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LOW TEMPERATURE PROCESSES FOR COAL DESULFURIZATION

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LOW TEMPERATURE PROCESSES FOR
COAL DESULFURIZATION

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(M. S. thesis)

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For Reference

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LOW TEMPERATURE PROCESSES FOR COAL DESULFURIZATION

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ABSTRACT

A number of processes have been proposed to remove sulfur from coal. Several of these are based upon treatment with aqueous solutions at low temperatures and pressures. The effectiveness of these latter methods to remove organic and inorganic sulfur from high sulfur Illinois #6 coal was studied. The effect of leaching agent temperature, reaction time, and particle size was determined. The leaching agents studied were 10% sodium hydroxide, and 0.5 M ferric sulfate.

The following major conclusions were drawn from this work:

1. Sodium hydroxide is effective in removing the major pyritic sulfur, but even at the highest temperatures studied was unable to remove more than 40% of the organic sulfur from Illinois #6 coal.

2. Ferric sulfate is very effective in removal of pyritic sulfur.

3. Oxygen appears to be a promising method but under the conditions used in this work, too much of the coal matrix was oxidized.
I. INTRODUCTION

A. Occurrence and Forms of Sulfur

Sulfur is present in coal in three different forms: as metallic sulfides, as metallic sulfates and as organic sulfur.

Pyritic sulfur in coal is present as the minerals pyrite and marcasite which have the same composition FeS₂, but differ in crystalline structure. Because it is difficult to distinguish between them, they are usually designated simply as pyrites or iron pyrites.

Pyrites are distributed in coal in many ways. They can occur in lenses and bands, balls or nodules, joints or cleats, and as finely dispersed particles. The size and distribution affect the amount that can be removed by conventional coal preparation methods. Coarse crushing may release much of the pyrites in the lenses, bands, cleats and joints, for subsequent removal by mechanical cleaning. In order to free the fine particles from the coal, it is necessary to grind the coal very fine prior to cleaning. However, this procedure has an adverse effect on process efficiency and severely restricts the methods of cleaning that can be applied.

The amount of sulfate sulfur in freshly mined coals in general is less than 0.05%, but it gradually increases due to oxidation of the pyrites. In fact its presence in more than small amounts indicates that the coal has been weathered. Because sulfate sulfur in commercial coals is so low, it is not an important factor in coal utilization.

Organic sulfur is distributed through the coal matrix as an integral part of the coal molecular structure and accordingly it can not be removed by conventional cleaning or preparation processes, but requires chemical treatment.
In general, organic sulfur is the predominant form of low-sulfur coals; however, as the total sulfur increases, both the organic and pyritic forms increase. There is no fixed direct relationship between the amounts of each form.

Although there is no exact knowledge of the forms in which organic sulfur is present in the coal matrix, some groups have been suggested as follows:

1. Bahtnagar and Duti\(^2\) reported mercaptans and disulfides in the extracts. However, the bulk of the sulfur compounds remained in the residue.

2. Roy\(^3\) obtained extracts from an Indian coal using benzene and ethylenediamine, in which he was able to identify mercaptans, sulfide, disulfides, and thiophenes. He also treated the Indian coal with \(\text{KMnO}_4\) and found that 70% of the sulfur remained in the oxidized residue, so he concluded that 70% of the sulfur is in ring structure.

3. Kavcic\(^4\) similarly concluded that 70% of the organic sulfur present in a high sulfur Yugoslavian coal is a part of the heterocyclic aromatic ring structure.

4. Gusev\(^5\) demonstrated the presence of both thioether and bis-thioether groups in Russian coals.

5. Postowsky\(^6\) demonstrated the presence of organically fixed thioether sulfur in coals.

6. Lissner and Nemes\(^7\) studying the distribution of sulfur in various fractions obtained when coal is carbonized in an atmosphere of nitrogen and steam or with steam alone at temperatures from 200 to 560°C, found that the organic sulfur occurs in four forms.
100-300°C sulfur is evolved from phenolic sulphur groups and probably from \( \equiv C - SH \) or \( \equiv C S C \equiv \) groups containing nitrogen. Superheated steam hydrolyzes sulfidic sulfur at 380°C, and retards the formation of new organic sulfur compounds with the evolution of inorganic sulfur.

Figure 1 displays a "representative coal molecule" of Hill and Lyon \(^8\) which includes sulfur-containing groups such as:

\[
\begin{align*}
\text{R} - \text{S} - \text{R}' \\
\text{C} - \text{C} -
\end{align*}
\]

In other "coal structure" proposed by Wiser \(^9\) shown in Fig. 2, the above groups are also present, but in addition Wiser includes:

\[
\begin{align*}
\text{R} - \text{S} - \text{S} - \text{R}'
\end{align*}
\]

where \( R \) and \( R' \) are in general cyclic compounds.

In general, the fraction of the sulfur present as mercaptans, sulfides, or as a part of a heterocyclic ring structure is unknown. This is unfortunate, because the form of the sulfur in coal has a great bearing on the chemical treatment necessary to remove it. When coal is coked Tiessen \(^10\) found that the coke product contained approximately 45% of the original organic sulfur. If coal is hydrodesulfurized at moderate temperatures and without catalysis (SRC process), around 40% of the organic sulfur remains in the coal. However, it is known that sulfur appearing in ring structures is more difficult to hydrogenate or to remove by decomposition than other forms of organic sulfur in coal. Thus, the above observations suggest that the major portion of the sulfur appearing in the coke and in the coal product originates from ring structure, and that the easily removed portion is other
\[
R^*N = \text{Alicyclic rings of } N \text{ carbons.} \\
RN = \text{Alkyl side chain of } N \text{ carbons.} \\
R'N = \text{Unsaturated alkyl side chain of } N \text{ carbons.} \\
CB = \text{Cross bonding by } O \text{ or } S \text{ to new heterocyclic groups with side chains.} \\
T = \text{Tetrahedral 3 dimensional } C-C \text{ bonds, } C-O \text{ bonds and } C-S \text{ bonds.}
\]

XBL 767-8684

Fig. 1. Model for high-volatile coal.
G. R. Hill, L. B. Lyon, ISEC (June, 1962)
Fig. 2. A model for bituminous coal structure.
W. H. Wiser, "Coal Cataysis"
forms of sulfur. It follows that approximately 40-60% of the organic sulfur in American coals is present in ring structure.

B. Chemistry of Organic Sulfur

Little quantitative information is available on either the amount or kind of sulfur compounds present in coal. Consequently the chemistry of model sulfur-containing compounds of the type believed to exist in the coal structure was studied.

1. Hydrogenation

Equilibrium constants for the hydrogenation of various type compounds to yield saturated hydrocarbons and hydrogen sulfide are summarized by Emmett and are plotted in Fig. 3 for the following reactions:

1. Ethanethiol
   \[ \text{CH}_3\text{CH}_2\text{SH} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_3 + \text{H}_2\text{S} \]

2. 2-Propanethiol
   \[ (\text{CH}_3)_2\text{CHSH} + \text{H}_2 \rightarrow (\text{CH}_3)\text{CH}_2\text{CH}_3 + \text{H}_2\text{S} \]

3. 3-Thiapentane
   \[ \text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3 + 2\text{H}_2 \rightarrow 2\text{CH}_3\text{CH}_3 + \text{H}_2\text{S} \]

4. Thiacycloexane
   
   \[ \text{CH}_2\text{CH} - \text{CH}_2 - \text{SH} + 2\text{H}_2 \rightarrow \text{H}_2\text{S} + \text{n-C}_5\text{H}_{12} \]

5. 3-4 Dithiaexane
   \[ \text{CH}_3\text{CH}_2\text{SSCH}_2\text{CH}_3 + 3\text{H}_2 \rightarrow 2\text{CH}_3\text{CH}_3 + 2\text{H}_2\text{S} \]

6. Thiophene
   \[ \text{CH} - \text{CH} \]
   \[ \text{CH} - \text{CH} + 4\text{H}_2 \rightarrow 4\text{H}_2\text{S} + \text{n-C}_4\text{H}_{10} \]
Fig. 3. Equilibrium constants for the hydrogenation of sulfur compounds to form H₂S.
The graph shows that hydrogenation of sulfur compounds in thermodynamically favorable, especially for disulfides, in the range of 700°K (427°C) and lower temperatures.

Some information on the relative hydrodesulfurization rates of various compounds is available from work done on petroleum fractions. Byrns, Bradley, and Lee\textsuperscript{12} observed that thiophenes were the most difficult sulfur compounds to decompose during the hydrodesulfurization of feed stocks in the gasoline boiling range.

Casagrande, Meerbott, Sartor, and Trainer\textsuperscript{13} found that hydrodesulfurization of a pressure distillate tops (0.34% S) under pressure over a tungsten-nickel sulfide catalyst, gave a good removal of sulfides, mercaptans, and disulfides. The residual sulfur compounds included thiophenic rings. Figure 4 shows their results.

