

THE CHEMISTRY OF SULFUR IN COAL—A HISTORICAL PERSPECTIVE

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Introduction

Coal represents 85–90% of the fossil energy resources in the United States, and a quarter of the world's coal resources (1). Yet the full utilization of these resources has been limited by the presence of high levels of sulfur in many of the major deposits. (Fig. 1) This has been a recognized problem for many years. In the early part of the century, high sulfur content made use of some coals unsuitable for making of coke for metallurgical purposes. In recent years, the high sulfur content of coal has been recognized as the source of air pollution problems (acid rain), particularly from electricity generation and in industrial boilers. The Clean Air Act Amendments of 1990 were enacted to mitigate these problems. Earlier legislation restricted allowable SO₂ emissions in new power plants. The 1990 act however requires phased in limitation of SO₂ emissions in all power plants of over 25 MW capacity beginning in 1995, and is projected to reduce annual SO₂ emissions by about 10 million tons by the year 2000. A wide variety of methods of limiting SO₂ in flue gas have been devised from wet and dry limestone scrubbers, hot scrubbers, fluidized bed combustors, limestone injection into burners or ducts and others. Many of these are being developed and tested on a commercial scale under the Clean Coal Initiative. Under the 1990 Clean Air Act utilization of high sulfur coal without scrubbers or other remedial measures will not be permitted, although credits for lower than permitted levels may be used to compensate for emissions over permitted levels. This legislation will be expensive in new investment and operating costs and consumers are going to feel it.

The Origin of Sulfur in Coal

Much of the sulfur in low sulfur coal derives from the sulfur content of the plant material making up the original peat. Sulfur contents greater than a few tenths of a percent have long been known to derive from the depositional environment. Sea water or brackish water in the coal beds contain sulfates. The sulfates undergo bacterial reduction to H₂S which reacts with iron in the water to form pyrite and with the organic material or the sulfate reducing bacteria to form the organic sulfur structures. The reactions involved are not understood, but isotopic sulfur ratios support this conclusion (2,3).

Sulfur in the Mineral Matter in Coal

It is well known that high sulfur coal usually contains both mineral sulfur which is largely pyrite, but can also include other metal sulfides and sulfates, and in some cases small amounts of elemental sulfur. It also contains sulfur in organic structures of a variety of types. (Table 1) There are well established methods for removal of much of the mineral sulfur compounds, based on density or wettability or other characteristics of the mineral.

Stock (4) and Buchanan (5,6,7) have shown that elemental sulfur is not present in pristine coal, but derives by oxidation of pyrite primarily. In any event, it is generally present in relatively small amounts even in oxidized coals.

The Organic Sulfur Structures in Coal

Removal of the organic sulfur is much more difficult than the pyritic sulfur, as it is part of the organic coal structure itself. Processes have been developed for removal of both organic and inorganic sulfur involving molten caustic at high temperatures (e.g., the TRW Gravimelt Process) or oxidizing agents such as air, or chlorine in the presence of strong alkali (e.g., the Ames, PETC and Ledgemont oxydesulfurization Processes). (8) None of these appear to be economically practical at the present time. All of them have been developed without any real knowledge of the chemistry of the organic sulfur they

are supposed to remove. In the Second Supplementary Volume of the "Chemistry of Coal Utilization" which came out in 1981 it says:

"Since there are few methods for determining the functionality of sulfur, especially in mixtures, and the few that are available either are ambiguous or give questionable results with coal, the nature and bonding of the organic sulfur in coal is still unknown."

Since that was written, much progress has been made by many researchers including our Storch Awardee and his coworkers. I am therefore going to devote the limited time I have to outline some of the scientific advances that have been made toward understanding the chemistry of the organic sulfur components, and the status of our knowledge of the organic sulfur structures in coal, as I perceive it today. This progress has been the result of development of a number of new analytical techniques that have become available and considerable research ingenuity by a number of coal scientists.

The organic sulfur in coal can vary from a few tenths of a percent to several percent. Usually, the pyritic sulfur content is similar to the organic sulfur content. In some rare coals however, the pyritic sulfur is very low and the organic sulfur very high. That is the case for two coals from Spain and Yugoslavia (see table 2) which have been the subject of considerable study by coal scientists because they allow the study of the organic sulfur with little interference from the pyrite (46,47,48). Similar coals exist from India and New Zealand.

It has been known for many years, that coal produces thiophenic compounds as tars upon coking, pyrolysis or in coal hydrogenation. That these heterocycles are actually part of the coal structure and not formed in the processing was demonstrated by Hayatsu (9,10) with sodium dichromate oxidation of a range of coal ranks from lignite to anthracite and converting the resulting acids to the methyl esters. Of some 141 aromatic structures obtained in this work were thiophene, benzothiophene, dibenzothiophene and a number of methyl substituted compounds of those same heterocycles. Since that time, Nishioka et al. (11, 12), Curt White (13,14), Sinnighe Damste and de Leeuw (15, 16) and a number of other workers have identified other heterocyclic structures either produced by solvent extraction, pyrolysis or coal hydrogenation. The development of Flame Photometric Detectors (FPDS) was important in some of this work. Winans and Neill (17) also found a number of multiple- heteroatom-containing sulfur compounds where there was oxygen or nitrogen or both in addition to the sulfur by flash pyrolysis of coal into a high resolution mass spectrometer (fig. 2). There can be little doubt that there are sulfur heteroatoms in the aromatic clusters of most high sulfur coals. But is that the only form of sulfur in the organic portion of coal?

When Pittsburgh 8 coal which contained about 1.5% organic sulfur was pyrolyzed by a pyroprobe into a high resolution mass spectrometer many sulfur containing products including low molecular weight compounds such as H_2S , CO , CH_3SH , SO_2 , and CS_2 as well as a whole range of heterocyclic structures from thiophene, benzothiophene, dibenzothiophene and many alkyl substituents of these heterocycles were detected. (18) When the same coal had over 90% of the mineral matter removed by a non-chemical process so as not to affect the organic structures present, a very similar set of pyrolysis products were produced with only the SO_2 and CS_2 largely eliminated. (Table 3) With the mineral sulfur compounds removed from the system, this suggests that the low molecular weight sulfur compounds are produced by breakdown of some relatively unstable organic sulfur structures in the coal, while the more stable heterocyclic sulfur structures pyrolyze into the mass spectrometer unchanged. What are these unstable sulfur structures?

Coal of course is a very heterogeneous material, consisting not only of mineral matter as I have already mentioned, but also quite distinct macerals, deriving from different components of the plant material which went into forming the coal. Raymond of Los Alamos (19,20) studied the organic sulfur content of the various macerals, without separation, from 8 different coals by electron probe microanalysis and showed that the sulfur content is not the same in the various macerals of a given coal. Wert et al. at the University of Illinois (21) made similar measurements on Illinois #5 coal by Transmission Electron Microscopy and showed that the sporinite contained twice as much sulfur as the vitrinite (Fig. 3). Purified

macerals prepared by Dyrkacz' (22) method for separating the various macerals from coal by Density Gradient Centrifugation have been shown by Dyrkacz and Wert (23) and Hippo and Crelling (24) to also have different organic sulfur contents in the various macerals of the same coal.

"Pure" macerals, we must remember still consist of mixtures of macromolecules having a rather random distribution of component molecules. In most cases these are cross-linked and insoluble and therefore intractable. Most researchers in the field therefore resort to trying to identify the various sulfur functional groups or substituents in coal without regard to the rest of the coal structure, since they are the components whose chemistry we want to identify and presumably remove.

