DOE/PC/92521--T217

RECEIVED
MAY 15 1995
OSTI

FINAL TECHNICAL REPORT
September 1, 1993 through November 30, 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 R. Palmer, SIUC
Other Investigator:	Gerald P. Huffman, University of Kentucky
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 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. The XANES spectra of less severely treated samples were similar, although not identical, to the untreated coal spectra. XANES of gasification chars indicated conversion of pyrite to pyrrhotite, removal of organic sulfide sulfur and dissolution of soluble inorganic sulfur species during gasification. Mild oxidation with peroxyacetic acid results in preferential oxidation of sulfide forms before thiophene forms but increasing oxidation severity leads to virtually all sulfur species being oxidized. Good agreement between W-band EPR and XANES data for aromatic sulfur contents were obtained. The temperature programmed reduction analysis of coal indicated that organic sulphur was present as alkyl-aryl sulfide, aryl-aryl sulfides, simple thiophenes and condensed thiophenes. TPR shows that non-thiophenic compounds are removed by PAA oxidation, and that the longer the oxidation is performed the greater is the removal of non-thiophenic sulfur structures. This agrees very well with the XANES analysis of the oxidized samples.

RECEIVED
USDOE/PETC
95 MAY 12 AM 11:06
ACQUISITION & ASSISTANCE DIV.

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

EXECUTIVE SUMMARY

The overall objective of this study was to combine advanced non-destructive and advanced destructive methods of sulfur analysis so as to provide detailed characterization of the organic sulfur in coal. To achieve this overall objective a number of specific objectives were 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 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.

Initial XANES and Mossbauer analyses 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.

Gasification chars were prepared from 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. A further eight samples were prepared using peroxyacetic acid oxidation. An oxidized IBC-101 and IBC-106 were prepared at room temperature for 6 hours while six other samples of IBC-101 were obtained at the boiling point of the oxidative

mixture. The boiling point samples were obtained at three different time intervals. Both the solubilized and residual component from each oxidation reaction was retained for analysis. Some samples were also prepared using alternative oxidants.

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 can be formed via an interaction between pyrolysing polyethylene and both pyrite and 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. This, together with the fact that very little pyrolyzate in generated from a gasification char by analytical pyrolysis, indicates that this sulfur characterization technique may not be best suited for the analysis of gasification chars.

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. The more severe treatments showed preferential attack of one or more sulfur-bearing phases in the original coal. For example, XANES analysis of the steam gasification chars indicate the following possible reactions: conversion of pyrite to pyrrhotite, extraction of organic sulfide sulfur into the gas phase, and dissolution and removal of soluble inorganic sulfur forms.

The room temperature peroxyacetic acid treatment oxidized organic sulfides to sulfones, without significantly affecting the thiophenic sulfur. When stronger oxidation conditions were used virtually all of the sulfur forms were converted to oxidized forms. The spectra of these highly oxidized samples can be fitted with three distinct components, sulfones, sulfonates, and sulfate, respectively. The preponderance of sulfate and sulfonate forms in the soluble fractions is consistent with the anticipated aqueous solubilities of oxidized sulfur forms: sulfonate > sulfate >> sulfone. The peak positions for the residual non-oxidized aromatic components in these fractions are significantly higher than those noted for thiophene components in coal spectra. It would appear that this non-oxidized residue is either non-thiophenic (thianthrene type structures would be a possibility) or that the thiophene, although not directly oxidized, has a highly oxidized functional group, such as carbonyl or carboxyl, at the alpha position. Both of these possibilities have been documented to result in peak positions that are higher than those observed for typical simple thiophenes.

Analysis of samples oxidized with potassium permanganate, sodium dichromate, nitric acid and hydrogen peroxide was also performed. With each of these oxidants the XANES spectra were strikingly similar to that of the original coal. Major peaks were attributed to aliphatic sulfides and thiophenes, while minor peaks were attributed to pyrite, elemental sulfur and oxidized sulfur forms. These spectra were slightly broader than those of the untreated coal which made it difficult to fit a pyrite peak to these spectra. This may indicate that there was no pyrite in these samples but this is ambiguous at this time. It is interesting to note that none of these oxidants were capable of significantly oxidizing the sulfur in this coal. Under identical conditions PAA oxidized virtually all of the non-thiophenic organic sulfur.

All samples were submitted to Professor R. Clarkson at The University of Illinois at Champaign-Urbana for W-Band EPR spectroscopy. 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, line-widths, and composition coefficients. This analysis method has been tested on coal blends of known sulfur content as well as on a variety of coals from the IBCSP and elsewhere. The precision of the method is conservatively ± 0.1% of the aromatic sulfur in the sample. Identical samples measured both by EMR and XANES gave nearly identical results.

As the result of the extension of this project by 3 months a collaborative arrangement with Professor Yperman's group at Limburgs Universitair Centrum in Belgium was established. This arrangement is still ongoing. Professor Yperman's group uses atmospheric pressure temperature programmed reduction (AP-TPR) to determine sulfur functionality. A number of samples have been examined in the extension period. Sulfur recoveries using the TPR set-up were found to be 76% for a raw IBC-106 sample, 50% for a IBC-106 sample oxidized for 6 hours and 35% for a IBC-106 sample oxidized for 24 hours. This unaccounted for sulfur is believed to be the difficult to reduce condensed thiophene structures. Thus these results suggest that the absolute amount of condensed thiophene structures increases as the IBC-106 coal is oxidized.

By comparing the TPR profile for the raw coal with those obtained for the two oxidized samples it can be determined that pyrite has been removed by the oxidative process. In addition, it appears that non-thiophenic compounds are removed by the oxidation, and that the longer the oxidation is performed the greater is the removal of non-thiophenic sulfur structures. This agrees very well with the XANES analysis of the oxidized samples which shows non-thiophenic sulfur forms oxidizing before the thiophenic sulfur forms. It appears that the condensed thiophenic compounds are not affected by the oxidative treatment. At this time the H_2S evolution profiles for the samples gives qualitative information about the sulfur forms present, but further work is needed to fully develop the quantitative aspects of this approach.

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 from them.

Specific Objectives

The specific goals and objectives of this study were:

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 were to be obtained from the Illinois Basin Coal Sample Program. Aliquots of each were to be micronized, sink/floated and solvent extracted. Aliquots of these samples were then to be selectively oxidized, mildly gasified and chemically desulfurized.

In addition, a mild gasification reactor was to be designed and constructed and used for the preparation of mild gasification chars. The object of task 1 was 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 was analytical pyrolysis. Both pyrolysis-gas chromatography /flame photometric detector (py-GC-FPD) and pyrolysis-gas chromatography mass spectroscopy (py-GCMS) were 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 were to be characterized by selective oxidation with sodium dichromate. Soluble oxidation products would be methylated and then analyzed for organic sulfur compounds using GC-FPD and GC-MS. Insoluble oxidation products would 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 were to be characterized by selective oxidation with peroxyacetic acid. Soluble oxidation products would be methylated and then analyzed for organic sulfur compounds using GC-FPD and GC-MS. Insoluble oxidation products would 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 were 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 would 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 characterization of organic sulfur.

