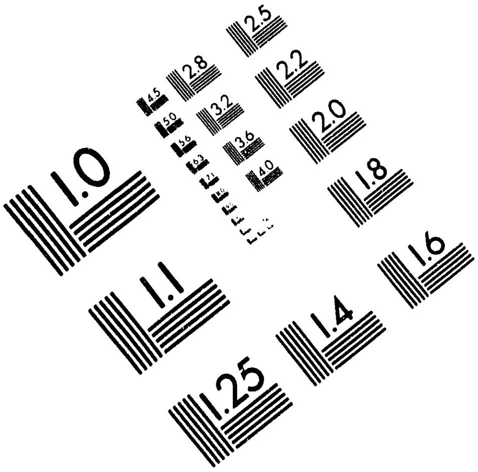

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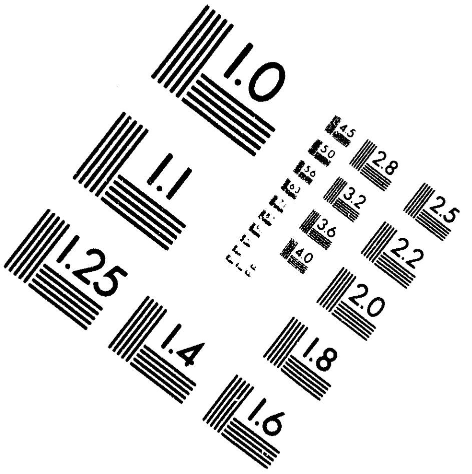

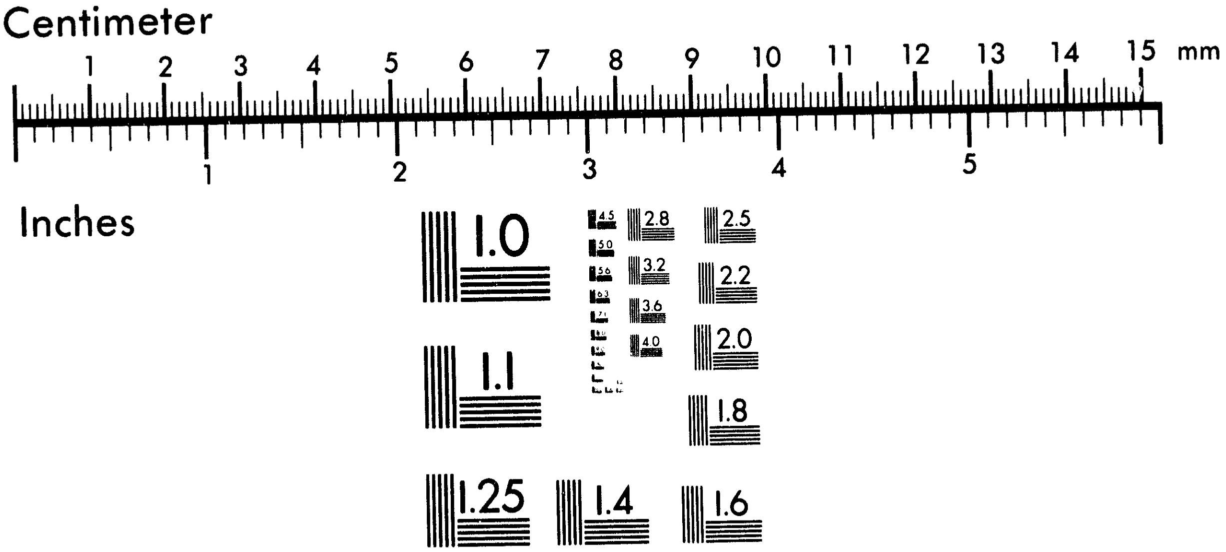

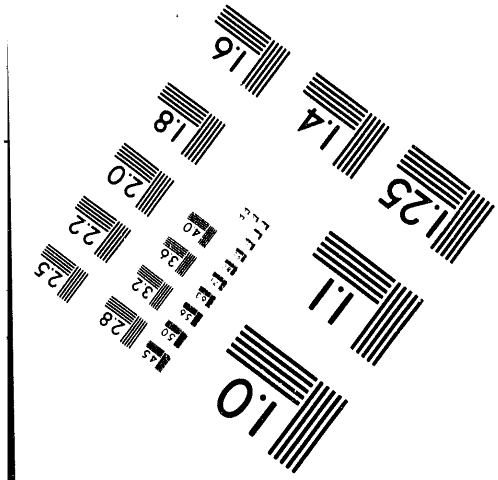

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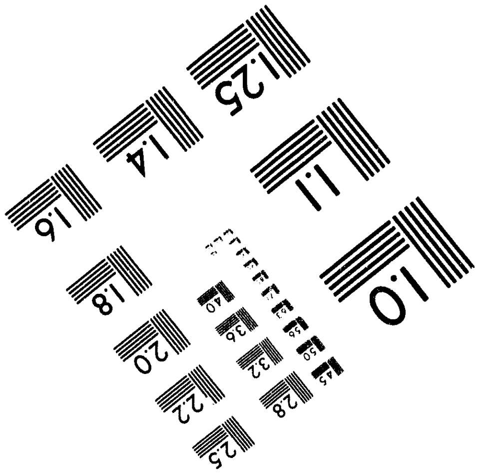

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DOE/PC/92521--T170

TECHNICAL REPORT
March 1, 1994 through May 31, 1994

Project Title: **ANALYZING ORGANIC SULFUR IN COAL/CHAR: INTEGRATED MILD DEGRADATION/XANES METHODS**

DOE Grant Number: DE-FC22-92PC92521 (Year 2)
ICCI Project Number: 93-1/6.1A-1P
Principal Investigator: Dr. Stephen R. Palmer, Department of Mechanical Engineering and Energy Processes, Southern Illinois University at Carbondale, Carbondale IL 62901.
Other Investigator: Dr. G. P. Huffman, Consortium for Fossil Fuel Liquefaction Science, 233 Mining and Mineral Resource Building, University of Kentucky, Lexington, KY 40506.
Project Manager: Ken Ho, Illinois Clean Coal Institute

ABSTRACT

The overall goal of this study is to improve our understanding of sulfur in coals/chars via the use of combined advanced non-destructive and advanced destructive methods of sulfur analysis. This study combines selective oxidation, analytical pyrolysis, and sulfur X-ray Absorption Near Edge Structure Spectroscopy (XANES) analysis.