2. Decomposition Reactions

The decomposition of the model compounds to yield unsaturated hydrocarbons and H\textsubscript{2}S can be represented by the following stoichiometric equations:

1. Ethanethiol

\[
\text{CH}_3\text{CH}_2\text{SH} \rightarrow \text{CH}_2 = \text{CH}_2 + \text{H}_2\text{S}
\]

2. 2-Propanethiol

\[
(\text{CH}_3)_2\text{CHSH} \rightarrow \text{CH}_3\text{CH} = \text{CH}_2 + \text{H}_2\text{S}
\]

3. 3-Thiapentane

\[
\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3 \rightarrow 2\text{CH}_2 = \text{CH}_2 + \text{H}_2\text{S}
\]

4. Thiacyclohexane

\[
(\text{CH}_2)_5\text{S} + \text{CH}_2 = \text{CHCH}_2\text{CH} = \text{CH}_2 + \text{H}_2\text{S}
\]
Fig. 4. Comparison of 50°F cuts of pressure distillate tops charge and product.
5. 3-4 Dithiahexane

\[ \text{CH}_3\text{CH}_2\text{SSCH}_2\text{CH}_3 + \text{CH}_2 = \text{CH}_2 + \text{CH} = \text{CH} + 2\text{H}_2\text{S} \]

The equilibrium constants for the reactions shown are summarized by Emmett\textsuperscript{11} and plotted in Figure 5.

From the graph it can be seen that the decomposition reactions are favored at high temperatures, but at lower temperatures reactions 1 and 2 are still possible.

Some of the works that confirm these data are:

(1) Woolhouse\textsuperscript{14} mentions that \( \text{H}_2\text{S} \) was produced by the decomposition of organic sulfur upon carbonization of a coal.

(2) Jolly\textsuperscript{1} studied the effect of rate of heating in the decomposition of the organic sulfur to give \( \text{H}_2\text{S} \).

(3) Powell\textsuperscript{15} concluded that one quarter to one third of the organic sulfur decomposes to give hydrogen sulfide at temperatures below 500°C. He also found that a small part of the sulfur was evolved as volatile organic sulfur compounds.

(4) Scott\textsuperscript{16} concluded that the heterocyclic sulfur bond is very stable, and that if the sulfur is not a part of an aromatic system, the C – S bond scission is relatively easy at low-temperature carbonization levels.

3. Oxidation

Mercaptans can be oxidized to sulfonic acids\textsuperscript{17} with various types of oxidizing agents, such as oxygen and hydrogen peroxide.

\[ \text{RSH} + \frac{1}{2} \text{O}_2 \rightarrow \text{RSO}_2\text{OH} \]
Fig. 5. Equilibrium constants for the decomposition of sulfur compounds to form $\text{H}_2\text{S}$. 
Alkylsulfides can react with $\text{O}_2$:

$$2\text{RSSR} + 2\text{H}_2\text{O} + 5\text{O}_2 \rightarrow 4\text{RSO}_3\text{H}$$

Wallace and Seckriesheim\textsuperscript{19} studied the oxidation of thiols and disulfides with $\text{O}_2$ under basic conditions. They conclude that both aliphatic and aromatic compounds can be oxidized to their corresponding sulfonic acids.

4. Sodium Hydroxide

Treatment with sodium hydroxide has been used for many years to remove mercaptans from gasoline cuts in the petroleum industry. The reaction that takes place\textsuperscript{20} is:

$$\text{RSH} + \text{NaOH} \rightarrow \text{RSNa} + \text{H}_2\text{O}$$

The solubility of the mercaptans in sodium hydroxide decreases as the molecular weight increases. The removal of mercaptans reaches a maximum at 2M concentration.\textsuperscript{21}

Some solubilities of mercaptans in 1N sodium hydroxide solution are:\textsuperscript{36}

<table>
<thead>
<tr>
<th>Mercaptan</th>
<th>Solubility, gm/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl to butyl</td>
<td>very soluble</td>
</tr>
<tr>
<td>Amyl</td>
<td>328.0</td>
</tr>
<tr>
<td>Hexyl</td>
<td>94.0</td>
</tr>
<tr>
<td>Heptyl</td>
<td>27.6</td>
</tr>
<tr>
<td>Octyl</td>
<td>8.0</td>
</tr>
<tr>
<td>Nonyl</td>
<td>2.3</td>
</tr>
</tbody>
</table>
When mercaptans are treated with steam in presence of NaOH, they can decompose as follows:

\[ \text{RSH} + \text{H}_2\text{S} + \text{R'}\text{CH} = \text{CH}_2 \]
\[ \text{H}_2\text{S} + 2\text{NaOH} \rightarrow \text{Na}_2\text{S} + 2\text{H}_2\text{O} \]

The overall reaction is:

\[ \text{RSH} + 2\text{NaOH} \rightarrow \text{Na}_2\text{S} + 2\text{H}_2\text{O} + \text{R'}\text{CH} = \text{CH}_2 \]

When mercaptans are treated with NaOH at 260°C two reactions can take place:

\[ \text{RSNa} + \text{NaOH} \rightarrow \text{ROH} + \text{Na}_2\text{S} \]

or

\[ 2\text{RSNa} \rightarrow \text{R}_2\text{S} + \text{Na}_2\text{S} \]

Sulfides can react in the following way:

\[ 2\text{RCH}_2\text{SCH}_2\text{R'} + 2\text{NaOH} \rightarrow \text{R} = \text{CH}_2 + \text{R'} = \text{CH}_2 + \text{Na}_2\text{S} + \text{H}_2\text{O} \]

Disulfides can decompose according to this stoichiometry:

\[ 2\text{RSSR} + 4\text{OH}^- \rightarrow 3\text{RS}^- + \text{RSO}_2^- + 2\text{H}_2\text{O} \]

The \( \text{RS}^- \) can decompose further to yield the \( \text{Na}_2\text{S} \) and the unsaturated hydrocarbon.

C. Chemistry of Inorganic Sulfur

1. Hydrogenation

Pyritic sulfur, FeS\(_2\), can be treated with hydrogen to yield FeS and hydrogen sulfide according to the equation:

\[ \text{FeS}_2 + \text{H}_2 \rightarrow \text{FeS} + \text{H}_2\text{S} \]

at temperatures greater than 230°C.
The reaction
\[
\text{FeS} + \text{H}_2 + \text{Fe} + \text{H}_2\text{S}
\]
is not very favorable\(^{26}\) because the equilibrium values \(K = \frac{P(\text{H}_2\text{S})}{P(\text{H}_2)}\) are 0.0008 and 0.003 at 723° and 994°C, respectively. It follows that the hydrogen sulfide partial pressure must be very small in order to make the latter reaction approach completion.

2. Oxidation

\(\text{FeS}_2\) can be easily oxidized with \(\text{O}\) to \(\text{FeSO}_4\), even at ordinary temperatures\(^{28}\).

\[
\text{FeS}_2 + 3\text{O}_2 \rightarrow \text{FeSO}_4 + \text{SO}_2
\]

\(\text{FeS}_2\) in presence of water and oxygen can react as follows:\(^{26,29}\)

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

\[
2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}
\]

Both sulfates are soluble in water. \(\text{FeS}_2\) can react with ferric sulfate as follows:\(^{26,30}\)

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

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

With \(\text{NaOH}\), the \(\text{FeS}_2\) can react as follows:\(^{27}\)

\[
8\text{FeS}_2 + 30\text{NaOH} \rightarrow 4\text{Fe}_2\text{O}_3 + 14\text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3 + 15\text{H}_2\text{O}
\]
D. Coal Desulfurization Processes

Several approaches to achieve the desulfurization of coal have been proposed. Among these are hydrogenation, oxidation, sodium hydroxide leaching. These will be considered separately.

1. Hydrogenation

Hydrodesulfurization appears to be the most successful treatment for the removal of sulfur from coal. The principal processes using hydrogen are:

Hydrocarbon Research, Inc. Process (H-Coal).\textsuperscript{31-32} In this process coal (-40 mesh) is slurried in a derived solvent oil, mixed with compressed hydrogen, and fed to an ebullated-bed reactor containing catalyst. The coal is catalytically hydrogenated as the dissolution occurs to form products which depend strongly on the reaction operating conditions and the particular type of coal used. Typical operating conditions are 850°F and 3000 psig. Gases and lighter hydrocarbons are separated using a flash drum. The slurry is separated using hydroclones, into an overhead recycle solvent stream of low solid content and an underflow stream containing mineral and undissolved carbonaceous matter. The latter stream is further processed using a precoated rotary drum filter, and the filtrate is subsequently separated by distillation. A schematic drawing of the process is shown in Fig. 6.

This process gives liquid and gaseous products, and reduces the sulfur content to as low as 0.1-0.2%. Mineral matter tends to accumulate on the catalyst, decreasing its activity so that catalyst regeneration is necessary.
Fig. 6. H-Coal process for fuel oil production—devolatilization plant.
Synthoil Process.\textsuperscript{31,32} In this process a slurry of recycled solvent and coal is mixed, preheated, and fed to a fixed-bed reactor with turbulently flowing hydrogen. The reactor is packed with a commercial catalyst as used in hydrodesulfurization of petroleum derivatives (cobalt-molybdate on silica-activated alumina catalyst). Operating conditions in the reactor are usually $840^\circ F$ and 2000-4000 psig. The effluent gases are separated from the extract oil in the high-pressure receivers, the hydrogen sulfide and ammonia are removed, and the hydrogen is recycled. The pressure in the extract oil is then reduced, followed by either centrifugation or filtration to remove mineral matter and undissolved organic matter. A flow sheet of the process is shown by Fig. 7.

The process yields a low sulfur oil that flows freely at room temperature. The sulfur present in the oil product is less than 0.3\% even for coals containing over 5\% sulfur.