In the late 1970s Attar and his coworkers (25,26,27) developed an interesting approach to determining the sulfur functional groups in coal by catalytic programmed temperature reduction to H₂S. He obtained "kinetograms" (fig. 4) which showed peaks of H₂S production at various temperatures which from model compound experiments he identified with the various sulfur functional groups which were present. This approach had the problem of requiring adequate contact of a solid catalyst with a solid coal, and recoveries of the sulfur were often low. However he did obtain discrete peaks which he associated with such functional groups as thiolic (mercaptan), thiophenolic, aliphatic sulfide, aryl sulfide, thiophenic and pyrite.

LaCount and coworkers (28,29) came up with a similar approach based on the programmed temperature oxidation of coal in which the sulfur components were oxidized to SO₂ which was detected by FTIR. SO₂ evolution peaks were obtained at various temperatures which were again related to specific sulfur functional groups by comparison with model polymeric sulfur compounds. Peaks were identified with pyrite, non-aromatic sulfur and aromatic sulfur, which presumably includes thiophenic sulfur. In a recent paper, LaCount showed the presence of significant amounts of non-aromatic sulfur groups which he found to be a larger proportion of the total organic sulfur in the low rank coals than in the higher rank coals.

Similar results were obtained in isothermal flash pyrolysis experiments (18). If model sulfur compounds are pyrolyzed at various temperatures at fast heat up rates and very short contact times, to avoid secondary reactions, a set of curves such as those shown in figure 5 are obtained. The aliphatic mercaptans, sulfides and disulfides break down to form H₂S at a much lower temperature than the aromatic sulfides and thiophenic compounds. When similar isothermal pyrolysis experiments are applied to coals, significant amounts of H₂S are produced at temperatures in the range where the aliphatic sulfur groups are unstable. The proportion of organic sulfur groups of the thermally unstable types are found to be higher in the low rank coals, and decrease as the rank increases. This suggests that coalification either converts the unstable sulfur structures of the coal to thiophenic structures, or destroys them leaving the thiophenic sulfur structures intact.

It would of course be desirable to have an analytical method for the various sulfur functional groups without the danger of thermally converting the sulfur compounds to other sulfur structures. In the process, as could be the case with the three methods I have described. At least two laboratories undertook to do this with X-ray methods. Gorbaty and coworkers at EXXON used Sulfur K edge X-ray absorption near edge structure spectroscopy (XANES) and X-ray Photoelectron spectroscopy (XPS) (30,31), and Huffman and coworkers at the University of Kentucky also used XANES (32,33). The EXXON group found it necessary to use a third derivative analysis of the XANES spectra to get a resolution of the aliphatic, aromatic and pyritic sulfur forms, while with the XPS they were able to deconvolute the original spectra into identifiable sulfur components. Table 4 shows the breakdown of sulfur types they obtained on the 8 Argonne premium coal samples. The Kentucky group after initially being unable to see the aliphatic structures were able to deconvolute the XANES spectra into component sulfur types at which time the presence of the aliphatic sulfur components became apparent (fig. 6). Suffice it to say that both aliphatic and aromatic or heterocyclic sulfur structures are resolvable in the various coals, and the previously observed trend of higher aliphatic sulfur in the low rank coals decreasing in the higher rank coals is also apparent.

Comparison of analysis of sulfur type on the same low pyrite-high organic sulfur coals by flash pyrolysis and X-ray methods shows quite a reasonable agreement concerning the content of the more reactive aliphatic sulfur components. (34) (Table 5) The higher aliphatic value for the Rasa coal by pyrolysis than by X-ray apparently is due to the presence of some aromatic disulfide which was shown to be less stable than other aromatic sulfides. Combined pyrolysis and X-ray studies also provided evidence that aliphatic sulfidic sulfur is thermally converted to aromatic or heterocyclic sulfur forms, supporting the view that coalification results at least in part in conversion of aliphatic to aromatic and heterocyclic sulfur. (35)

Recently, Brown of CANMET and coworkers (36,37) have introduced another X-ray method based on the sulfur L edge X-ray absorption near-edge spectra. This method offers the potential of greater resolution than the K edge analysis. It has the disadvantage of requiring high vacuum, (the K edge method can be run at atmospheric pressure) thereby limiting the range of samples that can be run. However the greater resolution makes further investigation of this technique worthwhile.

While unoxidized (pristine) coals clearly contain sulfur in the reduced state, the X-ray techniques can also distinguish among the oxidized forms of sulfur such as sulfoxides, sulfones, sulfonic acids and sulfate. This was utilized by both the EXXON (38) and U. of Kentucky groups (39) to show that the aliphatic sulfides are selectively oxidized to sulfoxides and sulfones, and in some cases sulfonic acids, if disulfides are present.

Hippo and the group at Southern Illinois University (40) have done oxidation studies on coals and coal macerals derived from them, using peroxyacetic acid which solubilized most of the coals. The oxidation products were methylated with diazomethane and analyzed in a gas chromatograph using a flame photometric detector. Ten or twelve sulfur compounds were detected, with methyl sulfonic acid being a major product, presumably derived from aliphatic disulfides or thiophene.

The existence of organic sulfur in coal as both aliphatic and aromatic or heterocyclic sulfur forms was dramatically demonstrated by Stock and coworkers together with the EXXON group. They showed that single electron transfer reagents such as potassium naphthalenide in tetrahydrofuran will attack and destroy heterocyclic sulfur compounds and not the aliphatic or sulfidic sulfur. (41) They also showed that strong organic bases such as n-butyl lithium and potassium t-butoxide in heptane remove the sulfidic sulfur from model compounds without affecting the thiophenic compounds. (42) They performed these treatments individually on Illinois #6 coal from which the pyrite had been removed, and showed that the organic sulfur type corresponding to the particular method of treatment was removed as shown by the XANES method. Also, stepwise treatment of the same coal with each reagent eliminated both sulfidic and heterocyclic sulfur types from the coal. (43)

As I have discussed, we now have considerable evidence that the sulfur in coal exists as both aliphatic and aromatic or heterocyclic forms, and several methods exist for the approximation of the amounts of each. Low rank coals contain more of the organic sulfur in aliphatic or labile forms, whereas higher rank coals contain predominantly heterocyclic sulfur. Reaction of coals with methyl iodide (18) suggests that at least some of the aliphatic sulfur is present as thioether, and some possibly as disulfides. Very little appears to be present as mercaptan.

Sulfur Removal from Coal

What are the implications of this information for the development of an effective high yield low cost process for sulfur removal from coal? Since there are at least two distinct organic sulfur forms, any process devised for such removal must take this into account. Palmer and Hippo et al. (44) found that a combination of peroxyacetic acid treatment and either thermal or base treatment removed much of the organic sulfur. Stock's two processes appear to be unlikely to be practical on a commercial scale, but may lead to similar lower cost methods. With the lower rank coals containing a larger percentage of the less stable aliphatic sulfur, removal of that portion of the organic sulfur together with the pyritic sulfur with strong alkali may be sufficient for most purposes. There is also a number of research programs

underway investigating bacteriological methods for sulfur removal (45). These might be expected to be slow but low in cost if the proper organisms are found.