Samples with a wide variety of sulfur contents, (0.63% to 4.40%) have been prepared for use in this study. This includes steam gasification chars, oxidized coals and desulfurized coals as well of the original unaltered coals. Mild pyrolysis and preliminary XANES data shows that the sulfur chemistry of gasification chars is significantly different from that of the original coals. Mild pyrolysis of the samples that were oxidized with peroxyacetic acid showed that the level of simple thiophene structures observed in the pyrolysis products declines with increasing levels of oxidation. Sulfur XANES spectra of treated samples showed various effects depending on the treatment severity. For the less severely treated samples (demineralization and solvent extraction), the XANES spectra were similar, although not identical, to the untreated coal spectra, whereas the more severe treatments (steam at 450°C; peroxyacetic acid at 25°C) showed preferential oxidation of one or more sulfur-bearing phases in the original coal. Additional samples have recently been examined by XANES and W-band EPR and the data is currently being processed and evaluated.

U.S. DOE Patent Clearance is <u>NOT</u> required prior to the publication of this document.

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EXECUTIVE SUMMARY

The release of sulfur oxides into the environment via the combustion of high sulfur coals is the primary cause of acid rain. To address this problem considerable effort has been expended on finding methods for the removal of sulfur from coal prior to combustion. Although some success has been achieved with the removal of inorganic sulfur forms (primarily pyrite), no technique is currently available for the cost-effective removal of organic sulfur.

Perhaps the single most important reason why organic sulfur removal is so difficult is the fact that the organic sulfur in coal remains very poorly characterized. Since different organic sulfur species are easier to desulfurize than others it is essential that a knowledge of the different types of organic sulfur and their distribution in coal be obtained. Only then will it be possible to design the required technologies for their effective removal.

Recently, two approaches have received considerable attention for the characterization of organic sulfur in coal. The first is the use of so-called `destructive' techniques which degrade the coal into small, more readily analyzable fragments. The second is the so-called `non-destructive' techniques which observe the sulfur in the whole coal without degradation. Each technique has advantages and disadvantages. For instance the destructive techniques such as chemical and thermal degradation can provide very detailed molecular structure information but they suffer from the inability to observe all of the sulfur at one time, and from the possibility that degradation induced rearrangement reactions may corrupt the structural information. On the other hand non-destructive techniques can observe all of the organic sulfur species simultaneously in situ and hence can provide the best overall picture of the organic sulfur distribution. However, non-destructive techniques often fail to provide the very detailed structural information such as substitution patterns, the nature of substituents and the nature of bonding between the different units that may be provided by the degradative methods. All information is needed if the organic sulfur in coal is to be adequately characterized.

The overall objective of this study is to combine advanced non-destructive and advanced destructive methods of sulfur analysis so as to provide complete characterization of the organic sulfur in Illinois Basin coals and mild gasification chars derived form them. To achieve this overall objective a number of specific goals and objectives can be identified. These are:

1. Obtain and analyze, by standard ASTM coal analysis methods, a series of Illinois Basin coals and mild gasification chars derived form them.

2. Use analytical pyrolysis techniques, dichromate and peroxyacetic acid oxidation and sulfur K-edge XANES analysis to compare and contrast the organic sulfur distribution of the coals and their mild gasification chars.

3. Use the organic sulfur distribution obtained to investigate any transformation of organic sulfur species that occur as a result of mild gasification.

4. Explore relationships between the organic sulfur species identified by the destructive techniques with those identified by the XANES analysis, thereby evaluating the combination of these techniques for organic sulfur characterization purposes.

5. To combine the information from all techniques to provide a detailed quantitative analysis of organic sulfur.

6. Screen the oxidation and analytical pyrolysis products for organic nitrogen compounds.

To achieve these specific goals the following tasks have been completed.

Steam gasification chars have been prepared from each of the freshly ground coals together with samples of floated and extracted coal derived from the IBC 101 and IBC-106 coals. A further six samples were prepared from the IBC-101 coal using peroxyacetic acid oxidation. Both the solubilized and residual component from each oxidation reaction was retained for analysis.

Aliquots of these samples were delivered to Dr. G.P. Huffman at the Consortium for Fossil Fuel Liquefaction Science, University of Kentucky, for sulfur K-edge XANES analysis during the March/April Brookhaven session and to Dr. R. Clarkson, University of Illinois, for W-Band EPR analysis. In addition, aliquots of these same samples are currently under investigation in laboratories at SIUC using the analytical pyrolysis and selective oxidation techniques.

Since the samples have a wide variety of sulfur contents. (0.63% to 4.40%) and differ in their method of preparation, this sample set should provide a good test for the various sulfur characterization techniques employed in this study.

All mild gasification chars (steam gasification at 550°C) show reductions in their sulfur contents when compared to their parent coal. As might be expected the gasification chars derived from the floated coals have much lower sulfur contents than the chars derived from the original coals.

To investigate possible transformations between sulfur forms as a result of mild pyrolysis two model sample mixtures were examined using the mild pyrolysis technique. These were a 1:1 mixture of polyethylene and pyrite and a 1:1 mixture of polyethylene and iron sulfate. It is clear that organic sulfur species are formed via an interaction between the pyrolyzing polyethylene and both the pyrite and the iron sulfate. Based on this observation it is clear that for mild pyrolysis data to be used for the characterization of organic sulfur species it is important that both the pyrite and iron sulfate contents of the sample being analyzed be as low as possible.

It is clear that the sulfur chemistry of gasification chars is significantly different from that of the original coals. This can be seen from a comparison of the analytical pyrolysis chromatograms of the IBC coals and their gasification chars and from the preliminary XANES results. Using the analytical pyrolysis technique, it is clear that the gasification char does not yield the alkyl and benzothiophenes that are abundant before gasification. Although this result is not too surprising, it clearly demonstrates that the distribution of sulfur species changes as a result of mild gasification.

In addition, examination of IBC-101 samples that were oxidized with peroxyacetic acid using the analytical pyrolysis technique shows that the level of simple thiophene structures observed in the pyrolysis products declines with increasing levels of oxidation. This observation would support our earlier findings which suggested that peroxyacetic acid was oxidizing simple thiophenes to methyl sulfonic acid.

From the XANES experiments conducted so far, the four original coal samples (IBC 101,102,106 and 109) were found to contain most of the organic sulfur in the form of thiophene derivatives, with a minor to significant amount present as organic sulfide. This is in agreement with previous XANES studies on Illinois coals. However, all of the coals were oxidized to some extent as the sulfate contents of the coals were significant. This result was also confirmed by Mössbauer spectroscopy, which showed that a significant fraction of the pyrite in the coal was oxidized. In the extreme case (IBC-102), sulfate sulfur constituted over 50% of the sulfur in the sample and over half the iron was also present as $FeSO_4 \cdot H_2O$ (szomolnokite). In comparison, the other coal samples examined showed less than 15% of the sulfur or iron in the form of sulfates. Freshly prepared samples have been re-examined.

