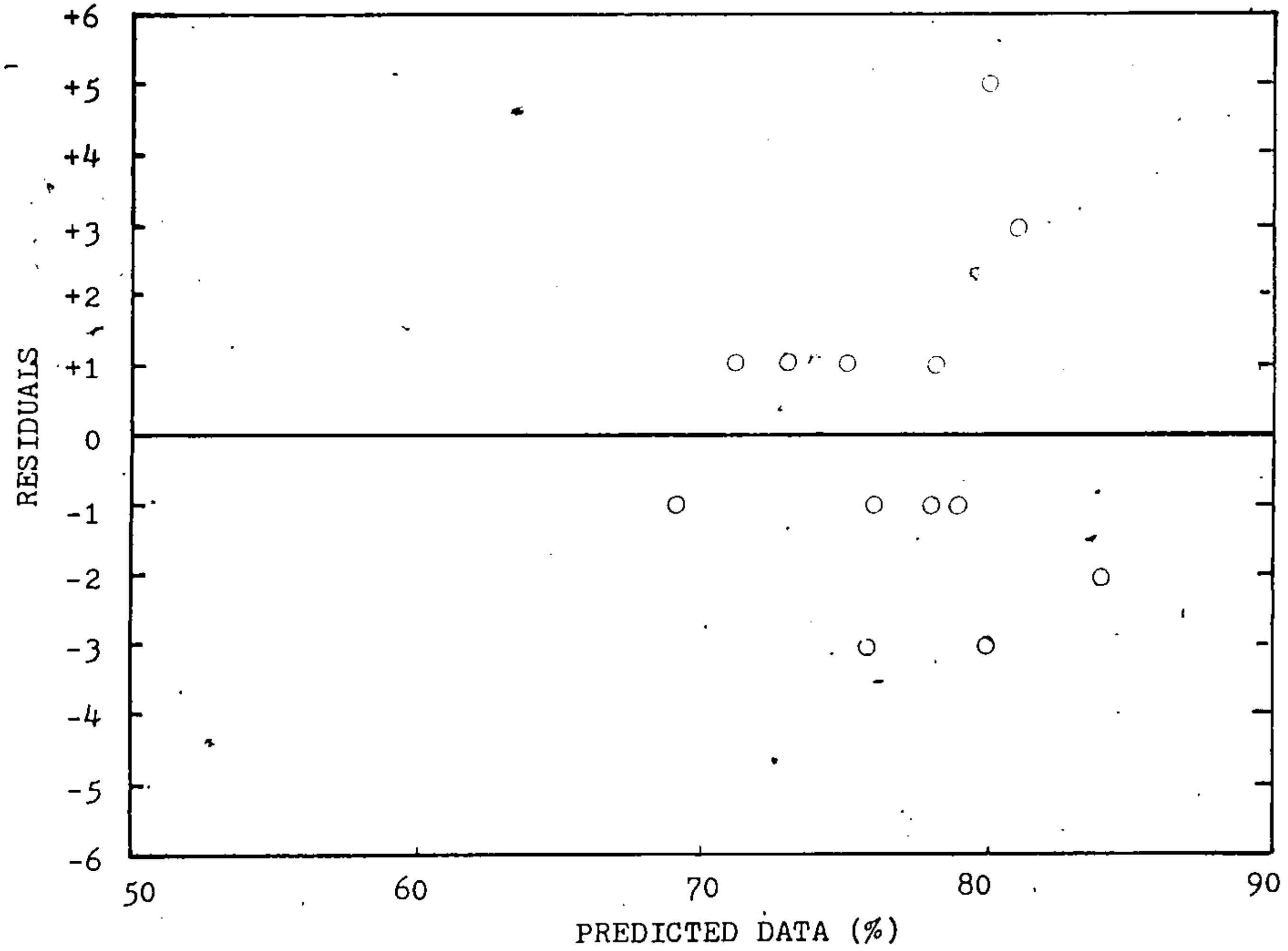

Figure III-3 Residual Plot for Cupric Sulfate Desulfurization Data