Summary and Conclusions

- 1) At least two classes of organic sulfur structures appear to be present in coals, with the low rank coals generally containing a larger percentage of the total sulfur as more reactive aliphatic sulfur components. As rank increases, the more stable heterocyclic sulfur structures increase and become predominant.
- 2) Analytical methods exist for approximating the amount of the two component classes, although more precise methods are needed.
- 3) We now have the fundamental basis and analytical methods for further development of processes for removal of organic sulfur from coal. Such processes must recognize the presence of the two types of sulfur structures.
- 4) We still do not understand the reactions occurring between H₂S and the biomass that formed the organic sulfur structures in the first place.
- 5) We also do not understand the reactions of H₂S and/or elemental sulfur with coal or char at elevated temperatures as has often been observed.

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Table 1. Sulfur Content Of Some United States Coals (Wt. %)

Type of Sulfur	Texas Lignite Martin Lake	Wyodak Subbit.	Hi Vol Bit.	
			Ill #6	Ohio #6
Pyritic	0. 14	0. 11	1. 06	1. 15
Sulfate	0. 03	0. 12	0. 12	0. 03
Organic	1. 05	0. 70	2. 17	2. 01
Total	1. 22	0. 93	3. 35	3. 19

Table 2. Total and Organic Sulfur Contents of Two High-Sulfur Low-Pyrite Coals

Coal	Country of Origin	% Carbon (maf basis)	% Total Sulfur	% Organic Sulfur
Mequinenza	Spain	68. 6	12. 6	11. 8
Rasa	Yugoslavia	80. 2	11. 8	11. 4

Table 3. Pyroprobe GC/MS Analysis of Pittsburgh 8 R & F High Sulfur Coal

Product	% Tot. Area	
	raw	90% of Pyrite Removed
H ₂ S	3. 03	4. 83
COS	0. 48	0. 31
CH ₃ SH	0. 32	0. 34
SO ₂	2. 13	0. 02
CS ₂	0. 27	0. 06
thiophene	0. 25	0. 22
methylthiophene-1	0. 34	0. 23
methylthiophene-2	0. 23	0. 10
dimethylthiophene-1	0. 49	0. 46
dimethylthiophene-2	0. 47	0. 38
dimethylthiophene-3	0. 38	0. 24
dimethylthiophene-4	0. 07	0. 05
trimethylthiophene-1	0. 19	0. 10
trimethylthiophene-2	0. 22	0. 16
tetramethylthiophene	low	0. 04
benzothiophene	0. 29	0. 24
methylbenzothiophene-1	0. 06	0. 04
methylbenzothiophene-2	0. 13	0. 15
methylbenzothiophene-3	0. 20	0. 19
methylbenzothiophene-4	0. 15	0. 14
methylbenzothiophene-5	0. 17	0. 12
methylbenzothiophene-6	—	0. 02
Dimethylbenzothiophene-1	0. 11	0. 11
dimethylbenzothiophens-2	0. 06	0. 05
dimethylbenzothiophene-3	0. 12	0. 14
dimethylbenzothiophene-4	0. 07	0. 10
dimethylbenzothiophene-5	0. 05	0. 04
dimethylbenzothiophene-6	0. 07	0. 08
dimethylbenzothiophene-7	0. 05	0. 04
dimethylbenzothiophene-8	0. 05	0. 03
dimethylbenzothiophene-9	0. 03	0. 02
dibenzothiophene	0. 08	+

Calkins, W. H. (18)

Table 4. Approximate Quantification of Organically Bound Sulfur Forms in Argonne Premium Coal Samples

Coal	%C dmmf	Mole percent (+10) by XANES		
		aliphatic	aromatic	thiophenic
Beulah-Zap	74. 05	35	25	38
Wyodak-Anderson	76. 04	33	22	45
Illinois #6	80. 73	33	26	41
Blind Canyon	81. 32	24	28	47
Pittsburgh 8	84. 95	22	34	44
Lewiston-Stockton	85. 08	19	20	60
Upper Freeport	88. 08	13	30	57
Pocohontas #3	91. 81	13	23	64

G. N. George, M. L. Gorbaty, S.R. Kelemen and M. Sansone (30)

Table 5. Percent of Organic Sulfur as Aliphatic Sulfur by Pyrolysis and X-ray Methods

coal	country of origin	% carbon (maf basis)	% total S	% organic S	by pyrolysis	% aliphatic sulfur		mol % H ₂ S by TPD
						by X-ray		
						XANES	XPS	
Mequinena	Spain	68.6	12.6	11.8	67	48	66	75
Beulah-Zap	USA	72.9	0.88	0.70	39	37	37	45
Wyodak-Anderson	USA	75.0	0.63	0.47	36	33	37	
Charming Creek	NZ	78.7	5.85	5.76	26	28	38	29
Rasa	Yugoslavia	80.2	11.8	11.4	47	30	26	40

Calkins, W. H. , Torres-Ordonez, R. J. , Jung, B. , Gorbaty, M. L. , George, G. N. and Kelemen, S. R. (34)

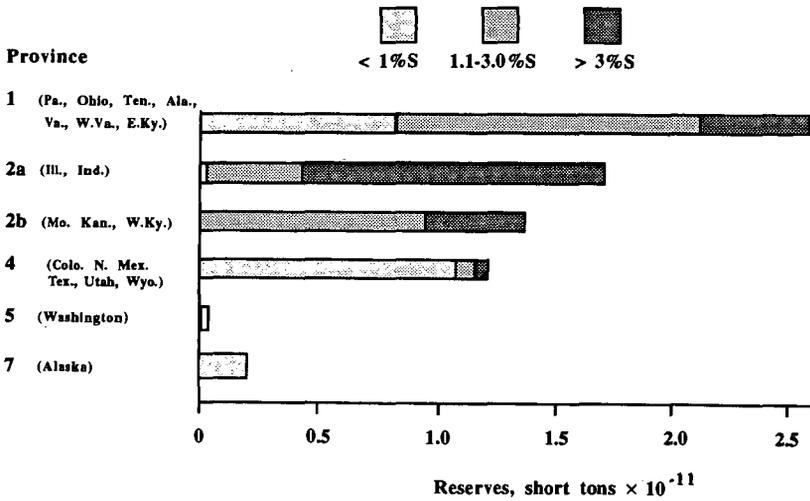


Figure 1. Distribution of U.S. bituminous coals by geological province and sulfur content.

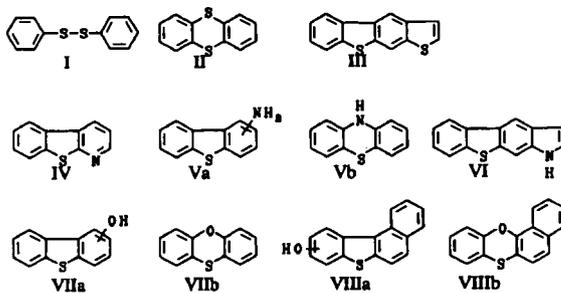


Figure 2. Possible Multiple-heteroatom-containing pyrolysis products. [R. E. Winans and P. H. Neill (17)]

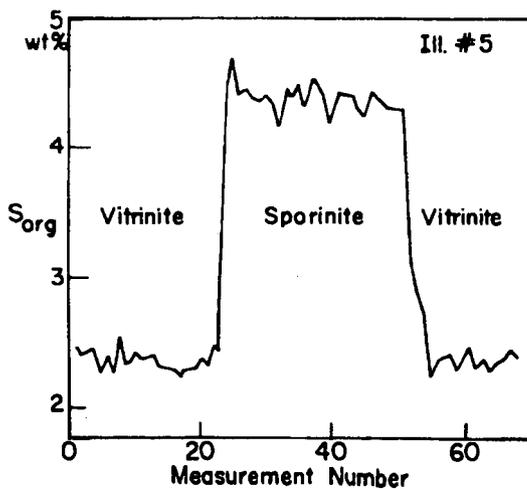


Figure 3. Change in organic sulfur concentration for a maceral of sporinite embedded in a maceral of vitrinite, Illinois #5 Coal. [C. Wert, Y. Ge, B. H. Tseng, and K. C. Hsieh (21).]