Sulfur XANES spectra of the treated samples showed various effects depending on the treatment severity. For the less severely treated samples (demineralization and solvent extraction), the XANES spectra were similar, although not identical, to the untreated coal spectra, whereas the more severe treatments (steam at 450°C; peroxyacetic acid at 25°C) showed preferential oxidation of one or more sulfur-bearing phases in the original coal. For example, the peroxyacetic acid treatment oxidized organic sulfides to sulfones, without significantly affecting the thiophenic sulfur, whereas the steam treatment appeared to largely alter the pyrite to pyrrhotite, along with some reduction of organic sulfide as well.

It should be noted that this study has received some attention from Professor Yperman's group at Limburgs Universitair Centrum in Belgium. Professor Yperman is attempting to characterized sulfur functionalities in coals using the Atmospheric Pressure Temperature Programmed Reduction (AP-TPR) technique. He is willing to examine the same set of samples used in this study. It is anticipated that this collaboration will provide additional sulfur functionality information on which to evaluate the characterization techniques.

OBJECTIVES

The overall objective of this study is to combine advanced non-destructive and advanced destructive methods of sulfur analysis so as to provide complete characterization of the organic sulfur in Illinois Basin coals and mild gasification chars derived form them.

Specific Objectives

The specific goals and objectives of this study are:

1. Obtain and analyze, by standard ASTM coal analysis methods, a series of Illinois Basin coals and mild gasification chars derived form them.
2. Use analytical pyrolysis techniques, dichromate and peroxyacetic acid oxidation and sulfur K-edge XANES analysis to compare and contrast the organic sulfur distribution of the coals and their mild gasification chars.
3. Use the organic sulfur distribution obtained to investigate any transformation of organic sulfur species that occur as a result of mild gasification.
4. Explore relationships between the organic sulfur species identified by the destructive techniques with those identified by the XANES analysis, thereby evaluating the combination of these techniques for organic sulfur characterization purposes.
5. To combine the information from all techniques to provide a detailed quantitative analysis of organic sulfur.
6. Screen the oxidation and analytical pyrolysis products for organic nitrogen compounds.

To achieve these goals a series of tasks were scheduled for completion within the contract period. These tasks include:

Task 1. Sample selection and preparation.

Four coals, IBC-101, IBC-102, IBC-106 and IBC-109 are to be obtained from the Illinois Basin Coal Sample Program. Aliquots of each are to be micronized, sink/floated and solvent extracted. Aliquots of these samples are then to be selectively oxidized, mildly gasified and chemically desulfurized.

In addition, a mild gasification reactor is to be designed and constructed and used for the preparation of mild gasification chars. The object of task 1 is to provide a variety of samples with different sulfur contents and distributions.

Task 2. Analytical pyrolysis.

The first sulfur characterization technique to be applied to the samples prepared in task 1 is analytical pyrolysis. Both pyrolysis-gas chromatography-flame photometric detector (py-GC-FPD) and pyrolysis-gas chromatography mass spectroscopy (py-GCMS) are to be used to characterized organic sulfur species present in the pyrolysis products.

Task 3. Coal/char oxidation with sodium dichromate.

The samples prepared in task 1 are to be characterized by selective oxidation with sodium dichromate. Soluble oxidation products will be methylated and then analyzed for organic sulfur compounds using GC-FPD and GC-MS. Insoluble oxidation products will be examined by XANES and W-Band EPR as described in task 5.

Task 4. Coal/char oxidation with peroxyacetic acid.

The samples prepared in task 1 are to be characterized by selective oxidation with peroxyacetic acid. Soluble oxidation products will be methylated and then analyzed for organic sulfur compounds using GC-FPD and GC-MS. Insoluble oxidation products will be examined by XANES and W-Band EPR as described in task 5.

Task 5. Sulfur XANES and Mössbauer analysis.

Samples prepared in task 1 and selected samples produced in tasks 3 and 4 are to be examined by sulfur K-edge XANES and W-Band EPR. By analyzing the samples before and after selective oxidation, mild gasification and desulfurization, it will be possible to determine which sulfur forms are released from the coal, those which remain and transformations between sulfur forms resulting from the various treatments.

Task 6. ASTM methods of coal/char analysis.

Selected samples from tasks 1-5 are to be analyzed by standard ASTM methods of analysis such as proximate, ultimate, sulfur forms and BTU analysis.

INTRODUCTION AND BACKGROUND

The release of sulfur oxides into the environment via the combustion of high sulfur coals is the primary cause of acid rain.(1) To address this problem considerable effort has been expended on finding methods for the removal of sulfur from coal prior to combustion. Although some success has been achieved with the removal of inorganic sulfur forms (primarily pyrite) (2,3), no technique is currently available for the cost-effective removal of organic sulfur.

Perhaps the single most important reason why organic sulfur removal is so difficult is the fact that the organic sulfur in coal remains very poorly characterized. Since different organic sulfur species are easier to desulfurize than others it is essential that a knowledge of the different types of organic sulfur and their distribution in coal be obtained. Only then will it be possible to design the required technologies for their effective removal.

There have been many attempts to characterize the organic sulfur in coal and some important progress has been made.(4) However, a universally excepted method for organic sulfur characterization has yet to be provided. The problem is due to the extreme complexity of the chemistry of coal, a fact that prevents any single characterization technique from providing all of the necessary information. The solution to this problem would therefore appear to be the use of a combination of several techniques such that the combined information would be sufficient for complete sulfur characterization. This idea serves as the basis for this current research program.

Recently, two approaches have received considerable attention for the characterization of organic sulfur in coal. The first is the use of so-called \`destructive' techniques which degrade the coal into small, more readily analyzable fragments. The second is the so-called \`non-destructive' techniques which observe the sulfur in the whole coal without degradation. Each technique has advantages and disadvantages. For instance the destructive techniques such as chemical and thermal degradation can provide very detailed molecular structure information but they suffer from the inability to observe all of the sulfur at one time, and from the possibility that degradation induced rearrangement reactions may corrupt the structural information. On the other hand non-destructive techniques can observe all of the organic sulfur species simultaneously in situ and hence can provide the best overall picture of the organic sulfur distribution. However, non-destructive techniques often fail to provide the very detailed structural information such as substitution patterns, the nature of substituents and the nature of bonding between the different units that may be provided by the degradative methods. All information is needed if the organic sulfur in coal is to be adequately characterized.

The current study combines selective oxidation strategies, analytical pyrolysis with subsequent GC-FPD and GC-MS analysis, and Sulfur X-ray Absorption Near Edge Structure Spectroscopy (XANES) analysis of Illinois Basin coals and mild gasification chars derived from them for the complete characterization of organic sulfur.

It is anticipated that this characterization approach will provide both the detailed molecular structure, and the overall quantitative distribution, of organic sulfur thereby leading to a more complete analysis of organic sulfur structures in coals and chars.

