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THE CHEMICAL CONVERSION OF VOLATILE
COAL SULFUR COMPOUNDS INTO NONVOLATILE
COMPOUNDS AT LOW TEMPERATURES

A Thesis
Presented for the
Master Of Science Degree
The University of Tennessee, Knoxville

William Thomas Hall

August 1986

ACKNOWLEDGEMENTS

I am deeply indebted to all those who have provided inspiration and waited with patience as this project was completed. Most particularly, my wife has been a well-spring of encouragement, and without the encouragement and forbearance of my family this degree would only be a wish.

Certainly, my thanks go to my advisor, George Frazier, whose guidance and patience made my graduate education interesting, enjoyable, and worthwhile, and to John Holmes and Wayne Davis for serving as members of my graduate committee.

ABSTRACT

The reactions of coal sulfur with and without calcium based sorbents have been studied. The coal used was Ky #9, (Paradise), and the samples were finely ground such that 100% of the ground coal would pass through an 80 mesh sieve and 80% would pass through a 100 mesh sieve. The calcium sorbent was Fredonia limestone, similarly ground. The experimental samples were prepared by portioning coal with no sorbent, with finely ground limestone, and with finely ground and freshly calcined limestone. The reactions were studied at room temperature, at 60c, and at 100c over a period of approximately five months.

The chemical analyses for pyritic sulfur, for sulfate sulfur, for total sulfur, and for organic sulfur were performed using standard American Society for Testing Materials (ASTM) methods. X-ray powder diffraction was used to search for metallic reaction products, and gas chromatography was used to search for gaseous reaction products. Pseudo first-order reaction kinetics were assumed, and the reaction rates and the Arrhenius activation energies were determined by statistical methods.

The reactions at room temperature were unaffected by sorbent addition, and the reactions at 60c were only marginally affected by sorbent addition, but the reactions at 100c were clearly related to sorbent addition. It was

found that coal sulfur conversions involve both the organic and the inorganic coal sulfur fractions, and that the reaction kinetics is more complex than the assumed pseudo first-order model. The primary reaction products depended on which sorbent was added to the coal sample.

TABLE OF CONTENTS

SECTION	PAGE
1.0 INTRODUCTION	1
1.1 Problem Statement	1
1.2 Coal Sulfur Conversion Reactions	6
1.2.1 Inorganic reactions	8
1.2.2 Organic sulfur conversions	10
2.0 SIGNIFICANCE	11
2.1 Energy Technologies For The United States	11
2.2 Coal As A Source Of Environmental Pollution	16
2.3 Pathways Of Sulfur In The Atmosphere ..	24
2.4 Atmospheric Sulfur Chemistry	27
2.5 Sulfur Deposition And The Effects Of Deposition	33
2.6 The Control Of Sulfur Emissions	40
3.0 BACKGROUND	43
3.1 Coal Petrology	43
3.1.1 The formation of coal.....	43
3.1.2 The organic matrix of coal	46
3.1.3 Mineral inclusions in coal	50
3.2 Iron Pyrite And Related Minerals (Disulfides)	52
3.2.1 Origin	52
3.2.2 Pyrite chemistry	54
3.3 Coal Beneficiation	56
3.3.1 Categories of beneficiation	57
3.3.2 Physical beneficiation methods ..	60
3.3.3 Coal washing methods	60
3.3.4 Deep cleaning	63

4.0	EXPERIMENTAL PROCEDURES AND EXPERIMENTAL DATA.	65
4.1	Objective	65
4.2	Sample Materials	68
4.3	Preliminary Description Of The Samples ..	69
4.4	Sample Preparation	73
4.5	Time Sequence Chemical Analysis For Sulfur	76
4.6	X-Ray Powder Diffraction Analysis	78
4.6.1	Sample preparation	78
4.6.2	A brief discussion of the theory and operation of an x-ray powder diffraction analyzer	79
4.7	Tests For Gaseous Sulfur Dioxide	85
5.0	RESULTS AND INTERPRETATIONS	91
5.1	Objectives	91
5.2	Time Sequence Chemical Analysis	91
5.2.1	Theory and results	91
5.2.2	An alternate description of the sulfate sulfur formation	104
5.2.3	Interpretation of the time sequence results	108
5.2.4	Organic sulfur	114
5.2.5	Closing mass balances	116
5.2.6	Sulfur dioxide	117
5.3	The Arrhenius Activation Energy: Theory And Determination	119
5.4	X-Ray Diffraction Analyses	121
5.4.1	Freshly ground coal	121
5.4.2	Aged coal samples	127
5.4.3	Coal plus sorbents aged at 60c ..	130
5.4.4	Detectability limits of minerals in coal	131

6.0	CONCLUDING DISCUSSIONS	135
7.0	SUMMARY	139
	REFERENCES	145
	APPENDIXES	151
	A. Selected Thermodynamic Data	152
	B. Fredonia Limestone Analysis	154
	C. Laboratory Results for ASTM Analyses for Pyritic and Sulfate Sulfur	156
	D. Percent Total Sulfur and Percent Organic Sulfur	160
	E. Summary of ASTM Analytical Procedures	162
	F. Statistical Table: Student's <u>t</u> Distribution ..	169
	G. Table of X-Ray Powder Diffraction Constants ..	171
	H. Selected X-Ray Powder Diffraction Spectrographs	177
	VITA	188

LIST OF TABLES

TABLE		PAGE
1.1	Heats Of Formation And Free Energies Of Formation Of Selected Inorganic Compounds ...	7
2.1	Estimation of Unit Costs for a Coal Conversion Plant	19
2.2	Ultimate Analyses in Mass Percent of Rep- resentative Coals of the United States	22
2.3	Rates of Homogeneous Oxidation of SO ₂ in the Atmosphere	31
3.1	The Origin Of Coal Macerals	45
3.2	Composition Of Extractable Coal Fractions ...	50
3.3	Minerals In Coal	53
4.1	Net Enthalpies Of Reaction And Net Free Energies Of Reaction For Equa- tions (4.4-4.11)	67
4.2	Identification Of Experimental Samples	75
4.3	Materials Prepared For X-Ray Diffrac- tion Analysis	80
5.1	Empirical Formulae By Regression Analysis Pyritic Sulfur Conversion	99
5.2	Empirical Formulae By Regression Analysis Increasing Sulfate Sulfur	100
5.3	Empirical Formulae By Regression Analy- sis; Increasing Sulfate Sulfur; Alterna- tive Model	109
5.4	Asymptotic Values Of Pyrite Sulfur Conversion	115

5.5	Percent Decrease In Pyrite Sulfur and Percent Increase In Sulfate Sulfur	118
5.6	The Arrhenius Activation Energy	122
7.1	Analytical Results for Pyrite Sulfur Reduction	142
7.2	Analytical Results for Sulfate Sulfur Formation	143
7.3	Arrhenius Activation Energy	144

LIST OF FIGURES

FIGURES		PAGE
2.1	Production of Bituminous Coal and Lignite, ... and Dollar Value of Production; 1973-1981	17
2.2	Coal Fields of the Conterminous United States	20
2.3	Sources of Sulfur Compounds in the Atmosphere	24
2.4	The Global Sulfur Cycle in the Biosphere	25
2.5	Implied Fraction of SO_2 Converted to Sulfate Along the East Coast of the United Kingdom, As a Function of Relative Humidity	28
2.6	Involvement of SO_2 in Atmospheric Chemical Reactions	32
2.7	Comparison of Rainfall pH to Other Common Substances	35
2.8	Major North American Storm Tracks	37
2.9	Precipitation pH And North American SO_2 Emissions	38
2.10	Average Concentration of SO_4^{2-} in North American Precipitation	39
3.1	A Representation of the Bituminous Polymeric Skeleton	47
3.2	Selected Biological Precursors of the Coal Matrix	48
3.3	Structures of Iron Pyrite and Marcasite	55
3.4	Phase Diagrams for the Fe-S-O-H System	57
4.1	Photoelectron Micrograph of Specimen Surface	70
4.2	Photoelectron Micrograph of A Band Isolated from Figure 4.1	70
4.3	X-Ray Emission Spectrum of Figure 4.2	72

4.4	Diagram of the Source, Sample, and Detector: Rigaku Geiger-Flex X-Ray Powder Diffractor...	83
4.5	Formation of the Bragg Double-angle: X-Ray Diffraction Analysis	84
4.6	The Rigaku Geiger-Flex Computer Program	86
4.7	Sulfur Dioxide Test Gas Chromatograms	89
5.1	Hypothetical First-order Curves Fitted To The Experimental Data	92
5.2	The Regressed Straight Lines Based on the Empirical Formulae	101
5.3	Typical Exponential Curves of the Form $Y = \exp[f(x)]$	105
5.4	Hypothetical Exponential Curves of the Form $Y = \exp(a - b/x)$ Fitted To The Data For Sample No. 1, Coal Aged At Room Temperature	106
5.5	The Dependency of the Arrhenius Acti- vation Energy on Composition	123
5.6	X-Ray Diffraction Scan of Coal Pyrite	125
5.7	X-Ray Diffraction Scan of Freshly Ground Coal	126
5.8	X-Ray Diffraction Scan of Coal Aged at Room Temperature	128
5.9	X-Ray Diffraction Scan of Coal Aged at 60°C Temperature	129
5.10	X-Ray Diffraction Scan of Coal Aged With Fredonia Limestone At 60 Degrees	132
5.11	X-Ray Diffraction Scan of Coal Aged With Calcined Fredonia Limestone At 60 Degrees	133

1.0 INTRODUCTION

1.1 Problem Statement

It has become apparent that the near-term growth and maintenance of the electric power industry will be via coal utilization. Coal is plentiful, relatively cheap, and available near the points of utilization. On the contrary, hydropower sites have been essentially 100% developed; the nuclear power industry is in dis-array due to technical and political problems; increasing demands on natural gas for basic chemical purposes are causing gas to become uneconomical for electric power production; and the so-called alternate energy sources such as solar energy, power from geothermal sources, the wind and the sea, are far from ready for general commercialization.

The problem with coal is simple: it is very dirty. The coal power industry is a mature industry with few technological problems and favorable economics. But there are huge quantities of ash that require disposal; and unfortunately, the coals that are nearest the points of utilization tend to be high in sulfur resulting in gaseous sulfur oxide emissions upon combustion.

The sulfur oxide emissions resulting from coal combustion return to the earth's surface as acidic depositions and seem to be wreaking havoc with certain delicate ecosystems in the northeastern United States, and also

Canada, Scandinavia, and Germany. Degrees of damage are also visible in the upper midwestern and Appalachian regions of the U.S. The reduction of acid rain, one form of acid deposition, is a current controversial subject with many political ramifications and numerous technological and economic considerations.

Almost all schemes designed to reduce the emissions of gaseous oxidized sulfur compounds include the use of lime or limestone. Most developmental work so far has been in post-combustion methodologies in which the produced gasses are reacted with a lime slurry. Other important control approaches include fluidized bed combustion methodologies and limestone injection or limestone pelletization, all of which rely on the co-introduction of a calcium based chemical additive with the fuel coal which quickly reacts with the sulfur oxidation products.

The chemistry and reaction kinetics of coal sulfur compounds at low temperatures, most particularly iron pyrite, have not been elucidated. The present study is an attempt to fill-in certain gaps in the knowledge of coal sulfur chemistry at low temperature with respect to reaction rate, reaction order, reaction products, and the apparent Arrhenius activation energy.

It is possible that where coal can be sized and stored for periods of time of 60 days, more or less, significant amounts of coal sulfur can be converted at

ambient conditions into a form which is stable at moderate combustion temperatures -- this is probably a sulfate salt. It is also possible that users of stoker coal, where pellitization with lime or limestone is appropriate, will find the information of this and similar studies useful.

The ambient air oxidation of iron pyrite (FeS_2) in coal has been known as a chemical phenomenon for some time, but only recently has the progress of the air oxidation reaction, or the auto-desulfurization reaction, been analyzed (1). Another study has investigated the catalysis of the ambient air oxidation reaction by alumina (2), and still another recent study by Wilcox (3) has demonstrated the increased rate of the oxidation of pyrite at ambient conditions in the presence of calcined limestone. In the Wilcox study the oxidation rate was determined to be first-order, and the first-order time constant for the conversion of 62.3% of the pyrite was determined to be approximately 20 days^{-1} for a moderately high sulfur coal and several different limestones. The analytical method for determining the pyrite conversion reaction used by Wilcox was thermogravimetric analysis.

Davis and Fiedler (4) have demonstrated that the sulfur of coal is retained in the combustion ash proportionately to the calcium content of the coal. Attempts are now under way to utilize the calcium retention of coal

sulfur by limestone addition at the time of combustion by the pelletization of coal with limestone before combustion (5) and by various lime/limestone injection processes during combustion.

The original intent of the Wilcox study was to investigate the retention of sulfur in the combustion ash as a function of calcium content, and to determine whether the chemical form of the calcium, i.e., lime or limestone, affected the retention rate. In the course of the investigation a noticeable drift in the results was observed over time, and it was speculated that the sulfur inherent in the coal was reacting with the calcined additive under ambient conditions, and also probably the uncalcined limestone as well. The good correlation of the data of the Wilcox study to first-order kinetics strongly suggests that only one sulfur compound was involved in the reaction, with the assumption being that the reactive species was iron pyrite. In fact, it was not confirmed by experiment that the increase in the mass of the ash produced over time by the thermogravimetric technique was due to sulfur conversion of iron pyrite.

Consequently, it was decided to study further the possible conversion of iron pyrite, or other sulfur compounds, in the presence of calcined limestone and limestone in an attempt to remove any ambiguities. This present report is the result of a study in which the iron

pyrite content of reacting coal samples was evaluated directly according to standard extractive procedures, and without resorting to combustion temperature reactions.

The iron pyrite content and the sulfate content of specially prepared coal samples were monitored over a period of 120 days by ASTM methods (6). By using the ASTM methodology the oxidation of iron pyrite, as well as any change in the organic sulfur content of the coal could be evaluated directly.

By X-ray diffractive techniques the iron pyrite oxidation products could be unambiguously determined. Although certain oxidation products of the FeS_2 -lime-limestone reaction system were determined to be present on materials from the Wilcox study, i.e., CaSO_4 ; it has not been established whether the oxidized salts resulted from the ambient oxidation of FeS_2 or from the combustion reactions (7).

In addition to observing the ambient oxidation of FeS_2 , other samples were observed at 60c and 100c in the present study. By observing the pseudo first order reaction at three temperatures the Arrhenius activation energy, E , could be determined. Other samples were semi-saturated with water to observe whether moisture level affects the conversion of pyritic sulfur in the presence of calcined lime or limestone. Only one type of coal was used in this study: Kentucky #9, (Paradise), which is a

high sulfur coal. The sample used was 3/4" top-size, with some evidence of weathering.

1.2 Coal Sulfur Conversion Reactions

In coal, sulfur exists in inorganic and organic chemical forms with small negative energies of formation. The sulfur in these forms is very reactive, and upon combustion of the coal the result is sulfur dioxide (SO_2). It is desirable to find a method whereby the sulfur may be transformed into a non-reactive moiety before combustion, such as calcium sulfate (CaSO_4). Calcium sulfate is stable at moderate combustion temperatures and SO_2 is not emitted. When the reactive coal sulfur is chemically oxidized before combustion or use, it is said to have been "converted" into a nonreactive form.

Since the reactions of coal sulfur at low temperature have been incompletely observed, there are few literature references. As can be seen from the short table of thermodynamic data for selected inorganic compounds (8), iron oxide, iron sulfate, and calcium sulfate are all thermodynamically stable compared to FeS_2 . However, FeS_2 alone does not auto-oxidize in air, and it is described as "inert at room temperature" (9). In the dry state, it has not been established whether FeS_2 and CaO or CaCO_3 react in any manner.

Although the data of Wilcox strongly suggest that

Table 1.1

Heats Of Formation And Free Energies Of Formation
Selected Inorganic Compounds

kcal/mol at 25c

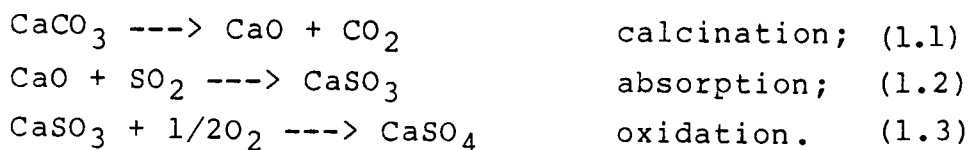
Compound	ΔH_f	ΔG_f
CaCO_3	-288.5	-269.8
CaO	-151.8	-144.3
Ca(OH)_2	-235.7	-214.8
CaS	-113.5	-112.3
CaSO_4	-339.5	-315.9
FeO	- 65.0	- 60.1
Fe_2O_3	-197.0	-177.4
Fe_3O_4	-267.3	-242.7
Fe(OH)_2	-136.0	-116.3
Fe(OH)_3	-196.7	-165.5
FeS	- 23.9	- 24.0
FeS_2	- 42.6	- 39.9
FeSO_4	-221.9	-197.2
$\text{S}_2(\text{g})$	30.8	19.1
$\text{S}_8(\text{g})$	24.2	11.8
$\text{SO}(\text{g})$	1.2	- 5.1
$\text{SO}_2(\text{g})$	- 70.9	- 71.8
$\text{SO}_3(\text{g})$	- 94.6	- 88.7

*Source: "Lange's Handbook Of Chemistry," ed. J.A. Dean, McGraw-Hill Book Co., New York, 1985.

only the FeS_2 was undergoing an ambient temperature reaction, the analysis of Chandra, et al (1), indicates that ambient conversion of organic sulfur compounds does occur, and to about the same extent as pyrite conversion. The results of Chandra were based on an examination of the sulfur moieties of a pile of coal exposed to the weather for four years. In such a case the conversion of organic coal sulfur by microbial action could be more noticeable than for dry coals under laboratory conditions.

1.2.1 Inorganic Reactions

It is hypothesized that at combustion temperatures gaseous oxidized sulfur products react with calcined limestone to produce CaSO_4 according to the following sequence:

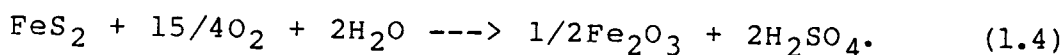


Calcination is necessary for good SO_2 absorption because the reaction of SO_2 with CaCO_3 is quite slow at temperatures below which CaCO_3 is stable (1400 F). The reaction may depend on pore structure, and pore structure depends mainly on the limestone type and the calcination conditions, primarily temperature. Generally, 1800 F is chosen as an optimum combustion temperature for the calcination-absorption-oxidation sequence (10). At lower temperatures, in the absence of additives in the coal, it

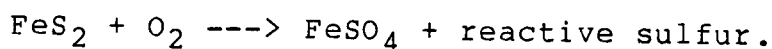
is believed that FeS_2 converts to FeSO_4 , either by bacterial action or by slow solid-solid reactions. The solid-solid reactions may in fact be aqueous and depend on the moisture in and around the coal particles.

Stenhouse and Armstrong observed microscopically that stable layers of Fe_2O_3 and Fe_3O_4 formed around granules of unreacted pyrite (11). The unreactivity of pyrite at room temperature is explained by the formation of this passive oxide film in which further oxidation of the pyrite granules is controlled by resistance to oxygen diffusion through the oxide layer. Comminution of fresh samples makes more surface area available for reaction with the resultant pseudo first-order behavior of the conversion process.

But the observed $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ film does not explain what happened to the sulfur. In fact, it is not certain that the observed films were, in fact, iron oxides. An appropriate stoichiometric reaction which satisfies this result is:



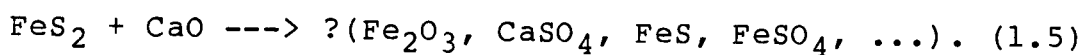
Others suggest a more simple approach:



Unfortunately, this begs the question of the net reaction. Burkin and Edward (12) observed rapid desulfurization at the pyrite grain boundaries and in impure and imperfect pyrite crystals, but offered no hypothesis with regard to

the chemical fate of the sulfur. Note that the formation of H_2SO_4 requires water from some source.

A similar problem arises with regard to the pyrite reactions in the presence of some additives, such as calcined or uncalcined limestone:



It is well established that sulfate content increases and that pyrite content decreases upon the exposure of coal to air. The exact species and mechanisms have not been established.

1.2.2 Organic Sulfur Conversions

The organic sulfur exists in functional groups within the organic matrix of the coal. The major functional groups are the mercaptans, sulfides, disulfides, and thiophenes. These functional groups are somewhat reactive chemically, and microbial metabolism could be expected to supply somewhat acidic waste products, perhaps further contributing to the conversion of inorganic sulfur.

There are no known satisfactory thermochemical reactions which account for the conversion of organic sulfur compounds at ambient temperatures. Consequently, it must be assumed that organic sulfur conversion is the result of microbial catalysis.

2.0 SIGNIFICANCE

2.1 Energy Technologies For The United States

It has become obvious that the future energy needs of the United States will require the full development of numerous technologies. Not only will a variety of technological approaches to the solution of the energy problem be required, but each approach must be consistent and compatible with environmental restrictions, industrial health and safety regulations, political realities, and public perceptions.

It is also necessary that each technology be capable of contributing a significant fraction of the total energy requirement in order to be economically attractive for development. A large portion of the total capital investment in the United States is allocated to energy production, and the cost of money, even in deflationary times, demands that energy be produced as cheaply and efficiently as possible.

Every known energy technology has some serious limitation to its exploitation. Hydro-electric power, for instance, is limited by the fact that almost all suitable sites have already been developed, and by the environmental concerns for the ecological damage done by dams and flooding. An example is the siltation that occurs behind dams and the lack of siltation below dams. A particularly

acute example of the damage done by changing a natural river cycle and by changing the siltation patterns is the Aswan High Dam of Egypt. Above the dam Lake Nasser is rapidly silting-up, resulting in a poor quality impoundment and an increase in the incidence rate of shistosomiasis. Below the dam the clean water is scouring the river bank increasing the corrosion rate, and the unusually clean water has led indirectly to a near total loss of the sardine harvest at the mouth of the Nile River (13).

Those technologies thought of as "clean," or "safe," because no expendable resources are necessary include solar power, wind power, geothermal heat sources, and natural thermoclines in the sea. However, those technologies are only in their infancy. Furthermore, the ecological impact may be far greater than supposed because clean technologies are also inefficient technologies, and huge expanses of physical plant will be required to produce a significant quantity of energy. To support the physical plants vast new networks of roadway for maintenance and wires for delivery networks will be required in the fragile eco-system of the desert and forest (14).

Fission nuclear power suffers from identifiable technical difficulties in the areas of metallurgy and control, from rapidly escalating development costs, from the environmental problems associated with waste disposal, and particularly from problems of politics and public perception.

Although nuclear energy offers many technical advantages, the current problems of the industry are severely limiting the exploitation of those advantages. It has been several years since a permit for a new nuclear plant has been filed with the appropriate regulating authority, and when units under present construction have been commissioned, the nuclear power industry in the U.S. will become dormant. For the foreseeable future nuclear power will provide only a few percent of the total electrical energy requirement of the United States; however, other nations are expected to continue the development of commercial nuclear energy.

Further development of petroleum and petroleum-related resources, such as natural gas, is impractical due to the limited resources available for use and the competition for those resources by uses other than energy production. Gasoline and diesel fuel -- the fuel for cars, trucks, trains and planes already accounts for 25% of the total of U.S. energy use. Increasing pressure on petroleum allocations for petro-chemicals and agri-chemicals combined with vehicle fuel production severely limits the amount of petroleum-like raw materials available for new energy production facilities.

The problems of further energy development from petroleum are compounded by the fact that the United States is less than self-sufficient in petroleum production.

Currently, about 20% of U.S. petroleum use is imported, with 10% of our imports coming from the region known as the Middle East. Although this figure is down from the 35% figure of a few years ago, additional use of petroleum as an energy source will necessitate additional imports (15). The so-called Arab Oil Embargo of 1973-1974, and the tremendous price escalation of crude oil during the same period, was a shocking lesson to Americans accustomed to flaunting their energy wealth. Consequently, further development of petroleum-based energy technologies is predicted to be in the areas of refinements of existing technologies. There will be continued strong pressure to conserve petroleum reserves, with probable downward pressure on the use curve for the next few years (16).

The difficulties in developing alternative energy technologies, the retrenchment of the nuclear power industry, the limitation of petroleum reserves, together with political uncertainties, have all combined, in a sense, to resurrect the coal industry. Coal is not a problem-free energy source, but it is readily available and the technology exists for immediate utilization. Coal can be utilized, with varying degrees of economy, not only as a raw energy source (combustion for heat) but also as a substitute for petroleum in the production of liquid fuels and as a chemical feedstock material. The conversion of

coal to synthetic liquid fuels is in the demonstration plant stage for several promising new processes, and the industry is reaching for industrial maturity, albeit with slower progress than many would like. The U.S. Synfuels Board, with many problems of its own, has only recently made its first cash awards for on-going syn-fuel projects (17).

Coal represents hazards to industrial safety and health and to environmental and ecological quality. Industrial safety and health considerations include the high accident rate of mining operations (particularly underground mining), black-lung disease, and the high accident rate associated with transportation by rail. Ecological and environmental damage occurs from the physical mining process (particularly strip mining), from mine drainage and run-off, and from air pollution after combustion of the coal. Air pollution also poses certain health risks to the general population. When coal is used as a chemical feedstock, it tends to produce carcinogenic by-products.

None the less, coal is available, and it is utilized in tremendous quantities. According to the Keystone Coal Industry Manual, coal utilization has shown considerable growth in the past decade from less than 600 million tons in 1973 to over 800 million tons in 1981. The coal production industry is adding an additional 514 million tons

capacity by 1990, in anticipation of continued growth in the industry (18). Marketed coal, in production tonnage and dollar value for this period, is illustrated graphically by Figure 2.1.

2.2 Coal As A Source Of Environmental Pollution

Coal utilization presents problems in each of the three well-known areas of environmental control: water pollution, air pollution, and solid waste disposal. The water pollution problems occur mainly from the mining process and coal washing operations. In both cases, the drainage and/or run-off waters tend to be acidic and toxic. Solid wastes are primarily associated with the combustion ash, which includes the combustion residue and the collected fly ash from air pollution control devices. The ash may contain concentrations of toxic minerals, such as cadmium, aluminum, or arsenic, which require stabilization or special disposal sites. Even when the waste is demonstrably biologically and chemically inert, it must go somewhere, often in huge quantities. Real estate used as a waste disposal site is an expensive, if not always complex, solution to the problem of solid wastes.

For the coal user, among the most complex and the most expensive unit operations in the plant will be air pollution control devices. For U.S. industry, approximately 50% of air pollution control expenditure has been

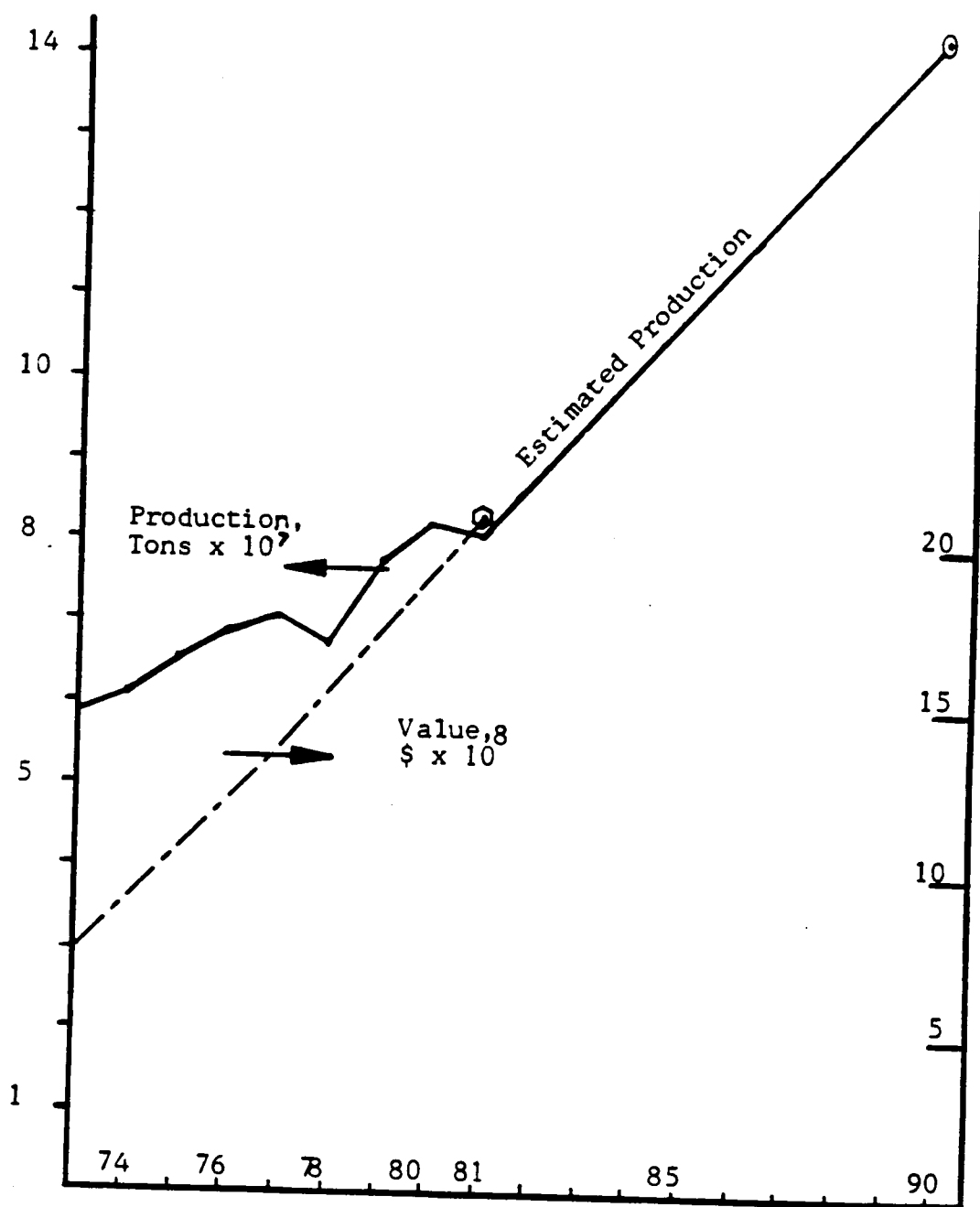


Figure 2.1*

Production of Bituminous Coal and Lignite,
and Dollar Value of Production; 1973-1981

*Source: "The Keystone Coal Industry Manual," McGraw-Hill Book Co., various issues.

for the control of particulate emissions from the combustion of coal. However, sulfur oxide control is becoming more expensive, relatively, than particulate control. Table 2.1 is an estimation of the unit costs for a syn-fuels plant project, illustrating the expensive nature of pollution control (19).

Although nitrogen is usually present in coal at about the same level as sulfur, the regulations controlling the emissions of nitrogen oxides (NO_x) are less stringent and less well-defined than the regulations controlling the emissions of sulfur dioxide (SO_2). In addition to the nitrogen in the coal, atmospheric nitrogen is converted to NO_x during the combustion process at high temperatures. In fact, it is modification and control of the combustion process, particularly control of the temperature of combustion, that is the primary method of NO_x control. Currently, there are no significant commercial secondary NO_x control methodologies in use in the United States, although Japan does require effective NO_x control (20).

Sulfur content in U.S. commercial coals varies from less than 0.5% to about 3%. As fate would have it, the coals that are nearest the large industrial centers, the Mid-Western and Appalachian coals, are the highest in sulfur content. The "Coal Fields of the Conterminous United States" are shown in Figure 2.2 (21), and the "Ultimate Analysis In Mass Percent Of Representative Coals Of

Table 2.1

Estimation of Unit Costs for a Coal Conversion Plant
(Costs in Millions of Dollars)*

Unit Description	Cost Variability
coal preparation, storage, and handling	46.5 - 75.2
gasification	44 - 65
oxygen plant	45 - 80
raw gas quench	19 - 50
sour water treatment**	19 - 58
shift conversion	31 - 52
acid gas removal**	108 - 117
sulfur recovery**	54 - 60
methanation	29 - 58
drying	0.8
water supply	17 - 25
steam and utilities	136 - 255
solids disposal**	3.3 - 8.9
general facilities	68 - 90
Total approximate cost	1000.00

** Represents a pollution control unit

Approximate sub-total of pollution control 208.1

Approximate percent invested in
pollution control 20.8%

*Source: G.A. Mills, Chemtech, July, 1977.

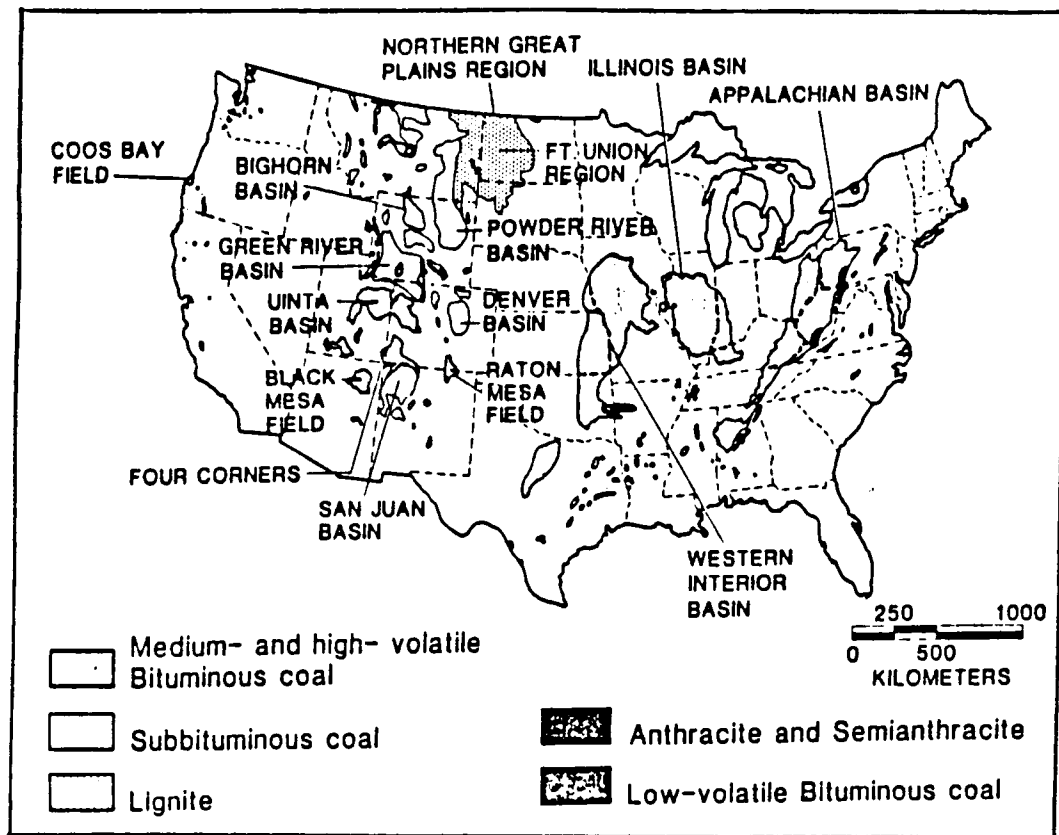


Figure 2.2*

Coal Fields Of The Conterminous United States

*Source: Averitt, U.S. Geological Survey Bulletin 1412, 1975.

The United States", illustrating the sulfur, nitrogen, and ash contents, is given in Table 2.2 (22). It may be seen from these illustrations that the sample Illinois and Appalachian bituminous coals are relatively high in sulfur and nitrogen content and moderate in ash content.

The sulfur in coal is converted almost stoichiometrically to a sulfur oxide upon combustion: usually 95% or more sulfur is converted. Davis and Fiedler (4) have studied the retention of sulfur in the fly ash from coal-fired boilers and found that the retained sulfur strongly correlated with lime (calcium) content of the coal ash. This fact is utilized in at least two SO₂ emission control schemes: pelletization of stoker coal with limestone prior to combustion and the addition of limestone during combustion in the atmospheric fluidized bed (ATFB) process. In both schemes the effect is to increase the calcium content of the ash in a special way.

The U.S. Environmental Protection Agency (EPA) regulates SO₂ control by emission standards. The current regulation in Tennessee, which is a typical regulation, is not more than 1.2 lbs./10⁶ BTU heat value (23). Recent strong associations of present levels of emitted SO₂ and long-term environmental damage may force a reduction in allowable emissions. For coal-fired electric utilities additional SO₂ emission reductions would result in estimated cost increases of from 6% up to 50%.

Table 2.2

Ultimate Analyses in Mass Percent of Representative Coals of the United States*

Component	Fort Union Lignite	Powder River Subbituminous	Four Corners Subbituminous	Illinois C Bituminous	Appalachia Bituminous
Moisture	36.2	30.4	12.4	16.1	2.3
Carbon	39.9	45.8	47.5	60.1	73.6
Hydrogen	2.8	3.4	3.6	4.1	4.9
Nitrogen	0.6	0.6	0.9	1.1	1.4
Sulfur	0.9	0.7	0.7	2.9	2.8
Oxygen	11.0	11.3	9.3	8.3	5.3
Ash	<u>8.6</u>	<u>7.8</u>	<u>25.6</u>	<u>7.4</u>	<u>9.7</u>
Total	100.0	100.0	100.0	100.0	100.0
GCV (MJ/kg)	15.6	18.4	19.6	24.9	31.2

* Source: Probststein and Hicks, "Synthetic Fuels," McGraw-Hill Book Co., 1977.

