ABSTRACT

The purposes of this work are threefold: 1) to improve techniques to separate coal macerals in order to characterize the sulfur-containing groups in each maceral type, 2) to determine the degree to which chemical characterization of organic sulfur species is improved by the use of maceral fractions in the analyses, and 3) to investigate the effects of the maceral separation processes on the sulfur compounds found in the macerals and the coal.

During this year, a centrifugal separator was designed and constructed to use the principle of magnetohydrostatics with a standard laboratory electromagnet rather than the superconducting magnet used in earlier studies for maceral separation. This new separator was designed for use with aqueous-based colloidal suspensions of magnetite as the separation medium.

Pyridine extracts of fresh samples as well as acid demineralized samples of a Herrin Seam hvC bituminous coal were separated on a neutral alumina column and then analyzed by GCMS and high resolution mass spectrometry. Minimal differences were observed in the separation yields between the fresh and the demineralized coals. Somewhat greater amounts of polar hetero-compounds are found in extracts from the acid demineralized coals. The aromatic sulfur compounds found in the coal do not appear to be affected significantly by the demineralization of the coal.
EXECUTIVE SUMMARY

The objective of this effort is to obtain a better understanding of the chemical properties of sulfur-containing compounds occurring in the various macerals derived from Illinois-Basin high-sulfur coals. The goal of the work to be carried out in 1987-1988 is to improve the techniques necessary to produce larger quantities of coal macerals than are currently available and to determine the changes the separation of coal into its maceral fractions makes in the nature of the chemically-bound sulfur species found in the coal.

Organically-bound sulfur is a significant problem in coal, in that it often accounts for 33 to 50% or more of the sulfur in Illinois coals. By characterizing the organic sulfur content in various maceral fractions of the coal, more innovative methods can be devised to remove that organic sulfur, as certain coal macerals have been found to be more easily desulfurized than others.

Development of the maceral separation technology has progressed to the point that a centrifugal separator was designed and constructed, which permits the use of a standard laboratory electromagnet rather than the liquid helium cooled superconducting magnet utilized in earlier designs. In addition, the centrifugal separator requires significantly shorter residence times for separation compared to earlier static designs. Extensive development of the centrifugal separator hardware was necessary to eliminate vibration problems associated with operation of the spinning centrifuge in the gap of specially designed pole caps installed on the electromagnet. These problems have now been eliminated, and the centrifuge has been operated with flow of liquid through the system. Time did not permit testing of the system with magnetic medium and macerals.

Pyridine extracts of fresh samples as well as acid demineralized samples from a Herrin Seam hvC bituminous coal have been separated on a neutral alumina column into compound types and characterized by gas chromatography/mass spectrometry (GCMS), and high resolution mass spectrometry, in order to investigate any possible alteration of the sulfur-containing species in coal as a result of the acid demineralization. The only differences in the yields of the alumina-separation fractions for the fresh and demineralized coals occur in the very non-polar and the very polar last fractions. Those fractions containing the heterocyclic sulfur compounds were not affected by the acid demineralization step. The acid demineralization does appear to result in the release greater amounts of polar oxygen-containing compounds such as carboxylic acids that could have been bound to the mineral matter in the un-demineralized coal.
OBJECTIVES

The objective of this effort is to obtain a better understanding of the chemical properties of sulfur-containing compounds occurring in the various macerals derived from Illinois Basin high-sulfur coals. The goal of the work to be carried out in 1987-1988 is to improve the techniques necessary to produce larger quantities of coal macerals than are currently available and to determine the changes that the separation of coal into its maceral fractions makes in the nature of the chemical-bound sulfur species found in the coal.

INTRODUCTION AND BACKGROUND

Coal is an extremely heterogeneous material that is difficult to characterize. Each of the distinct organic entities called macerals have a unique set of physical and chemical properties that contribute to the overall behavior of coal. Although much is known about the properties of minerals in coal, for example, the crystal chemistry, crystallography, magnetic, and electrical properties, surprisingly little is known about the properties of individual coal macerals.

Organically-bound sulfur in coal is a significant problem, in that it often accounts for 33 to 50% or more of the sulfur in Illinois coals. By characterizing the organic sulfur content in various maceral fractions of the coal, more innovative methods can be devised to remove that organic sulfur, as certain coal macerals have been found to be more easily desulfurized than others.