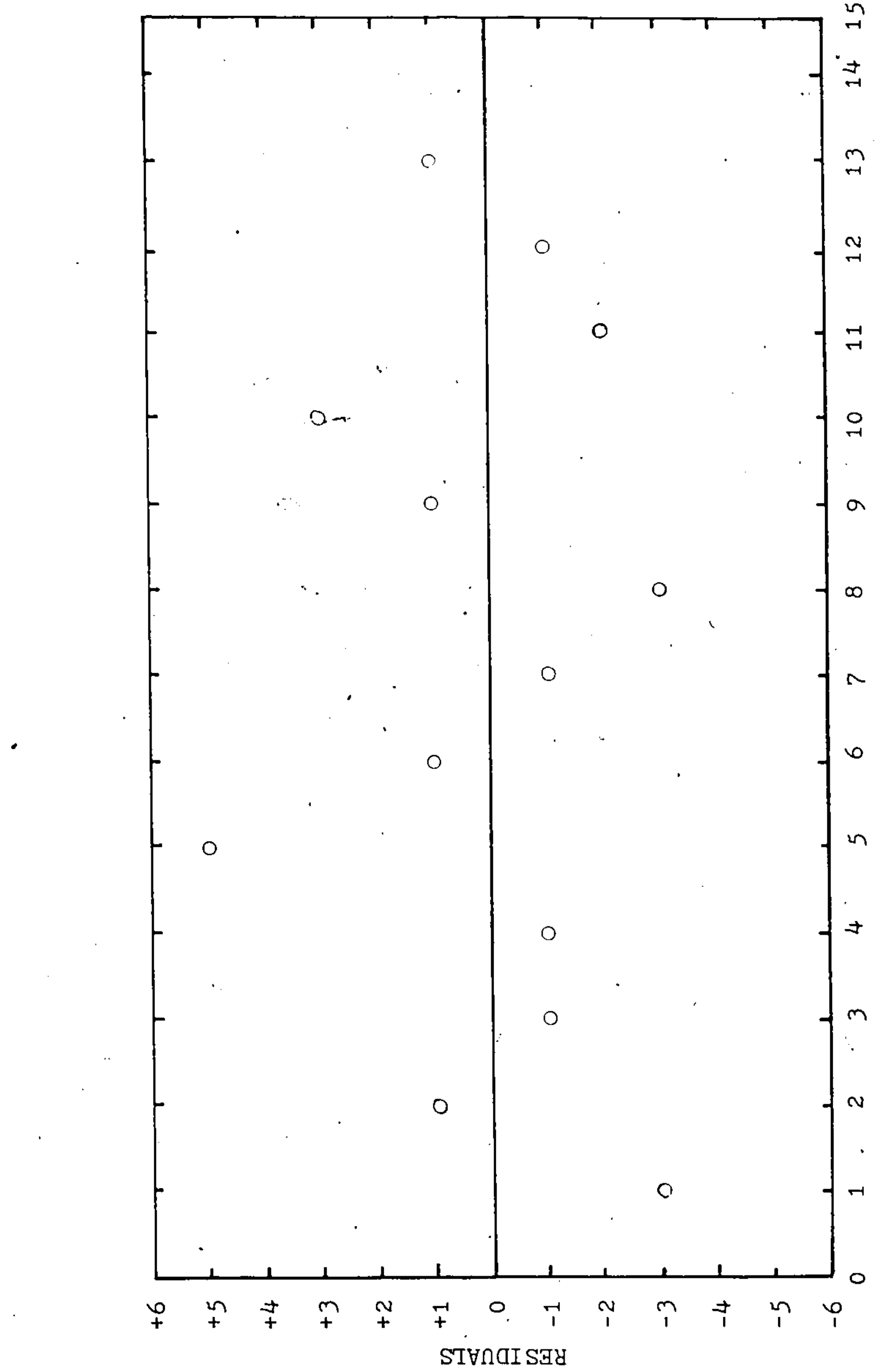

Figure III-4 Residual Plot for Cupric Sulfate Desulfurization Experiments