In this system, the hydrogenation is milder and there is less hydrogen consumption than the H-Coal process, but the amount of hydrogen recycle is large, leading to high compression costs. Further problems are that the bed plugs easily, and that the reactor must shutdown to replace catalyst.

Solvent Refined Coal (SRC).\textsuperscript{31,32} In this process coal ground to -200 mesh is mixed with three parts of a recycle solvent having a boiling range of about 550-850°F. This slurry is mixed with hydrogen preheated and fed into the reactor or dissolver where typical operating conditions are $825-850^\circ F$ and 1000-2000 psig. The reactor effluent is collected in a high pressure receiver where the gas and liquid
Fig. 7. Schematic drawing of the U.S. Bureau of Mines syntheoil process unit.
phases are separated. The liquid slurry is then filtered and the liquid is cooled until it solidifies. A flow sheet is shown in Fig. 8.

This process produces a low sulfur ash-free material, which has a very consistent heating value of 16,000 Btu/lb regardless of the coal feedstock processed. In this process all the pyritic sulfur and up to 70% organic sulfur is removed. Most of the carbon in the coal is dissolved in the reactor, and hydrogen consumption is 1-2% of the weight of the coal processed.

Advantages of this process are low hydrogen consumption, no catalyst, and operating costs lower than either H-Coal or the Synthoil process. The low cost is due principally to less severe operating conditions.

A major disadvantage of this process is that it gives a higher sulfur content in the coal product than the H-Coal and Synthoil process. Another problem area is that to date there appears to be no reliable and economical filter that can operate continuously at the conditions required. The filtration step is essential for the removal of the ash and the inorganic sulfur.

2. Oxidation

Another method for removing sulfur is to oxidize and leach out the sulfur compounds.

Dillon\textsuperscript{29} slurried coal with water and air at 620 psia and 175°C for 10 min. Initially the coal contained 2.55% total sulfur the 0.94% was organic sulfur, and after treatment it had only 0.48% total sulfur. All the pyritic and half of the organic sulfur was removed.
Fig. 8. Schematic flow sheet of the Southern Services, Inc. pilot plant.
Mukai\textsuperscript{33} reported that they removed practically 100\% of the pyritic sulfur from a bituminous coal by a room temperature treatment of the coal with a 3\% solution of hydrogen peroxide, without affecting the properties of the coal's coking ability.

Meyer\textsuperscript{30,34} proposed a process in which coal is mixed with either ferric sulfate or ferric chloride solution and fed to a reactor where the pyritic sulfur is selectively oxidized to sulfate and free sulfur. The reaction temperature is approximately 100°C. The aqueous solution containing sulfate ion is separated by filtration from the coal and washed to remove the residual ferric salt. The elemental sulfur is removed by steam or by solvent extraction (toluene). The oxidizing agent can be regenerated and recycled. A flow sheet of the process is shown in Fig. 9.

Meyers claims that the process can remove practically 100\% of the pyritic sulfur present in the coal without affecting the coal matrix; however, in order to achieve this removal, a multi-batch leaching process is needed. Otherwise a single batch of the order of 8 hr is needed to remove more than 80\% of the pyritic sulfur, although higher temperatures can shorten the time.

Kennecott Copper Corporation\textsuperscript{35} proposed a different process for removal of the pyritic sulfur. This process uses a coal slurry in a leaching reactor, where under the conditions of operation the pyritic sulfur is oxidized only to soluble sulfates and elemental sulfur. The slurry is then separated, and the coal fraction is washed with water. The water collected from the washings and the leaching operations is neutralized with lime or limestone. The insoluble iron compounds and gypsum are separated from the water and discarded, and the water is
Fig. 9. Schematic flow sheet of Meyers' process.
returned to the process. Reaction conditions are 300 psig of O₂ and 130°C, the reaction time is 2 hr. A flow sheet for the process is shown in Fig. 10. They claim that in some cases close to 100% of the pyritic sulfur is removed.

3. Sodium Hydroxide Treatment

Leo Kasehagen 37 studied the action of aqueous alkali at different concentrations and temperatures on a bituminous coal. He studied a range of temperatures from 250 to 400°C and concentrations ranging from 1N to 100% NaOH in water. His data are shown in Fig. 11.

The data show that for the dilute concentrations an increase in temperature gives an increase in the amount of organic sulfur removed, but the use of higher concentrations seems to have adverse effects on the amount of organic sulfur that is removed. Moreover the higher-concentration behavior with respect to temperature is opposite to that of the dilute solutions.

Battelle Process. 38, 39 Recently Battelle proposed a hydrothermal coal-treatment process to remove sulfur from coal using sodium hydroxide. In this process, coal is ground to permit 70% to pass through a 200 mesh screen. The coal is mixed in a slurry tank with the leaching agent composed of 5-10% sodium hydroxide and Ca(OH)₂ in water, pumped into the reactor at 350-2500 psig, and heated to 225-350°C. These conditions were necessary to extract the sulfur and a portion of the ash from the coal. The sulfur is mainly converted to sodium sulfide. The desulfurized coal is separated from the coal slurry in a centrifugal filter and transported to a dryer. A flow sheet of the process is shown in Fig. 12.
LEDGEMONT PROCESS FOR REMOVAL OF PYRITE SULFUR FROM COAL.
Fig. 11. Effect of temperature and concentration in removal of organic sulfur.
Fig. 12. Battelle hydrothermal coal process.
The leaching agent used is regenerated with carbon dioxide:

\[ \text{Na}_2\text{S} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{S} \]

The hydrogen sulfide is converted to elemental sulfur by the Clauss or Stretford process. Regeneration of the sodium hydroxide is completed by reacting the sodium carbonate solution with lime, yielding sodium hydroxide and a precipitate of calcium carbonate:

\[ \text{Na}_2\text{CO}_3 + \text{CaO} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{CaCO}_3 \]

The calcium carbonate is calcined to lime and CO₂:

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]

The developers claim that the leaching removes almost all the pyritic sulfur and depending on the coal up to 70% of the organic sulfur, and that if the product from the alkaline desulfurization is washed with dilute acid the majority of the ash is extracted.

The product from the hydrothermal treatment is a good stock for the commercial production of synthetic oils.

4. Other Proposals

Meyers⁴⁰ tried to remove the organic sulfur from coal using different chemical leaching agents. He found that weak-organic acids can remove part of the organic sulfur from coals. Among the weak organic acids investigated, it was found that the best is nitrobenzene, followed by cresol. Aqueous caustic removes small amounts of organic sulfur from some coals but not from others.

Hamersma and Meyers³⁴ found that p-cresol was a more efficient organic sulfur extraction agent than nitrobenzene. Organic sulfur removal at 200°C ranged from 10-50%. One serious problem in this process is the high level of solvent retention in the processed coal.
II. OBJECTIVES

A. Removal of Sulfur

The purpose of this work was to remove organic and inorganic sulfur at temperatures less than 300°C and low pressures, without appreciably affecting the coal matrix.

In order to understand how this could be accomplished, extensive bibliographic research was done to see the different approaches that have been tried, and the inherent problems in sulfur removal. The goal was to find a chemical leaching agent capable of removing sulfur compounds. Among the different agents that have been proposed, the most promising seemed to be sodium hydroxide. Previous investigations \(^\text{38}\) claim that this leaching agent can remove almost all the pyritic sulfur and up to 70% of the organic sulfur, and that it is possible to regenerate the sodium hydroxide. This leaching agent was studied and ways for improving its efficiency were investigated.

Other promising approaches that have been suggested are oxidation of the inorganic and organic sulfur with oxygen, \(^\text{44}\) and oxidation of the pyritic sulfur with ferric ions. \(^\text{34}\) These alternatives were also investigated and compared to the effectiveness of other methods of sulfur removal.

B. Study of Different Chemical Leaching Agents

1. Sodium Hydroxide Leaching

Preliminary experiments conducted by the author showed that a 10% sodium hydroxide leaching agent at 100°C dissolved appreciable amounts of the subbituminous coal. Seth \(^\text{41}\) treated the subbituminous coal with higher concentrations of sodium hydroxide, and found that
appreciable amounts of coal were dissolved. Because of the solubility and low sulfur content of the subbituminous coal, experiments were made only on the Illinois #6 bituminous coal.

In runs 1 through 11 the effects of particle size, temperature, and time of reaction on removal of the different forms of sulfur using an aqueous solution of 10% sodium hydroxide were studied. Run 12 was intended to study the effect of CaO in the removal of sulfur. This effect is important, because CaO will be used to regenerate the sodium hydroxide solution, and it is expected that CaO will be present in the regenerated sodium hydroxide solution. Run 13 was conducted under hydrogen pressure using 10% sodium hydroxide to see if the amount of sulfur removed would be increased. In run 14 a 10% sodium hydroxide solution in a 1:1 mixture by volume of methanol and water was tried to see if methanol, an organic polar solvent, would improve the amount of organic sulfur removed.

Experiment 21 was performed on the coal product produced from experiment 15 (described in Section B-2). The leaching agent used was a 10% sodium hydroxide solution. This experiment was run to examine the possibility that the oxidation treatment in experiment 15 had converted additional sulfur compounds to forms soluble in sodium hydroxide solutions. Hydrogen was introduced during this run as in experiment 13.

2. Oxygen Treatment

Oxygen treatment has been proposed as another approach for removal of sulfur. In order to study this alternative, runs 15-17 (differing in oxygen pressure and temperature) were conducted in Illinois #6 coal.
Here the coal was leached with water under oxygen pressure. Experiment 18 was carried out in a 10% sodium hydroxide solution under oxygen pressure.

