PRECOMBUSTION DESULFURIZATION OF COAL BY PHOTOCHEMICAL
METHODS AND PYRITE DEPRESSION IN FROTH FLotation

By

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(ABSTRACT)

The precombustion desulfurization of coal was investigated by photochemical methods and by the application of a novel pyrite depressant in froth flotation. Semiconductor photoelectrochemical catalysis was extensively examined. As much as 41% of the organic sulfur was removed and 72% overall desulfurization of micronized Illinois No. 2 coal was obtained. Zinc oxide, in colloidal suspension, produced a small increase in the overall desulfurization at longer reaction times when compared to direct photolysis. The major limiting factor in organic sulfur removal from coal appears to be accessibility rather than reactivity. Kinetic experiments conducted with the model organosulfur compound, dibenzothiophene, showed high photochemical reactivity with nearly complete conversion occurring in 5 minutes in a saturated solution at 25°C. Scanning electron microscopic examination of
product coals showed empty casts in places once occupied by iron pyrite.

Additionally, a novel process was developed for separating clean coal from metal sulfide minerals such as pyrite and marcasite. The process comprises depressing the metal sulfide minerals with a reagent resulting from the alkaline oxidation and polymerization of a polyphenol or a quinone, and selectively floating clean coal from the depressed metal sulfide minerals. The process was investigated using microflotation, conventional Denver cell flotation, and microbubble column flotation. Up to 90% pyritic sulfur rejection was achieved from a coal and coal pyrite synthetic mixture. The process efficiency is a function of pH with greater improvements generally occurring at acidic pH when compared with the results obtained in the absence of the quinonoid reagent. However, in the case of microbubble column flotation with micronized coals, the largest overall pyritic sulfur and ash rejection occurred under alkaline conditions. Data from x-ray photoelectron spectroscopy and calorimetry indicate the quinonoid reagent modified the surface properties of minerals by reversible adsorption.
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PART I

GENERAL INTRODUCTION, OBJECTIVES, 
AND REPORT ORGANIZATION

CHAPTER 1

Introduction

Environmental concerns such as the much publicized "acid rain" issue, as well as industrial specifications for coals intended for metallurgical processes, have prompted researchers to seek new methods for desulfurization of coal. Physical methods have proven to be somewhat effective for the removal of the pyritic sulfur fraction of coal, but these conventional processes of coal beneficiation are completely ineffective for the removal of the organic sulfur fraction.

The coal reserves of the United States are enormous, but the utilization of this important resource is being inhibited by the detrimental environmental effects of the sulfur oxides which are emitted into the atmosphere by the combustion of sulfur-contaminated coals. Post combustion removal of sulfur oxides from exhaust gases is proving to be very expensive on both a capital and operational cost basis. A more cost effective approach would be to remove
the sulfur in the preparation process. Photochemical processes and pyrite depression in froth flotation can provide new methods for the precombustion desulfurization of coals. Photochemical methods may include direct or sensitized oxidation, fragmentation, extrusion, rearrangement, addition and/or reduction reactions, used separately, or in combination to remove the pyritic and organic sulfur contaminants. Pyrite depression in froth flotation may be accomplished by adding a reagent which selectively binds to the naturally hydrophobic surface of the pyrite. This renders the surface hydrophilic and thereby depresses it.

Steel production is primarily dependent on low sulfur coals since high sulfur content coals produce a weak, inferior steel. After conventional coal cleaning processes a coal may still contain a pyritic and/or organic sulfur content which limits its use to the lower priced steam coal market. Development of an inexpensive method for the removal of this sulfur would make it possible to sell certain high sulfur coals on the more lucrative metallurgical market as well as providing an environmentally acceptable end product.
General Background

A provisional estimate of U.S. coal resources is a total of $3.228 \times 10^9$ tons ($67.4 \times 10^{18}$ BTU) (1). Unfortunately, much of this coal is contaminated with metallic sulfides, metallic sulfates, elemental sulfur, and organic sulfur. The metallic sulfur compounds can generally be removed, if the mineral is ground to liberation, by gravimetric and flotation separation techniques.

Unfortunately, the pyrite and marcasite minerals contained in run of mine coal, frequently expose hydrophobic surfaces upon fresh grinding. In flotation the hydrophobic sulfide minerals tend to assemble on the bubble surfaces and report in the froth phase with the hydrophobic coal concentrate. Hydrophilic gangue minerals, such as the silicates, tend to remain in the water column and are eventually discarded as tailings.

Organic sulfur, however, is distributed throughout the coal matrix as a part of the molecular structure and is not amenable to removal by physical methods. Organic sulfur requires chemical treatment to accomplish removal (2). The organic sulfur compounds found in coal are very diverse, but the heteroaromatic compounds such as dibenzothiophene and benzothiophene are among the most commonly detected (3). It is interesting to note that
compounds such as dibenzothiophene are also present in high concentration in some crude petroleum, therefore, some methods which have been applied to oil desulfurization may be applicable to coal desulfurization as well (4, 5). Organosulfur compounds found in coal frequently contain the functional groups:

\[ \text{R-S-R} \quad \text{R-SH} \quad \text{R-S-S-R} \]

It is estimated that 40 to 60% of the organic sulfur in U.S. coal is present in ring structures (2, 6). The total sulfur content of coals ranges from 0.1 to 10% sulfur by weight (4) and of this 90% may be in the organic sulfur form (3). Organic sulfides in bituminous coals comprise from 30 to 50%, and thiophenes including dibenzothiophenes compose from 10 to 75% -- averaging more than 30% of the organic sulfur content in most coals (6).

Reduction processes frequently proceed more readily and are more selective in the thiophene series than similar reactions among aromatic or benzene type compounds. This phenomenon is due in part to activation of the α-positions on the thiophene ring by the sulfur atom to become involved in the delocalization of both the positive and negative charge and the odd electron (3).
The average C – S bond is relatively weak (7). Therefore, sulfur extrusion reactions are possible which leaves the basic hydrocarbon skeleton of the molecule intact. These extrusion reactions may preserve the caloric content of the coal.
Objectives

In Part II of this study photochemical methods for the precombustion desulfurization of coals were investigated. Dye-sensitized photo-oxidation, photochemical halogenation, alcoholic photochemical reduction, and semiconductor photoelectrochemical catalysis are among the techniques employed. Effects of these processes upon product coals with respect to chemical and morphological properties are examined. Kinetics of photo-oxidation of the model organic sulfur compound, DBT, have been determined under various experimental conditions.

In Part III of this investigation a novel pyrite depressant was synthesized and its performance and chemical properties examined by several methods. Experiments to quantify the pyrite depression effects of the new reagent in the froth flotation of coal were performed in a microscale cell, Denver cell, and microbubble column. Chemical properties of the reagent were illucidated by instrumental methods such as mass spectroscopy, Fourier transform infrared spectroscopy (FT-IR), electron spectroscopy for chemical analysis (ESCA), and calorimetry. Morphological and elemental composition characteristics of coal and coal pyrite which pertain to the the mineral flotation behavior were determined by scanning electron microscopy (SEM) and energy-dispersive x-ray analyzer (EDAX).
Dissertation Organization

This study is divided into two major thrusts: photochemical desulfurization and pyrite depression by a novel reagent. These are two widely divergent fields, and therefore this investigation will be reported in two major parts. Part II will deal with photochemical desulfurization and Part III will contain coal desulfurization by pyrite depression in froth flotation with a novel reagent.

Part II, "Photochemical Desulfurization of Coal", contains a review of the literature, methods and materials, results and discussion, and conclusions chapters. Part III, "Pyrite Depression in Froth Flotation of Coal" has chapters of the same format as Part II. A final summary section combines major findings from the study in a concise form. A single reference section consecutively numbered and a single appendix section are used.
PART II

PHOTOCHEMICAL DESULFURIZATION OF COAL

CHAPTER 2

INTRODUCTION

Practically every conceivable method has been applied to coal in order to remove the contaminating sulfur. Many of the procedures, which are still topics of intense investigation today, were first examined many years ago.

An area which has received relatively little attention in the past is the use of ultraviolet and visible wavelength light to promote sulfur rejection from coal. In the past thirty years numerous papers have been published concerning the photochemical reactivity of various organic and inorganic compounds, but only in the last five years have reports on coal desulfurization with radiation chemistry techniques appeared in the literature. Therefore, photochemical methods appear to be a fertile field for original research in fossil fuel beneficiation.

The earth receives a tremendous amount of radiant energy from the sun each day in the visible and ultra-
violet frequencies. Chemical processes utilizing this cheap and abundant energy source could have a considerable economic advantage over processes powered directly or indirectly by fossil fuels.

In the first phase of this study, the methods of photohalogenation, alcoholic photochemical reduction, dye sensitized photo-oxidation, and semiconductor photoelectrochemical oxidation were investigated as possible methods for coal desulfurization. Experiments were performed with particulate coal under atmospheric pressure and generally very mild operating conditions.
CHAPTER 3

PHOTOCHEMICAL DESULFURIZATION

LITERATURE REVIEW

Coal Structure

The efficiency of coal desulfurization processes are dependent upon the distribution and reactivity of the various sulfur forms found in coal. The three dimensional configuration of the major hydrocarbon components of coal largely controls the access of reagent molecules to the sulfur containing moieties in the coal. Therefore, the current theories concerning coal structure, chemical composition, and chemical reactivity will be presented in this section.

The organic component of coal appears to be a complex polymer of aliphatic and aromatic monomers with considerable random cross linking between the main chains. Three models for the organic structure of coal are given in Figures 1-3 (8-10). A comparison of the model for a low rank coal, lignite, as shown in Figure 1, with higher rank coals as displayed in Figures 2 and 3, indicates an increase in aromaticity with increasing rank. Experi-
Figure 1. Proposed Structure of the Organic Structure of Lignite Coal (8).
Figure 2. Representation of the Organic Structure of Coal (9).
Figure 3. Representation of the Organic Structure of Bituminous Coal (10).
mental evidence from nuclear magnetic resonance, as shown in Figure 4 (11), and data gathered from chemical studies, given in Table 1 (12) tend to support this view. Obviously, a tightly coiled and crosslinked polymer presents a formidable obstacle to the diffusional access of sulfur minerals and sulfur containing organic functional groups to reagents in desulfurization processes.

Sulfur found in coal is generally divided into two classes. The first is the organic sulfur component, which is sulfur that is covalently bonded to the hydrocarbon polymeric matrix. The second is the inorganic sulfur which includes elemental sulfur, metallic sulfides, and sulfate salts.

Inorganic sulfur mainly occurs as iron disulfides, with smaller amounts of elemental sulfur and sulfate salts. Sulfates generally consist of the iron, calcium, and barium salts. Disulfides may occur as finely dispersed euhedral crystals, framboidal assemblies, or massive crystals and lens throughout the coal substance. There are two iron disulfide crystalline forms: pyrite and marcasite. Pyrite exists as a cubic structure, with a specific gravity of 5.0 while marcasite is rhombic with a specific gravity of 4.87. Marcasite crystals are intimately covered with coal hydrocarbons, while pyrite crystals are generally free of this contamination (6).
<table>
<thead>
<tr>
<th>Coal Rank</th>
<th>Carbon Aromaticity</th>
<th>Nature of Monomers</th>
<th>Nature of Crosslinks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignite</td>
<td>30-50%</td>
<td>Small, largely single-ring systems extensively substituted with O-functional groups (-COOH, -OH, -OCH₃). About one oxygen per 3 to 4 carbon.</td>
<td>Many hydrogen bonds, probably some other crosslinks. Possibly salt bonds as in COO-Ca-00C. Few aliphatic crosslinks. Gel-like; water is an important structural component.</td>
</tr>
<tr>
<td>Sub-bituminous</td>
<td>60%</td>
<td>Still mostly single-rings with some larger rings; O-groups on almost all rings (-COOH, -OH) less than on lignites. About one oxygen per 5 to 6 carbon.</td>
<td>Mixture of hydrogen bonds and probably ethers. Some aliphatic links through less important than ethers.</td>
</tr>
<tr>
<td>Bituminous</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>70%</td>
<td>Mixture of ring systems - single ring still most common. About one oxygen per 9 carbon mainly -OH functional groups.</td>
<td>Mixture of aliphatic and ether crosslinks.</td>
</tr>
<tr>
<td>B</td>
<td>75%</td>
<td>Significant increase in amount of larger rings. About one oxygen per 12 carbon, now almost entirely ring ether and -OH.</td>
<td>Mostly aliphatic-type, some scissile biphenyl-types?</td>
</tr>
<tr>
<td>C</td>
<td>75-80%</td>
<td>Degree of condensation of aromatics still greater. Very few O-groups. Down to about one oxygen per 20 carbon.</td>
<td>Non-reactive aliphatic bridges and biphenyl-type links?</td>
</tr>
<tr>
<td>Anthracite</td>
<td>95%</td>
<td>Highly condensed aromatics, graphitic, commonly multiple rings. Functional groups rare - only one oxygen to about 100 carbon.</td>
<td>Almost entirely direct aromatic-aromatic links.</td>
</tr>
</tbody>
</table>
Figure 4. NMR Spectra of Coal as a Function of Rank. The Spectra Include: A. Wyodak Subbituminous, B. Illinois Bituminous, and C. Anthracite (11).
However, Mossbauer spectroscopy has shown some interaction between pyrite and coal hydrocarbons which can be eliminated by heating the coal at 175°C for six hours (13). Pyrite is more stable and slightly less reactive than marcasite. Marcasite can be irreversibly converted to pyrite by heating to 450°C. However, the chemical properties of pyrite and marcasite are similar. Iron-sulfur compounds which have been found in coals are given in Table 2 (14).

Organic sulfur in coal is classified by the type of functional group within which it is contained. The five groups include:

(i) Mecaptan or Thiol, RSH

(ii) Thio-ether or Sulfide, RSR'

(iii) Disulfide, RSSR'

(iv) Thiophene rings in the aromatic systems,

(v) γ - Thiopyrone, \[ \text{\includegraphics[width=2cm]{thiopyrone.png}} \]

Where R and R' are alkyl or aryl groups. Thiophenic compounds which have been identified by high resolution mass spectroscopy in coal hydrogenation products are shown in Table 3 (15).
<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>Atomic Fe%</th>
<th>Atomic FeS_x</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeS</td>
<td>50.00</td>
<td>1.00</td>
<td>Troilite</td>
</tr>
<tr>
<td>Fe_{11}S_{12}</td>
<td>47.83</td>
<td>1.09</td>
<td>Troilite</td>
</tr>
<tr>
<td>Fe_{10}S_{11}</td>
<td>47.62</td>
<td>1.10</td>
<td>Hexagonal Pyrrhotite</td>
</tr>
<tr>
<td>Fe_{9}S_{10}</td>
<td>47.37</td>
<td>1.11</td>
<td>Hexagonal Pyrrhotite</td>
</tr>
<tr>
<td>Fe_{7}S_{8}</td>
<td>46.67</td>
<td>1.14</td>
<td>Monoclinic Pyrrhotite</td>
</tr>
<tr>
<td>Fe_{9}S_{11}</td>
<td>45.00</td>
<td>1.22</td>
<td>Smythite</td>
</tr>
<tr>
<td>Fe_{3}S_{4}</td>
<td>42.86</td>
<td>1.33</td>
<td>Gregite</td>
</tr>
<tr>
<td>Fe_{2}S_{3}</td>
<td>40.00</td>
<td>1.50</td>
<td>Gamma FeS</td>
</tr>
<tr>
<td>FeS_{2}</td>
<td>33.33</td>
<td>2.00</td>
<td>Pyrite, Marcasite</td>
</tr>
<tr>
<td><strong>Formula</strong></td>
<td><strong>Structure</strong></td>
<td><strong>Name</strong></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>--------------</td>
<td>-------------------------------</td>
<td></td>
</tr>
<tr>
<td>$\text{C}_5\text{H}_6\text{S}$</td>
<td><img src="image1" alt="Structure" /></td>
<td>Methyliothiophene</td>
<td></td>
</tr>
<tr>
<td>$\text{C}_8\text{H}_6\text{S}$</td>
<td><img src="image2" alt="Structure" /></td>
<td>Benzothiophene</td>
<td></td>
</tr>
<tr>
<td>$\text{C}<em>8\text{H}</em>{10}\text{S}$</td>
<td><img src="image3" alt="Structure" /></td>
<td>Tetrahydrobenzothiophene</td>
<td></td>
</tr>
<tr>
<td>$\text{C}_9\text{H}_8\text{S}$</td>
<td><img src="image4" alt="Structure" /></td>
<td>Methylbenzothiophene</td>
<td></td>
</tr>
<tr>
<td>$\text{C}<em>{10}\text{H}</em>{10}\text{S}$</td>
<td><img src="image5" alt="Structure" /></td>
<td>Dimethylbenzothiophene</td>
<td></td>
</tr>
<tr>
<td>$\text{C}<em>{11}\text{H}</em>{10}\text{S}$</td>
<td><img src="image6" alt="Structure" /></td>
<td>Benzylthiophene</td>
<td></td>
</tr>
<tr>
<td>$\text{C}_{12}\text{H}_8\text{S}$</td>
<td><img src="image7" alt="Structure" /></td>
<td>Dibenzo thiophene</td>
<td></td>
</tr>
<tr>
<td>$\text{C}<em>{13}\text{H}</em>{10}\text{S}$</td>
<td><img src="image8" alt="Structure" /></td>
<td>Methyldibenzothiophene</td>
<td></td>
</tr>
<tr>
<td>$\text{C}_{14}\text{H}_8\text{S}$</td>
<td><img src="image9" alt="Structure" /></td>
<td>Benzo[def] dibenzothiophene</td>
<td></td>
</tr>
<tr>
<td>$\text{C}<em>{16}\text{H}</em>{10}\text{S}$</td>
<td><img src="image10" alt="Structure" /></td>
<td>Naphthobenzothiophene</td>
<td></td>
</tr>
<tr>
<td>$\text{C}<em>{17}\text{H}</em>{12}\text{S}$</td>
<td><img src="image11" alt="Structure" /></td>
<td>Methylnaphtobenzothiophene</td>
<td></td>
</tr>
<tr>
<td>$\text{C}<em>{20\text{H}}</em>{12}\text{S}$</td>
<td><img src="image12" alt="Structure" /></td>
<td>Dinaphthothiophene</td>
<td></td>
</tr>
<tr>
<td>$\text{C}<em>{21\text{H}}</em>{14}\text{S}$</td>
<td><img src="image13" alt="Structure" /></td>
<td>Methyldinaphthothiophene</td>
<td></td>
</tr>
</tbody>
</table>
The total sulfur content ranges from 0.2% to 10% by weight in the coals of the United States (15), while most coals contain between 1.0 and 4.0%. The organic sulfur content is generally less than 2%, while pyritic sulfur content may be quite variable. In common coals, i.e., those with total sulfur contents less 4%, the organic sulfur content tends to be proportional to the pyritic sulfur, with a ratio of 2 organic/3 pyritic (16).

Chemical analyses of the sulfur containing functional groups found in bituminous coal indicates organic sulfides constitute 5-30% of the total organic sulfur (15, 17). In most coals, thiophenes constitute 10-75% of the organic sulfur content and are generally greater than 30%. The dibenzothiophenic content of Illinois #6 bituminous coal is 41.8%, while the single thiophenic sulfur content is 30.8%. On the other hand, a low rank Texas lignite coal contains 16.3% dibenzothiophenic and 57.1% single thio-
henic organic sulfur contents (15). The order of desulfurization reactivity is as follows:

Naphthabenzo thiophene > Benzothiophene > Thiophene >

Dibenzothiophene (6).
Pyrite Chemical Reactivity

The reaction of ore pyrite with air at 610°C yields a 50% desulfurized product. Two reactions responsible for this desulfurization are as follows:

\[ \text{FeS}_2 + \text{O}_2 \rightarrow \text{FeS} + \text{SO}_2 \]  \hspace{1cm} [1]

\[ \text{FeS}_2 + 3\text{O}_2 \rightarrow \text{FeSO}_4 + \text{SO}_2 \]  \hspace{1cm} [2]

At higher temperatures, from 810°C-910°C, nearly complete desulfurization occurs. FeS and FeSO\(_4\) react to form iron oxides as follows:

\[ 2\text{FeS} + 7/2\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 \text{ (or Fe}_3\text{O}_4) + 2\text{SO}_2 \]  \hspace{1cm} [3]

\[ 2\text{Fe}_2\text{SO}_4 \rightarrow \text{Fe}_2\text{O}_3 \text{ (or Fe}_3\text{O}_4) + 2\text{SO}_2 + 1/2\text{O}_2 \]  \hspace{1cm} [4]

Coal pyrites also react with oxygen in air in a similar way. At temperatures ranging from 350°C-450°C up to 90% desulfurization may be obtained in 10 minutes of treatment. Diffusion of oxygen into the coal matrix and the subsequent reaction with the pyrite is the rate controlling step. Coal heating value recoveries of 80% were obtained (19).

Steam reacts with ore pyrite at elevated temperatures (18). At temperatures between 380°C and 550°C the following reactions are responsible for desulfurization:
3FeS₂ + 2H₂O \rightarrow 3FeS + 2H₂S + SO₂ \quad [5]

2H₂S + SO₂ \rightarrow 2H₂O + 3S \quad [6]

Thus, the net reaction is:

3FeS₂ \rightarrow 3FeS + 3S \quad [7]

At higher temperatures, between 700-900°C, other reactions are proposed:

3FeS + 4H₂O \rightarrow Fe₃O₄ + 3H₂S + H₂ \quad [8]

2FeS + 3H₂O \rightarrow Fe₂O₃ + 2H₂S + H₂ \quad [9]

These reactions may reduce the sulfur content by 90% in ore pyrites.

The mixture of air and steam produces greater desulfurization than using air or steam alone at temperatures lower than 650°C. In coal desulfurization, Tsai (6) contends that steam minimizes heating value losses from the coal matrix by the dilution of the oxygen partial pressure in the gaseous steam. Steam is readily separated from the coal product, minimizing further processing costs. Steam increases coal permeability, so that increased access to pyrites is obtained. Desulfurization of West Kentucky, high volatile, bituminous coal is significantly greater with a mixture of air and steam versus air alone at 350°C.
The reaction of iron pyrite with gaseous chlorine has been investigated (6). The following chemical reactions are believed to be responsible for the observed desulfurization:

\[ \text{FeS}_2 + \text{Cl}_2 \rightarrow \text{FeCl}_2 + \text{S}_2\text{Cl}_2 \]  
\[ 2\text{FeS}_2 + 3\text{S}_2\text{Cl}_2 \rightarrow 2\text{FeCl}_3 + 10\text{S} \]  

Pyrite may be oxidized in aqueous solution with the sulfur forming elemental sulfur, sulfate, or sulfurous acid as given by the following equations:

\[ \text{FeS}_2 \rightarrow \text{Fe}^{2+} + 2\text{S}^0 + 2e \]  
\[ \text{FeS}_2 + 8\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ + 14e \]  
\[ \text{S} + 3\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 + 4\text{H}^+ + 4e \]

These half reactions have standard reduction potentials of +0.421, +0.362, and +0.45 volts respectively (20-22). The oxidation potential of the reagent determines which reaction predominates. Sulfur dioxide or sulfurous acid may oxidize pyrite to form elemental sulfur or sulfate, but oxidants with oxidation potentials greater than +0.45 volts such as \( \text{Fe}^{3+} \) or dissolved \( \text{O}_2 \) can further oxidize the sulfur products into sulfur dioxide.

Ferric ions react with ore pyrite in aqueous solution efficiently at low temperatures (23). Temperatures between
$90^\circ$ and $130^\circ$C are quite effective. A conversion of 92-96% requires 6-8 hours or longer. Reaction products include ferrous sulfate, sulfuric acid, and elemental sulfur. Governing reactions are as follows:

$$\text{FeS}_2 + 7\text{Fe}_2\text{(SO}_4\text{)}_3 + 8\text{H}_2\text{O} \longrightarrow 15\text{FeSO}_4 + 8\text{H}_2\text{SO}_4$$  \[15\]

$$\text{FeS}_2 + \text{Fe}_2\text{(SO}_3\text{)}_3 \longrightarrow 3\text{FeSO}_4 + 2\text{S}$$  \[16\]

The oxidant can be regenerated for subsequent use as a desulfurization reagent by air or electrochemically:

$$9.6\text{FeSO}_4 + 4.8\text{H}_2\text{SO}_4 + 2.4\text{O}_2 \longrightarrow 4.8\text{Fe}_2\text{(SO}_4\text{)}_3 + 4.8\text{H}_2\text{O}$$  \[17\]

$$\text{Fe}^{+2} \underset{+e}{\longrightarrow} \text{Fe}^{+3}$$  \[18\]

Pyrite reacts with dissolved oxygen in aqueous solution to form soluble iron sulfates at temperatures ranging from 100-300°C (25, 26). Pressures of 4.3 to 20 atmospheres increases solubility of oxygen in the solution. In two hours of reaction time, at 20 atmospheres and $130^\circ$C, more than 90% pyritic sulfur rejection can be obtained. Chemical reactions involved include:

$$2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4$$  \[19\]

$$4\text{FeSO}_4 + \text{O}_2 + 2\text{H}_2\text{SO}_4 \longrightarrow 2\text{Fe}_2\text{(SO}_4\text{)}_3 + 2\text{H}_2\text{O}$$  \[20\]

$$\text{Fe}_2\text{(SO}_4\text{)}_3 + 3\text{H}_2\text{O} \longrightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{SO}_4$$  \[21\]
Hematite formed in the third reaction creates a film on the pyrite crystal and thereby slows the rate of subsequent oxidation. The rate of reaction can be substantially increased by the addition of alkali, especially sodium carbonate (27). Addition of sodium carbonate doubles the desulfurization of the coal product which occurs at 150°C and 7.8 atmospheres in one hour of reaction time.

Hydrogen peroxide, a strong oxidant, reacts with pyrite quite readily (28). The reactions proceed as follows:

\[
2\text{FeS}_2 + 3\text{H}_2\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 4\text{SO}_4^2^- + 3\text{H}_2\text{O} \quad [22]
\]

\[
2\text{FeS}_2 + 15\text{H}_2\text{O}_2 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4 + 14\text{H}_2\text{O} \quad [23]
\]

Note the first reaction produces the water insoluble elemental sulfur product.

Pyrite reacts with aqueous alkali (29) or molten alkali (30, 31) at temperatures ranging from 200-400°C. The major product is sodium sulfide (90-93%). Minor products are thiosulfate and sulfates: \( \text{Na}_2\text{S}_2\text{O}_3 \), \( \text{Na}_2\text{SO}_3 \), and \( \text{Na}_2\text{SO}_4 \) (7-10%) (32, 33). The governing chemical reactions are (33, 29):


25
\[ 8\text{FeS}_2 + 30\text{NaOH} \rightarrow 4\text{Fe}_2\text{O}_3 + 14\text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3 + 15\text{H}_2\text{O} \] \[ 24 \]

\[ \text{FeS}_2(s) + 4\text{NaOH}(s) \rightarrow \frac{32}{33} (\frac{1}{2}\text{Fe}_2\text{O}_3(s) + 2\text{Na}_2\text{S}(s) + \] \[ 2\text{H}_2\text{O}(l)) + \frac{3}{33} (\frac{1}{3}\text{Fe}_3\text{O}_4(s) + 2\text{Na}_2\text{SO}_4(s) + 2\text{H}_2(g)) \] \[ 25 \]

A reaction similar to the first equation also occurs with sodium bicarbonate (33).