For the United States in 1970, SO_2 emissions generated by combustion processes have been estimated to have exceeded 35 million tons, and by the year 2000 emissions are expected to exceed 100 million tons if present emission regulations remain in force. About half the SO_2 emissions originate with electric energy generation, and about 60% of the sulfur dioxide air emissions result from coal combustion (24).

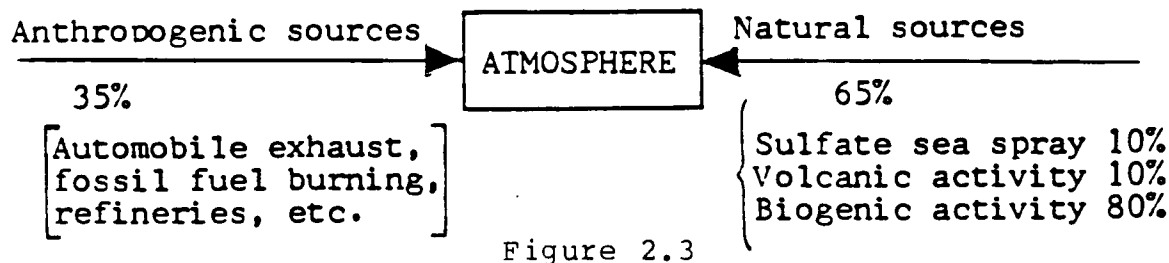
Emitted sulfur is reported as equivalent SO_2 whether it is emitted as SO_2 , sulfur trioxide (SO_3), or as a sulfate aerosol (SO_4^{2-}). Usually, well over 90% of emitted sulfur oxides are emitted as SO_2 , and SO_2 is considered environmentally hazardous and detrimental in itself. However, the SO_3 and SO_4^{2-} forms of sulfur are considered more potentially damaging than SO_2 in moderate concentrations.

There are three common pathways of atmospheric SO_2 which contribute to environmental quality deterioration: (1), it may be absorbed/adsorbed directly by the soil where it reacts to form acid sulfates, particularly with aluminum, or it may be metabolized adversely by plant life: (2), it may be photo-oxidized in the atmosphere to SO_3 and react with water vapor to form sulfuric acid mist: (3), it may combine with gaseous basic compounds, including nitrogen compounds, to form sulfate aerosols. Either droplets of sulfuric acid mist or air-borne sulfate

particles are candidates for becoming condensation nuclei, around which rain drops form, causing acid rain. Acid rain is one of the most controversial topics of our time.

2.3 Pathways of Sulfur In The Atmosphere

The sulfur burden of the atmosphere originates from both man-made (anthropogenic) sources and from natural sources. About 35% of the atmospheric sulfur burden is estimated to be of anthropogenic origin, and about 23% of the atmospheric sulfur burden is from coal combustion (27). The origins of atmospheric sulfur are illustrated by Figure 2.3 (28), and the global sulfur cycle in the biosphere is illustrated by Figure 2.4 (29).



Sources of Sulfur Compounds in the Atmosphere*

* Source: Aneja, Aneja, and Adams, Journal of the Air Pollution Control Association, 32,8.

Myers, Aneja, et al, Butler, and others (30,31), maintain that (1) overall the atmosphere has achieved

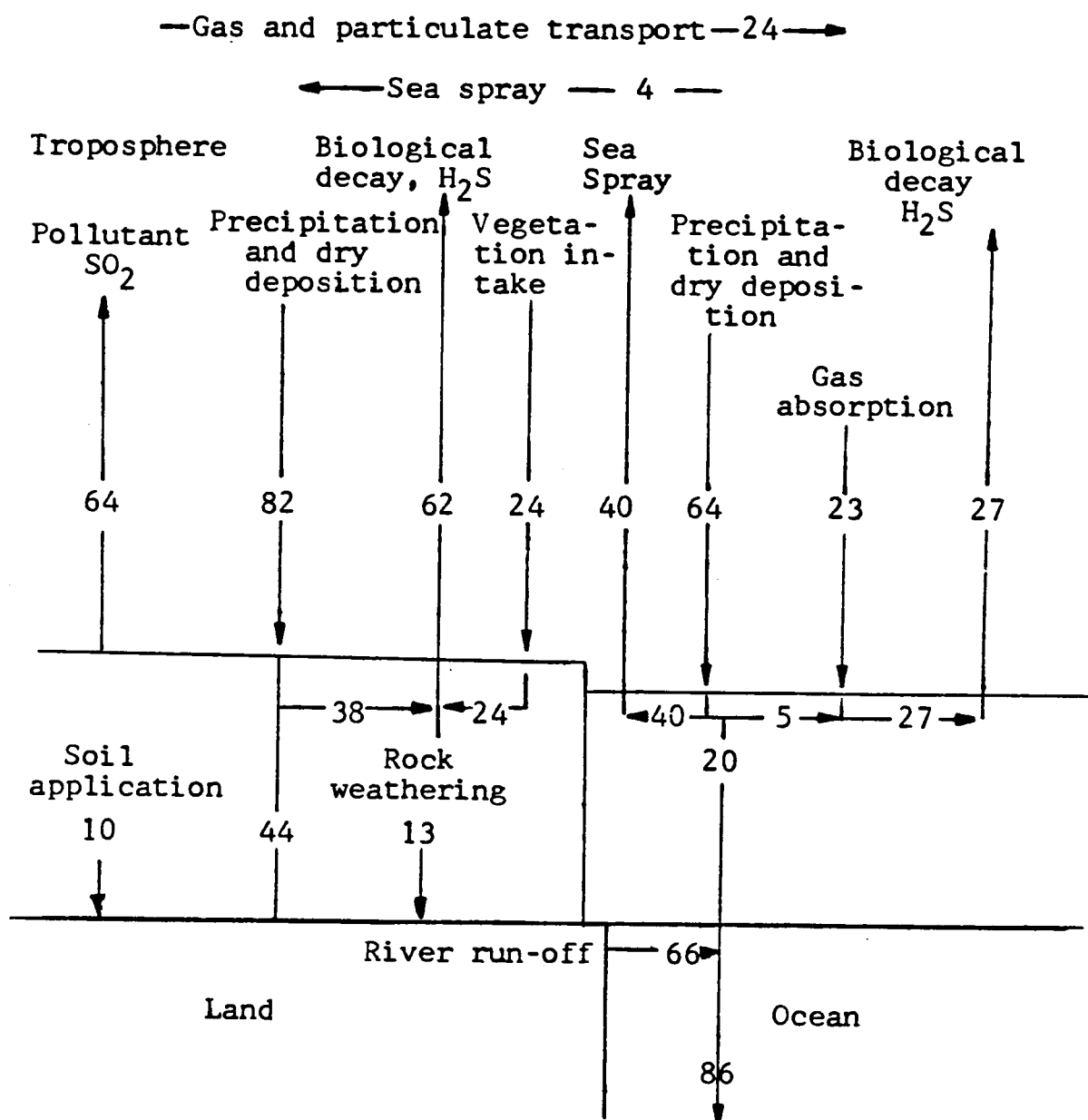


Figure 2.4*

The Global Sulfur Cycle in the Biosphere

($\text{kg} \times 10^9 \text{ year}^{-1}$)

*Source: Butler, "Air Pollution Chemistry," Academic Press, 1978.

steady-state with regard to the sulfur burden, (2) no matter in what form the sulfur is emitted it eventually will be oxidized to SO_2 , SO_3 , or SO_4^{2-} , and (3) the ocean is the ultimate sulfur sink for all the sulfur emitted. This cycle requires time, and when sulfur compounds are locally released into the atmosphere at such a rate that the compounds can not be time distributed into the sulfur-cycle, "the atmosphere-to-land portion of the sulfur cycle is unsound", (27).

It is typical that large coal combustion sources are concentrated in relatively small areas around the world. These areas are, of course, the large industrial cities and regions of the world, and it is from emissions from the large industrial complexes that the adverse ecological effects of sulfur pollution originate.

In contrast, the natural sources of sulfur emissions are spread over the entire surface of the earth. Active volcanism, for instance, releases huge quantities of sulfur in bursts which are of comparatively short duration, and the bursts are highly energetic. Consequently, the effects of volcanism, though measurable, are short-term. Much of the eruptive mass is distributed above 100,000 feet (28) and is rapidly absorbed into the background sulfur burden. On a yearly average basis, volcanism accounts for about 10% of natural sulfur emissions. The majority of the atmospheric sulfur burden originates in

biogenic activity, including the action of sulfur-releasing bacteria, plant metabolism, etc.

2.4 Atmospheric Sulfur Chemistry

In general, when atmospheric sulfur chemistry is considered, it is the role of SO_2 in atmospheric chemistry that is implied. For the case of sulfur pollution released from the combustion of coal, hydrogen sulfide (H_2S) and other sulfur compounds are not of much interest. The understanding of the involvement of sulfur dioxide in atmospheric reactions is not far advanced, and the oxidation of SO_2 to SO_4^{2-} may proceed via very complex mechanisms. Sulfur dioxide reactions have been identified which are dependent on photo-oxidation, relative humidity, metal aerosol catalysts, ozone, aerosol surfaces, and airborne ammonia concentrations (26). Figure 2.5 illustrates the fraction of SO_2 converted to sulfate as a function of relative humidity for one study (29).

The oxidation routes of SO_2 have been summarized by Roberts and Friedlander (30) as five probable mechanisms, and placed into two broad categories by Cox (31).

Class I: Heterogeneous oxidation either in aqueous cloud or fog droplets or on aerosol particles

- (1) liquid phase oxidation catalyzed by metals
- (2) catalyzed oxidation by absorption/adsorption on soot.

Class II: Homogeneous gas-phase oxidation, usually by photochemically initiated reactions

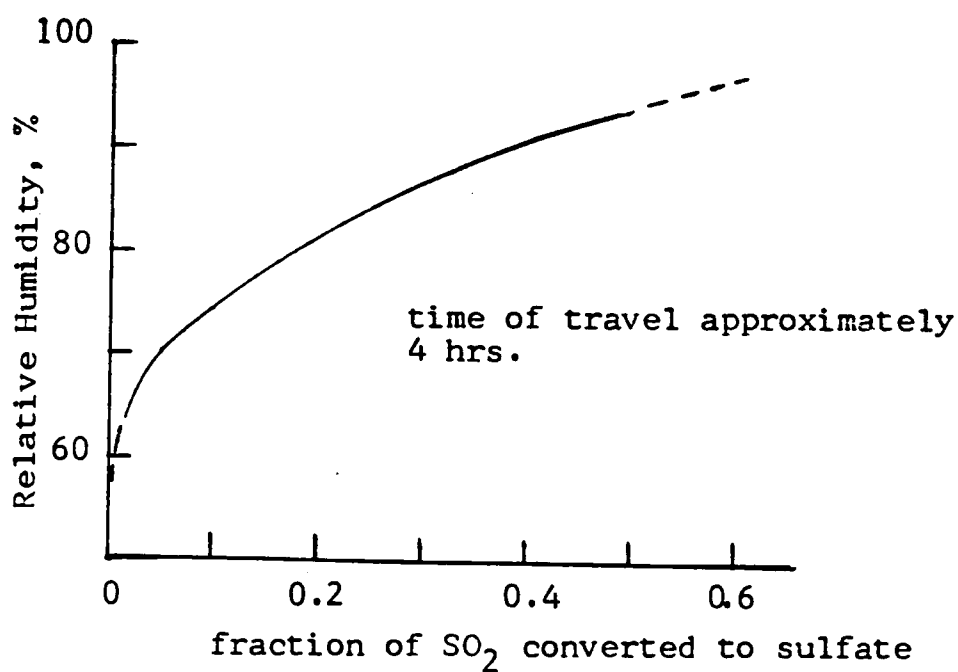


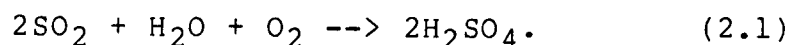
Figure 2.5*

Inplied Fraction of SO₂ Converted to Sulfate Along
The East Coast of the United Kingdom, as a Function of
Relative Humidity

*Source: Smith and Hunt, Proceedings of the International Symposium on Sulfur in the Atmosphere and Atmospheric Environment, 12, 1977.

- (3) homogeneous gas-phase oxidation by OH: radicals
- (4) homogeneous gas-phase oxidation by an intermediate of the ozone-NO_x-hydrocarbon photochemical reaction
- (5) homogeneous gas-phase oxidation by other intermediate species, e.g., HO₂, RO₂, RO.

Within a smoke plume, Class I, mechanisms (1) and (2) are thought to be very important. Even in a plume that has been drastically reduced in fly ash content a large number of particles will be present. Manganese and iron salts have been demonstrated as capable conversion catalysts in straight-forward conversion to sulfuric acid:



The water is available from the atmosphere, and as may be seen from Figure 2.5, when the relative humidity exceeds 70% the conversion rate is rapid.

Foster has studied catalytic SO₂ conversion in some detail -- centering on rate expressions (32). For the second-order manganese-catalyzed reaction, the reaction rate constant has been estimated as:

$$k_{i,\text{Mn}} = 2 \times 10^5 \text{ l}_{\text{H}_2\text{O}} \text{ mol min}^{-1}. \quad (2.2)$$

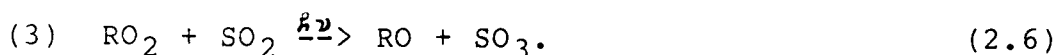
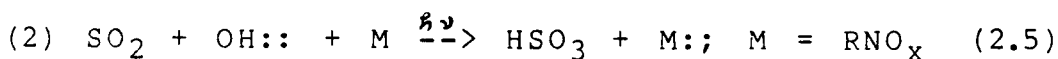
For the first-order iron-catalyzed reaction, the reaction rate constant has been estimated as:

$$k_{i,\text{Fe}} = 2 \text{ min}^{-1}. \quad (2.3)$$

The actual reaction sequence is hypothesized to occur via conversion of the SO₂ to SO₃²⁻ in aqueous solution, and then the reaction with iron salts forms intermediates

en route to SO_3 formation in the droplet. The SO_3 rapidly associates with the water to form H_2SO_4 . There is evidence that for iron, as the pH lowers, the reaction rate increases (33). It is assumed that the reactions on soot particles are similar to those for which metal salts act as catalysts.

Direct photochemical oxidation of SO_2 has been shown to be of low quantum yield in the lower atmosphere (26). Therefore, SO_2 conversion to a higher oxidized state of sulfur must proceed by reactions with intermediates. These are the Class II, mechanisms (3), (4), and (5) reactions:



For some specific cases, the rates of homogenous oxidation have been summarized by Cox (31), and are presented in Table 2.3; the atmospheric sulfur dioxide reactions are diagrammatically illustrated in Figure 2.6 (26).

There have been recent suggestions that hydrogen peroxide (H_2O_2) is involved in the oxidation of SO_2 . There is new evidence that H_2O_2 may be present in the northeastern U.S. atmosphere in concentrations as high as 40 ppb. It has also been suggested that H_2O_2 , HO and HO_2 radicals, and trace metal catalytic aerosols are all interrelated in the oxidation of SO_2 to H_2SO_4 (33).

Table 2.3*

Rates of Homogeneous Oxidation of SO₂
in the Atmosphere

reaction	rate constant cm ³ molecule ⁻¹ s ⁻¹	concentration of (active species) molecules cm ⁻³	100 × oxidation rate of SO ₂ h ⁻¹
(a) direct photooxidation SO ₂ (³ B ₁) + O ₂ → SO ₃ + O(³ P)	ca. 1.6 × 10 ⁻¹⁵ †	2.3 (SO ₂ [³ B ₁])‡	0.026
(b) free radical oxidation OH + SO ₂ → HOSO ₂	8 × 10 ⁻¹³	7 × 10 ⁶ § (OH) (7 × 10 ⁵)¶	2.0 (0.2)
HO ₂ + SO ₂ → OH + SO ₃	9 × 10 ⁻¹⁶	2 × 10 ⁹ § (HO ₂) (1 × 10 ⁸)¶	0.6 (0.03)
CH ₃ O ₂ + SO ₂ → CH ₃ O + SO ₃	5 × 10 ⁻¹⁵	2 × 10 ⁹ § (CH ₃ O ₂) (1.5 × 10 ⁷)¶	1.7 (0.03)
(c) ozone-alkene reaction RCHOO + SO ₂ → RCHO + SO ₃	—	2.5 × 10 ¹² [O ₃] 2.5 × 10 ¹¹ [C ₃ H ₆]	0.07

† 0.4 % of total quenching of SO₂[³B₁] at 50 % relative humidity.‡ Solar zenith angle = 40°; [SO₂] = 10 parts/10⁹.§ Typical maximum daytime OH and RO₂ concentrations computed for 50° N latitude, 1 July; see text.|| Extrapolated from laboratory measurements of O₃-propene-SO₂ system.

¶ Mean summertime concentrations in the background troposphere at 50° N latitude.

* Source: Cox, Philosophical Transactions of the Royal Society of London, 290, 1979.

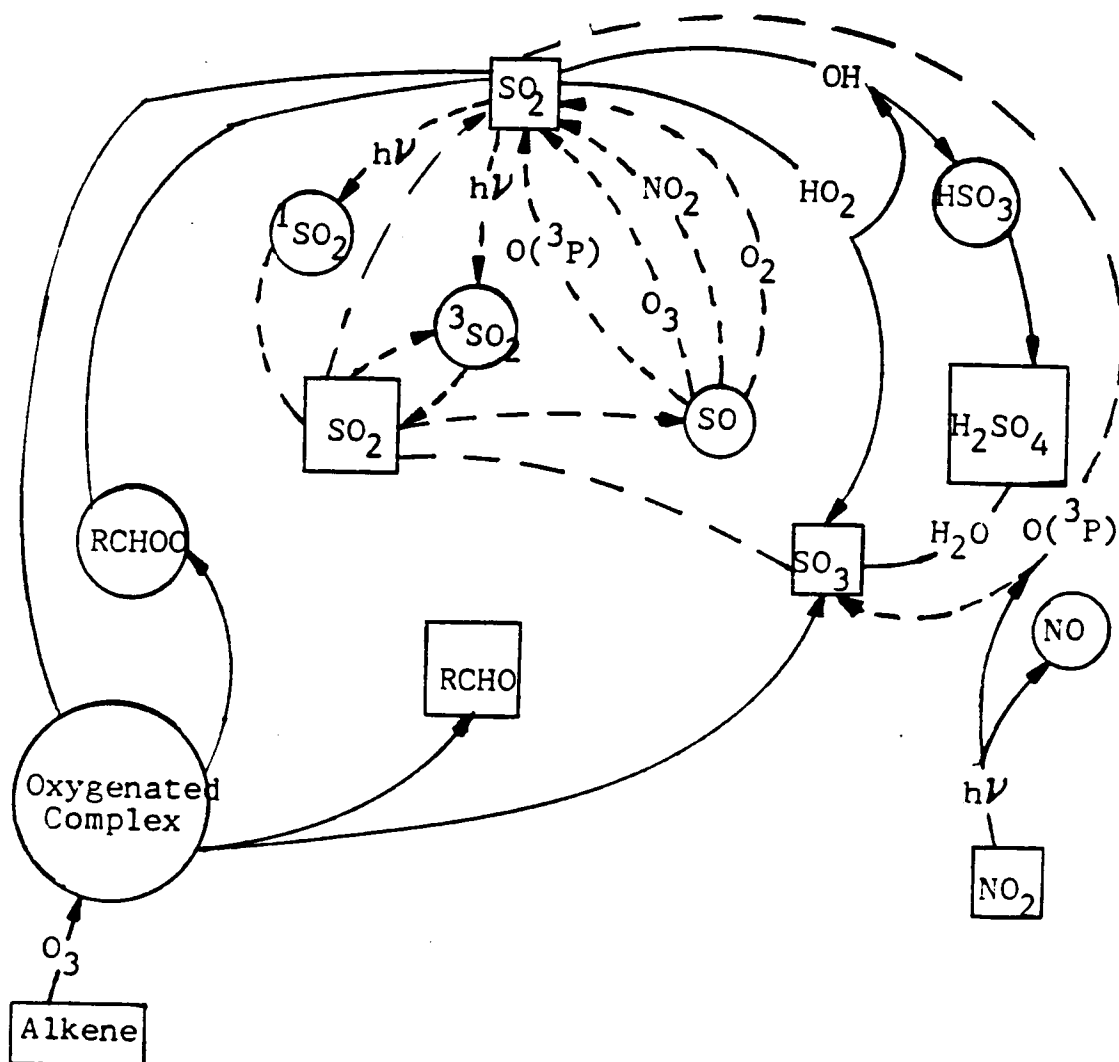


Figure 2.6

Involvement of SO₂ in Atmospheric Chemical Reactions*

*Source: Butler, "Air Pollution Chemistry," Academic Press, 1978.

2.5 Sulfur Deposition And The Effects Of Deposition

In obedience to the fundamental physical law, "what goes up, must come down," sulfur and nitrogen emitted to the atmosphere will return to the earth. Furthermore, they will return in an oxidized state. There are four mechanisms by which sulfur and nitrogen compounds, gaseous or particulate, are deposited on the earth's surface (34):

- (1) gravitational sedimentation;
- (2) turbulent transfer to the surface, followed by impaction, adhesion, sorption, or chemical reaction;
- (3) precipitation scavenging;
- (4) gas-solution exchange during wet periods.

Non-technically, but very descriptively, these mechanisms are divided into either of two categories: dry deposition or acid rain.

When the effects of acid deposition were first given serious consideration, it was primarily the direct effects of airborne sulfur oxides on foliage, erections, statuary, etc., or air pollution health effects that were considered. Little consideration was given to the degrading effects of long-time depositions on soils and inland waters from air concentrations below that which caused short-time measurable effects. It has now been established that soils are acidified over time as sulfuric acid and other pollutants are deposited in small quantities near the surface and gradually washed into the soil by precipitation.

When acid seeps through the soil, calcium and other basic cations are displaced by the incoming hydrogen ions and are transported or bound as sulfates (typically). As the soil becomes progressively more acidic due to the loss of basic cations, the incoming hydrogen ions can react with aluminum salts. The trivalent aluminum (Al^{3+}) in solution is toxic to plant life and to aquatic animal life (35). The current theory regarding the decline of freshwater lakes in the northeastern quadrant of North America and in North Europe is that organisms suffer both from pH intolerance and Al^{3+} poisoning (36) as aluminum is leached from the surrounding soils.

Recent studies have demonstrated that many organisms, particularly algae of the forest floor and certain conifers, are sensitive and susceptible to low precipitation pH alone (37,38). Although the implications of such studies are less obvious than they might seem, authorities universally agree that SO_2 and NO_x emissions from fossil fuel combustion, especially coal, are the great contributors to environmental acidification. Also, many authorities believe that acid rain is the major mechanism for returning acidic compounds to the earth's surface (39). Figure 2.7 illustrates the comparative acidity of various materials and is intended to give a sense of reference for acid rain (40).

SO_2 and NO_x are transported by air currents without

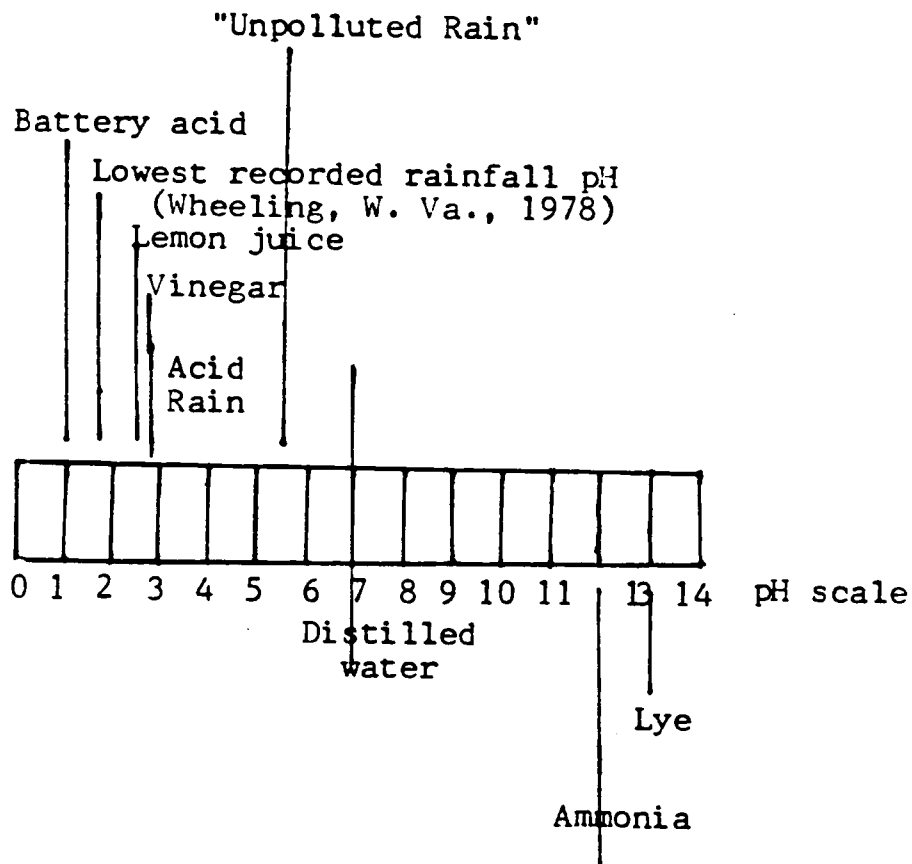


Figure 2.7

Comparison of Rainfall pH to Other Common Substances*

*Source: Record, Bubenick, and Kindys, "Acid Rain," Noyes Data Corp., 1982.

regard to national boundaries. Consequently, emissions from sources in Germany and the Netherlands are transported to Scandinavia; emissions from the United States are transported to Canada and become acid rain there. Emissions from Ohio are precipitated in Vermont and Maine. Resultantly, all around the world, pollution emissions are now international political issues.

Canada has perhaps the most intricate network for monitoring acid rainfall in the world. A two-year study indicates a significant southward shift in precipitation pH isopleths (41). However, if Figures 2.8 (42) and 2.9 (43) are compared, it may be seen that there is an obvious correlation between the intersections of North American storm tracks and precipitation pH. A two-year study is possibly a statistical short-sample, and the average pH isopleths likely vary several hundred miles year to year.

By comparing Figure 2.10 (44) and Figure 2.9, it may be seen that the average SO_4^{2-} concentration in North American precipitation exhibits a somewhat more variable pattern than might be expected from the pattern of SO_2 emissions and average rainfall pH.

Thorough reviews of the interactions among energy production -- pollution emission -- atmospheric reactions -- acid rain may be found in several recent publications, including the National Academy of Science (40,45,46).

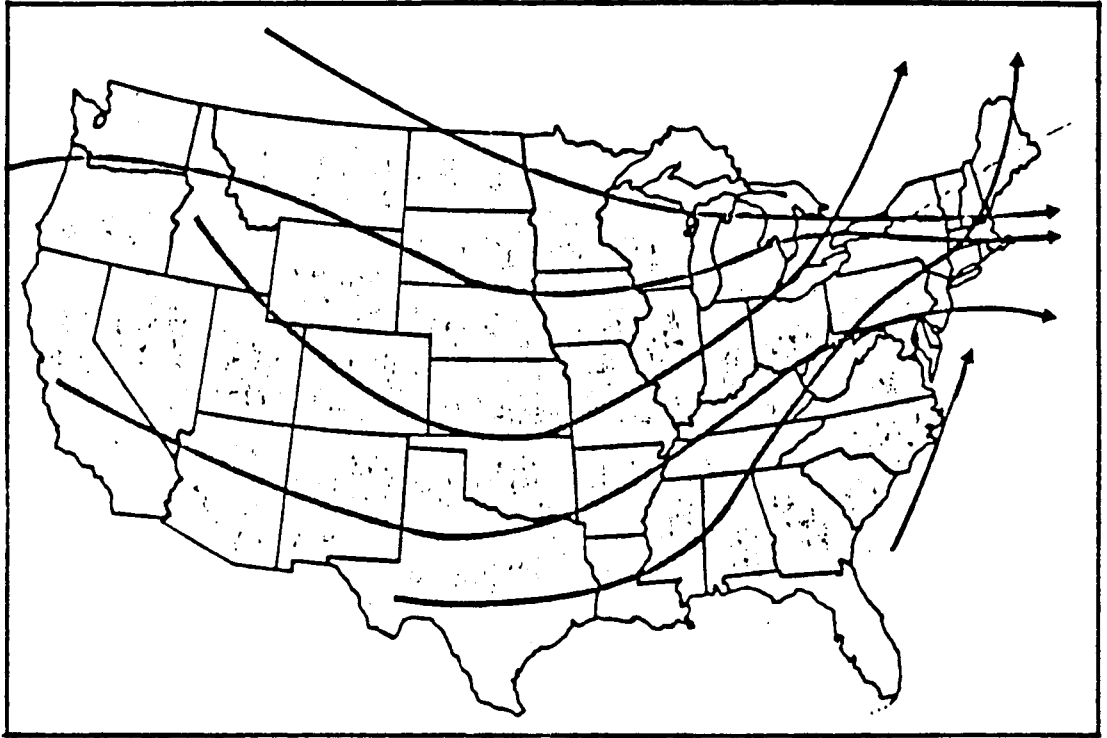


Figure 2.8

Major North American Storm Tracks*

* Source: Vishner, "Climatic Atlas of the United States,"
Harvard University Press, 1954.

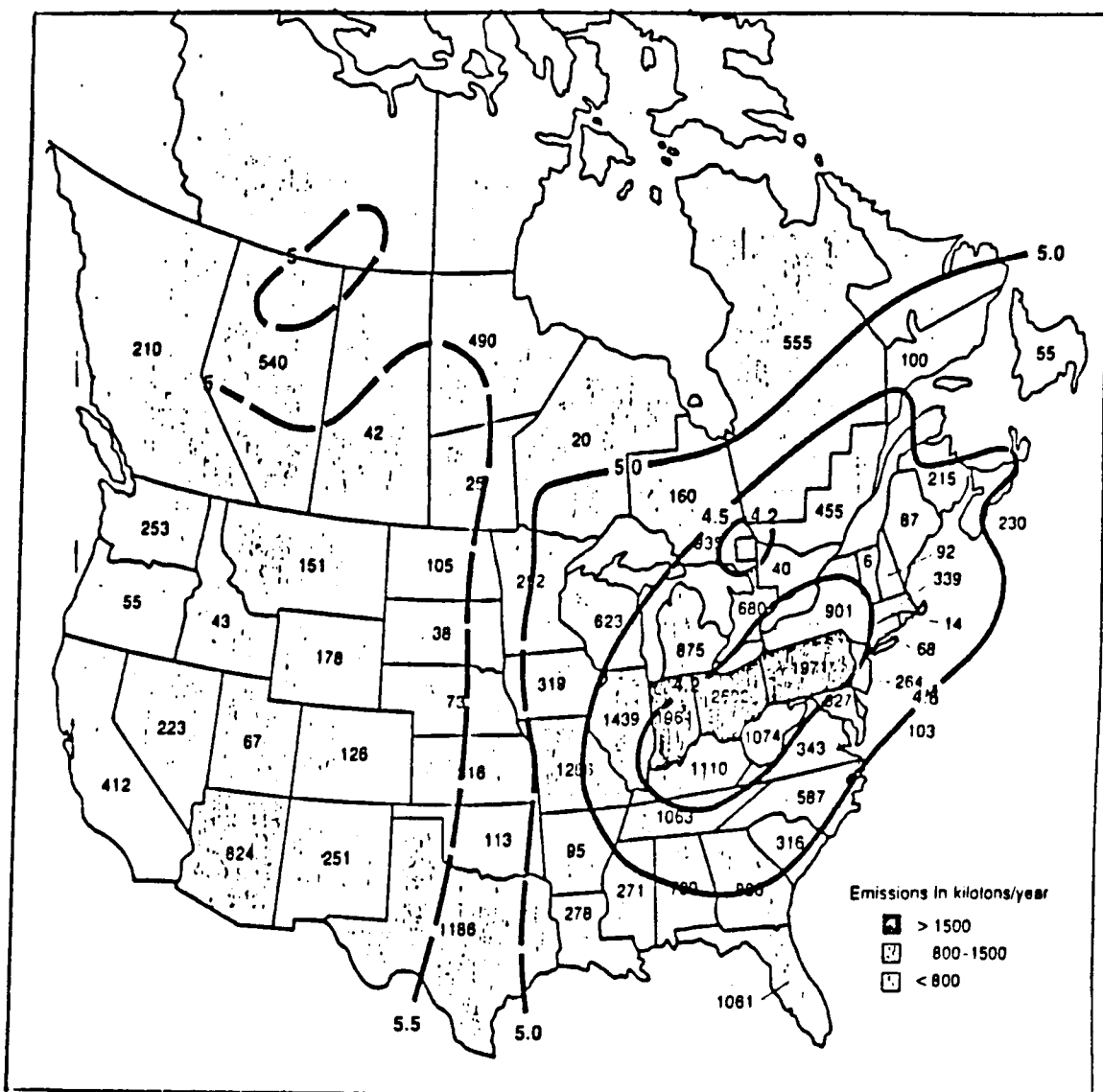


Figure 2.9

Precipitation pH and North American SO₂ Emissions*

*Source: Niemann in Proceedings of the Symposium on Acid Precipitation, Ann Arbor Science Publishers, 1982.

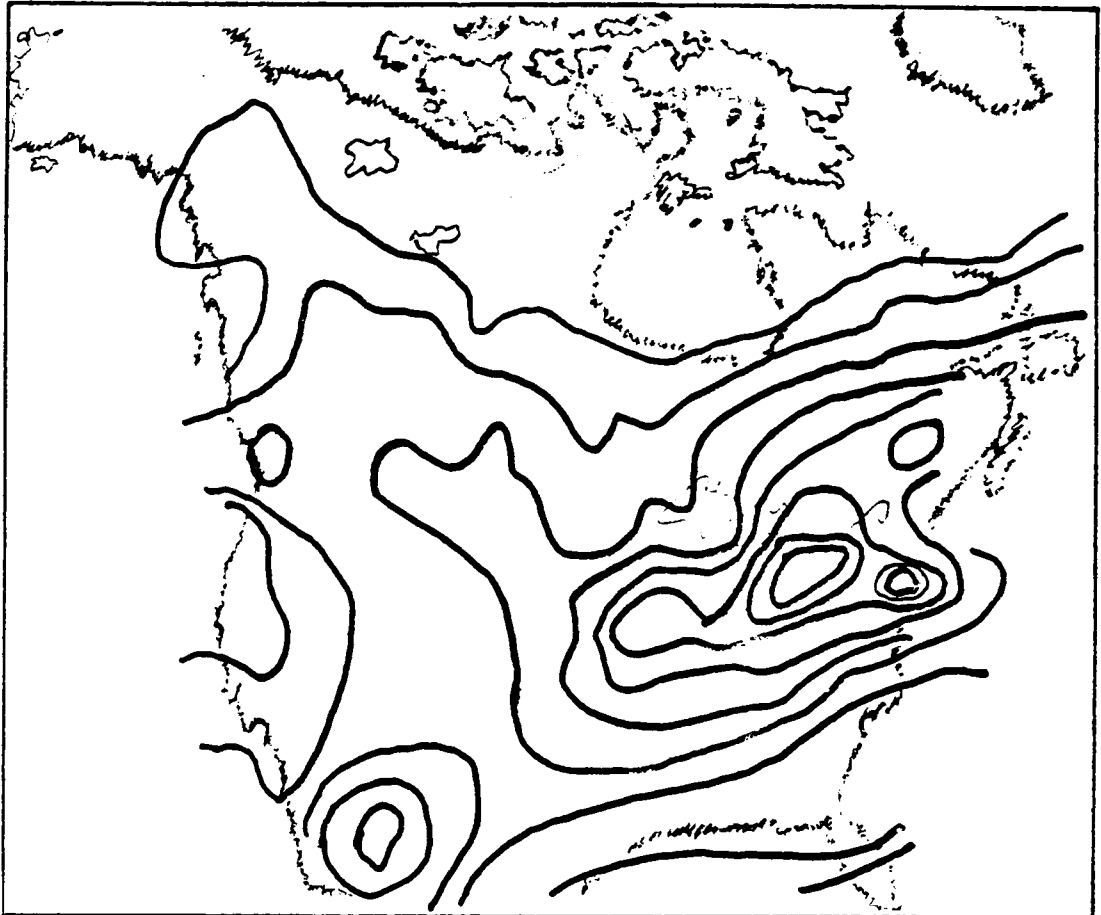


Figure 2.10

Average Concentration of SO_4^{2-} in
North American Precipitation*

* Source: Munger and Eisenreich, Environmental Science and Technology, 17, 1, 1983.

2.6 The Control Of Sulfur Emissions

Fossil fuel sources greater than 250×10^6 BTU/hr are limited by Federal regulation to a maximum of 1.2 lbs SO_2 / 10^6 BTU fuel. The regulations limit the actual allowable SO_2 emissions according to an adjustable scale that varies according to the SO_2 emission potential of the fuel being consumed as indicated by the following information.

<u>lb SO_2/10^6 BTU Fuel</u>	<u>control requirement</u>
0 - 2 lbs	70% removal; 0.6 lbs/ 10^6 max.
2 - 6 lbs	0.6 lbs/ 10^6 max.; 70 - 90% removal (sliding scale)
6 - 12 lbs	90% removal; 1.2 lbs/ 10^6 max.
> 12 lbs	1.2 lbs/ 10^6 maximum emissions

Using a coal with 1.5% by weight total sulfur, and 12,000 BTU/lb fuel value, and assuming stoichiometric conversion of the sulfur to SO_2 , uncontrolled emissions would be: $10^6/12,000 \times .015 \times 2 = 2.5$ Lbs SO_2 / 10^6 BTU.