3. **Ferric Sulfate Treatment**

The efficiency of ferric sulfate and the temperature effect on this efficiency on removal of pyritic sulfur was studied in runs 19 and 20. These runs were carried out using 0.5M ferric sulfate solution as the leaching agent. The elemental sulfur formed in the reaction was extracted with toluene.

4. **Organic Solvents**

Coal treated with oxygen in run 16 was leached with cresol (experiment 22) and with tetralin (experiment 23) under hydrogen pressure at 250°C, so see if the previous treatment had changed some of the insoluble sulfur to a form soluble in one of these organic solvents.

Samples from the Wyoming subbituminous coal, which were extracted with different solvents in the work done by Dean Draemel were analyzed to study the extent of sulfur removal achieved with these solvents.
III. PROCEDURES AND EQUIPMENT

A. Sampling of Coal

In dealing with coal, one serious problem is to obtain representative samples. For this reason, special care was taken when the coal was sampled to minimize segregation.

Two coals were studied: an Illinois #6 bituminous and a Wyoming subbituminous.

The Illinois #6 coal was received in a 55 gal. drum. All the coal was passed through a jaw crusher and a roller crusher to give a final size of about 1/4 in. The coal was mixed, shaped into a cone, and divided into quarters. Opposite quarters were removed and stored under nitrogen in 5 gal. paint cans to avoid further oxidation of the coal. The remaining two quarters were similarly mixed and divided. Half of this sample was also stored under nitrogen. The remaining half was passed through the roller crusher to reduce its size to pass a 4 mesh sieve. This portion was further subdivided by coning and quartering, and stored under nitrogen in 1 gal. paint cans.

For the experimentation and analysis, coal from a 1 gal. paint can was reduced to the desired size by a ball mill, and was separated into aliquote samples of about 60 grams using a riffler. These aliquots were stored in glass bottles and sparged with nitrogen. The coal needed for analysis or treatment was taken from the bottles.

The Wyoming coal was already available in 20 lb plastic bags. To obtain samples, half of the coal from a bag was ground to the desired size and then rifflerd to obtain aliquots of 60 gms, which were stored in glass bottles and sparged with nitrogen.
B. Coal Analysis

The coal used in this study was analyzed by three different laboratories: in the author's laboratory, the University of California microchemical analytical laboratory, and Commercial Testing and Engineering Company. The results are shown in Tables 1-4.

The analysis of ash in the Illinois coal reported by the Commercial Testing and Engineering Co. differs from those on Table 1 and 2. This difference can be explained on the grounds that the coal sent to the Commercial Testing and Engineering Co. was taken from the top of the 55 gal. drum without following the sample procedure recommended when sampling the coal. The values for total sulfur and moisture content are in better agreement. All further comparisons and discussions of results will be based on analysis performed by the author following the procedures given in Appendices A and B.

C. Apparatus

The reactions were carried out in a Parr minireactor capable of operating up to 2000 psia and 350°C. The reactor shown in Fig. 13 consisted of a cylinder and a head assembly of 316 stainless steel and had a capacity of about 600 ml. The reactor was equipped with a pressure gage, a safety rupture disc, a sampling valve, a charging valve, a pressure release valve, a stirrer, and a thermocouple.

Heat was supplied by a quartz fabric mantle that fit around the bomb cylinder, and the temperature was controlled by a signal from the thermocouple inserted through the bomb head. The reaction temperature could be controlled to within ±5°C, and could be monitored by a meter on the control panel. An internal cooling loop provided
Table 1. Analysis in author's laboratory.

<table>
<thead>
<tr>
<th>Coal</th>
<th>Moisture</th>
<th>Ash</th>
<th>Total Sulfur</th>
<th>FeS₄</th>
<th>S₃O₄</th>
<th>Org. Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illinois #6</td>
<td>11.0</td>
<td>20.0</td>
<td>4.38</td>
<td>1.84</td>
<td>0.44</td>
<td>2.10</td>
</tr>
<tr>
<td>Roland Seam</td>
<td>20.0</td>
<td>15.6</td>
<td>1.25</td>
<td>0.06</td>
<td>0.12</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Table 2. Analysis in University of California microanalysis laboratory.

<table>
<thead>
<tr>
<th>Coal</th>
<th>Ash</th>
<th>Total Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illinois #6</td>
<td>19.2</td>
<td>4.41</td>
</tr>
<tr>
<td>Roland Seam</td>
<td>16.6</td>
<td>0.96</td>
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</table>

<table>
<thead>
<tr>
<th>Proximate Analysis</th>
<th>As Received</th>
<th>Dry Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Moisture</td>
<td>12.62-12.67</td>
<td>---</td>
</tr>
<tr>
<td>% Ash</td>
<td>14.53-14.61</td>
<td>16.63-16.73</td>
</tr>
<tr>
<td>% Volatile</td>
<td>32.54-33.39</td>
<td>37.24-38.23</td>
</tr>
<tr>
<td>% Fixed Carbon</td>
<td>39.33-40.31</td>
<td>45.04-46.13</td>
</tr>
<tr>
<td>BTU</td>
<td>9988-10001</td>
<td>11431-11452</td>
</tr>
<tr>
<td>% Sulfur</td>
<td>3.64-3.95</td>
<td>4.17-4.52</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ultimate Analysis</th>
<th>As Received</th>
<th>Dry Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Moisture</td>
<td>12.62-12.67</td>
<td>---</td>
</tr>
<tr>
<td>% Carbon</td>
<td>56.03-56.31</td>
<td>64.16-64.44</td>
</tr>
<tr>
<td>% Hydrogen</td>
<td>3.89-3.92</td>
<td>4.45-4.49</td>
</tr>
<tr>
<td>% Nitrogen</td>
<td>1.15-1.17</td>
<td>1.32-1.34</td>
</tr>
<tr>
<td>% Chlorine</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>% Sulfur</td>
<td>3.64-3.95</td>
<td>4.17-4.52</td>
</tr>
<tr>
<td>% Ash</td>
<td>14.53-14.61</td>
<td>16.63-16.73</td>
</tr>
<tr>
<td>% Oxygen (difference)</td>
<td>7.42-7.85</td>
<td>8.49-8.98</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>As Received</th>
<th>Dry Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Proximate Analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Moisture</td>
<td>23.43-23.83</td>
<td>---</td>
</tr>
<tr>
<td>% Ash</td>
<td>10.40-11.49</td>
<td>13.64-15.08</td>
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<tr>
<td>% Volatile</td>
<td>29.04-35.52</td>
<td>37.93-47.23</td>
</tr>
<tr>
<td>% Fixed Carbon</td>
<td>30.16-36.17</td>
<td>39.60-47.23</td>
</tr>
<tr>
<td>BTU</td>
<td>8226-8372</td>
<td>10800-10931</td>
</tr>
<tr>
<td>% Sulfur</td>
<td>0.70-0.94</td>
<td>0.92-1.23</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Ultimate Analysis</strong></th>
<th>As Received</th>
<th>Dry Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Moisture</td>
<td>23.43-23.83</td>
<td>---</td>
</tr>
<tr>
<td>% Carbon</td>
<td>47.02-47.37</td>
<td>61.67-62.19</td>
</tr>
<tr>
<td>% Hydrogen</td>
<td>3.79-4.04</td>
<td>4.97-5.30</td>
</tr>
<tr>
<td>% Nitrogen</td>
<td>0.73-0.87</td>
<td>0.96-1.13</td>
</tr>
<tr>
<td>% Chlorine</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>% Sulfur</td>
<td>0.79-0.94</td>
<td>0.92-1.23</td>
</tr>
<tr>
<td>% Ash</td>
<td>10.40-11.49</td>
<td>13.64-15.08</td>
</tr>
<tr>
<td>% Oxygen (difference)</td>
<td>11.72-13.35</td>
<td>15.40-17.51</td>
</tr>
</tbody>
</table>
Fig. 13. Reactor.
a mean for removing heat from the reactor. Liners of nickel and glass were available.

A more detailed description of the apparatus is given in Appendix D.

D. General Procedure

A weighed amount of coal approximately 20 gms was slurried with 200 ml of leaching solution and charged into the reactor. The reactor was closed, and air was removed by passing a nitrogen purge for 20 min. The desired gas was then admitted into the bomb and brought to the desired pressure. The reactor was then transferred to the stand where the stirrer motor and heating mantle were mounted in preparation for a run.

Zero time for a run was arbitrarily selected as the time at which the reactor reached the reaction temperature. The heat-up time varied between 25 and 50 min. After the desired reaction time, the contents of the bomb were quickly cooled with the help of the cooling loop. Typically the temperature could be reduced 130°C in 5 min. The cold product mixture was vacuum filtered using a Buchner funnel, first with a coarse filter paper (Whatman 512), followed by a fine filter paper (Whatman 42). The coal was washed thoroughly with water and transferred to a vacuum oven where it was dried for 24 hr at 110°C in 25 Torr of nitrogen pressure. Subsequently it was cooled in a dessicator and weighed. This coal was analyzed for the distribution of sulfur and ash using the procedures given in Appendices A and B.
IV. RESULTS AND DISCUSSION

The effect of temperature, particle size, time of reaction, leaching agent, and pressure on the removal of the different forms of sulfur present in the coal were studied. Analyses of the coal samples were performed using ASTM methods described in Appendices A and B. The data obtained from these studies are presented in tabular form in Appendix C and in graphical form in this section.