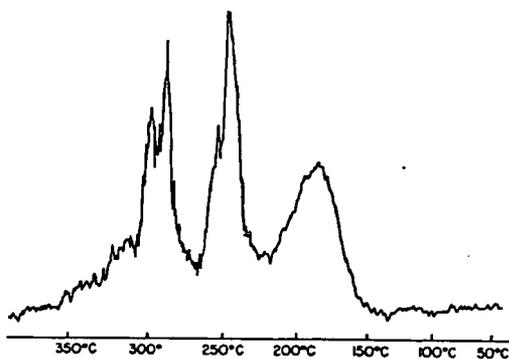


Figure 4. Reductive Kinetogram of Illinois #6 Coal. [A. Attar and F. Dupuis (25).]

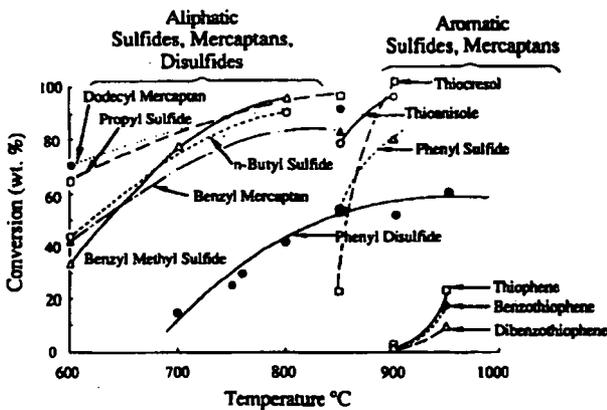


Figure 5. Pyrolysis of Model Sulfur Compounds (% Conversion vs. Temperature) 0.5 sec. Contact time. W. H. Calkins (18)

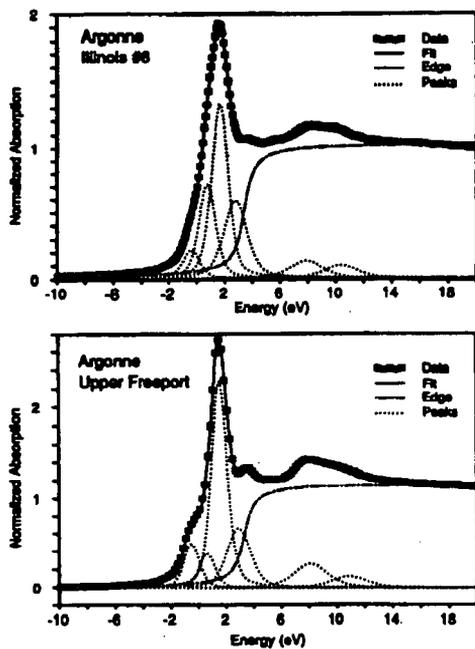


Figure 6. Least Squares Fits of the XANES of Illinois #6 and Upper Freeport Coals. [G. P. Huffman, S. Mitra, F. E. Huggins, N. Shah, S. Vaidya, and F. Lu (33).]

SULFUR SPECIATION STUDIES IN COAL AND OTHER FOSSIL ENERGY MATERIALS BY S K-EDGE XANES SPECTROSCOPY

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Keywords: sulfur speciation, XANES, XAFS, rubber, resids, coal.

ABSTRACT

Sulfur K-edge XANES spectroscopy has been shown to be an excellent technique for quantitative speciation of sulfur in fossil fuels. Earlier studies focused on establishing the method and applying it to sulfur speciation in coal. More recently, it has been applied to a variety of additional problems, including investigation of coal desulfurization processes, and speciation of sulfur in such materials as asphalts, kerogens/asphaltenes, coal liquefaction resids, and rubber. Some of the more interesting results from this research will be presented. Additionally, a comparison will be made of sulfur K-edge and L-edge XANES results for the same coal.

INTRODUCTION

Sulfur K-edge x-ray absorption fine structure (XAFS) spectroscopy has been shown to be an excellent method of speciating the sulfur in coal and related materials. Two methods have developed for sulfur speciation which involve analysis of the x-ray absorption near-edge structure (XANES) region of the XAFS spectrum. The method developed by Gorbaty and coworkers[1-3] analyzes the XANES by a third derivative method, which yields peaks whose heights are proportional to the percentages of sulfidic and thiophenic sulfur. In the method developed by our group[4-6], a direct least squares analysis of the XANES is carried out by fitting it to a series of mixed Lorentzian-Gaussian peaks. The peak areas are then used to determine the percentages of different sulfur forms present, using empirically determined calibration constants.

In the current article, we will briefly review some recent applications of this technique. These include speciation of sulfur in desulfurized coals, asphalts, coal liquefaction resids, and rubber. A comparison will also be made of sulfur speciation by sulfur K-edge and L-edge XANES spectroscopy for one coal.

RESULTS AND DISCUSSION

The experimental procedures used in these experiments have been discussed in detail elsewhere[3-6]. We will merely note that all experiments were carried out on beamline X-19A at the National Synchrotron Light Source (NSLS) in the fluorescent XAFS mode, using a Si(111) double crystal monochromator and a Lytle detector.

Desulfurization studies: XANES results for coals desulfurized by a number of methods have been summarized in recent papers[7,8]. Here we will briefly the principal results for different desulfurization methods.

Perchloroethylene(PCE) treated samples: Results have been obtained for a fairly large number of samples before and after extraction with boiling PCE. For the samples investigated to date, it is concluded that the primary effect of the treatment is to remove elemental sulfur. The samples which show elemental sulfur before treatment normally also exhibit a significant amount of sulfate, indicative of oxidation. Fresh coals are unaffected by PCE treatment, suggesting that an oxidative step is required to produce the elemental sulfur that is removed by PCE. These results are discussed in detail in reference 8.

Treatment with single electron transfer(SET) and basic reagents: Chatterjee and Stock have discussed the removal of organic sulfur by treatment with SET[9] and basic reagents[10]. A suite of these desulfurized coals have been investigated by XANES spectroscopy using both the third derivative method of Gorbaty et al.[11] and the least squares analysis method[7]. The results for the raw coal, an Illinois #6 from the Argonne Premium Coal Sample Bank, are similar to those reported earlier[4]. After treatment with lithium aluminum hydride(LAH), all of the pyrite is removed, and the percentage of organic sulfide appears to have decreased somewhat relative to thiophenic sulfur. Following SET treatment, the thiophenic sulfur percentage is significantly decreased, while the BASE treatment produces a substantial decrease in sulfidic sulfur, exactly as proposed by Stock and Chatterjee[9,10]. The results are obscured somewhat, however, by the appearance of an unidentified sulfide peak in the spectra of the treated coals, which is believed to be due to potassium sulfide.