**Organic Sulfur Reactivity**

Organic sulfur and oxygen occupy similar positions in the hydrocarbon coal matrix. However the chemical properties of sulfur and oxygen compounds are significantly different. Some of the differences include:

(i) Coals with high organic sulfur contents tend to contain less moisture than low organic sulfur coal of the same rank. This may be attributed to lower hydrogen bonding in the case of sulfur when compared to oxygen (34).

(ii) Pauling reports the electronegativity of oxygen to be 3.5 while sulfur is 2.5 (35). Therefore mercaptans and thiophenols do not hydrogen bond, thiophenols are approximately \(10^4\) times the acidity of phenols, and mercaptans exceed the acidity of alcohols (36, 37).
(iii) sulfur is more nucleophilic than oxygen.

(iv) sulfur may exist in numerous oxidation states and may polymerize to form chains of two or more atoms to link organic groups.

Thiophene is generally represented as:

\[
\text{[S]}
\]

However, this structure does not indicate the double-bond character of the carbon-sulfur bond which has been determined by microwave spectroscopy (38). The ultraviolet absorption spectrum of thiophene is similar to benzene (39). The sulfur atom appears to behave similarly to a -CH=CH- group. This is probably due to conjugation of the sulfur atom's lone pair of electrons with the aromatic \( \pi \) - electrons in the thiophene. This results in a bond distance which is shorter than an ordinary C-S single bond as shown in Table 4. Resonance energy of thiophene is 20 kcal/mole versus 37 kcal/mole for benzene. The data shown in Table 4 indicate the C-C bonds in benzene are equidistant while in thiophene they are quite variable. Table 4 indicates the C(2)-C(3) bond is more double bonded in character than in C(3)-C(4) bond. Therefore the C(2) carbon is quite susceptible to reactions with electrophilic reagents.
### Table 4. Structure of Thiophene and Benzene (39)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Bond</th>
<th>Distance(Å)</th>
<th>Bond</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiophene</td>
<td>C(2)H(2)</td>
<td>1.0776</td>
<td>C(5)SC(2)</td>
<td>92°10'</td>
</tr>
<tr>
<td></td>
<td>C(3)H(3)</td>
<td>1.0805</td>
<td>SC(2)C(3)</td>
<td>111°28'</td>
</tr>
<tr>
<td></td>
<td>C(2)S</td>
<td>1.7140</td>
<td>C(2)C(3)C(4)</td>
<td>112°27'</td>
</tr>
<tr>
<td></td>
<td>C(2)C(3)</td>
<td>1.3696</td>
<td>SC(2)(H)2</td>
<td>119°51'</td>
</tr>
<tr>
<td></td>
<td>C(3)C(4)</td>
<td>1.4232</td>
<td>C(4)C(3)H(3)</td>
<td>124°16'</td>
</tr>
<tr>
<td>Benzene</td>
<td>C(11)C(2)</td>
<td>1.397</td>
<td>C(2)C(1)C(6)</td>
<td>120°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C(1)C(2)H(2)</td>
<td>120°</td>
</tr>
</tbody>
</table>

**Pure C-C Single Bond** 1.504

**Pure C=C Double Bond** 1.334

**Pure C-S Single Bond** 1.812
Sublimed crystals of dibenzothiophene have been examined by x-ray diffraction to determine the molecular structure (40, 41). Results are given in Figure 5 using the cabazole numbering system. The bond lengths and angles are variable. The five and six membered rings, considered individually, are planar; however the entire molecule is slightly folded. Electron paramagnetic resonance (EPR) spectra of photoexcited triplet states of dibenzothiophene in ether glass, at liquid nitrogen temperature, shows that the sulfur atom contributes little to the conjugation of the aromatic rings. Also, the charge on the sulfur atom, as determined by x-ray spectroscopy, is similar to diphenyl sulfide (42, 43).

Organic Chemistry of Sulfur Compounds

Elemental sulfur can react with a hydrocarbon to form a mercaptan (44):

\[ \text{R-H} + \text{S} \rightarrow \text{R-SH} \]  \hspace{1cm} [26]

The resulting mercaptans may react:

\[ 2\text{R-SH} \rightarrow \text{R-S-R} + \text{H}_2\text{S} \]  \hspace{1cm} [27]

\[ \text{R-SH} + \text{R-H} \rightarrow \text{R-R} + \text{H}_2\text{S} \]  \hspace{1cm} [28]

But not all mercaptans react to form hydrogen sulfide, as the organic sulfide may be somewhat stable. A disulfide
Figure 5. Dibenzothiophene Structure. Bond Length is Reported in Angstroms (40, 41).
may be formed by the reaction of elemental sulfur with an organic sulfide:

\[ R-S-R + S \rightarrow R-SS-R \] \[29\]

\[ R-SS-R + 2R-H \rightarrow 2R-SH + R-R \] \[30\]

The resulting mercaptans may react further as previously indicated to yield hydrogen sulfide.

Thiols and mercaptans are acidic and can be neutralized by alkali:

\[ R-SH + OH^- \rightarrow RS^- + H_2O \] \[31\]

The ionized mercaptans of lower molecular weight are then water soluble (45).

Thiol compounds are the most easily desulfurized of the common organic sulfur forms found in coal. Thiols may be oxidized by air to form disulfide. Additionally, oxidation by aqueous chlorine may proceed as follows:

\[ R-SH + 4Cl_2 + 5H_2O \rightarrow R-OH + H_2SO_4 + 8HCl \] \[32\]

At high temperature and pressure oxygen may oxidize a thiol to a sulfonate (46):

\[ O_2, \text{Aqueous Na}_2\text{CO}_3 \]
\[ C_6H_5SH \rightarrow C_6H_5SO_3\text{Na (95\% yield)} \] \[33\]

150°, 1 Hr., 200 psi
While a similar reaction proceeds with peroxycfluoroacetic acid:

\[
\begin{align*}
\text{CF}_3\text{COOH/H}_2\text{O}_2 & \quad \rightarrow \\
\text{C}_6\text{H}_5\text{SH} & \quad \rightarrow \\
\text{C}_6\text{H}_5\text{SO}_3\text{H} & \quad \text{25°C, 15 min.}
\end{align*}
\]

The mechanism of attack upon thiols by aqueous alkali at 260°C has been proposed as follows:

\[
\begin{align*}
\text{HS}-\text{C}^-\text{C}-\text{Y} + \text{B}^- & \quad \rightarrow \\
\text{HS}^- & \quad \rightarrow \\
\text{HS}^- + >\text{C}=\text{C}-\text{Y} + \text{HB} & \quad \text{[35]}
\end{align*}
\]

The most important reaction of the disulfides (RSSR') is the reduction of the sulfur-sulfur bond. This results in partial desulfurization by the formation of hydrogen sulfide, thiols, and elemental sulfur. Thiols and elemental sulfur may then be removed by alkali and solvent extraction, respectively (6). Dialkyl disulfide (RSSR') is reduced at high temperature (496°C) as follows:

\[
\begin{align*}
\text{RSSR'} + \text{RH} & \quad \rightarrow \\
\text{RSSR'} & \quad \rightarrow \\
\text{RSH} + \text{RSR'} & \quad \text{[36]}
\end{align*}
\]

\[
\begin{align*}
\text{RSSR'} + 2\text{RH} & \quad \rightarrow \\
\text{RSSR'} & \quad \rightarrow \\
\text{RR} + \text{H}_2\text{S} & \quad \text{[37]}
\end{align*}
\]

While dibenzyl sulfide yields an unsaturated compound due to resonance stabilization of the product:

\[
\begin{align*}
(\text{C}_6\text{H}_5\text{CHS})_2 & \quad \text{270°C} \\
\rightarrow & \quad \text{C}_6\text{H}_5\text{CH} = \text{CHC}_6\text{H}_5 + \text{H}_2\text{S} + \text{S}^0
\end{align*}
\]

The ease of cleavage of the carbon-sulfur bond increases with increases in the number of phenyl groups attached to
the α - carbon. Upon distillation, dibenzhydral disulfide decomposes as indicated below:

\[
2[(C_6H_5)_2CHS]_2 \xrightarrow{\text{Distillation}} (C_6H_5)_2C=S + (C_6H_5)_2CH_2 + S + H_2S + (C_6H_5)_2C=C(C_6H_5)_2 \quad [39]
\]

In aqueous sodium carbonate, diphenyl sulfide is oxidized to the sulfonate (46):

\[
\begin{align*}
O_2, \text{aq., Na}_2\text{CO}_3 & \quad (C_6H_5S)_2 \xrightarrow{150^\circ C, 1\text{hr.}} C_6H_5SO_3^- & (92\% \text{ yield}) \quad [40]
\end{align*}
\]

While at higher temperature (300°C) diphenyl disulfide can be partially desulfurized to form sulfur dioxide instead of H₂S:

\[
(C_6H_5S)_2 + (C_6H_5)_2SO_2 \xrightarrow{} 2(C_6H_5)_2S + SO_2 \quad [41]
\]

In general, the oxidation of organic sulfides occurs in two steps. The first step is the oxidation of the sulfide to the sulfoxide and second is the oxidation of the sulfoxide to the sulfone:

\[
\begin{align*}
R_2S & \xrightarrow{} R_2SO \xrightarrow{} R_2SO_2 \quad [42]
\end{align*}
\]

Desulfurization of the sulfone may then be achieved by alkali treatment (6). Strong oxidizing agents such as fuming nitric acid, potassium permanganate, chromium trioxide in acetic acid, chromatosulfuric acid mixture,
hypochlorite, peroxysulfuric acid, and 30% hydroperoxide in acetone or glacial acetic acid (46, 47) may be employed. Sulfide is not oxidized by molecular oxygen in aqueous alkali except when a labile hydrogen is present, as in the case of a benzylic hydrogen. Benzylic sulfide is converted in the Ames' oxydesulfurization process by auto oxidation as follows (46):

$$\begin{align*}
200\text{psi } O_2, 0.2M \text{ Na}_2\text{CO}_3 \\
\text{C}_6\text{H}_5\text{CH}_2\text{SR} & \longrightarrow \text{C}_6\text{H}_5\text{COONa} + \text{C}_6\text{H}_5\text{CHO} \ [43] \\
150^\circ \text{C}, 1 \text{ Hr.}
\end{align*}$$

Sulfide may oxidized to the sulfoxide by halogenation (chlorine or bromine) followed by hydrolysis:

$$\begin{align*}
\text{R}_2\text{S} + \text{X}_2 & \longrightarrow \text{R}_2\text{SX}_2 \ [44] \\
\text{R}_2\text{S} \ \text{X}_2 + \text{H}_2\text{O} & \longrightarrow \text{R}_2\text{SO} + 2\text{HX} \ [45] \\
\text{where } \text{X} & = \text{Br or Cl} \ [46]
\end{align*}$$

The carbon-sulfur bond of alkyl sulfide cleaves at 300°C in aqueous alkali. The mechanism is believed to be similar to that of the mercaptan:

$$\begin{align*}
\text{RS-C-C-Y} + \text{B}^- & \longrightarrow \text{R}\text{-S-C-C-Y} \longrightarrow \text{RS}^- + >\text{C}=\text{C-Y} + \text{HB}^- \ [47] \\
\text{H} & \quad \text{HB}^-
\end{align*}$$

In organic synthesis, reductive cleavage of the benzyl group from the sulfur in sulfides is one of the most useful reactions which involves the cleavage of the
carbon-sulfur bond. This reaction may be accomplished by reaction with sodium/liquid ammonia, sodium alcohol, boiling acetic acid, or cold concentrated sulfuric acid. The ease of carbon-sulfur bond cleavage in sulfides is as follows:

\[ \text{CH}_3 \prec \text{C}_6\text{H}_5\text{CH} \prec (\text{C}_6\text{H}_5)_2\text{CH} < (\text{C}_6\text{H}_5)_3\text{C} \]  

[48]

The reaction of sulfides in boiling ethanol proceeds when catalysed by Raney nickel:

a) \( \text{R-S-R}' + \text{Ni(H)} \rightarrow \text{R-R} + \text{R-R} + \text{R}'-\text{R}' \)  

[49]

b) \( \text{R-S-R}' + \text{Ni(H)} \rightarrow \text{R-H} + \text{R}'-\text{H} \)  

[50]

In the presence of excess adsorbed hydrogen on the nickel catalyst only reaction (b) occurs (48). For example, the following reactions are known to occur:

\[ \text{C}_6\text{H}_5\text{SC}_6\text{H}_5 \rightarrow \text{Ni(H)} \rightarrow \text{C}_6\text{H}_6 \ (68\% \ yield) \]  

[51] Ethanol

\[ \text{C}_6\text{H}_5\text{SOC}_6\text{H}_5 \rightarrow \text{Ni(H)} \rightarrow \text{C}_6\text{H}_6 \ (75\% \ yield) \]  

[52] Ethanol

\[ \text{C}_6\text{H}_6\text{SO}_2\text{C}_6\text{H}_5 \rightarrow \text{Ni(H)} \rightarrow \text{C}_6\text{H}_6 \ (65\% \ yield) \]  

[53] Ethanol

In coal hydrogenation products the thiophenic compounds predominate. Therefore, they presumably predominate the organic sulfur content of most coals.
Unfortunately these compounds are generally less reactive than other organic sulfur compounds.

Dibenzothiophene is reportedly stable when heated in inert solvent at 150°C in the presence of bronze and oxygen (49). Under the same conditions diphenyl and dibenzyl sulfide yield insoluble precipitates. However, oxidation of dibenzothiophene with peracetic acid and peroxide readily proceeds. The oxidation products may be sulfoxides or sulfones dependent upon reaction conditions:

\[ 
\begin{align*}
\text{S} & \quad \xrightarrow{[\text{A}]} \quad \text{SO} \\
\text{S} & \quad \text{SO} \\
\end{align*}
\]

[54]

Kinetic studies of these reactions indicate that oxygen attack upon the sulfur atom is the rate limiting step (50, 51). Peracetic acid at 150°C to 60°C in acetic acid/benzene solution oxidizes dibenzothiophene to the sulfoxide in a 94% yield (50). With peroxide at 106°C, the sulfoxide product results in a 52% yield in 4 minutes, while a 47% yield of the sulfone occurs in 40 minutes. In trifluoroacetic acid and hydrogen peroxide or peroxytrifluoroacetic acid, dibenzothiophene is oxidized to the sulfone at 60°C with a 91% conversion occurring in 5 hours (46).
Biochemical oxidation of dibenzothiophene by *Pseudomonas jianii* or *Pseudomonas abikonensis* produces organic acids. Approximately 40% of the sulfur is converted to a water soluble form in one week of incubation (52).

Thiophene is more resistant to oxidation than dibenzothiophene since the lone pair of electrons on the sulfur atom of dibenzothiophene are in conjugation with the aromatic π-electrons. However, electron donating substitutions on the thiophene ring (such as methyl and phenyl groups) render it more susceptible to oxidation by perbenzoic or peracetic acid (53). While electron withdrawing substitutions on the thiophene ring (such as the nitro-group) hinders oxidation.

Dibenzothiophene shows great resistance to desulfurization by thermal decomposition. However the sulfone decomposes at high temperature as follows (54):

![Chemical Reaction](image)

Dibenzothiophene, benzo thiophene, and thiophene may be desulfurized by heating with an aluminosilicate catalyst at 400°-450°C. The resulting products are benzene, tar, and H₂S (55).
Thiophene and dibenzothiophene are more reactive with electrophilic reagents than their aromatic counterparts due to the electron donating property of the sulfur atom. The oxidation of the sulfur to the sulfoxide deactivates the molecule to subsequent electrophilic attack (6). As previously discussed, peroxyl trifluoroacetic acid or hydrogen peroxide readily oxidize dibenzothiophene to the dioxide. Peroxytrifluoroacetic acid, a powerful electrophilic oxidant, readily oxidizes alkylbenzenes to alkanoic acids. Since the divalent sulfur is more nucleophilic (or electron donating) than an aromatic ring, and the sulfoxide group is electron withdrawing, the benzene rings in the dibenzothiophene dioxide (sulfoxide) remain intact.

Dibenzothiophene reacts with nucleophilic reagents under harsh conditions. High alkali concentrations, temperatures, and pressures result in desulfurization reactions. The mechanism is proposed as follows (56):

\[ \text{[56]} \]

\[ \text{[57]} \]

\[ \text{[58]} \]
Dibenzothiophene is readily desulfurized in boiling alcohol in the presence of Raney nickel. A 66% yield of biphenyl is obtained in 3 hours (57, 58). Similar results are obtained with a sulfided CoMoO₃/γ-Al₂O₃ catalyst (59). However, 1,8-dimethyldibenzothiophene is unreactive under the same conditions. The methyl substitutions in the 1 and 8 positions is believed to produce steric hindrance to the adsorption of the sulfur atom to the active sites on the catalyst. Hydrodesulfurization activity is increased by methyl substitutions in the para (3 and 6) positions. This increased reactivity is attributed to the electron donating effects of the methyl groups. Two mechanisms of catalytic hydrodesulfurization of dibenzothiophene and its alkyl derivatives have been proposed. The first speculates the coordination of the sulfur atom with an active site on the catalyst (59) while the second proposes π-complex formation of a benzene ring with an active site on the catalyst (60, 61). The basic steps of these mechanisms are shown in Figure 6.
Figure 6. Proposed Mechanisms of Dibenzothiophene Reduction on a CoMo/Al₂O₃ Catalyst (60, 61).
Catalytic hydrodesulfurization of benzothiophene by Raney nickel (62), palladium on alumina (63), molybdenum disulfide (64), and cobalt molybdena (65) generally produces ethylbenzene and cyclohexane. Conversion rate and product selectivity is altered by methyl substitution. The conversion rate is retarded by methyl substitution and the ethylbenzene product is greatly favored.

Photochemistry of Organosulfur Compounds

Considerable research has been performed on the photochemistry of organosulfur compounds. Only a few reactions will be shown here that concentrate on the photoextrusion of sulfur from compounds of a similar nature to those contained in coal.

The action of sunlight on 3,5-diphenyl-[4H] thiopyran-4-one 1, 1-dioxide (I) yields the trimer t-1,t-4,c-5, c-8,t-8a,c-9a-hexaphenyloctahydro-r-1, 4:t-5,8-dimethano-fluorene-9,10,11-trione (II) (one isomer of which is shown below) with the extrusion of sulfur (66). Also under the action of sunlight (I) the desulfurized product dimethyl 3,6 diphenylbenzene-1,2-dicarboxylate (III) can form (67):
Sensitized irradiation of 2-(2-benzothienyl)ethyl-but-2-ynoate (I) yields a desulfurized naphthopyranone (II) as a major product (68):

Direct irradiation with a 450 watt medium pressure mercury lamp of 4,6-diphenyl-2,2-dioxo-1,2,3,5-oxathiadiazine (I) yields 2-phenyl-4(3H)-quinazolinone (II) (69):
Using benzene as a sensitizer the photodecomposition of the following sulfones (I) and (II) gives a [5-->4+1] retrocycloaddition product. The reactions are somewhat stereo-specific, giving a result which is derived from "conrotation." This result would have been expected for an "allowed" 6 electron cheletropic reaction for singlet states, but instead triplet sensitization is required (7, 70):

![Diagram of reaction]

Upon sensitized or direct irradiation dialkyl sulfides are subjected to primary C-S cleavage, and with thiirans, sulfur extrusion frequently occurs (71, 72):

![Diagram of reaction]

Investigators have examined the thermal or photochemical reaction between aryl azides and n-sulphynylanilines. The formation of $SO_2$ and elemental sulfur indicates $SO_2$ was probably generated during the reaction (73).
Ultraviolet radiation at 254 nm of o-ethyls-n-propyl-phosphonothioate in ethanol yields a rapid photoreductive cleavage of the P-S or the S-C bond. Photoreductive cleavage of the S-C bond is demonstrated by the formation of o-ethylphenylphosphonothioic acid, its oxygen analogue, and propane (74).

Photo-oxidation reactions proceed by the promotion of molecular oxygen to an excited singlet state. Usually a triplet photosensitized method is used, but direct excitation is possible by ultraviolet light. Strongly absorbing dyes are frequently used as photosensitizers, examples of these dyes include rose bengal, methylene blue, toluidine blue-o, and 10-methyl phenothiazine (7, 75, 76, 66). Alkyl and arylthiophenes when attacked by singlet oxygen may give rise to ring cleavage products (79).

Methylene blue-sensitized photo-oxidation of 2,5-dimethylthiophene (I) in chloroform yields a trans-diketone (II) and a cis-sulfine (III):

![Chemical Diagram]

[67]
Rose bengal sensitized photo-oxidation of 2,4,5-triphenyl-thiazole gives benzil and benzamide, while methylene blue sensitized photo-oxidation in chloroform results in thioamide (80).

Photochemical Processes

The Stark-Einstein law indicates that the absorption of one quantum of radiation yields one photo-excited molecule (81). The resulting photo-excited molecule may then participate in numerous photochemical processes which may be physical or chemical in nature.

Photochemical processes of particular interest in this study include: direct photolysis, direct excitation of reactive molecules in solution, sensitized photo-oxidation, semiconductor photoelectrochemical contact oxidations, and semiconductor photoelectrochemical reduction of oxygen. Direct photolysis is the absorption of photons by an organosulfur molecule causing the cleavage of bonds and subsequent fragmentation and/or rearrangement. The average C-S bond energy (66 kcal/mole) is relatively small when compared to the average C-C bond (83-85 kcal/mole) and C-H bond (96-99 kcal/mole) (7) as shown in Table 5. Thus sulfur extrusion reactions are possible while leaving the basic hydrocarbon skeleton of the molecule intact and thereby preserving the calorific content of the coal.
Direct excitation of molecular oxygen in solution by absorption of radiation may produce singlet oxygen (10) or ozone which are highly reactive species. In sensitization, organic molecules such as those present in the coal organic matrix, may absorb a visible frequency photon which promotes an electron from the singlet ground state to a short-lived excited triplet state (30). If a suitable acceptor molecule is present within range, such as oxygen, the absorbed energy is transferred to the acceptor. This produces a chemically reactive species with wavelengths of light much longer than those required for direct excitation of the acceptor.

A process of heterogeneous photocatalysis occurs when semiconductor particles are illuminated (82). In this case, oxidation and reduction occur simultaneously at the semiconductor photoelectrode surface as shown in Figure 7 (83). Oxidation of the chemical species may occur by contacting the holes \((h^+)\) produced on the n-type semiconductor surface. Oxygen reduction occurs on the semiconductor surface to form highly reactive species such as \(H_2O_2, \cdot OH,\) and \(\cdot HO_2\), which, in turn, may oxidize the sulfur species (84, 85). An example illustrating this process is the oxidation of sulfite by ZnO irradiated at the band gap wavelength or shorter (6):
<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Average Bond Energy (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C - H</td>
<td>96 - 99</td>
</tr>
<tr>
<td>S - H</td>
<td>82</td>
</tr>
<tr>
<td>C - C</td>
<td>83 - 85</td>
</tr>
<tr>
<td>C - S</td>
<td>66</td>
</tr>
<tr>
<td>C - O</td>
<td>85 - 91</td>
</tr>
<tr>
<td>C = O</td>
<td>173 - 181</td>
</tr>
<tr>
<td>C - N</td>
<td>69 - 75</td>
</tr>
</tbody>
</table>
Figure 7. Semiconductor Heterogeneous Photocatalysis (83).
(ZnO) + hv \rightarrow (ZnO) + h^+ + e \tag{68}

1/2\text{SO}_3^{2-} + 1/2\text{H}_2\text{O} + h^+ \rightarrow 1/2\text{SO}_4^{2-} + \text{H}^+ \tag{69}

1/2\text{O}_2 + \text{H}^+ + e \rightarrow 1/2\text{H}_2\text{O}_2 \tag{70}

1/2\text{H}_2\text{O}_2 + 1/2\text{SO}_3^{2-} \rightarrow 1/2\text{SO}_4^{2-} + 1/2\text{H}_2\text{O} \tag{71}

\[ \text{hv} + 1/2\text{SO}_3^{2-} + 1/2\text{O}_2 \rightarrow 1/2\text{SO}_4^{2-}. \tag{72} \]

A similar process is discussed by Adamson (85, 86) for titanium dioxide:

\[(\text{TiO}_2) + \text{hv} \rightarrow \text{e} + \text{h}^+ \tag{73}\]

\[\text{H}_2\text{O} + \text{h}^+ \rightarrow \cdot\text{OH} + \text{H}^+ \tag{74}\]

\[\text{H}^+ + \text{e} \rightarrow \cdot\text{H} \tag{75}\]

\[\text{O}_2 + \text{e} \rightarrow \cdot\text{O}_2^- \rightarrow \cdot\text{HO}_2^- \tag{76}\]

\[\text{HO}_2^- \rightarrow \text{h}^+ \rightarrow \cdot\text{HO}_2 \tag{77}\]

\[2 \cdot\text{HO}_2^- \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{OH}^- + \text{O}_2 \tag{78}\]

\[\text{RH} + \cdot\text{OH} (\text{or} \cdot\text{HO}_2) \rightarrow \text{ROH} + \cdot\text{H} \tag{79}\]

\[\text{RH} + \text{h}^+ \rightarrow \text{RH}^+ \rightarrow \text{RH}^{2+} \tag{80}\]

Platinized titanium dioxide particles have been reported to increase the rate of cyanide oxidation by a factor of 500 times when compared to the rate of semiconductor
photoelectrochemical catalysis with unplatinized anatase particles (84). The following mechanism is proposed:

\[ \text{TiO}_2 + 2hv = 2e + 2h^+ \] \hspace{1cm} [81]

\[ \text{CN}^- + 2\text{OH}^- + 2h^+ = \text{CNO}^- + \text{H}_2\text{O} \] \hspace{1cm} [82]

with simultaneous reduction of oxygen on dark surface:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e = 4\text{OH}^- \] \hspace{1cm} [83]
or

\[ \text{O}_2 + 2\text{H}_2\text{O} + 2e = \text{H}_2\text{O}_2 + 2\text{OH}^- \] \hspace{1cm} [84]

More recent experimental results indicate pure TiO\textsubscript{2} probably does not produce hydrogen peroxide when irradiated, while ZnO with acetate produces measurable hydrogen peroxide in a 10% quantum yield (87, 88).

**Radiation Chemistry of Coal**

The radiation chemistry of coal has been extensively studied. An early investigation by Weinstein (89) examined the radiation chemistry of coal in various atmospheres. In these experiments, dry coal was sealed in cadmium-shielded vessels in the presence of oxygen, ammonia, nitrogen or air. The samples were then subjected to gamma and fast-neutron radiation in a nuclear reactor. Hydrogen, methane and possibly ethane were determined to be products of radiolysis. Radiation increased the
oxidation rate of some coals in oxidizing atmospheres. This increase in oxidation was attributed to the formation of oxygen atoms or ozone during irradiation. Related studies by Mead (90), Petrenko (91), Golovina et al. (92), Roy (43), Smutkkins (94), and Rayk (95) reported significant property changes in coal by exposure to energetic and ionizing radiation. Tripathi et al. (96) report up to 68.4% oxidative desulfurization of an Indian coal in acidic aqueous slurry when exposed to gamma rays from a Co$_{60}$ source.