It was anticipated that this characterization approach would 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 included coal micronization, coal demineralization, coal flotation and solvent extraction. Micronization was achieved using a nitrogen powered fluid energy mill and was 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 were required. The acid treatment was performed by dispersing 100grams of the micronized coal in a 500mL mixture of HF and HCl (3:1). After the mixture had been stirred for 3 hours the coal was recovered by filtration and the residual acid washed away with hot distilled water until the filtrate was neutral.

To remove minerals such as pyrite that are insoluble in the HF/HCl mixture the sink/float procedure was employed. This involved dispersing the acid treated coal in a cesium chloride solution of specific density 1.6g/mL. This coal slurry was then centrifuged so that the mineral sank and the organic coal floated. The mineral-free coal (approximately 1-1.5% ash) was 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 were used. The first was a relatively mild oxidation which results in little coal dissolution. This was 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.

Typical mild selective oxidation with peroxyacetic acid involved 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 was then stirred at room temperature for six hours. After this time the oxidation product was recovered at the filter largely as undissolved coal solids. This material was washed with distilled water and dried.

The procedure used for more extensive oxidation used the same quantities of coal and reagents but this time the reaction was carried out under reflux. Samples of both soluble and insoluble coal were taken at 15 minutes, 6 hours and 24 hours time intervals. The solubilized oxidation products were recovered by first removing any residual undissolved material by filtration. Any excess peroxides in the oxidation products solution were then destroyed by the addition of 10mg of platinum on carbon (1% wt Pt). The peroxide free solution was then rotary evaporated to recover the soluble coal products. Any GC-FPD and GCMS analysis performed on these oxidation products required that they were 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.

As part of this project a mild gasification unit incorporating a fluidized bed was designed and built. Using this apparatus six experiments were performed on 2 grams coal aliquots at a temperature of 550°C using a 10mL per minute flow of nitrogen gas. These gasification runs were for 1 hour with 0.2mL/min of water introduced into the nitrogen gas stream using a HPLC pump.

Coal Desulfurization

The method of coal desulfurization used incorporated 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 was recovered by vacuum filtration, washed with distilled water and finally dried at 110°C. The oxidized coal (2g) was then dispersed in a suspension of 0.2g NaOH in 5mL methanol. This mixture was 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 was then collected at the filter, washed with distilled water and finally dried.

XANES Analysis

The sulfur XANES spectra were 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 were 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 were used to separate the XANES region from the XAFS spectrum. A least-squares fitting program (EDGFIT) was 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 were then converted to wt% sulfur in the various forms.

Temperature Programmed Reduction (TPR) Procedure

During the TPR procedure a linear temperature ramp of 5°C/min was applied to a reactor containing the sample (between 50mg and 100mg coal or coal product). It is mixed with a reducing solvent mixture (phenanthrene; resorcinol; 9,10-dihydrophenanthrene; tetralin and pyragallol).

Any hydrogen sulfide released from the reactor was detected by measuring the concentration of sulphide ion at a constant and precise pH in an alkaline sulphide anti-oxidant buffer solution using a sulphur selective electrode. The cell potentials and reactor temperatures were recorded continuously and the data presented as plots of the rate of sulphur evolution versus temperature or as the integrated signal.

RESULTS AND DISCUSSION

Sample Preparation

Initial XANES and Mossbauer analyses indicated that some of the original coal samples had been exposed to air during handling and storage and had subsequently oxidized to some degree. This can be seen from the large sulfate peaks in the XANES and Mossbauer spectra of the micronized IBC-102 (Figure 1.) Indeed, analysis of these spectra revealed that approximately 50% of the sulfur in this coal was in the sulfate form and approximately 8% was present as elemental sulfur. Both are products of pyrite oxidation. 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.

Gasification chars were prepared from 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.

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.

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

A further eight samples were prepared using peroxyacetic acid oxidation. An oxidized IBC-101 and IBC-106 were prepared at room temperature for 6 hours while six other samples of IBC-101 were obtained at the boiling point of the oxidative mixture. The boiling point samples were obtained at three different time intervals. Both the solubilized and residual component from each oxidation reaction was retained for analysis. This allows 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
IBC-101 oxidn. res. 6 hrs at RT	SO1
IBC-106 oxidn. res. 6 hrs at RT	SO6
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

The available ultimate and proximate data for the samples prepared in the this project 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.

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)

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.

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

Many of the samples prepared in this project have been examined by analytical pyrolysis GCMS. From the total ion chromatogram (TIC) for each pyrolysate single ion chromatograms (SIC) can be constructed for ions that are representative of sulfur containing compounds. Specifically we have used the ions (m/e) 98, 112, 126 and 146. These are characteristic ions for C_1, C_2, C_3 and C_4 substituted thiophenes respectively. 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 can be seen from Figure 2 which shows the ion intensity for the selected ions decreasing sharply from that of the raw coal to those for the oxidized coal. This finding supports the observation that peroxyacetic acid oxidizes simple thiophene structures to methylsulfonic acid.

As we can see from Figure 3. the pyrolysis TIC's for gasification chars are extremely weak. This is not that surprising since one would have expected much of the volatile matter in the samples to have been removed from the sample during gasification. For this reason it would appear that the mild pyrolysis method of sulfur characterization is not suitable for the analysis of gasification chars. Presumably the substituted thiophene 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 Figure 4.

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 prominent peaks in the FPD chromatogram are sulfur containing gases such as H_2S, but thiophene and C_1 thiophene are present in both samples. In addition C_2 and C_3 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

A summary of the sulfur K-edge XANES results obtained to date are given below by sample category.

Raw coals

The four original coals showed some oxidation of the sulfur forms. (see Figure 1.) 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. However, even the new set of pristine coals showed some degree of oxidation. (The XANES spectra for these coals are shown in Figure 5 together with a typical curve fitting plot showing the distribution of sulfur forms for the IBC-101 coal.) Whereas the amounts of sulfate in the IBC-101, 106 and 109 coals are relatively minor, the amount present in the IBC-102 sample is much more significant. It would appear that either this sample is oxidized at the source, or it oxidizes extremely rapidly on exposure to air. In addition to sulfate sulfur, this sample also appears to contain a small amount of elemental sulfur. The peak envelope for IBC-102 in the region -2 to 4 eV is clearly different from those of the other Illinois Basin coals, but it is quite similar to those that have been reported previously for other Illinois Basin coals that contain significant amounts of elemental sulfur (6). For the coals that are relatively free of oxidation, there are significant differences in the organic sulfide/thiophene ratio. The IBC-101 coal has the highest value (0.60) for this ratio, while the IBC-109 coal has the lowest (0.35) and the IBC-106 coal is intermediate (0.47). As has been previously reported, the ratio of organic sulfide/thiophene derived from XANES spectra is to first order reflective of rank. These three coals are consistent with that trend.

Micronized, Demineralized, floated and extracted coals.