A. Treatment with 10% Sodium Hydroxide Solutions

These results are shown in Figs. 14-18, and in Tables 6 and 7 in Appendix C. The results show that the coal particle size has no apparent effect on the amount of sulfur removed. At the highest temperature studied (300°C), a small difference between the values for the two different particle sizes is within analytical uncertainty. Also, the apparent difference in the amount of organic sulfur removed (shown in Fig. 16) is probable due to the fact that this value is determined by difference, and the errors accumulate.

The total sulfur in the coal decreases strongly as the temperature increases at constant reaction time over the range studied. This curve can be interpreted in the following way: most of the pyritic sulfur is removed as the temperature increases from 150-200°C. This accounts for approximately half of the sulfur. At 200°C the organic sulfur starts to be extracted and in the temperature range of 200-250°C the easily extractable forms are leached. Increasing the temperature further results in additional sulfur removal, but at reduced rates.
Original total sulfur content (AFB) = 5.46%
Time of reaction = 2 hr

- Δ 200 mesh
- ○ 28 mesh
- × CaO
- □ Methanol:water

Weight of coal to weight of 10% NaOH solution is 1 to 10

Fig. 14. Effect of temperature and particle size on removal of total sulfur.
Fig. 15. Effect of temperature and particle size on removal of pyritic sulfur.
Original organic sulfur content (APH) = 2.60%

○ 28 mesh
△ 200 mesh

Weight of coal to weight of 10% NaOH solution is 1 to 10
Time of reaction = 2 hr

Fig. 16. Effect of temperature and particle size on removal of organic sulfur.
To study the effect of reaction time on desulfurization, samples of -200 mesh coal were reacted with sodium hydroxide solution for different times at 250°C and 300°C. The data presented on Figs. 17 and 18 show respectively that the pyritic sulfur is removed in the first 15 min of reaction or less, whereas the organic sulfur is mostly removed in the first hour of the reaction. About half of the sulfate sulfur appears to be present in insoluble form.

The effect of CaO on the leaching solution efficiency was studied because CaO would be used to regenerate the sodium hydroxide. The data in Table 7 shows that it did not change the amount of sulfur removed by the sodium hydroxide solution alone.

Methanol, being a polar organic solvent, was tried in run 14, but because of pressure restrictions the experiment was done at 200°C. The amount of organic sulfur found after reaction was lower than that obtained by the use of aqueous solution, but the difference is not large. Perhaps at higher temperatures the methanol would be more effective. In the run it was also noticed that the nickel liner was chemically attacked to form a thin film on the interior of the liner. For this reason a high amount of ash and no appreciable weight loss was found in the coal after reaction.

In run 13, the effect of hydrogen was studied, but pressure restrictions permitted a maximum partial pressure of hydrogen of only 170 psia. No effect on the removal or organic sulfur was found.

In run 21 the previously oxidized coal was treated with sodium hydroxide solution and half of the organic sulfur was in the residue and half in the extract.
Original FeS$_2$ content (AFB) = 2.30%
Particle size = -200 mesh

Weight of coal to weight of 10% NaOH solution is 1 to 10

Fig. 17. Effect of temperature and time of reaction in removal of pyritic sulfur.
Fig. 18. Effect of temperature and time of reaction on removal of organic sulfur.
The amount of coal dissolved in these experiments does not agree with data from previous work done in bituminous coal treated with sodium hydroxide. Sharma and Wilson\textsuperscript{42} found that for reaction temperatures of 250°C and 300°C the highest amount of coal extracted were 16 and 24\% respectively. At the same temperatures Kasahagen\textsuperscript{26} found the amount of coal extracted to be 5 and 14\% respectively. In the present experiments the amounts of coal dissolved at the two temperatures were 25 and 40\%.

One possible explanation for the high solubility of coal found in our experiments is that the coal was oxidized for it is known that oxidized coal gives higher solubility in alkaline solutions. Another characteristic that supports this belief is that this Illinois #6 coal had a higher than usual content sulfur as sulfate (around 0.40\%) a property suggesting that the coal had been weathered.

\textbf{B. Oxygen Treatment}

Runs 15 and 16 were treated with oxygen under similar conditions. The data in Table 8 in Appendix C shows that the pyritic sulfur and a small amount of the organic sulfur was removed. Run 17 was carried out at lower oxygen pressure and removed less sulfur from the coal.

In these experiments the oxygen was charged only at the beginning of the reaction. At the end of runs 15 and 16 the pressure was 45 psig. Oxygen is likely to react completely, so possibly the remaining pressure is due to formation of CO$_2$.

The amount of oxygen charged into the reactor was in excess of that needed to oxidize the sulfur, so it is concluded that a part
of the oxygen was used to oxidize the coal rather than to oxidize the sulfur. This is supported by the fact that the treated coal was very soluble in sodium hydroxide.

The pyritic sulfur removed in these experiments was not as high as that reported by Kennecott\textsuperscript{35} but the conditions were slightly different. The temperature in this work was either 150 or 250°C, as opposed to a value of 130°C used by Kennecott. Also it is not clear whether the results reported by Kennecott correspond to runs in which oxygen pressure was maintained throughout the reaction, and whether the leaching agent was pure water.

C. Ferric Sulfate Treatment

The amount of pyritic sulfur removed was very sensitive to the temperature used. For example, at 100°C only 50% was removed whereas at 130°C almost 98% was removed.

The value for the organic sulfur content was increased after treatment because some of the elemental sulfur that was formed when the coal was treated with ferric sulfate solution was not removed in toluene extraction. The elemental sulfur will appear as organic sulfur in the analysis.

The data generated in these experiments agree in general with the results of Meyers\textsuperscript{34}

D. Organic Solvents

After treatment with oxygen to remove the pyritic sulfur, the possibility that some organic sulfur would be dissolved in organic solvents was looked at. Tetralin and p-cresol were tested under hydrogen pressure 250°C. The results were negative, only a small
portion of the pyritic sulfur was removed and it was more likely to be due to the hydrogen present. Samples from Draemel's work having the greatest amount of extraction with each solvent were analyzed to determine the amount of organic sulfur removed.

Phenol and tetralin extracted 30% of the total sulfur present in the original subbituminous Wyoming coal. Benzene and decalin did not show appreciable sulfur removal.
V. CONCLUSIONS

The sodium hydroxide process does not appear to be very promising for the removal of organic sulfur from Illinois #6 coal. The highest organic sulfur removal was 36% (AFB), and was only reached at the highest temperature and pressure used. The success of this process appears to depend largely on the form in which the organic sulfur is present in the coal.

Because approximately 80% of the pyritic sulfur was extracted at 200°C with the sodium hydroxide solution, this process appears to be effective for the removal of this form of sulfur. At this temperature, the pressure is only 175 psig, a very positive feature. Moreover, coal does not need to be finely ground to accomplish pyritic sulfur removal. The time needed to achieve this removal at 200°C is estimated to be less than 30 min although this needs to be studied in more detail.

The large amount of coal dissolved in these experiments would have been much less than that obtained if the coal had not been weathered.

This process is not suitable to use in subbituminous coal because of the lower rank coal has higher solubility in sodium hydroxide solutions.

Oxygen treatment could be promising if it were possible to increase the rate at which the pyritic sulfur oxidized with respect to the rate of oxidation of the coal matrix. This process has the advantage of being carried at low temperature and pressure.
Ferric sulfate treatment seems to be very promising for coals where only pyritic sulfur removal is necessary because almost 100% can be removed at low temperature and pressure.

None of the organic solvents at the conditions used seemed to be a good leaching agent for the sulfur.

In summary, when more than 40% of the organic sulfur must be removed, the high temperature high pressure hydrogen treatment appears to be necessary because these processes attacks the very stable sulfur forms encountered in coal. Therefore, it is recommended to study hydrogenation processes to find a catalyst that will work at low temperatures and pressures.
ACKNOWLEDGEMENTS

The author wishes to acknowledge the helpful criticisms and suggestions by Professors E. Peterson and T. Vermeulen. This work was done with support from the U. S. Energy Research and Development Administration.
APPENDIX A. SULFUR DETERMINATIONS

For the sulfur determinations the coal samples are ground to pass a -60 mesh sieve and dried in an oven that is kept at 110°C. Total Sulfur

One gram of sample is weighed and then placed in the oxygen bomb. An ignition wire is connected to the electrodes and allowed to come in contact with the coal sample, 1 cc of water is placed at the bottom of the bomb to saturate the oxygen used for the combustion. The bomb is closed and filled with oxygen. The oxygen is admitted slowly until the pressure in the bomb is 25 atmospheres. The bomb is then transferred to a recipient containing cooling water. The purpose of the recipient is to cool the bomb after the ignition.

After ignition and a subsequent 10 min cooling period, the residual gases are released slowly to avoid losses of sulfuric acid. Then the bomb is opened and all the interior parts, including the capsule are washed with a fine jet of distilled water containing methyl orange indicator. The washings are continued until no acid reaction is observed. All the wash water is collected in a 600 ml beaker and neutralized with NaOH solution (0.4N). After the neutralization, 1 ml of NH₄OH is added. The solution is heated to boiling for 1 min and then filtered. The residue is washed with hot water and collected as filtrate. To the filtrate, 1 ml of saturated bromine-water and enough HCl to make it slightly acidic are added. The solution is boiled for 5 min, and then neutralized with NaOH (2M). One ml of HCl (1+9) is added in excess and then the solution is heated to boiling. While boiling, 10 cc of BaCl₂...
solution (100 mg/lt) are added, to precipitate the \( \text{SO}_4^{2-} \) as \( \text{BaSO}_4 \). The solution is kept boiling for 10 min and then let at a temperature just below boiling for at least 2 hr.