A patent by Zavitsanos et al. (97) describes a process for coal desulfurization by microwaves in the 2.45 GHz range. In this process, moist coal is irradiated in air producing a 53.5% decrease in sulfur content. Later research showed that up to 80-90% desulfurization of coal could be accomplished with microwaves and NaOH (98, 99). Similar work by Yanagisawa (100) was less promising with only 5-15% sulfur removal occurring in an inert gas with microwave irradiation.

Sato et al. (101) reported on platinized titania-catalyzed production of hydrogen and carbon dioxide from Texas lignite and water during irradiation with ultraviolet light at 23°C. In a related study, Hashimoto et al. (102) investigated the semiconductor photocatalyzed oxidations of aliphatic and aromatic compounds, as well as
coal. Hydrogen and carbon dioxide were produced very early in the irradiation of model compounds and coal. The authors suggest direct oxidation of benzene by photo-generated holes and associated ring openings. They reported oxidation of benzene mainly to CO₂ and production of several other minor products.

Hayatsu et al. (103) performed ultraviolet photo-chemical oxidation of DBT in aqueous HCl solution with air. The radiation source was a high-pressure mercury vapor lamp. They reported a 57 ± 10% conversion of DBT. Styrene and thiophenol were the major oxidation products identified.

Coal desulfurization by photo-oxidation has been performed by Mathur et al. (104, 105). Finely-ground Illinois No. 6 coal was subjected to methylene blue sensitized photo-oxidation in 95% ethanol with O₂ bubbling. A xenon mercury lamp was the radiation source. After dye removal and drying, the photooxidized coal was hydrolyzed by water, acid or base. After the hydrolysis procedures, increased process efficiencies due to irradiation were 7.4, 3.4 and 23.7% respectively.

The second paper by Mathur et al. (105) investigated the effects of wavelength, solvent and sensitizer dye. In these experiments coal suspended in water, in 1 N sodium
hydroxide or 95% ethanol, was exposed to xenon light (800 watts) for four hours. The improvements in coal desulfurization were shown to be 16.5, 22.5 and 20.5%, respectively. Up to 42% maximum total desulfurization was achieved in 16 hours of irradiation in ethanolic slurry. The application of 254 nm wavelength light demonstrated an efficiency improvement of 35% versus 23% at 300-600 nm. The organic sensitizer dye was shown to have no significant effect on coal desulfurization efficiency.

In a patent by Soundararajan (106), a semiconductor photocatalyzed coal desulfurization process is described. In this process, crushed coal from 1 inch to 0.5 inches in diameter was exposed to radiation in an alkaline aqueous suspension with a photoelectric catalyst. The radiation sources for these experiments were Co57 yielding gamma radiation at 0.01 to 0.1 nm, or various lasers emitting radiation from 450-650 nm. The preferred catalyst was a combination of indium oxide and tin oxide, while reduced silicon dioxide was also suitable. A photocatalyzed free radical-type mechanism was proposed as shown in Figure 8. Greater than 92% of the total sulfur of a coal was claimed to be removed by the method of the invention. Elemental sulfur was reported to be a product of the reaction.
Figure 8. Proposed Semiconductor Photoelectrochemical Desulfurization of Coal Mechanism (106).
Review of Related Chemical Coal Desulfurization Processes

Halogenation

In an early paper by Moschopedis et al. (107) the halogenation of coal and humic acids is described. Chlorine or bromine was added to an aqueous coal slurry or humic acids. Addition of chlorine or bromine reactions were performed in the dark, in ultraviolet light, or in diffuse visible light. Halogenation rapidly proceeded with an introduction of the halogen to the coal. The resulting product was up to 25% halogen by weight in only 30 minutes of reaction time. Marked changes were observed in the infrared spectra of humic acids. Halogenation reduced the 1600 cm\(^{-1}\) band; while new bands appeared at 1640 cm\(^{-1}\) and in the 2850-3000 cm\(^{-1}\). No desulfurization results were reported. In related work by Tyutyunnikov, et al. (108) the chlorination of coals in aqueous suspension for 100 hours at 98°C produced 22.3% or 15.9% chlorine product. Chlorination increased the coal solubility in organic solvents. Honda et al. (109) reported that chlorination of low rank coals is accompanied by oxidation, and solvent solubility after halogenation is a function of coal rank.

Coal desulfurization by chlorination at room temperature was reported by Mukai et al. (110). The treatment
considerably reduced the sulfur content of the coals tested, but had a deleterious effect upon caking properties. Coal desulfurization by chlorinolysis at 74°C in methyl chloroform and at atmospheric pressure was studied by Hsu et al. (111). This method removed <70% of the organic sulfur and <90% of the pyritic sulfur. Up to 76% total rejection was obtained. After treatment, dechlorination of the coal product was obtained by steam. Later, Kalvinskas, Hsu and others (112, 114), coined the phrase: JPL coal desulfurization process and reported the desulfurization results for numerous coals of various ranks and presented plans for pilot plant equipment. Hsu et al. (115) were granted a patent on the process in 1978, (i.e. U.S. Patent 4,081,250). In a closely related patent by Kalvinskas et al. (116) coal desulfurization of aqueous slurries with chlorine gas was described, U.S. Patent 4,325,707, with up to about 50% sulfur rejection claimed.

Iron pyrite was oxidized by chlorine in aqueous and organic slurries by Vasilakos et al. (117). The reaction was mass transfer limited in organic solvents due to the low solubility of the products. The reaction in water was quantitative, could be described by first order kinetics, highly exothermic, and had a low activation energy of only 26.7 KJ Mole⁻¹.
Alcohol Treatment

The desulfurization of coal by alcohols grew out of work which was first directed towards the conversion of coals to liquid products. An early paper by Whitehead et al. (118) described the supercritical extraction of coal by coal tar or petroleum naptha fractions. Tugrul et al. (119) presented data obtained from supercritical gas extraction of lignite. This method extracted about 24% of the coal mass at completion. Extract analysis indicated numerous paraffins, alkanes, phenols, and oxygenated hydrocarbons. Slomka et al. (120) examined the extraction of high volatile bituminous coal by toluene. Kinetic analysis of the data indicated a good fit with the second order rate equation. A pilot plant study of supercritical toluene extraction by Maddocks, et al (121) reported efforts directed towards the optimization of coal liquefaction.

Supercritical extraction of coal by alcoholic solvents has also been reported. Makabe et al. (122) investigated the extraction of coal with ethanol-sodium hydroxide solutions to maximize extraction yield, without any sulfur data being reported. Gardner et al. (123) reported the reaction of methanol with a low volatile bituminous coal at high temperatures to produce coal gasification.
Apparently, the first reference to coal desulfurization by supercritical alcoholic solution was reported by Amestica et al. (124). They compared results obtained by toluene and ethanol extraction. Only a small percentage of sulfur was claimed to be removed. Later, Chen, Muchmore et al. (125-128) published a series of papers which indicated high organic sulfur removal was possible with supercritical alcohol reactions. The pretreatment of the coal with an alkali metal hydroxide or by adding the strong base to the alcohol during the reaction was demonstrated to have a strong beneficial effect in sulfur rejection. Generally, these experiments were conducted in a stirred autoclave at 250-350°C and pressures from 1750 psia to 4000 psia. Ethanol and methanol were both effective, with the latter demonstrating superiority as a desulfurization reagent. The authors speculate that the strong base may promote depolymerization of the coal matrix and thereby improve reagent access to the sites of sulfur compounds. This depolymerization would allow a greater efficiency in the extraction and conversion of the organosulfur compounds. This approach produces about 50% total sulfur reduction.

As briefly discussed in a preceding section, two very pertinent papers on photochemical coal desulfurization were written by Mathur et al. (104, 105). The initial
approach was quite interesting. First, finely ground coal was placed in 95% ethanol solution with methylene blue, a well known sensitizing dye. The resulting slurry was sparged with oxygen and exposed to radiation of wavelengths 300-600 nm from a xenon mercury lamp. Irradiation proceeded 10-16 hours and the resulting coal products were then subjected to hydrolysis by refluxing water, in hydrochloric acid, or in sodium hydroxide. Improvements over the dark reaction by irradiation were reported to be 7.4, 3.4, and 23.7%, respectively. The best total desulfurization result was 27.8%, which followed alkaline hydrolysis. Oxidation of organic sulfur moieties such as sulfide and thiol to sulfoxides, sulfones, and sulfonic acids is proposed. Resulting functional groups would then be subject to subsequent hydrolysis. A strong base would eliminate sulfonic acid from the sulfones and with greater difficulty from the sulfoxides. Pyritic sulfur was most likely affected by the hydrolysis procedure; while photolysis, under the conditions of these experiments, may not have any significant effect.

A second paper by Mathur (105) investigated the effects of radiation wavelength, solvent, and the presence or absence of the sensitizer methylene blue, on the efficiency of photochemical desulfurization of coal. In these experiments coal was suspended in water, in sodium
hydroxide, or 95% ethanol and exposed to xenon light (800 watts) for 4 hours. The improvements due to irradiation were observed to be 16.5, 22.5, and 20.5% respectively. In other experiments up to 41.9% maximum desulfurization was achieved in irradiated ethanolic slurry after 16 hours reaction time. The "photonic advantage" resulting when coal was irradiated with 254 nm light was 35% versus the result obtained at 300-600 nm which demonstrated a 23% photonic advantage. The sensitizer dye was shown to have no effect upon the efficiency of alcoholic photochemical desulfurization of coal.

**Oxidation of Coal**

Numerous papers have been published on the oxidation of coal. At the turn of the century oxidation of coal by air and oxidizing agents in the presence heat or alkalis and acids was examined (129-132). These early reports focused on the deleterious changes in coking properties and the formation of humic acids as a function of oxidation under various conditions. Later studies considered the kinetics of oxidation, more detailed molecular analysis of the oxidation products, and oxidation under high pressures and temperatures (133-163). Important observations contained in these papers include:
i) Coal oxidation yields innumerable aliphatic and aromatic products, many which contain hydroxyl or carboxylic acid functional groups or both.

ii) Reactivity of coal towards oxidation decreases with increasing rank.

iii) Accessibility of coal internal surface is an oxidation rate limiting constraint.

iv) Accessibility of internal coal surfaces decreases with increasing alkaline oxidation, which may be due to pore clogging by humic substances. These authors were concerned with illucidation of natural coal oxidation processes, coal geogenesis, and coal coking property decreases which occur as a result of coal storage and handling. They were not concerned with the development of coal desulfurization processes.

In an early investigation by Grunert in 1929 (164) the desulfurization of coal by high temperature steam was examined. Grunert proposed that iron pyrite reacts with steam and the pyritic sulfur is thereby converted to $\text{SO}_2$ and $\text{H}_2\text{S}$. The reaction was somewhat inhibited by the formation of a protective layer of inert iron oxide on the mineral surface.
In 1933, Nelson et al. (165) studied the oxidation of pyritic sulfur in bituminous coal. An Illinois bituminous coal assaying 17.6% ash, 0.94% sulfate sulfur, 2.58% pyritic sulfur, and 2.51% organic sulfur was used in these experiments. In the first series of experiments the coal crushed to 80.9% passing 100 mesh and suspended in an aerated aqueous slurry at 22°, 50°, 70°, and 90° for 1 to 7 days. The amount of pyritic sulfur oxidized varied from 6.7 to 79.0%, with the best result occurring at 7 days with the highest temperature. Efficiency of desulfurization improved with increasing temperature, while increasing aeration rate or the use of pure oxygen instead of air showed no effect. Effects of particle size was evaluated in the next series of experiments. Coal screened to 20-60, 60-100, 100-140, 140-200, and 200 x 0 mesh sizes and subjected to aerial oxidation for 24 hours at 50°C. Results indicated an increasing rate of desulfurization with decreasing coal particle size. The amount of pyritic sulfur oxidized was close to being inversely proportional to the mean diameter of the coal particles. An addition of ferric sulfate increased the rate of desulfurization and the effect improved with increasing temperature from 22° to 70°C. Application of chlorine gas to the coal slurry produced large amounts of desulfurization, and the efficiency of desulfurization decreased with increasing temperatures. Organic sulfur
content of this coal was largely unaffected by the application of any of these processes.

In experiments similar to Nelson (165), Teichmann (166) studied the oxidation of pyrite, coal, and coal-pyrite mixtures. These experiments were performed at elevated temperatures and in aerated aqueous slurries. The results indicated the oxidation rate of pure pyrites is considerably less than the case when the pyrites are mixed with coal. The addition of ferric chloride increased the oxidation of pyrites and produced sulfuric acid.

In an important series of reports, the great Soviet coal scientist, A.Z. Yurovskii, discussed several coal desulfurization processes (44, 167-169). In 1939, he reported laboratory and pilot plant experiments of steam-air treatments of coal at 350°C (167). This process produced 60-80% desulfurization with insignificant losses of heating values. However, significant decreases in coking properties were observed. In a second paper (168) it was noted that water instead of steam may be advantageously employed for the desulfurization of semi-coke and coke. Later, air-steam treatment was used to form pyrrhotite and iron oxide films on the surface of pyrite minerals which were liberated from the coal by grinding (169). The resulting films were magnetic and the pyritic sulfur was then removed from the coal by magnetic
separation. In the classic text, "Sulfur in Coal", Yurovskii (44) reports numerous chemical processes for coal desulfurization. Among these are ferric ion oxidation which produces significant desulfurization and ash rejection. Also an interesting radiochemical sorting technique is discussed. The radiochemical sorting technique employs the different permeabilities of hydrocarbon and gangue components of coal to automatically differentiate between the two so they may be mechanically separated by robotic sorting.

The use of molten alkali metal hydroxides and other compounds for the desulfurization of carbonaceous materials such as coal, char, coke, or petroleum was patented by Murphy in 1968, with the initial application occurring in 1965 (170). In his process a fluidized bed of molten alkali metal hydroxide, oxide, carbide, carbonate, or hydride is operated at 500-850°C. During treatment many sulfur compounds were volatilized or rendered soluble in water. Introduction of intermittent steam enhanced desulfurization and water washing of the product following treatment removed most of the rest of the sulfur. This process resulted in a 35-50% decrease of sulfur in the carbonaceous materials tested. Also in 1965, Masciantonio (30) reported a similar process using 1:1 NaOH/KOH at 250°C or higher to produce nearly complete pyritic sulfur
removal in five minutes. Markyszewski et al. (171) state that Masciantonio discovered the molten caustic process, however, they do not cite the Murphy patent or application, and were therefore apparently unaware of this prior claim. A very similar process was resurrected by Meyers in 1981 (31) under the name of "Gravimelt Process". A flurry of activity in several laboratories was initiated to determine process characteristics (172-182). Organic sulfur was observed to be reduced by 70-80% from coals by the application of the method. The molten caustic process is very efficient in the removal of ash and sulfur from coals, and has been very extensively studied. However, the problem of excessive processing cost has not been satisfactorily solved.

German research in World War II (183) was directed towards the production of a low ash product suitable for conversion to electrode carbon by hot aqueous caustic solutions. However, the discovery of aqueous caustic treatment as a coal desulfurization technique is attributed to Reggel et al. (29, 184). Reggel et al. reported desulfurization of coals with a 10% sodium hydroxide solution. They found most pyritic sulfur could be removed by this approach while organic sulfur was not attacked and occasional erratic increases in organic sulfur were found. About 45-95% pyritic sulfur rejection from Illinois #6
coals were obtained with an average yield of 91.5% (moisture and ash free, maf, basis). After caustic treatment, acidic extraction was performed with carbon dioxide, hydrochloric acid, sulfur dioxide, or sulfuric acid. A large percentage of the ash was removed from the coal by the acidification. One result with an Illinois #6 coal initially containing 9.8% ash indicated the ash content was reduced to 0.7% after acidification. These aqueous alkali experiments were conducted at temperatures ranging from 175° to 350°C, with most performed at 225°C. Optimum reaction times vary from coal to coal but 0.25 to 6 hours was generally sufficient. The reaction may be carried out in autoclaves, which can be stirred or rocked.

The method of Reggel et al. (184) employed inert gas atmospheres in the reaction vessel. Longanbach, working for Occidental Petroleum Corp., discovered that the addition of oxygen containing gas to hot aqueous caustic solutions greatly improved the desulfurization of carbonaceous materials (185). A U.S. patent was issued on the process in 1977. In this procedure, pulverized coal and aqueous alkali slurry is placed in an autoclave at temperatures ranging from 200° to 1600°F for 1 to 300 minutes. Oxygen was introduced at 800 psig. A ten minute treatment of a Hamilton high volatile bituminous coal, with an initial sulfur content of 2.63%, produced a 96%
sulfur reduction. However, the dry weight recovery was only 48.85% of the original coal weight (136).

A substantially similar process was invented by Stambaugh and Sachsel (187-191, 22, 6), which became known as the "Battelle Hydrothermal Process". The procedure is claimed to remove a substantial portion of the sulfate, pyritic, and organic sulfur and ash found in coals and cokes. It comprises mixing the carbonaceous material with an aqueous solution containing sodium, calcium, or ammonium carbonate, hydroxide, sulfide, or hydrosulfide, or a combination of the preceding, and heating the resulting mixture under increased pressure to leach out sulfur compounds and ash. The resulting product is then washed with water. For example, an Ohio coal (-200 mesh) treated at 250°C for two hours showed about 50% of the organic sulfur, 100% of the pyritic sulfur, and 70% of the sulfate sulfur were removed. The principal desulfurization reactions are proposed to be of the following types:

\[
8\text{FeS}_2 + 30\text{NaOH} \rightarrow 4\text{Fe}_2\text{O}_3 + 14\text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3 + 15\text{H}_2\text{O} \tag{85}
\]

\[
\begin{array}{c}
\text{g}
\end{array}
\quad + 2\text{NaOH} \rightarrow \begin{array}{c}
\text{s}
\end{array}
\quad + \text{Na}_2\text{S} + \text{H}_2\text{O} \tag{86}
\]

Similar reactions are also believed to be operating in the molten alkali leaching process.
Numerous oxydesulfurization processes have been reported in the literature. In general, these methods employ oxygen or air in aqueous solution at elevated temperature and pressure. Major processes include the Ledgemont Oxygen Leaching (LOL) process (26, 192-194), the Promoted Oxydesulfurization process (195-197), the Pittsburgh Energy Technology Center (PETC) oxydesulfurization process (25, 198, 199) and the Ames process (200-204). The fundamental desulfurization principle is dependent upon the oxidation of pyrite by dissolved oxygen and the formation of soluble sulfate products which can be readily separated from coal. This reaction scheme is given by the following equations:

\[ \text{2FeS}_2 + 7O_2 + H_2O \rightarrow \text{2FeSO}_4 + 2H_2SO_4 \]  \[ \text{87} \]

\[ \text{4FeSO}_4 + O_2 + 2H_2SO_4 \rightarrow \text{2Fe}_2(\text{SO}_4)_3 + 2H_2O \]  \[ \text{88} \]

\[ \text{Fe}_2(\text{SO}_4)_3 + 3H_2O \rightarrow \text{Fe}_2O_3 + 3H_2SO_4 \]  \[ \text{89} \]

Claims of limited organic sulfur removal have also been made.

In the LOL process (26, 192-194) comminuted coal is treated with dissolved oxygen in aqueous slurry under 10-20 atmospheres pressure at 130°C for 1-2 hours. The treatment is conducted under mildly acidic conditions or alkaline conditions. The alkaline condition produced by
the addition of 1-3 M ammonium hydroxide. Greater than 90% pyritic sulfur rejection can be achieved in 2 hours of treatment with low to high rank coals. Up to 99% pyritic sulfur removal has been reported from Illinois #6 coal in 2 hours of treatment. No organic sulfur was removed under mildly acidic conditions. However, approximately 80-85% of the pyritic and 30-40% of the organic sulfur are removed from certain coals under alkaline conditions. The reaction of pyrite with ammonia and oxygen is as follows:

\[ \text{FeS}_2 + 4\text{NH}_3 + \frac{7}{2} \text{H}_2\text{O} + \frac{15}{4} \text{O}_2 \rightarrow 2(\text{NH}_4)_2\text{SO}_4 + \text{Fe(OH)}_3 \] [90]

Unfortunately, higher heating value losses occur under alkaline conditions when compared to acidic treatment conditions. Efficiency of pyritic sulfur removal is apparently independent of rank, while oxygen uptake is a function of rank. In general, higher rank coals take up less oxygen than lower rank coals. Elemental sulfur is not believed to be a product of this treatment process.

The Promoted Oxydesulfurization process (195-197) is closely related to the LOL process. It uses oxygen at 20 atmospheres in acidic slurry at 120°C for one hour. The primary difference in the two processes is an iron complexing reagent such as oxalic acid or a salt of oxalic acid is added to promote the reaction. In the case of the
Promoted Oxydesulfurization process nearly complete pyritic sulfur, 94% iron, and 50% ash removal may be achieved by the process. Up to 35% organic sulfur removal can be obtained when the slurry is heated to 350°C for one hour.

The PETC Oxydesulfurization process (25, 198, 199) differs from the LOL process by the use of air and more severe conditions. Higher temperatures, 180-200°C, and higher pressures, 34-68 atmospheres, are employed. Under these more rigorous conditions, desulfurization is quite rapid. Nearly complete pyritic sulfur removal occurs, by conversion to sulfuric acid in an hour or less. Up to 40% organic sulfur removal was reported with certain coals. Heating value losses were usually less than 10% ash rejection was as high as 20%. However, coking values are lost by this severe oxidation treatment.

The Ames process (200-204) is performed in a similar manner. Alkaline solutions of 0.2 M sodium carbonate are utilized at 150°C and oxygen at 14 atmospheres. Up to 95% pyritic sulfur can be removed from certain coals in one hour of treatment. Organic sulfur removal varies with each coal, but up to 50% removal can be obtained if a second treatment is performed under nitrogen atmosphere at 240°C or higher. Only thiols and benzylic sulfides are reported to be converted to sulfonates. Thiophenes and sulfides are reportedly resistant. The pyritic sulfur is
removed as the sulfate, which leaves a residue of hematite (Fe₂O₃). The rate of pyritic sulfur removal is mass transfer controlled, i.e., limited by the diffusion of dissolved oxygen through the shell of hematite which develops around the core of unreacted pyrite.
CHAPTER 4

PHOTOCHEMICAL DESULFURIZATION

METHODS AND MATERIALS

Equipment

Coals used in these experiments were ground in a hammer mill and then wet screened to the desired particle size, or hammer milled coals were reground in a stirred ball mill with 1/16" stainless steel balls at 500 rpm with the mill jacket cooled by circulating tap water to produce micronized coals. The resulting particle size of micronized coals were determined by an Elzone analyzer. Sulfur contents were analysed by the Leco and ASTM D2492 methods. Heating value of coals were determined by a Leco AC-300 automatic bomb calorimeter.

Infrared spectra were obtained using a Perkin Elmer 1710 Fourier Transform Infrared (FT-IR) spectrophotometer using a Mercuric Cadmium Telluride (MCT) detector. The Attenuated Total Reflectance (ATR) method was employed with a KRS-5 (Thallium Iodide Bromide) internal reflection element.
A Cambridge Instruments 120 Scanning Electron Microscope (SEM) was used to examine coals for morphological changes. The instrument was equipped with a Kevex Energy Dispersive X-ray Microanalysis (EDAX) analyzer to determine elemental composition.

Photochemical experiments were performed in a custom made photochemical reaction assembly as displayed in Figure 9. The radiation source was an Ace-Hanovia medium pressure mercury vapor lamp with spectral characteristics given in Table 6. Filtered light experiments were conducted with a Corning No. 7740 (Chemical Pyrex) glass sleeve which covered the lamp. The transmission characteristics of this filter are shown in Figure 10.

Gas chromatography for kinetics experiments was performed with a Tracor 560 operated under the following conditions: oven temperature 200°C isothermal; carrier gas = \( N_2 \) at 1.5 setting; detector temperature = 250°C; injector temperature = 225°C; column = 2m, 4mm I.D., packed glass column (5% SP-2100 100/120 Supelcoport); and detector - Flame Ionization with air at 300 ml/min and hydrogen at 30 ml/ min. DBT was extracted from reaction mixtures by iso-octane. The emulsion resulting from the iso-octane extraction was very stable and was broken by centrifugation at 20000 rpm at 25°C for 15 minutes.
Figure 9. Simplified Schematic of the Photochemical Reaction Assembly.
<table>
<thead>
<tr>
<th>Far U.V.</th>
<th>Middle U.V.</th>
<th>Near U.V.</th>
</tr>
</thead>
<tbody>
<tr>
<td>220-280nm</td>
<td>280-320nm</td>
<td>320-400nm</td>
</tr>
<tr>
<td>27.0 w</td>
<td>28.7 w</td>
<td>28.0 w</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Visible</th>
<th>Infrared</th>
<th>Total Radiated Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>400-600nm</td>
<td>1000-14000nm</td>
<td>175.8 w</td>
</tr>
<tr>
<td>75.7 w</td>
<td>16.4 w</td>
<td>175.8 w</td>
</tr>
</tbody>
</table>
Figure 10. Transmission Characteristics of the Corning No. 7740 (Pyrex) Glass Filter.
Gas chromatography/mass spectroscopy for product identification was performed in the biochemistry department of Virginia Tech. Products were extracted with methylene chloride and concentrated by evaporation at room temperature under a stream of nitrogen.

Zinc oxide, bromine, iodine, ethanol, and toluene employed in the experiments were the Fisher products. Titanium dioxide was Degussa P-25, anatase with a particle size of 0.015-0.040 μm and a surface area of 50± 15 m²/g. Zinc oxide and titanium dioxide are n-type semiconductors, with bandgap widths of 3.2 eV and 3.0 eV (300K) for ZnO and TiO₂ respectively.

Typical Experimental Procedure

Coals, typically run-of-mine (ROM), were stored in a freezer at -10°C. A sample of this coal was obtained by cone and quarter, and riffled to minimize bias. Resulting representative samples were hammer-milled to approximately 75 μm mean size and then ground in a stirred ball mill for the time required to produce the desired particle size. Ball mill grinding times ranged from 15 minutes to more than one hour. Resulting coals were preliminarily dewatered by vacuum filtration and then oven or vacuum dried. Dry products were then stored in a freezer for subsequent use.
A coal sample was mixed in a beaker with water, catalysts, or other chemicals as desired, to form a slurry by mechanical agitation. The resulting slurry was then pH adjusted by the addition of hydrochloric acid, sodium hydroxide, or potassium hydroxide. The finished slurry was then poured into the outer water jacketed vessel of the photochemical reaction assembly, see Figure 9. Water flowing through the jacket was heated or cooled by the circulating water bath to maintain the desired solution temperature, while cool tap water constantly bathed the quartz glass inner lamp jacket to dissipate the heat generated by the operation of the medium-pressure mercury vapor lamp. A quartz glass inner lamp jacket was then inserted into the outer water jacketed vessel. Stirring was maintained by a teflon coated stir-bar driven by a stirring plate located beneath the reaction assembly. A stir-bar was generally rotated at approximately 300 rpm as determined by tachometer. A thermometer and gas sparging tube were then inserted. The exterior of the vessel was covered with aluminum foil to prevent visual impairment and burns by radiation leakage from the reaction assembly, as well as the reflection of light back into the vessel. Gas flow rates were adjusted with a calibrated flowmeter, and when the solution temperature was at the desired level the current to the lamp was initiated. Approximately ten minutes of operating time was required for the lamp to
develop full brightness. With rapid model compound kinetics, this variable output in the first minutes of operation presented a difficulty. This problem was resolved by starting the lamp at least 15 minutes before insertion into a model compound solution, while carefully shielding the quartz glass inner lamp jacket with foil to prevent injury until insertion. Timing of an experiment began with starting of the lamp or insertion of the lamp assembly.