Biological desulfurization: XANES has been used to investigate two samples of Illinois #6 coal before and after biodesulfurization using the microbe *Rhodococcus rhodochrous* by Kilbane[12]. Pyrite was removed from the coal before biotreatment, leaving a sulfur distribution that consisted of approximately 48% thiophenic sulfur, 31% sulfidic sulfur, 10% sulfate and minor amounts of other components. Following biotreatment, the organic sulfur content was reduced by approximately 2 wt.% and 1 wt.% for two separate samples. The relative percentages of the various sulfur functional forms, however, was unchanged within the error of the measurement(\pm 5%), indicating that the biotreatment does not discriminate between different sulfur forms.

Molten caustic leaching: A molten caustic leaching process has been developed by TRW Corporation for the removal of sulfur and ash from coal[13]. The results obtained by least squares analysis of the XANES for a Kentucky #9 and a Pittsburgh #8 coal subjected to this process establish that the forms of sulfur are drastically changed and reduced[7]. Specifically, no pyrite or organic sulfide remain, and thiophenic sulfur, which is the dominant organic sulfur form in the original coals is reduced to only about 0.1% in the treated coals. Elemental sulfur, sulfone, and sulfate are the dominant sulfur species remaining at levels of approximately 0.2%, indicating rather severe oxidation.

Sulfur speciation in asphalts: The sulfur functional groups present in a

number of asphalt samples were determined by least-squares analysis of their sulfur K-edge XANES spectra[14]. In unoxidized asphalts, oxidized sulfur forms are generally absent, and the principal sulfur form observed is thiophenic. Thiophenic sulfur varied from 54% to 78% of the total sulfur, with the balance being primarily sulfidic. Oxidation tests aimed at mimicing asphalt ageing were carried out at the Western Research Institute. Comparison of the sulfur forms before and after oxidation shows that only the aliphatic sulfur oxidizes to sulfoxide.

Sulfur speciation in rubber: Recently, we completed an XANES analysis of the sulfur forms in rubber tread material provided by Michelin. This is the same rubber used by Farcasiu and Smith in experiments on the coliquefaction of rubber and coal[15]. The XANES spectrum of this rubber is shown in Figure 1. As seen, the major feature of the spectrum can be deconvoluted into the $s \rightarrow p$ transition peaks of polysulfide(0.0 eV), monosulfide(0.8 eV), and thiophenic sulfur(1.5eV). The conversion of peak area percentages into sulfur percentages gives the following results: polysulfides - 38%; sulfides - 29%; thiophenes - 27%; and sulfoxides - 5%. The polysulfides, and possibly the sulfides, are believed to be the sulfur chains formed between polymer chains during vulcanization. A more detailed summary of this work will be prepared for publication elsewhere.

Sulfur speciation in coal liquefaction resids: Sulfur speciation has been carried out on THF soluble extracts from a series of coal liquefaction resids from Wilsonville and on the resids themselves. In the resids, pyrrhotite derived from added iron catalyst is the dominant sulfur form. In the extracts, thiophenic sulfur is dominant, sulfidic sulfur is low relative to the original coals, and most samples exhibit some oxidized sulfur, principally sulfoxide and sulfone.

Comparison of sulfur K-edge and L-edge results: Recently, Brown et al.[15] have examined the sulfur in coal by sulfur L-edge XANES spectroscopy. Analysis of the sulfur forms in Mequinenza lignite[16] by L-edge XANES gave the following results: 40% thiophenic(4.0 wt%), 20% aryl sulfide, 20% aliphatic sulfide, and 20% disulfide(2.0 wt.% for each sulfide form). The K-edge spectrum of this sample is shown in Figure 2. The major white line component was fitted to three peaks that correspond, with increasing energy, to di/polysulfide, organic sulfide, and thiophenic sulfur. Minor amounts of sulfoxide and sulfate are also observed. The results for the percentages of total sulfur and the wt.% of sulfur in each sulfur form identified are summarized in Table 1. Generally speaking, the results for sulfur speciation by K-edge and L-edge spectroscopy agree within the error of the measurements if the aryl and aliphatic sulfide categories of the L-edge measurement are combined for comparison to the K-edge organic sulfide category.

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Table 1
Results of Least-Squares Fitting of
Sulfur K-edge Spectrum of Mequinenza Lignite

<u>Sulfur Form</u>	<u>% of Total Sulfur</u>	<u>Wt% S in Lignite¹</u>
Pyritic Sulfur	nd	(<0.5)
Di-sulfide	10	1.0
Sulfide	33	3.3
Thiophenic	42	4.2
Sulfoxide	9	0.9
Sulfone	0	0.0
Sulfate	5	0.5

¹Based on 10.0 wt% (dry) non-pyritic sulfur in lignite. nd - Not determined

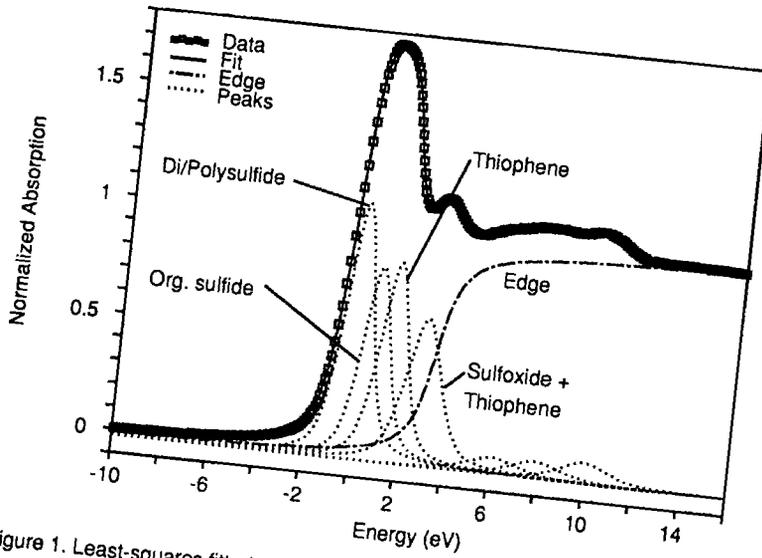


Figure 1. Least-squares fitted sulfur K-edge XANES spectrum of rubber tread material.

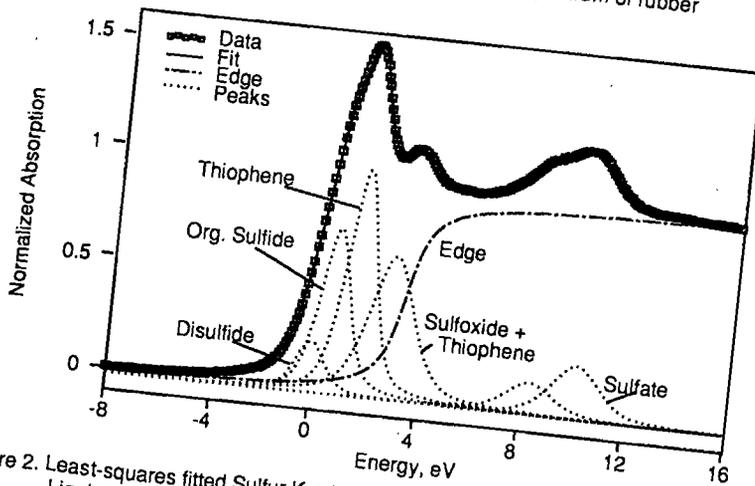


Figure 2. Least-squares fitted Sulfur K-edge XANES spectrum of Mequinenza Lignite

DETERMINATION OF SULFUR COMPOUNDS IN COAL BY
MASS SPECTROMETRY, CORRELATED WITH XANES AND XPS*

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Keywords: Macerals, Sulfur, High Resolution Mass Spectrometry, XANES, XPS

INTRODUCTION

The objective of this study is to identify important organic sulfur-containing compounds in the Argonne Premium Coals and in selected, separated coal macerals. In-source, desorption/pyrolysis high resolution mass spectrometry is being used to characterize the volatile species of whole coals, macerals, and their extracts. To examine the possibility of secondary reactions and undesirable selectivity, the MS data is compared to data from direct techniques, XANES and XPS. The MS results correlate very well which supports the suggestion that the species seen are indigenous to the original sample. Therefore, specific structural assignments to the sulfur species can be made.