Figure 6a shows the distribution of sulfur forms for the IBC-106 coal before and after micronization. As can be seen from Figure 6a. micronization does not lead to any major changes in sulfur form distribution. There is some increase in sulfate and sulfoxide content together with a small reduction in pyrite, sulfide and thiophene contents. This indicates some oxidation takes place during micronization. Interestingly the increase in the sulfate content is greater than the reduction in the pyrite content. This suggests that some of the additional sulfate came from an organic source. It is not immediately clear how this would happen. Figure 6b. shows the sulfur forms distribution for the IBC-101 before and after floatation and solvent extraction. Once again some oxidation is indicated by the presence of sulfate and sulfoxide sulfur forms in the treated sample. As expected, the XANES peak due to pyrite is eliminated by this treatment. There is also a reduction in the organic sulfide and thiophene contents after treatment. This may be partly due to oxidation to sulfoxides but may also be due to removal during the solvent extraction procedure.

Gasification chars

The XANES spectra obtained for the gasification chars are shown in Figure 7 together with the curve resolved spectrum for the gasification char derived form the IBC-101 coal. The spectra resemble the coal spectra except for the prominent peaks at -2 eV which arise from pyrrhotite, a decomposition product of pyrite. Naturally this peak is absent in the spectra of the samples derived from the floated coals. 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. Very minor amounts of sulfate are present in some of the samples. The main peak in the gasification spectra appears to arise entirely from thiophene sulfur with an apparently negligible contribution from organic sulfides. Figures 8a and 8b show sulfur distributions before and after gasification for the IBC-101 and IBC-106 respectively. Both figures 8a and 8b show the same trends. Pyrrhotite is formed, the pyrite content is lowered and organic sulfides are completely removed (or converted into something else). It is interesting that the reductions in the pyrite sulfur contents do not equal the amount of pyrrhotite sulfur that is formed. This suggests that at least part of the pyrrhotite does not come from the decomposition of pyrite. However this discrepancy may be due to the relative difficulty in deconvoluting the pyrite peak versus the pyrrhotite peak from the XANES spectra. In addition, it should be noted that the large sulfate component present in the sulfur XANES spectrum of IBC-102 coal is not found in the spectrum of the char sample. Hence, the steam treatment also removes this component as well. As was determined in earlier XANES and Mossbauer studies, szomolnokite, a water soluble iron sulfate, constitutes much of the sulfate sulfur in IBC-102 coal. Hence, the removal of sulfate sulfur during steam treatment is not unexpected. The steam treatment does not appear to induce any additional oxidation of the sample.

Desulfurized coal

Figure 9 shows the sulfur distribution for the IBC-101 coal before and after desulfurization. It can be clearly seen that 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% most of the thiophene types of sulfur must also have been removed since the original sulfur content assigned to thiophenes for this coal is 2.2%. This can be observed from Figure 9.

Oxidized coals

Examination of the XANES data for the coals that received the mild peroxyacetic acid (PAA) oxidative treatment (6 hours at room temperature) 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. Under stronger oxidation conditions however most of the sulfur forms report as oxidized sulfur species. Indeed, only around 15% of the sulfur remains in an unoxidized form in the insoluble residues and only 8% in the soluble material. This is regardless of the length of oxidation (15 minutes, 6 hours or 24 hours). This result suggests that the soluble material is more oxidized than the insoluble material and that sulfur oxidation is virtually complete after the first 15 minutes of oxidation under these reflux conditions. The XANES spectra for the oxidized coals (reflux conditions) are shown in Figure 10. It is clear that they are significantly different from those of the raw coals and the gasification chars.

These spectra can be fitted with three distinct oxidized components as shown by the profiles of the spectra between 6 and 12 eV. The spectra of the soluble and insoluble fractions are characteristically different in two major ways: first, the peak areas of the three components for the insoluble fractions decrease with increasing energy (i.e. as the sulfur becomes more oxidized, there is less of it), whereas the peak areas for the soluble residues are significantly greater for the peaks at higher energy (more highly oxidized forms); and second, the positions for the peaks in the XANES spectra of the soluble fractions are 0.2 to 0.5 eV higher in energy than the corresponding peaks for the insoluble fractions. Based on previous work, in which the peak positions of various standard sulfur forms were determined, it would appear that the three peaks correspond to sulfone, sulfonate, and sulfate, respectively, although it should be noted that we have never determined a standard sulfate with a peak at an energy as high as 10.8 eV. The highest peak position we have observed is for potassium sulfate at 10.3 eV. The preponderance of sulfate and sulfonate forms in the soluble fractions is consistent with the anticipated aqueous solubilities of oxidized sulfur forms: sulfonate > sulfate >> sulfone. It should be noted that the positions of the peaks (at 1.8 - 2.0 eV) for the residual non-oxidized aromatic components in these oxidized fractions are also significantly higher (by 0.3 - 0.5 eV) than those noted for thiophene components in coal spectra. It would appear that this non-oxidized residue is either non-thiophenic (thianthrene type structures would be a possibility) or that the thiophene, although not directly oxidized, has a highly oxidized functional group, such as carbonyl or carboxyl, at the alpha position. Both of these possibilities have been documented to result in peak positions that are higher than those observed for typical simple thiophenes.

Analysis of samples oxidized with potassium permanganate, sodium dichromate, nitric acid and hydrogen peroxide was also performed. With each of these oxidants the XANES spectra were strikingly similar to that of the original coal. Majors peaks were attributed to aliphatic sulfides and thiophenes, while minor peaks were attributed to pyrite, elemental sulfur and oxidized sulfur forms. These spectra were slightly broader than those of the untreated coal which made it difficult to fit a pyrite peak to these spectra. This may indicate that there was no pyrite in these samples but this is ambiguous at this time. It is interesting to note that none of these oxidants were capable of significantly oxidizing the sulfur in this coal. Under identical conditions PAA oxidized virtually all of the non-thiophenic organic sulfur.

^{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 was 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

All samples were 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.

This new basic scientific knowledge in turn allowed us accurately to analyze the W-band EMR spectra from coal, desulfurized coal, and a variety of coal derived materials. We developed an automated computer program (based on spin quantum mechanics) which can analyze the EMR spectra and which reports the aromatic sulfur content of the coal as well as key spectral parameters. This analysis method has been tested on coal blends of known sulfur content as well as on a variety of coals from the IBCSP and elsewhere. The precision of the method is conservatively ± 0.1% of the aromatic sulfur in the sample. Identical samples measured both by EMR and XANES gave nearly identical results. The EMR technique has the twin advantages of simplicity and absolute concentration readout; an analysis takes less than five minutes to perform.

TPR Analysis

The TPR data obtained from a range of model compounds has enabled temperature ranges to be defined that correspond to the different sulphur functionalities thought to be present in coal and its derivatives. The TPR H_2S evolution profiles for the raw IBC-106 coal and two selectively oxidized IBC-106 samples (6hrs at room temperature and 24 hrs at room temperature) are shown in Figure 11. The recoveries of the sulfur amounts by the TPR set-up are 76% for the raw IBC-106 sample, 50% for the sample oxidized for 6 hours and 35% for the sample oxidized for 24 hours. In absolute sulfur concentration terms 0.9%, 1.1% and 1.3% weight percent sulfur remains unaccounted for in the raw, 6 hour oxidized and 24 hour oxidized samples respectively. This unaccounted for sulfur is believed to be the difficult to reduce condensed thiophene structures. Thus these results suggest that the absolute amount of condensed thiophene structures increases as the IBC-106 coal is oxidized.