For a number of years, ANL has had an on-going program funded by U.S. DOE, Division of Basic Energy Sciences, related to high resolution separation and characterization of coal macerals using density gradient centrifugation, which separates macerals based on their density differences. Using this technique, and variations thereof, only limited amounts (milligram to gram quantities) of materials can be separated and isolated in a single run. Using CRSC funding, a continuous maceral separation technique is being developed, using the principle of magnetohydrostatics. In previous years this concept has been demonstrated, although precise separation was not obtained because of inadequacies in the magnet pole configuration and the separator. Late in 1986-1987, a new magnet design and centrifugal separator were conceived and construction initiated.

In this new system, a conventionally powered laboratory magnet is used, rather than the earlier liquid helium cooled superconducting magnet. In this way, cost of operation is significantly reduced. However, with this type of magnet, the maximum magnetic field intensity is more than a factor of ten smaller than that of the superconducting magnet. As a result, the fluid magnetic medium must have a magnetic susceptibility greater than that of the manganese chloride solution used in the original tests. A colloidal suspension of magnetite has a magnetic susceptibility up to 1000 times greater than that of transition metal salt solutions. In addition, this greater magnetic susceptibility allows separation in shorter residence times. Addition of the centrifugal separator further reduces the residence times for separation.
The major effort of 1987-1988 is to determine the effects that the maceral separation processing steps have on the nature of the sulfur-containing species found in the whole coal and macerals. Acid demineralization is used prior to maceral separation, and during separation, the coal particles are suspended in an alkaline medium containing colloidal magnetite and high concentration of surfactants. Any of these agents could modify the organic sulfur species found in the coal and macerals.

EXPERIMENTAL PROCEDURES

A) Maceral Separation

The 12-inch laboratory electromagnet used in the separation studies has water-cooled coils for continuous operation and 11.9 inch diameter poles with a maximum air gap of 5.4 inches. The pole caps and centrifuge are located within this 5.4 in. gap. The magnet is powered by a 5-kw regulated power supply.

In this system, the magnetic field is configured to exert a constant force on the magnetic fluid throughout the volume of the centrifuge. The shape of the pole pieces and the spacing between them determines both the strength and shape of this zone of constant force. The pole caps were designed by the Electromagnetic Technology Group here at Argonne in such a way as to produce a force uniform within 10% over a donut shaped volume with an outside diameter of 4 inches, an inside diameter of 2.34 inches, and a width of 0.66 inches. This volume, which is enclosed by the centrifuge, is where the actual maceral separation takes place. Use of a tolerance of less than 10% in the zone of constant force would result in a zone significantly smaller in size, and would adversely affect the size, and hence the throughput of the centrifugal separator.

A schematic diagram of the electromagnet and centrifuge is shown in Fig. 1. The pole caps, centrifuge, drive shaft, bearings, and motor are labeled in this figure. In this figure, the distance between the pole caps (the air gap) has been exaggerated for clarity. The centrifuge, fabricated from fiberglass-reinforced plastic, is 8.5 inches in diameter and 0.9375 inches wide. It holds about 25 mL of liquid and solids when operating. The unit operates at 7000 rpm with a coal slurry feed rate of 18 mL/minute (corresponding to a coal residence time of 82 seconds). The magnetic field strength in these tests equals 1.7 Tesla.

A cross-sectional view of the pole cap configuration chosen for these tests is shown in Fig. 2. This particular pole cap design was chosen because it permitted the use of a centrifuge considerably greater in width than that envisioned in our earlier conceptual designs. By increasing the width of the centrifuge, the likelihood is decreased that the coal particles will "short circuit" the separation zone and immediately pass out of the centrifuge before being separated. Hence the coal throughput to the centrifuge can be increases. One drawback of increasing the width of the centrifuge is that the air gap is increased. The magnetic flux density correspondingly decreases, increasing the residence time needed to separate the coal particles.
To operate this system, a coal/magnetite slurry is fed to the centrifuge through the adjustable feed line. The slurry then passes through the centrifuge (where the coal macerals are separated) and is then discharged over the outside weir. This stream is collected by a splash guard and routed to a collection tank. The dense maceral fraction is separated from the slurry and held at the outside wall of the centrifuge chamber. To remove the dense coal fraction from the centrifuge, the centrifuge is removed, and the coal fraction is removed from the wall. This centrifuge design does not provide a continuous solids removal system in order to keep the design simple and the construction cost at a minimum.