Section A. The solution is filtered using an ashless paper filter and washed with hot water until a drop of the washings does not precipitate \( \text{AgCl} \) from a silver nitrate solution.

The filter paper is placed in a weighted porcelain crucible and put in a muffle furnace. The temperature is raised to 925° C and kept at this temperature for 1/2 hr. The crucible is then taken out of the muffle and cooled in a desiccator. The crucible is then weighed when it is cold. A blank is done without coal following the same procedure.

The percent of total sulfur in the coal is calculated from the amount of \( \text{BaSO}_4 \) found in the precipitate:

\[
\% \text{ Total Sulfur} = \frac{A - B}{C} \times 13.735
\]

where:  
\( A \) = gms of \( \text{BaSO}_4 \) precipitated  
\( B \) = gms of \( \text{BaSO}_4 \) precipitated in the blank  
\( C \) = gms of sample used  
13.735 = gravimetric factor \times 100 = \frac{S}{\text{BaSO}_4}

Sulfate Sulfur

Approximately 3 gms of a dry coal sample are weighed and put into an erlenmeyer flask. Fifty ml of HCl (2+3) are added and a cold-finger condenser is fitted into the flask. The solution is boiled for 30 min using a hot plate. After the 30 min boiling period, the solution is filtered and washed six times with HCl (1:23). The
filtrate and washings are received in a 600 ml beaker.

The residual coal in the filter is retained for the determination of pyritic sulfur.

To the filtrate are added 10 ml of saturated bromine-water (to reduce all the iron from Fe^{+2} to Fe^{+3}) and boiled for 5 min. Then while stirring NH_{4}OH is added in excess. The beaker is covered with a watch glass and boiled for 1 min. The solution is filtered and washed with hot water that has a small amount of NH_{4}Cl and NH_{4}OH.

The filtrate is neutralized with HCl conc and 1 ml is added in excess.

The solution is heated to boiling and while boiling, BaCl_{2} solution is added to precipitate the sulfate as BaSO_{4}. The solution is kept boiling for 15 min and then maintained at a temperature just below boiling for at least 2 hr. Procedure A is continued.

The sulfur combined as SO_{4} is given by:

\[
\%_{S_{SO_{4}}} = \frac{(A - B)}{C} \times 13.735
\]

where:  
A = gms of BaSO_{4} precipitated  
B = gms of BaSO_{4} precipitated in the blank  
C = gms of sample used.

**Pyritic Sulfur**

The filter paper and residue from the HCl extraction are transferred to a 250 ml erlenmeyer flask and 50 ml of HNO_{3} (1-7) are added to the flask. A cold-finger condenser is fitted into the flask and the flask is put on a hot plate to boil the contents for 30 min. After boiling, the solution is filtered and washed several times with HNO_{3} (1-7). The residue in the filter is discarded.
The filtrate and washings are received in a 600 ml beaker, 2 ml of 30% \( \text{H}_2\text{O}_2 \) are added and the solution is boiled for 5 min. The solution is neutralized with concentration \( \text{NH}_4\text{OH} \), 5 ml are added in excess and boiled for 1 min to coagulate the precipitate of ferric hydroxide. The precipitate is filtered and washed with hot water that has a trace of \( \text{HN}_4\text{OH} \) and \( \text{NH}_4\text{Cl} \), and retained for the volumetric determination of FeS. The filtrate is neutralized with HCl and added 1 ml in excess. The solution is heated to the boiling point and while boiling 10 cc of a solution of \( \text{BaCl}_2 \) (100 gm/lt) are added to precipitate and sulfates as \( \text{BaSO}_4 \). The boiling is maintained for another 15 min and then the solution is kept at a temperature just below boiling for at least 2 hr. Procedure A is then continued. The percent of sulfur present as \( \text{FeS}_2 \) is given by:

\[
\% \text{S}_{\text{FeS}_2} = \frac{(A - B)}{W} \times 13.735
\]

where

- \( A \) = gms of \( \text{BaSO}_4 \) precipitated
- \( B \) = gms of \( \text{BaSO}_4 \) precipitated in the blank
- \( W \) = gms of sample used

The ferric hydroxide precipitate is dissolved from the filter paper using 25 cc of hot HCl \((2 + 3)\). The filter paper is washed with hot water. The filtrate and washings are received in a 500 ml erlenmeyer flask and heating to boiling. Solution of \( \text{SnCl}_2 \) (5 gms of \( \text{SnCl}_2 \), 10 ml of conc. HCl and diluted to 100 ml with water) is added drop by drop until the resolution is colorless, 2 drops are added in excess and it is quickly cooled to room temperature.
The iron is reduced by the SnCl₂:

\[ 2Fe^{+3} + Sn^{+2} \rightarrow 2Fe^{+2} + Sn^{+4} \]

The excess of Sn⁺² is removed by the addition of a saturated solution of mercuric chloride:

\[ Sn^{+2} + HgCl₂ \rightarrow Sn^{+4} + 2HgCl + 2Cl⁻ \]

The solution is allowed to rest 2 min and then 10 ml of H₂SO₄-H₃PO₄ mixture (150 ml of conc. H₂SO₄, 150 ml of conc. H₃PO₄ diluted to 1 lit with water), 3 drops of diphenylamine sulfonate, and water are added to make a total volume of 200 ml. The iron is titrated with 0.05 N K₂Cr₂O₇. The end point is reached when the color persists for 15 sec. The reaction is:

\[ Cr₂O₇^{+2} + 6Fe^{+2} + 14H^{+1} \rightarrow 6Fe^{+3} + 2Cr^{+3} + 7H₂O \]

A blank is done without coal following the same procedure.

The percent of sulfur present as FeS₂ is given by:

\[ \% S_{FeS₂} = \frac{(A - B)}{C} \times N \times 6.412 \]

where:

A = cc of K₂Cr₂O₇ used for the titration of iron

B = cc of K₂Cr₂O₇ used for the titration of the blank.

C = gms of sample

N = normality of the K₂Cr₂O₇

6.412 = volumetric factor \times 100

The results obtained for the pyritic sulfur determination by both methods are compared and in case of a difference the value obtained by the volumetric method is taken.
Organic Sulfur

The organic sulfur is determined by subtracting the sum of the sulfate and pyritic sulfur from the total sulfur.
APPENDIX B. ASH DETERMINATION

A sample of dry coal is weighed (3 to 5 gms) in a porcelain capsule and placed in a cold muffle where it is heated gradually so that the temperature reaches 500°C in 1 hr and 750°C in 2 hr.

The sample is maintained at 750°C for 1 hr. The sample is stirred two or three times with a platinum wire to assume that all the coal is ignited. An ample supply of air in the muffle is assured by not closing it completely. The sample after ignition is cooled in a desiccator and weighed.

The ash content is given by:

\[
\% \text{ ash} = \frac{A}{B} \times 100
\]

where: \( A = \text{gms of ash} \)

\( B = \text{gms of sample} \).
APPENDIX C. TABLES OF DATA

Reporting values for sulfur content in coal is more meaningful if they are reported based on the heat content of the coal because that value is the one that tells if the coal can be burned.

Since a calorimeter was not available, sulfur was reported on an ash free basis. This gives the percent of sulfur on the basis of the organic matter present which is related to the calorific value of the coal.

The values obtained for pyritic sulfur by the gravimetric method were used to check the values obtained by the volumetric method and were not done in all the cases. The gravimetric values are not very reliable because some organic sulfur can be oxidized to sulfate when the coal is treated with the nitric acid.

The experimental data generated in this work are presented in tabular form in the following tables.
Table 6. Sodium hydroxide treatment.**