From the information above it may be calculated

$$\frac{2.5 - 0.6}{2.5} \times 100\% = 76\% \text{ required } \text{SO}_2 \text{ removal.}$$

There are several ways to accomplish the control:

- (1) by cleaning the flue-gas stream;
- (2) by treating the coal at the time of combustion;
- (3) by removing the sulfur prior to combustion;
- (4) by burning low sulfur coal.

In general, up until now, commercial boilers have had flue

gas scrubbers for sulfur emission control; this is a post-combustion technique. There is increased and growing interest in methods that control sulfur emissions at the time the coal is burned, especially among those who are considering converting from fuel oil to coal slurries. Pre-combustion sulfur removal has mostly been a method by which coal producers could meet sales specifications by crushing and washing the coal. Pre-combustion methods which are capable of lowering the coal sulfur per cent to a low level have been chiefly of interest to those who use coal as a chemical feedstock, where the sulfur (and nitrogen) could act as catalytic poisons.

As reductions in SO_2 emissions are now being contemplated, the debate is centering on whether to require emissions controls or to allow the reductions to be achieved by burning lower sulfur coal. The question seems to be as political as technological. Eastern coal miners have presented a strong lobby in the U.S. Congress to require that reductions in SO_2 be achieved by scrubbing (flue gas desulfurization). This is an attempt to prevent a massive shift to the use of lower sulfur western coals, because the economics of regional coal importation are favorable when compared to scrubbing. If scrubbers are actually required for operation, the effect may be to inhibit the development of more sophisticated sulfur removal techniques, including chemical desulfurization of

movál techniques, including chemical desulfurization of coal prior to combustion. Since the entire issue of SO₂ emissions, acid rain, and controls is hotly contested from all sides, it is unlikely that any resolution will be immediately forth-coming.

The applicability of a desulfurization technique depends on many factors, including the chemical and physical forms of the sulfur in the coal. In the following sections the petrology of coal and coal sulfur and selected desulfurization techniques will be reviewed.

3.0 BACKGROUND

3.1 Coal Petrology

3.1.1 The Formation Of Coal

Coal formed when organic matter, both plant and animal, was deposited in sufficient quantity in wet, chemically reducing conditions for a long period of time. The result was a highly carbonized, heterogenous aggregate material composed of organic and inorganic compounds having a macroscopically similar appearance and certain similar useful chemical properties.

Most bituminous coals were deposited in eutrophic swamps, peat bogs, or the like, and are termed autochthonous, meaning that they were formed in situ, or in place. The organic growth was generally nurtured by regular flooding of rivers, lakes, or the sea, and simultaneously resulted in the removal of soluble matter from the decaying detritus, in mineral deposition, and in the formation of layers of gravel and marl bands. Some coal seams formed when fluvial matter was transported away from its site of origin and redeposited. Coals that formed in this manner are termed allochthonous (47).

The process of natural conversion has been called "coalification", and the process consists of two stages. The first stage of coalification is the laying-down of materials accompanied by active bacterial, plant, and

animal metabolism. The second stage of coalification is the consolidation stage, which may be caused or accompanied by geological changes, such as the formation of mountains or the receding of a sea. During the second stage the organic silts are shielded from further decay by increasingly thick inorganic deposits, called "overburden". Overburden pressures physically form the plastic material into seams and chemically alter the coal by heat. The degree of coalification is termed the "rank" of the coal and is the single most important property. Ranks of coal are lignite, subbituminous coal, bituminous coal, and anthracite (24).

There is no precise compositional make-up of a coal seam; the material may vary considerably in chemical composition, hardness, inclusions, ash content, appearance, and other characteristics within any given coal seam. Those portions of the coal that are visibly similar are termed "macerals," from the French after the Latin, for macerated plant matter. Maceral groups are categorized according to their reactive and compositional characteristics and consist, basically, of an organic matrix and inorganic inclusions within the organic matrix.

The reactive maceral groups are termed either "vitrinite" or "exinite," depending on their origin, and the nonreactive macerals are termed "inertinite." Coal macerals and their materials of origin are listed in Table 3.1.

Table 3.1

The Origin of Coal Macerals*

Maceral	Submaceral	Origin
Vitrinite	Telinite	cellular structures derived from vegetable materials such as trunks, stems, branches, leaves, and roots.
	Collinite	true gel — structureless; frequently fills the space between the identifiable cell walls from tellinite; believed to originate from humic solutions
	Vitrodetrinite	identifiable detritus particles that originate from a humus-peat complex; rare
Exinite	Sporinite	the fossilized skins of spores and pollens
	Cutinite	the outer layers of leaves, stalks, shoots, thin stems, and nettles; from cuticles
	Resinite	the essential oils of plants, particularly conifers
	Alginite	from certain types of algae and found only in a very limited kinds of coal
	Liptodetrinite	a collective term for fragments or degradation residues which can not be definitely assigned to one of the other groups
Inertinite	Fusinite	the result of pyrolysis during coalification; charred plant tissues
	Macrinite	an amorphous, rarely occurring, high carbon cement-like material that binds together other maceral particles
	Micrinite	very small grains of undefined origin and unreactive
	Schlerotinite	fungal remains
	Inertodetrinite	extremely small particles of the inertinite group which can not be assigned to a specific submaceral due to the fine size

* Source: Stach, et al., "Coal Petrology," Gebrüder Bontraeger Pub., Berlin, 1982.

More than 70% of the composition of American coals is vitrinite, having been formed from peats or woody plants. Exinite is limited to a few percent, and inertinite usually is present on the order of 10-15% (22).

3.1.2 The Organic Matrix Of Coal

Coal has been described as "an extraordinarily complex, insoluble organic mixture," and as an "organic rock" (48, 49). It is usual to consider the organic portion of coal in two parts: (1) the highly cross-linked macro-molecular (gel-like) polymorphic structure of particle molecular weight greater than 10000 and (2) varying amounts of small molecular weight materials (MW <1000) which are extractable in organic solvents such as pyridene (49). Secondly, the various chemical functional groups are considered when the reactivity of a particular coal is being classified.

Purists argue the ultimate worth of attempting to describe bituminous coals as some "average" polymeric structure laced around semi-liquid droplets. None the less, for many practical purposes, an average structure describing a hypothetically typical configuration well illustrates the structural nature of the organic coal matrix. Figure 3.1 is the current best representation of the coal structure found in bituminous vitrinite (50), but Larsen emphasizes that this representation is not a true

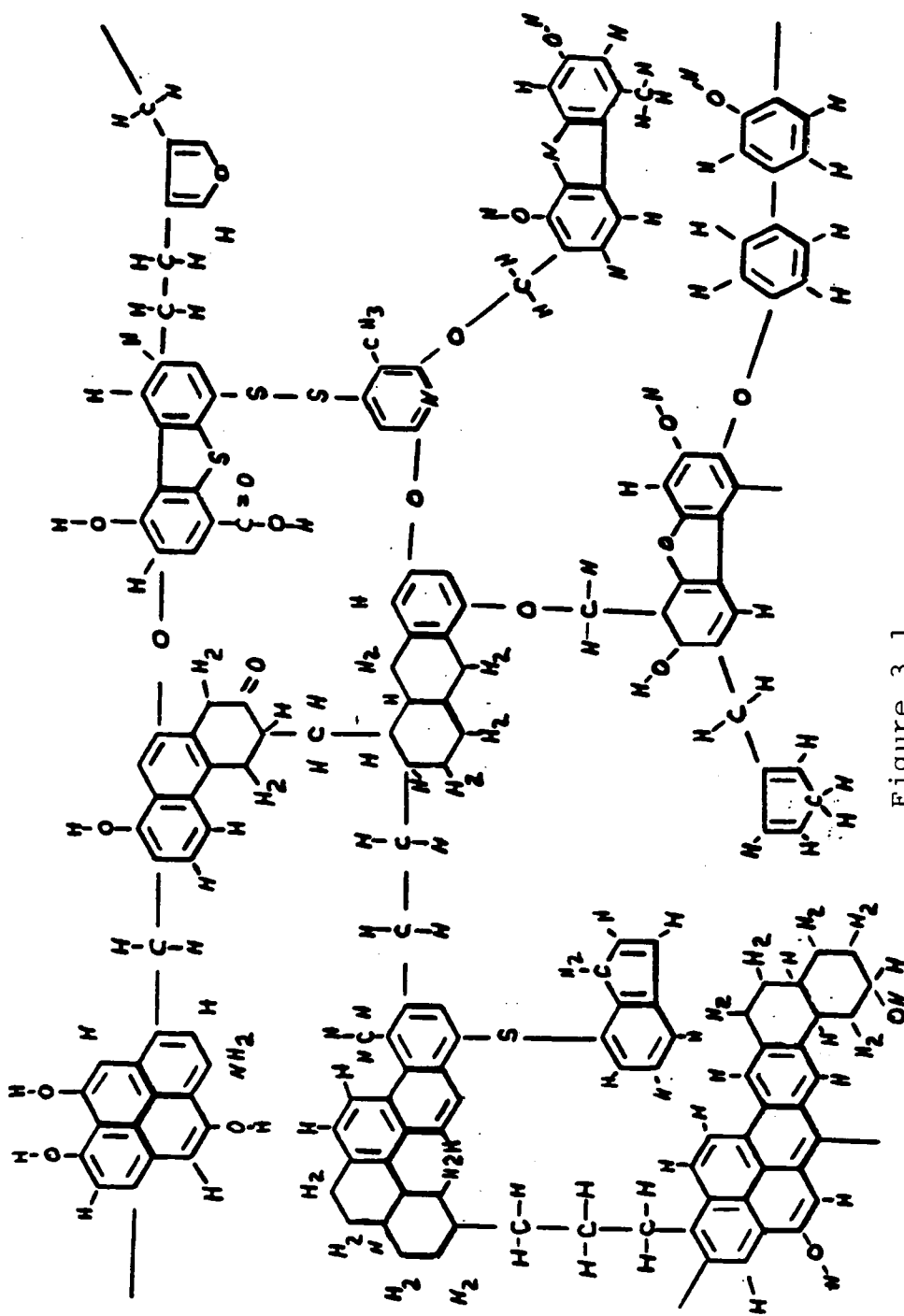


Figure 3.1

A Representation of the Bituminous Polymeric Skeleton*

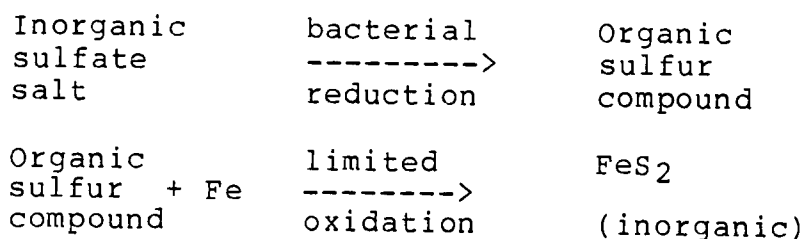
* Source: Green, et al., in "Coal Structure," ed. R.A. Myers, Academic Press, 1982.

coal structure. It is "a collection of the types of structures thought to be present and written down in a way which satisfies the bulk analytical data" (51).

There are a large number of condensed polycyclic aromatic and hydroaromatic units connected by various methylenes and ethers. The aromatic and hydroaromatic units form the carbon skeleton of the matrix, and the connectors form the linkages in the polymeric structure.

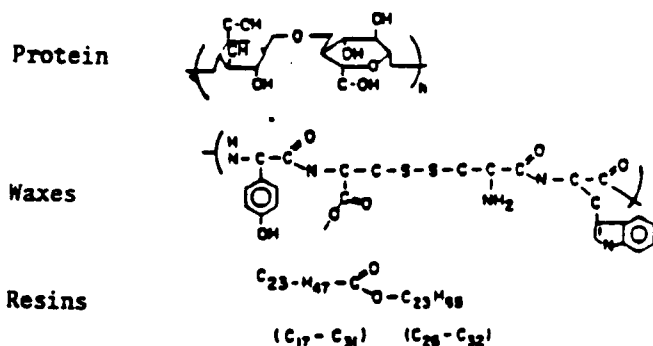
The organic materials in coal are direct descendants of the naturally produced materials of living organisms. Cell walls, protoplasts, exuded coatings, etc., have all contributed to the organic composition of coal. Cellulose, protein, waxes, etc., are called "precursors", and typical structures for the major coal precursors are illustrated by Figure 3.2 (52).

Stach, et al, suggests that the organic sulfur components largely originate from severe bacterial activity on protein-rich and part animal substances. He further suggests that syngenetic pyrite and marcasite results from bacterial reduction of sulfate ions in the presence of iron (47). The sequence suggested is:



Lumpkin (53) has analyzed the extractable fraction of

Aliphatics



Aromatics

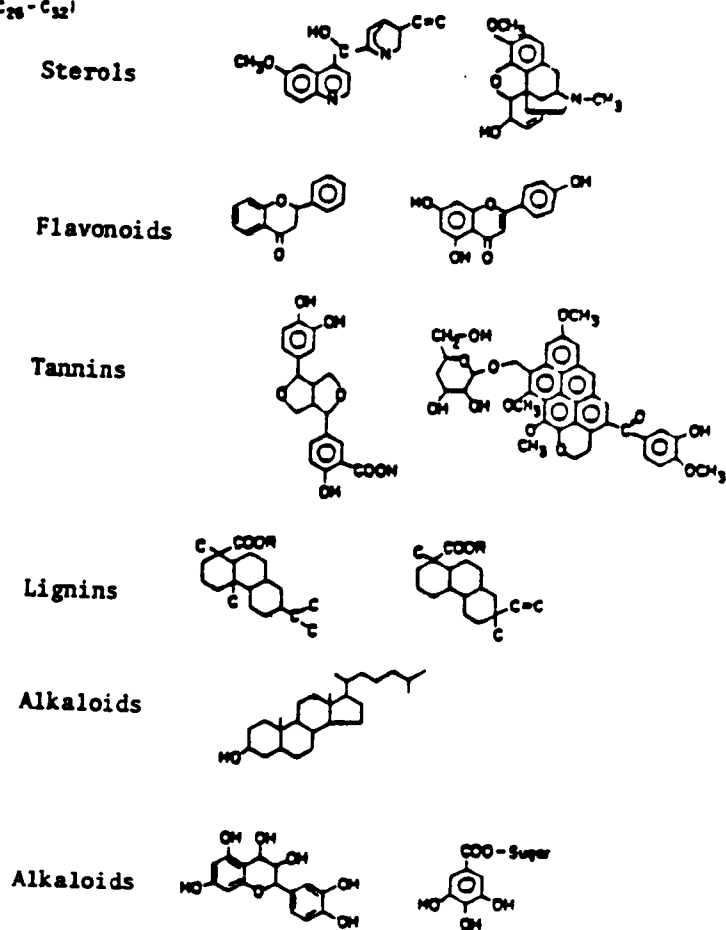


Figure 3.2

Selected Biological Precursors of the Coal Matrix*

* Source: D.D. Whitehurst in "The Organic Chemistry of Coal," 1978.

some coals and found that organic sulfur is concentrated in nonaromatic compounds and in aromatic compounds of five rings or less. These data are summarized by Table 3.2, from which it may be seen that two-thirds of the organic sulfur is concentrated in one- or two-ring aromatics.

Table 3.2
Composition Of Extractable Coal Fractions

	Hydrocarbons	Sulfur Compounds	Oxygen Compounds	Totals
Nonaromatics	0.0	0.144	0.0	0.144
1-Ring Aroms.	20.960	0.517	2.235	23.712
2-Ring Aroms.	35.919	0.611	3.465	40.996
3-Ring Aroms.	15.644	0.153	2.202	17.999
4-Ring Aroms.	12.388	0.067	1.470	13.925
5-Ring Aroms.	1.997	0.020	0.208	2.225
6-Ring Aroms.	0.856	-----	0.084	0.940
7-Ring Aroms.	0.068	-----	-----	0.068
Totals	88.832	1.512	9.664	100.008

Source: Lumpkin and Aczel in "The Organic Chemistry of Coal," American Chemical Society, 1978.

3.1.3 Mineral Inclusions In Coal

Mineral matter is classified according to its origin of formation. If the mineral matter was formed in the first stage of coalification, it is called "syngenetic"; if the mineral matter was deposited in the coal in the second stage of coalification, it is called "epigenetic" (47). Also considered minerals are all elements except ter how they are combined chemically within the coal. In

North American coals, mineral matter varies from a few percent to over 30%. The average mineral matter content of North American coals is about 15%.

The mineral matter of coal is important because it affects the BTU value of the fuel, because it affects the operational characteristics of heat transfer systems, because it affects the environment, and because it produces effects on conversion processes. The higher the mineral content, the lower the fuel value for a given amount of coal. For certain conversion processes and certain mineral compositions, the conversion process may be somewhat self-catalyzed by the mineral matter (50). Iron pyrite is an interesting catalytic agent in some coals and for some conversion processes, and it has been observed that pyrite containing coals liquify more readily than "clean" coals (22). Unfortunately, it is more often necessary to remove the mineral matter to protect downstream catalytic systems from gaseous sulfur compounds.

Heat transfer systems are affected due to deposits on and the corrosion of heating surfaces. Deposits result from the reaction of evaporated alkalis with SO_2 or SO_3 combustion products which then condense as complex sulfate salts. Where water or steam is present, the sulfate salts may corrode a metallic surface. The problems associated with deposits and/or corrosion are particularly serious when significant quantities of the clay minerals illite

and sericite are present. Much attention has been given to the environmental effects resulting from coal utilization. The compounds of several metals, including beryllium, cadmium, and mercury, and certain mineral compounds such as asbestos, are recognized as biologically hazardous in relatively small amounts, while the aforementioned oxides of sulfur and nitrogen are environmentally detrimental in larger amounts.

Virtually all minerals have been identified in coals. The more important groups include clays, carbonates, sulfides, oxides, quartzes, phosphates, and heavy minerals. The important mineral groups and their origins of occurrence are summarized in Table 3.3 (55). From Table 3.3 it may be seen that the important disulfide minerals are pyrite, marcasite, melnikovite, galena, and chalcopyrite. It is unusual when the inorganic sulfur is not nearly all pyrite, and usually all inorganic sulfur compounds are considered pyrites with regard to sulfur oxide emissions.

3.2 Iron Pyrite and Related Minerals (Disulfides)

3.2.1 Origin

Syngenetic disulfides are believed to originate from a sequence of bacterial action on proteinaceous materials followed by partial oxidation in the presence of metal salts, particularly iron, or from the bacterial reduction of sulfate salts of fluvial origin.

Table 3.3
Minerals In Coal

Mineral Group	First stage of coalification (syngenetic)	Second stage of coalification (epiinetetic)
Clays	kaolinite, illite, sericite, montmorillonite, tonstein	illite, chlorite
Carbonates	siderite, dolomite, calcite, ankerite	ankerite, calcite, dolomite, ankerite in fusite
Sulfides	pyrite, melnikovite, marcasite, sulfides of copper, zinc, and iron in concretions	pyrite from the transformation of syngenetic concretions of FeCO_3
Oxides	hematite	goethite, lepidocrocite
Quartz	quartz grains, chalcedony, feldspar, mica	quartz
Phosphates	apatite, phosphorite	
Heavy minerals and accessory minerals	zircon, rutile, tourmaline, orthoclase, biotite	chlorides, sulfates, and nitrates

Source: J.J. Renton in "Coal Structure," Academic Press, 1982.

The geological formation of epigenetic pyrite is less certain, but it is believed by some to occur as a transition from iron carbonate (FeCO_3). Pyrite is usually concentrated in the lowest and uppermost strata of coal seams or in old washouts (47).

3.2.2 Pyrite Chemistry

Pyrites are dimeric structures containing discrete S_2 units with an S-S bond distance almost exactly equal to that expected from a single S-S bond. The crystalline structure contains S_2^{2-} ions which are formally analagous to the peroxides, and they may also be considered as salts of the hydride, H_2S_2 .

Burdett and McLane have studied the structure of various MX_2 systems, and their illustrations of pyrite and marcasite structure are shown in Figure 3.3 (56). In the figures the small filled circles represent iron atoms, and the wedges represent S_2 dimers, with the broad end of the wedge nearer to the reader.

It is obvious from Figure 3.3 that the only difference in pyrite and marcasite is the spatial arrangement of the atoms. In fact, under thermal stress marcasite converts to pyrite.

The S-S dimers essentially make one sulfur atom available for reaction as atomic sulfur, while retaining one sulfur atom in the FeS system. Continued thermal

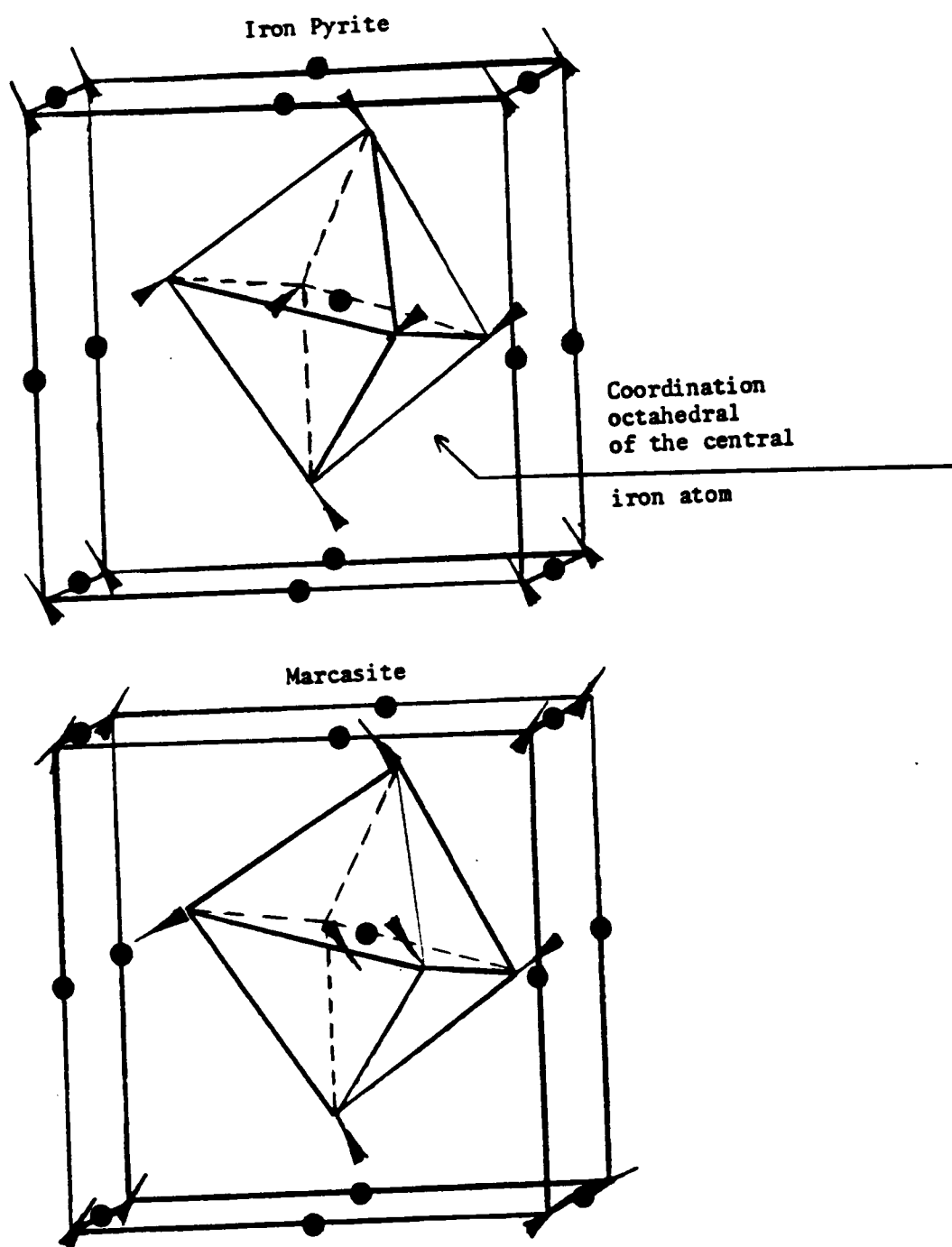


Figure 3.3
Structures of Iron Pyrite and Marcasite

Source: Burdette and McLane, Inorganic Chemistry, Vol. 21, No. 3, 1982.

stress of pyrites results in pyrrhotites, which are reduced ratio Fe_nS_m systems. Whole number stoichiometries from Fe_7S_8 through $\text{Fe}_{11}\text{S}_{12}$ have been identified by Richey (57), who has investigated the kinetics of the Fe-S-O-H system.

Phase diagrams for the Fe-S-O-H system, from 327c to 527c are shown in Figure 3.4. The axes are the log fugacity of sulfur ($\log f_{\text{S}_2}$), and the log fugacity of oxygen ($\log f_{\text{O}_2}$).

These diagrams have the most potential application in coal liquefaction applications. They also illustrate the increasing stability of $\text{FeS}_2\text{-Fe}_2\text{O}_3$ at lower temperatures. This stability indicates that the measurable conversion of iron pyrite to iron oxide is probably a catalytic conversion in the air oxidation of coal.

3.3 Coal Beneficiation

The processes which produce a fuel-coal that is more suitable for use are called "beneficiation" processes. These processes may be designed to reduce the ash content or to improve the chemical or combustion characteristics of the coal. "Beneficiation" always implies treatment of coal prior to its use. In this report only beneficiation processes which result in a reduction of emissible coal sulfur will be considered.

Since coal sulfur beneficiation methods have been

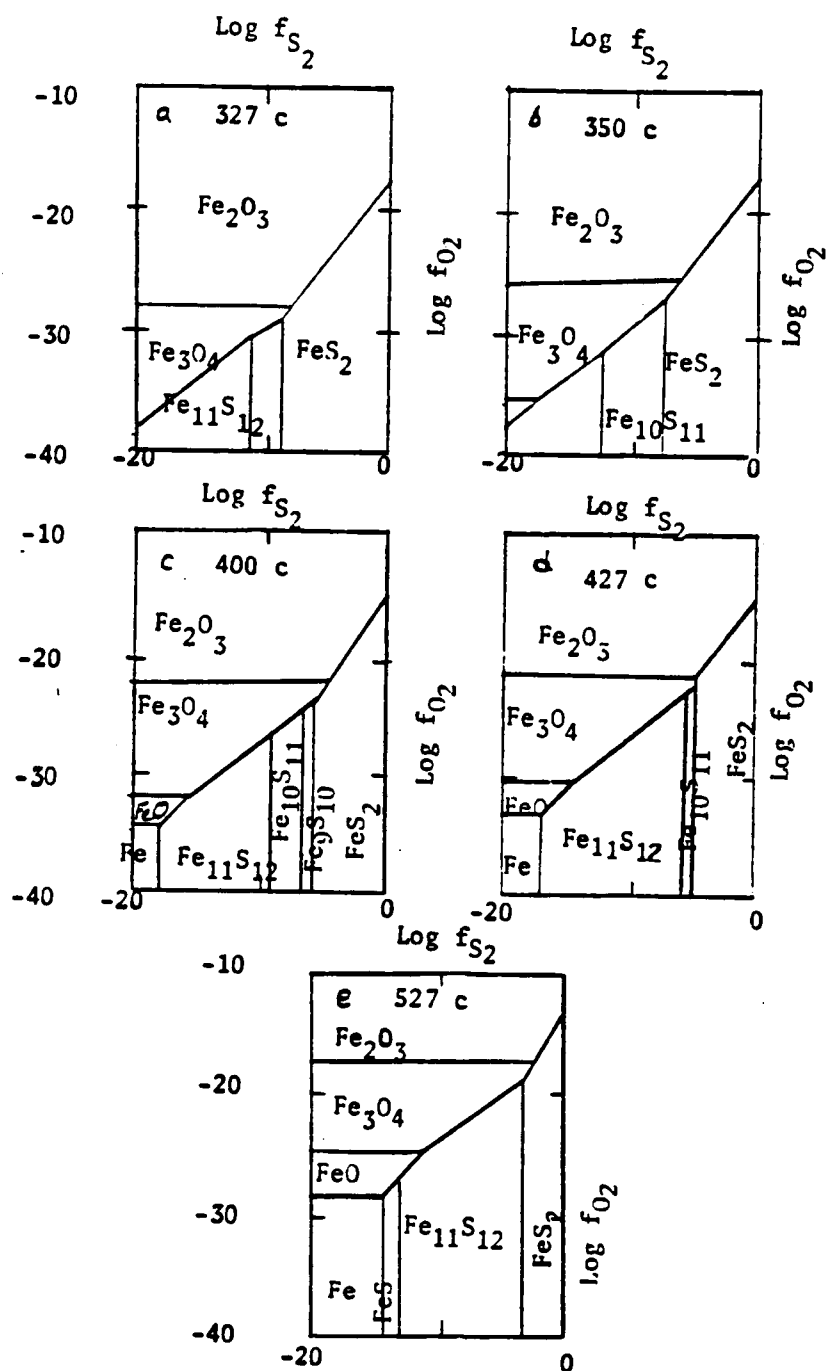


Figure 3.4

Phase Diagrams for the Fe-S-O-H System

Source: W.D. Richey in "New Approaches In Coal Chemistry," American Chemical Society, 1981.

discussed in detail by Meyers (24) and Wheelock (58), and most recently by Tsai (59), and since these methods were recently reviewed by Wilcox (3), only a brief review is included here for the convenience of the reader.

3.3.1 Categories Of Beneficiation

The beneficiation categories are rather obvious:

- (1) physical;
- (2) chemical; and
- (3) biological.

Physical processes rely on variant methods of comminution, washing, or separation by the use of electric fields. Coal desulfurization by physical separation methods is most appropriate when the pyrites exist as relatively large and discrete crystals, and when the reduction of only the inorganic sulfur fraction is a satisfactory control strategy. Usually, up to 75% of the inorganic sulfur fraction may be removed by physical methods. Probably 90% of industrial beneficiation processes include some relatively simple combination of grinding, sieving, and washing, either at the use site or at the mine. A substantial beneficiation may be achieved by size reduction to fractional centimeters followed by washing. The disadvantages include the generation of acidic runoff, large quantities of unusable fine particles, complex and costly mechanical equipment, and high energy consumption in the unit processes required to comminute and move the product.

Chemical processes rely on the relatively large negative ΔG that exists between inorganic disulfides or organic sulfides and sulfates. The coal is usually treated with a liquid solution of some chemical species under heat and pressure to improve the reaction kinetics, but simple controlled heating is also utilized on occasion. Chemical beneficiation processes are most appropriate where physical methods alone will not provide sufficient beneficiation. High percentages of reduction for inorganic sulfur is usually achieved, accompanied by organic sulfur reduction varying from 10-70%.

The disadvantages are the capital expenses of the process equipment, the necessity to physically comminute to a rather small sieve number before treatment, and the cost of the expendable treatment materials. Chemical beneficiation is, at present, only marginally cost competitive with flue gas desulfurization.

Biological beneficiation, primarily relying on the bacterium Ferrobacillus ferrooxidans, is of academic interest and shows promise for specific applications, but in general biological conversion of FeS_2 to FeSO_4 is encountered as a problem when run-off at the mine becomes acidic.

Some significant beneficiation processes are reviewed in a little detail in the following sections.

3.3.2 Physical Beneficiation Methods

All physical methods assume that the coal has been comminuted to some appropriate screen size or top size, and that the comminution effectively fractures the coal into coal particles and particles high in mineral content, causing a difference in specific gravity, a difference in surface properties , or a different response to an electric field. There are sub-categories of physical separation methods depending on whether the coal beneficiation may suitably be performed on coarse or fine coal, where fine coal is arbitrarily defined as passing a 50 mesh screen, or whether the method is a dry separation method or a wet or oily separation method.

It is interesting to note that all methods of physically cleaning coarse coal, whether wet methods or dry methods, are referred to as "coal washing" techniques. In a sense, the dry methods wash the coal with a gas. Selected methods of physical beneficiation are discussed below.

3.3.3 Coal Washing Methods

Jigs

The most widely applied method of cleaning coal is by jig. Up to 50% of the coal that is cleaned in the United States is washed in one of several kinds of jigs. Jigs are devices which use alternately pulsating jets of gas or

liquid to separate suspended ground coal according to specific gravity in a fluid (gas or liquid) bath. Jigs are highly versatile and economical, and are used on coal ground to a mixed-size range up to 8 inches top size. Most jigs are used to separate particles of specific gravity >1.3 . Particles having a specific gravity < 1.3 are retrieved in the float, and particles with a specific gravity > 1.3 descend into a refuse bin.

Dry jigs use a bed of feldspar, or some hard rock, through which the refuse materials migrate. The dry jig, sometimes called a dry table separator, requires a much smaller top size and a somewhat more uniform particle size than a wet jig, usually $1/2$ inch to 50 mesh. For jigs, coal recovery is on the order of 90%, typical pyrite reduction is about 70%, and the total ash reduction is about 50%.

Wet concentration tables

Tables are sluice boxes with sloping bottoms. The heavier fractions accumulate along the low side of the bottom permitting a cut into a light fraction, middlings, and a heavy fraction. There is a density distribution vertically in the suspended slurry as well as a horizontal distribution along the bottom, allowing for a quite selective cut of the sluice.

Wet tables usually operate on coal ground to $3/8$ " top

size. Coal recovery is in the 98% range for the coarser fraction, and about 90% for coal as small as 100 mesh. Used alone, wet concentration tables are somewhat more efficient in pyrite removal and ash reduction than jigs, but in tandem with other units, such as froth flotation cells, and with selected coals, pyrite reductions approaching 90% and ash reductions approaching 70% may be achieved for fine coal washing.

Froth flotation and oil agglomeration

Froth flotation and oil agglomeration are the best known methods of cleaning fine coal. The optimum coal particle sizes for froth flotation are reported to be 48 to 150 mesh, but coal as fine as 325 mesh has been successfully treated. Oil agglomeration is more effective on particles of 200 mesh or smaller than any other well-known method.

Froth flotation and oil agglomeration are both effective due to the hydrophobic quality of the surface of the coal particles, and to the hydrophylic quality of the surface of the mineral particles. In froth flotation organic surfactants or detergents are added to a coal-water slurry and air bubbles are injected into the slurry. The coal particles are selectively attracted to the air bubble - slurry interface where they attach and are removed (skimmed) with the froth. In oil agglomeration droplets

of oil or selected polymer are emulsified in the slurry. The coal particles are attached to the oil, and by repeated particle collision and by growth of the agglomerate, the agglomerate settles to the bottom of the slurry. The agglomerated particles are removed by screening, while the fine mineral particles either pass the screen or are removed with the slurry liquid.

Since any method that requires size reduction produces a certain amount of small particle coal, these methods are becoming popular when used in tandem with other methods such as jigs. They are also attractive for use in extracting coal from the waste ponds of old operations.

By froth flotation, recovery of the fuel-coal has varied from 50-100% in controlled experiments, while the reduction in pyritic sulfur has varied from 14-73%. Oil agglomeration studies show product coal recovery has consistently been around 90% and pyrite reduction about 50% (59).

3.3.4 Deep Cleaning

Methods which remove or convert coal sulfur to nearly 100% usually involve all the following

- (1) elevated temperature
- (2) elevated pressure
- (3) chemical waste problems
- (4) capital intensive equipment
- (5) high operating costs.

Furthermore, the coal must be comminuted to a truly fine

size, frequently <200 mesh, and the energy cost of comminution is considerably greater than for physical methods. Although deep cleaning methods typically remove 99% of the pyritic sulfur and up to 75% of the organic sulfur, up to 20% of the energy value of the coal is also lost. As mentioned earlier, no cost-competitive chemical cleaning method has been demonstrated; hence, no method of deep cleaning is really available on a commercial scale.

The attention given to deep cleaning in the literature seems to follow personal preferences. Myers, who has a patented process (24), has published considerable material on the subject of chemical cleaning. Others, such as Elliot and Schweiger, dismiss chemical methods with a sentence or two (61).

4.6 EXPERIMENTAL PROCEDURES AND EXPERIMENTAL DATA

4.1 Objective.

There were two primary objectives to be met in this study: (1) to examine the kinetics of the pyrite conversion in fine coal in the ambient temperature range, and (2) to examine some possible reaction mechanisms for the pyrite conversion. With regard to objective (1), previous work (by indirect methods) has indicated a probable first order reaction rate. The data of Wilcox's (3) work were fit to a curve of the form for exponential fractional conversion,

$$[\text{FeS}_2] = c[1 - \exp(-at)], \quad (4.1)$$

where c and a are empirically derived constants, and t is in days. Note that the previous effort in quantifying the FeS_2 conversion reaction did not actually measure any of the chemical species of interest, but examined the change with time of the ash weight after controlled combustion. The Wilcox study was limited to coal to which fine calcined limestone had been added. Three samples of limestone were used by Wilcox with varying results, but it was not possible to establish the role of the lime in the sulfur conversion reactions. Consequently, for this study experiments were devised to examine the change in pyrite sulfur directly with time, hypothesizing a first order form:

$$\frac{-d[\text{FeS}_2]}{dt} = k[\text{FeS}_2]. \quad (4.2)$$

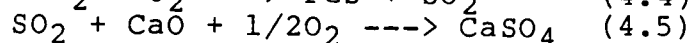
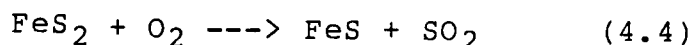
In this study only one limestone sample was used, uncalcined and calcined, and only one coal sample was used. The results will be compared to the conversion of sulfur in fine coal to which no sorbents have been added.

By examining the pyrite conversion with time at various temperatures, it should be possible to determine the coordination constant, A and the activation energy, E , for the Arrhenius form of the rate constant:

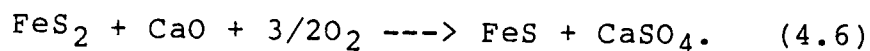
$$k = A \exp[-E/RT], \quad (4.3)$$

where k refers to the first order reaction rate constant.