EXPERIMENTAL PROCEDURES

Sample Preparation

Typical coal preparation includes coal micronization, coal demineralization, coal flotation and solvent extraction. Micronization is achieved using a nitrogen powered fluid energy mill and is necessary to liberate the mineral component of coal from the organic component. Approximately 200 grams of each coal were micronized. To remove minerals from the coal acid treatments with HCl and HF, and a subsequent sink/float procedure are required. The acid treatment is performed by dispersing 100grams of the micronized coal in a 500mL mixture of HF and HCl (3:1). After the mixture has been stirred for 3 hours the coal is recovered by filtration and the residual acid washed away with hot distilled water until the filtrate is neutral.

To remove minerals such as pyrite that are insoluble in the HF/HCl mixture the sink/float procedure was employed. This involves dispersing the acid treated coal in a cesium chloride solution of specific density 1.6g/mL. This coal slurry is then centrifuged so that the mineral sinks and the organic coal floats. The mineral free coal (approximately 1-1.5% ash) is collected by filtration, washed sequentially with dil. HCl and hot distilled water and finally dried. Solvent extraction was performed on aliquots of the demineralized coal using an azeotropic mixture of methanol and chloroform. Soxhlet apparatus was used.

Coal Oxidation

Two selective oxidation procedures have been used. The first is a relatively mild oxidation which results in little coal dissolution. This is used to provide samples for subsequent XANES, W-Band EPR and analytical pyrolysis analysis. The second procedure is more extensive and results in almost complete dissolution of the coal. This procedure is used for sulfur characterization by GC-FPD and GCMS.

Typical mild selective oxidation with peroxyacetic acid involves dispersing 2 grams of the solvent extracted coal sample in a mixture of 50mLs glacial acetic acid and 50mLs 30% (wt/v) hydrogen peroxide. The mixture is then stirred at room temperature for six hours. After this time the oxidation product is recovered at the filter largely as undissolved coal solids. This material is washed with distilled water and dried.

The procedure used for subsequent GC-FPD and GCMS analysis used the same quantities of coal and reagents but this time the reaction is carried out under reflux for 24 hours. After this time the coal is almost completely in solution. The solubilized oxidation products are recovered by first removing any residual undissolved material by filtration. Any excess peroxides in the oxidation products solution are then destroyed by the addition of 10mg of platinum on carbon (1% wt Pt). The peroxide free solution is then rotary evaporated to recover the soluble coal products. For GC-FPD and GCMS analysis these oxidation products are first methylated with diazomethane.

Coal Gasification

A preliminary mild gasification experiment was performed by sealing 2g of the IBC-101 micronized sample in a 10mL stainless steel micro-reactor with 2 mL of water. After purging the reactor with nitrogen it was sealed and heated to 450°C in a fluidized sand bath for 1 hour. After this time the reactor was cooled and the product recovered at the filter where it was washed with distilled water and dried.

Using the mild gasification unit constructed in the previous quarters, a total of twelve gasification chars have been prepared. Six experiments were performed on 2 grams coal aliquots at a temperature of 450°C and 550°C using a 10mL per minute flow of nitrogen gas. Another six experiments were performed at a temperature of 550°C for 1 hour with 0.2mL of water introduced into the nitrogen gas stream using a HPLC pump.

Coal Desulfurization

The method of coal desulfurization used incorporates an oxidative pretreatment step followed by an alcohol/base desulfurization reaction. The pretreatment step involved dispersing coal (50g) in glacial acetic acid (200mL) and adding 50mL of 30% (wt/v) hydrogen peroxide solution. After stirring this mixture for 6 hours at room temperature the oxidized coal is recovered by vacuum filtration, washed with distilled water and finally dried at 110°C. The oxidized coal (2g) is then dispersed in a suspension of 0.2g NaOH in 5mL methanol. This mixture is placed in a 10 mL stainless steel micro-reactor, purged with nitrogen, sealed and then heated to 350°C for 1 hour. The resulting desulfurized coal is then collected at the filter, washed with distilled water and finally dried.

XANES Analysis

The sulfur XANES spectra are measured at beam-line X-19A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, NY. This beam line is well suited for soft X-ray measurements because the X-rays are in vacuum right up to the sample and are therefore minimally absorbed before interacting with the sample. Spectra are collected in fluorescence geometry and stored in a MicroVAX II computer at NSLS before being transferred to a similar computer at the University of Kentucky. Standard computerized methods are used to separate the XANES region from the XAFS spectrum. A least-squares fitting program (EDGFIT) is then applied to the XANES spectrum to determine the contribution of different sulfur forms to the spectrum. The areas under the peaks in the fitted spectrum are then converted to wt% sulfur in the various forms.

RESULTS AND DISCUSSION

Sample Preparation

XANES and Mossbauer analyses, as reported in the previous quarterly report, indicated that some of the original coal samples had been exposed to air during handling and storage and had subsequently oxidized to some degree. To eliminate problems concerning the influence of this oxidation on the characterization techniques new pristine coal samples were obtained from the IBCSP sample bank. These four coals (IBC 101, 102, 106 and 109) were ground under nitrogen and resubmitted for XANES, W-band EPR, selective oxidation and mild pyrolysis.

In addition, gasification chars have been prepared from each of these fresh ground coals together with samples of floated and extracted coal derived from the IBC 101 and IBC-106 coals. In each case the coal was gasified at 550°C using steam with an inert nitrogen carrier gas. The yields of char are given in Table 1.

Table. 1. Steam gasification char yields

Coal Sample	Code Name	Char Yield
IBC-101	GCR1	57.4
IBC-102	GCR2	53.3
IBC-106	GCR6	51.8
IBC-109	GCR9	60.4
IBC-101FE	GCF1	53.0
IBC-106FE	GCF6	50.0

FE = floated and extracted

As expected the char yields obtained using steam gasification are about 10-15% below those obtained by gasifying the coals in a stream of nitrogen gas (pyrolysis). This is, of course, due to the carbon/steam gasification reaction. Since this study is primarily concerned with identifying the sulfur forms in the coals and their gasification chars, no attempt was made to measure the composition of the gases produced by the steam reaction.

A further six samples were prepared from the IBC-101 coal using peroxyacetic acid oxidation. These samples were obtained under three different oxidation conditions. Both the solubilized and residual component from each oxidation reaction was retained for analysis. This will allow for the distribution of the sulfur forms between the soluble and insoluble phases to be compared. The samples prepared are listed in Table 2.

Table 2. List of oxidized samples prepared.

Sample description	Code name
oxidn. res. after 15 mins at 100°C	OXRA
oxidn. sol. after 15 mins at 100°C	OXSA
oxidn. res. after 360 minutes at 100°C	OXRB
oxidn. sol. after 360 minutes at 100°C	OXSB
oxidn. res. after 24 hours at 100°C	OXRC
oxidn. sol. after 24 hours at 100°C	OXSC

Aliquots of these samples were delivered to Dr. G.P. Huffman at the Consortium for Fossil Fuel Liquefaction Science, University of Kentucky, for sulfur K-edge XANES analysis during the March/April Brookhaven session and to Dr. R. Clarkson, University of Illinois, for W-Band EPR analysis. In addition, aliquots of these same samples are currently under investigation in laboratories at SIUC using the analytical pyrolysis and selective oxidation techniques.