<table>
<thead>
<tr>
<th>Run</th>
<th>Size</th>
<th>Temp. °C</th>
<th>Time Hours</th>
<th>Pressure psig</th>
<th>Ratio Coal/Sol</th>
<th>% L.W.</th>
<th>% Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-28</td>
<td>150</td>
<td>2</td>
<td>0</td>
<td>55</td>
<td>1:10</td>
<td>8.0</td>
</tr>
<tr>
<td>2</td>
<td>-28</td>
<td>200</td>
<td>2</td>
<td>0</td>
<td>175</td>
<td>1:10</td>
<td>11.5</td>
</tr>
<tr>
<td>3</td>
<td>-28</td>
<td>250</td>
<td>2</td>
<td>0</td>
<td>440</td>
<td>1:10</td>
<td>25.0</td>
</tr>
<tr>
<td>4</td>
<td>-28</td>
<td>300</td>
<td>2</td>
<td>0</td>
<td>1000</td>
<td>1:10</td>
<td>49.0</td>
</tr>
<tr>
<td>5</td>
<td>-200</td>
<td>200</td>
<td>2</td>
<td>0</td>
<td>175</td>
<td>1:10</td>
<td>9.9</td>
</tr>
<tr>
<td>6</td>
<td>-200</td>
<td>250</td>
<td>2</td>
<td>0</td>
<td>440</td>
<td>1:10</td>
<td>24</td>
</tr>
<tr>
<td>7</td>
<td>-200</td>
<td>300</td>
<td>2</td>
<td>0</td>
<td>1000</td>
<td>1:10</td>
<td>60</td>
</tr>
<tr>
<td>8</td>
<td>-200</td>
<td>250</td>
<td>0.25</td>
<td>0</td>
<td>440</td>
<td>1:10</td>
<td>15.3</td>
</tr>
<tr>
<td>9</td>
<td>-200</td>
<td>250</td>
<td>0.50</td>
<td>0</td>
<td>440</td>
<td>1:10</td>
<td>16.0</td>
</tr>
<tr>
<td>10</td>
<td>-200</td>
<td>250</td>
<td>1.0</td>
<td>0</td>
<td>440</td>
<td>1:10</td>
<td>16.0</td>
</tr>
<tr>
<td>11</td>
<td>-200</td>
<td>300</td>
<td>1.0</td>
<td>0</td>
<td>1000</td>
<td>1:10</td>
<td>40.0</td>
</tr>
<tr>
<td>12</td>
<td>-200</td>
<td>250</td>
<td>2.0</td>
<td>0</td>
<td>440</td>
<td>1:10</td>
<td>16.0</td>
</tr>
<tr>
<td>13</td>
<td>-200</td>
<td>250</td>
<td>2.0</td>
<td>200</td>
<td>610</td>
<td>200</td>
<td>1:10</td>
</tr>
<tr>
<td>14</td>
<td>-200</td>
<td>200</td>
<td>2.0</td>
<td>0</td>
<td>350</td>
<td>0</td>
<td>1:10</td>
</tr>
<tr>
<td>21*</td>
<td>-200</td>
<td>250</td>
<td>2.0</td>
<td>55</td>
<td>445</td>
<td>55</td>
<td>1:20</td>
</tr>
</tbody>
</table>

In this reaction hydrogen was introduced into the reactor to give a pressure of 55 psig at 25°C, and the reaction carried out for 1 hr. After cooling the reactor to ambient temperature the pressure was 20 psig. The reactor was again pressurized with hydrogen to a pressure of 55 psig without removing the coal or leaching solution, and the reaction was conducted again for another hour at 250°C.

** A linear of nickel was used in these reactions.

The coal used in these experiments was Illinois #6.

I = Initial pressure at room temperature.
W = Pressure at the temperature of reaction.
F = Final pressure at room temperature.
L.W. = Loss on weight.
Table 7. Sodium hydroxide treatment.

<table>
<thead>
<tr>
<th>Run</th>
<th>% Sulfur Content Moisture and Ash Free Basis</th>
<th>% of Sulfur Removed Moisture and Ash Free Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S_T$</td>
<td>$SO_4$</td>
</tr>
<tr>
<td>1</td>
<td>4.47</td>
<td>0.34</td>
</tr>
<tr>
<td>2</td>
<td>3.26</td>
<td>0.34</td>
</tr>
<tr>
<td>3</td>
<td>2.59</td>
<td>0.34</td>
</tr>
<tr>
<td>4</td>
<td>2.52</td>
<td>0.38</td>
</tr>
<tr>
<td>5</td>
<td>3.16</td>
<td>0.29</td>
</tr>
<tr>
<td>6</td>
<td>2.54</td>
<td>0.31</td>
</tr>
<tr>
<td>7</td>
<td>2.24</td>
<td>0.39</td>
</tr>
<tr>
<td>8</td>
<td>2.89</td>
<td>0.36</td>
</tr>
<tr>
<td>9</td>
<td>2.74</td>
<td>0.39</td>
</tr>
<tr>
<td>10</td>
<td>2.67</td>
<td>0.36</td>
</tr>
<tr>
<td>11</td>
<td>2.45</td>
<td>0.40</td>
</tr>
<tr>
<td>12</td>
<td>2.56</td>
<td>0.31</td>
</tr>
<tr>
<td>13</td>
<td>2.62</td>
<td>0.36</td>
</tr>
<tr>
<td>14</td>
<td>3.29</td>
<td>0.60</td>
</tr>
<tr>
<td>21</td>
<td>2.63</td>
<td></td>
</tr>
</tbody>
</table>

$S_T$ = Total sulfur
$S_{Org}$ = Organic sulfur
$S_{Fe}$ = Pyritic sulfur volumetric
$S_{FeG}$ = Pyritic sulfur gravimetric
$SO_4$ = Sulfate sulfur
Table 8. Oxygen treatment.

<table>
<thead>
<tr>
<th>Run</th>
<th>Size</th>
<th>Temp. °C</th>
<th>Time Hours</th>
<th>Pressure Psig</th>
<th>Ratio Coal/Sol</th>
<th>% L.W.</th>
<th>% Ash</th>
<th>Coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>-200</td>
<td>150</td>
<td>2.0</td>
<td>220 150 50</td>
<td>1:10</td>
<td>0.0</td>
<td>21.7</td>
<td>Illinois #6</td>
</tr>
<tr>
<td>16</td>
<td>-200</td>
<td>150</td>
<td>2.0</td>
<td>215 150 45</td>
<td>1:10</td>
<td>1.7</td>
<td>19.2</td>
<td>Illinois #6</td>
</tr>
<tr>
<td>17</td>
<td>-200</td>
<td>250</td>
<td>2.0</td>
<td>80. 500 20</td>
<td>1:10</td>
<td>2.41</td>
<td>54.5</td>
<td>Illinois #6</td>
</tr>
<tr>
<td>18</td>
<td>-200</td>
<td>250</td>
<td>2.0</td>
<td>225 445 40</td>
<td>1:10</td>
<td>66.0</td>
<td>54.5</td>
<td>Illinois #6</td>
</tr>
</tbody>
</table>

I = Initial pressure at room temperature.
W = Average pressure at reaction temperature.
F = Final pressure at room temperature.
L.W. = Percent of loss on weight.

<table>
<thead>
<tr>
<th>Run</th>
<th>$S_T$</th>
<th>$SO_4$</th>
<th>$S_{Fe}$</th>
<th>$S_{FeG}$</th>
<th>$S_{Org}$</th>
<th>$S_T$</th>
<th>$SO_4$</th>
<th>$S_{Fe}$</th>
<th>$S_{Org}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>3.14</td>
<td>0.23</td>
<td>1.25</td>
<td>1.31</td>
<td>1.66</td>
<td>42.5</td>
<td>58.9</td>
<td>45.7</td>
<td>36.1</td>
</tr>
<tr>
<td>16</td>
<td>3.51</td>
<td>0.23</td>
<td>1.16</td>
<td>1.21</td>
<td>2.12</td>
<td>35.7</td>
<td>58.9</td>
<td>49.6</td>
<td>18.5</td>
</tr>
<tr>
<td>17</td>
<td>3.27*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>2.48</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*This value is in moisture free basis.

$S_T$ = total sulfur
$SO_4$ = sulfate sulfur
$S_{Fe}$ = pyritic sulfur volumetric
$S_{FeG}$ = pyritic sulfur
$S_{Org}$ = organic sulfur
Table 10. Ferric sulfate treatment.

<table>
<thead>
<tr>
<th>Run</th>
<th>Size</th>
<th>Temp. °C</th>
<th>Time Hours</th>
<th>Ratio Coal/Sol</th>
<th>% L.W.</th>
<th>% Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>28</td>
<td>100</td>
<td>2</td>
<td>1:10</td>
<td>7.0</td>
<td>18.3</td>
</tr>
<tr>
<td>20</td>
<td>28</td>
<td>130</td>
<td>2</td>
<td>1:10</td>
<td>8.0</td>
<td>20.0</td>
</tr>
</tbody>
</table>

L.W. = Percent of loss on weight.

Table 11. Ferric sulfate treatment.

<table>
<thead>
<tr>
<th>Run</th>
<th>$S_T$</th>
<th>$SO_4$</th>
<th>$S_{Fe}$</th>
<th>$S_{Org}$</th>
<th>% Sulfur Removed Moisture and Ash Free Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>4.10</td>
<td>0.21</td>
<td>1.09</td>
<td>2.8*</td>
<td>24.9 62.5 52.6 -21.7*</td>
</tr>
<tr>
<td>20</td>
<td>3.30</td>
<td>0.20</td>
<td>0.06</td>
<td>3.0</td>
<td>39.6 64.3 97.4 0.0</td>
</tr>
</tbody>
</table>

* Look at Discussion for explanation of these values.