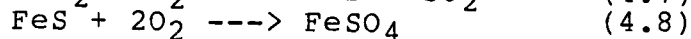
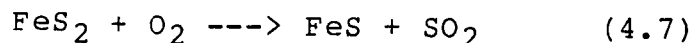
With regard to objective (2) various reaction mechanisms have been hypothesized. In the presence of calcium compounds one possibility is



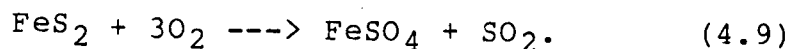
or for the overall reaction



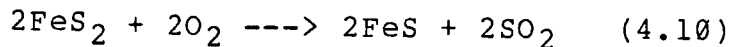
Another possibility, in the absence of calcium compounds, is

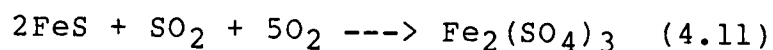


or for the overall reaction

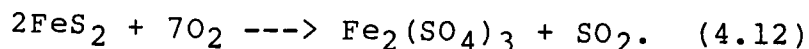


One final probable mechanism is





or for the overall reaction



Hammer (62) blames the accumulation of heat from reactions (4.4-4.11) (and reactions similar to them) for the spontaneous ignition of coal dust in mines, but there are no studies in the literature indicating that any of these reaction mechanisms have been verified.

As may be seen from the Table 4.1, the values for the net enthalpies of reaction and the values for the net changes in the Gibbs free energy for reactions (4.4-4.11) are all quite large negative numbers, indicating that the reactions would proceed exothermically and spontaneously once the Arrhenius activation energy level has been attained. A short list of the enthalpies of formation and the free energies of formation is included in Appendix A.

Table 4.1

Net Enthalpies of Reaction and Net Free Energies
of Reaction for Equations (4.4-4.11)

Reaction Equations	ΔH° kcal/mol	ΔG° kcal/mol
(4-6)	-152.85	-170.50
(7-9)	-229.05	-250.25
(10-11)	-572.75	-645.35

A further objective was to establish enough detail about the reactions to determine a plausible reaction mechanism(s) for desulfurization supported by data.

The analytes for this study are listed below:

- pyrite sulfur;
- sulfate sulfur;
- total sulfur;
- organic sulfur (by difference);
- calcium sulfate, CaSO_4 ;
- ferric oxide, Fe_2O_3 ;
- ferric sulfate, $\text{Fe}_2(\text{SO}_4)_3$;
- ferrous sulfate, FeSO_4 ;
- ferrous sulfide, FeS ;
- sulfur dioxide, SO_2 .

By observing the change with time of any or all of the above analytes it should be possible to establish reactions (4-12), or perhaps establish a more tenable reaction mechanism hypothesis. The necessary data for equations 4.2 and 4.3 would be measured directly.

4.2 Sample Materials

In order to limit the scope of the study only one coal sample and only one limestone sample were used. As identified in the introduction, this coal was Ky #9 (Paradise) -- a high sulfur coal with some evidence of weathering. Fifty pounds of this coal sized 0/.5" were received gratis from the Tennessee Valley Authority (TVA).

The limestone used in the present study is the same Fredonia limestone sample used in the Wilcox study and also in a study by Frazier and Badin (38). In the Wilcox work this limestone produced considerable data scatter, and Wilcox described the results using this limestone as "uncertain." However, two reasons for using Fredonia limestone were that a sample was on-hand and the characteristics of the Fredonia limestone material were known.

4.3 Preliminary Description Of The Samples

Since the present study uses a limestone from a previous sample which has already been analytically described, no analyses were performed on the limestone. The limestone has been determined to be 93.29% calcium carbonate, 1.76% magnesium carbonate, and various other constituents. A complete analysis performed by personnel at the Oak Ridge National Laboratory is included in Appendix B.

Bits and chunks of the coal often had a yellowish sheen. Under an optical microscope the surfaces of many of the coal particles appeared to be streaked (in varying degree) by thin veins of metallic yellow crystals. Several chunks of coal were mounted in an epoxy base, sawn to expose new surfaces, and polished using metallographic techniques. Figures 4.1 and 4.2 are electron photomicrographs of a 6.5 mm specimen (.25") made with a Phillips electron microscope after a carbon film was applied by

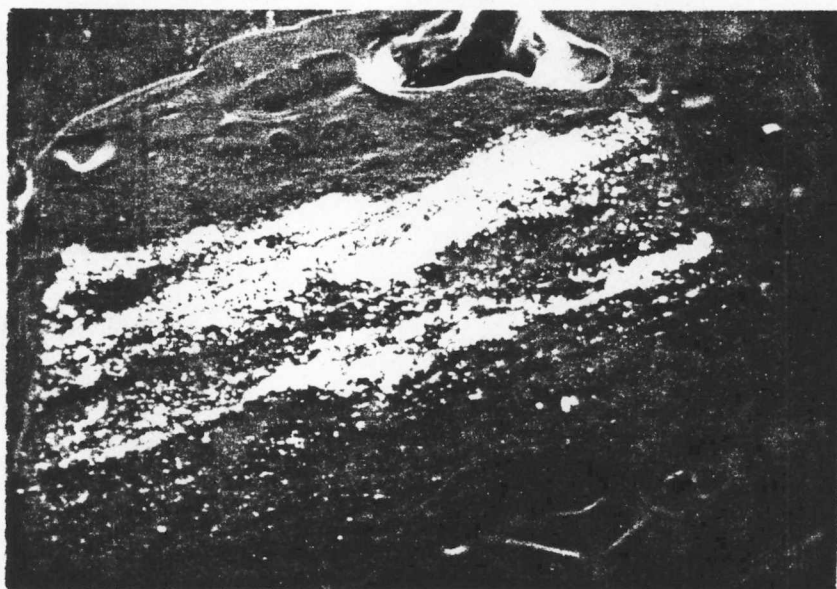


Figure 4.1

Photoelectron Micrograph of Specimen Surface
Magnification Approximately 20x

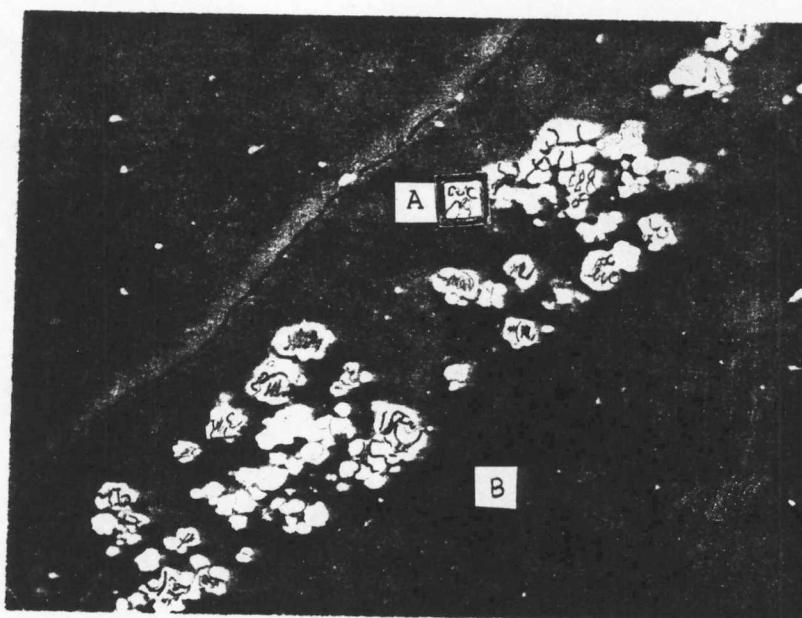


Figure 4.2

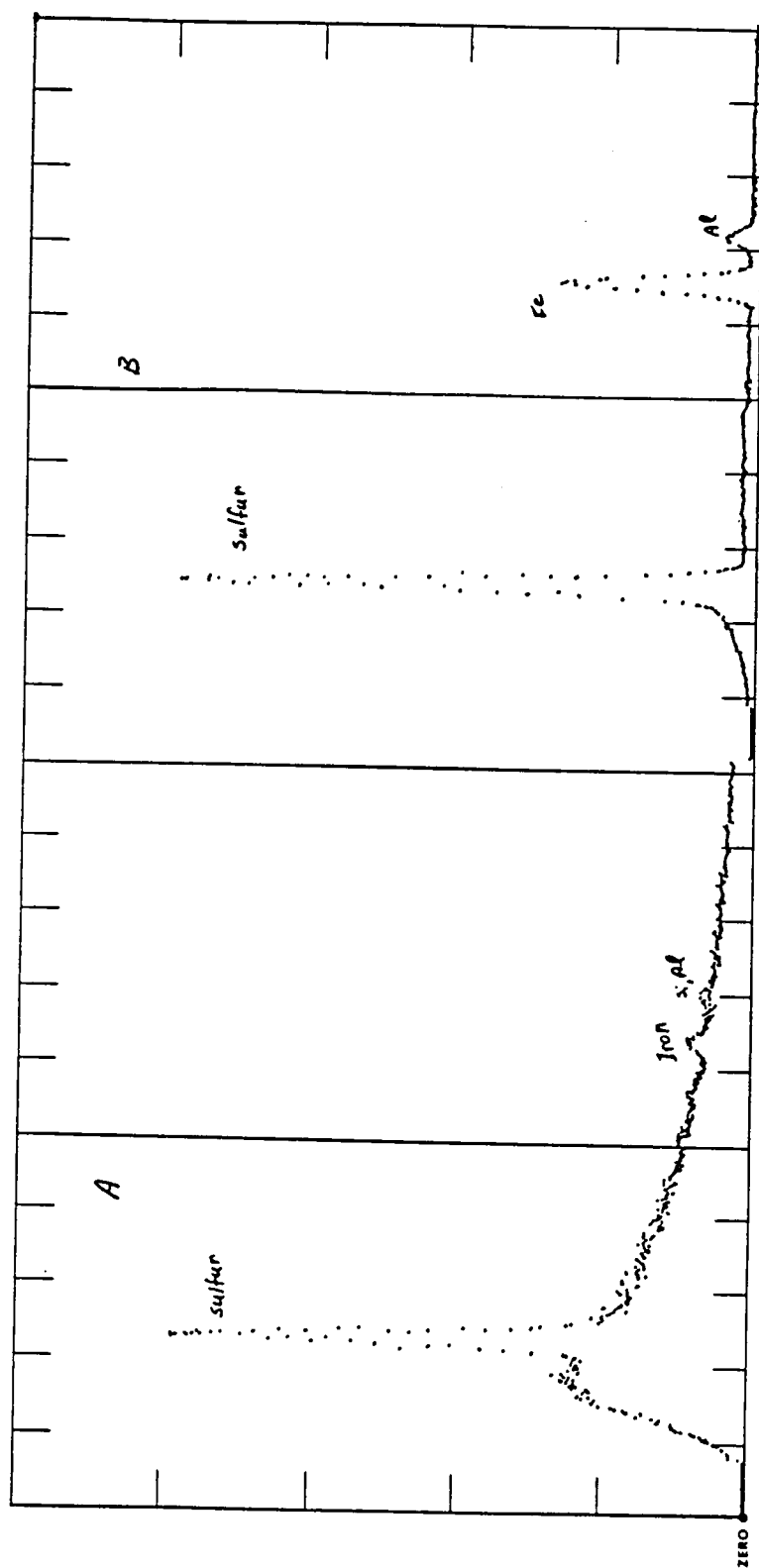
Photoelectron Micrograph of a Band Isolated from Figure 4.1
Magnification Approximately 2500x

vacuum deposition, and they clearly show that the supposed iron pyrite is oriented in parallel bands. In Figure 4.2 a band is isolated and magnified. It may be seen that the band is composed of discrete crystals which have, in some cases, grown and occluded.

In Figure 4.2 two areas are indicated which were selected for further observation by x-ray emission analysis. The x-ray emission spectrum of Area A, the clear area, shows primarily sulfur with minor amounts of iron, aluminum, and silicon. Emissions from the lighter non-metals, including carbon and oxygen, are not detected by the instrument used. In contrast, the crystal in Area B shows mostly sulfur and iron, in an approximate 2:1 ratio, with minor amounts of aluminum. That is, the crystal has been shown to be nearly pure iron pyrite (FeS_2). The X-ray emission charts for Areas A and B are included as Figures 4.3A and 4.3B.

The density of several bits and chunks of the coal was determined by using Avogadro's Principle and water at 25°C. The average density for the coal was determined to be 1.32 g/cm^3 , a moderately heavy coal as expected from the above surface examination.

The moisture and ash content of freshly ground coal samples were determined according to methods published by the American Society for Testing Materials (ASTM). The moisture content of the coal was determined according to



A. Emission Spectrum of Area A

B. Emission Spectrum of Area B

Figure 4.3

X-Ray Emission Spectrum of Figure 4.2

ASTM D 3173-73(1979), and found to be 5.42% moisture, and the ash content of room temperature air-dried coal was determined according to ASTM D 3174-82 and found to be 14.6%. Reactive calcium was determined by extraction with aqua-regia and found to be less than 0.5%.

4.4 Sample Preparation

In general, coal ground to less than size 60 mesh is considered fine coal. The literature on fine coal treatment frequently mention coals "as fine as 200 mesh," indicating a size range for fine coal as 60/200 mesh. For this study the coal was ground such that 100% of the ground coal passed through an 80 mesh sieve, and 90% passed through a 100 mesh sieve. The limestone was prepared in such a manner that 100% passed through an 80 mesh screen.

The limestone was ground first, and divided into two portions, with one portion being immediately calcined at 850c for 12 hours. The coal was then ground and sized and divided into three portions of 600 grams each: portion one was labeled as ground coal, to portion two was added 9% by weight ground limestone, and to portion three was added 8.5% by weight ground and calcined limestone. The amount of additive was intended to be approximately twice the total sulfur content.

After the portions were thoroughly mixed in a rotary

mixer, they were subdivided into three portions each, containing 200 grams of coal, and labeled as the samples for study. One sample from each portion was stored at room temperature, one at 60c, and one at 100c. The samples are identified by number, composition, and temperature in Table 4.2.

The three experimental temperatures of ambient, 60c, and 100c were chosen in order to take advantage of available laboratory ovens and to reduce the possibility of bacterial catalysis of the pyrite. Temperatures in the 40-60c range would have been preferable in order to establish the kinetics at near ambient temperatures. The samples were stored in more or less air-tight containers without predrying; resultantly, the moisture content remained approximately constant throughout the course of the experiment. To insure a nearly constant concentration of air the containers were opened and the contents stirred about twice weekly during the course of the experiment. Although the small amount of moisture present presents the possibility of water participating in a chemical reaction, this represents the natural case and it was decided to use the ground coal on an "as is" basis. The moisture content of freshly ground coal was found to be 5.42%, but the coal quickly dried to about 2.1% moisture at room temperature and remained steady. The room temperature coal was stored over a desiccant.

Table 4.2
Identification Of Experimental Samples

Sample #	Composition	Temperature
1	pure coal	room temp. (23c)
2	200g coal plus 18g ground Fredonia limestone	room temp.
3	200g coal plus 19g ground and calcined Fredonia limestone	room temp.
4	pure coal	60c
5	200g coal plus 18g ground Fredonia limestone	60c
6	200g coal plus 19g ground and calcined Fredonia limestone	60c
7	pure coal	100c
8	200g coal plus 18g ground Fredonia limestone	100c
9	200g coal plus 19g ground and calcined Fredonia limestone	100c

Notes:

- (a) The coal particle size range is 100%/80 mesh, 80%/100 mesh.
- (b) The limestone particle size is 100%/80 mesh.

4.5 Time Sequence Chemical Analysis For Sulfur

The primary emphasis in this study has been given to the disappearance of pyrite sulfur and to the formation of sulfate sulfur, with periodic analysis of total sulfur. The analytical scheme for the time sequence analysis is outlined below.

- (1) The coal samples listed in Table 4.2 were stored in air-tight bottles at room temperature, 60c, and 100c for five months.
- (2) The samples were opened and stirred twice weekly to assure nearly constant O₂ in air concentrations in contact with the samples.
- (3) Periodically, representative samples were taken from the bottles for analysis.
- (4) The analysis of a freshly ground coal sample was begun within two hours of grinding in order to establish the base level concentrations of each analyte.
- (5) The moisture content of the coal at the time of the sulfur analysis was determined.
- (6) Total sulfur was analyzed by ASTM procedure D 3177-75. Sulfate and pyrite sulfur analysis was determined by ASTM procedure D 2492-29, "Forms of Sulfur in Coal." (39)

In the total sulfur procedure a 1.0 gram sample was ignited in an electric muffle furnace with Eschka's mixture, which is a mixture of two parts by weight of light calcined magnesium oxide (MgO) and one part by weight of anhydrous sodium carbonate (Na₂CO₃). The collected sulfur was precipitated from an acidic solution as barium sulfate (BaSO₄), collected by filtration on ashless filter paper, and ashed in an electric muffle furnace. The precipitated

and purified BaSO_4 was weighed, and the sulfur was determined from the stoichiometric fraction of sulfur in BaSO_4 divided by the weight of the original coal sample. The weight of the original sample was corrected for the addition of sorbent such that the determined total sulfur percentage was the percentage of total sulfur in the normalized coal sample, not the percentage of total sulfur in coal plus sorbent. The Eschka method presumes that all heat sensitive sulfur compounds are converted into SO_2 which then reacts with the Eschka mixture to form magnesium sulfate.

According to ASTM test procedure D 2492-79 the sulfate sulfur and the pyritic sulfur may be separated by refluxing a coal sample in 7.5% hydrochloric acid (HCl). This is because FeS_2 is insoluble in dilute HCl , but all other commonly encountered iron compounds and sulfate anions are soluble in dilute HCl . The sulfate sulfur may be precipitated from the acidic solution as BaSO_4 and the sulfate sulfur determined as in the total sulfur method.

The pyritic sulfur determination method is an indirect method whereby the pyritic iron content is measured directly and the pyritic sulfur content deduced from the stoichiometry of FeS_2 . The coal residue from the sulfate sulfur test was used in the pyrite sulfur determination. It was assumed that the sulfate extraction procedure removed not only the sulfate anions but also all

ferrous and ferric cations, leaving only iron as iron pyrite, FeS_2 , in the residue. Iron pyrite has very limited solubility in dilute HCl but may be removed quantitatively by dilute nitric acid (HNO_3). According to ASTM test procedure D 2492-79, the FeS_2 may be removed from the coal residue by refluxing with 8.5% HNO_3 and separated from the residue by filtration. The iron content of the resulting solution was determined by atomic absorption spectroscopy, using a Perkin-Elmer Model 503 instrument. From the FeS_2 stoichiometry the sulfur concomitant with the pyritic iron was deduced and divided by the original coal sample weight to establish the fraction of pyritic sulfur.

Samples which had a sorbent added were normalized to an equivalent pure coal weight by dividing by 1.085 for the limestone additions, and by 1.090 for the calcined limestone additions. The laboratory data for the time-sequence sulfur analyses are listed in Appendix C for sulfate and pyritic sulfur and in Appendix D for total sulfur. The ASTM test procedures are summarized in Appendix E; please refer to ASTM Volume 26 for the complete procedures (40).

4.6 X-Ray Powder Diffraction Analysis

4.6.1 Sample Preparation

At the end of the five-month period of the chemical

time-sequence analysis, fresh coal samples were prepared as discussed in Section 4.4. Portions of the freshly prepared samples and portions of the aged samples were mixed with a mixture of light grease and solvent to a putty-like consistency, and the coal putty was tamped into specially-made sample holders for a Rigaku "Geiger-flex" x-ray diffraction analyzer. As the solvent (acetone) evaporated, a firm specimen was available for analysis by x-ray diffraction. In addition to the coal sample specimens, a group of standard chemical specimens representing some of the analytes of interest were also prepared. Finely powdered silicon was used as a standard for calibrating the x-ray machine. Table 4.3 lists the materials that were prepared and analyzed by x-ray powder diffraction, and the standard data from an atlas of x-ray powder diffraction for a broader list of analytes is included in Appendix F. The x-ray spectrographs for analysis are included in Section five.

4.6.2 A Brief Discussion Of The Theory And Operation Of An X-Ray Powder Diffraction Analyzer

For a crystalline material there are numerous possible imaginary parallel planes of atoms. These planes are denoted according to their distance from the origin of an arbitrary set of three dimensional Cartesian coordinates, x , y , and z , and usually denoted (hkl) . Thusly, an imaginary plane of atoms that is (110) passes through one unit

Table 4.3

Materials Prepared For X-Ray Diffraction Analysis

Sample #	Identification
1	Coal aged at room temperature
2	Coal aged at room temperature + 2% Fe_2O_3
3	Coal aged at room temperature + 5% Fe_2O_3
4	Coal aged at room temperature + 10% Fe_2O_3
5	Coal aged at room temperature + 20% Fe_2O_3
6	Coal + calcined Fredonia limestone aged together at 60c
7	Coal + uncalcined Fredonia limestone aged together at 60c
8	Coal aged at 60c
9	Finely powdered mineral pyrite, aged
10	Finely powdered mineral pyrite, fresh
11	Freshly ground coal
12	Fredonia limestone
13	FeSO_4
14	Coal aged at room temperature + 10% FeSO_4
15	FeS
16	Coal aged at room temperature + 10% FeS
17	$\text{Fe}_2(\text{SO}_4)_3$
18	Coal aged at room temperature + 10% $\text{Fe}_2(\text{SO}_4)_3$
19	Calcined Fredonia limestone
20	Coal pyrite

along the h axis, one unit along the k axis, and at the origin of the l axis. The numbers associated with the (hkl) notation, i.e., (110) , are called the Miller indices. Crystal planes which are at an angle to the parallel direction of an incident monochromatic x-ray beam will diffract the beam in a predictable manner; the diffraction angles of a particular material depend on the wavelength (λ) of the incident x-ray beam and the distance between the crystalline planes (d). In the powder diffraction method each appropriate particle is a minute crystal oriented at random to the collimated x-ray beam, and by random chance some of the particles will be correctly oriented for reflection from their (100) planes, other particles will be correctly oriented for reflection from their (110) planes, and so on, such that all (hkl) planes are available for reflecting the beam.

The advantage of this method is that mixtures of crystalline substances may be examined since each material reflects the beam in a particular fashion and since all the crystalline planes of each substance are available for diffraction, the percentage of the beam that is reflected is much greater than for a single crystal of the same mass and material. Consequently, relatively small quantities may be detected. On the Rigaku instrument used, usually about 5% by mass is detectable, but for some materials considerably less than 5% can be detectable.

Figure 4.4 is a representation of the source, sample, and detector of the Rigaku machine. The sample was mounted vertically and rotated parallel to the incident x-ray beam. When the (hkl) planes were properly oriented to the incident beam, the beam would be partially reflected to the detector. From Figure 4.5 it is clear that the angle observed from a reflection is twice the incident angle of the beam with the sample. The strip-chart record produced by the Rigaku instrument records the double angle (2θ) directly. Since the wavelength of the monochromatic beam is known, it is possible to substitute into the familiar Bragg's Law expression,

$$\lambda = 2d \sin \theta . \quad (4.1)$$

For a particular set of conditions the equation may be rewritten as

$$\sin \theta = \lambda / 2d \quad (4.2)$$

and from direct measurements d may be calculated. For many materials d has been tabulated and the values of d for some of the analytes of interest in this study are included in Appendix G. Of course, the resultant chart may be compared to the chart of a standard material. For the Rigaku machine the wavelength is 1.542 angstroms.

From Appendix D for iron pyrite the value of d for the 100% peak has been determined to be 1.632 angstroms. Substituting values into equation (4.2) we have

$$\sin \theta = 1.542 / 2 (1.6332), \quad (4.3)$$

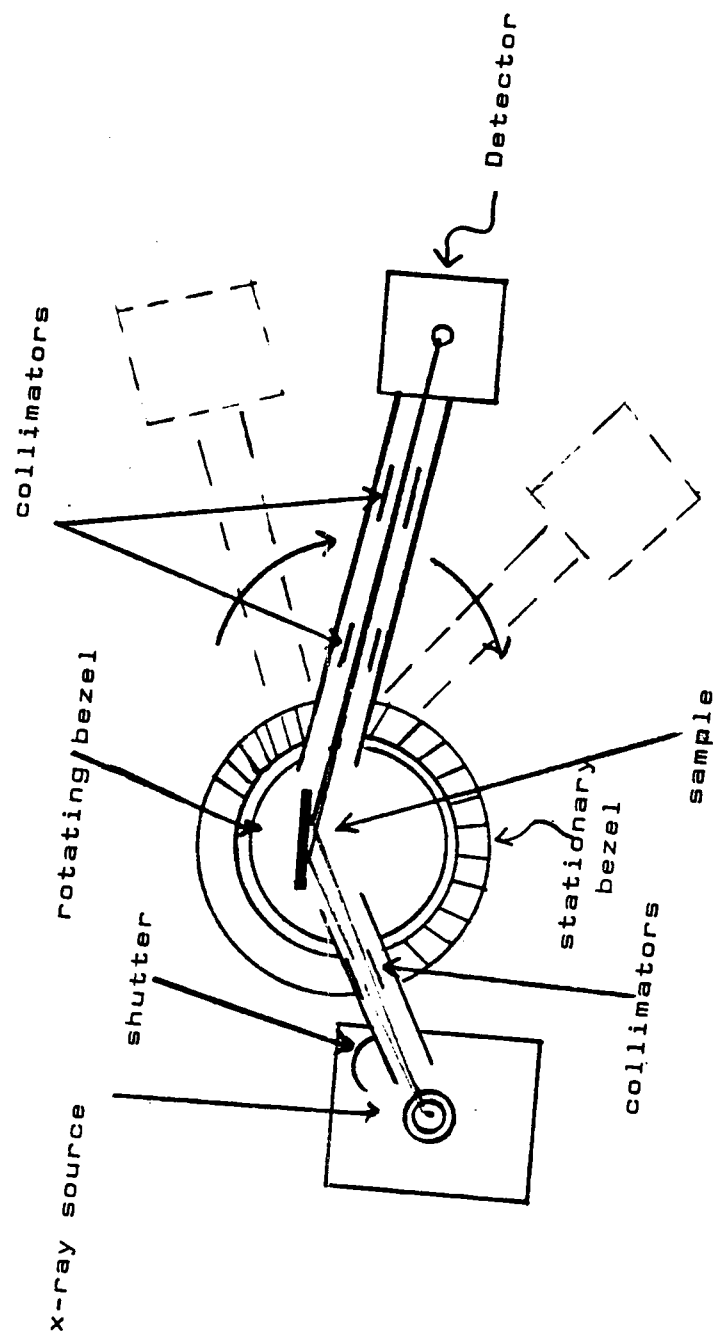


Figure 4.4

Diagram of the Source, Sample, and Detector
Rigaku Geiger Counter

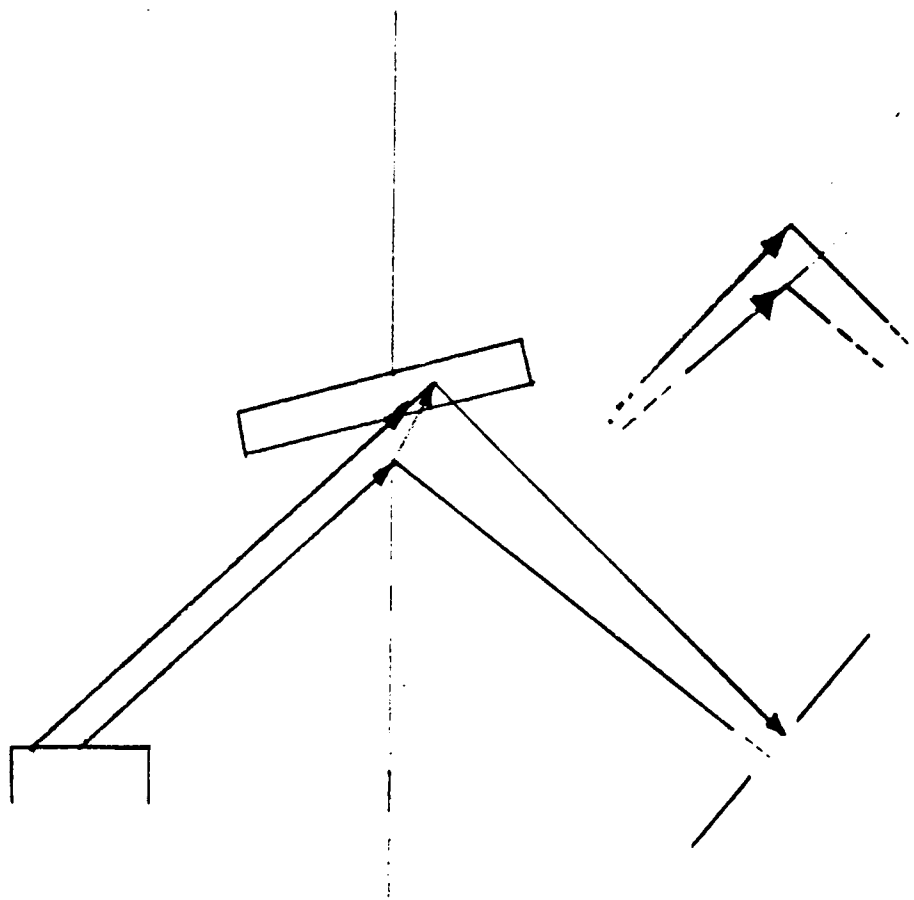


Figure 4.5
Formation of the Bragg Double-angle:
X-Ray Diffraction Analysis

which becomes upon inverting, 28.67° . However, recalling that the strip-chart record of the x-ray diffractor records the double angle we may expect to see the 100% pyrite peak at 2θ , or 56.34 degrees of scan. The values listed in Appendix G have all been converted to the double angle, and the values have all been computed for 1.542 angstroms (the published data relate a number of wavelengths).

The operation of the Rigaku Geiger-flex is controlled by a small built-in computer. The degrees of rotation of the sample in the beam, scan rate, chart speed, etc., were selected after a series of trials to determine optimum operating conditions.

The instrument was set to scan from 10° to 60° , and the chart speed was set at 6 cm per minute. The machine-printed operational data parameters are reproduced in Figure 4.6.

4.7 Tests For Gaseous Sulfur Dioxide

On occasion the odor of SO_2 was noticed when a sample jar was opened to remove a sample. In addition, the possible mechanisms of pyrite coal conversion may involve an intermediate step whereby the FeS_2 is first reduced to FeS and SO_2 . It was decided that an analysis of the air space above the coal in the sample jars should be checked by gas chromatography (GC) for the presence of gaseous SO_2 .

PROGRAM NO.	5
MODE	1
RECYCLE	1
AXIS	1
START ANGLE	10.00
STOP ANGLE	60.00
SCAN SPEED	8
FULL SCALE	5
TIME CONST	2
CHART SPEED	6

Figure 4.6
The Rigaku Geiger-Flex Computer Program

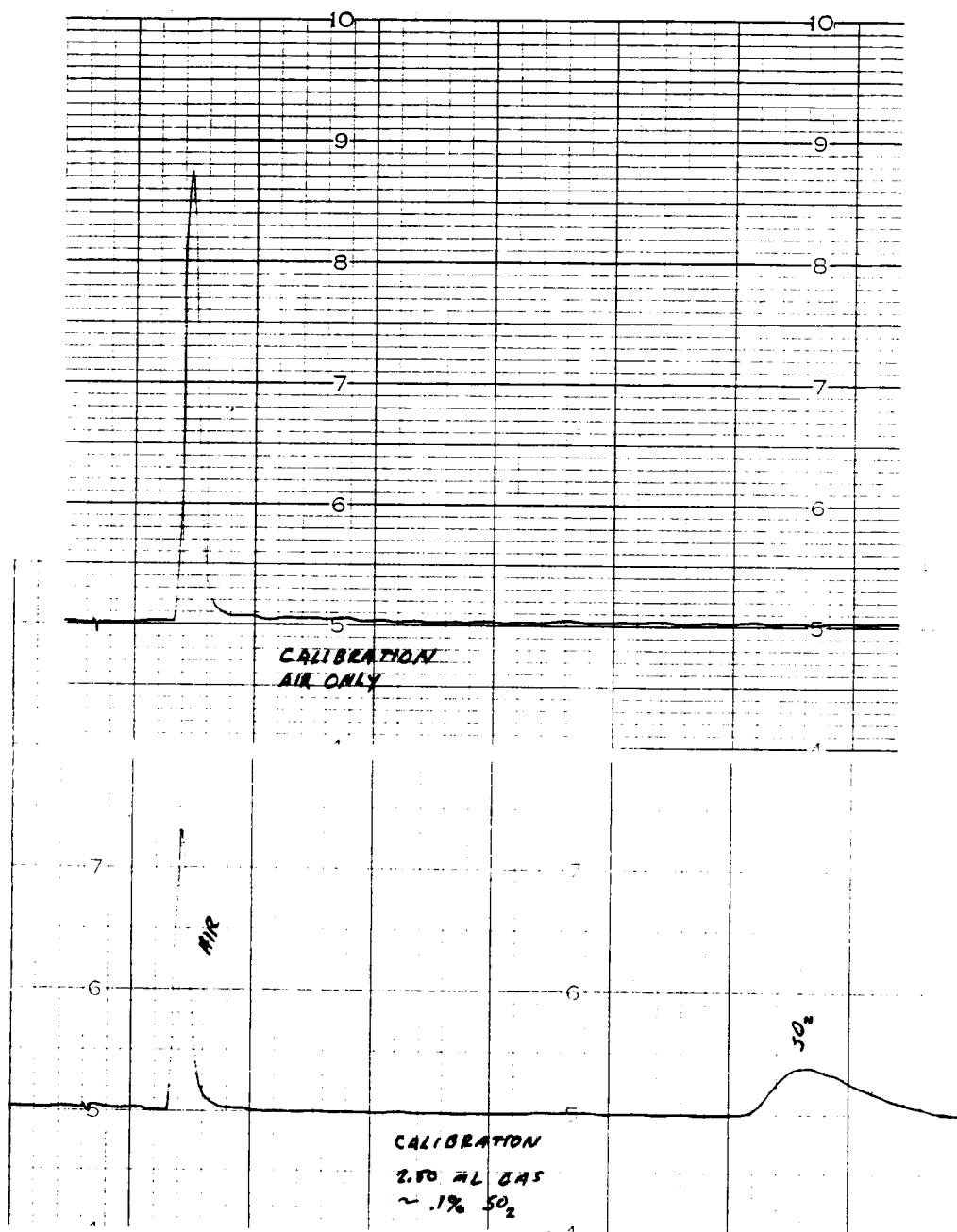
A 76 cm teflon column packed with preconditioned Poropak "Q" polymer beads and equipped with stainless steel fittings was constructed and mounted in a Wilkins Aerograph gas chromatograph with a thermal conductivity detector. The packing was preconditioned for 24 hours at 230°C using helium at 50 ml/min, in accordance with published instructions (41). This column and instrument arrangement was tested with various mixtures of SO₂ and air and found to have a trace sensitivity of 0.02% (200 ppm) SO₂ in air.

A 3.5 cc gas sample from the original ground coal sample (approaching one year old) was collected and injected into the gas chromatograph. Gas samples collected from aged coal mixed with limestone or calcined limestone were not demonstrated to contain sulfur dioxide in detectable quantity. Since the presence of SO₂ was indicated in the pure coal sample, a more organized experiment was planned which included grinding and preparing other fresh coal samples. For this experiment the containers were modified in the following manner:

- (1) a special silicone rubber which is chemically inert to most gasses, including SO₂, was chosen to seal the specimen jar;
- (2) a hole was drilled in the lid of each specimen jar and a septum of the above silicone rubber was forced and glued into the opening;
- (3) a gasket of the same silicone rubber compound was cut for each jar so that when the lid was fitted the container would be air-tight.

Sample masses of 200 grams of coal were placed in the (250 ml) jars and stored as prepared in Section 4.4. Periodically over a three month span a 3.5 ml gas sample was withdrawn from the jars through the septa and injected into the gas chromatograph. Also, 3.5 ml of fresh air replacement was reinjected into the jar, and the coal was shaken routinely. These steps were taken to insure that the concentration of oxygen remained approximately constant throughout the duration of the experiment.