B) Maceral Characterization

The coal sample used in this study is the Argonne Premium Coal Sample #3, which is an Illinois Herrin Seam hvC bituminous coal. A description on how the sample was acquired and processes is available(1). This coal is the same material as the Illinois Coal Sample Program Sample No. 5. The elemental composition of this -100 mesh sample fresh, demineralized, and the pyridine extracts and residues from these two samples is given in Table 1. All demineralizations and extractions have been carried out under a nitrogen atmosphere.

Table 1. Elemental Compositions of samples used in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Number</th>
<th>%C</th>
<th>H</th>
<th>S</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Herrin hvC Bituminous Coal</td>
<td>RM-67-L-3</td>
<td>77.70</td>
<td>77.2</td>
<td>1.15</td>
<td>1.51</td>
<td>13.03</td>
</tr>
<tr>
<td>Demineralized Coal</td>
<td>RM-10-M-1</td>
<td>75.00</td>
<td>93.8</td>
<td>1.00</td>
<td>1.60</td>
<td>13.50</td>
</tr>
<tr>
<td>Pyridine Extract(Demineralized)</td>
<td>RM-11-M-1</td>
<td>77.40</td>
<td>88.2</td>
<td>1.00</td>
<td>4.00</td>
<td>10.90</td>
</tr>
<tr>
<td>Pyridine Extract(Fresh)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For demineralization, 75 g of coal is stirred with a mixture of 400 ml of 37% aq. HCl and 400 ml of 48% aq. HF in a teflon flask under nitrogen for 5 days. The sample is washed with water and vacuum dried at 60°C. The coal samples, 20 g, were extracted for 48 hrs in refluxing pyridine under nitrogen. After separation from the residue by centrifugation the pyridine solution with evaporated to dryness under vacuum at 50°C. The yields of pyridine extracts in wt% were 18.7±1.9 for the demineralized coal and 28.5±0.9 for the fresh sample.

The total pyridine extracts were characterized by high resolution mass spectrometry (HRMS) using two approaches. In both cases the spectrometer, a Kratos MS-50 was operating at 40000 dynamic resolving power scanning at 100 sec/decade. In the first approach the extract was introduced into an all-glass heated inlet system, heated to 300°C, and the volatiles leaked into the mass spectrometer. In the second approach the sample was heated to 300°C and then flash heated to 600°C. The second method, as one would expect, gave a greater yield of higher mass material. In both cases the internal yield standard consisted of the Diels-Alder adduct of D10-anthracene and maleic anhydride. Upon heating, the compound cleanly reverts to D10-anthracene which is easily distinguished in the precise mass mode in which we are operating. The appropriate scans are averaged and the data sorted according to heteroatom content and hydrogen deficiency (HD, equals number of rings + number of double bonds).
The pyridine soluble extracts were then separated into five fractions by low pressure liquid chromatography using a technique modified from that presented by Later, et al. (1). Neutral alumina was coated with 2 g of the extract by dissolving the extract in pyridine, adding 30 g of the alumina to the solution and rotatory evaporating it to dryness. The column was packed with 40 g of alumina in hexane and the coated alumina was added to the top, also in hexane. The column was sequentially eluted with 250 ml hexane, 500 ml benzene, 700 ml chloroform, 500 ml of 10% ethanol in THF and, finally, with 500 ml of pyridine. Each fraction with evaporated to dryness and weighed.

Appropriate LC fractions were analyzed by GCMS on a VG-Trio 3(20-250T) triple quadrupole mass spectrometer interfaced to an HP5890 GC. A 30 m x 0.25 micron DB-5 column was used for the GC separation. In addition, the benzene and chloroform LC fractions were analyzed by HRMS.

RESULTS AND DISCUSSION

A) Maceral Separation

During 1987-1988, development continued on the equipment and technology to permit large scale separation of coal into its constituent macerals. Early in this year, a centrifuge and drive system was designed and fabricated using the conventional electromagnet described earlier. However, during operation of this system, excessive vibration and bearing noise were encountered, at approximately 5000 rpm.