Quantitative speciation of organic sulfur in coals has been accomplished by both XANES^{1,2} and XPS² with what appears to be good reliability. Mass spectrometry approaches provide more detailed molecular information, but suffer from problems with sampling.³ In the past we have found it difficult to isolate aliphatic sulfur compounds by thermal desorption or pyrolysis due to their thermal transformation to aromatic species. However, recently we have found that with in-source pyrolysis the occurrence of secondary reactions is reduced significantly. Results from both a selected set of the Argonne Premium Coal Samples and a set of three macerals from the Lewiston-Stockton coal (APCS 7) will be discussed.

Table 1. Analysis of the APCS 7 Macerals.

	%C(maf)	H	Per 100 Carbons			
			N	S	O	fa
Whole Coal	85.5	76	1.6	.3	8.9	.76
Liptinite	81.7	110	1.0	.5	8.3	.56
Vitrinite	80.2	78	1.7	.3	11.5	.75
Inertinite	85.4	46	1.3	.7	7.5	.89

EXPERIMENTAL

The preparation of the macerals by a continuous flow density gradient technique has been discussed and analysis of these samples is presented in Table 1.¹ The XANES and XPS methods have also been published.²

The desorption chemical ionization (DCI) and desorption electron impact (DEI) mass spectra were obtained on a three-sector high resolution, Kratos MSS0 spectrometer operating at 10,000 resolving power. This lower resolution was used to enable a more rapid scanning rate (10 sec/decade). In the CI experiments iso-butane was the reagent gas. Samples are deposited on a small platinum coil that is inserted directly into the source body adjacent to the electron beam and heated electrically at 100°C/minute from 200° to 700°C.

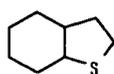
Table 2. Sulfur Distribution in a Selected Set of Argonne Premium Coal Samples.

Coal	%C	S/100C	XANES		XPS		HRMS	
			Al	Ar	Al	Ar	Al	Ar
Lignite	74.1	0.4	37	63	45	55	31-41	69-59
Upper Freeport	88.1	0.3	13	87	19	81	5-7	93-95
Pocahontas	91.8	0.2	13	87	0	100	3-4	96-97

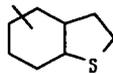
RESULTS AND DISCUSSION

Initially, a set of pyridine extracts was examined by DEIHMS. Extracts have been found to be quite representative of the whole coal and they typically give higher yields of volatiles compared to the whole, unextracted coals. The results for a lignite and two high rank coals are shown in Table 2 along with the published XANES and XPS results.² Although the MS results are only semi-quantitative, they agree very well with the directly obtained data. The trend of decreasing aliphatic sulfur with increasing rank is evident. It can be concluded that the sulfur containing species seen in the mass spectrometer are likely to represent most of the coal.

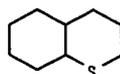
There are some interesting trends in the aliphatic sulfur species seen in the lignite coal. Molecules containing eight and nine carbons tend to dominate. This is especially true at a hydrogen deficiency (rings + double bonds = HD) of two. Possible structures could be:



I

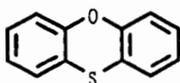


II

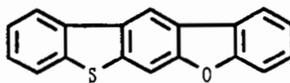


III

Thiolanes (I and II) have been observed in sediments.³ In addition, partially reduced thiophenes such as dihydrobenzothiophenes are also quite abundant.



I V



V

In the higher rank coals polycyclic thiophenes and sulfur-oxygen species (for example IV or V) dominate. There is evidence that phenoxathiim (IV) occurs in high sulfur bituminous coals.⁶ The distribution for the Pocahontas Iv bituminous coal is shown in Figure 1.

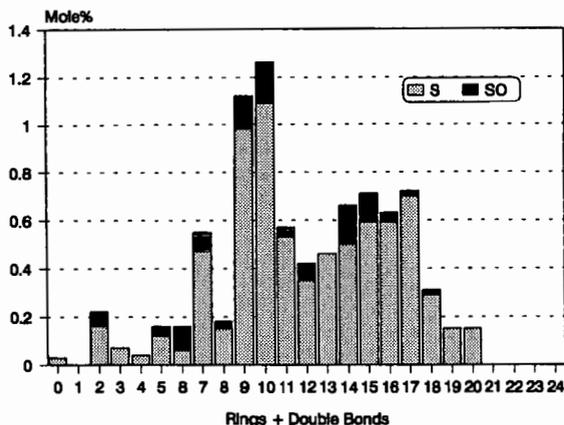


Figure 1. Distribution of organic sulfur containing species as a function of hydrogen deficiency.

XANES and the first XPS results for a set of separated macerals are shown in Table 3. Huffman and co-workers have examined a different set of macerals by XANES.⁴ They found, as is shown in this study, that sporinites typically contain much more aliphatic sulfur compared to either vitrinite or inertinite. The amounts are very similar to those found in lignite coals (Table 2). Since these sporinite macerals have been subjected to more rigorous coalification conditions than the lignite, the sulfur compounds such as those seen in lignite (i.e., thiolanes) would be aromatized. Initial examination of the MS data shows a lack of these compounds. The sulfur compounds are possibly incorporated into extended straight²chair aliphatic networks, which has been observed with alginites.³ As expected the inertinites contain more aromatic thiophenes similar to those seen in the high rank coals. Analysis of this data is continuing.

Table 3. Sulfur Distribution in Lewiston-Stockton Coal and Separated Macerals.

	XPS		XANES		HRMS	
	Al	Ar	Al	Ar	Al	Ar
Whole Coal	14	86	20	80		
Liptinite	35	65	50	50		
Vitrinite	8	92	0	100		Pending
Inertinite	9	91	0	100		

CONCLUSIONS

Results on the distribution of sulfur compounds determined by in-source pyrolysis HRMS correlates very well with organic sulfur data from XANES and XPS.

ACKNOWLEDGMENT

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TOWARD ORGANIC DESULFURIZATION

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Keyword: Desulfurization

INTRODUCTION

Advances in the organic desulfurization of coals and resids depend upon the discovery of methods for the secure definition of the sulfur forms in fossil fuel materials as well as upon the discovery of innovative chemical desulfurization strategies. This report deals with the coupling of selective chemical methods with XANES in an investigation of the desulfurization of Illinois No. 6 bituminous coal and Rasa subbituminous coal.

EXPERIMENTAL PART

The Argonne National Laboratory Premium sample of Illinois No. 6 bituminous coal and a sample of Rasa subbituminous coal that was provided by Ljiljana Ruscic were used in these experiments. The Illinois No. 6 coal contains 81% C (maf) with 2.0%S in organic compounds and 2.8%S in pyrite. The Rasa coal contains 73%C (maf) with 11.7%S in organic compounds.

The procedures that we used for selective desulfurization with lithium aluminum hydride (1-3), potassium naphthalene (-1), (3), and n-butyllithium-potassium t-butoxide (4) have been described previously. Conventional isolation procedures were used in most experiments, however, the facility with which some of the residual sulfur-containing compounds underwent air oxidation prompted us to protect the reaction products from oxygen in certain experiments.