$S_T$ = total sulfur
$SO_4$ = sulfate sulfur
$S_{Fe}$ = pyritic sulfur volumetric
$S_{Org}$ = organic sulfur
<table>
<thead>
<tr>
<th>Run</th>
<th>Size</th>
<th>Temp. °C</th>
<th>Time Hours</th>
<th>Pressure Psig</th>
<th>Ratio Coal/Sol</th>
<th>% L.W.</th>
<th>% Ash</th>
<th>Coal</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>-200</td>
<td>250</td>
<td>2</td>
<td>250 450 245</td>
<td>1:20</td>
<td>2.5</td>
<td>19.4</td>
<td>Illinois #6</td>
<td>Cresol</td>
</tr>
<tr>
<td>23</td>
<td>-200</td>
<td>250</td>
<td>2</td>
<td>250 440 250</td>
<td>1:20</td>
<td>0.8</td>
<td>18.0</td>
<td>Illinois #6</td>
<td>Tetralin</td>
</tr>
<tr>
<td>24*</td>
<td>-28</td>
<td>300</td>
<td>4</td>
<td></td>
<td>1:50</td>
<td>15.0</td>
<td>16.5</td>
<td>Wyoming Coal</td>
<td>Phenol</td>
</tr>
<tr>
<td>25*</td>
<td>-28</td>
<td>350</td>
<td>4</td>
<td></td>
<td>1:50</td>
<td>26.5</td>
<td>18.1</td>
<td>Wyoming Coal</td>
<td>Tetralin</td>
</tr>
<tr>
<td>26*</td>
<td>-28</td>
<td>200</td>
<td>4</td>
<td></td>
<td>1:50</td>
<td>4.6</td>
<td>15.7</td>
<td>Wyoming Coal</td>
<td>Decalin</td>
</tr>
<tr>
<td>27*</td>
<td>-28</td>
<td>250</td>
<td>4</td>
<td></td>
<td>1:50</td>
<td>6.6</td>
<td>15.6</td>
<td>Wyoming Coal</td>
<td>Benzene</td>
</tr>
</tbody>
</table>

* Runs done by Dean Draemel.

I = Initial pressure at room temperature.
W = Pressure at average reaction temperature.
F = Final pressure at room temperature.
Table 13. Organic solvent leaching.

<table>
<thead>
<tr>
<th>Run</th>
<th>S&lt;sub&gt;T&lt;/sub&gt;</th>
<th>SO&lt;sub&gt;4&lt;/sub&gt;</th>
<th>SFe</th>
<th>SFeG</th>
<th>S&lt;sub&gt;Org&lt;/sub&gt;</th>
<th>S&lt;sub&gt;T&lt;/sub&gt;</th>
<th>SO&lt;sub&gt;4&lt;/sub&gt;</th>
<th>SFe</th>
<th>S&lt;sub&gt;Org&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>3.11</td>
<td>0.31</td>
<td>0.77</td>
<td>0.94</td>
<td>2.03</td>
<td>11.4</td>
<td>-34.1</td>
<td>33.6</td>
<td>4.2</td>
</tr>
<tr>
<td>23</td>
<td>3.11</td>
<td>0.24</td>
<td>0.78</td>
<td>0.90</td>
<td>2.04</td>
<td>11.4</td>
<td>-26.1</td>
<td>33.3</td>
<td>4.2</td>
</tr>
<tr>
<td>24</td>
<td>1.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>26.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>1.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>28.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>1.38</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>1.42</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S<sub>T</sub> = organic sulfur.
SO<sub>4</sub> = Sulfate sulfur.
SFe = pyritic sulfur volumetric.
SFeG = pyritic sulfur volumetric.
S<sub>Org</sub> = organic sulfur.
### APPENDIX D. APPARATUS

#### Bomb Cylinder and Closure

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>452HC3</td>
<td>Bomb cylinder, 600 ml</td>
</tr>
<tr>
<td>A455HC</td>
<td>Split ring, pair</td>
</tr>
<tr>
<td>455HCF</td>
<td>Cap screw</td>
</tr>
<tr>
<td>A456HC</td>
<td>Drop band</td>
</tr>
<tr>
<td>456HCF2</td>
<td>Cone pointed screw</td>
</tr>
</tbody>
</table>

#### Bomb Heat Assembly

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A818HC</td>
<td>Bomb heat assembly, complete</td>
</tr>
<tr>
<td>48HC</td>
<td>Gasket, silver</td>
</tr>
<tr>
<td>A92 HW</td>
<td>Tube connector</td>
</tr>
<tr>
<td>A122VB</td>
<td>Needle valve, straight</td>
</tr>
<tr>
<td>A146VB</td>
<td>Needle valve, angle</td>
</tr>
<tr>
<td>420HC</td>
<td>Adapter</td>
</tr>
<tr>
<td>454HC</td>
<td>Compression ring</td>
</tr>
<tr>
<td>457HC2</td>
<td>Head gasket, Teflon</td>
</tr>
<tr>
<td>A472E3</td>
<td>Thermocouple, 11-1/2 in.</td>
</tr>
<tr>
<td>593HC2</td>
<td>Pressure gage, 3000#</td>
</tr>
<tr>
<td>818HC</td>
<td>Bomb heat bare</td>
</tr>
<tr>
<td>822HC3</td>
<td>Stirrer shaft (600 ml)</td>
</tr>
<tr>
<td>831HC3</td>
<td>Cooling loop (600 ml)</td>
</tr>
<tr>
<td>832HC3</td>
<td>Dip tube (600 ml)</td>
</tr>
<tr>
<td>Part</td>
<td>Description</td>
</tr>
<tr>
<td>------------</td>
<td>------------------------------------------------------</td>
</tr>
<tr>
<td>A833HC</td>
<td>Thermocouple connector</td>
</tr>
<tr>
<td>A834HC</td>
<td>Tube connector</td>
</tr>
<tr>
<td>835HC</td>
<td>Adapter tee</td>
</tr>
<tr>
<td>836HC</td>
<td>Gage adapter</td>
</tr>
<tr>
<td>A837HC</td>
<td>Propeller with screw</td>
</tr>
<tr>
<td>A840HC</td>
<td>Stirrer bearing and gland assembly (see separate listing for individual parts)</td>
</tr>
<tr>
<td>A888HC</td>
<td>Rupture disc assembly</td>
</tr>
</tbody>
</table>

A840HC Stirrer Bearing and Gland Assembly

<table>
<thead>
<tr>
<th>Part</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>238A</td>
<td>O-ring</td>
</tr>
<tr>
<td>345HC</td>
<td>Packing cone, Rulon</td>
</tr>
<tr>
<td>354HC2</td>
<td>Ball bearing</td>
</tr>
<tr>
<td>356HC</td>
<td>Snap ring</td>
</tr>
<tr>
<td>394HC</td>
<td>Spacer ring</td>
</tr>
<tr>
<td>503HC</td>
<td>Spring</td>
</tr>
<tr>
<td>510HC2</td>
<td>Leak detector tube</td>
</tr>
<tr>
<td>718HC</td>
<td>Splined coupling</td>
</tr>
<tr>
<td>819HC</td>
<td>Stirrer drive hub</td>
</tr>
<tr>
<td>821HC</td>
<td>Bearing support hub</td>
</tr>
<tr>
<td>822HC3</td>
<td>Stirrer shaft (600 ml)</td>
</tr>
<tr>
<td>823HC</td>
<td>Face seal</td>
</tr>
<tr>
<td>824HC</td>
<td>Snap ring</td>
</tr>
<tr>
<td>825HC</td>
<td>Snap ring</td>
</tr>
<tr>
<td>826HC</td>
<td>Stirrer gland housing</td>
</tr>
</tbody>
</table>
827HC  O-ring
828HC  Cooling sleeve
829HC  Hose nipple
842HC  Snap ring
889HC  Washer
Fig. 19. Bomb assembly.
Fig. 20. Stirrer housing assembly.
Fig. 21. Stirrer housing.
APPENDIX E. EVALUATION OF SULFUR ANALYSIS AND SAMPLING

In order to evaluate the uniformity of the samples and the repeatability of the analysis, samples were analyzed and the data compared. The range R (the difference between the largest observation and the smallest observation) rather than the standard deviation is calculated because the small number of observations. In order to characterize better the significance of the range, this value is divided by the average value and multiplied by 100. This value is tabulated as %R and will give us an idea of the magnitude of the value of R.

Values accepted by the ASTM for the range are:

<table>
<thead>
<tr>
<th>%S</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>less than 2</td>
<td>0.05</td>
</tr>
<tr>
<td>more than 2</td>
<td>0.10</td>
</tr>
</tbody>
</table>

In the following tables, letters refer to samples taken from the same bottle and numbers indicate samples taken from different bottles.

(1) Wyoming coal. This is a low-sulfur coal where the organic sulfur represents about 85% of the total sulfur. The following data are in wet bases.
The data in the tables show that no appreciable segregation occurred and that repeatability is good. The large value obtained for the $\% R$ in the pyritic sulfur determinations is a result of the small percent of sulfur present as FeS$_2$ in the coal, but the result is well within ASIM specifications.

(2) Illinois #6 coal. This is a high sulfur coal having substantial amounts of both organic and pyritic sulfur. The following determined data are on a dry basis.
The collective averages are:

<table>
<thead>
<tr>
<th>Sample</th>
<th>$% S_{\text{tot}}$ vol</th>
<th>$% S_{\text{FeS}_2}$ vol</th>
<th>$% S_{\text{SO}_4}$ vol</th>
<th>$% S_{\text{Org}}$ vol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>4.38</td>
<td>1.84</td>
<td>1.83</td>
<td>0.44</td>
</tr>
<tr>
<td>R</td>
<td>0.12</td>
<td>0.50</td>
<td>0.60</td>
<td>0.01</td>
</tr>
<tr>
<td>%R</td>
<td>2.70</td>
<td>2.80</td>
<td>3.20</td>
<td>2.20</td>
</tr>
</tbody>
</table>

For this coal some values of the range fall outside of the ASTM limits, but the %R shows that a significant error is not introduced. Furthermore, it is seen from the data that the gravimetric determination of $\text{FeS}_2$ give similar results than the volumetric, so the former can be used to check the values obtained by volumetric determination. The value for the organic sulfur is more susceptible to errors because it is not analyzed directly but is found by difference.
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