The TPR profile for the raw IBC-106 coal (profile 1 in figure 11) has two major peaks and two major shoulders. The signal at 460°C can be attributed to alkyldisulfides and alkyl-aryl monosulfides while the peak at 595°C is attributed to di-aryl monosulfides and disulfides. The shoulder at 540°C is due to the reduction of pyrite while the shoulder at 730°C comes from the reduction of simple thiophenes. At this time it is difficult to provide the distribution of these sulfur forms since a satisfactory deconvolution program is not currently available for their resolution.

By comparing the TPR profile for the raw coal with those obtained for the two oxidized samples it can be determined that pyrite has been removed by the oxidative process (minimums at 540°C in the profiles for the oxidized samples). In addition, it appears that non-thiophenic compounds are removed by the oxidation, and that the longer the oxidation is performed to greater is the removal of non-thiophenic sulfur structures. This agrees very well with the XANES analysis of the oxidized samples which shows non-thiophenic sulfur forms oxidizing before the thiophenic sulfur forms. It appears that the condensed thiophenic compounds are not affected by the oxidative treatment. Indeed as mentioned earlier they appear to be formed during oxidation. This is somewhat unlikely since the oxidation are low temperature. At this time the reduction temperatures for various sulfones in the TPR system are unknown. It is possible that some of these structures may not be reduced and hence contribute to the condensed thiophene value. The examination of several sulfone model compounds is to be attempted.

CONCLUSIONS AND RECOMMENDATIONS

Steam gasification chars were prepared from IBC coals 101, 102, 106, and 109. Other samples were prepared using peroxyacetic acid under various oxidation conditions. Both the solubilized and residual component from each oxidation reaction was retained for analysis. A desulfurized coal and coals oxidized with other oxidants were also prepared.

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 pyrite and 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. This, together with the fact that very little pyrolyzate in generated from a gasification char by analytical pyrolysis, indicates that this sulfur characterization technique may not be suited for the analysis of gasification chars.

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. The more severe treatments showed preferential attack of one or more sulfur-bearing phases in the original coal. For example, XANES analysis of the steam gasification chars indicated the following possible reactions: conversion of pyrite to pyrrhotite, extraction of organic sulfide sulfur into the gas phase, and dissolution and removal of soluble inorganic sulfur forms. The room temperature peroxyacetic acid treatment oxidized organic sulfides to sulfones, without significantly affecting the thiophenic sulfur. When stronger oxidation conditions were used virtually all of the sulfur forms were converted to oxidized forms. Oxidants such as potassium permanganate, sodium dichromate, nitric acid and hydrogen peroxide were found to be less effective in oxidizing organic sulfur than peroxyacetic acid with the XANES spectra being strikingly similar to that of the original coal. Under identical conditions PAA oxidized virtually all of the non-thiophenic organic sulfur.

All samples were submitted to Professor R. Clarkson at The University of Illinois at Champaign-Urbana for W-Band EPR spectroscopy. An automated computer program which can analyze the EMR spectra and which reports the aromatic sulfur content of the coal was developed. The precision of the method is conservatively 0.1% of the aromatic sulfur in the sample. Identical samples measured both by EMR and XANES gave nearly identical results.

As the result of the extension of this project by 3 months a collaborative arrangement with Professor Yperman's group at Limburgs Universitair Centrum in Belgium was established. This arrangement is still ongoing. At this time the H_2S evolution profile for the samples gives qualitative information about the sulfur forms present, but further work is needed to fully develop the quantitative aspects of this approach. The TPR data shows that non-thiophenic compounds are removed by oxidation, and that the longer the oxidation is performed the greater is the removal of non-thiophenic sulfur structures. This agrees very well with the XANES analysis of the oxidized samples.

ACKNOWLEDGEMENTS

This work was prepared with the support, in part by grants made possible by the Illinois Department of Energy and Natural Resources through its Coal Development Board and Illinois Clean Coal Institute, and by the U.S. Department of Energy (Grant Number DE-FC22-92PC92521). However, any opinions, findings, conclusions, or recomendations expressed herein are those of the authors and do not necessarily reflect the views of IDENR, ICCI and the DOE.

REFERENCES

1. Record, F., Bebenick, D. and Kindya, R.J. 1982. Acid Rain Information Book; Noyes Data Corp., Park Ridge, NJ.

2. Aplan, F.F., 1977. In Coal Desulfurization. Chemical and Physical Methods. (Wheelock T.D (Ed)), ACS Symp. Ser. No.64, American Chemical Society, Washington DC, p70.

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

4. Orr, W.L. and White, C.M. (Eds). 1990, Geochemistry of sulfur in fossil Fuels. ACS Symp. Ser. No. 429, American Chemical Society, Washington DC.

5. Palmer, S.R., Hippo, E.J., Kruge, M.A. and Crelling J.C. 1992, "Characterization and selective removal of organic sulfur from Illinois Basin coals." Coal Preparation, 10, p93-106.