The available ultimate and proximate data for these new samples plus that for the samples prepared in the first two quarters are listed in Table 3. (The data is reported on a dry basis.)

As can be seen from the data in Table 3 samples have been prepared which have a wide variety of sulfur contents. (0.63% to 4.40%) In addition, since the methods of preparation vary, it is likely that the sulfur compound distributions in each sample will vary also. This sample set should therefore provide a good test for the various sulfur characterization techniques employed in this study.

Table 3. Ultimate and proximate composition data.

Sample	Elemental Composition				Ash
	%C	%H	%N	%S	wt%
101M	72.41	4.51	1.30	4.40	10.82
102M	73.71	4.33	1.44	3.27	10.73
106M	79.41	4.94	1.79	3.90	9.06
109M	74.90	3.78	1.70	1.10	8.30
101FE	65.49	4.68	1.25	3.22	2.63
106FE	70.43	4.88	1.64	2.68	3.71
101SO	63.07	4.64	1.21	2.84	7.84
106SO	66.07	4.46	1.47	1.95	6.55
101MG1	74.50	3.09	1.36	3.16	9.23
101MG2	71.00	2.98	1.30	3.09	15.32
101MG3	87.16	2.55	1.68	2.28	2.29
102MG1	74.53	3.52	1.91	3.09	10.33
106MG1	71.61	2.94	1.98	2.67	13.29
109MG1	78.94	3.49	2.19	1.21	10.38
101DES1	75.38	5.08	1.17	0.77	13.98
GCR1	71.29	2.39	1.36	2.89	
GCR2	77.85	2.61	1.83	1.89	
GCR6	74.05	2.37	1.86	2.73	
GCR9	78.03	2.49	2.12	0.63	
GCF1	84.22	2.35	1.63	1.89	
GCF6	74.19	1.95	1.41	0.86	
OXRA	61.17	4.41	1.43	2.49	
OXSA	48.52	4.38	1.28	3.28	
OXRB	62.17	4.42	1.11	1.91	
OXSB	52.42	4.91	1.37	2.72	
OXRC	61.81	4.19	1.64	1.84	
OXSC	50.28	4.37	1.57	2.79	

M = micronized, FE = floated + extracted, SO = selectively oxidized, MG = mild gasification char (Table 1), DES = desulfurized.

The oxidation treatment with peroxyacetic acid lowers the sulfur content of the coals, primarily by the dissolution of pyrite, but also by reaction with the organic sulfur. Previous investigations showed that between 10 and 20% of the organic sulfur in these coals was removed by peroxyacetic acid oxidation. (5)

All mild gasification chars (steam gasification at 550°C) show reductions in their sulfur contents when compared to their parent coal. For example, both the IBC 101 and 106 samples have reductions in sulfur contents around 30% while the IBC 102 and 109 samples show a sulfur content reduction of around 40%. As might be expected the gasification chars derived from the floated coals have much lower sulfur contents than the chars derived from the original coals. It is interesting to note the difference in sulfur contents between the chars from the floated and those from the original coals is about equal to the amount of pyrite in the original coals. This would suggest that all the pyritic sulfur remains in the char upon gasification. However, this sulfur may not be pyritic after gasification since the pyrite may be transformed into another form during the gasification process.

Analytical Pyrolysis

Each of the samples prepared has or is being examined by analytical pyrolysis GCMS. From the total ion chromatogram (TIC) for each pyrolysate single ion chromatograms (SIC) are constructed for ions that are representative of sulfur containing compounds. Previously it had been shown that as the level of selective oxidation increases so the abundance of substituted thiophenes decreases in the pyrolysis chromatograms. This finding supports the observation that peroxyacetic acid oxidizes simple thiophene structures to methylsulfonic acid. The mild gasification char prepared by a steam treatment at 450°C for 1 hour also has a low abundance of substituted thiophenes. Presumably these structures were removed from the coal during gasification or converted into other sulfur forms. The reduction in the sulfur content supports the removal theory but a conversion to another sulfur form cannot be ruled out.

The use of mild pyrolysis to characterize organic sulfur species in a material relies on the thermal breakdown of that material is such a way as that the sulfur species are released as volatile units that are structurally unchanged. If structural changes accompany thermal breakdown and volatilization then these changes must occur in a known way for the information to be structurally meaningful.

To investigate possible transformations between sulfur forms as a result of mild pyrolysis two model sample mixtures were examined using the mild pyrolysis technique. These were a 1:1 mixture of polyethylene and pyrite and a 1:1 mixture of polyethylene and iron sulfate. Since polyethylene does not have any sulfur and since pyrite and iron sulfate are both involatile in the py-GCMS system, any organic sulfur species identified in the pyrolysis products must be a product of an interaction between the pyrolysing polyethylene and the inorganic sulfur species. The py-GC-FPD chromatograms are shown in Figures 1 and 2.

It is clear that organic sulfur species are formed via an interaction between the pyrolysing polyethylene and both the pyrite and the iron sulfate. The most prominant peaks in the FPD chromatogram are sulfur containing gases such as H_2S, but thiophene and C1 thiophene are present in both samples. In addition C2 and C3 thiophenes can be detected in the pyrolysis products from the polyethylene/pyrite mixture. From the intensity of the thiophene peaks it appears that it is easier to form the thiophenes from the pyrite containing mixture than from the sulfate containing mixture.

Although these test mixtures are exceptionally high in sulfur content compared to the coals and gasification chars, it is possible, if not likely, that the same reactions could take place between the organic coal molecules and any pyrite or iron sulfate that the coal contains. Since gasification reactions usually employ temperatures similar to those used in mild pyrolysis it is possible that the mild pyrolysis technique could be used to explore transformation between sulfur species that takes place during gasification.

Based on these observation it is clear that for mild pyrolysis data to be used for the characterization of organic sulfur species it is important that both pyrite and iron sulfate have a low concentration in the samples being analyzed. This of course does not eliminate the possibility that transformations between organic sulfur species may occur.

Sulfur K-edge XANES Results

The sulfur K-edge XANES results for the ten sample submitted during the first quarter were reported in the second quarterly report. The second series of sixteen samples has been examined at Brookhaven and the XANES spectra obtained. The data is currently undergoing processing and a full data set will be available for the next report. A summary of the XANES data processed so far is given below.

Raw coals

The four original coals showed some oxidation of the sulfur forms. In the worst case, IBC-102 coal, the analysis shows that 52% of sulfur is in the sulfate form and that substantial sulfur (8%) is present as elemental sulfur, generated as a product of pyrite oxidation. A new set of pristine raw coals was examined and the levels of oxidation were found to be much reduced.