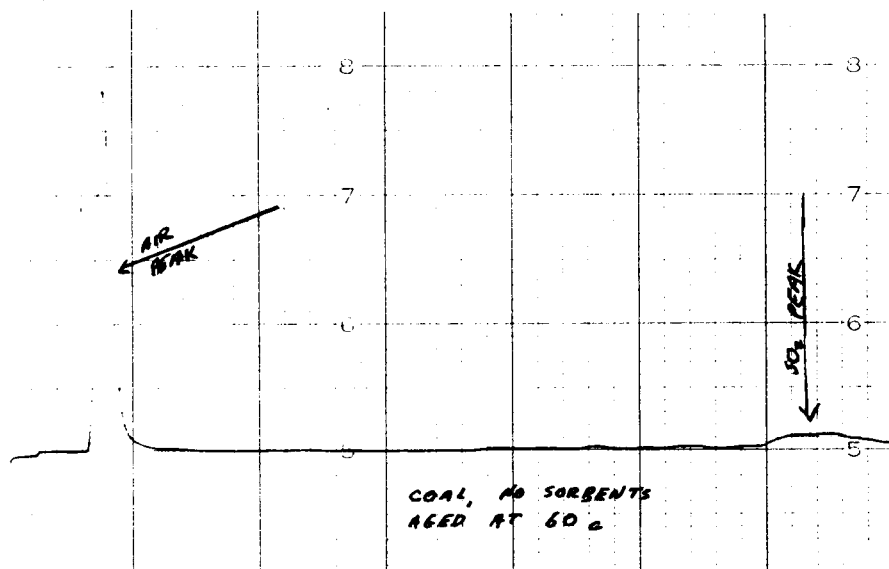
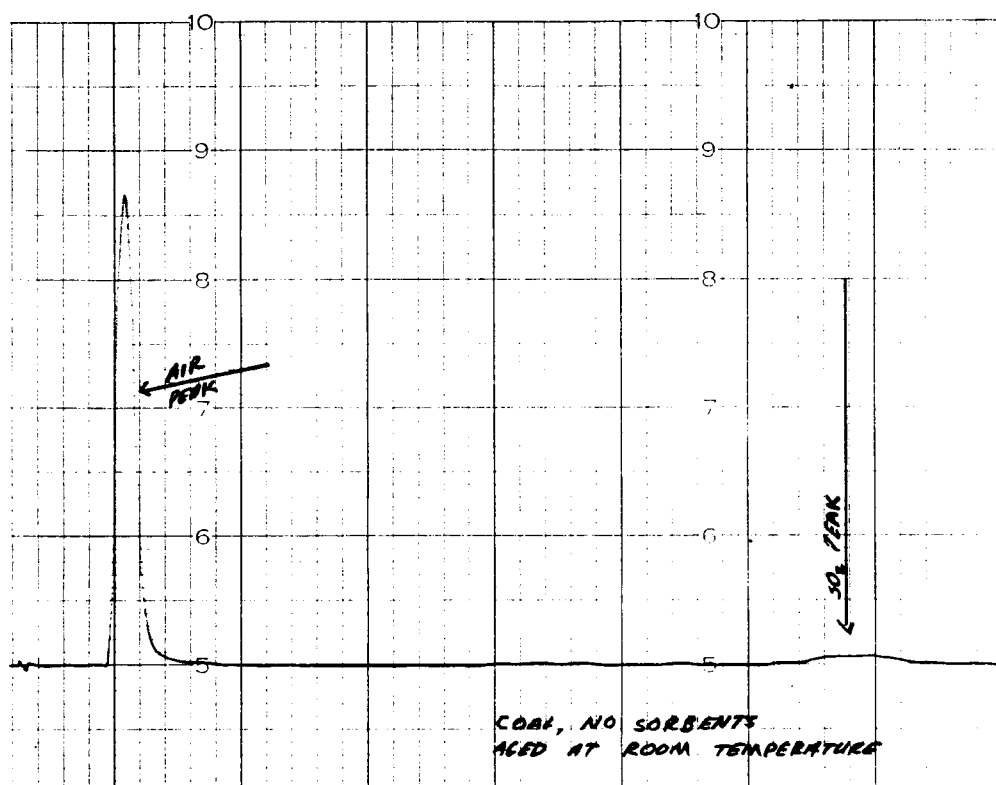
The gas chromatographs produced by this experiment follow as Figures 4.7-A and 4.7-B. The gas chromatographs are discussed in Section 5.2.3.



A. Calibration gas chromatograms

Figure 4.7

Sulfur Dioxide Test Gas Chromatograms



B. Experimental gas chromatograms

Figure 4.7 (continued)

5.0 RESULTS AND INTERPRETATIONS

5.1 Objectives

The results of the procedures described in the "Experimental Procedures" section will be discussed in detail. In particular the analyses of the results from the time sequence chemical analysis, from the results of the x-ray diffraction experiment, and from the sulfur dioxide experiment will be developed.

The time sequence chemical analysis will be interpreted statistically according to regression analysis procedures. An expression for reaction rate for each sample at each temperature will be developed and the reaction rates so produced will be graphically interpreted to obtain the Arrhenius activation energy.

The x-ray diffraction results will be scrutinized for the presence of specific compounds, and the SO₂ gas chromatographic results will be used in support of hypothetical reaction mechanisms for the conversion of pyrite sulfur.

5.2 Time Sequence Chemical Analysis

5.2.1 Theory And Results

Hypothetical smooth curves sketched through the datum points of the analytical data, as in Figure 5.1, suggest a simple exponential decay curve for the pyritic sulfur concentration and show a flattening toward an asymptotic

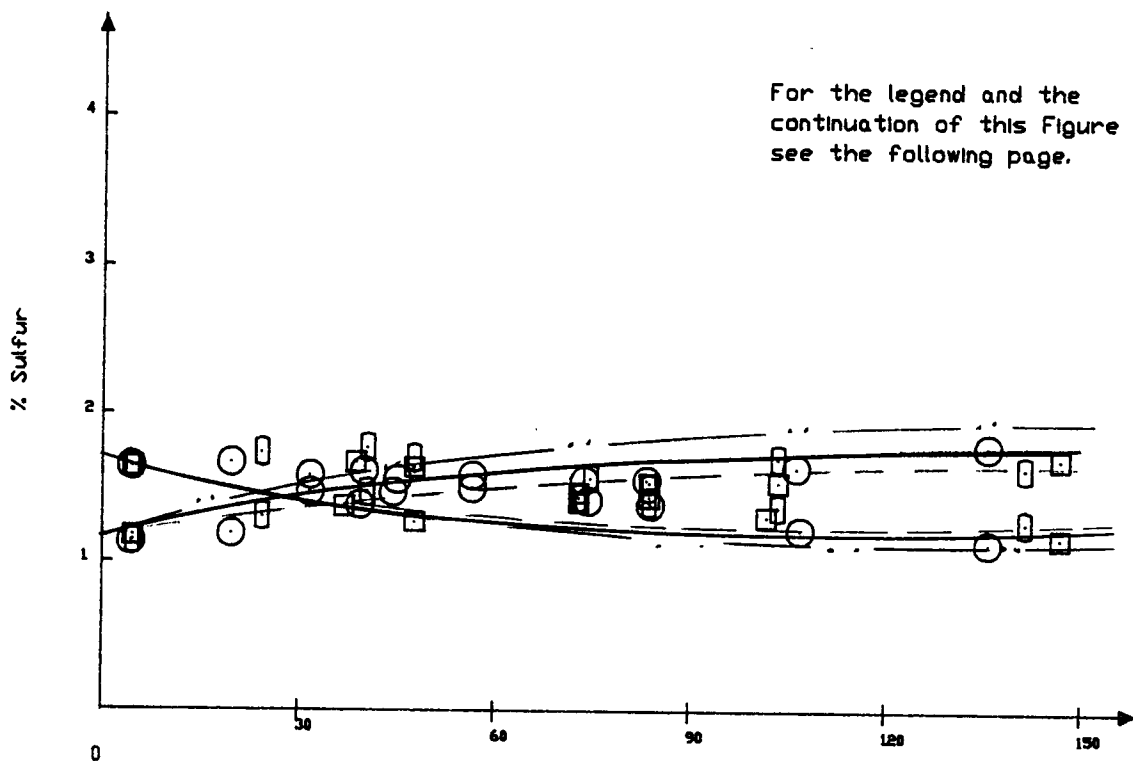


Figure 5.1-A, room temperature

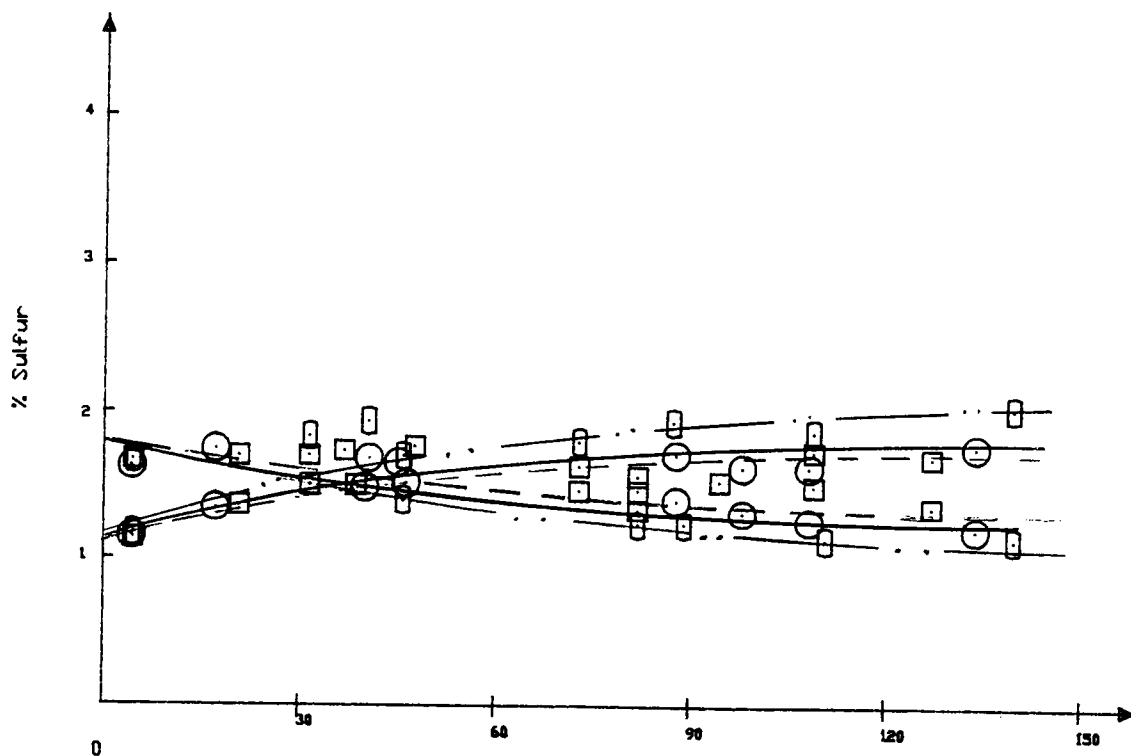


Figure 5.1-B, 60c

Figure 5.1

Hypothetical First-Order Curves Fitted
to the Experimental Data

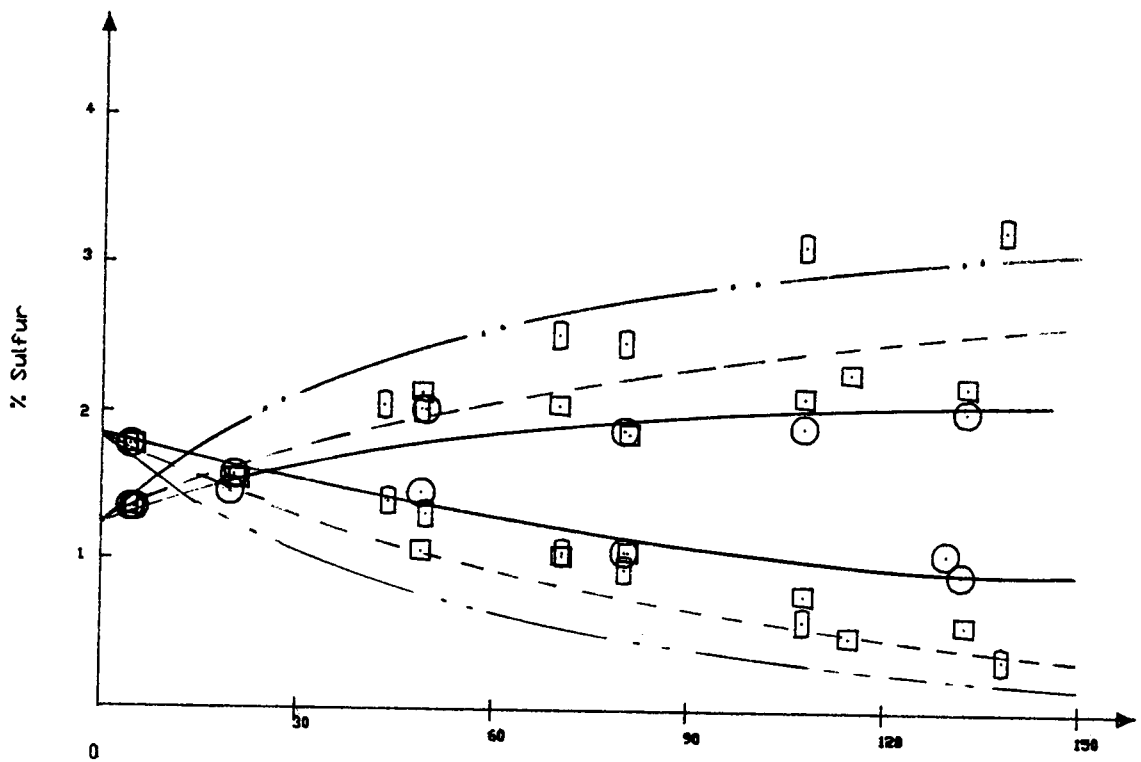


Figure 5.1-C, 100c

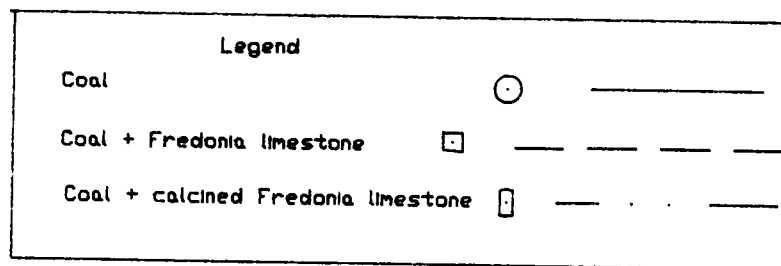


Figure 5.1 (continued)

value for sulfate sulfur growth. A relationship where the analyte varies with time is expected to exhibit first order exponential behavior if the chemical reaction is truly second order but one of the reacting constituents is essentially constant with time. For a reaction of the form



and the reaction is assumed to be elementary, then the differential change (disappearance) of A with time may be expressed as

$$\frac{d[A]}{dt} = -k[A][B]. \quad (5.2)$$

But if the concentration of B remains essentially constant or if the concentration of B is much greater than A, then

$$\frac{d[A]}{dt} = -k'[A] \quad (5.3)$$

where k' is an apparent first order rate constant. Note that the true chemical equation is not zero order in B, but is only apparently so. The technique of flooding a second order reaction with a concentration of one constituent such that $[B] \gg [A]$, or the technique of holding $[B]$ constant during the progress of the reaction will satisfy the requirements of (5.3); chemical kinetic expressions represented by equation (5.3) are known as pseudo first order expressions. In this study the oxygen concentration for the hypothetical reactions described by equations (4.4-4.11) was held approximately constant.

The differential equation described by (5.3) is easy to evaluate by the separation of the variables and integrating from time zero to time t , and from the initial concentration of A, $[A]_0$, to an instantaneous concentration of A, $[A]_i$, which is generally simply written as $[A]$.

$$\int_{[A]_0}^A \frac{d[A]}{[A]} = \int_{t=0}^t -k' dt \quad (5.4)$$

$$\ln[A] - \ln[A]_0 = -k't \quad (5.5)$$

$$\ln[A] = \ln[A]_0 - k't \quad (5.6)$$

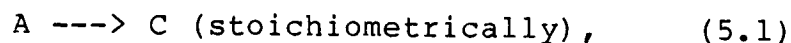
Equation (5.6) may be exponentiated to yield

$$[A] = [A]_0 \exp(-k't). \quad (5.7)$$

Equations (5.6) and (5.7) are exponential decay curves. Although (5.6) has the convenient form of a straight line, the exponential relationship of the physical data is best suggested by (5.7). To evaluate the first order rate constant and to determine the best statistical value for $[A]_0$, equation (5.6) may be regressed using a linear least squares technique.

From equations (5.6) and (5.7) it is seen that the independent variable is the present concentration of sulfur, the intercept with the ordinate is the logarithm of the initial pyritic sulfur concentration ($\ln[A]_0$), and the negative slope is the value for the reaction rate constant, k . Since equation (5.7) represents a pseudo first order equation, the units of k are inverse days.

If it is desirable to express the kinetics of the formation of the product, $\underline{C}$, in equation (5.1), the formation of $\underline{C}$ may be expressed in terms of the disappearance of $\underline{A}$ by using the following equivalency substitutions in equation (5.7):



$$[A] + [C] = [A]_0 \quad (5.8)$$

(both $\underline{A}$ and $\underline{C}$ approach asymptotic concentrations),

$$\text{at } t=0, [C] = [C]_0, \quad (5.9)$$

$$[C] = [C]_0 + [A]_0. \quad (5.10)$$

Recalling equation (5.7)

$$[A] = [A]_0 \exp(-kt), \quad (5.7)$$

and substituting for $[A]$

$$[A]_0 - [C] = [A]_0 \exp(-kt) \quad (5.11)$$

and rearranging

$$[C] = [A]_0 - [A]_0 \exp(-kt) \quad (5.12)$$

which may be written

$$[C] = [A]_0 \{1 - \exp(-kt)\}. \quad (5.13)$$

But at $t=0$, $[C] = [C]_0$, so finally

$$[C] = [A]_0 \{1 - \exp(-kt)\} + [C]_0. \quad (5.14)$$

Equation (5.14) may be alternately expressed as

$$[C] = [A]_0 \{1 - \exp(-kt + b)\} \quad (5.15)$$

where $\underline{b}$ is a constant related to $[C]_0$ such that at $t = 0$,

$$1 - \frac{[C]}{[A]_0} = \exp(b) = [C]_0. \quad (5.16)$$

Where $[A]_0$ is known explicitly, equation (5.13) may

be linearized to the form

$$\ln \left(1 - \frac{[C]}{[A]_0} \right) = (-kt). \quad (5.17)$$

The left side of equation (5.17) may be linearly regressed against time (t) to establish the best fit line where the slope is proportional to the formation reaction rate constant, k, and the intercept is related to the initial concentration of product. Note that if $[C]_0$ is substantial equation (5.17) fails, but the reaction rate constant may still be determined by substituting for [C]

$$[C] = [C] - [C]_0 \quad (5.18)$$

if $[C]_0$ is known explicitly.

In cases where $[C]/[A]_0 \geq 1$, and $[C]_0$ is known explicitly, equation (5.14) may be linearized into the form

$$\ln \left(1 - \frac{[C] - [C]_0}{[A]_0} \right) = -kt. \quad (5.19)$$

Equation (5.19) fails in the case where

$$\frac{[C] - [C]_0}{[A]_0} \geq 1. \quad (5.20)$$

However, based on the simple derivations presented, equation (5.19) could only fail in the impossible case where more than 100% of $[A]_0$ has been converted into [C]. Rejecting the impossible implication, upon the failure of (5.19) it must be concluded that not all the formation of product is due to the reaction of A, but must include the parallel reaction of some unknown reactant.

Since these reactions represent pseudo first order

relationships, the units of the reaction rate constants are inverse days. Using the models of equations (5.6) and (5.16), the data from Appendix C have been analyzed according to a standard bivariate, linear, least-squares regression program for samples 1-6. For sample Nos. 7, 8, and 9, the mean value for $[C]_0$ obtained from the regression of the data for samples 1-6 (regressed) was inserted into equation (5.18) for regression.

There are a number of least-squares regression programs available for use; in this study several microcomputer programs were used, including Lotus 1-2-3, Statgraphics, and several custom programs.

The equations of the lines generated by the least squares technique and the accompanying correlation coefficients for decreasing pyritic sulfur percentage are listed in Table 5.1, and for the growth of the sulfate sulfur percentage in Table 5.2 for each sample. The lines are graphically presented in Figure 5.2.

It has been hypothesized that the formation of sulfate is directly related to the disappearance of pyrite sulfur; if the hypothesis is correct, the formation of sulfate sulfur should have the form of equation (5.12). Assuming that the laboratory techniques for sulfate sulfur analysis and pyrite sulfur analysis produce similar data scatter and if pyrite sulfur is converting to sulfate sulfur, the correlation coefficients for the regressed

Table 5.1

Empirical Formulae By Regression Analysis
Pyritic Sulfur Conversion

Sample No.	Pyritic Sulfur %	Initial % Pyrite Sulfur	Time Constant	Correlation Coefficient
1.	$y' = .554 - .0028t$	1.740	357 days	-.987
2.	$y' = .575 - .0029t$	1.777	345 days	-.978
3.	$y' = .583 - .0029t$	1.791	345 days	-.974
4.	$y' = .574 - .0029t$	1.775	345 days	-.973
5.	$y' = .536 - .0033t$	1.709	303 days	-.921
6.	$y' = .562 - .0033t$	1.754	303 days	-.951
7.	$y' = .514 - .0048t$	1.672	208 days	-.984
8.	$y' = .681 - .0095t$	1.976	105 days	-.944
9.	$y' = .693 - .0129t$	2.000	76 days	-.991

sample No. 1, coal aged at room temp

sample No. 2, coal plus Fredonia limestone, room temp.

sample No. 3, coal plus calcined limestone, room temp.

sample No. 4, coal aged at 60c

sample No. 5, coal plus Fredonia limestone, 60c

sample No. 6, coal plus calcined limestone, room temp.

sample No. 7, coal aged at 100c

sample No. 8, coal plus Fredonia limestone, 100c

sample No. 9, coal plus calcined limestone, 100c

$$y' = \ln[\text{pyritic sulfur \%}]$$

$$\text{intercept} = \ln(\text{initial pyritic sulfur \%})$$

Mean initial pyritic sulfur percentage, 1.796%
standard deviation, .061

Table 5.2

Empirical Formulae By Regression Analysis
Increasing Sulfate Sulfur

Sample No.	Sulfate Sulfur %	Initial % Sulfate Sulfur	Time Constant	Corr. Coeff.
1.	$y' = -1.244 - (6.680 \text{ EE } -3)t$	1.280	150 days	.922
2.	$y' = -1.085 - (7.082 \text{ EE } -3)t$	1.191	141 days	.954
3.	$y' = -1.151 - (1.015 \text{ EE } -2)t$	1.230	99 days	.920
4.	$y' = -1.299 - (8.854 \text{ EE } -3)t$	1.308	113 days	.866
5.	$y' = -1.280 - (7.113 \text{ EE } -3)t$	1.299	141 days	.909
6.	$y' = -1.057 - (1.656 \text{ EE } -2)t$	1.174	60 days	.989
7.	$y' = -1.186 - (2.864 \text{ EE } -3)t$	1.247	349 days	.858*
8.	$y' = -1.186 - (6.809 \text{ EE } -3)t$	1.247	146 days	.964*
9.	$y' = -1.186 - (2.100 \text{ EE } -2)t$	1.247	48 days	.968*

$$y' = \ln \left[1 - \frac{(\text{sulfate sulfur } \%)}{(\text{initial pyrite sulfur } \%)} \right]$$

Mean initial sulfate percentage, 1.247%
standard deviation, .057

* By Eq. 5-19 using 1.247% as $[C]_0$

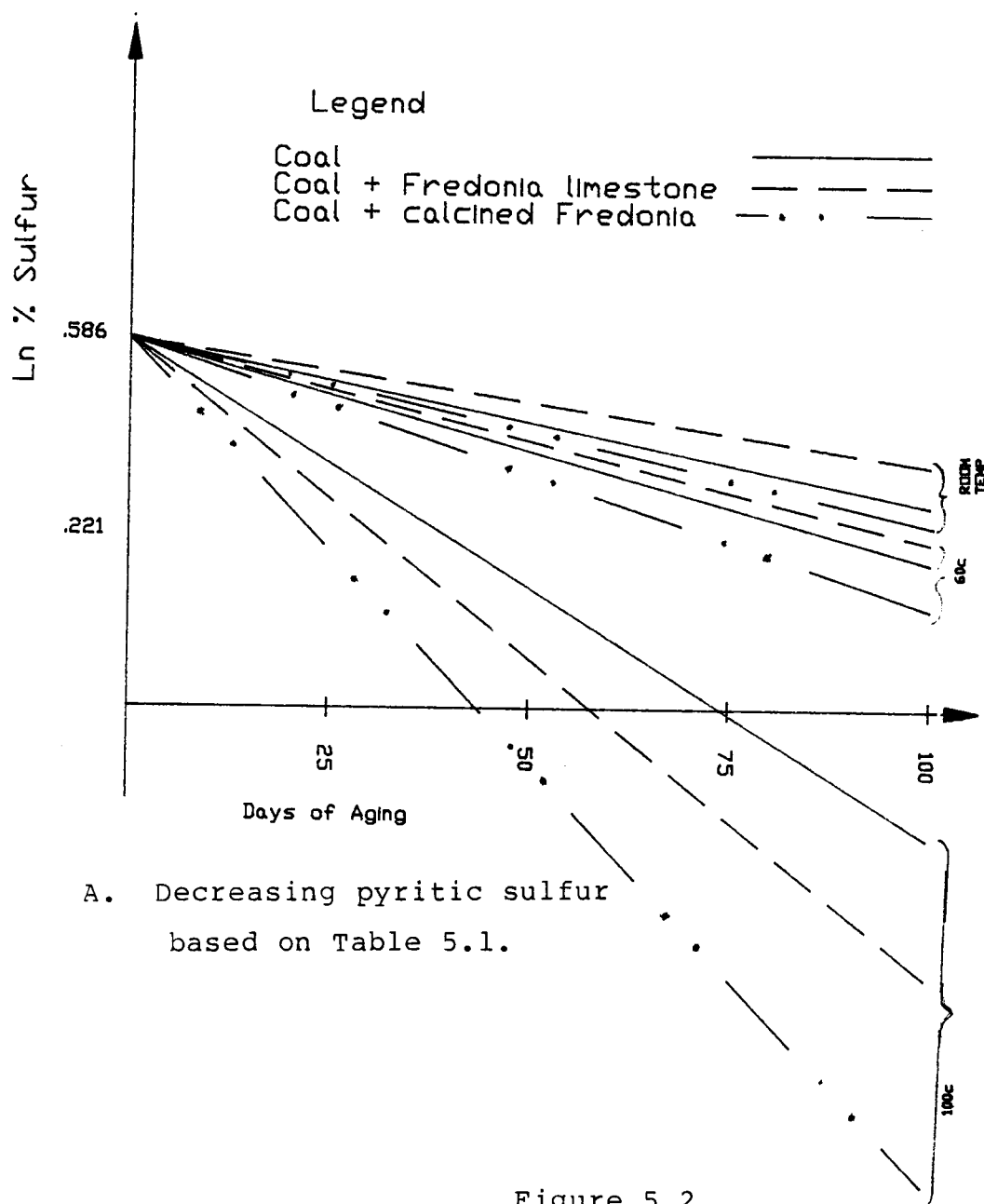
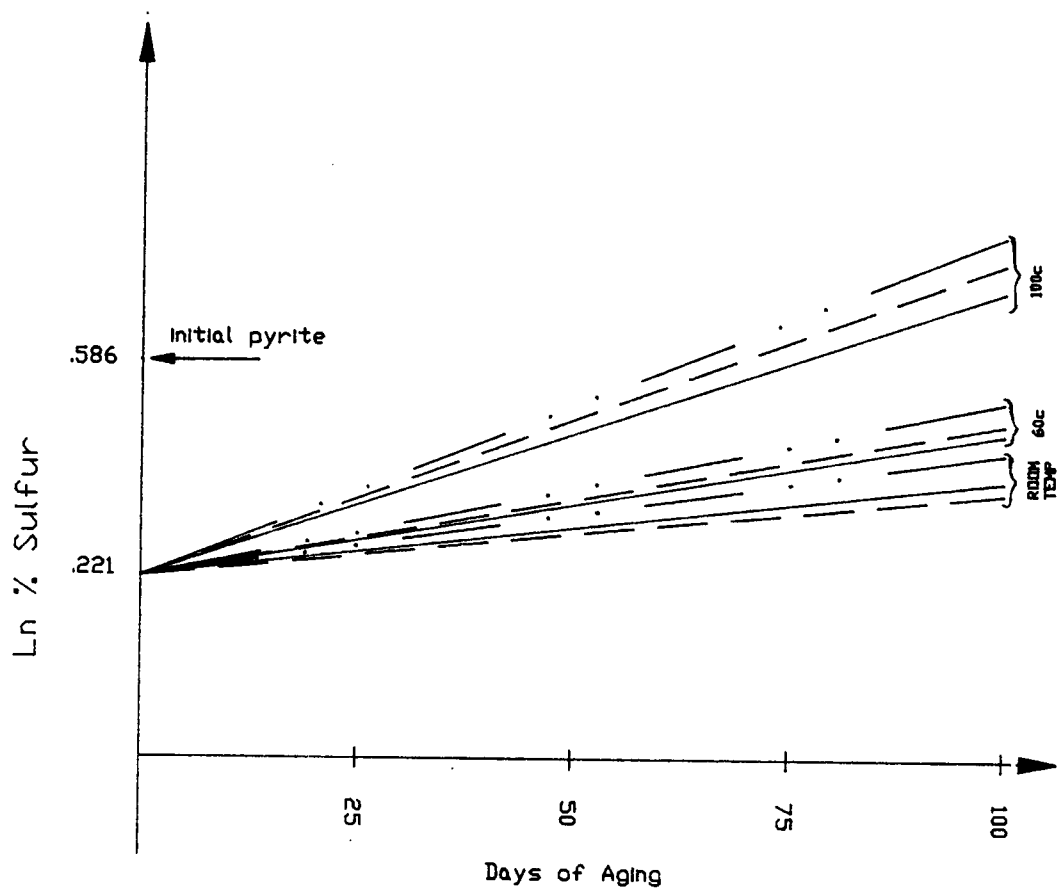


Figure 5.2

The Regressed Straight Lines Based on
the Empirical Formulae



Legend

Coal	—————
Coal + Fredonia limestone	- - - - -
Coal + calcined Fredonia	

B. Increasing sulfate sulfur based on Table 5.2.

Table 5.2 (continued)

lines from equation (5.6) and (5.16) should have similar values, and furthermore, the sum of pyrite sulfur and sulfate sulfur will be constant. Also, the rate coefficients from (5.6) and (5.15) should be similar if equation (5.1) accurately represents the reaction.

From Appendix D, it may be seen that the sum of pyritic and sulfate sulfur is nearly constant, but a comparison of the correlation coefficients of Table 5.1 for pyritic sulfur dissipation with those of Table 5.2 for sulfate sulfur increase reveals that the correlation coefficients of the sulfate sulfur increase are somewhat less than the correlation coefficients for the corresponding pyritic sulfur disappearances. The mean correlation coefficient for pyritic sulfur decrease is $r = .967$ and a standard deviation of $.023$, while the mean correlation coefficient for the sulfate sulfur increase is $r = -.925$, with a standard deviation of $.044$. There are two correlation coefficients for the sulfate sulfur increase experiment which are quite low; sample 4 has a correlation coefficient of $-.866$ and sample 7 has a correlation coefficient of $-.858$. For these samples the r^2 value of about $.75$ indicates that only about 75% of the variance is accounted for by the regression analysis.

It may be concluded that the agreement between the results for the regression analyses of equation (5.6) and (5.16) is good, but not outstanding. Consequently, it is

worthwhile to investigate whether an empirical relationship which does not rely on the assumptions of equations (5.1), (5.8), and (5.9) can better describe the sulfate sulfur increase in coal with time.

5.2.2 An Alternate Description Of The Sulfate Sulfur Formation

Various exponential curves of the form $Y = \exp[f(x)]$ are illustrated in Figure 5.3. Note that a hypothetical smooth curve fitted through the data could be drawn to closely resemble the S-shaped curve of the type

$$Y = \exp(a - b/t). \quad (5.21)$$

Such a hypothetical smooth curve for sample No. 1 is included as Figure 5.4. This model is discussed below.

A model which retains the exponential growth characteristics at short times is desirable. A model which reduces to the initial concentration for SO_4^{2-} and approaches an asymptotic value for SO_4^{2-} as $t \rightarrow \infty$ is

$$[C] = [C]_0 + \exp(a - b/t), \quad (5.22)$$

where $[C]$ represents the sulfate concentration. Clearly, as $t \rightarrow 0$, $\exp(a - b/t) \rightarrow 0$, and as $t \rightarrow \infty$ $\exp(a - b/t)$ must approach $\exp(a)$, such that $\{[C]_0 + \exp(a)\}$ represents the asymptotic value, $[C]_f$. Equation (5.22) may be rearranged to give

$$[C] - [C]_0 = \exp(a - b/t) \quad (5.23)$$

which may be linearized by logarithms to yield

$$\ln ([C] - [C]_0) = a - b/t. \quad (5.24)$$

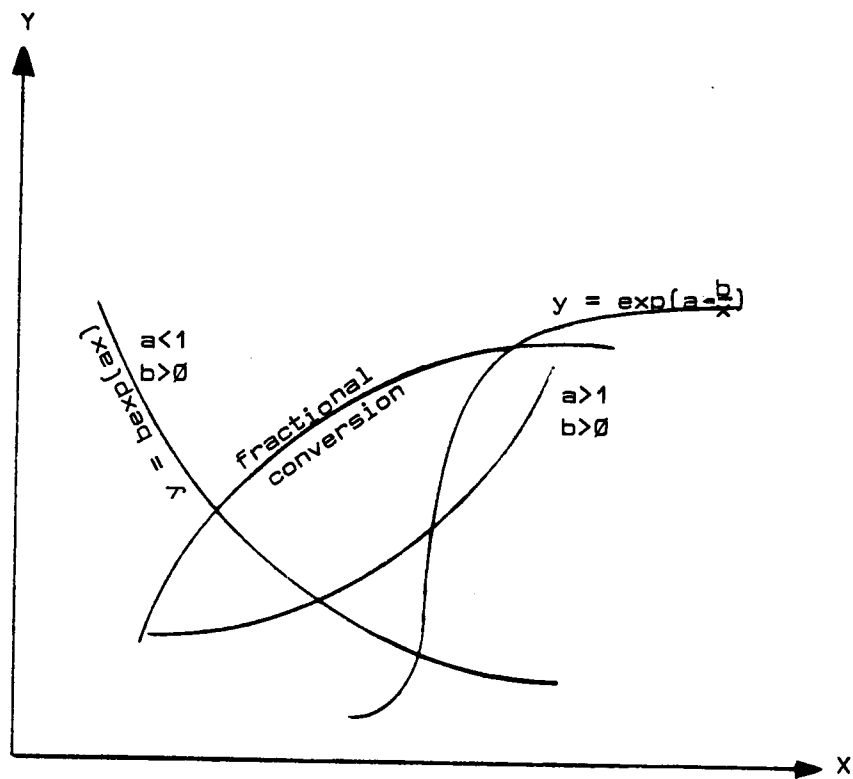


Figure 5.3
Typical Exponential Curves of the Form
 $Y = \exp[f(x)]$

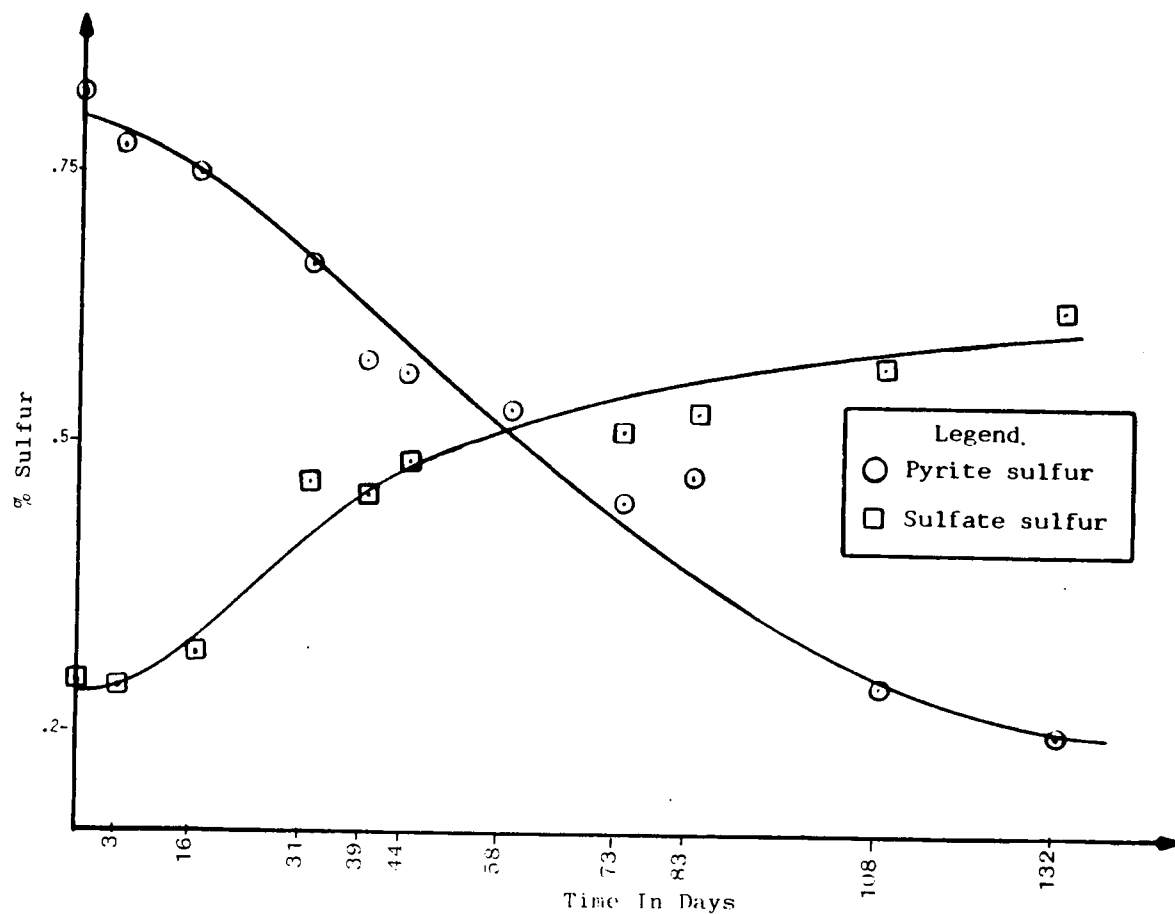


Figure 5.4

Hypothetical Exponential Curves of the Form
 $Y = \exp(a - b/x)$ Fitted to the Data for
 Sample No. 1, Coal Aged at Room Temperature

If $[C]$ and $[C]_0$ are known explicitly for the sulfate concentrations ($[C]_0 = \text{constant}$) equation (5.24) may be regressed as

$$\ln [Y] \text{ vs } 1/t \quad (5.25)$$

to determine the values for a and b in equation (5.21).