Upon irradiation of a coal slurry for a desired time, the lamp was switched off and the contents of the outer water jacketed vessel were recovered by wet screening (for large particles, i.e. >500 mesh) or filtration (for small particles, i.e. <500 mesh). The coal products were frequently washed with one part HCl plus 3 parts H₂O solutions, to remove soluble sulfates, for 20 minutes at room temperature, filtered while washing with distilled water, and dried. After drying the coal products were often extracted with hot toluene, ~97°C, held constant by a boiling water bath; and filtered again while rinsing with fresh toluene. The resulting coal product was oven dried, and typically assayed for sulfur, ash, and/or caloric contents.
Sulfur Analysis

Total sulfur contents of feed and product coals were determined by the Leco method. In this method the coal is burned at 2700°F in a ceramic vessel atmosphere. Resulting gases are dried and then passed through an infra-red detector. The quantity of sulfur oxides thus determined resulting from the combustion of a known amount of coal is used to calculate the total sulfur content.

Sulfur forms analysis were conducted in accordance with the American Society of Testing and Materials Standard (ASTM D 2492). This procedure employs the so called "Difference Method."

ASTM D 2492 uses extraction of the sulfate sulfur from coal with dilute hydrochloric acid. Sulfate thus extracted is then precipitated as the insoluble barium salt which is then determined gravimetrically. Pyrite and organic sulfur is unaffected by dilute hydrochloric acid.

Coal residue resulting from sulfate analysis is then extracted with hot, diluted nitric acid which completely oxidizes the pyrite liberating the iron as the ferric ion. Iron concentrations can then be determined by titration or atomic absorption spectrophotometry. The pyrite content is then back calculated based upon the knowledge of pyrite stoichiometry.
Organic sulfur content may then be calculated by the "Difference method." The formula is as follows:

\[
\text{Organic Sulfur} = \text{Total Sulfur} - (\text{sulfate sulfur} + \text{pyritic sulfur}).
\]

[91]

No standard method is presently available for the determination of elemental sulfur in coal.

**Isolation and Identification of DBT Oxidation Products**

Slurries of DBT crystals (0.1g/700 ml water) were suspended in DBT saturated solutions. Various other experimental conditions used for the preceding kinetics experiments were utilized, i.e. results displayed in Figure 30, with the exception of reaction time which was lengthened to one hour. After the reactions in darkness, U.V. light, U.V. and TiO₂, and U.V. and ZnO; the remaining DBT and catalysts (if any) were removed by filtration through borosilicate glass. Resulting filtrates were exhaustively extracted with 10 ml of methylene chloride in a separatory funnel, without grease in the fittings. Methylene chloride extracts were evaporated to a small volume under a stream of nitrogen at room temperature. Extracts were then analysed using the GC/MS facilities in the Virginia Tech Biochemistry Department with the equipment set at the highest sensitivity. In addition to the reaction product extracts, DBT in methylene chloride and
methylene chloride alone were also analysed. The high purity methylene chloride solvent showed no contamination which would interfere with reaction product identification.
CHAPTER 5

PHOTOCHEMICAL DESULFURIZATION

RESULTS AND DISCUSSION

In this section the results of the survey of several photochemical desulfurization processes will be presented and discussed. Methods to be considered include halogenation, alcoholic reduction, dye-sensitized oxidation, and semiconductor catalysed photo-oxidation. Data obtained from the processing of various coals from sub-bituminous to bituminous in rank will be presented. Kinetic studies with the model compound dibenzothiophene (DBT) were performed utilizing the alcoholic reduction, dye-sensitized photo-oxidation, and semiconductor catalysed photo-oxidation methods. Reaction products resulting from alcoholic reduction and semiconductor catalysed photo-oxidation were determined by gas chromatography and mass spectroscopy.

Inorganic chemical and morphological changes were determined for certain coal reaction products by SEM and EDAX. Organic chemical changes for some coal products were determined by infrared spectroscopy.
Proposed chemical mechanisms shall be presented for each of the photochemical desulfurization procedures. Flowcharts utilizing these desulfurization procedures in potential industrial applications will be given at the end of each section.

COAL DESULFURIZATION BY PHOTOCHEMICAL HALOGENATION

A halogen may form a highly reactive radical by the addition of heat or light as follows:

\[
X_2 \xrightarrow{U.V. \text{ or } 250^\circ-400^\circ} 2X^* \tag{92}
\]

The radicals thus formed readily participate in electrophilic reactions. The order of reactivity of the halogens is \(F_2 > Cl_2 > Br_2 > I_2\). For example, bromine is only 1/250,000 as reactive towards methane as chlorine. A general observation concerning selectivity is: "In a set of similar reactions, the less reactive the reagent, the more selective it is in its attack" (205). It might reasonably be expected that bromine would show much greater selectivity in reactivity with coal components than chlorine which has been typically used in previous coal desulfurization by halogenation experiments. Desulfurization by the JPL halogenation process results in large chlorine content (23-26% chlorine by weight) in the product coals, (111)
chlorination in aqueous media at room temperatures resulted in low sulfur removal efficiencies, and (110) high temperature gas phase chlorination resulted in both inorganic and organic sulfur rejection but at a 20% caloric content decrease (206, 207).

Upon consideration of the results of these previous coal desulfurization processes, a group of experiments were performed with the less reactive and presumably more selective bromine and iodine reagents in aqueous solution. In lieu of operating at elevated temperatures, ultraviolet light was applied to the reaction vessel to promote the formation of free radicals, in an inert nitrogen atmosphere. Temperatures were maintained near ambient.

Representative results of the photochemical free-radical halogenation of Illinois #6 and Pittsburgh #8 bituminous coals at 40°C are displayed in Table 7. Coals which had been subjected to various chemical and physical pre-cleaning procedures still responded favorably to photochemical halogenation. The sulfur forms analysis results with Illinois #6 and Pittsburgh #8 coals indicates significant reductions in organic sulfur. The test result with Illinois #6 shows iodine to be a less powerful desulfurization reagent than bromine.
Table 7. Representative Results of Coal Desulfurization by Photochemical Free-Radical Halogenation

<table>
<thead>
<tr>
<th>Amount Processed (grams)</th>
<th>Particle Size (μm)</th>
<th>Reaction Time (hrs)</th>
<th>Halogen</th>
<th>Initial Sulfur Content (%)</th>
<th>Product Sulfur Content (%)</th>
<th>Total Sulfur Removal Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Total</td>
<td>Pyritic</td>
<td>Organic</td>
</tr>
<tr>
<td>1</td>
<td>1.0</td>
<td>10</td>
<td>0.25</td>
<td>20mlBr₂/H₂O</td>
<td>3.31</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>5</td>
<td>0.08</td>
<td>50mlBr₂/H₂O</td>
<td>4.53</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>5</td>
<td>0.08</td>
<td>5mlBr₂/H₂O</td>
<td>4.58</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>5</td>
<td>0.08</td>
<td>100mlBr₂/H₂O</td>
<td>4.53</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>5</td>
<td>3.00</td>
<td>150mlBr₂/H₂O</td>
<td>4.58</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>5</td>
<td>0.08</td>
<td>Br₂(l)</td>
<td>4.53</td>
<td>2.39</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>5</td>
<td>1.00</td>
<td>1.23g I₂</td>
<td>4.58</td>
<td>--</td>
</tr>
<tr>
<td>8</td>
<td>2.0</td>
<td>--</td>
<td>1.00</td>
<td>150mlBr₂/H₂O</td>
<td>1.41</td>
<td>0.50</td>
</tr>
<tr>
<td>8</td>
<td>2.0</td>
<td>--</td>
<td>1.00</td>
<td>150mlBr₂/H₂O</td>
<td>1.25</td>
<td>0.29</td>
</tr>
</tbody>
</table>

1 Illinois #6 - Product of dye-sensitized photo-oxidation (rose bengal).
2 Illinois #6 - Run of Mine (ROM).
3 Pittsburgh #8 - Physically cleaned by froth flotation.
4 Pittsburgh #8 - Physically cleaned and product of chemical and electrochemical process.
The observed desulfurization results are believed to be the result of free radical reactions. These free radical reactions are initiated at near ambient temperatures by the influence of ultraviolet radiation, as follows:

\[ \text{Br}_2 + h\nu \longrightarrow 2\text{Br}^- \]  \[\text{[93]}\]

The reactions with inorganic sulfur may proceed:

\[ \text{FeS}_2 + 4\text{Br}^- \longrightarrow \text{FeBr}_2 + \text{S}_2\text{Br}_2 \]  \[\text{[94]}\]

\[ 2\text{FeS} + 14\text{Br}^- \longrightarrow 2\text{FeBr}_3 + 4\text{SBr}_2 \]  \[\text{[95]}\]

\[ 2\text{FeS}_2 + 10\text{SBr}_2 \longrightarrow 2\text{FeBr}_3 + 7\text{S}_2\text{Br}_2 \]  \[\text{[96]}\]

\[ \text{S}_2\text{Br}_2 + 8\text{H}_2\text{O} + 5\text{Br}_2 \longrightarrow 2\text{H}_2\text{SO}_4 + 12\text{HBr} \]  \[\text{[97]}\]

While organic sulfur reactions might proceed:

\[ \text{R-SH} + \text{Br}^- \longrightarrow \text{R-Br} + \cdot\text{SH} \]  \[\text{[98]}\]

\[ \cdot\text{SH} + \text{R-H} \longrightarrow \text{H}_2\text{S} + \text{Alkene} \]  \[\text{[99]}\]

Photochemical halogenation of coal could be scaled up to an industrial level for the purpose of coal desulfurization. A flow chart outlining this process is shown in Figure 11. In this method, coal which is physically cleaned to the extent practical, is subjected to photochemical free radical bromination. The brominated product must then be dehalogenated, perhaps by steam
Figure 11. Halogen Photosubstitution Method for Coal Desulfurization.
treatment or alkaline hydrolysis. The resulting coal product would then be dewatered for transportation and subsequent utilization.

In spite of the high efficiency of the desulfurization of coal, certain serious deleterious effects of halogenation on product coals are observed. First volatile matter is completely eliminated and serious caloric value losses occur. Second, even though improved selectivity of attack upon sulfur species was anticipated, the experimental results indicated large amounts of bromine was taken up by the coal organic matrix. This covalently bonded bromine proved to be quite difficult to remove. If sufficient dehalogenation can not be achieved, upon combustion bromine would be released into the atmosphere. Upon emission into the atmosphere the threat to the environment would likely be more serious than the sulfur which it replaced. This effect was in evidence when the strong pungent odor of bromine was liberated into the room when halogenated coal products were burned for total sulfur analysis in the Leco Sulfur Determinator.

Application of alcoholic reflux followed by alkaline hydrolysis was only partially effective in the dehalogenation of processed coals. Hsu et al. (111) proposed the use of superheated steam to effect dehalogenation in their process. However, the application of superheated steam is
a powerful desulfurization procedure in itself and has few of the serious side effects of halogenation.

In light of the serious deleterious effects on product coals, the well known toxicity of halogenated organic compounds, and difficulties involved in efficient dehalogenation of product coals, further efforts with the photochemical halogenation desulfurization of coal were curtailed. Other photochemical processes present opportunities for effective desulfurization without such negative effects.

PHOTOCHEMICAL ALCOHOLIC REDUCTION

Muchmore et al. (127, 128) have demonstrated relatively high organic sulfur removal efficiency with supercritical alcohol extraction. Underlying mechanisms of this process are thermal in nature. If thermal activation of coal and alcohol reactions are effective in coal desulfurization, then perhaps photochemical activation could have equal or even superior efficiency. A series of experiments were performed with coal and alcohols utilizing photochemical activation at temperatures near ambient, to evaluate the potential of such processes for the industrial desulfurization of coals. Kinetics of the photochemical transformation of DBT in alcoholic solutions were determined. The products
of the alcoholic photochemical reduction of DBT were identified by gas chromatography/mass spectroscopy.

The organic matrix of coal, as it presents a black appearance, obviously absorbs many frequencies of light. The absorption of a photon of sufficient energy by an organic molecule will cause the formation of an excited triplet state which may directly result in a chemical reaction with other chemical species. Additionally, the photochemically excited organic molecule may transfer the energy to a suitable ground state acceptor molecule in a process of "sensitization". An acceptor molecule, excited by photochemical sensitization, may then participate in various chemical reactions which could include the formation or breakage of covalent bonds. If a photon of sufficient energy is absorbed, generally of the ultraviolet wavelengths or shorter, a direct homolytic cleavage of covalent bonds may occur in an organic molecule. In homolytic cleavage, one electron which was formerly involved in the covalent bond remains with each fragment yielding two radicals. Radicals thus formed are quite unstable and will react with any suitable molecule with which collision in the proper physical orientation occurs. All these preceding processes may be reasonably expected to occur in an irradiated coal slurry.
Electrochemical reactions are frequently performed in basic alcoholic solutions for organic synthesis. Two important reactions have been observed to proceed with high efficiency under these conditions. The first is known as the "Kolbe reaction" and was discovered in 1847 (208). The Kolbe reaction is believed to occur as follows:

\[
\begin{align*}
\text{RCOO}^- & \quad \xrightarrow{\text{electrochemical oxidation}} \quad \text{RCOO}^- \quad [100] \\
\text{RCOO}^- & \quad \xrightarrow{} \quad \text{R}^+ + \text{CO}_2 \uparrow \quad [101]
\end{align*}
\]

The second reaction may occur simultaneously. This reaction is "alkoxylation". For example, thiophene in basic methanolic solution yields 2,5-Dimethoxy-2,5-dihydrothiophene and malealdehyde tetramethyl acetal upon electrochemical oxidation (210). Note that the second product of alkoxylation of thiophene is desulfurized. Thiophene is a well known component of the coal organic matrix.

A metallic oxide such as titanium dioxide or zinc oxide produces a positive charge on an surface which is illuminated with band gap wavelength or shorter light. This positive surface may cause electrochemical oxidations of organic compounds such as the Kolbe and alkoxylation reactions. Photo-Kolbe decarboxylation of coals would be a positive effect as floatability could be improved,
perhaps even to the point where lower rank coals could be made amenable to the highly efficient flotation cleaning process. The desulfurization of thiophenic compounds by photochemical alkoxylation and hydrodenation would produce reductions in the difficult to remove organic sulfur component of coal.

Photochemically Induced Degradation of DBT in Alcoholic Solution

Dibenzothiophene, DBT, is a commonly used model compound in coal desulfurization research. This compound has been identified in coal hydrogenation products and is believed to constitute a large percentage of the organic sulfur in many coals. However, in situ, the DBT molecule would be a monomer in the complex polymer of which the organic matrix of coal is composed.

DBT exhibits strong absorption of ultraviolet light, as the absorption spectrum given in Figure 12 indicates. This absorption spectrum was obtained at an ambient pH in a saturated solution of distilled water. DBT is only sparingly soluble in water, with an apparent solubility of 2 mg/l or less at room temperature in distilled water. Fortunately, DBT is quite soluble in ethanol and therefore kinetics and product identifications were not complicated by poor signals due to low concentrations.
Figure 12. Absorption Spectrum of DBT in Water.
Since DBT exhibits good direct absorption of ultraviolet light in the range of wavelengths capable of homolytic cleavage, high reactivity was anticipated in alcoholic solutions. Experiments were performed to determine the kinetics of the degradation of DBT in alcoholic solution by gas chromatography. The results of these experiments are shown in Figure 13. Examination of the data in Figure 13 indicates complete degradation of a 100 mg/l DBT in alkaline ethanolic solution is possible in only one hour of irradiation with ultraviolet light, under a nitrogen atmosphere.

The course of the ultraviolet photochemical degradation of DBT in alkaline ethanolic solution under a nitrogen atmosphere is clearly indicated in a sequence of chromatograms shown in Figure 14. In the absence of irradiation, no significant degradation of DBT was observed in an identical solution in one hour of reaction time. In Figure 14 at t=0 the DBT signal is that which is found at retention time = 8.32 minutes; while the first large peak is the solvent ethanol. At t=15 minutes of irradiation time, the DBT peak has significantly eroded with the formation of at least three small product peaks which precede the DBT peak. At t=30 minutes of irradiation time the DBT peak has eroded into a well formed doublet with the three product peaks still evident. After
Figure 13. Degradation of 100mg/l of DBT in Ethanol With KOH sparged with N₂ gas and irradiated with ultraviolet light at 30°C.
Figure 14. Gas Chromatograms of the 100mg/l DBT in Basic Alcoholic Solution as a Function of U.V. Irradiation Time, 30°C, and Nitrogen Sparging.
45 minutes of irradiation, a prominent product peak at 3.86 minutes is observed as well as other products. After 60 minutes of irradiation the solvent peak has broadened with this low resolution packed column and no further trace of DBT nor individual products is in evidence. At this stage the solution exudes the strong odor of acetaldehyde indicating the oxidation of the ethanolic solvent to the aldehyde product. Examinations of gas chromatograms obtained at lower oven temperatures, to spread out the components, indicate the complete degradation of the DBT substrate at longer irradiation times. All products appear to be very low molecular weight compounds residing in the solvent peak or volatilized from the solution. At intermediate irradiation times a biphenyl product has been identified by retention time comparison with the parent compound. Of course, it is impossible to rule out high molecular weight polymer products which may be non-volatile. The quartz glass immersion well which encloses the medium pressure mercury vapor lamp frequently shows the formation of an oily residue in longer runs with alcoholic solvents under reducing atmospheres. This residue probably contains higher molecular weight polymers.

The semiconductor photoelectrochemical degradation of DBT in basic ethanolic solution was investigated. Titanium dioxide, anatase, in form of a finely divided
colloidal suspension was employed as the catalyst. The distribution of reaction products was similar to that observed with direct photolysis. A high resolution capillary column chromatogram of the reaction products is shown in Figure 15. In this Figure, the solvent and low molecular weight products are peaks preceding peak #89.

The peak labeled 89 is likely to be hexamethyl cyclo-trisiloxane. Siloxanes are common column bleeding components. The unknown's mass spectrum is shown in Figure 16 compared to the library spectrum with a high probability of match.

The peak labeled #226 in Figure 15 appears to be desulfurized alkene product. The mass spectrum of the unknown is compared to a library match of 2,4 Dimethyl-1-decene in Figure 17. However, it is suggested that the molecule may be 5, 6-Dimethyl-1-decene, C_{12}H_{24} (molecular weight 168):
Figure 15. Capillary Gas Chromatogram of TiO₂ Catalysed Photochemical Reaction Products of DBT in Basic Ethanolic Solution.
Figure 16. Mass Spectrum of Compound Eluting #89 With Library Match Spectrum Below.
Figure 17. Mass Spectrum of Compound Eluting #226 Compared to the Computer Generated Library Match Below.
Alkane fragmentation is favored at carbon atoms which are more highly substituted, since such fragments are more able to stabilize the resulting positive charge (211). Therefore cations of m/e = 83, 57, 112, and 168 may be reasonably expected from 5, 6-Dimethyl-1-decene supporting this identification of the unknown compound. Unfortunately, a standard mass spectrum of 5, 6-dimethyl-1-decene is not available in the spectral libraries consulted.

A peak labeled #524 in Figure 15 is most likely biphenyl. The unknown compound's mass spectrum is compared to a library mass spectrum in Figure 18. A computer generated match possesses a high probability of fit and is an expected product. This compound exists in the original DBT solution as a trace contaminant, however the signal intensity is significantly greater following photochemical treatment.

Peaks labeled 732 and 742 appear to be a group of related ring reduction products. The mass spectra of the unknown compounds are given in Figures 19 and 20. Computer library matches of these spectra were poor in quality and are given with other chromatographic and mass spectral data in Appendix I. A peak labeled #732 contains a major ion at m/e = 190 which may be the molecular cation of cyclohexylbenzthiophene, C_{12}H_{14}S, m.w. 190:
Figure 18. Mass Spectrum of Compound Eluting #524 Compared to the Computer Library Match Below.
Figure 19. Mass Spectrum of Compound Eluting #732 Compared to the Computer Generated Library Match Below.
Figure 20. Mass Spectrum of Compound Eluting #742 Compared to the Computer Generated Library Match Below.
Loss of butane from the cyclohexane ring would yield a cation of m/e = 134, while the loss of ethane yield a cation with m/e = 162. Loss of CS from the aromatic and thiophene ring would yield a cation with m/e = 146. DBT (m.w. 184), for example, is known to fragment in mass spectroscopy as follows:

A peak labeled #742 in Figure 15 may be a partial ring reduction product: 1, 4, 5, 6-tetrahydro-dibenoazathiophene or a closely related isomer with a molecular weight of 188 and formula C_{12}H_{12}S. The proposed structure for #742 is:
Loss of C₄H₆ as indicated:

Would yield the prominent cation observed at m/e 134 by a retro-Diels-Alder reaction.

Peaks labeled #816-835 in Figure 15 are of the substrate compound dibenzothiophene. The mass spectra of the compound is shown in Figure 21 compared to the computer library match.

A low hump of compounds with higher retention times (presumably more polar) follows the DBT peak in Figure 15, most of these compounds are contaminants resulting from the synthesis of DBT. Prominent among these is the peak labeled #1014. This compound is proposed to be an ethoxylated compound, 2-ethoxy-cyclohexylbenzothiophene, m.w. 234, C₁₄H₁₈S₂O:

As similar weak signals exist in the original DBT mixture, this compound is not considered to be a photochemical reaction product at this time. The mass spectrum of the unknown compound is displayed in Figure 22. The loss of ethoxy would yield the cation m/e 189. A retro-Diels-
Figure 21. Mass Spectrum of Compound Eluting #816 in Gas Chromatogram of Reaction Mixture Compared to the Computer Generated Match Below.
Figure 22. Mass Spectrum of Compound Eluting #1014.
Alder reaction gives the cation m/e 134. Formation of the cation at m/e 147 may be more complicated as proposed in the following:

\[
\begin{array}{c}
\text{[104]} \\
\text{[104]} \\
\text{[104]} \\
\end{array}
\]

For example, 3-methyl-benzothiophene has been demonstrated to undergo the ring expansion as previously described (212). The cation m/e 147 observed in the mass spectrum of compound eluting #732 may also have resulted from a similar process.

**Proposed Mechanisms of DBT Photo-Degradation in Alcoholic Solution**

A group of products are observed to form as photolysis of DBT proceeds. The general trend in both direct photolysis and in semiconductor photocatalysis is that smaller and less polar molecules are formed the longer the reaction proceeds.
The observed degradation of DBT upon ultraviolet irradiation in basic ethanolic solution is a complicated reaction as indicated by the large number of products formed as indicated in Figures 14 and 15. There are two basic mechanisms believed to involved. The first reaction type is free radical. The free radical mechanisms are involved in the direct photolysis process. In direct photolysis the DBT molecule absorbed a photon of sufficient energy such that homolytic cleavage of a covalent bond occurs. Homolytic cleavage yields highly reactive radicals. From the literature we know that radical-site preference in organic molecules follows the order:

\[ N > S, O, \pi, R^\cdot > Cl, Br > H \] (211)

This fortunately may lead to radical formation at the sulfur in organo-sulfur molecules, eventually resulting in desulfurized products. The second reaction type is semi-conductor photoelectrochemical catalysis. In this process, the semiconductor becomes positive on the illuminated side, while the dark side becomes negative. Illuminated particles may then act as electrodes upon which electrochemical oxidation and reduction reactions may proceed. Electrochemical reactions in alcoholic media may also produce desulfurized products by successive hydrogenation and alkoxylation as previously discussed.
The early products of ultraviolet photolysis of DBT with colloidal anatase in basic ethanolic solution are believed to be as follows:

\[
\text{5,6-dimethyl-1-decene} \\
\text{m.w. 168} \\
\text{C}_{12}\text{H}_{24}
\]

\[
\text{biphenyl} \\
\text{m.w. 154} \\
\text{C}_{12}\text{H}_{10}
\]

\[
\text{cyclohexylbenzothiophene} \\
\text{m.w. 190} \\
\text{C}_{12}\text{H}_{14}\text{S}
\]

\[
\text{1,4,5,6-tetrahydro-dibenzothiophene} \\
\text{m.w. 188} \\
\text{C}_{12}\text{H}_{12}\text{S}
\]

These products are likely the results of direct photolytic free radical reactions and semiconductor catalysed photoelectrochemical reactions occurring simultaneously.

The ring hydrogenation products, cyclohexylbenzo thiophene and 1,4,5,6-tetrahydrodibenzothiophene may have resulted from interaction with solvated electrons derived from the dark sides (cathodic) of the illuminated anatase photoelectrodes. Solvated electrons have been detected in ethanol/water systems by ESR studies (213). The mechanism could follow the path:
\[
TiO_2 + h\nu \rightarrow TiO_2 + h^+ + e \quad [105]
\]
\[
e (\text{photocathode}) + \text{EtOH} \xleftarrow{\rightarrow} e (\text{EtOH}) \quad [106]
\]
\[
\cdot (\text{EtOH}) + \begin{array}{c}
\begin{array}{c}
\text{S}
\end{array}
\end{array} \xrightarrow{\rightarrow} \begin{array}{c}
\begin{array}{c}
\text{S}
\end{array}
\end{array} + \text{EtOH} \quad [107]
\]
\[
\text{EtOH} + 2 \begin{array}{c}
\begin{array}{c}
\text{S}
\end{array}
\end{array} \xrightarrow{\rightarrow} 2 \begin{array}{c}
\begin{array}{c}
\text{S}
\end{array}
\end{array} + \text{CH}_3\text{CHO} \quad [108]
\]
\[
\cdot (\text{EtOH}) + \begin{array}{c}
\begin{array}{c}
\text{H}
\end{array}
\end{array} \xrightarrow{\rightarrow} \begin{array}{c}
\begin{array}{c}
\text{H}-
\end{array}
\end{array} + \text{EtOH} \quad [109]
\]
\[
\text{EtOH} + 2 \begin{array}{c}
\begin{array}{c}
\text{S}
\end{array}
\end{array} \xrightarrow{\rightarrow} 2 \begin{array}{c}
\begin{array}{c}
\text{S}
\end{array}
\end{array} + \text{CH}_3\text{CHO} \quad [110]
\]

And these reactions may continue stepwise until the observed products are achieved.

Alternatively, the electron could be obtained by direct contact with the cathodic side of the colloidal photoelectrodes. The mechanism may be visualized as follows:

\[\text{EtOH} + \cdot \\begin{array}{c}
\begin{array}{c}
\text{S}
\end{array}
\end{array} \xrightarrow{\rightarrow} \begin{array}{c}
\begin{array}{c}
\text{S}
\end{array}
\end{array} + \text{CH}_3\text{CHO} \quad [112]\]

Photoelectrohydrogenation could also occur by an indirect method:
\[ R^+ + \text{EtOH} \rightarrow R\text{-OEt} + H^+ \] \[ 2H^+ + 2e \rightarrow H_2 \text{ or } 2H^\cdot \]
\[ H^\cdot + R^\cdot \rightarrow R\text{-H} \]

This pathway is not expected to be important as the solution is alkaline. Acidic conditions would favor this mechanism.