When the centrifuge and shaft were dismantled and inspected, two problem areas were identified. Evidence of bending of the shaft during operation was observed, as well as inadequacies in the needle bearing assemblies in properly locating the shaft.

To determine if bending of the shaft is possible, the systems' natural frequencies, bending modes and dynamic response at 6500 RPM were calculated with a computer program called Beam IV. This program was developed by the Mechanical Engineering Department, Virginia Polytechnic Institute and State University, Blacksburg, Va. To provide a basis for comparison, the first model developed was for the system as designed. Then, several variations were modeled and the results compared with the original design. These variations included 1) the use of a stiff coupling to replace the flexible coupling, 2) the addition of a third bearing located between the two existing bearings, 3) the use of a hollow shaft instead of the existing solid shaft, and 4) the addition of a flywheel on the end of the shaft opposite the centrifuge rotor. Based on a preliminary review of these models, it became evident that the shaft was susceptible to bending at several locations.

Preliminary calculations completed while the system was being designed indicated no natural vibrational frequencies at the operating speed of 7000 RPM. However, this analysis indicates the first, and sometimes the second, natural frequency may be below the operating speed of the centrifuge. As the centrifuge is brought up to speed, it passes through these natural frequencies, which may add some bending and vibration to the system. If the natural frequency lies within 20% of the operating speed, the operation may be unstable. In some of the models evaluated, including the basic system model, one of the natural frequencies lies between 6000 and 6500 RPM. This may be one of the reasons why our operation is unstable at these speeds.
The two major modifications made to the design were 1) increasing the shaft diameter from 0.75 to one inch and 2) replacing the needle bearings with ball bearings. By increasing the shaft diameter to one inch, the shaft stiffness was increased, which increased the natural vibrational frequencies of the system. Through modeling of this new design, the first natural frequency was estimated to be 10,700 RPM, and the second natural frequency 43,000 RPM. Since our operating speed is expected to be 7000 RPM, we will be operating below the first critical frequency. The maximum shaft deflection predicted by the program is 0.0002 inches, which will occur in the shaft at a location between the two bearings. This is a significant improvement over the original design, which had a first natural frequency of approximately 7000 RPM.

The second modification was to substitute ball bearings for the needle bearings. Since the ball bearing diameter (7/8 inch) was too large to be located in the pole cap (like the needle bearings), it was mounted in a hole machined into the face of one of the poles. The purpose of this modification was to increase the expected lifetime of the bearing system as well as to improve the rigidity of the centrifuge shaft system.

Following installation of the shaft, bearings, and motor, preliminary tests were completed without pumping water into the rotor. Tests were conducted successfully at speeds up to 7200 RPM. After these preliminary tests, the splash shield was installed around the rotor, the rotor was brought up to 6280 RPM, and then water was pumped into the rotor at 43 mL/min. The rotor speed decreased to 6140 RPM during this test because of the additional water weight in the rotor. A second water test was completed at 6450 RPM, which showed that the rotor speed only varied by ± 20 RPM. Both water tests were a success, with the collector operating as designed. Misting was not a problem as long as the water feed nozzle was located correctly inside the rotor.

B) Maceral Characterization

An objective of this study is to investigate any possible alteration to the sulfur containing species in coals as a result of acid demineralization. An examination of Table 1 shows that the overall organic sulfur-carbon ratio remains constant in the extracts with demineralization. One should note that there is an increase in oxygen content in the extract from the acid treated coal. This is most likely due to the release of compounds with very polar oxygen functionality which are complexed by the mineral matter. For example, acid treatment is typically done to release carboxylic acids in most geological samples(1). Further evidence of this fact is found in the presence of greater contents of oxygen-containing hetero-species, as found by GCMS of extracted fractions obtained from demineralized coal. This point will be discussed later in this report.