Due to the significant data scatter in the laboratory results for sulfate sulfur analyses, the best value for use in the regression analysis of equation (5.24) is not the experimentally determined initial sulfate sulfur percentage. There are two alternatives:

- (1) perform a multiple regression for all datum values for time greater than zero and assuming a value for $[c]_0$, then varying $[c]_0$ until the best correlation coefficient is obtained, or
- (2) use the regressed results for $[c]_0$ determined in Section 5.2.1 as listed in Table 5.2.

While it is possible to generate very good correlation coefficients from the first approach, this approach is in fact specious because no consideration is given to the analytically determined values for $[c]_0$, and the second value (for $t = 3$ days) is assumed to be nearly correct; in fact, the best correlation coefficient is obtained when the value for $[c]_0$ is slightly less than the value for $t = 3$ days. The first approach does produce empirical relationships which mimic the experimental data quite well, and consequently the asymptotic values for sulfate conver-

sion should be quite reliable. The results of the second approach produce correlation coefficients which are improvements to those listed in Table 5.2, and the results obtained for the asymptotic sulfate conversion and for sulfate formation from the approach using the $[C]_0$ value listed in Table 5.2 are listed in Table 5.3.

Although the model of equation (5.21) can be linearized for convenient mathematical analysis, a complex reaction kinetics that can not be ascribed to pseudo first order reactions is projected by the exponential inverse time model.

5.2.3 Interpretation Of The Time Sequence Results

Analytically, the pyritic sulfur content for freshly ground coal was determined to be 1.762% (Table 4.2). If it is assumed that the intercepts for pyritic sulfur and sulfate sulfur in Table 5.1 are randomly distributed then

$$\bar{Y} = \frac{\sum Y_i}{n} = 16.195/9 = 1.799\% \text{ sulfur, and}$$

$$S_y = \sqrt{\frac{\sum (Y_i - \bar{Y})^2}{n-1}} = .113.$$

That is, the regressed value for the initial pyritic sulfur percent of 1.799 % .113% includes the analytically determined value of 1.762%. Similarly, for sulfate formation the regressed time-zero results are 1.248% % .057%, compared to an analytically determined value of 1.280%. The standard deviations are in the range of 6-8

Table 5.3

Empirical Formulae By Regression Analysis;
Increasing Sulfate Sulfur;
Alternative Model

$$Y = \exp(a - b/t)$$

$$y'' = \ln [\text{sulfate sulfur \%} - \text{initial sulfate sulfur \%}]$$

$$y'' = a - b/t$$

Sample No.	$y'' = (a - b/t)$	Asymptote	Correlation Coefficient
1.	$y'' = -.9809 - 18.05/t$	1.590%	-.967
2.	$y'' = -1.252 - 17.08/t$	1.486%	-.847
3.	$y'' = -.9452 - 18.13/t$	1.589%	-.929
4.	$y'' = -.7848 - 18.65/t$	1.656%	-.939
5.	$y'' = -.8637 - 18.15/t$	1.622%	-.927
6.	$y'' = -.6722 - 18.79/t$	1.711%	-.982
7.	$y'' = -.0728 - 20.59/t$	2.130%	-.921
8.	$y'' = -.0496 - 20.97/t$	2.251%	-.989
9.	$y'' = -.5880 - 22.55/t$	3.000%	-.977

percent of the reported value. The excellent agreement of the means and the moderate standard deviations are good indications that the analytical errors are mostly statistically random in nature, but no statement can be made with regard to the accuracy of the results.

It may be noticed from Table 5.1-A that the results for room temperature and 60c are not too dissimilar. To determine if the values at 60c are statistically dissimilar from the room temperature results -- that is, to investigate whether the change in temperature actually results in a statistically significant concomittant increase in reaction rate -- the data were fitted to a form of the t test. Since the reaction rate constant, k, is a small number and the differences in the values of k are also quite small, the data used for the statistical test were the data for the first-order time constant.

The Student's t distribution formula for testing the hypothesis that the difference between the means of two normally distributed populations having the same unknown variance is d, may be taken from Walpole and Myers (63) as

$$t = \frac{(\bar{X}_1 - \bar{X}_2) - d_0}{s_p \sqrt{(1/n_1) + (1/n_2)}} \quad (5-26)$$

In the above equation the degrees of freedom are defined as

$$v = n_1 + n_2 - 2 \quad (5-27)$$

and it is assumed that

$$\sigma_1 = \sigma_2 , \text{ but unknown.} \quad (5-28)$$

The hypotheses are:

the null hypothesis, H_0 $\mu_1 - \mu_2 = d_0$
the alternative hypothesis, H_1 $\mu_1 - \mu_2 \neq d_0$.

In this case the null hypothesis will assume that there is no difference in the means for room temperature and 60°C, or

$$\mu_1 - \mu_2 = 0.$$

When the data for the first-order time constants of Table 5.1-A are substituted into equation 5-26 it is found that

$$t = 2.198.$$

Comparing the value $t = 2.198$ to the critical region of the t distribution of Appendix D where the critical region is

$$t < -t_{\alpha/2} \text{ and } t > t_{\alpha/2} \quad (5.29)$$

for $v = 4$ it is found that $t = 2.198$ is not in the range of a .1 level of significance but is in the range of a .05 level of significance. That is, it is possible to reject the null hypothesis and state that there is a difference in the results with 90% certainty, but not with 95% certainty.

Using the t statistic equation for paired observations,

$$t = \frac{\bar{d} - d_0}{s_d \sqrt{n}}; \quad v = n-1 = 2 \quad (5.30)$$

and computing for

$$\mu_d = d_0$$

it is found that

$$\underline{t} = 3.2 \quad \text{and} \quad \underline{d}_0 = 32 \text{ days.}$$

Comparing to the critical values of the $\underline{t}$ distribution table it may be concluded with greater than 90% confidence that the average first order time constant at room temperature is 32 days longer than the average first-order time constant at 60c.

A comparison of the data of Tables 5.1 and 5.2 with the results illustrated by Figure 5.2 shows that in the neighborhood of ambient temperatures, reaction rates are little affected by the addition of sorbent, and at temperatures near ambient, random variations in the analytical procedure probably account for all the observed differences in the reaction rate results for pyritic sulfur conversion and for a part of the differences in the results for sulfate formation.

The only unambiguous results are for 100c, in which case there was a modest improvement in sulfate formation when using calcined limestone, and a more dramatic increase in the rate of pyritic sulfur dissipation for all cases. At 100c for pyritic sulfur conversion the rate was approximately double for limestone and 2.7 times for calcined limestone compared to the rate of conversion for plain coal.

It may be concluded that at near ambient temperatures the addition of calcium sorbent has little

effect on the sulfur conversion reactions; this applies to the dissipation of pyritic sulfur and to the formation of sulfate salts. From the results listed in Table 5.1, the first order time constant is 357 days at room temperature, which is much slower than the results from the Wilcox study.

In order to compare the asymptotic conversion of iron pyrite from the present study and the Wilcox study it is necessary to convert the data for pyrite conversion to percent sulfur reacted. Assuming the first-order model

$$Y^* = P - P \exp(-kt) \quad \text{or} \quad (5.31)$$

$$Y^* = P[1 - \exp(-kt)] \quad (5.32)$$

where:

Y^* = percent pyrite sulfur remaining

t = sample age, days

P = percent pyrite sulfur reacted

k = rate coefficient, inverse days.

The value of Y^* is merely

$$Y^* = \frac{Y_0 - Y_i}{Y_0} \times 100\% \quad (5.33)$$

where

Y_0 = initial concentration pyritic sulfur, and

Y_i = instantaneous concentration of pyritic

sulfur. Experimental values for Y^* may be calculated from the data available in Appendix C.

Equation (5.32) must be linearized in order to perform the regression analysis. By the rearrangement of equation (5.32)

$$1 - \frac{Y^*}{P} = \exp(-kt). \quad (5.34)$$

The above result may be linearized by logarithms:

$$Z = \ln(1 - Y^*/P) = -kt. \quad (5.35)$$

If a value of P is assumed, equation (5.35) may be regressed linearly by Z vs t. In order to determine the most appropriate percent conversion the following algorithm was used:

- (1) assume $0 \leq P \leq 100\%$,
- (2) regress Z vs t,
- (3) determine the correlation coefficient, r,
- (4) retain the value of P which gives the correlation coefficient nearest to 1.00.

This algorithm is well suited to computer application, and a short program was written to determine the best value of P. Since the left hand side of equation (5.31) is merely a manipulation of the left hand side of equation (5.7), with the percent conversion of A substituted for [A], the regression of equation (5.31) yields correlation coefficients and values for the slopes which were each identical to the values listed in Table 5.1. The results for this procedure yielded an asymptotic value for percent conversion of approximately 66% for sample No. one. The complete listing of the asymptotic values for pyrite conversion follows in Table 5.4.

5.2.4 Organic Sulfur

A two-tailed t-test on the sum of sulfate and pyritic sulfur (from Appendix D) yields a better than 95% probability

Table 5.4

Asymptotic Values Of Pyrite Sulfur Conversion

Sample No.	Asymptotic Percent Pyrite Sulfur Conversion
1.	66%
2.	59%
3.	63%
4.	59%
5.	55%
6.	50%
7.	82%
8.	85%
9.	100%

ity that for periods of 50 days or less the sum of pyrite sulfur plus sulfate sulfur is constant for all samples. However, there is an apparent decrease in the pyrite sulfur plus sulfate sulfur sum for the duration of the testing for all samples except sample No. 9, coal with calcined limestone aged at 100c. Referring to Appendix C it may be seen that sample No. 9 exhibits an increase in sulfate sulfur that is 165% of the decrease in pyrite sulfur. For the other samples the increase in sulfate sulfur and the decrease in pyritic sulfur are approximately equal, but from Appendix D a decrease in organic sulfur is evident from all samples. For the room temperature samples (Nos. 1,2,3) an average total decrease of about 13.5% is observed for the total testing period.

5.2.5 Closing Mass Balances

Accepting the first-order exponential model as accurately depicting both the pyrite sulfur dissipation and the sulfate sulfur increase for moderate time periods, the changes in percent sulfur have been computed for 50 days based on the regression formulae of Tables 5.1 and 5.2, and these changes have been listed in Table 5.5. On the average, 102% of the change in pyritic sulfur appears to have been converted into sulfate sulfur.

The asymptotic reduction in pyritic sulfur and the asymptotic increase in sulfate sulfur may be conveniently

compared from Table 5.4 and Table 5.3. These figures have been regrouped in Table 5.5, and the results for asymptotic time may be seen to be somewhat inconsistent with the short-term results.

From Table 5.5 it may be seen that for short time intervals the sulfate sulfur increases more rapidly than the pyritic sulfur decreases, but over long time intervals the sulfate sulfur increase is less than the pyritic sulfur increase. This result is also visible when the first-order time constants listed in Table 5.1 and 5.2 are compared. With some irregularities - most likely attributable to experimental error - the first-order time constants for pyritic sulfur decrease are longer than for sulfate sulfur increase. In fact, the average first-order time constant for pyritic sulfur decrease is 194 days longer than the average first-order time constant for sulfate increase.

It is clear that organic sulfur is converting for the calcined limestone sorbent (sample No. 9) at 100°C. From the mass balance data it appears that organic sulfur is reacting, but it is not necessarily being converted to stable sulfates.

5.2.6 Sulfur Dioxide

In addition to an apparent mass imbalance, on several occasions when a sample container was opened in the

Table 5.5

Percent Decrease in Pyrite Sulfur and
Percent Increase In Sulfate Sulfur

Sample No.	Percent Decrease In Pyrite Sulfur	Percent Increase In Sulfate Sulfur	% Change Based On Pyrite
50 days			
1	15.8	22.3	141.1
2	14.4	24.2	168.1
3	24.6	26.4	107.3
4	14.5	27.7	191.0
5	19.3	27.3	141.4
6	17.2	36.3	211.0
7	26.8	56.6	211.2
8	31.6	67.3	213.0
9	41.6	144.3	346.9
Asymptotic Time			
1	66	27.5	42
2	59	19.2	33
3	63	27.4	44
4	59	32.8	56
5	55	30.1	55
6	50	37.2	75
7	82	70.8	86
8	85	80.5	95
9	100	140.6	141

laboratory an apparent odor of sulfur dioxide was noticeable. Since some plausible reaction mechanisms postulate an intermediate conversion to sulfur dioxide, the above observations made it desirable to investigate whether SO_2 would be formed in measurable quantities in a sealed reacting system.

A jar which had been closed and sitting for several months with about one pound of fine coal was on hand. A 2.50 ml sample of the air above the coal was drawn into a syringe and injected into a gas chromatograph, and the presence of SO_2 was clearly indicated.

As described in the "Procedures" section, 200 gram quantities of samples 1 through 6 were freshly prepared, and at the end of 50 days 2.50 ml of air from each sample was analyzed by gas chromatography. As may be seen from Figures 4.7-A and 4.7-B traces of SO_2 were detectable from samples 1, 4, and 5, but there were no indications of SO_2 in samples 2, 3, and 6. The results of this experiment could be considered indicative, but not determinate, of support for the sulfur dioxide hypothesis. This support is weak due to the evidence for organic sulfur conversion. The mechanisms of organic sulfur conversions are not considered in this study.

5.3 The Arrhenius Activation Energy: Theory And Determination

An examination of the rate expression of equation

(5.2)

$$\frac{d[A]}{dt} = -k[A][B]$$

reveals no obvious temperature dependency. The traditional temperature varying term is considered to be the rate constant, k , which is postulated for an elementary reaction as

$$k = CT^n \exp(-U/RT) \quad (5.36)$$

where:

C is a term very weakly dependent on temperature,
 U has dimensions of energy, and
 n usually is 0, 1/2, or 1, depending on the form
of the theoretical model chosen.

A plot of kt^{-n} vs T^{-1} will be linear with a slope of $-U/R$ when (5.36) is cast in the logarithmic form:

$$\ln(k/T^n) = \ln C - (U/R)T^{-1}. \quad (5.37)$$

The most common form of (5.36) is the Arrhenius form, where $n = 0$ and " C " is replaced by " A ",

$$k = A \exp(-E/RT), \quad (5.38)$$

where E is the activation energy of the reaction. The activation energy, E , is the energy which must be absorbed by the reactants before any reaction may be initiated. If the reaction of interest is carried out at specific temperatures, then all terms of (5.38) are constant except E . The logarithm of both sides of (5.38) yields

$$\ln k = \ln A - (E/RT), \quad (5.39)$$

and by the same simple variable transform as before, with A

assumed nearly constant, equation (5.39) is quickly recognized as the form of a straight line in which the slope relates directly to E, the Arrhenius activation energy.

"A" is termed a "pre-exponential factor," which reduces to a so-called "frequency factor," with units of time^{-1} for unimolecular reactions. The pseudo first-order case is apparently unimolecular, consequently $A = \text{time}^{-1}$.

From Table 5.1 the values of k for each temperature have been ascertained according to statistical techniques. For each reacting system (coal, coal + limestone, coal + calcined limestone) the value of k may be regressed against the inverse temperature to produce a value for E. Using the three datum points available for each reacting system and the same linear least squares correlation program as before the values of Table 5.6 have been obtained, and the results tabulated in Table 5.6 have been plotted in Figure 5.5. Note from equation (5.38) that the units of E are dependent on the units of the universal gas law constant. The values of Table 5.6 are based on SI units:

$$R = 8.314 \times 10^3 \text{ Joules/Kg.MOl.K.}$$

5.4 X-Ray Diffraction Analyses

5.4.1 Freshly Ground Coal

Recall from section 4.6 that the strip-chart record produced by the Rigaku x-ray diffractor indicates the double angle. The x-ray diffraction chart of a sample of

Table 5.6
The Arrhenius Activation Energy

Analyte	Slope of ln k vs 1/k	Arrhenius Activation Energy	Correlation Coefficient
Coal	- 733.1	6.095×10^6	-.854
Coal plus limestone	-1621.5	1.348×10^7	-.874
Coal plus	- 2033.6	1.691×10^7	-.864

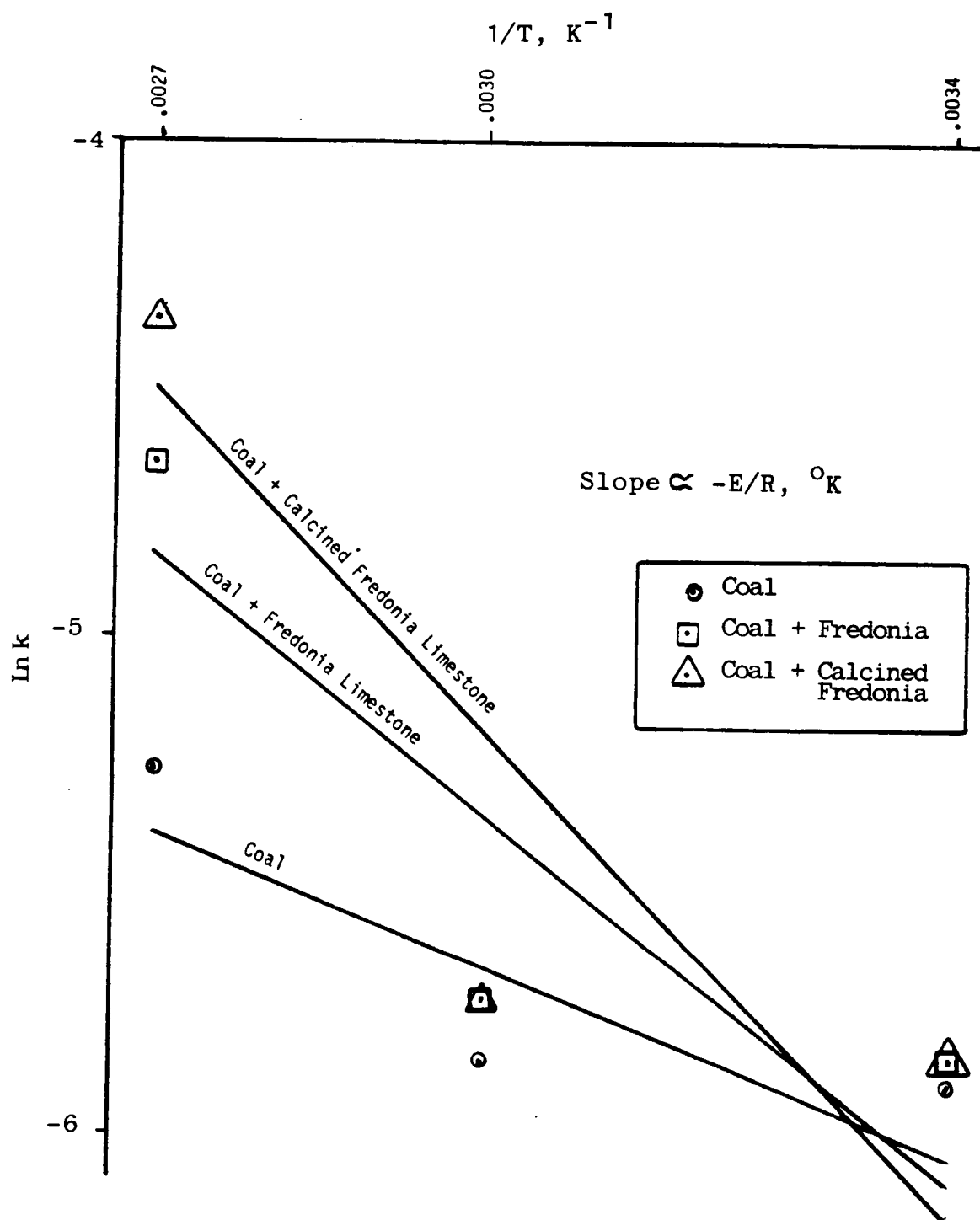


Figure 5.5

The Dependency of the Arrhenious Activation Energy on Composition

iron pyrite follows as Figure 5.6. It may be noted from the chart that there are peaks at 33.4, 37.5, 41.2, and 56.7 degrees of scan. From the information in Appendix G, we find angles of 33.07, 37.11, 40.80, and 56.34 degrees of scan, which correlate well with the quality control sample. Note that the quality control sample has a slight shift of 0.4 degrees to the left.

Also note from the information in Appendix G that the peak height response is predictable. For instance, the double angle of 56.34 degrees is the reference double angle for iron pyrite. At this angle the maximum response to incident x-ray beams is indicated and is considered to be the 100% peak height line. At the double angle of 37.11 degrees the peak height is predictably 66% of the value for 56.34°. As is usual for analytical responses the peak height is proportional to the percentages of analyte present in the sample.

It should be possible to observe the peak heights of pyrite in a coal sample that is heavy in iron pyrite. From section 5.2 it is possible to determine that the percentage of iron pyrite in the coal is 3.37 %. From Figure 5.7, the x-ray diffraction scan of freshly ground coal, the pyrite peaks at 56.4° (100%) and at 33.4° (84%) are quite visible compared to the background noise of the scan. The peaks at 37.5° (66%), 41.2°, and the peak at 37.5° are less clearly differentiable from the background.

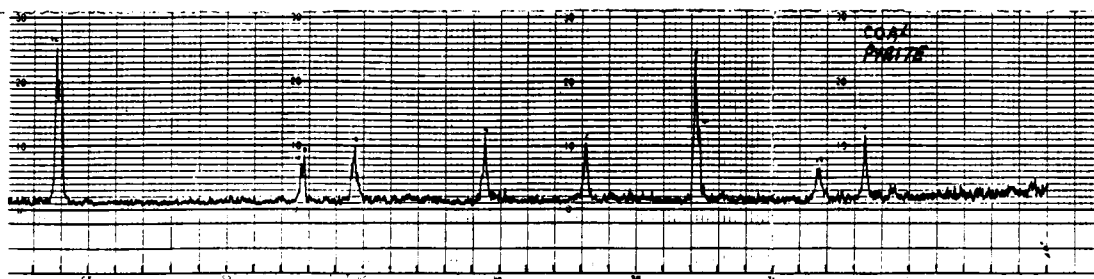


Figure 5.6
X-Ray Diffraction Scan Of
Coal Pyrite*

*Courtesy of G.F. Frazier

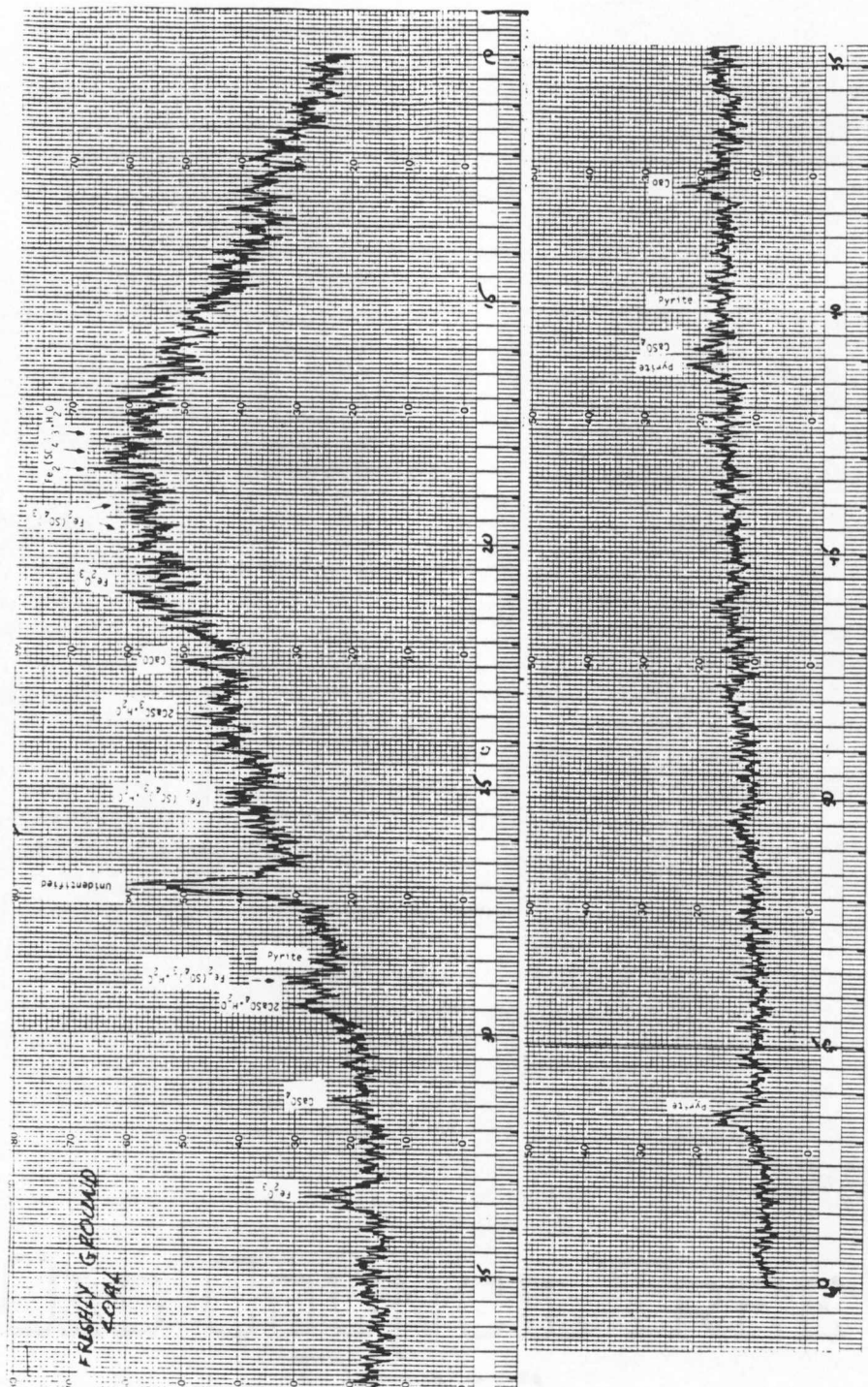


Figure 5.7
X-Ray Diffraction Scan of Freshly Ground Coal

There are no peaks identifiable corresponding to Marcasite, which is a chemical homolog of pyrite.

There is a large diffraction peak in the coal sample at 27° and numerous small peaks which rise somewhat above the freshly ground coal x-ray diffraction scan background. These peaks remain unidentified and are not necessarily peaks due to inorganic minerals. The only inorganic mineral unequivocally detectable in a freshly ground sample of the coal used in this study is iron pyrite. There are weak peaks for the minerals commonly found in coal including the following:

calcite	(calcium carbonate);
gypsum	(calcium sulfate dihydrate);
iron (III) oxide	(hematite).

There may be weak indications for iron (III) sulfide (troilite), and other minerals, but the resolution of all the peaks for the mineral compounds from the background is questionable.

5.4.2 Aged Coal Samples

The major diffraction peak that occurs for freshly ground coal at 27° appears on the chart for aged coal at 26.5° . As may be seen from Figures 5.8 and 5.9 the peak height varies but the shape and the surrounding background clearly differentiate this peak.

The x-ray charts for the aged coal samples show a diminution of the major pyrite peak at 56.2° , and peaks at

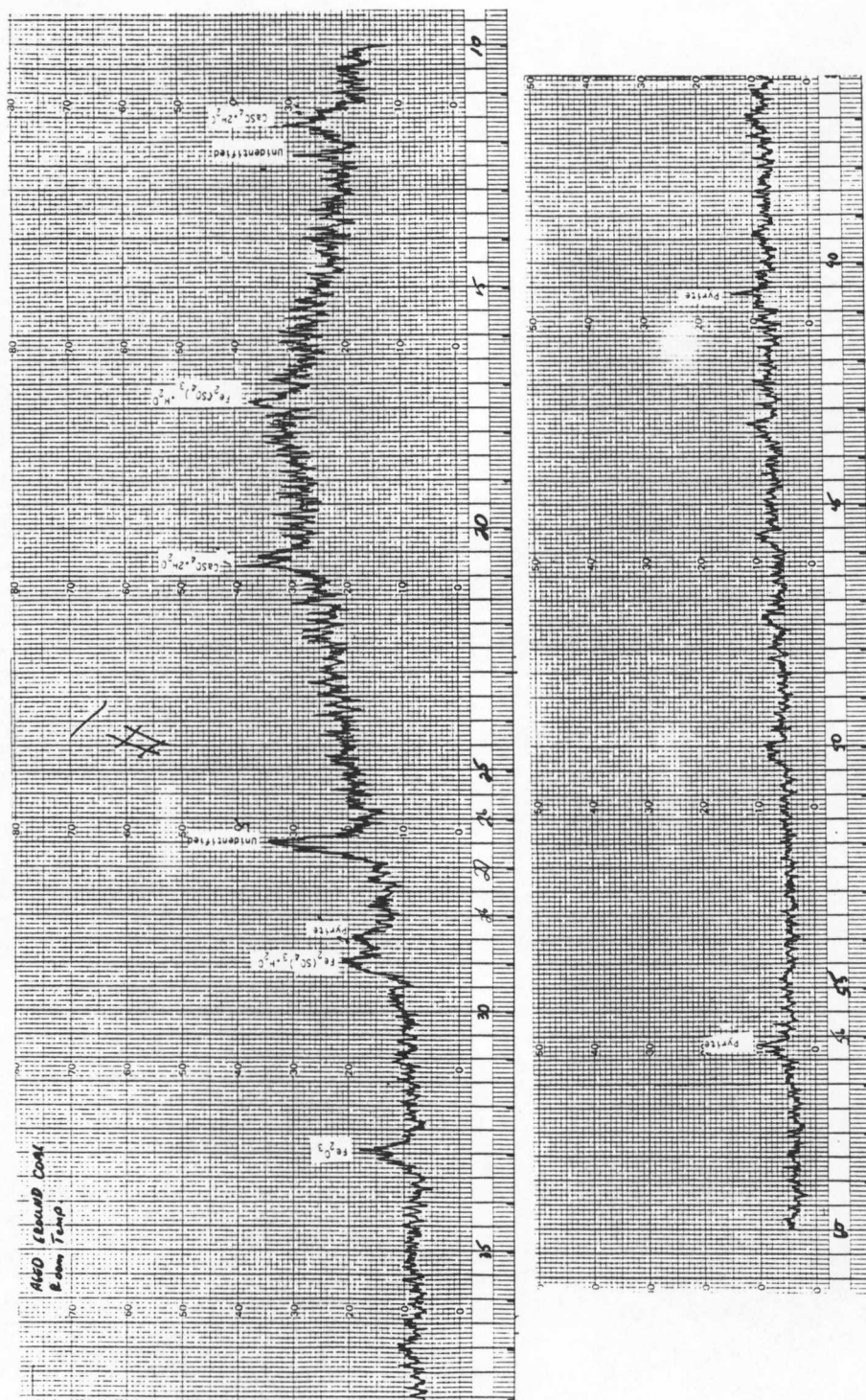


Figure 5.8
X-Ray Diffraction Scan of Coal Aged at Room Temperature

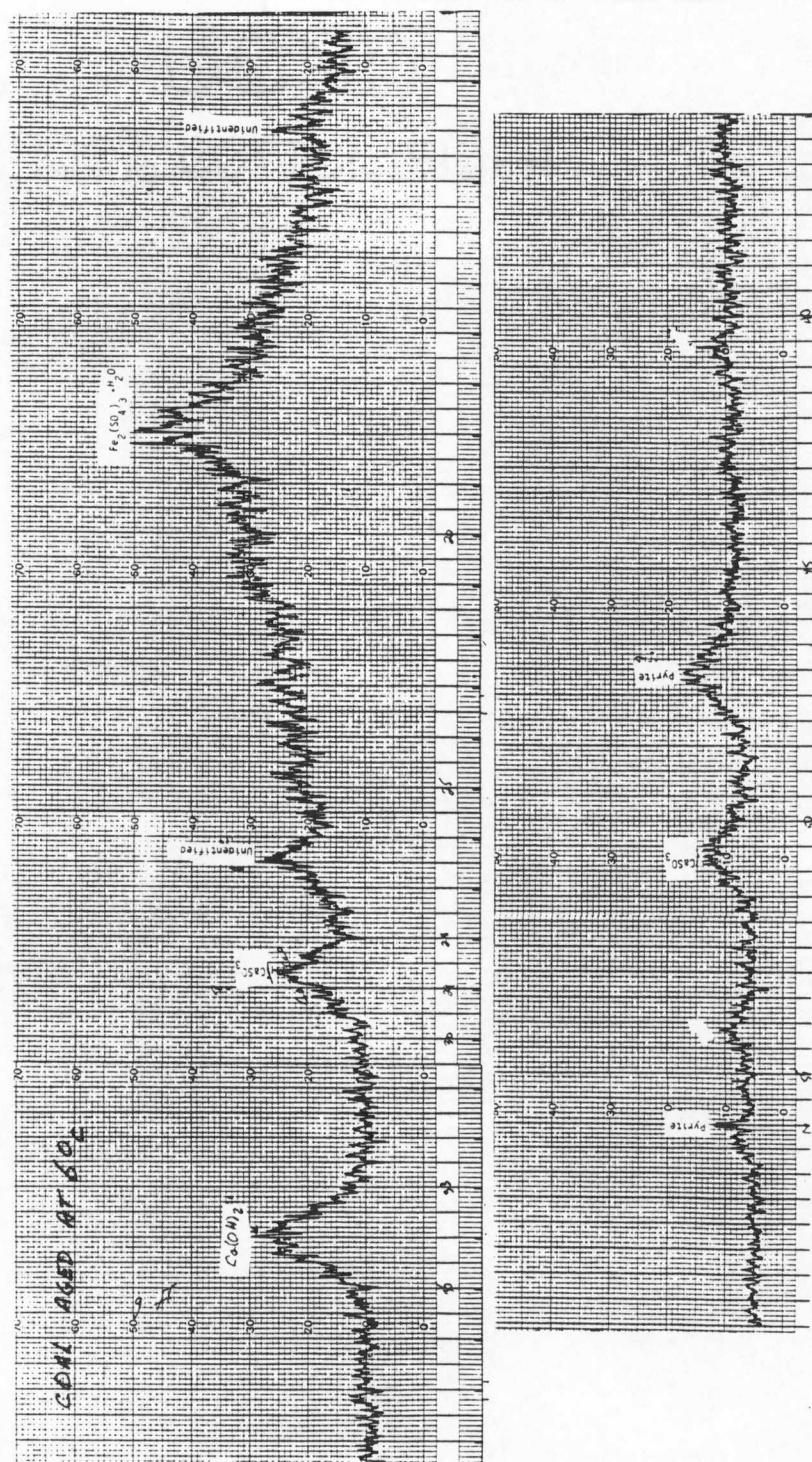


Figure 5.9
X-Ray Diffraction Scan of Coal Aged at 60°C Temperature

11.7°, 17.5°, 29°, and 33° appear. These peaks correlate well with the published data for gypsum and various iron sulfates, and perhaps portlandite (Ca(OH)_2), as listed in the atlas of powder diffraction constants contained in Appendix G. There are also possibilities for Fe_2O_3 correlated from a sample of coal plus hematite. The coal plus hematite spectrograph is contained in Appendix H.

The spectrographs for the aged coal samples show about the same pyrite reduction, but the mineral peaks and the overall shape of the curves vary both in magnitude and for specific peaks. Therefore, although the aging effect on the pyrite is about the same, the chemical reactions are apparently not the same at room temperature and at 60c.

5.4.3 Coal Plus Sorbents Aged At 60c

The large unidentified peak appears on these scans at 26.5°. However, in contrast to the pure coal sample charts which indicated the presence of peaks for several minerals, particularly various iron compounds, the coal plus sorbent sample charts show primarily peaks for gypsum (calcium sulfate dihydrate). Although the initial peak at 11.4° for $\text{Fe}_2(\text{SO}_4)_3$ is difficult to distinguish from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, there are several other peaks on both the scan for coal plus Fredonia limestone and coal plus calcined Fredonia limestone that correlate well with the scan for

iron (III) sulfate, and with the published data for gypsum. The scans of the coal plus sorbents aged at 60°C follow as Figures 5.10 and 5.11, and an x-ray diffraction chart for $\text{Fe}_2(\text{SO}_4)_3$ is included in Appendix H.

Note that the peaks corresponding to the peaks of the limestone and calcined limestone are considerably reduced, but the major pyrite peak at 56.4° is only slightly reduced. The x-ray scans for uncalcined and calcined Fredonia limestone are also contained in Appendix H.