6. Huggins, F.E., et al., Fuel Proc. Tech., 1993, 35, 233-257

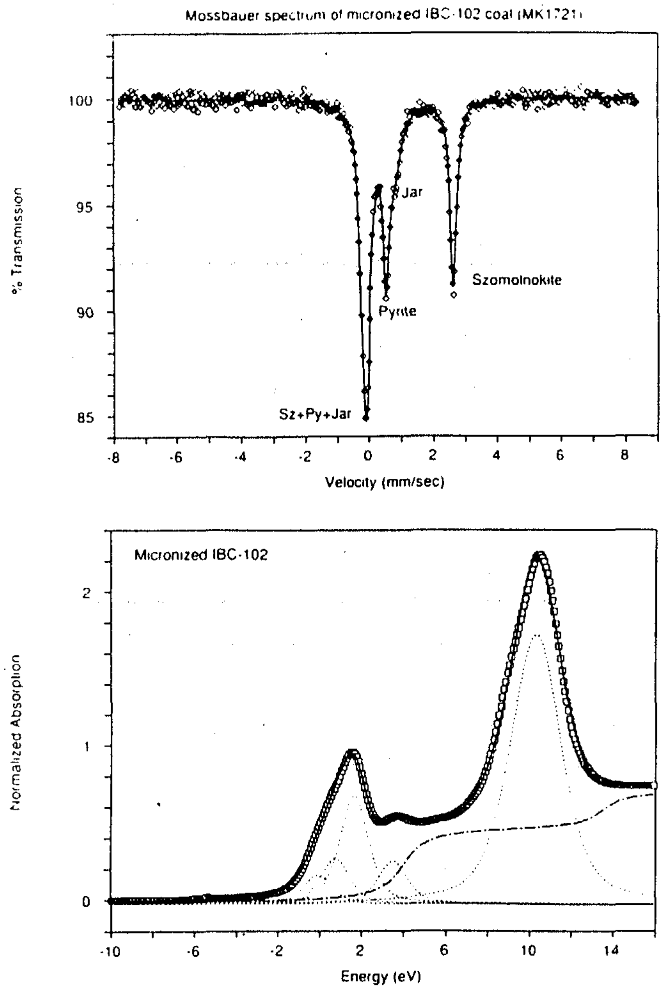


Figure 1. Mossbauer (TOP) and XANES (BOTTOM) spectra for micronized IBC-102

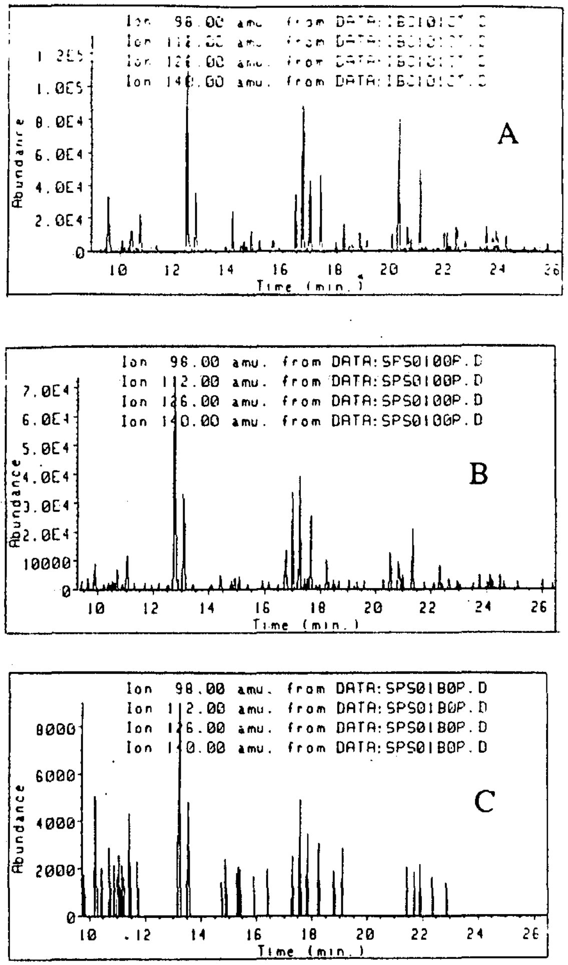


Figure 2. Single ion chromatograms for C1, C2, C3 and C4 substituted thiophenes derived from analytical pyrolysis of: A = IBC-101 coal, B = oxidized IBC-101 (room temp. 6 hrs) and, C = oxidized IBC-101 (104°C, 15 mins).

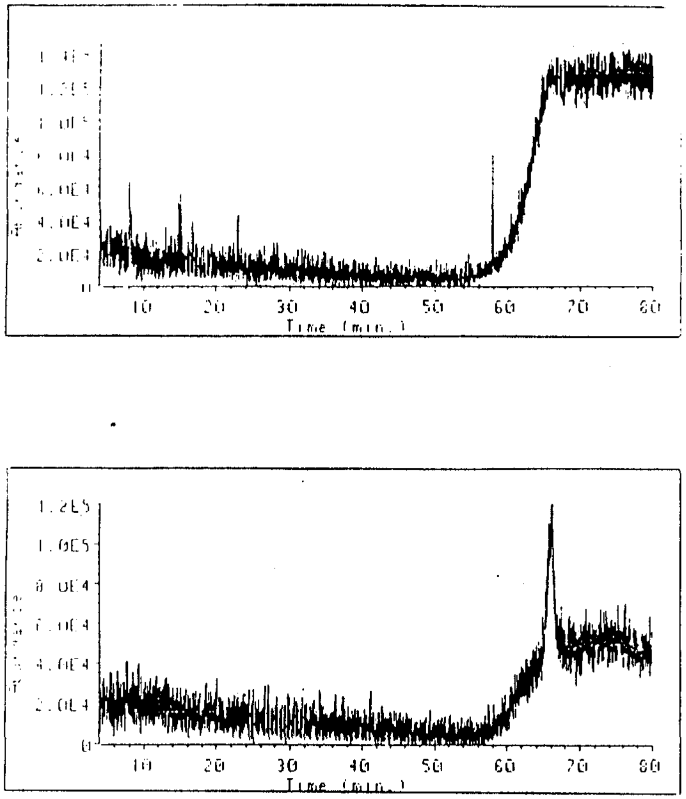


Figure 3. Py-GCMS TIC's of gasification chars. IBC-109 (TOP) and Floated IBC-101 (BOTTOM).

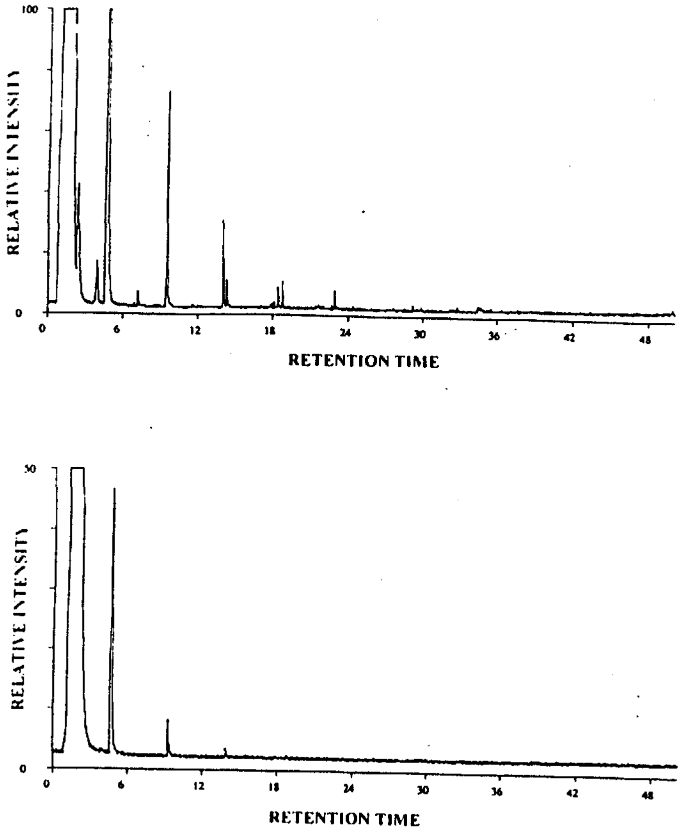


Figure 4. Py-GCMS TIC chromatograms of a polyethylene/pyrite 1:1 mixture (TOP) and a polyethylene/iron sulfate 1:1 mixture (BOTTOM).