The high nitrogen content in the extracts is due to residual pyridine which is factored out in the mass spectrometry analysis. The yield of the extracts is significantly lower for the demineralized sample. Some of the extractables may be lost in the acid treatment, but there may be changes in the physical properties which can reduce extractability.
Averaged scans for the four MS experiments are shown in Figure 3a-d. Typically over 1000 peaks are found in the range of 90-500 thus demonstrating the need for high resolution spectra. Also, a significant number of ions are observed in the higher mass range (>300). Note that the larger ions are still quite abundant in the 600°C experiments, suggesting that thermal degradation is not destroying these species. In the HRMS analysis the following heteroatoms or combination of heteroatoms were searched for:

<table>
<thead>
<tr>
<th>None</th>
<th>Sulfur</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>2 Sulfurs</td>
<td>Fluorine</td>
</tr>
<tr>
<td>2 Oxygens</td>
<td>Sulfur-Oxygen</td>
<td>Chlorine-35</td>
</tr>
<tr>
<td>3 Oxygens</td>
<td>Sulfur-Nitrogen</td>
<td>Chlorine-37</td>
</tr>
</tbody>
</table>

There were no fluorine containing compounds in either extract, ruling out the possibility of fluorination during the acid treatment. A small amount of organic chlorine species were found, but they appear in both samples and are most likely indigenous to the coal extract.

The distributions of ions containing a sulfur and containing both a sulfur and oxygen are shown in Figures 4a,b and 5a,b for the 300°C and 600°C experiments respectively. Based on HD number and the number of carbons reasonable structures can be assigned for the various alkylated series. The parent molecules for selected HD numbers could be:

<table>
<thead>
<tr>
<th>HD number</th>
<th>Carbon number</th>
<th>Molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>4</td>
<td>Thiophene</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>Thiophenol</td>
</tr>
<tr>
<td>6</td>
<td>8</td>
<td>Benzo thiophene</td>
</tr>
<tr>
<td>9</td>
<td>12</td>
<td>Dibenzothiophene</td>
</tr>
<tr>
<td>12</td>
<td>16</td>
<td>Naphthobenzothiophene</td>
</tr>
</tbody>
</table>

It is interesting to note that the most abundant sulfur species in both samples has a HD number of 10 and starts at 13 carbons (Figure 4a). This is also found for the combination sulfur and oxygen. For a single sulfur distributions are similar for the two samples at 300°C but are much closer at the 600°C devolatilization. Benzo thiophenes are much more abundant in both samples at the higher temperature. At 300°C the S0 species appear to be very different with more ions found in the demineralized sample. However, at 600°C the opposite is true with fresh sample yielding more S0 containing ions especially with high HD numbers.

The selected ion peaks containing sulfur as a function of HD (Z) number are shown in Figures 6 and 7 for the fresh and demineralized samples, respectively. The patterns seen are very similar for both samples. For example, benzothiophene starts at 8 carbons as expected and the most abundant ion at 12 carbons and the largest m/z at 24 carbons. Significant ions at HD>12 are only seen in the fresh sample.

The direct high resolution mass spectrometric (HRMS) analysis of the extracts discussed above suggested that the demineralization step did not have a major effect on the distribution of sulfur compounds found in the extracts. However, since these compounds are minor constituents in the extracts, quantitation is difficult. In order to address this problem a class
separation technique was used which has been applied to coal liquefaction products(2) and also to extracts(3). The neutral sulfur containing hetero-aromatics were found in the second (benzene) fraction in these studies. Since pyridine extracts are being investigated in this project, the fifth elution solvent, pyridine, was added to the procedure. Averaged yields from the LC separation are presented as bar graph in Figure 8. It is important to note that the yields for the second (benzene) and third (chloroform) fraction are very similar for both fresh and demineralized coal extracts. The only major differences are seen in the very non-polar first fraction and the very polar last fraction. Some of the light hydrocarbons in the first fraction could be lost in the workup after the demineralization. The greater yield of polar molecules in the demineralized coal extract may be related to the greater oxygen content seen in this extract. Polar oxygen functionality such as carboxylic acids are released from attachment to the mineral matter in the coals during demineralization.

The benzene and chloroform fractions were analyzed by GCMS. The EtOH/THF and pyridine fractions did not have sufficient volatility to be analyzed by the GCMS. The resulting chromatograms were quite complex, but it is possible to examine the data for specific molecules using selected ion chromatograms. In the benzene fraction, the more abundant sulfur hetero-aromatics found in coal extracts are benzo- and dibenzothiophene and their alkylated analogues. Dimethyl and ethyl benzothiophenes were found to be quite abundant. The molecular ions (m/z=162) and a loss of a proton (m-1, m/z=161) are typically major peaks for these molecules. Also, the 161 peak is found in the C3-benzothiophenes. The selected ion chromatograms for these two ions is shown in Figure 9 for both the fresh coal extract and the demineralized coal extract. The two samples are very similar. Note that the 162 ion is the most abundant in scan 470 for both samples and scan 512 for ions with m/z=161. The mass spectra for scan 512 is also shown in Figure 9 and is identified as a C3-benzothiophene. Figure 10 shows the selected ion chromatograms for m/z=184 which could be the molecular ion for dibenzothiophene. The mass spectra at scan 363 was identified to be dibenzothiophene. As was seen in the previous figure the two samples are very similar.