Chemically treated coals

1. Demineralized, floated and solvent extracted coals. This mild treatment to remove mineral matter and the mobile phase from coal does not have much impact on the distribution of various sulfur forms in coals. The IBC-101 floated and extracted coal shows some oxidation during this treatment as the concentration of the oxidized forms (sulfoxide and sulfate) have increased and the sulfide and thiophene concentrations have decreased. As expected, the XANES peak due to pyrite is eliminated by this treatment.

2. Desulfurized coal. The desulfurization treatment (mild oxidation followed by alcohol/base treatment at 350°C) apparently removes all sulfide forms of sulfur from coal. The concentration of the oxidized forms of sulfur do not appear to have increased significantly during this process. Since the sulfur content of this particular sample is only 0.77% some of the thiophene types of sulfur must also have been removed since the original sulfur content assigned to thiophenes for this coal is approximately 1.7-2.0%.

3. Peroxyacetic acid oxidation. Examination of the XANES data indicated that sulfide forms of sulfur are converted to their sulfones by peroxyacetic acid. This is supported by the oxidation of sulfide model compounds to their sulfones under similar conditions. The thiophenic sulfur forms however appear to be unchanged by the oxidation. This is surprising because previous mild degradation and analytical pyrolysis results suggest that simple thiophenes are oxidized by this treatment. It is expected that the discrepancy is due to the differences in the sensitivity of the different analytical methods to minor changes in sulfur form distributions, and from the fact that the sample that was analyzed by XANES received only a very mild oxidative treatment. It is anticipated that stronger oxidation conditions will reveal changes in the thiophene content as determined by XANES analysis. Samples that received a more severe oxidative treatment have been examined by the XANES technique and the data is currently being evaluated.

4. Steam treatment at 450°C. This treatment converts pyrite to pyrrhotite. Since the pyrrhotite peak is better isolated from the sulfide and thiophene peaks than the pyrite peak (at -0.5 e), it is easier to deconvolute it from the sulfur XANES spectra. Thus, although both pyrite and pyrrhotite have similar calibration constants, the pyrrhotite percentages are usually more accurate than the pyrite percentages in XANES analysis. The steam treatment does not appear to induce any additional oxidation of the sample.

^{57}Fe Mössbauer Spectroscopy

As mentioned earlier, because of lower calibration constants, XANES analysis has poorer sensitivity for pyrite and pyrrhotite forms than other forms of sulfur. Fortunately, Mössbauer spectroscopy is an excellent technique for identifying and quantifying these forms of iron in coal. Room temperature Mössbauer spectroscopy on all of the raw coal samples have been carried out to further quantify these forms.

Mössbauer spectroscopy confirms the XANES data in that oxidation of the original four coals is observed. Jarsonite and szomolnokite are iron sulfate forms produced as a product of pyrite oxidation. They compromise the sulfate peaks in the sulfur K-edge XANES spectra of these coals.

W-Band EPR Spectroscopy.

As mentioned earlier all samples have also been submitted to Professor R. Clarkson at The University of Illinois at Champaign-Urbana for W-Band EPR spectroscopy. Each sample is placed in a 0.3mm ID quartz sample tube and the interaction of the unpaired electron spins with the local environment (including the heteroatomic species) observed using a very high field strength magnet (95 GHz, 3.4T). This very high frequency spectrometer is essential for the potential resolution of the interaction of different heteroatom environments with the unpaired electrons. The complex line shapes that are obtained for typical Illinois coals are the result of contributions from several molecular populations including those which contain sulfur. The current mode of data reduction and analysis is to use computer programs to simulate real coal spectra by manipulating various spectral parameters such as g-values, linewidths, and composition coefficients. In addition, the examination of model compounds that contain heteroatoms such as sulfur and oxygen, using the W-band EPR spectrometer has prepared the foundation for the interpretation of coal EPR spectra in terms of heteroatom distribution.

CONCLUSIONS AND RECOMMENDATIONS

Steam gasification chars have been prepared from each freshly ground coal together with samples of floated and extracted coal derived from the IBC 101 and IBC-106 coals. A further six samples were prepared from the IBC-101 coal using peroxyacetic acid oxidation. Both the solubilized and residual component from each oxidation reaction was retained for analysis.

Aliquots of these samples were delivered to Dr. G.P. Huffman at the Consortium for Fossil Fuel Liquefaction Science, University of Kentucky, for sulfur K-edge XANES and to Dr. R. Clarkson, University of Illinois, for W-Band EPR analysis. In addition, aliquots of these same samples are currently under investigation in laboratories at SIUC using the analytical pyrolysis and selective oxidation techniques.

All mild gasification chars (steam gasification at 550°C) show reductions in their sulfur contents when compared to their parent coal. As might be expected the gasification chars derived from the floated coals have much lower sulfur contents than the chars derived from the original coals.

It is clear that organic sulfur species can be formed via an interaction between pyrolysing polyethylene and both the pyrite and the iron sulfate. Based on this observation it is clear that for the mild pyrolysis data to be used for the characterization of organic sulfur species it is important that both pyrite and iron sulfate contents of the samples being analyzed should be as low as possible.

In addition, it is clear that the sulfur chemistry of gasification chars is significantly different from that of the original coals. This can be seen from a comparison of the analytical pyrolysis chromatograms of the IBC coals and their gasification chars and from the preliminary XANES results. Using the analytical pyrolysis technique, it is clear that the gasification char does not yield the alkyl and benzothiophenes that are abundant before gasification.

Examination of IBC-101 samples that were oxidized with peroxyacetic acid using the analytical pyrolysis technique shows that the level of simple thiophene structures observed in the pyrolysis products declines with increasing levels of oxidation. This observation would support our earlier findings which suggested that peroxyacetic acid was oxidizing simple thiophenes to methyl sulfonic acid.

XANES spectra of the treated samples showed various effects depending on the treatment severity. For the less severely treated samples (demineralization and solvent extraction), the XANES spectra were similar, although not identical, to the untreated coal spectra, whereas the more severe treatments (steam at 450°C; peroxyacetic acid) showed preferential oxidation of one or more sulfur-bearing phases in the original coal. For example, the peroxyacetic acid treatment oxidized organic sulfides to sulfones, without significantly affecting the thiophenic sulfur, whereas the preliminary steam treatment (450°C) appeared to largely alter the pyrite to pyrrhotite, along with some reduction of organic sulfide as well.

The next phase of this project is to compare and contrast the analytical data collected via the different analytical techniques used in this study so that an evaluation of the different sulfur characterization techniques can be made.