An alkoxylated product could arise in the following manner from reduction on the TiO\textsubscript{2} catalyst:

\[ \text{EtOH} + e \rightarrow \text{EtO}^- + \text{H}_2\text{O} \]

or alternatively:

\[ \text{EtO}^- + \text{EtOH} + e \rightarrow \text{EtO}^- \text{EtO}^- + H^+ \]
The biphenyl product could be produced by a free radical mechanism:

\[
\text{hv} + \begin{array}{c}
\text{S} \\
\end{array} \rightarrow \begin{array}{c}
\text{S} \\
\end{array} \text{[123]}
\]

\[
\text{EtOH} + \begin{array}{c}
\text{S} \cdot \\
\end{array} \rightarrow \begin{array}{c}
\text{S} \\
\end{array} + \text{CH}_3\text{CHO} \text{[124]}
\]

\[
\text{hv} + \begin{array}{c}
\text{SH} \\
\text{SH} \\
\end{array} \rightarrow \begin{array}{c}
\text{SH} \\
\text{SH} \\
\end{array} + \text{S} \cdot \text{[125]}
\]

\[
2 \text{SH} \cdot + \text{EtOH} \rightarrow 2\text{H}_2\text{S} + \text{CH}_3\text{CHO} \text{[126]}
\]

\[
\text{EtOH} + 2 \begin{array}{c}
\text{S} \\
\end{array} \rightarrow 2 \begin{array}{c}
\text{S} \\
\end{array} + \text{CH}_3\text{CHO} \text{[127]}
\]

Radical formation at the sulfur is favored, and extrusion of small molecules such as H$_2$S is frequently observed in free radical fragmentation reactions.

The formation of the alkene product may be more complex. Not only does sulfur appear to have been extruded but symmetric ring opening has apparently occurred.

Since from the literature it is known that (214):

\[
\begin{array}{c}
\text{[128]}
\end{array}
\]

The following reaction might occur:

\[
\begin{array}{c}
\text{hv} + \begin{array}{c}
\text{S} \\
\end{array} \rightarrow \begin{array}{c}
\text{S} \\
\end{array} \text{[129]}
\]

and with photocathodic reduction:
By homolytic cleavage of the carbon sulfur bonds and reaction with hydrogen atoms or abstraction of hydrogen from the ethanol:

\[ \text{[132]} \]

The double bonds are successively reduced:

\[ \text{[133]} \]
\[ \text{[134]} \]
\[ \text{[135]} \]

or alternatively:

\[ \text{[136]} \]

Finally yielding the observed alkene product 5,6-methyl-1-decene, after successive reductions:
The eventual disappearance of the higher molecular weight products upon prolonged direct photolysis or semiconductor catalysed photolysis may be explained by successive homolytic cleavage of sigma bonds followed by hydrogenation of the products. This may be illustrated in this manner:

\[ \text{Products} \]

and etc.

The residue on the immersion well can be explained by free radical polymerization. The photopolymerization could occur in this way:

\[ \text{Chemical Equations} \]

118
and so forth, eventual building large cross linked polymers of high boiling points. The solvent was shown involved in the preceding polymerization scheme. However, nothing would preclude the DBT molecule's participation in similar processes.

**Photochemical Alcoholic Desulfurization of Coals**

To determine the effectiveness of photochemical alcoholic reduction as a coal desulfurization method a series of experiments were performed with and without semiconductor catalysis. The results obtained by direct ultraviolet radiation photolysis are displayed in Table 8. Microbubble products of Pittsburgh #8 were fairly resistant to this approach. This may be due to the near complete removal of pyritic sulfur, leaving only organic sulfur which is more difficult to remove. No great advantage for any particular alcoholic solvent was observed. Though methanol may show a slight improvement in desulfurization efficiency.

Comparison of the dark reaction, the semiconductor catalysed reaction with pyrex filter, and the direct reaction with ultraviolet light with regard to coal desulfurization efficiency was made. Results of these experiments are given in Table 9. An order of desulfurization efficiency was shown to be semiconductor catalysed
Table 8. Representative Results of the Desulfurization of Pittsburgh #8 Coal
By Direct Ultraviolet Photochemical Alcoholic Reduction

<table>
<thead>
<tr>
<th>Particle Size</th>
<th>Alcohol</th>
<th>Alcohol Concentration (%)</th>
<th>Reaction Time (hrs)</th>
<th>Temperature °C</th>
<th>Initial Total Sulfur</th>
<th>Total Sulfur Removal Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>100x0</td>
<td>Ethanol</td>
<td>6.25</td>
<td>2.75</td>
<td>40</td>
<td>1.46</td>
<td>24</td>
</tr>
<tr>
<td>100x0</td>
<td>Ethanol</td>
<td>6.25</td>
<td>2.00</td>
<td>40</td>
<td>1.46</td>
<td>16</td>
</tr>
<tr>
<td>100x0</td>
<td>Methanol</td>
<td>6.25</td>
<td>1.67</td>
<td>40</td>
<td>1.46</td>
<td>17</td>
</tr>
<tr>
<td>--</td>
<td>2-Propanol</td>
<td>6.25</td>
<td>1.00</td>
<td>40</td>
<td>0.935</td>
<td>9</td>
</tr>
<tr>
<td>--</td>
<td>2-Propanol</td>
<td>6.25</td>
<td>2.33</td>
<td>40</td>
<td>0.935</td>
<td>10</td>
</tr>
<tr>
<td>--</td>
<td>Methanol</td>
<td>6.25</td>
<td>1.00</td>
<td>40</td>
<td>0.935</td>
<td>10</td>
</tr>
<tr>
<td>--</td>
<td>Methanol</td>
<td>3.13</td>
<td>5.00</td>
<td>40</td>
<td>0.935</td>
<td>12</td>
</tr>
</tbody>
</table>

NOTE: pH 11.8 (Adjusted by KOH)

1 Conventionally precleaned.
2 Microbubble product.
Table 9. Comparison of Alcoholic Desulfurization Efficiency of Pittsburgh #8 Coal (400x500) Under Various Conditions

<table>
<thead>
<tr>
<th>pH</th>
<th>Light</th>
<th>Catalyst</th>
<th>Ethanol Concentration (%)</th>
<th>Feed Sulfur (%)</th>
<th>Product Sulfur (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.8</td>
<td>None</td>
<td>None</td>
<td>100</td>
<td>4.24</td>
<td>4.02</td>
</tr>
<tr>
<td>11.8</td>
<td>Pyrex</td>
<td>2g TiO₂</td>
<td>100</td>
<td>4.24</td>
<td>3.58</td>
</tr>
<tr>
<td></td>
<td>Filtered</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.8</td>
<td>U.V.</td>
<td>None</td>
<td>100</td>
<td>4.24</td>
<td>3.93</td>
</tr>
</tbody>
</table>

Note: Temperature = 40°C
Reaction Time = 4 Hrs.
direct ultraviolet > dark. The feed size of the Pittsburgh #8 coal was 400x500 mesh. Therefore, efficient separation of the catalyst could be obtained by screening. Results indicate titanium dioxide catalysed reaction with pyrex filtered light was more than twice as efficient in coal desulfurization (i.e. 15.6%) than the direct ultraviolet reaction (7.3%) or the dark reaction (5.2%). The mechanisms responsible for these results may be those outlined in the preceding section discussing the photolysis of the model compound DBT, and well as reactions with iron pyrite similar to those observed by Muchmore et al., except photochemically initiated.

Other results obtained with Pittsburgh #8 coal in ethanolic photochemical desulfurization are given in Table 10. These experiments were performed utilizing colloidal TiO₂ semiconductor catalysts. The first two results are back calculated as efficient separation of the catalyst from the micronized coal could not be achieved. The third result was determined after separation of the coal product from the catalyst by screening. A decrease in particle size, and the corresponding increase in surface, appears to have greatly increased the desulfurization efficiency when compared to other coal products obtained of larger particle sizes.
Table 10. Representative Results of the Desulfurization of Pittsburgh #8 Coal by Semiconductor Catalysed Photochemical Alcoholic Reduction

<table>
<thead>
<tr>
<th>Particle Size</th>
<th>Alcohol(^2) Concentration (%)</th>
<th>Catalyst</th>
<th>Reaction Time (Hrs)</th>
<th>Temperature (°C)</th>
<th>Initial Total Sulfur Content (%)</th>
<th>Total Sulfur Removal Efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 μm Ethanol</td>
<td>90</td>
<td>5g TiO(_2)</td>
<td>4.0</td>
<td>40</td>
<td>0.927</td>
<td>98(^1)</td>
</tr>
<tr>
<td>5 μm Ethanol</td>
<td>100</td>
<td>5g TiO(_2)</td>
<td>2.5</td>
<td>40</td>
<td>0.945</td>
<td>47(^1)</td>
</tr>
<tr>
<td>140x400 Ethanol</td>
<td>100</td>
<td>5g TiO(_2)</td>
<td>2.0</td>
<td>25</td>
<td>1.77</td>
<td>22</td>
</tr>
</tbody>
</table>

\(^1\)Not separated from catalyst, back calculated.

\(^2\)With potassium hydroxide (2g).
Potential Industrial Application of Alcoholic Photo-chemical Desulfurization

A scheme for the potential industrial utilization of a photochemical process employing alcohol in a reducing atmosphere is shown in Figure 23. Alternatively sunlight could be used to drive the reaction with a semiconductor catalyst such as colloidal titanium dioxide. However use of the catalyst would require a catalyst separation step which would increase processing costs. Fortunately, a catalyst such as TiO₂ is corrosion resistant and could be repeatedly recycled.

DYE SENSITIZED PHOTO-OXIDATION OF COAL

The dye sensitized photo-oxidation of organic compounds is well documented in the literature. Thiophenic compounds have been desulfurized by methylene blue sensitized photo-oxidation. These methods may also produce desulfurization of coals in similar ways. The highly reactive singlet oxygen produced could attack organo-sulfur compounds and pyrite yielding the water soluble sulfate products which then can be readily separated from the coal product by filtration or screening. A series of experiments were performed to determine the efficiency of such processes.
Figure 23. Alcohol - U.V. Process for Coal Desulfurization.
The organic sensitizer dyes used for these experiments are known by the common names: Rose bengal and methylene blue. The structures of these molecules are given in Figure 24. These dyes are strong absorbers of visible wavelength light which promotes the singlet ground state molecule to an excited triplet state. The excited triplet state molecules may then return to the singlet ground state by the transfer of the absorbed energy to a suitable acceptor molecule such as oxygen. Oxygen, contrary to most molecules, has a triplet ground state. Therefore energy absorbed by oxygen creates an excited singlet state. Excited singlet state oxygen is extremely reactive and will attack most organic molecules. Production of singlet state oxygen by dye sensitization occurs at wavelengths much longer than is possible by direct absorption of light by oxygen.

Kinetics of Dye Sensitized Photo-Oxidation of Dibenothiophene

Dye sensitized photo-oxidation of DBT was conducted in a neutral aqueous solution which was sparged with oxygen. The change in DBT concentration was determined by iso-octane extraction followed by gas chromatography. The results of methylene blue sensitized photo-oxidation of DBT at 30°C and 80°C are shown in Figures 25 and 26.
Figure 24. Molecular Structures of the Sensitizer Dyes Employed in Photo-oxidation Experiments.

Methylene Blue:

\[
\begin{array}{c}
\text{CH}_3 \text{N}
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3 \\
\text{N}
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3 \\
\text{N}
\end{array}
\]

\[
\begin{array}{c}
\text{Cl}^-
\end{array}
\]

3,7-Bis(Dimethylamino)Phenothiazin-5-i um Chloride

Rose Bengal:

4,5,6,7-Tetrachloro-2,4',5,7'-Tetraiodo-Flourescein

Sodium Salt
Figure 25. Percent Removal of DBT Versus Time in a Saturated Solution at 30°C Using 30 mg/l Methylene Blue, 400 Watts Tungsten Light Source, 240 ml/min O₂ in Pyrex Flask and Neutral pH.
Figure 26. Percent Removal of DBT Versus Time in a Saturated Solution of 80°C Using 30 mg/l Methylene Blue, 400 Watts Tungsten Light Source, 240 ml/min O₂ in Pyrex Flask and Neutral pH.
the increase in temperature from 30°C to 80°C produced a large increase in the rate of degradation of DBT.

Speculated Mechanism for the Dye Sensitized Photo-oxidation of DBT

The methylene blue sensitized photo-oxidation of 2,5-Dimethylthiophene in chloroform yields a trans-diketone and a cis-sulfine (80):

Therefore, a similar mechanism for DBT photo-oxidation appears likely. This process could proceed as follows:

\[
\text{Dye} + \text{hv} \longrightarrow \text{Dye}^1 \longrightarrow \text{Dye}^3
\]

\[
\text{Dye}^3 + \text{O}_2 \longrightarrow \text{Dye} + \text{O}_2^1
\]
The resulting biphenone could be reduced to the corresponding biphenol.

**Desulfurization of Coal by Dye Sensitized Photo-Oxidation**

The use of dye sensitized photo-oxidation as a method for the desulfurization of several bituminous coals was evaluated. Illinois #6, Pittsburgh #8 from two sources, and an extremely high sulfur Pittsburgh seam coal from Northern West Virginia were tested. Representative results from these experiments are displayed in Table 11. Unfortunately, methylene blue (an organosulfur compound) when used in high concentration was found to produce increases in sulfur contents of some coals by adsorption. This phenomenon was especially prevalent in tests of short duration. As a result, most tests were run with rose bengal which contains no sulfur.

The dyes used in these experiments were quite unstable under alkaline conditions, being rapidly oxidized to brownish products. As a result, the solutions were maintained in the neutral to slightly acidic range. Also, even when neutral conditions were maintained the dyes faded with irradiation time as they were themselves photo-oxidized. The pH of distilled water rapidly declined while the photo-oxidation of high sulfur coals proceeded.
<table>
<thead>
<tr>
<th>Coal</th>
<th>Dye</th>
<th>Feed Size</th>
<th>Feed Sulfur(%)</th>
<th>Reaction Time(Hrs)</th>
<th>Total Sulfur Removal(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illinois #6</td>
<td>1</td>
<td>5 μm</td>
<td>4.53</td>
<td>5.75</td>
<td>27</td>
</tr>
<tr>
<td>Pittsburgh #8</td>
<td>1</td>
<td>400X0 Mesh</td>
<td>1.55</td>
<td>6.00</td>
<td>21</td>
</tr>
<tr>
<td>Pittsburgh #8</td>
<td>1</td>
<td>5 μm</td>
<td>0.90</td>
<td>1.00</td>
<td>12</td>
</tr>
<tr>
<td>Pittsburgh #8</td>
<td>1</td>
<td>5 μm</td>
<td>0.90</td>
<td>2.00</td>
<td>16</td>
</tr>
<tr>
<td>Pittsburgh</td>
<td>2</td>
<td>100X0 Mesh</td>
<td>9.73</td>
<td>1.00</td>
<td>10</td>
</tr>
<tr>
<td>Pittsburgh</td>
<td>2</td>
<td>200X0 Mesh</td>
<td>10.50</td>
<td>2.00</td>
<td>28</td>
</tr>
</tbody>
</table>

1 = Rose Bengal  
2 = Methylene Blue  
3 = RL
The kinetics of Pittsburgh #8 coal desulfurization by dye sensitized photo-oxidation was determined at two particle sizes. The results of these experiments are shown in Figures 27 and 28. Consideration of these data indicate that smaller particles, with higher surface areas are more rapidly desulfurized than larger particles, with less surface area. Also, Figure 27 indicates the rate of desulfurization proceeds rapidly at first and then slows considerably as irradiation time increases. This may be due to the exhaustion of readily accessible organo-sulfur and pyrite molecules near the surfaces of the coal particles.

The efficiency of coal desulfurization by dye sensitized photo-oxidation appears to be quite limited when compared to many other photochemical or chemical processes. These results may be due to the extremely short lifetime of singlet oxygen in aqueous solution, which is only 2 μ seconds (7). In 2 μ seconds, the singlet oxygen could not diffuse far into the pores or polymeric matrix of a coal particle. Thus, coal desulfurization by singlet oxygen would be limited to that sulfur on or near the surfaces of coal particles. This would leave the interior of coal particles unaffected, thereby seriously limiting the desulfurization efficiency.
Figure 27. Dye Sensitized Photo-oxidation of Pittsburgh Seam Coal (100x0), Initial S = 4.50%, 250 mg/l Rose Bengal, O₂ at 100 ml/min, pH 8.5, Temperature = 50°C, 1 g Coal.
Figure 28. Dye Sensitized Photo-oxidation of Pittsburgh #8 Coal (200x0), Initial S = 3.76%, 250 mg/l Methylene Blue, O₂ at 100 ml/min, pH 8.0, Temperature = 40°C, 1 g Coal.
Potential Industrial Application of Coal Desulfurization by Dye Sensitized Photo-Oxidation

A scheme for the employment of dye-sensitized photo-oxidation for the desulfurization of comminuted coals is shown in Figure 29. In this process, finely ground coal in a dye containing slurry is agitated by aeration in shallow ponds while exposed to sunlight. The soluble sulfate products would be removed from product coals by filtration screening, or centrifugation.

A process of this type would be most feasible in the case of a coal whose sulfur contents only slightly exceed the desired level. If the sulfur content only exceeded the target sulfur content after conventional cleaning by 10-15% this dye sensitized photo-oxidation procedure would likely be indicated.

Final Discussion of Desulfurization of Coal by Dye Sensitized Photo-Oxidation

Total coal desulfurization efficiency by dye sensitized photo-oxidation was disappointingly low. Stability of the sensitizer dyes was poor; which would cause high dye consumption for small benefits. However, the use of atmospheric oxygen as an inexpensive desulfurization reagent, in aqueous slurry, powered by sunlight remained an attractive process alternative. This led to the next
Figure 29. Dye Sensitized Photo-oxidation Process for Coal Desulfurization.
phase of research, the use of corrosion resistant metallic oxides to catalyse photoelectrochemical oxidation reactions which could result in coal desulfurization.

COAL DESULFURIZATION BY SEMICONDUCTOR PHOTOELECTROCHEMICAL CATALYSIS

The Stark-Einstein law indicates that the absorption of one quantum of radiation yields one photo-excited molecule. A resulting photo-excited molecule may then participate in numerous photochemical processes which may be physical or chemical in nature.

Photochemical processes of particular interest in this phase of study include: direct photolysis, direct excitation of reactive molecules in solution, sensitized photo-oxidation, semiconductor photoelectrochemical direct oxidations, and semiconductor photoelectrochemical reduction of oxygen.

An example of direct photolysis would be the case of photons absorbed by an organosulfur molecule causing the cleavage of bonds and subsequent fragmentation and/or rearrangement. Direct excitation of molecular oxygen in solution by absorption of shortwave ultraviolet radiation produces a highly reactive species.
Organic molecules, such as those present in the coal organic matrix, may absorb a visible frequency photon which promotes an electron from the singlet ground state to a short-lived excited triplet state. If a suitable acceptor molecule, such as oxygen, is present within range, the absorbed energy is transferred to the acceptor. Production of a chemically reactive species occurs with wavelengths of light much longer than those required for direct excitation of the acceptor. This process is an example of sensitization.

A process called heterogeneous photocatalysis occurs when semiconductor particles are illuminated (82). In this case, oxidation and reduction occur simultaneously at the semiconductor photoelectrode surface. First, direct oxidation of a chemical species may occur by contacting the n-type semiconductors illuminated surface. Second, oxidation of chemical species formed by the reduction of oxygen, i.e., \( \text{H}_2\text{O}_2 \) and its decomposition products, \( \cdot\text{OH} \), \( \cdot\text{HO}_2 \), etc. (84, 85).

Model Compound Kinetics of Photoelectrochemical Degradation

The model organosulfur compound DBT was used in saturated aqueous solution to determine the rates of degradation under various conditions. There is consider-
able scatter in the data, probably due to extraction variability, as shown in Figure 30. No significant DBT absorption or degradation was observed in the dark with the semiconductor colloidal suspensions without aeration over the duration of the kinetics experiments.

Consideration of the data shown in Figure 30 indicates DBT is rapidly degraded by photochemical processes. Zinc oxide shows the highest rate of degradation with this improvement, probably due to the fact that the rate observed is due to the linear superposition of the dark reaction, the ultraviolet radiation reaction, oxidation on the illuminated semi-conductor surface and oxidation by hydrogen peroxide resulting from the photoheterocatalytic reduction of oxygen. A good rate is also exhibited by titanium dioxide; however, the rate observed is a linear superposition of the dark reaction, direct ultraviolet radiation reaction, and oxidation on the semi-conductor surface without the H₂O₂ or its radical decomposition products. TiO₂ is not known to produce H₂O₂ when illuminated in aqueous solution, while ZnO is quite efficient at its production with a 10% quantum yield in oxygen-saturated solution, and no H₂O₂ production is observed in the absence of illumination (Hoffman et al.) (87, 88).

A kinetics experiment performed with zinc metal and 1.2 x 10⁻⁴M H₂O₂ at the same mass of the zinc oxide
Figure 30. Kinetics of DBT Oxidation in Alkaline Aqueous Solution. Experimental parameters included: pH 11 with KOH, Temperature at 25°C, O₂ at 70 ml/min, 6.67 g/l Semiconductor Catalyst, and DBT Saturated Solution.
experiments and other experimental details being identical to the zinc oxide experiment, indicated a similar rate of reaction to that observed with zinc oxide. Data are shown in Figure 31. These results support a \( \text{H}_2\text{O}_2 \) mechanism for ZnO catalysed photo-oxidation.

A DBT kinetic experiment performed in the dark under oxygen saturated alkaline conditions was repeated. A low disappearance rate under these relatively mild operating conditions was quite unexpected as other researchers had reported great stability for this compound; Tsai (1982) and etc. Analysis of the results displayed in Figure 32 indicate excellent reproducability. DBT does not exhibit high stability under these experimental conditions.

Since ZnO oxide showed the highest rate of degradation in the preceding experiments, an attempt was made to identify intermediate organic products by gas chromatography and mass spectroscopy. These attempts were seriously hampered by the extremely low solubility of DBT in aqueous solution, i.e. perhaps 1.4 x 10\(^{-5}\) M or ~2.0 mg/l by Kilbane, 1989. To overcome the poor signals obtained by the typical 1:20 iso-octane extraction of 10 ml aliquots previously used in this study, an entire reaction solution (about 700 ml) was extracted by methylene chloride. The methylene chloride extract was then evaporated under a stream of nitrogen to a volume
Figure 31. Comparison of the Rates of DBT Photo-oxidation Catalysed by ZnO or in the Presence of Granulated Zinc Metal and Hydrogen Peroxide (1.2x10^-4M). Other Experimental Conditions Were Identical to Those Given in Figure 30.
Figure 32. Reproducability of DBT Oxidation in Dark Oxygen Aerated Alkaline Solution. Other Experimental Parameters are Identical to Those Given in Figure 30.
near 1 ml. These data are contained in Appendix II. Upon first examination the chromatogram looked very promising. However all the major peaks turn out to be from the solvent or siloxanes from stopclock grease or volatilizing from the stationary phase of the column. High molecular weight products would not be expected to persist in an alkaline solution irradiated with ultraviolet light, and containing a ZnO catalyst. Sato et al. (101) observed CO₂ production when lignite was subjected to semiconductor photo-electrochemical oxidation. Therefore the weak signals from the starting compound and the absence of intermediate degradation products are as expected, since the production of low molecular weight products including CO₂ is favored under these reaction conditions.

To overcome the problems associated with the low solubility of DBT in aqueous solution, with regards to product identification, a new sequence of experiments were performed. In these experiments slurries of DBT crystals were suspended in DBT saturated solutions. The various other experimental conditions used for the preceding kinetics experiments were utilized, i.e. results displayed in Figure 30, with the exception of reaction time which was lengthened to one hour.

The DBT-methylene chloride solution gas chromatogram, shown in Figure 33, indicates the distribution of com-
Figure 13. Gas Chromatogram of DBT in Methylene Chloride.
pounds in the starting material which was reported by the manufacturer to be 95% DBT. Figures 34-37 display the chromatograms of the methylene chloride extracts of the DBT slurry filtrates after oxidation in the dark, direct U.V. photo-oxidation, TiO₂ catalysed photo-oxidation, and ZnO catalysed photo-oxidation. Examination of the chromatograms show marked similarities in the distribution of compounds eluting after DBT, the large peak with retention time about 10 minutes. The methylene chloride solvent is the first large peak to elute. However, the area between the solvent and DBT does show significant differences. Chromatograms of the region between about 4 minutes and 9.5 minutes are given in Figures 38-42 for the starting compound mixture and the various reaction extracts. These chromatograms are normalized to the largest peak in the region displayed.

Each of the chromatograms shown in Figures 38-42 show the same two compounds eluting last. These compounds are apparently stable under these experimental conditions and can be used to judge the relative changes in the concentrations of the compounds eluting before them. Computer library matches for these two compounds are 4-(1-methyl-1-phenyl-ethyl)-phenol and 2,3-dihydro-1,1,3-trimethyl-3-phenyl-1H-indene, respectively.
Figure 34. Gas Chromatogram of Methylene Chloride Extract of DBT Slurry Filtrate After Alkaline Oxidation in the Dark.
Figure 35. Gas Chromatogram of Methylene Chloride Extract of DBT Slurry Filtrate After Direct U.V. Photolysis.
Figure 36. Gas Chromatogram of Methylene Chloride Extract of DBT Slurry Filtrate After TiO₂ Catalysed Photo-oxidation.
Figure 37. Gas Chromatogram of Methylene Chloride Extract of DBT Slurry Filtrate After ZnO Catalysed Photo-oxidation.
Biphenyl is found in all the chromatograms in Figures 38-42 with the exception of the chromatogram derived from the direct U.V. photo-oxidation reaction mixture. Peaks labeled #158, 173, 170, and 167 in Figures 38, 39, 41, and 42, respectively are biphenyl. There is a curious absence of large concentrations of products eluting before phenol and indene type compounds in the direct U.V. irradiated extract chromatogram. This may be the result of rapid direct absorption of U.V. radiation by the compounds formed from the degradation of DBT and the efficient production of CO₂ and water. Biphenyl observed in the semiconductor catalysed photo-oxidation reaction extract chromatograms may be due to oxidation of DBT as has been proposed in microbial processes (215):

\[
\begin{array}{c}
\text{[152]}
\end{array}
\]

However, neither the DBT sulfone nor the 2,2'-dihydroxy-biphenyl products have been identified in any of the extracts. These products may not be stable under these experimental conditions, i.e. short lived intermediates, and escapes isolation as a result. Survival of biphenyl
Figure 38. Normalized Chromatogram of Region Preceeding DBT in a DBT-Methylene Chloride Solution.
Figure 39. Normalized Chromatogram of Region Preceding DBT in the Methylene Chloride Extract of a Filtrate Resulting From the Dark Alkaline Oxidation of DBT.
Figure 40. Normalized Chromatogram of Region Preceding DBT in the Methylene Chloride Extract of a Filtrate Resulting From the Direct U.V. Photo-oxidation of DBT.
Figure 4.1. Normalized Chromatogram of Region Preceding DBT in the Methylen Chloride Extract of a Filterate Resulting from the TiO2 Catalysed Photo-oxidation of DBT.
Figure 42. Normalized Chromatogram of Region Preceding DBT in the Methylene Chloride Extract of a Filtrate Resulting From the ZnO Catalysed Photo-oxidation of DBT.
in illuminated solution may be somewhat enhanced in semiconductor catalysed reactions by shielding due to the presence of shadows cast by the colloidal semiconductor particles.