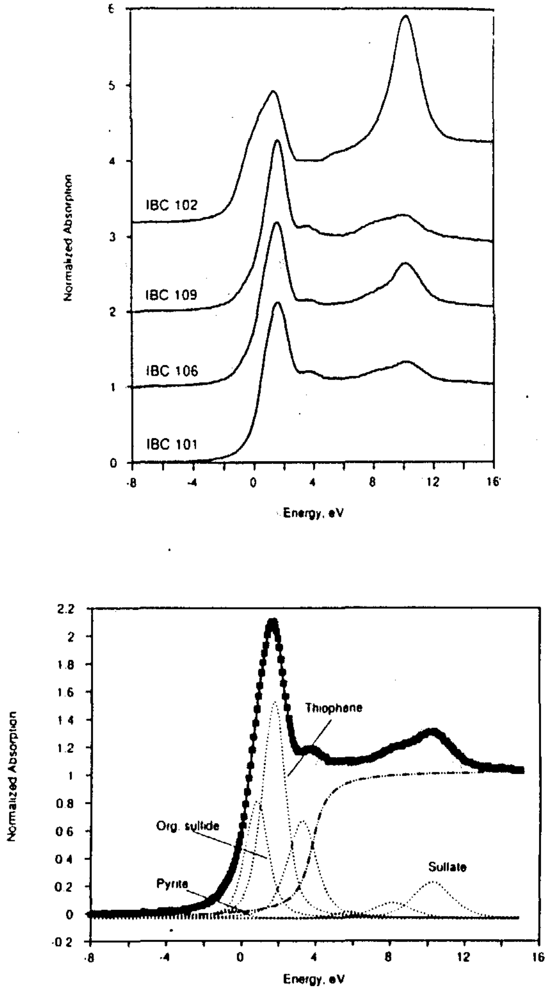


Figure 5. Sulfur XANES of four coals from the IBC Sample Program coal Bank (TOP) and, LSQ-fitted sulfur XANES spectrum of IBC-101 coal (BOTTOM).

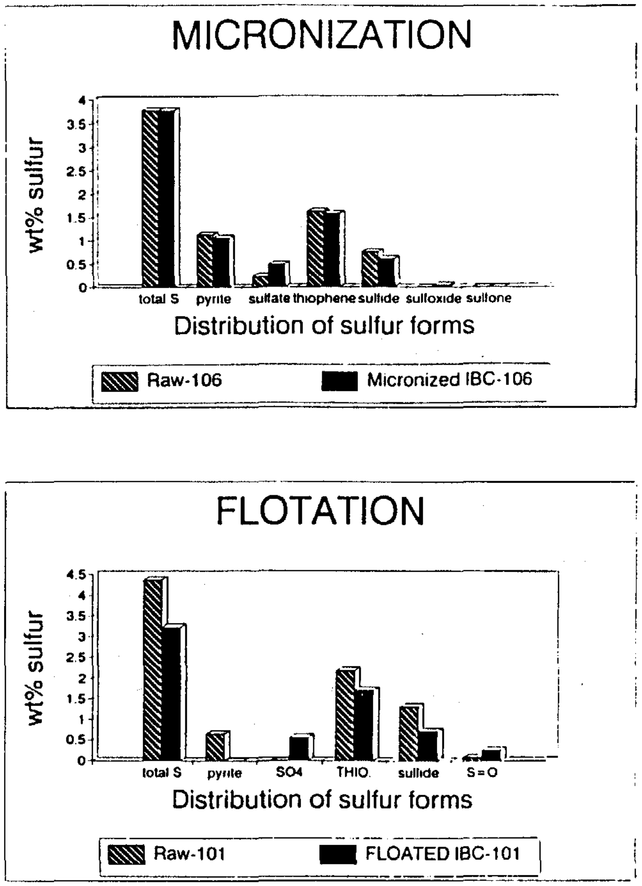


Figure 6. a) XANES sulfur distributions before and after micronization (IBC-106).
b) XANES sulfur distributions before and after floatation and extraction (IBC-101).

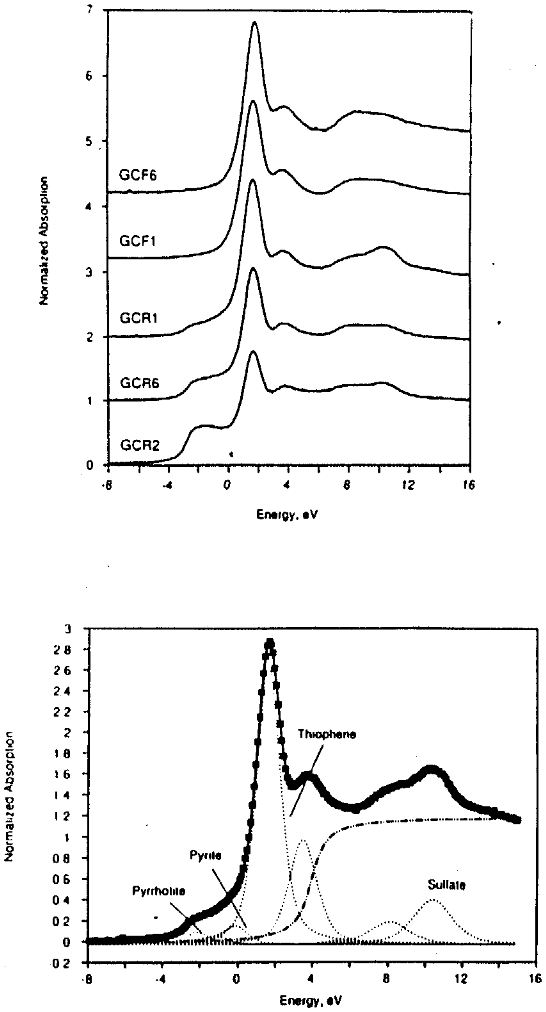


Figure 7. Sulfur XANES of gasification chars derived from the IBC coal samples (TOP) and, LSQ-fitted sulfur XANES spectrum of gasification char derived from IBC-101 coal (BOTTOM).

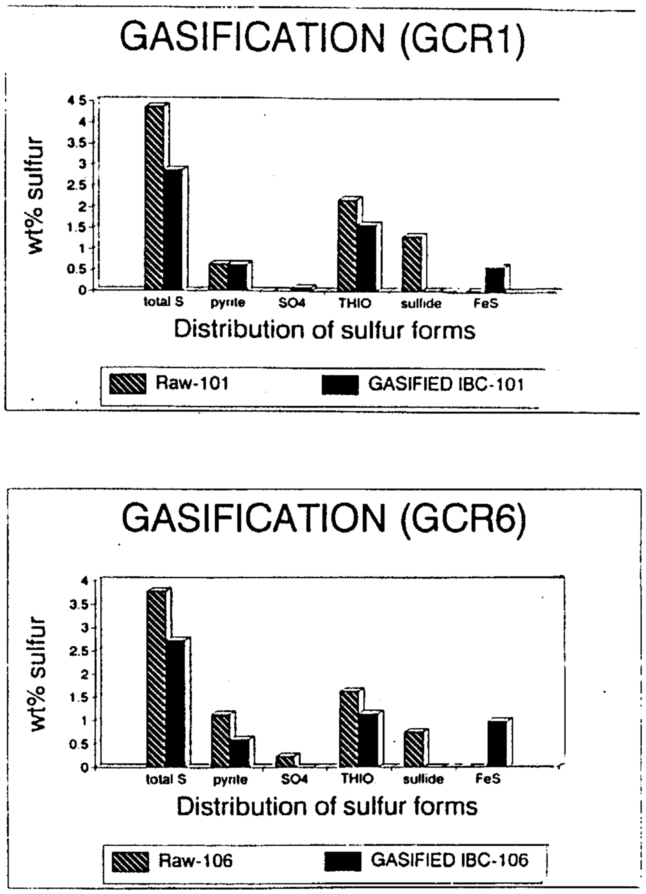


Figure 8. a) XANES sulfur distributions before and after steam gasification (IBC-101).
b) XANES sulfur distributions before and after steam gasification (IBC-106).