It should be noted that this study has received some attention from Professor Yperman's group at Limburgs Universitair Centrum in Belgium. Professor Yperman is attempting to characterized sulfur functionalities in coals using the Atmospheric Pressure Temperature Programmed Reduction (AP-TPR). He is willing to examine the same set of samples used in this study. It is anticipated that this collaboration will provide additional sulfur functionality information on which to evaluate the characterization techniques.

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3. Chugh, Y.P and Caudle, R.D. 1987, Processing of High Sulfur Coal II. Elsevier, NY.

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Figure 1. Py-GC-FPD chromatogram of a polyethylene/pyrite 1:1 mixture.

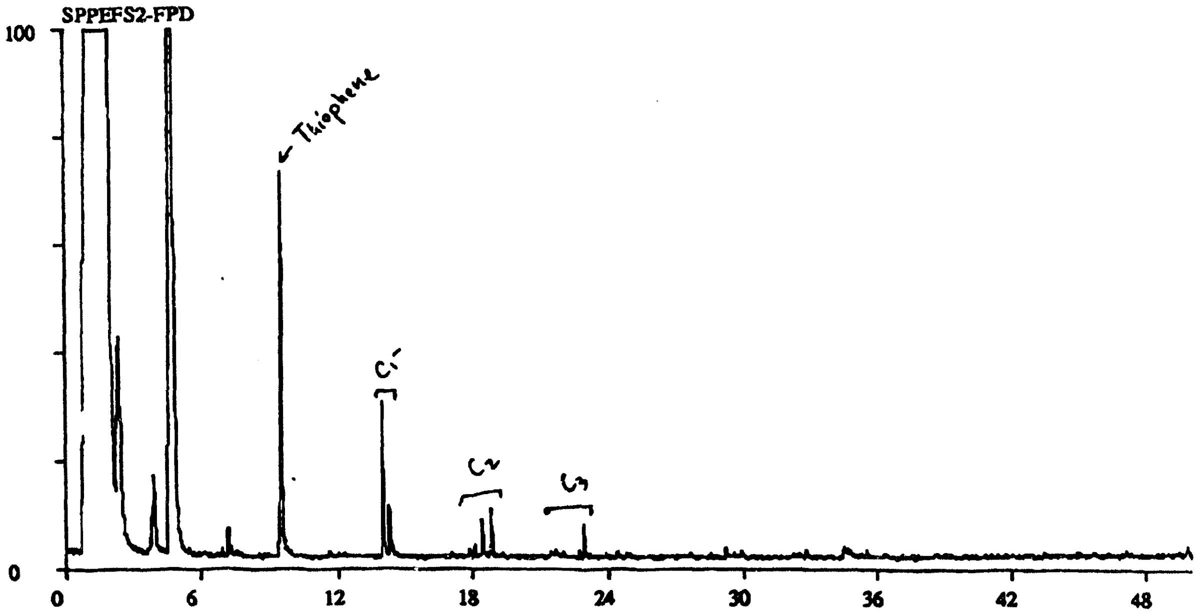
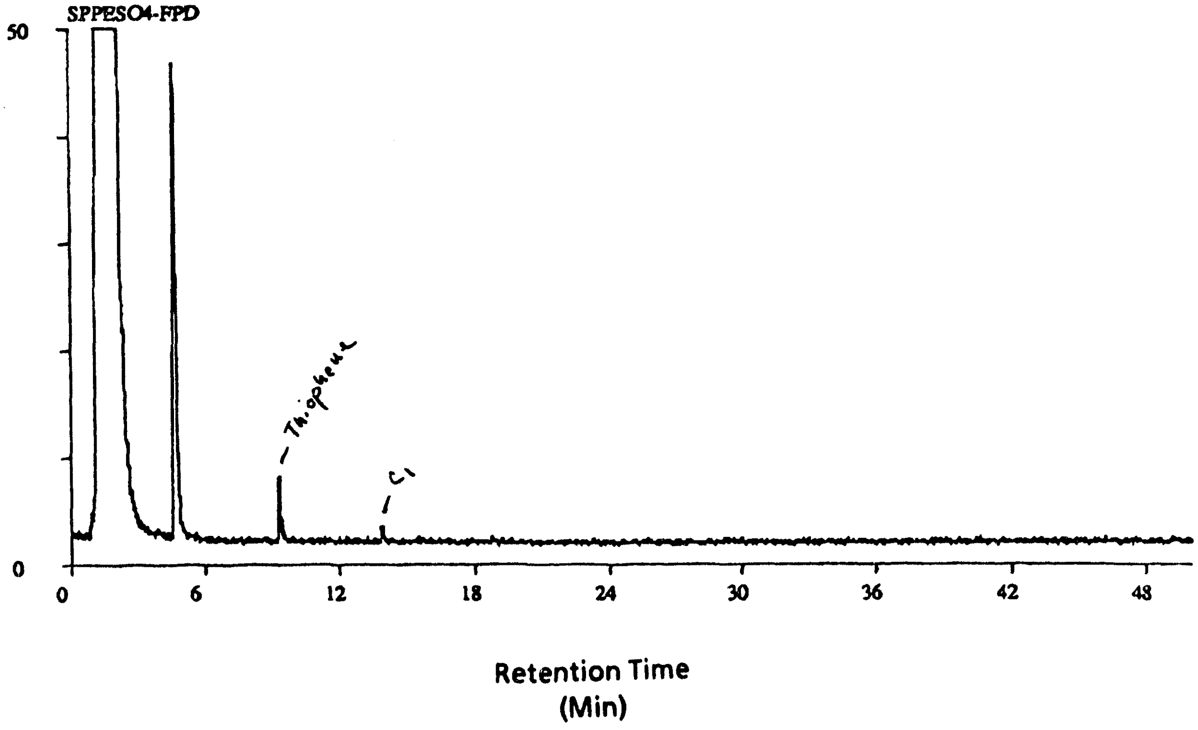


Figure 2. Py-GC-FPD chromatogram of a polyethylene/iron sulfate 1:1 mixture.