5.4.4 Detectability Limits Of Minerals In Coal

Extensive tests were not conducted. However, several tests were conducted using coal and laboratory grade chemicals. For the addition of Fe_2O_3 , FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$, 2% addition to the freshly ground coal was clearly visible, and by 10% addition of the mineral the coal peaks were overwhelmed by the peaks of the mineral addition. Included in Appendix H are the charts for coal plus 2%, 5%, and 10% ferric oxide. There is also a noticeable shift toward the right for increasing concentration. Experiments for pyrite addition and sorbent addition were less dramatic in result. About 2% additional pyrite was necessary to produce a consistently noticeable major peak, and about 3% addition of sorbent is necessary to clearly define either the limestone or the calcined limestone from the background. It may be concluded that even though it

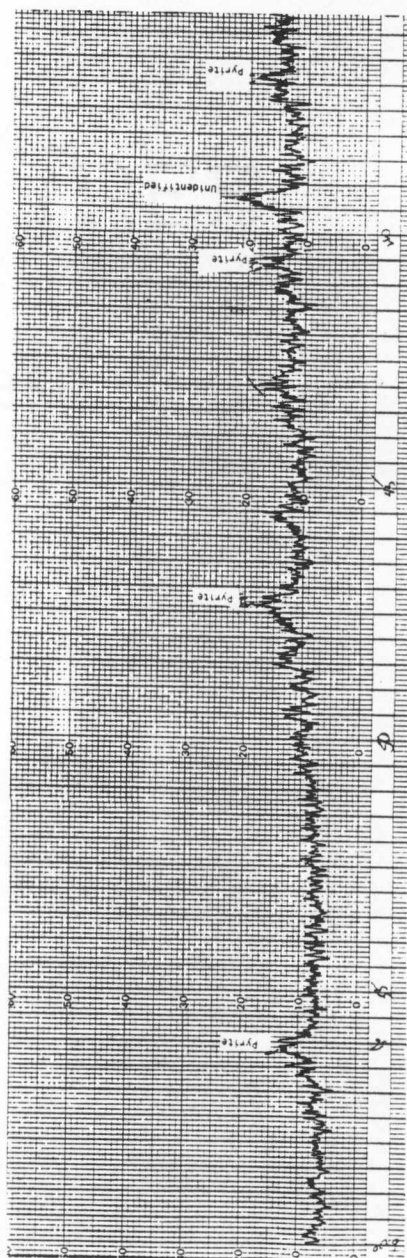
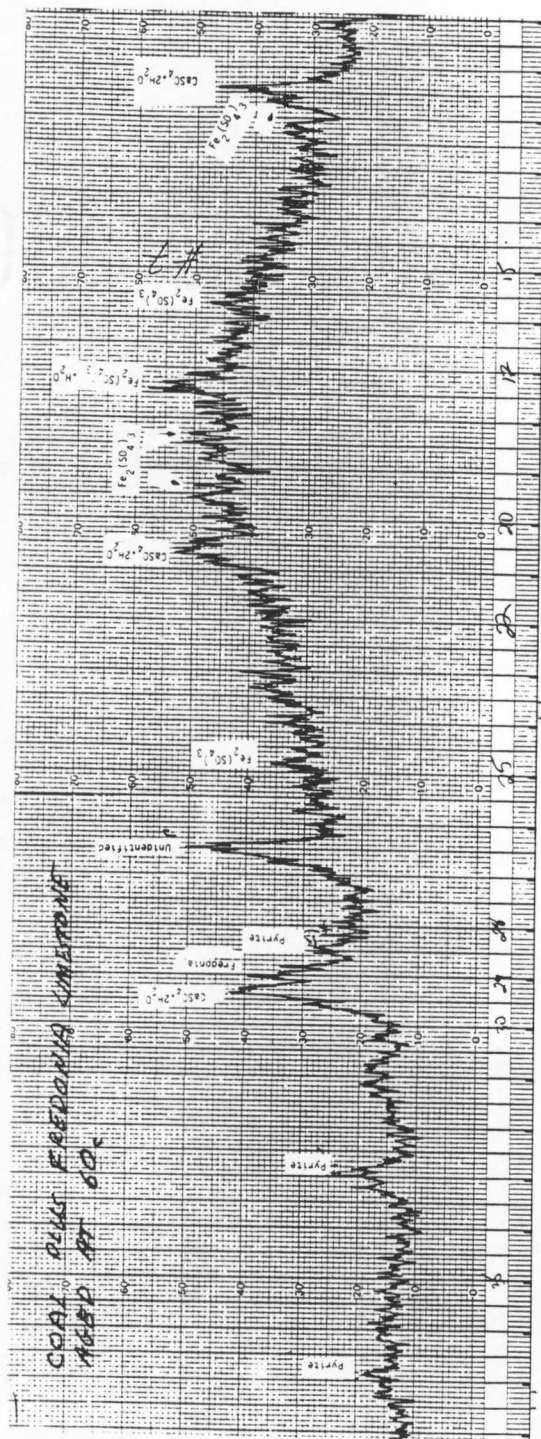


Figure 5.10

X-Ray Diffraction Scan of Coal Aged With Fredonia Limestone at 60 Degrees

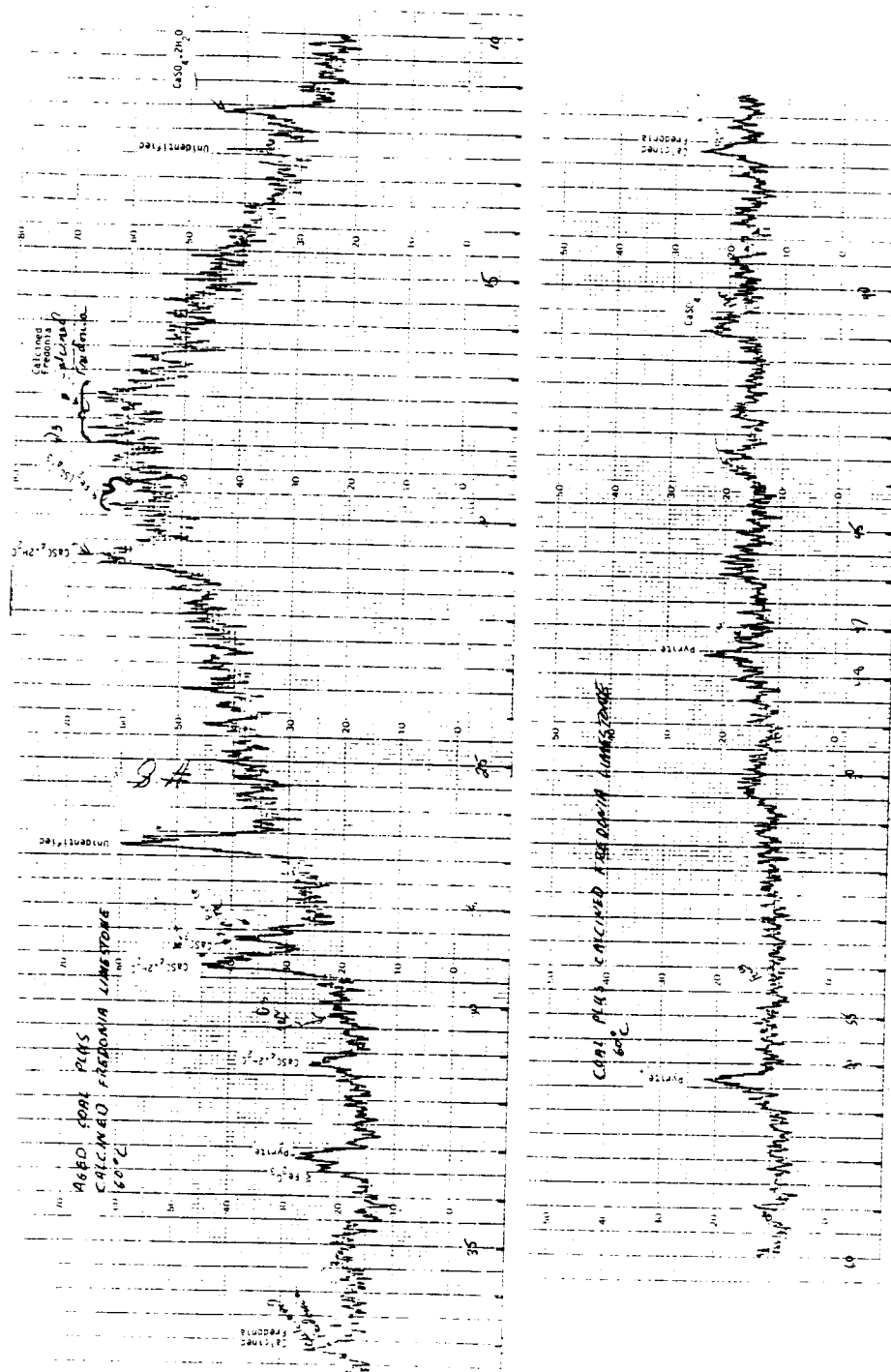


Figure 5.11
X-Ray Diffraction Scan of Coal Aged with Calcined
Fredonia Limestone at 60 Degrees

has been reported that about 5% mineral inclusion is near the lower detectability limit, a value of 2% for the transition metal minerals and a value of 3% for calcium minerals for the Rigaku machine seem more realistic. The detectability limits mentioned above were the approximate upper limits of mineral inclusion and addition for this study, and no quantitative measurements were performed.

6.0 CONCLUDING DISCUSSIONS

Using fine coal at temperatures near ambient, the addition of calcium based sorbents has little effect, if any, on the rate of iron pyrite sulfur conversion. At a temperature somewhat above ambient, the effect of sorbent addition is noticeable, but slight. At 100°C the effect of sorbent addition is much accelerated, i.e., uncalcined sorbent vs. calcined sorbent becomes important at 100°C.

For the particular high-sulfur coal used in this experiment, the formation of sulfate salts has been demonstrated to occur more rapidly than the pyrite sulfur reduction. The average first-order time constant for pyrite sulfur reduction was 265 days, and the average first-order time constant for sulfate formation was 139 days, or half the average first-order time constant for pyrite sulfur reduction. The results listed in Table 5.4 clearly indicate that long-term, the fate of the pyrite sulfur is mostly not sulfate. The results of this project indicate that the formation of sulfate salts is largely independent of pyrite sulfur conversion.

The fact that the rate of formation of sulfate with time is very different from the rate of pyrite sulfur conversion, and the observation that the sulfate forms mainly in the early times of the reaction, may indicate that the sulfate formation is a chemical reaction that de-

- (1) the sensitivity of the gas chromatograph used was too low to obtain reliable quantitative results, and
- (2) the length of the experiment was confined to the period when most of the sulfate formation was occurring.

A modern instrument with a more sensitive detector and a longer experiment at more varied conditions could conceivably produce data to elucidate the origin and interactions of the SO_2 .

The x-ray spectrographs very graphically depict overall changes in the coal samples with time; however, no strong and easily identifiable peaks are visible on the charts except iron pyrite and gypsum. When no sorbent was present, the reaction products are apparently several iron compounds, including various hydrated iron sulfates. The major reaction product when a sorbent was present was calcium sulfate dihydrate (gypsum), although when the sorbent was uncalcined Fredonia limestone there were a variety of iron compounds as well as gypsum evident in the x-ray spectrograph. There are weak indications for the formation of several sulfates and oxides, perhaps indicating that there are at least several series and/or parallel reactions occurring. Since it is easy to assume that some of the supposed reactions are more sensitive to temperature than others, the existence of parallel reactions may account for the rather low correlation coefficient of the

Arrhenius activation energy regression analysis, and generally supports the hypothesis that a shift in the dominant kinetics occurs in the vicinity of 100c.

It is evident from the x-ray spectrographs that the sorbents are reacting in ways that are independent from the conversion of iron pyrite. The level of sorbent addition was 9% -- a level well within the detectability limits of the Riagaku x-ray diffractor -- but the expected peaks for CaCO_3 and CaO due to the addition of limestone and calcined limestone are very weak. Particularly in the case of the calcined sorbent, it is believed that solvation reactions occur due to the natural moisture available in the freshly ground coal. The slower and long-term sulfate production may be due to interactions with SO_2 or interactions with the reaction products of pyrite.

The limit of quantitative sensitivity for the Rigaku x-ray diffraction instrument was about 2% for the analytes of interest, but the maximum concentrations of all the analytes of interest except iron pyrite were below this level. Consequently, only trace level measurements were possible. It is probable that an experiment designed around this instrument using standard additions or chemical and/or physical concentration methods could produce more revealing results.

Generally, coal users who must maintain a significant inventory of coal find it most convenient to store the

coal in top-sizes greater than 100-200 mesh. However, where fine coal is used in the formulation of a product such as a coal pellet, the comminution of the coal to a fine size could easily allow the conversion of significant quantities of volatile coal sulfur compounds into nonvolatile sulfur compounds before the product is used. If the average time before the product is used may be measured in months, then a somewhat higher sulfur coal could be utilized. Where the product is to be stored at ambient conditions there is little reason to add a calcium sorbent, but if a sorbent is desirable for purposes of flue gas desulfurization calcined limestone is the apparent choice because the calcium sulfate which forms is more heat stable than the various iron sulfates which form under the other conditions.

7.0 SUMMARY

The coal sulfur reactions at ambient temperature, at 60c, and at 100c were investigated in a high sulfur Western Kentucky coal which was ground to a fine mesh size such that 80% of the ground coal would pass through a 100 mesh sieve. The initial total sulfur content of the coal was 5.05%, the initial pyrite sulfur content was 1.796%, and the initial sulfate sulfur % was 1.247%.

The analytical samples were prepared by dividing the ground coal into three portions: portion number one was maintained as ground coal, to portion number two was added 9% by weight freshly ground Fredonia limestone, and to portion number three was added 8.5% by weight freshly ground and freshly calcined Fredonia limestone. Each portion was divided into three equal parts (approximately 200 grams each) and stored at room temperature, at 60c, and at 100c. Every few days over a period of five months samples were withdrawn from each of the prepared coal portions and analyzed for pyrite sulfur, sulfate sulfur, total sulfur, and by difference, organic sulfur. The analytical methodologies were standard ASTM methodologies.

The rate of pyrite sulfur conversion was interpreted in terms of a pseudo first-order rate expression:

$$\text{rate} = \frac{d[\text{pyrite sulfur}]}{dt} = -k[\text{pyrite sulfur}]$$

where: rate = rate of pyrite sulfur conversion from the

coal, % basis, and

k = first-order rate coefficient, inverse days
[pyrite sulfur] = % pyrite sulfur at time t .

In a multicomponent reacting system, the rate is proportional to the concentration of each reacting species; however, if all reactants but one are held constant with time the rate form may be assumed to approach first-order behavior. During the course of the experiment, each sample was opened and stirred at least twice weekly to provide a nearly constant supply of atmospheric oxygen, and the concentration of sorbent in those samples to which sorbent had been added was assumed to be always much higher than the concentration of reacting pyrite.

The pseudo first-order rate equation was integrated to the linear form

$$\ln[\text{FeS}_2] = \ln[\text{FeS}_2]_0 - kt,$$

and the analytical data was fit to this form by linear regression to establish a value for the pseudo first-order rate constant, k . The first order time constant, or the time for the reaction to approach 63.3% completion, is the inverse of the rate constant,

$$\text{time constant, days} = 1/k.$$

By hypothesizing that the reacting pyrite sulfur conversion was directly into sulfate a linear expression for sulfate formation of the form

$$\ln \left(1 - \frac{[\text{sulfate sulfur}]}{[\text{initial pyrite sulfur}]} \right) = -kt.$$

The analytical data for sulfate sulfur formation were fit to this form by linear regression to establish the first-order rate constant for sulfate formation. The results for each analytical sample are listed in Tables 7.1 and 7.2.

The air space above the experimental samples at room temperature and at 60°C were examined for the presence of sulfur dioxide by gas chromatography, and for the coal (only) samples, the presence of sulfur dioxide was confirmed. Sulfur dioxide was not found to be present in the samples to which a sorbent had been added.

There was sufficient information available from the analytical data to determine the Arrhenius Activation Energy, E , for each reacting system, coal, coal plus limestone, and coal plus calcined limestone. The Arrhenius formula,

$$k = A \exp(-E/RT),$$

can be linearized to the form

$$\ln k = \ln A - (E/RT),$$

where A is a term that is nearly constant (weakly dependent on temperature), and k has been determined for each set of conditions. For explicitly known temperatures and ignoring the small variance of A , the data may be examined by linear regression to determine E . The determined Arrhenius Activation Energies for each reacting system are listed in Table 7.3.

Table 7.1

Analytical Results For Pyrite Sulfur Reduction

Sample I.D.	time constant pyriteconversion	asymptotic pyriteconversion	correlation coefficient
Room Temperature			
coal	357 days	66%	-.987
coal + Fredonia limestone	345 days	59%	-.978
coal + calcined Fredonia limestone	345 days	63%	-.974
Aged at 60c			
coal	345 days	59%	-.973
coal + Fredonia limestone	303 days	55%	-.921
coal + calcined Fredonia limestone	303 days	50%	-.951
Aged at 100c			
coal	208 days	82%	-.984
coal + Fredonia limestone	105 days	85%	-.944
coal	76 days	100%	-.991

Table 7.2

Analytical Results For Sulfate Sulfur Formation

Sample I.D.	time constant pyrite conversion	asymptotic pyrite conversion	correlation coefficient
Room Temperature			
coal	150 days	28%	.922
coal + Fredonia limestone	141 days	19%	.954
coal + calcined Fredonia limestone	99 days	27%	.920
Aged at 60c			
coal	113 days	33%	.866
coal + Fredonia limestone	141 days	30%	.909
coal + calcined Fredonia limestone	60 days	37%	.989
Aged at 100c			
coal	349 days	71%	.858
coal + Fredonia limestone	146 days	81%	.964
coal	48 days	141%	.968

Table 7.3

Arrhenius Activation Energy		
System	Arrhenius Activation Energy joules/Kg.mol	Correlation Coefficient
Coal	6.095×10^6	-.854
Coal plus limestone	1.348×10^7	-.874
Coal plus calcined limestone	1.691×10^7	-.864

Freshly ground coal, coal aged at room temperature, coal aged at 60c, coal plus limestone aged at 60c, and coal plus calcined limestone aged at 60c, were examined by x-ray powder diffraction methods to determine the presence of solid reaction products. The major reaction products for coal (with no sorbent added) are various iron sulfates, but there was no strongly identifiable peak on the x-ray spectrographs. For coal with limestone added, there is a mixture of iron sulfates and gypsum, and for coal with calcined limestone added the major reaction product is clearly gypsum.

However, the x-ray spectrographs do not show a strong relationship between the reduction of pyrite content and the formation of calcium sulfate (gypsum).

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APPENDIXES

APPENDIX A

Selected Thermodynamic Data *

<u>Compound</u>	<u>ΔG_f°, 298</u> <u>Kcal/mole</u>	<u>ΔH_f°, 298</u> <u>Kcal/mole</u>
CaCO_3 (s)	-269.70	-288.50
CaO (s)	-144.25	-151.8
$\text{CaO} \cdot \text{Fe}_2\text{O}_3$ (s)	-337.67	-363.37
$2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ (s)	-478.44	-511.30
$\text{Ca}(\text{OH})_2$ (s)	-214.75	-235.70
CaS (s)	-112.30	-113.50
CaSO_4 (s)	-313.00	-341.00
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (s)	-371.70	-418.90
CO (g)	-32.81	-26.42
CO_2 (g)	-94.26	-94.05
FeCO_3 (s)	-159.35	-177.00
FeO (s)	-60.10	-65.00
Fe_2O_3 (s)	-177.40	-197.00
Fe_3O_4 (s)	-242.70	-267.30
$\text{Fe}(\text{OH})_3$ (s)	-166.50	-196.70
FeS (s)	-24.00	-23.90
FeS_2 (s)	-39.90	-42.60
Fe_7S_8 (s)	-178.90	-176.00
FeSO_4 (s)	-197.20	-221.90
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (s)	-599.97	-720.50
$\text{Fe}_2(\text{SO}_4)_3$ (s)	-540.90	-617.00
SO_2 (g)	-71.75	-70.95

*Source: "Lange's Handbook of Chemistry," 15th ed., J.A. Dean, editor, McGraw-Hill, New York (1985).

APPENDIX B

Fredonia Limestone Analysis*

Calcium carbonate (CaCO_3)	93.29%
Magnesium carbonate (MgCO_3)	1.76%
Silica (SiO_2)	3.45%
Sulfur (as SO_3)	409 ppm
Aluminum (Al)	0.35%
Iron (Fe)	0.22%
Moisture (H_2O)	0.14%
Potassium (K)	0.11%
Sodium (Na)	0.03%
Chlorine (Cl)	136 ppm

* This analysis was originally performed for B.C. Wilcox, March 8, 1980, by the Oak Ridge National Laboratory.

APPENDIX C

Laboratory Results Of ASTM Analyses
For Pyritic And Sulfate Sulfur

Days of Aging	% Sulfate	% Sulfate Sulfur	% Pyritic Iron	% Pyritic Sulfur	% Sulfate S + % Pyrite S
Sample No. 1					
0	3.920	1.280	1.535	1.762	3.042
3	3.647	1.191	1.488	1.708	2.899
16	2.273	1.254	1.474	1.692	2.948
31	3.958	1.438	1.403	1.611	3.049
39	4.232	1.410	1.333	1.530	2.940
44	4.390	1.463	1.321	1.517	2.980
58	4.454	1.484	1.296	1.488	2.968
73	4.041	1.515	1.228	1.410	2.925
83	4.475	1.491	1.245	1.429	2.920
108	4.065	1.524	1.087	1.248	2.772
132	4.697	1.565	1.055	1.211	2.776

coal, sorbent = plain coal, no sorbent
temperature = room temperature

Sample No. 2					
0	3.920	1.280	1.535	1.762	3.042
3	3.647	1.191	1.488	1.708	2.899
36	4.119	1.345	1.477	1.696	3.041
46	3.951	1.290	1.353	1.553	2.843
72	4.340	1.417	1.240	1.424	2.841
83	4.312	1.408	1.228	1.410	2.818
113	4.747	1.550	1.106	1.270	2.820
140	4.869	1.590	1.045	1.200	2.790

coal, sorbent = uncalcined Fredonia limestone
temperature = room temperature

Sample No. 3					
0	3.920	1.280	1.535	1.762	3.042
3	3.647	1.191	1.488	1.708	2.899
22	3.941	1.287	1.469	1.687	2.974
36	4.052	1.323	1.484	1.704	3.027
46	4.658	1.540	1.382	1.587	3.127
72	4.759	1.554	1.253	1.439	2.993
82	4.597	1.501	1.238	1.422	2.923
108	5.059	1.652	1.102	1.265	2.917
132	4.955	1.618	1.092	1.254	2.872

coal, sorbent = calcined Fredonia limestone
temperature = room temperature

Sample No. 4

0	3.835	1.280	1.535	1.762	3.042
3	3.568	1.191	1.488	1.708	2.899
19	3.790	1.265	1.524	1.750	3.015
39	4.461	1.489	1.420	1.630	3.119
44	4.824	1.610	1.305	1.498	3.108
89	4.854	1.620	1.248	1.433	3.053
96	4.725	1.577	1.134	1.302	2.879
116	4.788	1.598	1.097	1.260	2.858
141	4.896	1.634	1.034	1.187	2.821

coal, sorbent = plain coal, no sorbent
temperature = 60c

Sample No. 5

0	3.920	1.280	1.535	1.762	3.042
3	3.647	1.191	1.488	1.708	2.899
19	4.040	1.346	1.420	1.630	2.976
31	4.424	1.474	1.420	1.630	3.104
36	4.235	1.411	1.402	1.610	3.021
46	4.493	1.497	1.439	1.652	3.149
72	4.582	1.527	1.225	1.407	2.934
83	4.616	1.538	1.232	1.415	2.953
108	4.538	1.512	1.187	1.363	2.875
116	4.619	1.539	1.258	1.444	2.983
133	4.889	1.629	1.193	1.370	2.999

coal, sorbent = uncalcined Fredonia limestone
temperature = 60c

Sample No. 6

0	3.920	1.280	1.535	1.762	3.042
3	3.647	1.191	1.488	1.708	2.899
31	4.229	1.409	1.396	1.603	3.012
43	4.451	1.483	1.418	1.628	3.111
46	4.457	1.485	1.333	1.530	3.015
72	4.883	1.627	1.098	1.261	2.888
83	4.751	1.583	1.141	1.310	2.893
113	5.132	1.710	1.019	1.170	2.880
140	5.225	1.744	1.000	1.148	2.892

coal, sorbent = calcined Fredonia limestone
temperature = 60c

Sample No. 7

0	3.920	1.280	1.535	1.762	3.042
3	3.647	1.191	1.488	1.708	2.899
22	4.268	1.442	1.289	1.480	2.922
46	6.036	2.011	1.097	1.260	3.271
83	5.707	1.903	1.002	1.151	3.054
113	5.924	1.974	0.887	1.021	2.995
133	6.017	2.005	0.740	0.850	2.855

coal, sorbent = plain coal, no sorbent
temperature = 100c

Sample No. 8

0	3.920	1.280	1.535	1.762	3.042
3	3.647	1.191	1.488	1.708	2.899
22	4.475	1.491	1.351	1.551	3.042
36	5.399	1.799	1.243	1.427	3.226
46	5.457	1.818	1.106	1.270	3.088
72	6.011	2.003	0.959	1.101	3.104
83	6.180	2.059	0.897	1.030	3.089
113	6.276	2.091	0.546	0.627	2.718
119	6.492	2.163	0.428	0.491	2.654
133	6.426	2.141	0.368	0.422	2.563

coal, sorbent = uncalcined Fredonia limestone
temperature = 100c

Sample No. 9

0	3.920	1.280	1.535	1.762	3.042
3	3.647	1.191	1.488	1.708	2.899
43	6.144	2.047	1.060	1.217	3.264
46	6.098	2.032	0.984	1.130	3.162
72	7.626	2.541	0.721	0.828	3.369
83	7.455	2.484	0.662	0.760	3.244
113	9.333	3.110	0.400	0.460	3.570
140	9.384	3.127	0.226	0.259	3.386

coal, sorbent = calcined Fredonia limestone
temperature = 100c

APPENDIX D

Percent Total Sulfur and Percent Organic Sulfur

Basis: Moisture Free Coal

[Organic sulfur = total sulfur - (pyrite S + sulfate S)]

<u>Days</u> <u>Of Aging</u>	<u>Sample Identity</u>									
	<u>total sulfur</u>		<u>organic sulfur</u>		<u>total sulfur</u>		<u>organic sulfur</u>		<u>total sulfur</u>	
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	
0	5.05 2.01	5.05 2.01	5.05 2.01	5.05 2.01	5.05 2.01	5.05 2.01	5.05 2.01	5.05 2.01	5.05 2.01	
3	5.11 2.21	5.11 2.21	5.11 2.21	5.11 2.21	5.11 2.21	5.11 2.21	5.11 2.21	5.11 2.21	5.11 2.21	
16	5.02 2.07			5.00 1.99			4.92 2.00			
30		5.01 1.97			4.96 1.86			4.90 1.77		
39	4.91 1.97	4.83 1.79								
46			4.84 1.71			4.61 1.60			4.53 1.37	
59				4.63 1.55			4.51 1.56			
73	4.53 1.61	4.46 1.62								
83	4.35 1.43		4.29 1.37							
108	4.37 1.50									

APPENDIX E

Analytical Calculations

Sulfate Sulfur

$$\text{sulfate sulfur, \%} = [(A-B) \times 13.735]/W$$

where:

A = grams BaSO_4 precipitated

B = grams BaSO_4 in the blank

W = weight of sample used

13.735 = a stoichiometric factor

Pyritic Sulfur

$$\text{pyritic sulfur, \%} = \frac{C - A}{B - A} \times \frac{4.59}{W}$$

where:

A = absorbance of the blank

B = absorbance of standard

C = absorbance of sample

W = weight of sample used

4.59 = a stoichiometric factor

from concentrations - for instruments so equipped

$$\text{pyritic sulfur, \%} = \frac{D \times V \times 0.0001148}{W}$$

where:

D = concentration of iron in standard,
ppm

V = volume of analytical solution

W = weight of sample represented by
this solution

0.0001148 = a stoichiometric factor

For example, if a 2.0 g sample of coal is extracted, the filtrate diluted to 200 ml, and a 50 ml aliquot diluted to 100 ml, the weight of coal represented by the 100 ml of analytical solution would be 0.5g.

Total Sulfur in Coal

$$\text{total sulfur, \%} = \frac{(A - B) \times 13.738}{C}$$

where:

A = grams of BaSO_4 precipitated

B = grams of BaSO_4 blank correction

C = grams of sample used

13.738 = stoichiometric factor

Sulfate Sulfur In Coal
ASTM D2492-79

Extraction

1. Transfer approximately 5g of thoroughly air dried coal sample to a 250 ml Erlenmyer flask.
2. Add 50 ml HCl (2+3).
3. Fit the cold-finger condenser to the flask.
4. Boil for 30 minutes.
5. Rinse the cold-finger into the flask with HCl (1+23).
6. Filter through a medium-texture, double acid washed filter paper into a 400 ml beaker.
7. Transfer all residue in the flask to the paper by washing with HCl (1+23).
8. Use a total of about 35 ml HCl and about six washings.
9. Save the residue for pyritic sulfur determination.
10. To the filtrate add 10 ml saturated bromine water.
11. Cover with a watch glass and boil for 5 minutes.
12. Slowly add NH_4OH (sp. gr. 0.90) until a slight excess is present, then add 5 ml more with constant stirring.
13. Cover with a watch glass and boil for 1 minute.
14. Filter through a medium-texture ashless filter paper into a 600 ml beaker.
15. Wash the filtrate several times with hot water which has had a trace of NH_4Cl and NH_4OH added.
16. Retain the filtrate; discard the residue from step 15.

Analysis of Sulfate Extract

- (1) Neutralize the filtrate with concentrated HCl using methyl orange indicator; add 1 ml excess acid.
- (2) Heat to boiling.
- (3) Add dropwise, with stirring, 10 ml BaCl_2 solution.
- (4) Boil for 15 minutes.
- (5) Turn-down the heat, and allow the solution to stand for two hours just below boiling.
- (6) Filter through ashless paper and wash with hot water until silver nitrate solution shows no precipitate with one drop of solution.
- (7) Preweigh a porcelain crucible.
- (8) Place filter paper with residue into the crucible.
- (9) Place the covered crucible into a muffle furnace and "smoke" the paper away gradually.
- (10) After the paper is nearly consumed raise the temperature to 925c and heat to constant weight.
- (11) The remaining mass will be used to determine the sulfate sulfur from the stoichiometry of BaSO_4 .
- (12) A blank sample or a sample of known sulfate content is to be run alongside the analytical samples.

Pyritic Sulfur In Coal

ASTM D2492-79

Extraction

- (1) Use the sulfate from the sulfate extraction procedure.
- (2) Transfer the sample to a 250 ml Erlenmyer flask and add 50 ml HNO_3 (1+7).
- (3) Fit the cold-finger condenser to the flask and either (a) boil 30 minutes, or (b) let stand overnight.
- (4) Rinse the cold-finger into the flask with HNO_3 (1+7).
- (5) Filter into a 600 ml beaker and wash six times with HNO_3 (1+7).
- (6) Retain the filtrate; discard the residue.

Analysis of Pyritic Sulfur Extract

- (1) Dilute the filtrate to 200 ml with iron-free water.
- (2) Transfer a 50 ml aliquot to a 100 ml volumetric flask.
- (3) Add 10 ml lanthanum solution and dilute to volume with iron-free water.
- (4) Use atomic absorption spectroscopy to determine iron at 372 nm.
- (5) Calculate the pyritic sulfur.

Total Sulfur In Coal

ASTM D3177

Eschka Method

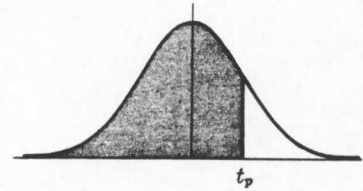
A mixture of 2 parts by weight of calcined magnesium oxide (MgO) and 1 part of anhydrous sodium carbonate (Na_2CO_3) is known as the ESCHKA MIXTURE.

1. Thoroughly mix 1g of sample coal (to nearest 0.1 mg) and 3 g of Eschka mixture in a porcelain crucible.
2. Cover the mixture with about 1 g of Eschka mix.
3. Place the crucible in a cold electric muffle furnace and gradually raise the temperature to $800^{\circ}C$ - plus or minus $25^{\circ}C$ - in about one hour.
4. Heat for 1 1/2 hours, or until on stirring all black particles have disappeared.
5. Transfer the contents of the crucible to a 200-ml beaker and digest with 100 ml of hot water for 3/4 hour while stirring occasionally.
6. Decant through a medium filter paper into a 400-ml beaker and wash the insoluble matter with hot water. Decant and wash five times with hot water.
7. Transfer the insoluble matter to the filter paper and wash five more times with hot water.
8. Accumulate about 250 ml of filtrate.
9. To the filtrate add 10-20 ml of saturated bromine water.
10. Make slightly acid with 1:1 HCl , and boil to expel the liberated bromine. The solution turns bright yellow, and turns white on boiling.
11. Make just neutral with saturated sodium carbonate solution using ethyl orange indicator solution.
12. Add 1 ml of 1:9 HCl . If the solution is not slightly acidic add another ml of 1:9 HCl .
13. Bring to boiling and add slowly from a pipet with constant stirring 10 ml or more $BaCl_2$ solution. The barium chloride solution must be in excess.

14. If much more than 10 ml BaCl_2 solution is required reduce the sample to about 0.5g and repeat.
15. Continue boiling for 15 minutes, then cover with a watch glass and allow to stand overnight at a temperature just below boiling.
16. Filter through an ashless paper and wash with hot water until 1 drop of silver nitrate solution produces no more than a slight opalescence with 10-15 ml of filtrate.
17. Place the wet filter in a weighed porcelain crucible and place in an electric muffle furnace.
18. Raise the temperature gradually, smoking away the paper without flame.
19. After the paper is practically consumed raise the temperature to 925c and heat to constant weight.
20. Correct the procedure by a blank or a sample with known sulfate content.

APPENDIX F

**PERCENTILE VALUES (t_p)
for
STUDENTS t DISTRIBUTION
with ν degrees of freedom
(shaded area = p)**



ν	$t_{.995}$	$t_{.99}$	$t_{.975}$	$t_{.95}$	$t_{.90}$	$t_{.80}$	$t_{.75}$	$t_{.70}$	$t_{.60}$	$t_{.55}$
1	63.66	31.82	12.71	6.31	3.08	1.376	1.000	.727	.325	.158
2	9.92	6.96	4.30	2.92	1.89	1.061	.816	.617	.289	.142
3	5.84	4.54	3.18	2.35	1.64	.978	.765	.584	.277	.137
4	4.60	3.75	2.78	2.13	1.53	.941	.741	.569	.271	.134
5	4.03	3.36	2.57	2.02	1.48	.920	.727	.559	.267	.132
6	3.71	3.14	2.45	1.94	1.44	.906	.718	.553	.265	.131
7	3.50	3.00	2.36	1.90	1.42	.896	.711	.549	.263	.130
8	3.36	2.90	2.31	1.86	1.40	.889	.706	.546	.262	.130
9	3.25	2.82	2.26	1.83	1.38	.883	.703	.543	.261	.129
10	3.17	2.76	2.23	1.81	1.37	.879	.700	.542	.260	.129
11	3.11	2.72	2.20	1.80	1.36	.876	.697	.540	.260	.129
12	3.06	2.68	2.18	1.78	1.36	.873	.695	.539	.259	.128
13	3.01	2.65	2.16	1.77	1.35	.870	.694	.538	.259	.128
14	2.98	2.62	2.14	1.76	1.34	.868	.692	.537	.258	.128
15	2.95	2.60	2.13	1.75	1.34	.866	.691	.536	.258	.128
16	2.92	2.58	2.12	1.75	1.34	.865	.690	.535	.258	.128
17	2.90	2.57	2.11	1.74	1.33	.863	.689	.534	.257	.128
18	2.88	2.55	2.10	1.73	1.33	.862	.688	.534	.257	.127
19	2.86	2.54	2.09	1.73	1.33	.861	.688	.533	.257	.127
20	2.84	2.53	2.09	1.72	1.32	.860	.687	.533	.257	.127
21	2.83	2.52	2.08	1.72	1.32	.859	.686	.532	.257	.127
22	2.82	2.51	2.07	1.72	1.32	.858	.686	.532	.256	.127
23	2.81	2.50	2.07	1.71	1.32	.858	.685	.532	.256	.127
24	2.80	2.49	2.06	1.71	1.32	.857	.685	.531	.256	.127
25	2.79	2.48	2.06	1.71	1.32	.856	.684	.531	.256	.127
26	2.78	2.48	2.06	1.71	1.32	.856	.684	.531	.256	.127
27	2.77	2.47	2.05	1.70	1.31	.855	.684	.531	.256	.127
28	2.76	2.47	2.05	1.70	1.31	.855	.683	.530	.256	.127
29	2.76	2.46	2.04	1.70	1.31	.854	.683	.530	.256	.127
30	2.75	2.46	2.04	1.70	1.31	.854	.683	.530	.256	.127
40	2.70	2.42	2.02	1.68	1.30	.851	.681	.529	.255	.126
60	2.66	2.39	2.00	1.67	1.30	.848	.679	.527	.254	.126
120	2.62	2.36	1.98	1.66	1.29	.845	.677	.526	.254	.126
∞	2.58	2.33	1.96	1.645	1.28	.842	.674	.524	.253	.126

Source: R.A. Fisher and F. Yates, "Statistical Tables for Biological, Agricultural, and Medical Research", Oliver and Boyd Ltd., Edinburgh.