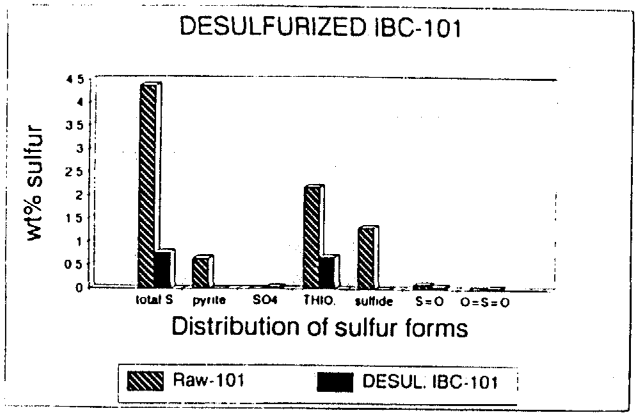


Figure 9. XANES sulfur distributions before and after desulfurization (IBC-101).

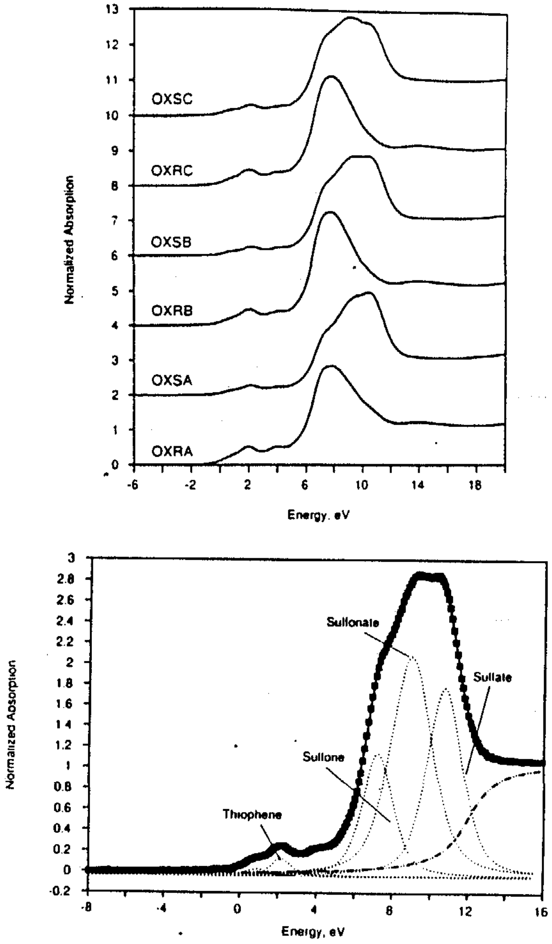


Figure 10. Sulfur XANES of oxidation products derived from the IBC-101 coal samples (TOP) and, LSQ-fitted sulfur XANES spectrum of oxidized residue derived from IBC-101 coal (BOTTOM).

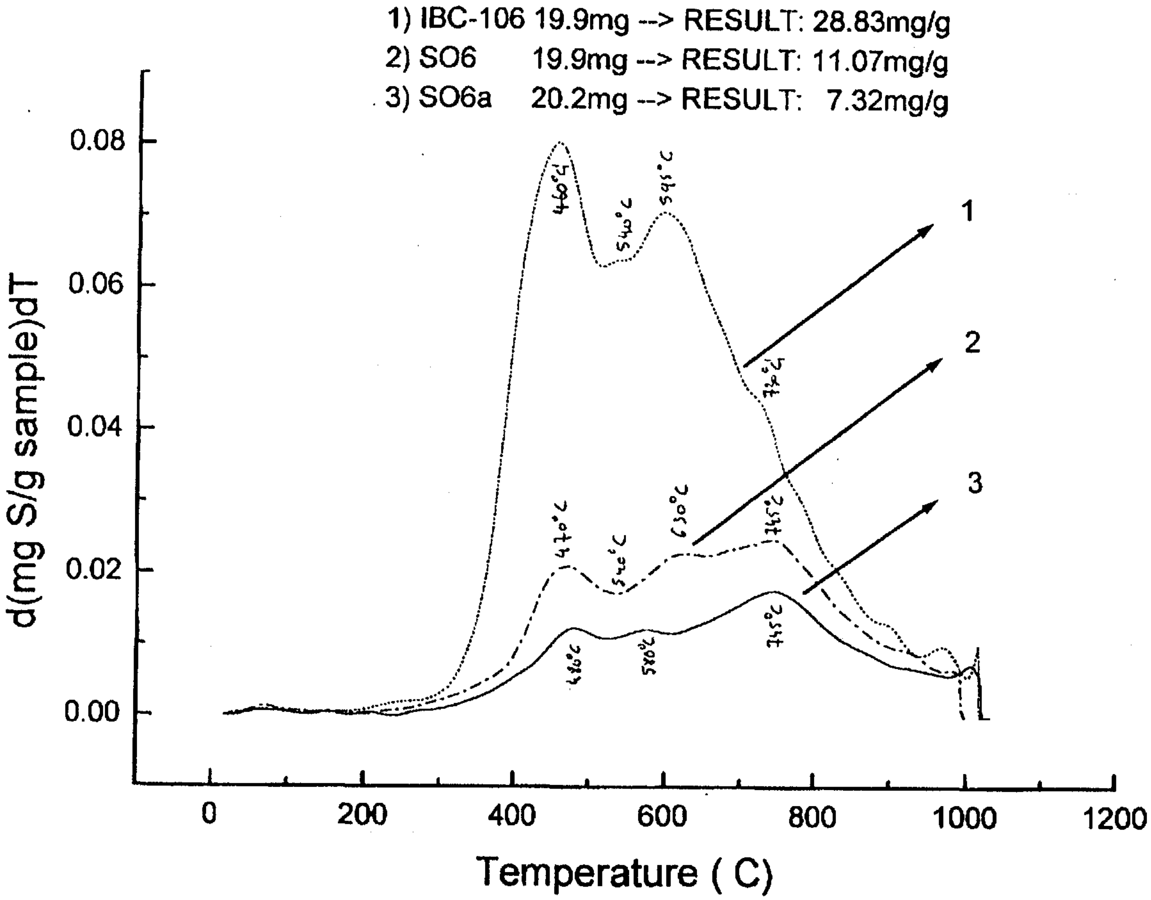


Figure 11. Temperature programmed reduction profiles for raw and PAA oxidized IBC-106

PROJECT MANAGEMENT REPORT
June 1, 1994 through November 30, 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 Mechanical Engineering and Energy Processes Southern Illinois University at Carbondale
Project Manager:	Ken Ho, Illinois Clean Coal Institute

COMMENTS

Due to a delay in the initiation of a journal contract between Southern Illinois University at Carbondale and the University of Kentucky, a project extension of three months (November 30th, 1994) was requested and subsequently approved. This extension has allowed further tests to be performed through an international collaborative effort at no extra cost to the ICCI.