PROJECT MANAGEMENT REPORT
March 1, 1994 through May 31, 1994

Project Title: **Analyzing Organic Sulfur in Coal/Char: Integrated Mild Degradation/Xanes Methods**

DOE Grant Number:	DE-FC22-92PC92521 (Year 2)
ICCI Project Number:	93-1/6.1A-1P
Principal Investigator:	Stephen Palmer Department of Geology Southern Illinois University at Carbondale
Project Manager:	Ken Ho, Illinois Clean Coal Institute

COMMENTS

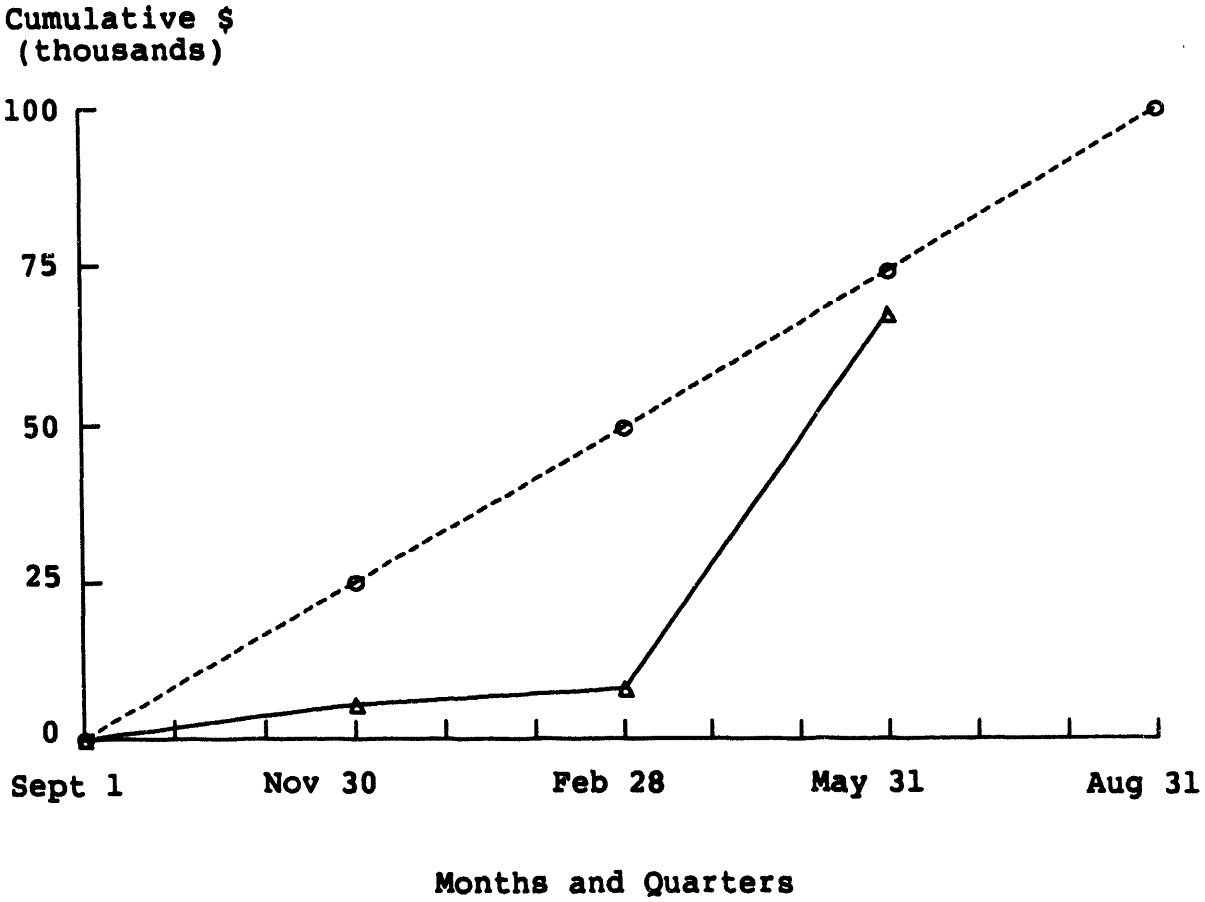
Projected and Estimated Expenditures by Quarter

Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials & Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1993 to Nov. 30, 1993	Projected	6,151	1,710	1,500	0	0	13,122	2,248	24,731
	Estimated	2,550	0	426	0	0	2,045	502	5,523
Sept. 1, 1993 to Feb. 28, 1994	Projected	12,302	3,421	3,000	0	0	26,244	4,497	49,464
	Estimated	2,772	0	1,475	0	0	3,102	735	8,084
Sept. 1, 1993 to May 31, 1994	Projected	18,545	5,132	4,500	0	0	39,366	6,754	74,297
	Estimated	9,150	1,094	2,793	538	0	47,997	6,157	67,729
Sept. 1, 1993 to Aug. 31, 1994	Projected	24,606	6,842	6,000	1,000	0	52,489	9,094	100,031
	Estimated								

*Cumulative by Quarter

COSTS BY QUARTER

Analyzing Organic Sulfur in Coal/Char: Integrated Mild Degradation/Xanes Methods

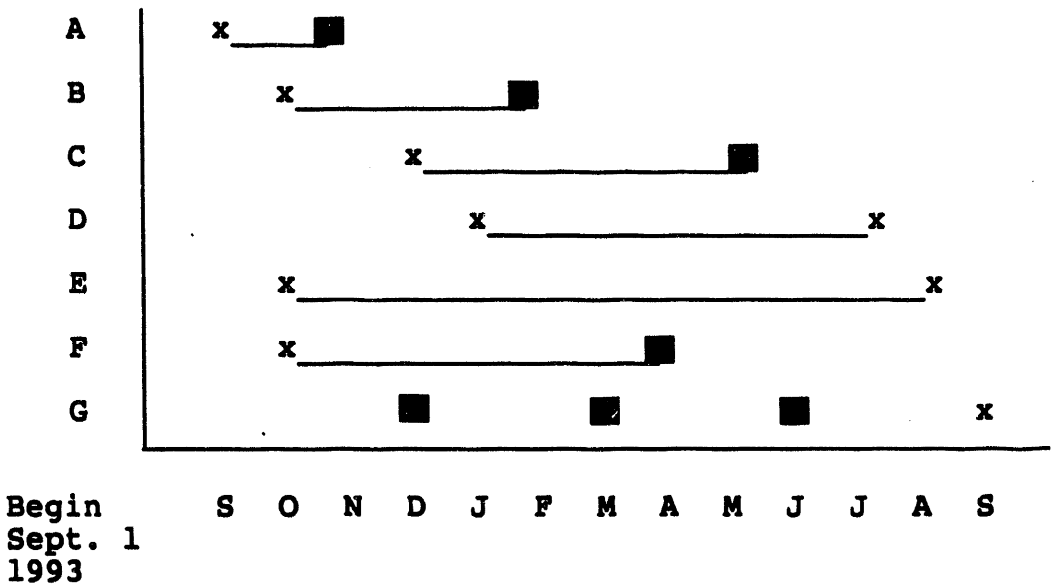


O = Projected Expenditures ---------

Δ = Estimated Actual Expenditures ________

Total Illinois Clean Coal Institute Award $100,031

SCHEDULE OF PROJECT MILESTONES



Milestones:

A. Task 1. Sample preparation.
B. Task 2. Analytical pyrolysis.
C. Task 3. Coal/char oxidation with sodium dichromate.
D. Task 4. Coal/char oxidation with peroxyacetic acid.
E. Task 5. Sulfur XANES analysis.
F. Task 6. ASTM methods of coal analysis.
G. Task 7. Reporting.

DATE
FILMED
10/17/94

END