All of the sulfur analyses were performed by Commercial Testing and Engineering of South Holland, IL.

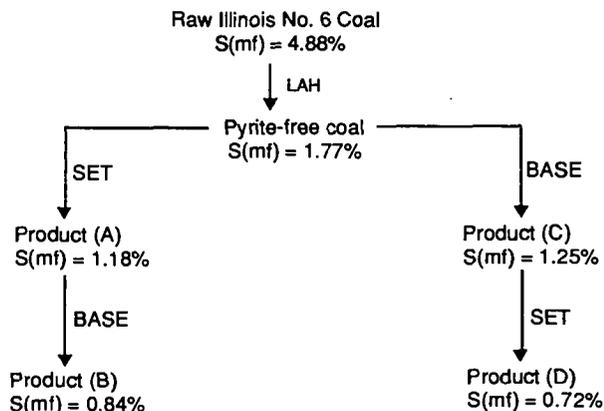
The XANES measurements were carried out by Gorbaty and his associates (5).

RESULTS AND DISCUSSION

The Illinois No. 6 coal was treated with lithium aluminum hydride to remove pyrite (1-3). As already reported, this method reduces the iron content of this coal to less than 0.1% by weight without altering the organic sulfur content. Several lines of evidence secure this point. First, pyrite reflections are absent in X-ray spectrum. Second, the XANES spectra of the product and the starting material indicate that the distribution of the sulfur forms is unchanged.

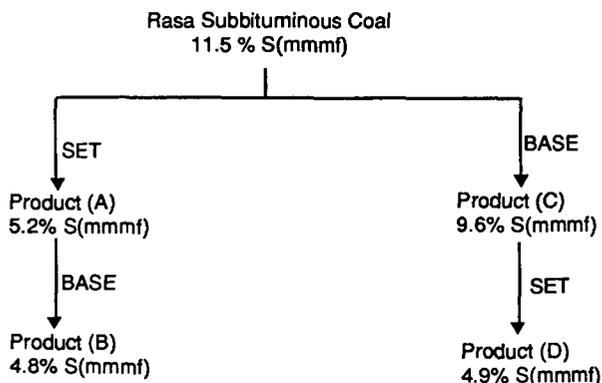
The pyrite-free coal was then treated with a single electron transfer reagent (SET) to react selectively with aromatic sulfur compounds including the sulfur heterocycles (3). We used potassium naphthalene(-1) in tetrahydrofuran at 67°C for 24 hours in most experiments. In an attempt to remove sulfidic sulfur, we used Lochmann's base (BASE), a very reactive mixture of *n*-butyllithium and potassium *t*-butoxide, in heptane at 98°C for six hours (4).

The results of the desulfurization experiments, which have been reported elsewhere (6), are summarized in the equation.



The XANES spectra of each product were recorded by Gorbaty and his colleagues at the Exxon beamline at National Synchrotron Light Source at Brookhaven National Laboratory (6). In brief, Gorbaty has shown that the sulfur XANES spectra of pyrite-free, unoxidized coals exhibit key features near 2469.6 and 2470.5 eV. The feature at 2469.6 eV arises from sulfidic sulfur compounds such as aromatic and aliphatic thiols, aliphatic sulfides, and aryl alkyl sulfides. The feature near 2470.5 eV is dominated by sulfur bound to sp² hybridized carbon atoms. The sulfur heterocycles and diaryl sulfides exhibit their absorptions in this region of the spectrum. The pyrite-free Illinois No. 6 coal contains 65 mole % aromatic sulfur and 35% sulfidic sulfur (7). As already reported, SET selectively reduces the aromatic sulfur content and the signal at 2470.5 eV is selectively decreased. On the other hand, BASE removes certain sulfidic forms that contribute to the intensity at 2469.6 eV.

With these results in hand, we turned our attention to the Rasa coal. The work with this subbituminous coal provided the results shown in the equation.



The Rasa coal undergoes extensive desulfurization with the SET reagent. It removes 55% of the sulfur when it is used as the first reagent and 41% of the sulfur when it is used as the second reagent. BASE is much less effective. It removes only 17% of the sulfur when it is employed as the first reagent, and even less, 3%, of the sulfur when it is used after the SET reagent. We also found that when the Rasa coal was treated with BASE and SET and

then treated with SET again, the sulfur content was reduced to 2.2%. When the BASE treatment was omitted entirely, dual SET reactions again reduced the sulfur content to 2.2%.

The XANES spectra for selected products were recorded. It was found that the sulfur bonded to sp^2 carbon in diaryl sulfides and heterocycles is virtually eliminated in the dual SET reactions, but that the feature at 2469.6eV remains.

In the course of our studies with the Illinois coal, we also found that the sulfur compounds that remained after SET and BASE reactions were thermally labile, and were also decomposed by vigorous acid hydrolysis.

CONCLUSIONS

Although space limitations do not permit a full discussion of all the results, the chemical and spectroscopic observations when coupled with information about the known chemistry of SET and BASE suggest the following conclusions.

First, the SET reagent selectively removes sulfur from heterocyclic sulfur compounds and aromatic sulfides. BASE does not remove the sulfur from the heterocycles but does react with sulfur compounds such as alkyl aromatic sulfides that are susceptible to base catalyzed elimination reactions. Neither of these reagents is effective for the removal of sulfur from aliphatic thiols under the mild conditions that were used in these experiments.

Second, the sulfur compounds that remain after the treatment with SET and BASE are probably aliphatic substances including alkyl and allylic thiols.

Third, BASE can be effective for partial organic desulfurization in some coals, but, generally speaking, the SET reactions, while slow, are more effective and purge sulfur selectively from the organic compounds in these coals without appreciable loss in the heat content.

ACKNOWLEDGEMENT

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Quantification of Nitrogen Forms in Argonne Premium Coals

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Abstract

X-ray Photoelectron Spectroscopy (XPS) was used to investigate the organic nitrogen forms present in fresh Argonne premium coals. In addition to the anticipated presence of pyrrolic and pyridinic nitrogen forms, a detailed analysis of the nitrogen (1s) line shape indicates the presence of quaternary type nitrogen species. A trend of decreasing level of quaternary nitrogen type with increasing coal rank is observed.

1. Introduction

The ability to quantify heteroatom functionalities in complex carbonaceous systems such as coal and petroleum residua can provide valuable insight into the organic macromolecular structure. Direct spectroscopic probes such as X-ray Photoelectron Spectroscopy (XPS) [1, 2] and X-ray Absorption Near Edge Structure (XANES) spectroscopy [3-7] have proven to be viable nondestructive techniques for organic sulfur speciation in non-volatile and solid carbonaceous materials. Results from these direct probes for organic sulfur have been compared to results based on pyrolysis methods [8]. XANES and XPS has been used to study the thermal chemistry of sulfur in coal [2] and these results provide insight into the transformations of organic sulfur that occur during pyrolysis based analytical probes. These results also provided insight into some of the processes at work during coal metamorphism [9].

A similar understanding of the chemistry of nitrogen in coal has not yet emerged. Progress has been made with XPS [10-14] and XANES [15] in the quantification of organic nitrogen forms. Development of both of these techniques is essential for a more complete understanding of chemical reactivity of coal. Mass transport of reactants and products is always a concern when dealing with coal. XPS has the advantage of being a probe the near surface (e.g. first 50 Angstroms) while XANES can derive its signal from the entire sample.