Through HRMS analysis of the benzene fraction of the pyridine extract, a large number of dibenzothiophene derivatives can be identified. Table 2 summarizes the dibenzothiophene and alkyl-substituted dibenzothiophene contents found in that fraction of both fresh and demineralized coal. A greater amount of these compounds was found in the demineralized coal fractions, as shown in the larger relative abundances listed in Table 2. However, the relative proportions of the substituted dibenzothiophenes compared to unsubstituted dibenzothiophene are very similar, showing that the acid treatment did not modify the nature of the dibenzothiophenes occurring in the coal.
Table 2  
Dibenzothiophene and Alkyl-substituted Dibenzothiophenes  
Found in Benzene Fraction of Pyridine Extracts from  
Fresh and Demineralized Coal

<table>
<thead>
<tr>
<th>Formula</th>
<th>m/z</th>
<th>Δamu(1)</th>
<th>RA(2)</th>
<th>Δamu</th>
<th>RA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}<em>{16}\text{H}</em>{18}\text{S}$</td>
<td>184.0334</td>
<td>-1.3</td>
<td>9.0</td>
<td>-0.2</td>
<td>3.4</td>
</tr>
<tr>
<td>$\text{C}<em>{14}\text{H}</em>{11}\text{S}$</td>
<td>211.0565</td>
<td>-1.6</td>
<td>31.9 (M-1)(3)</td>
<td>-0.4</td>
<td>8.4</td>
</tr>
<tr>
<td>$\text{C}<em>{15}\text{H}</em>{14}\text{S}$</td>
<td>226.0807</td>
<td>-0.9</td>
<td>38.7</td>
<td>-1.8</td>
<td>9.5</td>
</tr>
<tr>
<td>$\text{C}<em>{16}\text{H}</em>{16}\text{S}$</td>
<td>240.0938</td>
<td>-3.5</td>
<td>13.3</td>
<td>-3.7</td>
<td>3.2</td>
</tr>
<tr>
<td>$\text{C}<em>{16}\text{H}</em>{15}\text{S}$</td>
<td>239.0876</td>
<td>-1.8</td>
<td>7.1 (M-1)</td>
<td>-2.0</td>
<td>2.5</td>
</tr>
<tr>
<td>$\text{C}<em>{17}\text{H}</em>{18}\text{S}$</td>
<td>254.1129</td>
<td>0.0</td>
<td>4.2</td>
<td>-0.5</td>
<td>1.2</td>
</tr>
<tr>
<td>$\text{C}<em>{17}\text{H}</em>{17}\text{S}$</td>
<td>253.1035</td>
<td>-1.6</td>
<td>1.2 (M-1)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{C}<em>{18}\text{H}</em>{20}\text{S}$</td>
<td>268.1280</td>
<td>-0.6</td>
<td>1.0</td>
<td>-1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>$\text{C}<em>{18}\text{H}</em>{19}\text{S}$</td>
<td>267.1197</td>
<td>-1.1</td>
<td>0.0 (M-1)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{C}<em>{19}\text{H}</em>{22}\text{S}$</td>
<td>282.1438</td>
<td>-0.4</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{C}<em>{19}\text{H}</em>{21}\text{S}$</td>
<td>281.1336</td>
<td>-2.8</td>
<td>0.1 (M-1)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Notes
(1) Difference between theoretical and observed mass, in milli-mass units.
(2) Relative Abundance – Intensity of the observed peak compared to the most intense peak in the mass spectrum, which is assigned a RA value of 100.
(3) One hydrogen has been removed from the original species during the ionization process in the mass spectrometer.

The content of various species containing only sulfur as heteroatom found in the benzene fraction of the pyridine extract is shown in Figure 11a. A greater concentration of thiophene (HD=6) was found in the demineralized coal fraction, as well as dibenzothiophene (HD=9). Although thiophene and dibenzothiophene are not especially polar, it is still possible that greater amounts of these compounds are found in the demineralized coal because of retention by the mineral matter of the fresh coal.