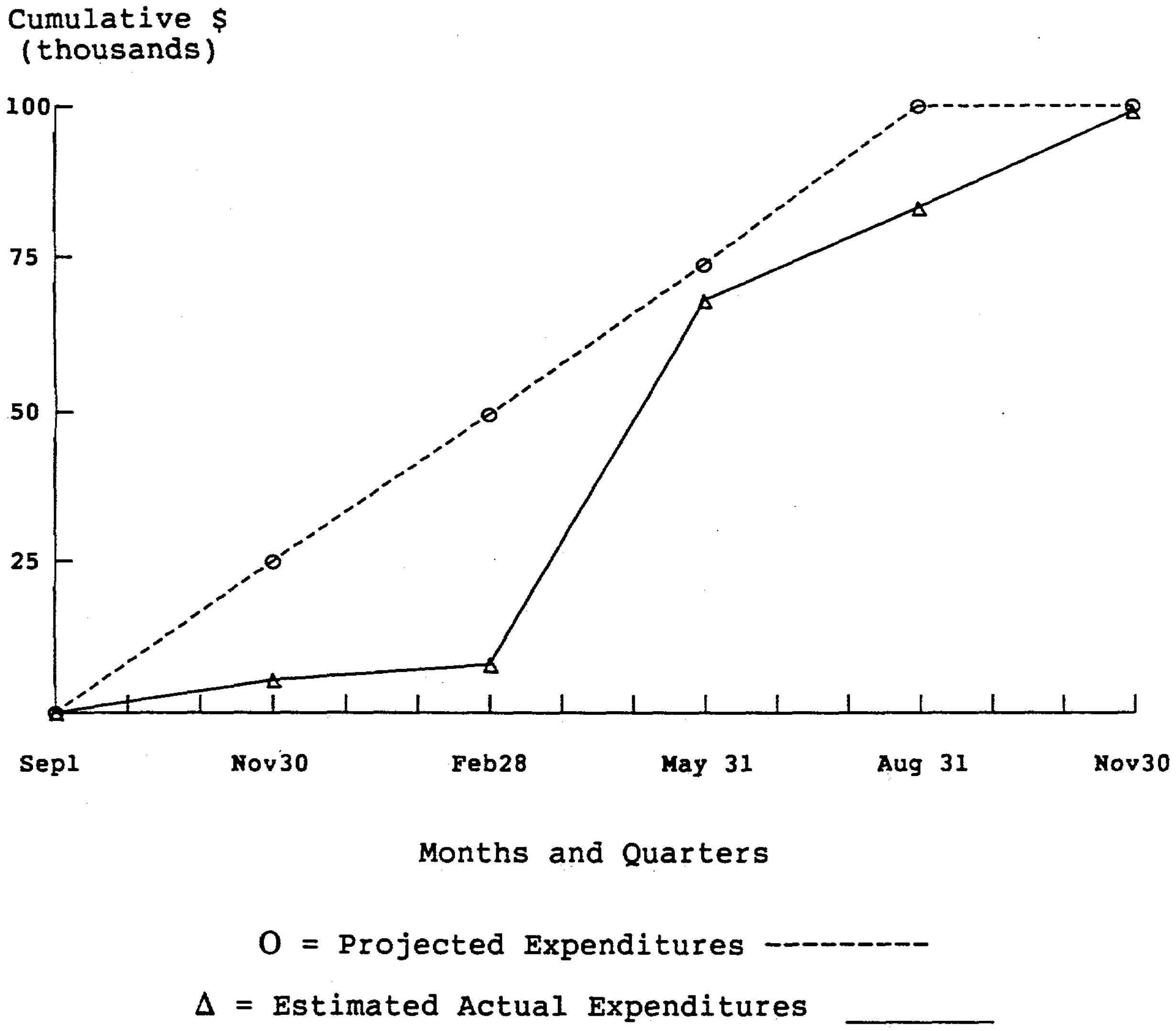
Projected and Estimated Expenditures by Quarter

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	18,717	2,944	4,376	795	0	48,451	7,528	82,811
Sept. 1, 1993 to Nov. 30, 1994	Projected	24,606	6,842	6,000	1,000	0	52,489	9,094	100,031
	Estimated	24,600	6,806	5,850	793	0	52,313	9,036	99,398

*Cumulative by Quarter

COSTS BY QUARTER

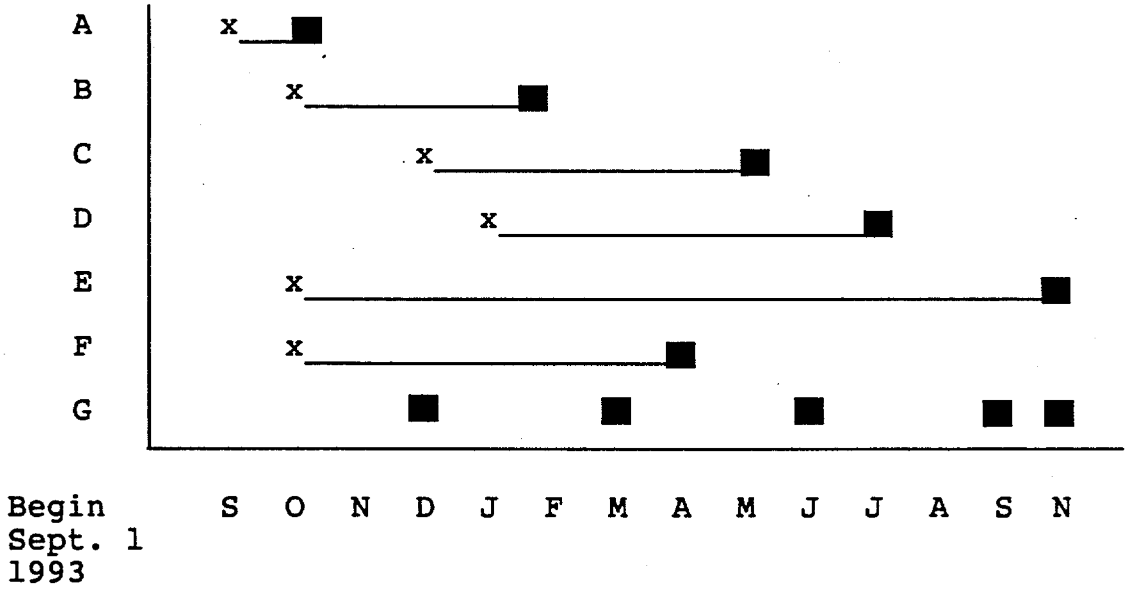
Analyzing Organic Sulfur in Coal/Char: Integrated Mild Degradation/Xanes Methods



Total Illinois Clean Coal Institute Award $100,031

*This graph represents five quarters extending from September 1, 1993 to November 30, 1994.

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 + AP-TPR analysis.
F. Task 6. ASTM methods of coal analysis.
G. Task 7. Reporting.