Semiconductor catalysed photo-oxidation of DBT reaction extracts contain products not observed in significant concentration in the DBT/methylene chloride solution, the dark reaction, or the direct U.V. reaction. These include what appears to be: (1) two propanoic acids eluting just before biphenyl, (2) a substituted phenol, eluting #202 in the ZnO extract chromatogram (Figure 42), and #206 in the TiO₂ extract chromatogram (Figure 41), and (3) ethyl phthalate, eluting #247, in the ZnO extract chromatogram, and #252, in the TiO₂ extract chromatogram. It is interesting to note the relative concentrations of these compounds is higher in the case of TiO₂ catalysed photo-oxidation versus the results of ZnO catalyses photo-oxidation when compared to the indene and phenol compounds, eluting last in these regions, which may be used as bases for comparison. The zinc oxide rate of photo-oxidation catalysis is clearly much higher than TiO₂ as clearly shown in Figure 30. Therefore intermediate oxidation products would not be expected to be as persistent in the presence of the more efficient ZnO catalyst.
A stepwise display and computer identification of the peaks eluting in the DBT/methylene chloride solution chromatogram and the extract from the zinc oxide catalysed photo-oxidation experiment in the previously described region of special interest is given in Figures 43 and 44. Additional GC/MS data on compounds eluting after DBT in these solutions is given in Appendix III. Chromatograms and other selected mass spectra from the chromatograms are also given in this Appendix.

No simple mechanism may be used to explain the unique products which are observed in the semiconductor catalysed photo-oxidation of DBT. The phenolic and carboxylic acid products are likely to occur by the attack of hydroxy radicals, oxygen, and hydrogen peroxide. Rearrangements have also apparently occurred simultaneously.

The product extracted from the catalysed reaction mixtures identified as ethyl phtalate may be a major intermediate product. A speculated mechanism for its production is as follows:

\[
\begin{align*}
\text{Catalyst} & \quad \text{DBT} \quad 2\text{H}_2\text{O}_2 \quad \left[ \begin{array}{c}
\text{Phenyl} \\
\text{Carboxylic acid}
\end{array} \right] \quad \rightarrow \quad \text{Phenyl succinate} \\
\text{s}^2^- + \text{O}_2 & \rightarrow \text{SO}_2
\end{align*}
\]
Figure 43. Mass Spectrum of Compound Eluting #158 in Chromatogram of DBT/Methylene Chloride Extract (Figure 38), With Computer Library Identification.
Figure 43b. Mass Spectrum of Compound Eluting #190.
Figure 43c. Mass Spectrum of Compound Eluting #226.
Figure 43d. Mass Spectrum of Compound Eluting #271.
Figure 43e. Mass Spectrum of Compound Eluting #274.
Figure 43f. Mass Spectrum of Compound Eluting #278.
Figure 44a. Mass Spectrum of Compound Eluting #157 in Chromatogram of Methylene Chloride Extract From the ZnO Catalysed Photo-oxidation of DBT (Figure 42), with Computer Library Identification.
Figure 44b. Mass Spectrum of Compound Eluting #165.
Figure 44c. Mass Spectrum of Compound Eluting #167.
Figure 44d. Mass Spectrum of Compound Eluting #199.
Figure 44e. Mass Spectrum of Compound Eluting #202.
Figure 44f. Mass Spectrum of Compound Eluting #232.
Figure 44g. Mass Spectrum of Compound Eluting #247.
Figure 44h. Mass Spectrum of Compound Eluting #269.
Figure 44i. Mass Spectrum of Compound Eluting #283.
Figure 44j. Mass Spectrum of Compound Eluting #287.
None of the intermediates would be expected to be long lived in irradiated alkaline aqueous solution. Oxidation, fragmentation and rearrangement reactions would eventually convert the intermediates into carbon dioxide, sulfate, and water.

Desulfurization of Coal by Semiconductor Catalysed Photo-Oxidation

Coal desulfurization experiments were conducted in alkaline solutions using the apparatus shown in Figure 9. The experiments were conducted at an aeration rate of 70 ml/min STP. The results obtained with Pittsburgh #8 Bell Ohio coal under conditions of darkness, Pyrex-filtered light, and Pyrex-filtered light with ZnO catalyst are given in Figure 45. It can be seen that there is an improvement in overall desulfurization with the application of light and a smaller but consistent improvement with light in combination with ZnO. The improved sulfur rejection brought about by the irradiation of filtered light may be due to direct photolysis and to the excitation of molecular oxygen by coal matrix sensitization which, in turn, helps oxidize the sulfur exposed near the surface.

In the presence of ZnO, oxidation by \( \text{H}_2\text{O}_2 \), or by oxygen-containing radicals formed by direct photochemical
Figure 45. Kinetics of coal desulfurization by darkness, filtered light, and filtered light with semiconductor catalyst reactions. Experimental conditions were as follows: pH 11 with KOH, O₂ at 70 ml/min, ZnO 4 g/700 ml, temperature = 40°C ± 2°C, 4 g Pittsburgh No. 8 Bell Ohio coal at ~75 μm mean size and initial sulfur content of 4.26%, coal products extracted with dilute HCl and hot toluene.
excitation of $\text{H}_2\text{O}_2$ may be responsible for the increased rate of sulfur rejection. Similar experiments conducted with TiO$_2$ did not produce consistent improvement over the results obtained with direct illumination alone, which may be due to the inability of TiO$_2$ to produce peroxides which are free in solution.

The results obtained with several other coals under various reaction conditions are given in Table 12. For tests conducted with micronized coal using TiO$_2$ as the photocatalyst, the percent sulfur in the product was back-calculated from the assays of the product coal containing the TiO$_2$ powder since it was difficult to separate them. When using ZnO as the photocatalyst, on the other hand, it was readily separated from the micronized coal with dilute hydrochloric acid. Most coal desulfurization experiments were performed with micronized coals, since a significant improvement in desulfurization efficiency was observed with decreasing coal particle size. For example, ZnO-catalyzed photo-oxidation of Pittsburgh #8 Bell Ohio coal assaying 4.26% total sulfur produced only 13% desulfurization at -70+100 mesh, while a 22% desulfurization was obtained at -325+400-mesh in one hour as shown in Figure 46. All coals tested responded favorably to the reaction conditions employed. In the experiments conducted with Illinois #6, Illinois #2 and Pittsburgh #8 Bell Ohio
Table 12. Results of Semiconductor Photoelectrochemical Desulfurization Tests

<table>
<thead>
<tr>
<th>Coal Seam</th>
<th>Particle Size (μm)</th>
<th>Catalyst</th>
<th>Reaction Time (hrs)</th>
<th>Initial Sulfur Content (%)</th>
<th>Product Sulfur Content (%)</th>
<th>% Sulfur Removed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Total Pyritic</td>
<td>Organic</td>
<td>Sulfate</td>
</tr>
<tr>
<td>Pittsburgh</td>
<td>5</td>
<td>TiO₂</td>
<td>12</td>
<td>4.50</td>
<td>2.49</td>
<td>2.02</td>
</tr>
<tr>
<td>Pittsburgh #8</td>
<td>5</td>
<td>TiO₂</td>
<td>3</td>
<td>1.47</td>
<td>0.50</td>
<td>0.96</td>
</tr>
<tr>
<td>Pittsburgh #8 Bell Ohio</td>
<td>5</td>
<td>ZnO</td>
<td>12</td>
<td>4.76</td>
<td>2.37</td>
<td>1.97</td>
</tr>
<tr>
<td>Pittsburgh #8</td>
<td>5</td>
<td>TiO₂</td>
<td>10</td>
<td>1.13</td>
<td>0.22</td>
<td>0.89</td>
</tr>
<tr>
<td>Illinois #6</td>
<td>1.5</td>
<td>TiO₂</td>
<td>2</td>
<td>3.40</td>
<td>2.12</td>
<td>1.20</td>
</tr>
<tr>
<td>Illinois #2</td>
<td>1.2</td>
<td>ZnO</td>
<td>38</td>
<td>3.08</td>
<td>1.98</td>
<td>0.98</td>
</tr>
<tr>
<td>Widow Kennedy</td>
<td>100</td>
<td>ZnO</td>
<td>12</td>
<td>0.83</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Note: All reaction temperatures were 30°C ± 2°C, except for Illinois No. 2 which was processed at 50°C ± 2°C.

1Run-of-mine coal from an open pit in northern West Virginia (Pittsburgh).

2Pre-cleaned by microbubble flotation to remove most of the liberated pyrite; mine site unknown (Pittsburgh # 8).

3Run-of-mine coal from Bell Ohio Seam (Pittsburgh # 8 Bell Ohio).

4Pre-cleaned by microbubble flotation to remove liberated pyrite; mine site unknown (Pittsburgh # 8).
Figure 46. The effect of coal particle size upon desulfurization efficiency in the ZnO photo-oxidation of Pittsburgh #8 B.O. (4.26 = S_i) pH 11, 1 Hr. reaction, 4 g ZnO/700 ml, 30°C.
coals, the product coals were contacted with hot toluene to extract the water-insoluble sulfur products, perhaps including elemental sulfur, formed during the photo-chemical reactions. Toluene extraction produced notable decreases in the sulfur content after photo-oxidation.

A Pittsburgh #8 coal, -400+500 mesh, was photo-oxidized at pH 11, in the presence ZnO at 30°C. The resulting product showed ~30% sulfur rejection. Zinc oxide was removed from the solution by filtration, and the resulting filtrate was acidified heated with the addition of barium chloride, which upon cooling yielding a barium sulfate precipitate which was recovered, weighed, and from which the soluble sulfate percentage shown in Table 13 was calculated. The acid soluble sulfate precipitate value was determined by HCl extraction of the coal followed by precipitation of the barium salt. Elemental sulfur content was determined by the difference in sulfur value in the product coal after extraction by hot toluene.

A series of experiments were performed with ZnO catalysed photo-oxidation of Pittsburgh #8 coal to determine the influence of temperature upon desulfurization efficiency. Results of these tests are shown in Table 14. No trend is discerned in the consideration of the data.
<table>
<thead>
<tr>
<th>Sulfur Form</th>
<th>Percentage of the Sulfur Rejected in That Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble Sulfate</td>
<td>69.4</td>
</tr>
<tr>
<td>Acid Soluble Sulfate Precipitates</td>
<td>19.0</td>
</tr>
<tr>
<td>Elemental Sulfur</td>
<td>3.6</td>
</tr>
<tr>
<td>Sulfur Unaccounted For</td>
<td>8.0</td>
</tr>
</tbody>
</table>
Table 14. The Effect of Temperature Upon the ZnO Photo-oxidative Desulfurization of Pittsburgh #8 Coal

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Effect of Temperature η%</th>
<th>Product S %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10°</td>
<td>22.5</td>
<td>3.30</td>
</tr>
<tr>
<td>30°</td>
<td>24.2</td>
<td>3.23</td>
</tr>
<tr>
<td>50°</td>
<td>21.6</td>
<td>3.34</td>
</tr>
<tr>
<td>70°</td>
<td>23.5</td>
<td>3.26</td>
</tr>
</tbody>
</table>

ZnO Photo-Oxidation of Pittsburgh #8 Belle Ohio (S% = 4.26), +500 mesh, pH 11, 4g ZnO/700 ml, Stirred @ 700 rpm, 1 Hour Reaction, O₂ @ 70 ml/min.
Experimental results indicated a significant increase in overall desulfurization efficiency with increasing base strength. For example, an increase in sodium hydroxide concentration from 0.0 to 1.0 N produced an improvement of 12.4% in sulfur removal efficiency with Pittsburgh #8 Bell Ohio coal (+500 mesh) in one hour of reaction time with ZnO photochemical catalysis as indicated in Table 15. Therefore, ZnO photo-oxidation experiments were performed with Pittsburgh #8 Bell Ohio in a 1 N solution of NaOH, as shown in Figure 47. Good desulfurization results were obtained at a relatively large mean particle size of 75 m. A similar experiment was performed with Illinois #6 coal (+500) in the presence of TiO₂ at pH 11.3 as displayed in Figure 48.

The calorific content of photochemically-treated product coals were consistently high under the relatively mild test conditions. For example, a Pittsburgh #8 Bell Ohio coal (-400+500 mesh) was subjected to ZnO photo-oxidation at pH 11 and 25°C for five hours. This produced a 32% decrease in total sulfur content with only a 1.1% Btu loss. The calorific content of the Pittsburgh #8 Bell Ohio feed coal was 13082 btu/pound while the photochemical product coal's heat content was 12945 btu/pound.

ATR-FTIR spectra of Illinois #6 and Herrin #6 coals subjected to photoelectrochemical oxidation were obtained,
### Table 15. Effect of Alkalinity Upon ZnO Catalysed Photo-oxidative Desulfurization of Pittsburgh #8

<table>
<thead>
<tr>
<th>Normality of NaOH</th>
<th>n(%)</th>
<th>Sulfur Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>12.9</td>
<td>3.71</td>
</tr>
<tr>
<td>0.025</td>
<td>13.9</td>
<td>3.67</td>
</tr>
<tr>
<td>0.111</td>
<td>16.2</td>
<td>3.57</td>
</tr>
<tr>
<td>0.500</td>
<td>23.0</td>
<td>3.28</td>
</tr>
<tr>
<td>1.000</td>
<td>23.7</td>
<td>3.25</td>
</tr>
</tbody>
</table>

ZnO Photo-oxidation of Pittsburgh #8 Bell Ohio (+500 mesh), 40°C, 1 Hour Reaction, O₂ @ 70 ml/min., 4g/700 ml
Figure 47. Kinetics of ZnO photoelectrochemical desulfurization of coal in 1N NaOH. Experimental conditions were as follows: ZnO 4 g/700 ml, U.V. radiation, O₂ at 70 ml/min, 40°C ± 2°C, 4 g Pittsburgh No. 8 Bell Ohio coal at ~75 μm mean size and initial sulfur content of 4.26%. Coal products were extracted with dilute HCl and hot toluene.
Figure 48. Kinetics of titanium dioxide catalysed photoxidation of Illinois #6 (~75 μm mean size), initial S = 4.10%, 4 g Degussa p-25/800 ml, pH 11.3 with KOH, and O₂ at 70 ml/min.
Figure 49. ATR spectra of Illinois #6 coal at ~400 + 500 mesh, photooxidized for 12 hours with TiO₂ catalyst, U.V. radiation, pH 11.0 with KOH, temperature = 50°C, A = Feed, B = Product, C = Difference Spectrum.
Figure 50. ATR spectra of Herrin #6 coal (micronized) product of ZnO catalysed photo-oxidation, A = Feed, B = Product, C = Difference Spectrum.
as shown in Figures 49 and 50. A difference spectrum which resulted from the subtraction of the feed and ash product spectra shows negative peaks in the region of 2900 cm\(^{-1}\), indicating decreases of C-H functional groups, and positive peaks in the 1700 cm\(^{-1}\) region, indicating corresponding increases in C=O functional groups. The Illinois #6 photo-oxidation product spectrum also showed a significant decrease in the Si-O absorption bonds at about 1100 cm\(^{-1}\). This result indicates a decrease in ash-forming silicate minerals in the product coals. Unfortunately, organo-sulfur bonds do not possess significant absorption bands in I-R region. Therefore, C-S bonds cannot be quantified with current I-R technology.

SEM examination of the feed and the product from a semiconductor photoelectrochemical process shows significant morphological differences especially in the areas containing pyrite inclusions. Some of the representative photomicrographs are displayed in Figure 51 (a-d). A Pittsburgh #8 Bell Ohio coal shows a framboidal pyrite inclusion before processing (Fig. 51a). After treatment, the same coal shows empty casts once occupied by pyrite crystals (Fig. 51b). Similarly, a Widow Kennedy coal (Fig. 51c) shows pyrite crystals as light cube-like inclusions (many shining beneath the surface in this backscatter-mode photomicrograph) before processing,
Figure 51. SEM photomicrographs of Pittsburgh No. 8 and Widow Kennedy coals before and after semiconductor photoelectrochemical desulfurization.
Figure 51. SEM photomicrographs of Pittsburgh No. 8 and Widow Kennedy coals before and after semiconductor photoelectrochemical desulfurization.
while it shows mostly empty casts which the pyrite had once occupied after the sample was processed (Fig. 51d). Note, however, that a few crystals are still visible, albeit greatly reduced in size. The elemental composition of the mineral bodies in these images were verified by EDAX. Accessible pyrite is efficiently oxidized and removed from coals by photo-oxidation in alkaline solutions, as clearly indicated by these photomicrographs.

Compressed pellets of Pittsburgh #8, Illinois #2, and Widow Kennedy feed and ZnO photo-oxidation product coals were carbon coated prior to analysis by EDAX. The EDAX spectra for these coals are displayed in Figures 52, 53, and 54. In all cases the peak intensities for iron and sulfur are decreased in the photochemical product coals. Appearance of the chlorine peak in the product coals result from the hydrochloric acid extraction of sulfate precipitates from the coals. Silicate signals increase slightly in the Illinois #2 and Pittsburgh #8 photo-oxidation product coals due to removal of iron which interfered with silicon and aluminum electron excitation and subsequent x-ray fluorescence, even though significant ash rejection in silicates had occurred, as evidenced by ash and FT-IR analyses.

The large decrease in the silicon, aluminum, and potassium peaks in the EDAX spectrum of Widow Kennedy
Figure 52. EDAX spectra of Illinois #2 feed coal versus the ZnO photochemical product.
Figure 53. EDAX spectra of Pittsburgh #8 feed coal versus the ZnO photochemical product.
Figure 54. EDAX spectra of Widow Kennedy feed coal versus the ZnO photochemical product.
coal after ZnO photo-oxidation in alkaline solution is quite interesting. Widow Kennedy coal was subjected to oxidation by an oxygen plasma produced by radio frequency excitation (low temperature ashing or LTA). The resulting inorganic residue, which is structurally almost identical to that contained in the original coal, shows the presence of pyrite framboids as displayed in the SEM photomicrograph, Figure 55a. Upon oxidation of the residue in a 1:7 nitric acid solution to completely remove iron pyrite, an framework of potassium, aluminum silicate cementation minerals are revealed by SEM as given in Figure 55b. Composition of this silicate framework is clearly shown in the EDAX spectrum given in Figure 56. The identity of this mineral is probably kaolinite. These observations are consistent with those of Scheining et al. (1978) who observed kaolinite interstitial networks within pyrite framboids of the Megs Creek coal of Ohio. A significant portion of the 70% ash rejection which was observed when the Widow Kennedy coal is subjected to ZnO photo-oxidation in NaOH may be due to oxidation of the pyrite in framboids. This pyrite oxidation would reveal the fragile kaolinite cementation mineral only about 1 mm thick as measured by SEM, which would decompose into small fragments by mechanical abrasion under turbulent conditions. These fragments would then be readily removed by screening.
Figure 55a. Pyrite framboids from LTA of Widow Kennedy Coal.

Figure 55b. Kaolinite cementation minerals from nitric acid extracted framboids of the Widow Kennedy LTA.
Figure 56. EDAX spectrum of the silicate cementation mineral from nitric acid extracted pyrite framboids of the Widow Kennedy LTA.
Therefore, with certain coals, significant ash rejection may be observed in addition to desulfurization as shown in Table 16.

Photochemical experiments conducted with the model organo-sulfur compound, i.e. DBT, indicate high reactivity. Yet, experiments with coal indicate slow rates of desulfurization and limited removal efficiency. This may be due to the limited accessibility of the sulfur functional groups and pyrite inclusions by the reactive species formed in the solution. It would be difficult for the reactive species to diffuse into the tightly cross-linked polymeric coal matrix. Also, the internal sulfur functional groups may not contact the holes on the illuminated semiconductor surface. For these reasons, photochemical methods would be more efficient with depolymerized coals or coal pyrolysis products where accessibility would be limited by steric hinderance alone.

Proposed Mechanisms

Desulfurization of coal by photochemical methods is probably the result of several processes occurring simultaneously. Analysis of the data shown in Figure 45 indicates that approximately 87% of the sulfur removed after 3 hours in darkness can be accounted for by dark
Table 16. Photochemical Ash Liberation and Desulfurization of Widow Kennedy Coal (-70 + 200 Mesh, 1N NaOH, ZnO, 12 Hour, 40°C)

<table>
<thead>
<tr>
<th>Init</th>
<th>hv Prod</th>
<th>η%</th>
<th>Wet Screen Prod</th>
</tr>
</thead>
<tbody>
<tr>
<td>S%: 0.825</td>
<td>0.691</td>
<td>16.55</td>
<td>--</td>
</tr>
<tr>
<td>ASH%: 33.0</td>
<td>8.9</td>
<td>73.00</td>
<td>24.1</td>
</tr>
</tbody>
</table>
oxidation. A further sulfur rejection of 10.6% is obtained upon illumination with Pyrex-filtered light. When ZnO photoelectrochemical catalyst is added, the sulfur rejection improved by another 3.3%. Obviously, the bulk of the reactions are simple dark oxidation reactions of the type (22):

\[
\text{FeS}_2 + \text{H}_2\text{O} + 3 \text{1}/2\text{O}_2 \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \quad [155]
\]

\[
8\text{FeS}_2 + 30\text{NaOH} \rightarrow 4\text{Fe}_2\text{O}_3 + 14\text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3 + 15\text{H}_2\text{O} \quad [156]
\]

\[
2\text{R-SH} + 2\text{O}_2 \rightarrow 2\text{R-OH} + \text{SO}_2 + \text{S}^0. \quad [157]
\]

The increase in coal desulfurization observed when a coal slurry is irradiated can be attributed to direct and sensitized reactions. Direct photochemical excitation of oxygen and subsequent desulfurization reactions may be written as follows:

\[
\text{O}_2^3 + \text{hv} \rightarrow \text{O}_2 \quad [158]
\]

\[
2\text{R-SH} + 2\text{O}_2 \rightarrow 2\text{R-OH} + \text{SO}_2 + \text{S}^0 \quad [159]
\]

\[
\text{FeS}_2 + \text{H}_2\text{O} + 3 \text{1}/2\text{O}_2 \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+. \quad [160]
\]

The organic component of coal represented by the generic formula, C, may act like a highly light-absorbent sensitizing dye in the following manner:

\[
\text{C}^1 + \text{hv} \rightarrow \text{C}^3 \quad [161]
\]

\[
\text{C}^3 + \text{O}_2^3 \rightarrow \text{C}^1 + \text{O}_2 \quad [162]
\]
Highly reactive singlet oxygen may then attack the organosulfur compounds and pyrite as previously described for direct photochemical excitation of oxygen.

The small improvement in efficiency of coal desulfurization exhibited by the addition of the ZnO catalyst during irradiation is believed to be a result of semiconductor photoelectrochemical catalysis. Irradiation of a semiconductor with band gap light causes the formation of holes in the semiconductor valence band by promotion of an electron to the conduction band. Solution species scavenge valence band holes before electron-hole recombination can occur in the semiconductor. Semiconductor electroneutrality is maintained by reduction of oxygen or other species in solution by conduction band electrons (82). Thus, the formation of holes and reactive species in the aerated solution can be represented as follows (85):

\[(\text{ZnO}) + \text{hv} \rightarrow \text{e} + \text{h}^+ \quad [163]\]

\[\text{H}_2\text{O} + \text{h}^+ \rightarrow \cdot\text{OH} + \text{H}^+ \quad [164]\]

\[\text{H}^+ + \text{e} \rightarrow \cdot\text{H} \quad [165]\]

\[\text{O}_2 + \text{e} \rightarrow \cdot\text{O}_2^- \quad \quad \quad \quad \quad \quad \rightarrow \cdot\text{HO}_2^- \quad [166]\]

\[\cdot\text{HO}^- + \text{h}^+ \rightarrow \cdot\text{HO}_2 \quad [167]\]

\[2\cdot\text{HO}_2^- \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \quad \rightarrow \cdot\text{OH} + \text{OH}^- + \text{O}_2 \quad [168]\]
Holes on the illuminated surface may oxidize compounds which contact the semiconductor yielding a cation radical:

$$\text{R-SH} + h^+ \rightarrow \text{RSH}^+ \rightarrow \text{ROH} + \text{SO} + \cdot \text{H} \quad [169]$$

Also, the reactive species formed in solution may be involved in the desulfurization reactions as follows:

$$\text{R-SH} + \cdot \text{OH} \rightarrow \text{ROH} + \text{SO} + \cdot \text{H} \quad [170]$$

$$2\text{FeS}_2 + 3\text{H}_2\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 4\text{SO} + 3\text{H}_2\text{O} \quad [171]$$

The preceding reactions suggest that insoluble elemental sulfur is formed as the oxidation product. Elemental sulfur removal may be the reason for the improved sulfur rejection after toluene extraction. A proposed mechanism of semiconductor catalysed coal desulfurization is illustrated in Figure 57.

**Proposed Scheme for the Desulfurization of Coal by ZnO Catalysed Photoelectrochemical Oxidation**

Industrial application of a semiconductor catalysed photo-oxidation process for the desulfurization of particulate coal could be accomplished as illustrated in Figure 58. However, sulfate products would eventually build up in the reaction slurry requiring the periodic or continuous removal of these products by ion exchange, precipitation, or other means. If high desulfurization efficiency is required, acidic extraction and organic solvent extraction would follow the screening step.
Figure 57. Proposed mechanism for coal desulfurization by ZnO catalysed photo-oxidation.
Figure 58. Proposed process for coal desulfurization by ZnO catalysed photo-oxidation.
CHAPTER 6

PHOTOCHEMICAL DESULFURIZATION

CONCLUSIONS

General Observations

Application of photochemical processes to the problem of coal desulfurization presents many obstacles. The most serious obstacle to coal desulfurization arises from the constraint of dealing with a particle of poor diffusivity. It is possible to photochemically generate reactive species in solution, which if granted access to sulfur moieties within the coal particle could easily produce desulfurized products; or if directly irradiated, the compound could be desulfurized by photolysis. This process is demonstrated by the rapid degradation of DBT in several photochemical environments, despite results indicating high stability previously reported by other researchers under other chemical conditions. However, diffusion access in the organic polymer is severely limited, and desulfurization efficiency is also limited as a consequence. The main solution to this problem was determined to be comminution of the feed coals.
Another difficulty encountered in photochemical experiments with coal is the high optical density of coal slurries. As the mean particle size decreases the optical density of the slurry increases when the total mass is held constant. Since particle size was found to be important in desulfurization efficiency, i.e. the smaller the mean particle size the higher the desulfurization efficiency at any given reaction time, experiments were typically performed with the smallest mean size particles practical. Micronized coals presented the most problems since the associated optical densities of the slurries were very high. High optical densities limited the mass of micronized coal which could be processed in the photochemical reaction assembly, at any one time, to only a few grams. This small mass seriously limited the number of destructive analyses which could be performed on the coal product of any given experiment.