Figures 11b and 11c show the contents of sulfur-only and sulfur + oxygen-containing species found in the chloroform fraction of the pyridine extracts. In general, there is little difference between the sulfur-containing species found in this fraction of the fresh vs the demineralized coal, with the notable exception of HD=7 (Fig. 11b). The nature of this compound has not been identified. Note also that a significantly increased amount of material corresponding to HD=7 was found in the benzene fraction of the demineralized coal (Fig. 11a). This species also has not been identified, but may be different from that noted in Fig. 11b.

In the case of compounds containing both sulfur and one oxygen (Fig. 11c) in the chloroform fraction, greater quantities are also found in the
deminerlalized coal fractions. These species are quite polar, so finding
greater amounts if fractions obtained from deminerlalized coals is consistent
with the concept of retention of polar species by the mineral matter in the
fresh coal.

It is difficult to envision oxidation during the deminerlalization of the coal
as the source of the increased levels of polar, and especially sulfur +
oxxygen-containing species found in the pyridine fractions obtained from acid
treated coal. The acid treatment in these studies was carried out at ambient
temperature in a nitrogen atmosphere to guard against oxidation. In
addition, the pyridine extractions were all carried out in nitrogen.

Lytle et al (4) reported significant modification of species found in a solid
c coal that had been deminerlalized by acid treatment. These measurements were
obtained by plasma desorption mass spectrometry (PDMS) which permits analysis
of high molecular weight samples. However, one must be careful while
interpreting data from PDMS of complex mixtures, since there are matrix
effects that are poorly understood. Lytle found that a series of species in
the 595-900 mass range, with a Δm/z of 44 was destroyed by acid treatment of
the coal. High resolution mass spectrometry was not used, so this series of
species could not be identified. However, the acid treatment step in this
study was carried out at 100°C. It was not reported as to whether a nitrogen
atmosphere was used or not. Acid treatment at this temperature is
significantly more severe than the conditions used in our study, and
modification of the coal structure is possible at those temperatures.

CONCLUSIONS

A centrifuge system has been constructed for the separation of coal macerals
using a colloidal suspension of magnetite as the separation medium in a
conventional laboratory electromagnet, with specially designed pole caps.
Operation of the centrifuge under design conditions was confirmed, but time
did not permit testing of the system with coal macerals.

Analysis by GC/MS and HRMS of extracts obtained from fresh and acid
deminerlalized Herrin Seam hvC bituminous coal samples showed that increased
amounts of sulfur- and oxygen-containing species are found in the extracts
from the acid treated coal, but the relative proportions and the structures
of the identified species are very similar for both the fresh and the treated
coals. Therefore, the conclusion can be drawn that the acid treatment has
little effect of the chemistry of the hetero-species occurring in the coal.

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Fig. 1. Overall Schematic of Magnet and Centrifuge System
Fig. 2. Detail of Electromagnet, Centrifuge, Slurry Feed, and Slurry Recovery System
Fig. 3a. Averaged High Resolution Mass Spectra (Fresh - 300°C)
Fig. 3b. Averaged High Resolution Mass Spectra (Demineralized - 300°C)
Fig. 3c. Averaged High Resolution Mass Spectra (Fresh - 600°C)
Fig. 3d. Averaged High Resolution Mass Spectra (Demineralized - 600°C)
Fig. 4a. Distribution of Ions at 300°C Containing One Sulfur
Fig. 4b. Distribution of Ions at 300°C Containing Sulfur + Oxygen
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Fig. 6. Selected sulfur containing ions as a function of Z number for the fresh sample extract.
Fig. 7. Selected Sulfur Containing Ions as a Function of Z Number for the Demineralized Sample Extract
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Fig. 9. Selected Ion Chromatograms for m/z = 162 and 161 from GC/MS.
Fig. 10. Selected Ion Chromatograms for m/z = 184
from GC/MS
Fig. 11. Hetero-atom Species Content in Selected Fractions of Pyridine Extracts
a. Benzene Fraction, S-containing Species
b. Chloroform Fraction, S-containing Species
c. Chloroform Fraction, S + O-containing Species