APPENDIX G

Table Of X-Ray Powder Diffraction Constants*

<u>Species</u>	<u>Reference</u>	<u>dA</u>	<u>2θ</u>	<u>I/I₀,%</u>
Calcium Carbonate (aragonite)	5-0453	3.396	26.24	100
		3.273	27.25	52
CaCO ₃		2.700	33.18	46
$\lambda = 1.54 \text{ \AA}$		1.977	45.91	65
		1.742	52.54	25
Calcium Carbonate (calcite)	5-0586	3.042	22.36	100
		2.635	34.02	42
CaCO ₃		1.863	48.89	33
$\lambda = 1.54 \text{ \AA}$		1.589	58.05	27
Calcium Ferrate CaFeO ₄	3-0804	3.71	24.00	15
		2.81	31.85	25
$\lambda = 1.54 \text{ \AA}$		2.70	33.18	100
		1.95	46.50	40
		1.86	48.98	15
Calcium Hydroxide (portlandite)	4-0733	4.90	18.11	74
		2.63	34.12	100
Ca(OH) ₂		1.927	47.17	42
$\lambda = 1.54 \text{ \AA}$		1.796	50.84	36
		1.687	54.39	21
Calcium Iron Oxide CaFe ₄ O ₇	12-145	5.03	17.63	15
		3.00	29.78	35
$\lambda = 1.54 \text{ \AA}$		2.76	32.44	35
Calcium Iron Oxide Solid solution CaO.2FeO	6-0602	2.59	34.64	35
		2.24	40.27	100
$\lambda = 1.79 \text{ \AA}$				

<u>Species</u>	<u>Reference</u>	<u>dA</u>	<u>2θ</u>	<u>I/I₀,%</u>
Calcium Iron Oxide	6-0562	2.75	32.56	40
CaO+10%FeO		2.243	40.21	100
Solid solution				
$\lambda = 1.79 \text{ \AA}$				
Calcium Oxide	4-0777	2.778	32.22	34
(lime)		2.405	37.40	100
CaO		1.701	53.19	45
$\lambda = 1.54 \text{ \AA}$				
Calcium Sulfate	6-0226	3.498	25.47	100
(anhydrite)		2.849	31.40	33
CaSO ₄		2.328	38.68	22
$\lambda = 1.54 \text{ \AA}$		2.208	40.87	20
Calcium Sulfate	6-0046	7.56	11.71	100
(dihydrate)		4.27	20.80	51
(gypsumn)		3.059	29.20	57
CaSO ₄ ·2H ₂ O		2.867	31.20	27
$\lambda = 1.54 \text{ \AA}$		2.679	33.45	23
Calcium Sulfate	14-453	6.01	14.74	95
(hemihydrate)		3.46	25.75	45
(bassanite)		3.00	29.79	100
2CaSO ₄ ·H ₂ O		2.802	31.94	50
$\lambda = 1.54 \text{ \AA}$		1.842	49.49	12
Calcium Sulfide	8-464	2.846	31.44	100
(oldhamite)		3.144	45.04	68
CaS		1.644	55.94	21
$\lambda = 1.54 \text{ \AA}$				
Calcium Sulfite	4-0599	3.12	28.61	100
CaSO ₃		2.94	30.41	20
$\lambda = 1.54 \text{ \AA}$		2.56	35.06	30
		2.09	43.30	40
		1.79	51.03	60

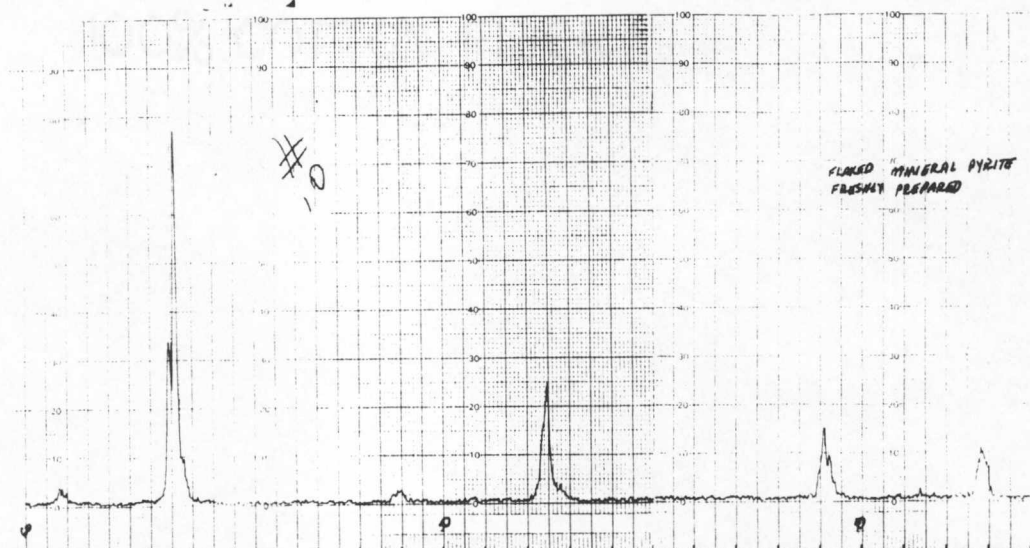
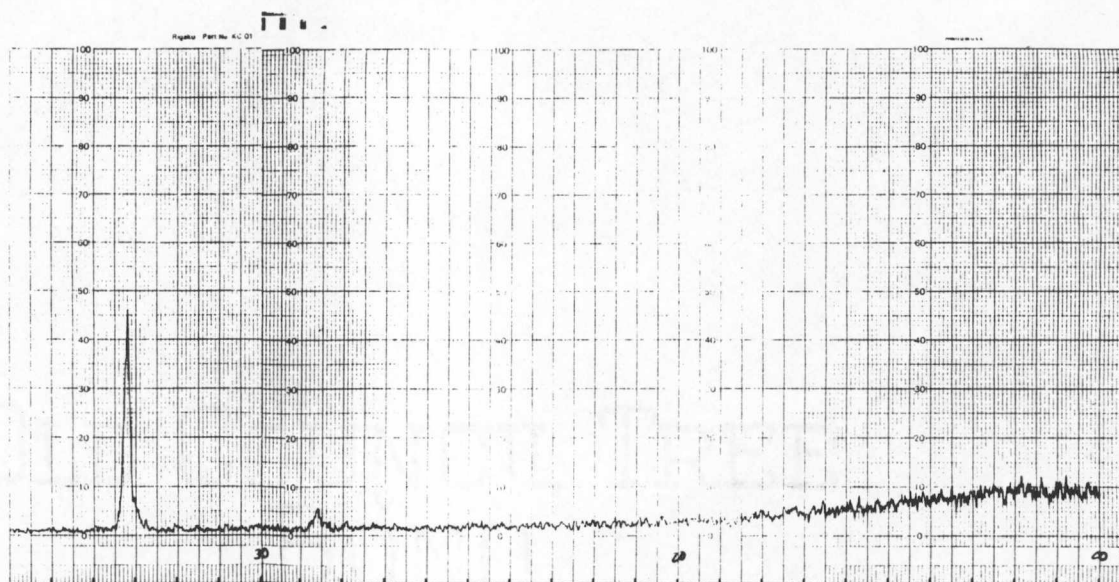
<u>Species</u>	<u>Reference</u>	<u>dA</u>	<u>2θ</u>	<u>I/I₀,%</u>
Calcium Sulfite (hemihydrate)	1-0772	3.80	23.41	32
		3.16	28.24	100
2CaSO ₃ ·H ₂ O		2.62	34.23	60
λ = 0.709 Å		1.85	49.26	40
Iron Disulfide (marcasite)	3-0799	3.44	25.90	40
		2.71	33.06	100
FeS ₂		1.91	47.47	30
λ = 0.709		1.76	51.96	63
		1.59	58.01	20
Iron Disulfide (pyrite)	6-0710	3.128	28.54	36
		2.709	33.07	84
FeS ₂		2.423	37.11	66
λ = 1.54 Å		2.212	40.80	52
		1.916	47.47	40
		1.633	56.34	100
		1.564	59.07	14
Iron(II) Oxide (wustite)	6-0615	2.486	36.13	80
		2.153	41.97	100
FeO λ = 1.79 Å				
Iron(III) Oxide (hematite)	13-534	3.65	24.39	25
		2.69	33.31	100
Fe ₂ O ₃		2.51	35.78	50
λ = 1.7902		1.838	49.60	40
Iron(II) Sulfate (hydrate)	13-103	5.48	16.18	90
		4.50	19.73	100
(rozenite)		3.979	22.35	80
FeSO ₄ ·H ₂ O		3.41	26.14	80
λ = 1.54 Å		2.973	30.06	80

<u>Species</u>	<u>Reference</u>	<u>dA</u>	<u>2θ</u>	<u>I/I₀,%</u>
Iron(II) Sulfate	12-226	4.84	18.33	90
(hydrate)		3.771	23.60	40
(szomolnokite)		3.441	25.90	100
FeSO ₄ ·H ₂ O		3.109	28.71	90
λ = 1.936 Å		2.528	35.51	80
		2.231	40.44	70
		1.996	45.45	70
Iron(III) Sulfate	1-0551	3.53	25.23	100
(hydrate)		3.35	26.61	50
Fe ₂ (SO ₄) ₃ ·H ₂ O		3.20	27.88	60
λ = 0.709		3.11	28.71	20
Iron(III) Sulfate	10-444	5.93	14.94	40
(basic hydrate)		5.05	17.56	50
(karphosiderite)		3.11	28.71	100
Fe ₂ (SO ₄) ₃ ·(OH) ₅ ·H ₂ O		3.06	29.19	100
λ = 1.54 Å		1.975	45.96	50
Iron(III) Sulfate	8-63	7.23	12.24	50
(octahydrate)		6.87	12.89	100
Fe ₂ (SO ₄) ₃ ·8H ₂ O		4.84	18.33	70
λ = 1.79		3.58	24.87	70
Iron Sulfide	15-37	5.03	17.63	100
(mackinawite)		2.97	30.09	80
FeS		2.31	38.00	80
λ = 1.54 Å		1.808	50.48	80
		1.562	59.15	30
Iron Sulfide	4-0832	2.98	29.89	90
(pyrrhotite)		2.93	30.51	50
FeS		2.67	33.57	90
λ = 2.29 Å		2.52	33.63	30

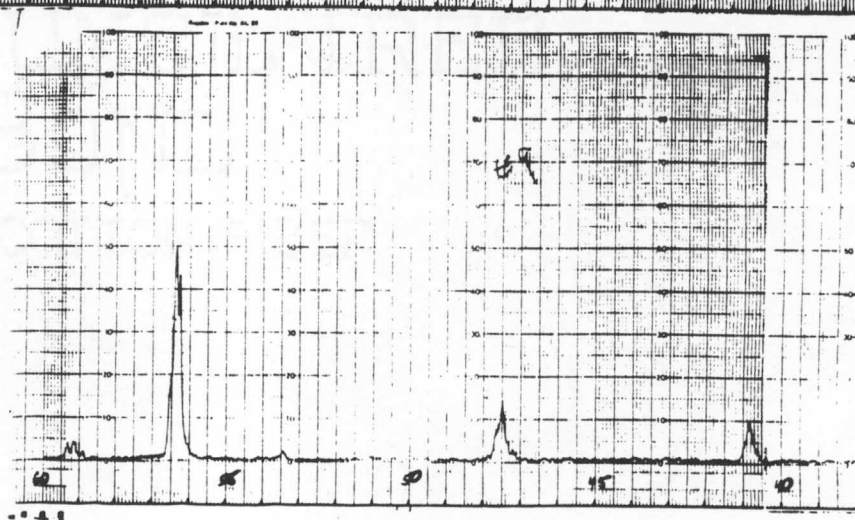
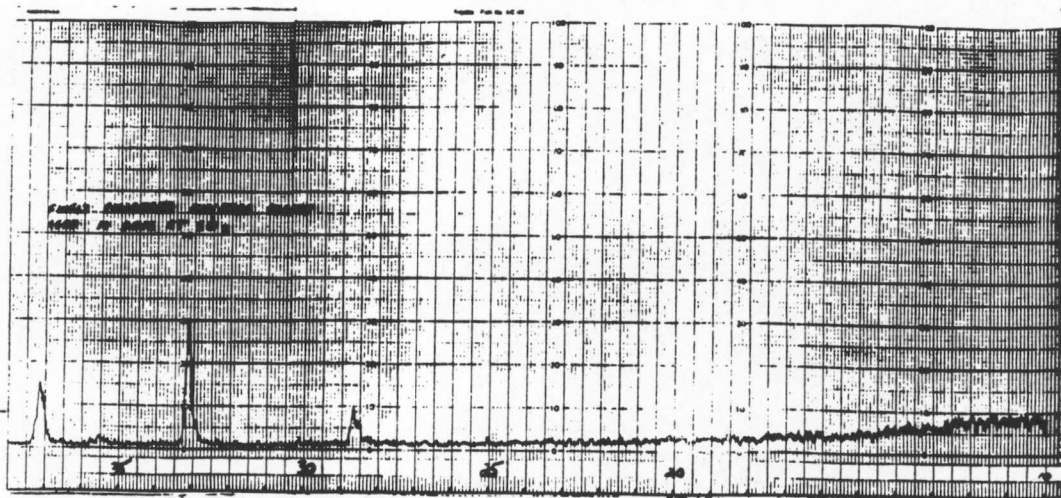
<u>Species</u>	<u>Reference</u>	<u>dA</u>	<u>2θ</u>	<u>I/I₀,%</u>
Iron Sulfide	11-151	5.4	16.42	20
(troilite)		2.98	29.98	40
FeS		2.66	33.57	60
$\lambda = 1.94 \text{ \AA}$		2.09	43.30	100

Source: ASTM, "X-Ray Powder Data File," 1960.

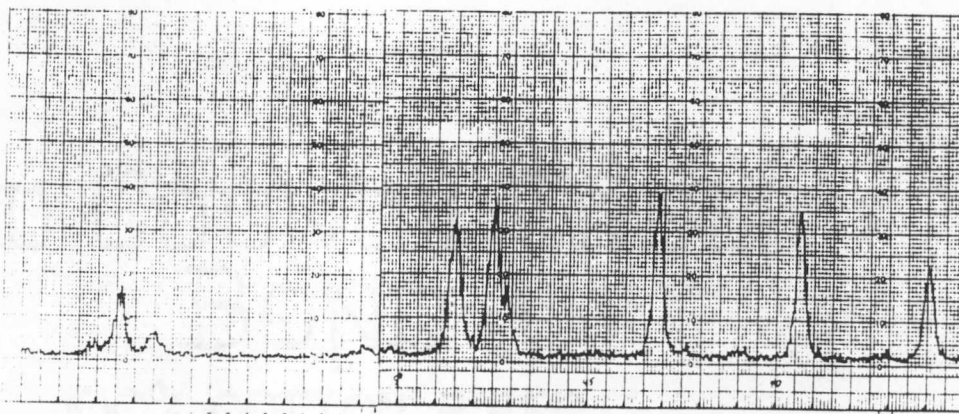
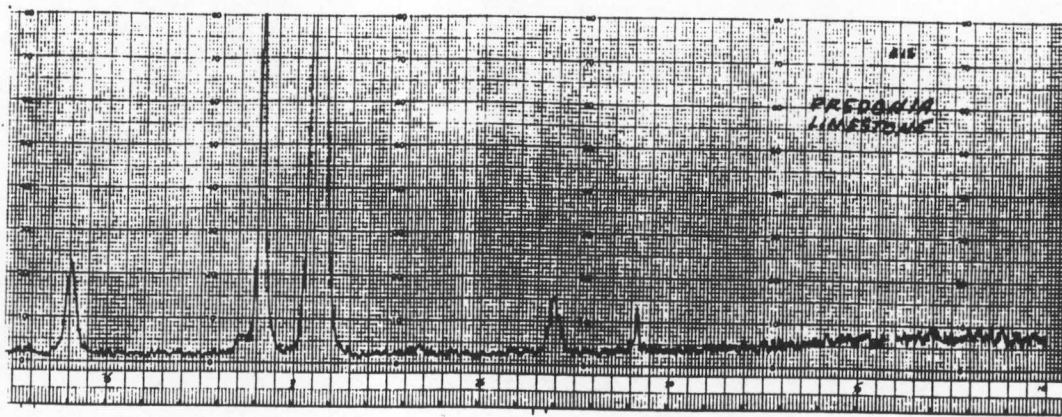
APPENDIX H



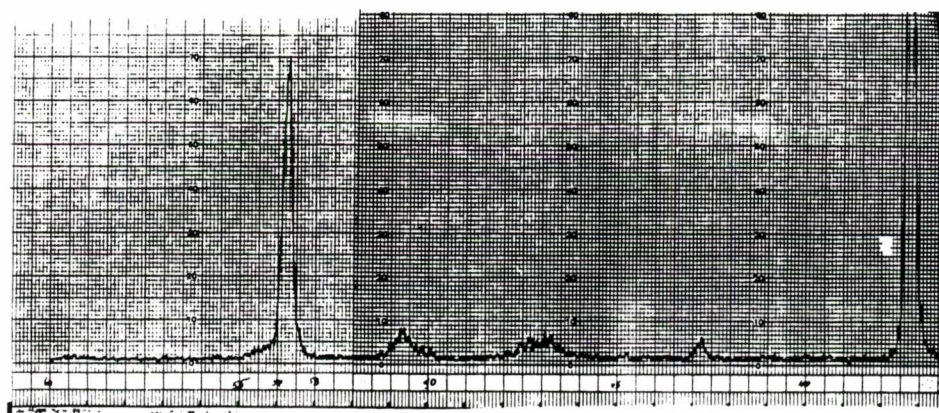
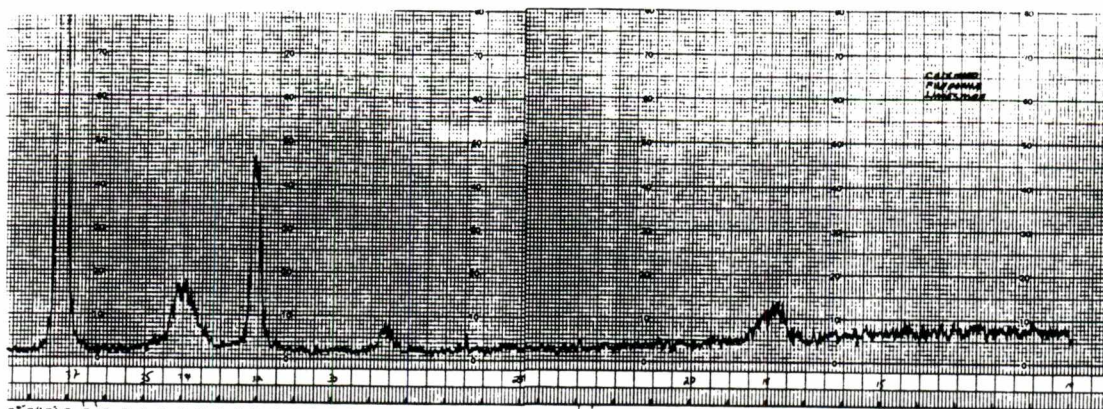
X-Ray Diffraction Scan Of
Mineral Pyrite, Freshly Prepared



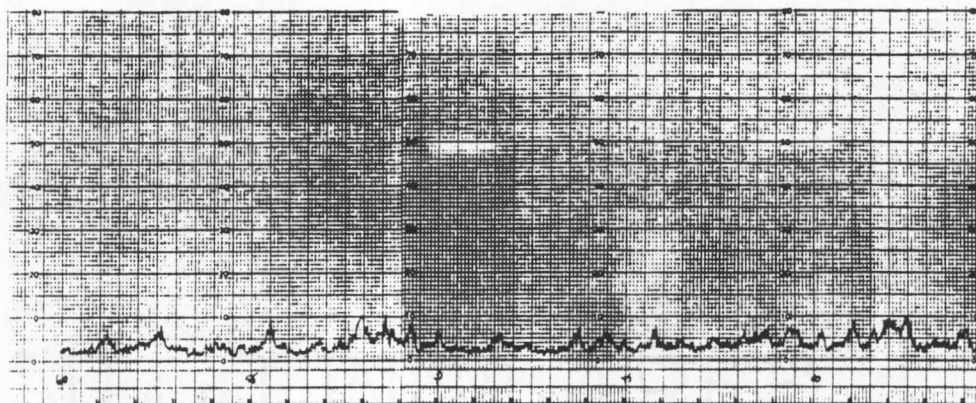
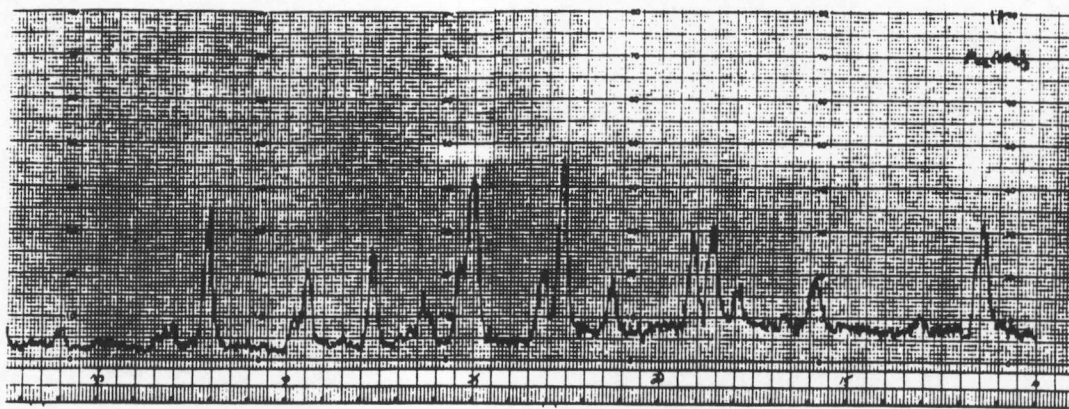
X-Ray Diffraction Scan Of
Mineral Pyrite, Aged 10 Days At 60c



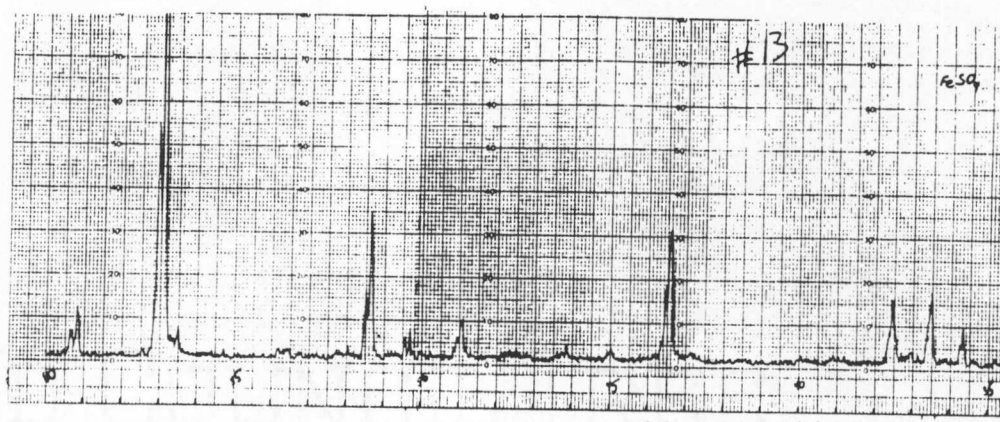
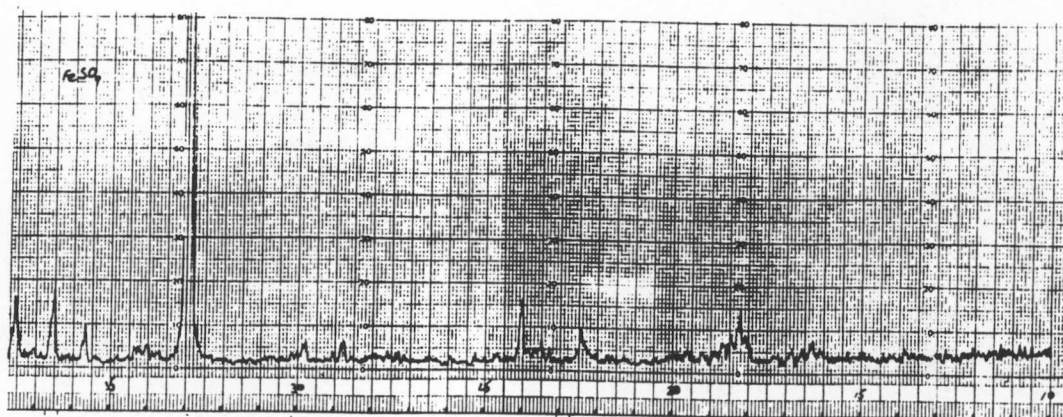
X-Ray Diffraction Scan Of
Fredonia Limestone



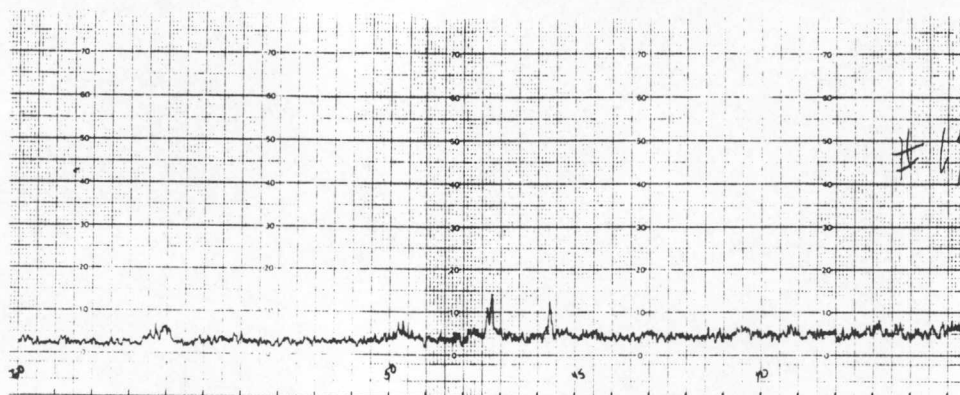
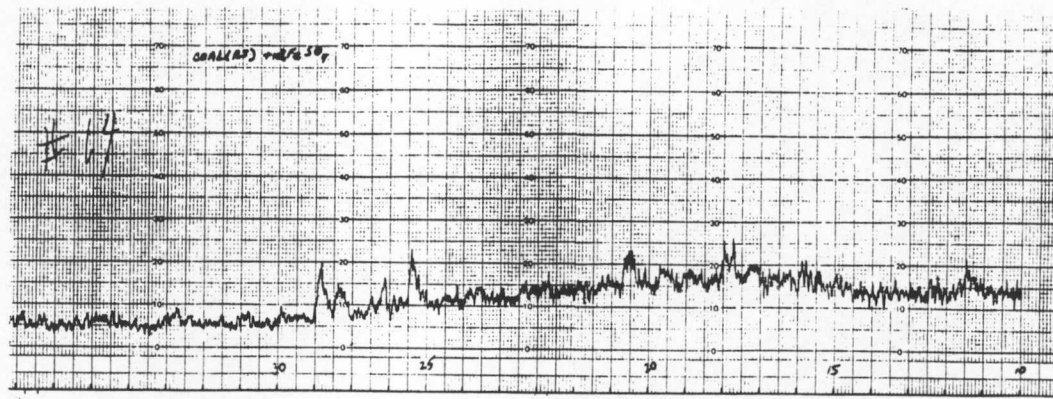
X-Ray Diffraction Scan Of
Calcined Fredonia Limestone



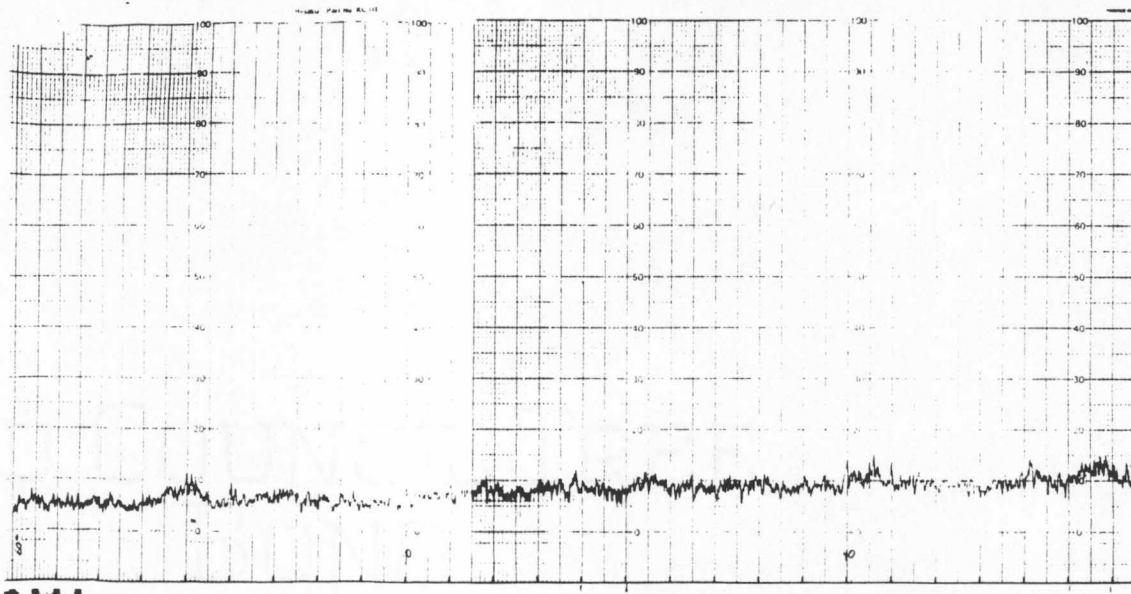
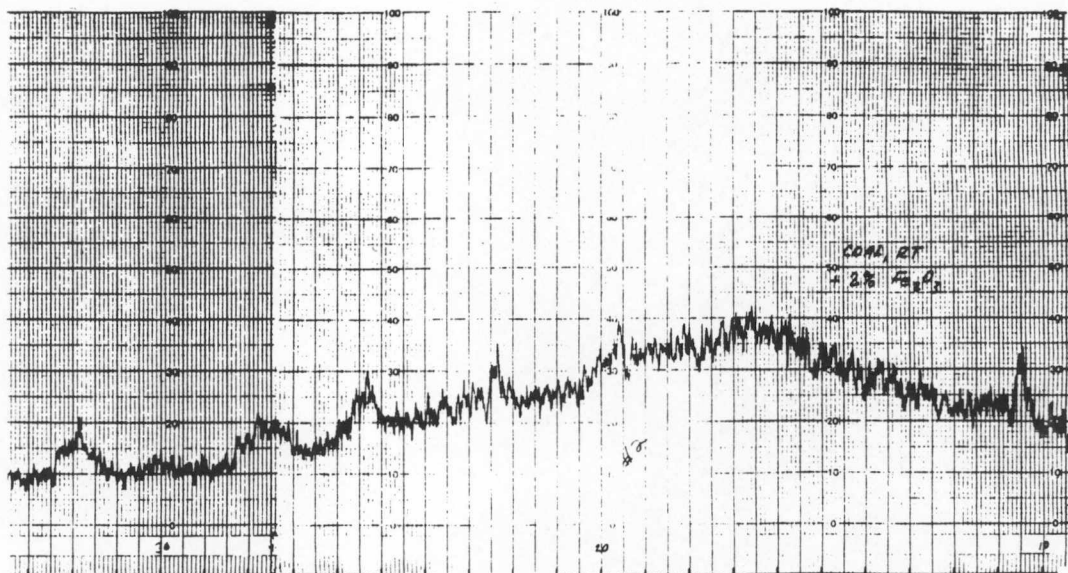
X-Ray Diffraction Scan Of Iron (III) Sulfate



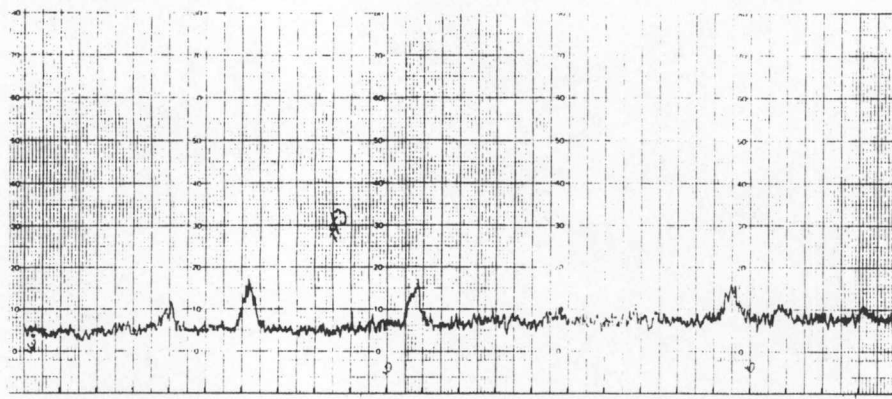
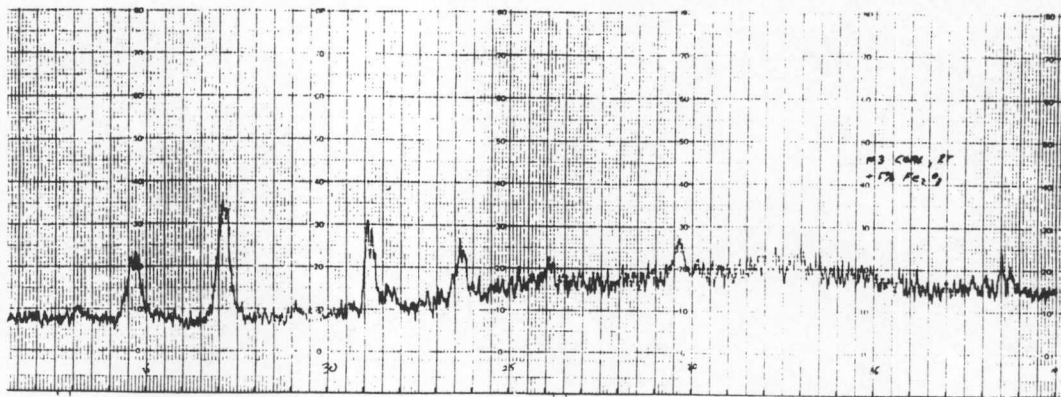
X-Ray Diffraction Scan Of
Ferrous Sulfate



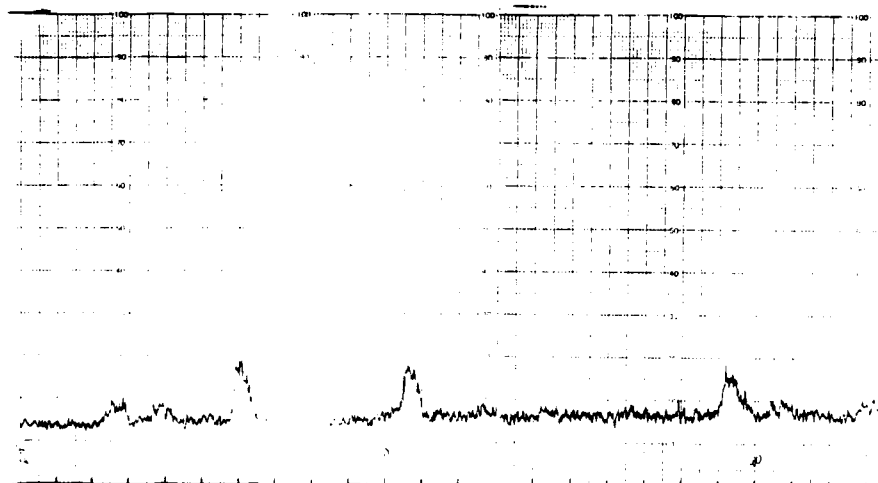
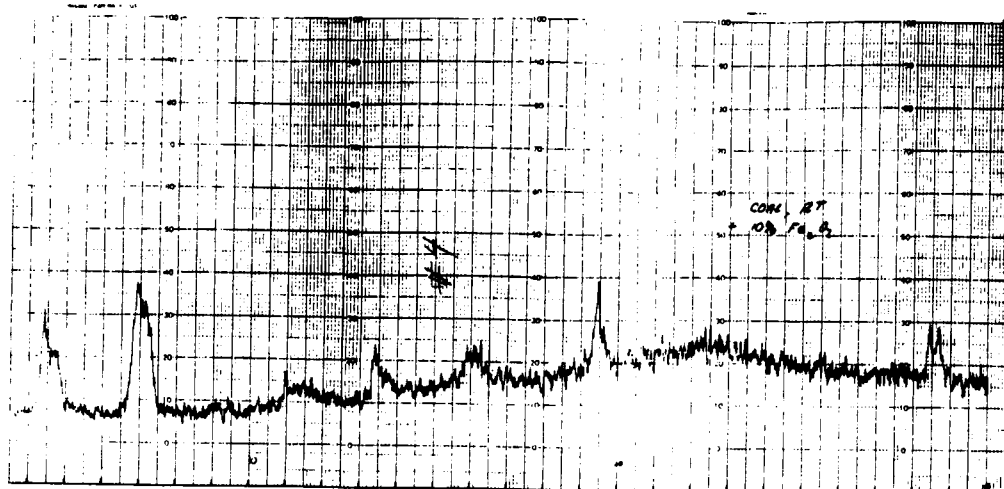
X-Ray Diffraction Scan Of
Coal Aged At Room Temperature + 10% Ferrous Sulfate



X-Ray Diffraction Scan Of
Coal Aged At Room Temperature + 2% Ferric Oxide



X-Ray Diffracton Scan Of
Coal Aged At Room Temperature + 5% Ferric Oxide



X-Ray Diffraction Scan Of
Coal Aged At Room Temperature + 10% Ferric Oxide

VITA

William Thomas Hall was born in Nashville, Tennessee, on October 29, 1941. He graduated from Corinne L. Cohn High School in that city in 1959. After a four year enlistment in the Air Weather Service he enrolled in college and graduated from Middle Tennessee State University in 1970 with a Bachelor of Science degree with a major in chemistry.

He has been employed with a State regulatory agency, in industry, and as a consulting engineer/chemist. He is a registered professional engineer in the State of Tennessee.

After five years as a pollution control engineer in Saudi Arabia, he returned to The University of Tennessee for a second bachelor's degree in chemical engineering. He began work on the Master of Science degree in Chemical Engineering in 1983. This degree was awarded in August, 1986.