Catalysts and sensitizer dyes present stability and separation difficulties. ZnO particles, a powerful photo-oxidation catalyst, is amphoteric and tended to corrode in experiments. TiO₂ is strongly corrosion resistant, though a much weaker photo-oxidation catalyst. Organic dyes such as rose bengal and methylene blue faded as experiments proceeded as they were irreversibly oxidized, and under alkaline conditions they were almost
instantly destroyed. Separation of colloidal semiconductor catalysts from +500 mesh coals is efficiently obtained by screening. However micronized coals are not amenable to screening. ZnO can be removed from micronized product coals by acidic extraction. With TiO₂ catalysis no suitable method for the separation of photo-oxidized, micronized coals was discovered. Flotation and coagulation processes fail in the separation, as photo-oxidized coals are hydrophilic and do not assemble on bubbles nor do they coagulate with high efficiency.

The sulfur forms analysis for coal (ASTM D 2492) appears to be somewhat unreliable. Reproducibly among the analyses was quite poor. The results of sulfur forms analyses for photochemical product coals sometimes showed the erratic behavior which has been previously reported by Reggel et al. (29, 58, 104). The data presented in Tables 7 and 12 show sulfur forms analyses results indicating organic sulfur reduction in photochemical product coals. Coal Halogenation produces sulfur reductions so great that organic sulfur reduction has probably occurred. Even so, dilution of the coal matrix by the uptake of halogen must account for a portion of the apparent desulfurization. Semiconductor photoelectrochemical oxidation of coals produces results which are much less impressive. Only in the case of the long term processing of Illinois #2 is the
apparent reduction in organic sulfur beyond reasonable doubt. In both photochemical halogenation and alkaline oxidation treatments of coal, the majority of observed desulfurization (in all sulfur forms) is probably due to thermal activated attack by halogen, strong base, and/or oxygen rather than some special virtue of photochemical activation. For example, the data displayed in Figure 45 clearly indicates only modest improvements in coal desulfurization by the addition of radiation in alkaline slurry.

However, the total sulfur content of the product coals can be reliably determined. The Leco method of total sulfur analysis for coal appears to possess both accuracy and precision. The total sulfur values reported in this study are presented with high confidence.

All coals tested responded favorably with regards to desulfurization by the photochemical methods employed, i.e. all coals were desulfurized to some extent. The use of halogens for coal desulfurization, even though highly efficient, should be avoided. Halogens which would be liberated upon combustion of product coals are likely to produce environmental impacts far more serious than the sulfur they replace. Alcoholic photochemical reduction produces fair desulfurization results but consumes expensive alcohol reagents, and if semiconductor catalysts
are employed, separation of product coals and catalyst would increase operating costs. The use of dye sensitized photo-oxidation produces low desulfurization efficiencies. The dyes are unstable and undergo auto-oxidation. Of the methods tested, photo-oxidation under strongly alkaline conditions appears to show the most promise as an industrial process. Not only is desulfurization efficiency high with this process but the application of light produced a significant improvement when compared to the dark reaction under similar conditions. The addition of a semiconductor catalyst is difficult to justify since separation costs would be greatly increased for a small increase in coal desulfurization efficiency. However, semiconductor catalysts did show remarkable increases in the rates of model compound degradation, therefore a potential exists for the future development with these methods.

**Coal Desulfurization by Photochemical Processes**

Consideration of the results obtained from the experiments involving the photochemical desulfurization of coal has lead to the following conclusions:

A. Photochemical Halogenation
1. Photochemical halogenation of coal produces large decreases in the total sulfur contents of product coals.

2. Photochemical halogenation of coal removes volatile matter from product coals.

3. Large amounts of halogen are incorporated into the organic matrix of photochemical halogenation coal products.

4. High concentrations of halogen may be released into the atmosphere upon the combustion of photochemical halogenation coal products.

B. Alcoholic Photochemical Reduction

1. Photochemical treatment of coals under reducing atmospheres produces fair to moderate desulfurization.

2. Addition of a titanium dioxide catalyst irradiated with pyrex filtered light produces greater coal desulfurization than the dark reaction or U.V. irradiation alone.

3. DBT degradation under irradiation in the presence of TiO₂ and alcoholic solution yields some desulfurized organic products.
4. The rate of direct photolysis of DBT under irradiation in alcoholic solution is high.

C. Dye Sensitized Photo-Oxidation

1. Dye sensitized photo-oxidation of coals produces fair desulfurization results.

2. Organic sensitizer dyes are unstable and subject to rapid and irreversible photo-oxidation.

D. Semiconductor Photoelectrochemical Oxidation

1. Illumination produces increased coal desulfurization when compared to the dark oxidation mechanism alone.

2. Illumination with a colloidal suspension of ZnO produces a small increase in the desulfurization of coal when compared to illumination alone.

3. The addition of colloidal semiconductor catalysts increases the rate of photo-oxidation of DBT when compared to direct photolysis or dark oxidation.

4. Increasing base strength produces increasing photochemical coal desulfurization efficiency.

5. Decreasing particle size increases photochemical coal desulfurization.
6. Coal calorific content may be largely preserved in photochemical desulfurization.

7. Photochemical coal desulfurization efficiency is limited by accessibility to sulfur containing functional groups and not reactivity under the mild operating conditions employed.
PART III

COAL DESULFURIZATION BY PYRITE DEPRESSION

IN FROTH FLOTATION

CHAPTER 7

PYRITE DEPRESSION

INTRODUCTION TO THE DESULFURIZATION OF COAL BY PYRITE DEPRESSION IN FROTH FLOTATION

Coal is a complex and heterogeneous material. It is frequently contaminated with sulfide, silicate and carbonate minerals, i.e., gangue minerals. The sulfur content of coal from different geographic locations varies from less than 0.5% to greater than 5.0%. The distribution of sulfur forms between organic sulfur, pyritic sulfur, sulfate sulfur, and elemental sulfur is also quite variable. The two major sulfur forms found in coal are organic and pyritic. Organic sulfur levels commonly range from about 0.3% to slightly more than 2.0% while pyritic sulfur content may be from about 0.1% to about 4.0%. When coal is burned the various sulfur forms are converted to gaseous oxides which are emitted to the atmosphere. Sulfur oxides in the air will react with atmospheric water to form sulfuric acid which is eventually returned to the
ground as deleterious "acid rain". Coal is also employed in the manufacture of steel where high sulfur contents render it unfit for this purpose. High-sulfur coals yield weak and inferior steels. Therefore, coal desulfurization is crucial for protection of the environment from degradation by acidic rain and for provision of metallurgical quality coals.

Coal preparation is generally accomplished by gravity separation and froth flotation processes. Large and intermediate sizes are treated by gravity techniques while fine coals, usually less than 100 mesh, are cleaned by froth flotation.

In present industrial practice, coal is ground to a fine size to liberate the gangue minerals and frothed in water containing certain additives which assist in concentrating the clean coal particles in the froth while allowing the gangue to sink. The resulting froth contains the clean coal values which are then dewatered by various methods for subsequent industrial utilization. The froth flotation exploits the differences in the surface properties of the various components to separate the mineral matter from a run-of-mine (ROM) coal. The hydrocarbon component, the desired clean coal product, is generally quite hydrophobic and readily attaches to the bubbles of the froth. While hydrophilic minerals, such as the sili-
icates and carbonates, do not readily attach to bubbles of the froth. Unfortunately, coal pyrite, even when it is fully liberated from the desired hydrocarbon clean coal product, is somewhat hydrophobic. Therefore, coal pyrite will also attach to bubbles and report to the froth with the desired clean coal product. To assist in the separation of clean coal and gangue, agents known as frothers and collectors are employed in said froth flotation. Depressants are not widely used in industry in said flotation.

Frothers are added to cause formation of a froth in which the clean coal concentrate collects. The most common frothers used industrially include higher aliphatic alcohols such as 4-methyl-2-pentanol (MIBC), and synthetic frothers such as polypropylene glycol.

Collectors are agents which assist in the assimilation of coal concentrate particles in the froth. Hydrocarbon oils such as kerosene and fuel oil are commonly used as collectors for coal. Coals of high natural hydrophobicity do not require the addition of a collector for beneficiation by froth flotation.

Depressants are agents used to inhibit as far as possible the collection of metal sulfide minerals with clean coal in the froth. Numerous methods have been
scientifically tested for the selective depression of pyrite in the froth flotation of coal.

However, these techniques are not effective for all coals and the performance varies from coal to coal. Also, every effective depressant so far developed equally depresses coal (Perry and Aplan, 1985), is ineffective in selective depression of coal sulfide minerals, or is prohibitively expensive.

The present study relates to froth flotation processes for recovering clean coal from ROM coals contaminated with pyrite. It is more particularly concerned with a process wherein coal is froth floated while sulfide minerals, mainly pyrite, with which it naturally occurs are depressed by a novel class of selective quinonoid depressants.
CHAPTER 8

PYRITE DEPRESSION

LITERATURE REVIEW DEPRESSION OF PYRITE IN FROTHER FLOTATION

Froth Flotation of Coal and Pyrite Depression

In the late 19th century several flotation processes were in use (216). However, froth flotation for coal beneficiation was not employed until 1918 (217). A patent was issued Feb. 3, 1920 (U.S. 1,329,493) to R. Bacon for the concentration of coal by froth flotation.

To produce metallurgical quality coals sulfur must be removed to very low levels. Unfortunately, coal pyrite which is liberated by comminution from the hydrocarbon may also report in the froth phase with the desired clean coal product. As early as 1935, Yancy and Taylor (219), employed ferric salts, \( \text{H}_2\text{SO}_4 \), and lime as pyrite depressants in the froth flotation of coal. These reagents produced a slight decrease in the ash and sulfur contents of the clean coal concentrates. They postulated mechanical entrainment was responsible for the limited efficiency.
A method of reverse flotation of coal was reported in 1934 by Bierbrauer and Popperle (220). In this process the coal hydrocarbons were converted to hydrophobic humic acids by superficial oxidation. Potassium permanganate at 250-500g/ton was used as the oxidation reagent. The ash minerals were then floated by PhOH as a frother. Low rank coals require no pre-oxidation treatment to utilize this process.

In 1958, Karpova (221) reported the use of Cr(NO₃)₃, FeSO₄ changed the behavior of the surfaces of particles. Potassium permanganate, at 250g/ton, seriously oxidized coal surfaces and decreased recovery in froth flotation. CuSO₄ and Na₂SiO₃ together reportedly improved sulfur rejection. The maximum sulfur rejection obtained was ~20%.

In 1964, Kun et al. (222), characterized the pyrite content of comminuted Hungarian Coal into 3 groups: 1) ~50-60% is internally bound to the coal, 2) ~10-15% is bound to ash minerals, and 3) ~30% liberated pyrite. The floatability of each of these groups were found to be significantly different. Use of CaO and NaCN as depressants, ethyl and butyl xanthates as collectors, and CuSO₄ and Na₂S as activators was examined. The highest efficiency reported for any reagent employed was only a 0.2% decrease in pyritic sulfur. The authors reported
that pyrite which is internally mixed with the coal, as in class one above, cannot be removed by flotation processes.

In 1971, Baker and Miller (223), investigated the use of hydrolysed metal ions as pyrite depressants in the froth flotation of coal. The results indicated that FeCl₃, AlCl₃, CrCl₃, and CuSO₄ are potential pyrite depressants. Optimum pH and concentration was different for each reagent tested. Pyrite depression was best at a pH of 4.5-7.0 with FeCl₃, at 5.8-7.0 with AlCl₃, at 6.4-7.1 with CrCl₃, and at 6.4-7.4 with CuSO₄. Approximately 2-5 x 10⁻⁵ moles/liter of reagent were required for pyrite depression. These salts also produced significant coal depression. A Lower Freeport coal could be reduced from ~2.51 to <0.60% sulfur with recovery >83% with these methods. The mechanism of depression was postulated to be the adsorption of positively charged colloidal metal hydroxide at the pyrite-water interface.

In 1973, Miller (224, 225, 226, 228) reported the results of a reverse flotation process. In this procedure coal is depressed by a proprietary polymeric depressant AERO 633 and pyrite is floated by the addition of a xanthate collector. Excellent desulfurization results are reported. However, reagent costs are quite high due to the reagent required for depression of the major component, i.e. coal.
Boateng et al. (227), examined in 1977 use of lime as a pyrite depressant. Up to 90% pyritic sulfur rejection was claimed at 75% coal recovery. At <94.4% coal recovery a 18.2% pyritic sulfur rejection was achieved. Improved ash rejection was also observed by the application of lime.

Celik and Somasundaran (229) reported the effects of pretreatment with KMnO₄ and SnCl₂ upon the flotation and electrokinetic properties of coal. Both these reagents produced coal depression. SnCl₂ depressed coal at the pH of precipitation. Ultrasonic treatment restored the flotation of depressed coal by attrition. No correlation was observed between the ZETA potential (electrophoretic mobility) and flotation. The mechanism of depression may be attributed to surface contamination and oxidation.

In 1979, Patterson et al. (230, 231), reported pre-oxidation by 1-3% sodium carbonate and air at 80°C for 15 minutes. Increased pyritic sulfur rejection was produced, while coal still reported in the froth, with high recovery.

The effectiveness of various chemical pretreatments was investigated by Le (232) in 1981. Addition of NaCN, FeCl₃, Na₂H₂ EDTA, and NH₄SCN produced some pyrite depression over a wide range of pH. Use of the frothing
agent methyl iso-butyl carbinol (MIBC) increased the recovery of both coal and pyrite. The mechanism of depression appears to be an adsorption phenomena, as electrophoretic mobility measurements indicate. As previously reported by Celik and Somasundaran (229), no correlation between the ZETA potential and floatability was observed.

Use of carboxymethylcellulose, CMC, as a pyrite depressant was reported by Laskowski et al. (233). Use of the CMC depressant, kerosine as a collector, and MIBC as a frother produced up to 55% pyritic sulfur rejection at a mean particle size ≤38 μm, in the froth flotation of coal.

Surface modification of coal pyrite by microbial action was examined by Attia et al. (234) in 1985. A decrease in pyrite flotation of 40% was observed when coals were conditioned with Thiobacillus ferroxidans at a pH of 2 for 15 minutes or less at 30°C. Coal did not suffer any depression by the application of this process.

Application of polysaccharides and xanthated polysaccharides has been investigated by Aplan and co-workers (235, 236). In the first case, starches and starch derivatives were used to depress coal while pyrite was floated by a xanthate collector. In the second case, polysaccharides and xanthated polysaccharides were used as pyrite depressant in the froth flotation of coal.
Laskowski et al. (237) report the addition of humic acids may improve flotation selectivity. In these experiments coals were treated with humic acids. Although initially severely depressed, these coals floated well with higher selectivity after the addition of a suitable amount of hydrocarbon collector. A patent was issued to Abadi (U.S. 4,702,824) (238) on a process utilizing a reagent package for pyrite depression. In this scheme, a depressant mixture consisting of xanthan gum 0.01-10%, hydrocarboxylic acid 0.1-69%, and sodium silicate at 0.0-0.5 ratio to the acid, is used to depress pyrite in the froth flotation of coal.

Numerous techniques have been applied to the froth flotation of coal to improve desulfurization results. However, the effectiveness of these approaches are quite variable with different coals. Differences in desulfurization efficiencies may be attributed to the liberation and complex surface chemistry characteristics of each coal and coal pyrite type. Perry and Aplan (236) assert that every effective depressant thus far developed equally depresses coal or requires prohibitively high reagent dosages. Therefore, research directed towards the goal of a selective and cost effective pyrite depressant is necessary.
Mechanisms of Mineral Depression by Organic Macromolecular Depressants

Macromolecular organic depressants generally cause depression by binding to the surface of the hydrophobic mineral surface. Drost-Hansen (244) proposed a model for water structure at a hydrophobic mineral surface and at mineral surfaces covered with a hydrophilic depressant as shown in Figure 59.

There are three major components of the interaction forces between a bubble and the depressant coated mineral (246):

1) Dispersion forces which are a function of particle size and the composite Hamaker constant,

2) Electrostatic forces which are dependent upon surface charges of the bubble and particle and the double layer characteristics, and,

3) Structural hydration repulsion forces which are associated with the adsorbed hydrophilic surface layer upon the mineral particle.

In the froth flotation of coal, the dispersion forces and hydrophobic structural forces (260, 261) would tend to attract particles to the surfactant covered bubble surface while an anionic surface coating would tend to be repul-
Figure 59. Models of the water structure at the interface of: a. Hydrophobic pyrite surface (M) showing clathrate like ordering (E) at the interface and a small disordered region (I). Structural entities in the bulk water are shown as pentagons and partial pentagons (B). These pentagonal structural entities are in equilibrium with monomeric water, which are represented by arrows. b. Hydrophobic pyrite surface (M) which is coated with a hydrophilic depressant (D) which causes ordering of the water molecule by dipole-dipole large entropic region (I) (244).
sive to an air-bubble, which is generally negatively charged. In the case of macromolecular depressant films, such as tannins and polyphenols, the molecules contain numerous hydrophilic groups. Polar functional groups may through strong ion-dipole effects impose a structure on the nearby water as seen in Figure 59. This "ordered structural zone" may cause strong repulsive forces which could repel air-bubbles and prevent contact. The distance and the strength which these repulsive forces propagate into the solution is dependent upon the conformation and type of adsorbed polymer. Obviously, if the sum of repulsive forces is greater than the sum of attractive forces, bubble-particle adhesion does not occur. However, if dispersion forces, electrostatic forces (such as the case which occurs at low pH where mineral surfaces become positively charged), and ordered structural hydration forces are sufficiently weak, bubble-particle attachment occurs.

**Mechanisms of Quinonoid Compounds Bonding to Mineral Surfaces**

Quinonoid compounds are known to form complexes with clays, alumino-silicates, metal ions, coal, graphite, and metal sulfides (245). Leja (247) suggests that ionization of phenolic groups causes the adsorption of these compounds on cationic mineral surface sites. This is
followed by strong lateral hydrogen bonding. The surface is thereby converted to a negatively charged hydrophilic surface. Giles (248-250) proposes the forces responsible for adsorption from solution are: 1) Dispersion forces (non-polar Van der Waals attraction) 2) Formation of hydrogen bonds 3) Covalent bonding on coal surface between hydroxyl, carbonyl, and phenolic groups. π-bonding interactions the aromatic rings and hydrophobic sites are also possible (251), as are charge transfer complexes (252).

QUINONOID CHEMISTRY

Alkaline oxidation of quinone, its products and mechanisms have been extensively studied (Herdman and Granath, 1954 (239), Flaig and Salfeld, 1960 (240), Eigen and Matthies, 1961 (241)). A general consensus appears to be that hydroquinone and quinone follows a reaction sequence similar to the following in alkaline aqueous solution:

\[
\begin{align*}
\text{PHOH} & \rightarrow \text{PH}^+ \rightarrow \text{P}^2+ \rightarrow \text{O}^2+ \rightarrow \text{O}^2+ + \text{O}^2+ \\
\rightarrow & \text{PH} \rightarrow \left[ \text{HO} \right]_n \rightarrow \left[ \text{HO} \right]_n
\end{align*}
\]

[172]

Dodgson (242) found strong evidence in 1914, for an addition reaction between sulphurous acid and quinone:
Hydroquinone sulfonic acid was isolated and characterized. A similar reaction was also reported by Ogata et al. (243) in 1968 with sodium thiosulfate:

The rate of the addition of thiosulfate to quinone was found to be affected by the acidity of the media. The reaction showed general acid catalysis. The mechanism of the reaction appears to be nucleophilic addition of the thiosulfate ion.
CHAPTER 9

PYRITE DEPRESSION

METHODS AND MATERIALS

Synthesis of the Quinonoid Depression Reagent

The present study is concerned with improved depressants for use in the froth flotation of clean coal from ROM coals containing various amounts of gangue minerals including metal sulfides. The improved depressants comprise a group of compounds derived from the alkaline oxidation of polyphenols or quinones. These compounds result from mixing amounts of polyphenol or a quinone and an alkali metal hydroxide, or other hydroxide such as ammonium hydroxide, in aqueous solution. The resulting complex mixture is brown in color and contains active quinonoid derivatives and various inactive compounds.

Synthesis of the reagent of this study from a polyphenol follow this procedure: a) \(10^{-2}\) mole (per liter of final solution) of polyphenol, such as hydroquinone, is added to 60% of the desired final reagent volume of distilled water in an open, stirred glass vessel. b) \(10^{-2}\)
mole (per liter of final solution) of base is added to a vessel containing 20% of the desired final reagent volume. c) The two previous solutions are mixed and diluted to the final reagent volume. d) The solution is stirred for 24 hours while exposed to the atmosphere. In the course of the ensuing reaction, the originally colorless polyphenol solution darkens and becomes dark brown. The resulting solution may be used directly as is, or may be dried by evaporation under reduced pressure to yield a dark brown crystalline solid which retains depressant properties indefinitely. Obviously, many variations upon this synthesis scheme may be used.

In this synthesis the polyphenol is first oxidized to the corresponding quinone. The resulting quinone is then subjected to various hydroxyl addition reactions around the ring. Quinone and the quinonoid compounds, which result from hydroxyl additions, may also polymerize yielding "quinone humic acids". Polymeric compounds resulting from a synthesis with hydroquinone with this method are apparently of relatively low molecular weight, ranging from ~110-631 as determined by mass spectroscopy.

Synthesis of the reagent from a quinone, may proceed as follows: 1) $10^{-2}$ mole (per liter of final solution) of a quinone is added to 60% of the desired final reagent volume of distilled water in a stirred, closed glass
vessel. 2) $10^{-2}$ mole (per liter of final solution) of a base is added to 20% of the final desired reagent volume of distilled water. 3) The previous two solutions are mixed and diluted to the final reagent volume. 4) The solution is stirred in a closed glass vessel for 24 hours. The original quinone is sparingly soluble, but upon addition of base, the quinone is rapidly oxidized and solubilized to yield a dark brown solution. The resulting solution may be used directly or may be dried. As previously indicated innumerable variations on this synthesis scheme may be employed.

The quinones in this synthesis scheme are subjected to hydroxyl substitutions and polymerization as previously described in the case of synthesis from the polyphenol. The reagent may be referred to as NBQ hereafter for convenience.

The brown color of the NBQ reagent solution disappears at low pH (HCl) with the addition of powdered zinc. This yields a colorless solution by complete reduction of the quinonoid polymers.

**Grinding and Sample Preparation**

Mineral pyrite from Huanzala, Peru was ground using an agate mortar and pestle, sieved to obtain 65x100 mesh
size and used immediately. A sample of coal pyrite, Pocahontas #3 was taken from a Diester table. It was received in the form of thick slurry which was wet sieved and vacuum dried to obtain the 65x100 mesh size fraction. The product was then passed through a dry magnetic separator to remove the non-magnetic particles. The sample which assayed 2.5% hydrocarbon material by low temperature ashing (LTA) was kept in a freezer at \(-10^\circ C\) for subsequent utilization. Pocahontas #3 coal received in lump form, was prepared by crushing in a jaw crushe followed by a roll crusher and wet screened to obtain the 65x100 mesh size fraction. The product which assayed 8.9% ash and 0.9% sulfur was stored in a freezer. Other coals used in these experiments were ground, sieved, and stored in the same way.

Flotation Techniques

Flotabilities of 65x100 mesh mineral pyrite, coal pyrite and raw coal were determined using a 120-ml column cell (23x220mm) with a fine frit and magnetic stirrer. In each test, 0.8 gram of mineral pyrite, coal pyrite samples and 0.5 gram of coal samples were used in the microflotation tests. Samples were conditioned in 120 ml of solution containing the desired chemical for 5 min and floated with 4-methyl-2-pentanol (MIBC, 99% + purity
purchased from Aldrich Chemicals) for 2 minutes using nitrogen at a flow rate of 40 cm$^3$/min.

Larger scale flotation tests were conducted using a bench scale Denver flotation cell. Solids were conditioned for 10 minutes in 2 liters distilled water followed by one minute of conditioning with 50 mg/l of MIBC. The slurry was also conditioned for one minute in the presence of 8x10$^{-6}$ M of NBQ.

An experiment was also performed in the microbubble flotation column of Yoon (253). In this test, a synthetic mixture of 90% Pocahontas #3 and 10% Pocahontas #3 coal pyrite was ground to a mean size of 4.5 $\mu$m. The resulting slurry was floated in the microbubble column. This column was 2" in diameter and 60" in height, with a collector zone of 20" and a recovery zone of 40". Solids were conditioned in a tank for 15 minutes in the presence and absence of 3.4 pounds per ton of NBQ at a pH of 5. The conditioned slurry was then pumped into the column at various feed rates on a continuous basis until steady state conditions were attained. At each feed rate, Dow Froth M150 was supplied at ~4 lbs/ton of coal.
Other Depressant Chemicals Used in the Study

ORFOM D8, a product of Phillips Chemicals, is a water soluble sulfide mineral depressant. The active component is disodium carboxymethyl trithiocarbonate. Because of its unique structure it was considered as a potential coal pyrite depressant. M is a proprietary reagent of American Cyanamid Company. The purified form of it was obtained from Aldrich Chemicals.

Instrumental Methods of Analysis

Mechanisms of the interaction of NBQ with pyrite and coal were investigated using several methods. These include x-ray photoelectron spectroscopy (XPS), FT-IR (Perkin-Elmer), electrophoretic mobility measurements (ZETA meter), adsorption studies with visible wavelength spectrophotometer (Beckman) and flow microcalorimeter (Microscal).

The morphology of coal pyrite was determined by SEM (Cambridge). Elemental analysis of objects under examination were determined by EDAX (Kevex). Sulfur content, ash, and BTU values were determined by Leco equipment.
CHAPTER 10

PYRITE DEPRESSION

RESULTS AND DISCUSSION

Microflotation Tests

The data presented in Figure 60 show the flotation recovery of Pocahontas #3 coal, Pocahontas #3 coal pyrite, and ore pyrite from Peru in the absence of frother. Ore pyrite shows practically no flotation except at pH 1.9, where the surface of the pyrite would be rendered strongly positive and may attach to air-bubbles by electrostatic interaction. The extremely hydrophobic Pocahontas #3 coal does not show the typical bell shaped flotation recovery curve, generally reported for bituminous coals. The hydrophobic character of this coal overwhelms the effects of surface charging which occurs as a function of pH. As pH increases the surface tends to acquire a negative charge, while conversely, as the pH declines the surface tends to acquire a positive charge, both of which may produce depression. The unusually high floatability of this sample of Pocahontas #3 coal pyrite is as that typically reported for coal. The reason for this behavior
Figure 60. Flotation recovery of Pocahontas #3 coal, Pocahontas #3 coal pyrite, and Peruvian ore pyrite in the absence of Frother. Experimental conditions include: 65x100 mesh particle size, conditioning time: 5 minutes, flotation time: 2 minutes, and temperatures = 23° ± 1°C.
becomes clear upon examination of the coal pyrite particles by SEM as shown in Figure 61. Electron photomicrographs show numerous hydrocarbon inclusions in the pyrite. Also, even particles which appear at first to be liberated, may actually possess a hydrocarbon film or lens. Hydrocarbon inclusions and lens appear to dominate the flotation behavior of Pocahontas #3 coal pyrite.

Results shown in Figure 62 indicate ore pyrite floats, without a depressant, with much higher recovery in the presence of the MIBC frother. This phenomenon may be attributed to the adsorption of the frother of the mineral surface increasing the probability of successful adhesion on the surfactant coated bubble, and by the increased probability of bubble-particle collision resulting from a decrease in mean bubble size by the frother addition, while the air volume with time passing thru the cell remains constant, i.e. the number of bubbles available for adhesion increases. The decrease in flotation recovery of ore pyrite with increasing pH is consistent with those results reported by Yoon et al. (254).

Figure 62 also shows the response of the ore pyrite to various depressants. The commercial depressant ORFOM D8 shows significant depression over the entire pH range tested. ORFOM D8 pyrite depression increases with increasing pH. The proprietary depressant M shows good
Figure 61a. SEM photomicrographs of Pocahontas #3 coal pyrite.
Figure 61b. SEM photomicrographs of Pocahontas #3 coal pyrite.
Figure 6lc. SEM photomicrographs of Pocahontas #3 coal pyrite.
Figure 62. Floatability of ore pyrite as a function of pH in the presence of various depressants. 50 mg/l MIBC was used as a Frother.
ore pyrite depression over the entire pH range test, with slight increases in depressant action observed at higher pH. The novel depressant NBQ shows complete depression of ore pyrite in the strongly acidic region, moderate to no depression in the neutral region, and enhanced recovery at alkaline pH. Results indicate the commercial depressants ORFOM D8 and M cannot produce the complete depression of pyrite with this concentration at any pH, while NBQ can produce complete ore pyrite depression at pH less than 6.

REDOX potentials of the M, NBQ, and ORFOM D8 solutions were +250mV, +80mV, and -170mV, respectively, at pH 7. Results shown in Figure 62 show no correlation between the REDOX potentials and the ore pyrite depression efficiencies of these reagents. These results contradict the notion that pyrite depression is generally better in solutions of high reducing potential (255).

Results of microflotation tests of Pocahontas #3 coal and coal pyrite in presence and absence of various depressants are displayed in Figure 63. Flotations were performed with 50 mg/l MIBC as a frother. In the absence of depressants, the coal and coal pyrite show near complete recovery over the entire range of pH. This behavior of coal pyrite is in sharp contrast to the flotation of ore pyrite as shown in Figure 62. The addition of ORFOM D8 and M have no significant effect
Figure 63. Floatability of Pocahontas #3 coal and Pocahontas #3 coal pyrite as a function of pH in the presence and absence of various depressants. 50 mg/l of MIBC was used as a Frother.
upon the flotation recovery of Pocahontas #3 coal pyrite under these experimental conditions. The addition of NBQ at two dosage levels shows remarkable depression of coal pyrite at lower pH; while coal recovery remains relatively high. Addition of NBQ appears to have no effect on coal or coal pyrite recovery at very high pH.

The effect of NBQ reagent dosage upon Pocahontas #3 coal and coal pyrite recovery at pH 5.3 in microflotation is given in Figure 64. Results indicate good pyrite depression may be obtained with reagent dosages as low as $10^{-4}$ moles per liter. Data displayed in Figure 65 indicates that coal depression with NBQ may be significant at short flotation times. If flotation time is increased the recovery of coal improves dramatically, while coal pyrite recovery remains quite low. Addition of kerosene as a collector has also been shown to improve flotation recovery coal, however a smaller increase in sulfur recovery is also observed.

The effect NBQ conditioning time upon the flotation recovery of Pocahontas #3 coal and coal pyrite is shown in Figure 66. Analysis on this data indicates a short conditioning time is required for coal pyrite depression with NBQ. In fact, the full depression effect is observed in one minute or less of conditioning time.
Figure 64. The floatability of Pocahontas #3 coal and Pocahontas #3 coal pyrite as a function of NBQ concentration at pH 5.3.
Figure 65. Flotation kinetics of Pocahontas #3 coal and Pocahontas #3 coal pyrite in the presence of 8x10^-4 M of the quinonoid depression reagent.
Figure 66. Flotation recovery of Pocahontas #3 coal and Pocahontas #3 coal pyrite as a function of conditioning time with $8 \times 10^{-4}$ M NBQ.
To show the potential for separating liberated coal and coal pyrite a series of flotation tests were performed at various pH values with $8 \times 10^{-4}$ NBQ. Results of these experiments are given in Figure 67. Comparison of these values with those obtained with the results obtained with the individual components shown in Figure 63 show they are practically identical. Results clearly indicate that selective coal pyrite depression in a completely liberated system is possible. Greater than 90% desulfurization can be achieved by the application of NBQ in froth flotation, with good coal recovery.

Denver Cell Flotation Tests

To more closely simulate current industrial coal beneficiation practice, a series of experiments were performed in a bench scale Denver flotation cell. The first experiments were performed with and without NBQ at an order of magnitude lower concentration than had been used in the micro scale flotation experiments. Ten grams of 100×140 mesh Pocahontas #3 coal and Pocahontas #3 coal pyrite were individually floated in a bench scale Denver flotation cell. The solids were conditioned for 10 minutes in 2 liters distilled water followed by one minute conditioning with 50 mg/l of MIBC. The slurry was then conditioned for one minute in presence of $8 \times 10^{-6}$ M NBQ.
Figure 67. Floatability of the synthetic mixtures of Pocahontas #3 coal and Pocahontas #3 coal pyrite as a function of pH with $8 \times 10^{-4}$ M of the quinonoid depression reagent.
Analysis of the data shown in Figure 68 indicates the coal floats at essentially the same rate in the presence or absence of 8x10^-6 NBQ. However coal pyrite is significantly depressed with less than 18% recovery in 8 minutes of flotation time while coal recovery was about 98% at the same flotation time. The flotation rate constant for Pocahontas #3 coal in the presence and absence of the depression reagent was approximately 16 min^-1. Pocahontas #3 coal pyrite showed a rate constant of 13 min^-1 in the absence of NBQ, while a rate constant of only 1 min^-1 in the presence of the reagent.

ROM Pocahontas #3 coal was ground to 75-micron mean size and floated in a bench-scale Denver flotation cell. Ten-gram samples were conditioned for five minutes in two liters of distilled water. Then NBQ, at 0.17 pounds/ton, was added with one minute of conditioning time at pH 5, followed by one minute of conditioning with 2.5 pounds/ton of MIBC. Flotation then proceeded to exhaustion. Data are presented in Table 17. Results show this low-sulfur coal, with a small amount of liberated pyrite, can be significantly desulfurized. A 6.3% improvement compared with flotation in the absence of the novel reagent was obtained with no significant decrease in recovery. The sulfur rejection result is a 17% decrease in the pyritic sulfur content of this coal. This is nearly all the
Figure 68. Flotation kinetics of Pocahontas #3 coal and Pocahontas #3 coal pyrite in a Denver cell with and without the quinonoid depression reagent.
Table 17. Results of Flotation Tests on a Pocohontas #3 Seam Coal

<table>
<thead>
<tr>
<th></th>
<th>Recovery (%)</th>
<th>Ash (%)</th>
<th>Sulfur (%)</th>
<th>Btu/lb</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROM Feed</td>
<td>-</td>
<td>11.86</td>
<td>0.941</td>
<td>13992</td>
</tr>
<tr>
<td>Product (w/o reagent)</td>
<td>95.26</td>
<td>7.94</td>
<td>0.941</td>
<td>14726</td>
</tr>
<tr>
<td>Product (w/reagent)</td>
<td>92.39</td>
<td>6.32</td>
<td>0.882</td>
<td>15024</td>
</tr>
</tbody>
</table>
liberated pyrite which is contained in this size coal, as is clearly demonstrated by SEM examination of the flotation products. Further improvements in pyrite rejection can only be achieved by finer grinding to liberate more pyrite. A significant increase in ash rejection is also observed, i.e., a 13.7% improvement compared with flotation in the absence of the novel reagent.

In this experiment, ROM Illinois #6 coal was floated as in the preceding experiment except 3 lb/ton of kerosene was added as a collector. The data, given in Table 18, show that Illinois #6 coal can be desulfurized with a 14.6% improvement over the flotation product in the absence of the NBQ reagent. At this relatively large particle size, 75 micron mean size, the pyrite in Illinois #6 is not well liberated and middlings containing large amounts of pyrite inclusions and ash minerals are rendered hydrophilic by the process and no longer report to the froth phase as indicated by the decrease in recovery at exhaustion. A 15.1% increase in ash rejection was also observed by application of the process.

A synthetic mixture of Pocahontas #3 coal (100x140 mesh) and Pocahontas #3 coal pyrite (Diester table refuse 100x140 mesh) was made by adding nine grams of the coal and one gram of the coal pyrite. The resulting ten gram sample was floated in a bench-scale Denver cell as in the
<table>
<thead>
<tr>
<th></th>
<th>Recovery (%)</th>
<th>Ash (%)</th>
<th>Sulfur (%)</th>
<th>Btu/lb</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROM Feed</td>
<td></td>
<td>24.51</td>
<td>4.08</td>
<td>10622</td>
</tr>
<tr>
<td>Product (w/o reagent)</td>
<td>92.30</td>
<td>13.17</td>
<td>4.17</td>
<td>12387</td>
</tr>
<tr>
<td>Product (w/reagent)</td>
<td>85.30</td>
<td>9.47</td>
<td>3.56</td>
<td>12800</td>
</tr>
</tbody>
</table>
preceding test, except 0.2 lb/ton of the NBQ depression reagent and pH 3 were employed. Results are shown in Table 19. The novel process produced 36.6% improvement when compared to flotation in the absence of the reagent, and a 76.1% overall desulfurization.

To demonstrate the potential for conditioning at low pH and floating at higher pH, the following experiments were performed. In this example, 0.8 grams of Pocahontas #3 coal pyrite (65x100 mesh) was preconditioned for one minute at pH 3 in the presence of \(8 \times 10^{-4}\) M of NBQ, and then rinsed and filtered to remove all traces of the solution. Resulting solids were resuspended in 120 ml of distilled water, adjusted to various pH by the addition of hydrochloric acid or sodium hydroxide, and conditioned as in the preceding flotation test. The results are presented in Table 20. Analysis of the data show that once the pyrite is rendered hydrophilic by the novel reagent treatment at low pH it is not reversed to a great extent when the solution is removed and flotation is promptly carried out at another pH. However, the data also indicates a small increase in recovery as the pH of flotation is increased.
<table>
<thead>
<tr>
<th></th>
<th>Recovery (%)</th>
<th>Sulfur (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>-</td>
<td>5.43</td>
</tr>
<tr>
<td>Product (w/o reagent)</td>
<td>83.27</td>
<td>2.05</td>
</tr>
<tr>
<td>Product (w/reagent)</td>
<td>83.79</td>
<td>1.30</td>
</tr>
</tbody>
</table>
Table 20. Effect of pH on Pyrite Recovery for a Pocohontas #3 Coal Pyrite Sample Floated With 8x10^{-4}M NBQ

<table>
<thead>
<tr>
<th>Flotation pH</th>
<th>Pyrite Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.10</td>
<td>1.9</td>
</tr>
<tr>
<td>5.10</td>
<td>4.0</td>
</tr>
<tr>
<td>8.30</td>
<td>16.6</td>
</tr>
<tr>
<td>10.40</td>
<td>17.4</td>
</tr>
</tbody>
</table>
Microbubble Flotation Tests

A synthetic mixture of 90% Pocahontas #3 coal and 10% Pocahontas #3 coal pyrite (Diester table refuse) was ground to a mean particle size of 4.5 µm. The resulting slurry was floated in a microbubble flotation column. The column described by Yoon et al., 1988, was 2" in diameter and 60" in height, with a collector zone of 20" and a recovery zone of 40". Solids were conditioned in a tank for 15 minutes in the presence and absence of 3.4 pounds per ton of the NBQ reagent at pH 5. A conditioned slurry was then pumped into the column at various feed rates on a continuous basis until steady state conditions were attained. At each feed rate, Dowfroth M150 was supplied at approximately 4 pounds per ton of coal. Results are illustrated in Figure 69 and additional data are contained in Appendix V. The microbubble flotation process using the NBQ reagent consistently produced lower sulfur levels, at equal coal recoveries, when compared to flotation results in the absence of the NBQ pyrite depression reagent.

Coal Coagulation Experiments

Coal coagulation experiments have shown the NBQ reagent produces better ash rejection than commercial dispersants such as sodium silicate, sodium hexametaphosphate, and carboxymethylcellose in identical
Figure 69. Grade recovery curves for synthetic mixtures of Pocahontas #3 coal and Pocahontas #3 coal pyrite in microbubble flotation with and without 3.4 lbs/ton of the NBQ depression reagent.
dosages, at pH 9 and 11. Therefore, the NBQ shows significant promise as a dispersant as well a pyrite depressant.

**Electrophoretic Experiments**

Electrophoretic mobility measurements (i.e. ZETA potential) were made with coal and coal pyrite in the presence and absence of NBQ. Results of these tests are presented in Figure 70. In the absence of the quinonoid depression reagent the Pocahontas #3 coal and Pocahontas #3 coal pyrite exhibit isoelectric points (IEP) at pH 4.8 and pH 3.9, respectively. Measured IEP values are within the range reported for coal and mineral pyrite by other researchers (256-258). Addition of NBQ yielded negative ZETA potentials throughout the pH range. The ZETA potentials for both coal and coal pyrite were similar in the presence of NBQ over the entire pH range.

The preceding ZETA potential measurement results suggest NBQ binds to both coal and coal pyrite. This binding to the surface renders it negatively charged from nearly pH 2-12. To demonstrate the charge on the NBQ reagent molecules, an electrophoretic experiment was performed. In this test a thick piece of filter paper was cut into a rectangle and soaked in a saturated potassium chloride solution. To opposite ends of the rectangle the
Figure 70. Electrophoretic mobility of Pocahontas #3 coal and Pocahontas #3 coal pyrite in the presence and absence of the quinonoid depression reagent.
wires from the ZETA meter were attached by alligator clips attached by alligator clips and current applied. A drop of NBQ was placed in the center of the paper, making a dark brown mark which was readily visible. As time passed the brownish material migrated en masse towards the positive pole. Neither visible light nor U.V. light examination of the paper showed any significant separation of the reagent into separate components.

**Instrumental Analyses**

Attempts to identify the molecular components by gas-chromatography/mass spectroscopy were thwarted, as many of the components of the NBQ depression reagent are non-volatile at ordinary injection port temperatures. An experiment with a heated probe containing NBQ inserted directly into the mass spectrometer, desorption chemical ionization (DCI), indicated the NBQ reagent at pH 3 (by HCl addition) apparently contained components of molecular weights: 110 (11.6%), 203 (29.6%), 287 (30.6%), 361 (22.6%), 575 (3.6%) and 631 (1.8%). The mass spectral data from this experiment is contained in Appendix IV.

The quinonoid reagent does not possess any distinctive absorption band in the infra-red region. Transmission, ATR, and external reflection techniques all fail to give worthwhile signals for interpretation.
X-ray photoelectron spectroscopy (XPS) was employed to examine ore pyrite samples with and without NBQ treatment. The spectra indicate the presence of a carbon compound on the surface of the pyrite after NBQ treatment. However, no significant shifts in the sulfur peak were observed which might be indicative of covalent bonding between the quinonoid compound and the sulfur of the pyrite. This mechanism of covalent bonding to sulfur early in this study seemed a plausible explanation for the binding of the depression reagent to sulfide mineral surfaces. Especially since the depressant effect of NBQ on pyrite is enhanced at high acidity (low pH) and thiosulfate addition to quinone shows acid catalysis. Thiosulfate type compounds may exist on pyrite surfaces providing sites of binding for NBQ. Even with the evidence of microcalorimetry, to be discussed later in this section, which shows the NBQ binding to be reversible, cannot be used to completely dismiss this possibility. Even though this mechanism may not play a dominant role, it could still make a smaller contribution.

A visible wavelength spectrophotometer was adjusted to radiate 506 nm light, and a light transmission calibration curve was obtained with three concentrations for the quinonoid reagent. The resulting curve showed good agreement with Beer's Law. A known mass of graphite
(surface area = 0.75M², at 50x80 mesh) was agitated with 10⁻³M of the quinonoid reagent, at pH 4.1, for 30 minutes, the product was separated by centrifugation. The supernatant was placed in the spectrophotometer to determine the change in concentration by comparison of the absorption of the unknown versus the calibration curve results. A pyrite sample (ore pyrite, Peru, 50x80 mesh, surface area = 0.00498M²/g) was treated in the same way.

Results of the preceding experiments indicated that the mass of quinonoid reagent per unit surface area on pyrite is approximately 19 times that which occurs on graphite, specifically: 0.0361g/M² on graphite and 0.6930g/M² on pyrite.

Experiments were performed in the flow microcalorimeter (Microscal Ltd.) to determine the heats of adsorption and desorption on both graphite and pyrite. Examination of the thermogram illustrated in Figure 71A shows the quinonoid reagent binds to graphite reversibly. Reagent binding occurs over a relatively short interval, approximately 6.5 minutes, and liberates little heat. Heat liberated during adsorption is approximately equal to that absorbed during desorption. The heat of adsorption of the quinonoid reagent appears to be about 10mJ/g on graphite. The thermogram shown in Figure 72B indicates the quinonoid reagent reversibly binds with pyrite. This
Figure 71. Thermograms of the adsorption and desorption of the quinonoid depression reagent:
a. graphite and b. ore pyrite.
binding occurs over a relatively long time interval, approximately 26 minutes or so, and generates much more heat than observed with graphite. The heats of adsorption and desorption on pyrite are approximately equal. The heat of adsorption of the quinonoid reagent is apparently about 48 mJ/g on pyrite.

Proposed Mechanisms of Depression and Dispersion

Results obtained with pyrite are consistent with the view of Leja (247), where he states: "Ionization of the phenolic and carboxylic groups leads to adsorption of these compounds," i.e. polyphenols and derivatives, "on cationic surface sites, followed by strong lateral hydrogen bonding and conversion of mineral surfaces to negatively charged hydrophilic surfaces." Our own electrophoretic mobility measurements indicate minerals are rendered negatively charged by the quinonoid reagent.

The selectivity displayed in froth flotations of coal by the quinonoid reagent may be explained by the density of adsorption of the reagent on a carbon compound versus a metallic sulfide. The number of hydrophilic reagent molecules which adsorbs per unit of surface area of pyrite is many times that which probably occurs on coal; that is, if graphite and ore pyrite can be considered as model
compounds similar in reactivity to coal and coal pyrite, respectively.

Binding of the quinonoid reagent with graphite appears to be much weaker than observed with pyrite. It is proposed that the quinonoid reagent binds to the surface of graphite by hydrophobic bonding.

Decrease in the flotation rate constant of a naturally hydrophobic and flotable mineral is likely to be directly proportional to the mass of hydrophilic quinonoid reagent molecules adsorbed per unit of mineral surface.

The reagent, by binding to the mineral surface, converts the surface to an anionic state. This tends to electrostatically repel the negatively charged, surfactant coated air bubble. The reagent also causes ordering of the water molecules near the mineral particle, propagating a repulsive structural force deep into the surrounding medium. This ordered hydration layer may resist thinning upon the approach of a bubble due to its semi-crystalline (ice-like) nature. Combination of these two repulsive forces tends to overwhelm the weaker attractive dispersion forces and thereby inhibits bubble-particle attachment.

Another aspect of this reagent which may explain the reagent selectivity of depression between coal and coal pyrite is the relatively low average molecular weight.
The average molecular weight for NBQ appears to be only about 275. When related compounds, humic acids (molecular weight >600) and tannic acids (molecular weight about 1600) acids, have been tested on coals, severe coal depression was observed. If the number of potential binding sites on a coal particle is some given constant and all these sites are occupied by a molecule of molecular weight 275 in one case and 1600 in the other. It is reasonable to expect the higher molecular weight molecule would produce significantly greater depression due to: 1) greater surface area coverage due to bulk, 2) potentially more ionization functional groups to produce repulsive electrostatic forces, and, 3) propagation of a stronger repulsive structural force into the surrounding solution.

In addition to the improved desulfurization, which is the primary objective, the process also increases significantly the ash rejection with some coals. Mechanisms involved in the beneficial increase in ash rejection may include:

1) Desliming coal particles by imparting negative charges by binding of the quinonoid molecules on the coal and ash-forming gangue particles. The negatively-charged particles would then be repelled from one another by electrostatic repulsion. Therefore, ash-forming
gangue particles would no longer be buoyed to the froth by attachment to hydrophobic coal particles.

2) Decreased entrainment of ash particles in the coal coagula. Fine coal tends to coagulate and, at the same time, to entrain other particles in the coagula. The reagent of this study binds to coal, rendering it more negative, as evidenced by electrophoretic mobility measurements. Binding of the reagent to the coal partially inhibits the formation of coal coagula, but not bubble-particle adhesion to any substantial degree.

3) The reagent binds to the surface of the ash-forming gangue minerals such as the silicates. The reagent of this study generally possesses a negative charge which aids in the dispersion of the ash-forming particles by electrostatic repulsion and inhibits bubble-particle adhesion by covering the mineral with strongly polar molecules, rendering it more hydrophilic. The ash rejection effect appears to be a function of pH. Higher pH yields greater ash rejection when compared to the results identically obtained except for the application of the novel process. The mechanism of increased ash rejection as the pH of the flotation pulp increases may be ascribed to increased ionization of the various hydroxyl groups on the molecules of the NBQ reagent.
CHAPTER 11

PYRITE DEPRESSION

CONCLUSIONS

Consideration of the experimental results of the use of a novel quinonoid pyrite depression reagent has lead to the following conclusions:

1) Liberated pyrite can be separated from bituminous coal in froth flotation by the addition of a reagent resulting from the alkaline oxidation of hydroquinone or quinone, and thereby producing significant desulfurization.

2) Ash rejection in the froth flotation of run-of-mine coals may be significantly increased by the addition of the quinonoid reagent.

3) The hydrophilic quinonoid reagent produces pyrite depression by selectively binding to the pyrite surface, producing a much higher adsorption density on the pyrite versus coal.

4) The mechanism of the NBQ reagent binding to pyrite may include: a) Attraction to cationic sites on the
mineral surface by electrostatic interactions with ionized oxygen groups on the depressant molecule, and
b) Subsequent strong hydrogen bonding of the reagent molecule to the mineral surface.

5) The mechanism of NBQ reagent binding to coal may be largely due to hydrophobic bonding of the aromatic rings of the reagent to similar functional groups on the coal surface.

6) The novel depression reagent produces greater ore pyrite depression than the commercial depression reagents, M and ORFOM D8.

7) The depression reagent is a mixture of quinonoid compounds ranging in molecular weight from 110 to 631, with an average molecular weight of ~275.
PART IV

MAJOR FINDINGS AND SUGGESTIONS FOR FUTURE RESEARCH

CHAPTER 12

MAJOR RESEARCH FINDINGS

During the survey of photochemical methods for the desulfurization of coal several interesting facts emerged. First, semiconductor photoelectrochemical and direct photolysis chemical processes are very efficient in the degradation of the model organo-sulfur compound DBT in solution. Thiophenic compounds of this type are reputedly the most resistant organic sulfur forms found in coal. However, these same photochemical processes produced only limited improvements in coal desulfurization when compared to the dark reactions. The major obstacle to chemical coal desulfurization is diffusional access to the sulfur imbedded deep in the polymeric matrix of the coal and not the reactivity of sulfur compounds found in the coal. Second, the efficiency of coal desulfurization is largely dependent upon the alkalinity of the solution, i.e. higher concentrations of strong base produce much greater desulfurization than lower alkalinity coal slurries. Third,
the mechanisms of model compound degradation in the presence of semiconductor catalysts is apparently complicated. In some cases, the molecule appears to bind to the surface of the catalyst and symmetrical ring opening occurs, in addition to the expected oxidation, rearrangement, or hydrogenation.

The use of the novel quinonoid reagent produces significant sulfur and ash rejection in the froth flotation of coal. This anionic, polymeric surfactant, reversibly binds to mineral surfaces and renders them more hydrophilic and simultaneously imparts a strong negative charge. Coal recovery remains high in processes employing the new pyrite depressant.

With further development, both photochemical and selective depression techniques show promise as commercial coal desulfurization processes. Continued research and development directed towards the improvement of process efficiency and more thorough understanding of the fundamental mechanisms involved should be continued. Only through the development and implementation of new technologies can our environment be protected from the deleterious effects of the combustion of fossil fuels.
Suggestions for Future Work

Promising new photochemical methods for the precombustion desulfurization of coal have been described. These procedures could utilize sunlight, a cheap and abundant energy source to drive the reaction. Coal slurries in shallow ponds or reaction tanks could be diffused with the appropriate gas could be photochemically treated to further remove sulfur which was not previously rejected by conventional coal preparation techniques. Research directed towards this goal should be continued.

Since coal desulfurization appears to be limited by access rather than reactivity experiments could be directed towards the solution of this problem. For example solvents such as n-propylamine are known to expand the coal matrix considerably, perhaps an approach similar to this could be employed to increase diffusity and thereby internal access. Also, depolymerization of the organic coal matrix could produce products more amenable to photochemical procedures.

Products of coal liquefaction or liquid petroleum could be desulfurized by photo-oxidation techniques. In this process the hydrocarbon liquid would be contacted with an aerated alkaline aqueous media. This media would consist of an aerated semiconductor catalyst slurry with
irradiation at band gap wavelengths. Stereo specific oxidation of sulfur containing compounds in the hydrocarbon liquids would occur at the boundary of the immiscible phases. The polar oxidation products such as sulfate would tend to accumulate in the aqueous slurry phase.

Semiconductor catalysts demonstrate marked improvements in the photo-degradation of DBT. Perhaps doping of the familiar semiconductors could produce further improvements in degradation rates and associated desulfurization efficiencies. The discovery of more effective metallic oxide catalysts may also improve kinetics.

The novel reagent NBQ has demonstrated considerable commercial promise as a pyrite depressant and ash dispersant. Experiments directed towards the synthesis of similar yet more selective and powerful depression reagents may produce an even more useful reagent than NBQ. The exact molecular composition of the depression reagent has yet to be determined, more work with the DCI mass spectroscopic technique may provide the data required for complete characterization. The models of bubble-particle interaction which have been thus far developed are not fully quantitative, nor are they based on first principles. Further work is needed to simplify and unify the existing theories so that they may be used by engineers in process control.
REFERENCES


APPENDIX I

GC/MS ANALYSIS OF THE TiO$_2$ CATALYSED PHOTOLYSIS
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APPENDIX II

GC/MS ANALYSIS OF FIRST ATTEMPT TO ISOLATE PRODUCTS FROM ZnO/hv REACTION MIXTURE
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DCI MASS SPECTROSCOPY OF NBQ AT pH 3
APPENDIX V

DATA FROM MICROBUBBLE FLOTATION TESTS
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VITA

Michael L. Stallard was born October 13, 1954 in Hamilton, Ohio. He obtained his Bachelor of Science degree in Biology from Virginia Commonwealth University, Richmond. Upon graduation, he worked five years with the Jewell Ridge Coal Corporation Division of the Pittston Company as an environmental technician before entering Virginia Polytechnic Institute and State University in 1983 to obtain a Master of Science degree in Environmental Engineering. Following the successful completion of the Masters degree in 1986, he began pursuit of the Doctor of Philosophy degree in Civil Engineering (Environmental Engineering) also at Virginia Polytechnic Institute and State University. He is a member of the American Society of Civil Engineers, American Water Works Association, and the Water Pollution Control Federation.