XPS methods have been widely used in the study of nitrogen forms in coal. Initial studies established that the energy position of the nitrogen (1s) signal was close to that expected for pyrrolic nitrogen [10,11]. It was possible to further curve resolve the XPS nitrogen (1s) spectra of coal into two peaks corresponding to pyrrolic and pyridinic types [10-13]. In a more recent study of a series of eight UK coals covering the range of 80-95 Wt% carbon it was found that the XPS nitrogen (1s) spectra could be curve resolved into two major components, pyrrolic and pyridinic [14]. The XPS sensitivity for nitrogen in this study was estimated at 0.1 atom % nitrogen and the total nitrogen content of the coals ranged from about 0.8 to 2.0 atom % [14]. In another recent XPS study of nitrogen, pyrrolic and pyridinic were the major forms identified in coal and its derived products with only minor unidentified components present in some samples at higher binding energy [13]. The first XANES studies of coal and petroleum asphaltenes supports the position that pyrrolic and pyridinic groups are the most abundant nitrogen forms in these materials [15]. An error estimate based on the unnormalized XANES nitrogen fraction, is considered to be about 10% [15].

A detailed analysis of the XPS nitrogen (1s) line shape has been used to quantify both the major and minor forms of nitrogen present in fresh Argonne premium coals. Changes in the distribution of nitrogen functionalities

due to pyrolysis and hydrolysis have been examined for Illinois #6 bituminous and Wyodak subbituminous coal. The relevance of these results toward understanding coal metamorphism will be discussed.

II. Experimental

XPS spectra were obtained with a Vacuum Generators (VG) ESCA Lab system using MgK alpha non-monochromatic radiation and a either a single or a five channel detection arrangement. The five channel signal system provided a five times greater XPS signal for the same X-ray exposure time. The coal and model compound samples were made into fine powders and mounted to a metallic sample block by means of Scotch double sided non-conducting tape. An energy correction was made to account for sample charging based on the carbon (1s) peak at 284.8 eV. All spectra were obtained at an analyzer pass energy of 20 eV and a constant analyzer transmission mode. Under these conditions the full width at half maximum (FWHM) of 1.7 eV was obtained for the carbon (1s) spectrum of Argonne premium Pocahontas coal. The carbon (1s) line shape of Pocahontas coal is dominated by signal from hydrocarbons because of the very low total heteroatom content.

The nitrogen (1s) signal was curve resolved using a mixed Gaussian-Lorentzian line shape and a FWHM of 1.7 (eV). With these parameters it was possible to fit the nitrogen (1s) signal from pure model compounds, where nitrogen exists in a single chemical environment, with a single peak having these characteristics. The nitrogen (1s) spectra from coal were more complex. These spectra were curve resolved using the same theoretical line shape using peaks at 398.7, 400.2 and 401.3 (± 0.05)(eV). These peaks correspond to the energy positions found for pyridinic, pyrrolic and quaternary type nitrogen functionalities respectively [13]. The peak shape and peak energy positions were fixed and only the amplitudes of these peaks varied to obtain the best fit to the experimental XPS data.

Elemental data for the coal samples were obtained from the Users Handbook for the Argonne Premium Sample Program [16]. Other elemental analytical data were obtained from Galbraith Analytical Laboratories, Knoxville, TN. Elemental data was also derived from XPS measurements from the areas of the XPS peaks after correction for atomic sensitivity. The sensitivity factors were obtained from VG sensitivity tables and experimentally measured standards. The elemental concentrations are presented relative to carbon.

Pyrolysis experiments were done in a quartz lined reactor in helium at 1 atm. The reactor temperature was raised to 400°C at approximately 0.5°C/sec. and held for 5 min. Under these conditions, little of the ultimate amount of hydrocarbons expected from the volatile matter determination are released while much of the oxygen as CO₂, H₂O and CO evolves [2]. Hydrolysis was accomplished in a closed reactor pressurized at room temperature to 70 atm. with a 95% hydrogen 5% helium mixture. The reactor temperature was raised to 427°C at a heating rate of 0.05°C/sec. and held for 30 min. These conditions favored the retention of coal hydrocarbon components and hydrocarbon products in the hydrolysis chars.

III. Results

The amount of nitrogen measured by XPS for the fresh coal samples was compared to bulk elemental data. The results are shown in Table I and there is excellent agreement for all coals except Illinois #6 and Lewiston coals. The generally good agreement indicates that there is no systematic enhancement or depletion of nitrogen at the coal surface. Illinois #6 and Lewiston coals gave lower nitrogen values with XPS. The origin for the difference with bulk

value for these two coals is not yet resolved. The precise nature of the XPS results was demonstrated by numerous measurements on fresh coals of different particle sizes. The XPS nitrogen values for Illinois #6 coal were consistent throughout thermal and reductive treatment. Previous XPS investigations of other coal samples gave reasonable agreement between XPS and bulk values for nitrogen [10-14, 17, 18]. A tendency toward lower XPS values was noted [11, 13, 14] and a possible uncertainty in the XPS sensitivity factor for nitrogen was suggested as one possible cause for the discrepancy. This is an inadequate explanation in the present case of Argonne premium coals. Nevertheless, XPS has good precision for nitrogen quantification and the results are significant for identification of chemical changes in coal functionality.

The XPS nitrogen (1s) signals for the fresh Argonne premium coal samples is shown in Figure 1. Included in Figure 1 are the results of the curve resolution analysis for nitrogen forms. In each case the individual peaks and the total simulated spectrum are shown with the actual spectrum. The anticipated pyrrolic (402.2 eV) and pyridinic (398.7 eV) nitrogen forms were the most abundant species identified. The two forms could almost completely describe the nitrogen (1s) spectrum from a high rank coal such as Pocahontas, however, in all other cases it was necessary to include a peak for quaternary nitrogen ion (401.3 eV). Notice the relatively good signal to noise (S/N) characteristics of each spectrum and how well the sum of theoretical peaks fit the actual data. There are limited degrees of freedom in the curve resolution methodology, described in the experimental section. Data with good (S/N) provide a good test for the curve resolution methodology. Additional samples of fresh Argonne Premium coal were prepared, the XPS nitrogen (1s) signal recorded and curve resolved using the same methodology the gave essentially the same result, namely, that it was necessary to include in all cases a peak representative of quaternary nitrogen in addition to the ones representative of pyrrolic and pyridinic species. The estimated experimental precision for nitrogen forms is (\pm) 3.0 mole %.

The average numerical results of the curve resolution analysis are shown in Table 2. In all cases pyrrolic and pyridinic species are the dominant nitrogen forms in agreement with previous findings for coal [10-14]. There is a significant contribution of quaternary nitrogen signal, especially in the lower rank Argonne premium coals. The data from each individual curve resolution analysis for nitrogen forms was plotted as a function of the weight % carbon in coal. Figure 2 shows these results. The solid and open points were obtained using a five and a single channel detection system respectively. These results show a distinct trend of decreasing relative amount of quaternary nitrogen with increasing coal rank for Argonne premium coals. A distinct trend for the relative level of pyrrolic nitrogen is not evident but there appears to be a tendency for the relative level of pyridinic nitrogen to increase with increasing coal rank.

The changes in the total level of organic nitrogen and oxygen following pyrolysis and hydrolysis of Illinois #6 and Wyodak coal were examined. The results of total nitrogen in the residual pyrolysis and hydrolysis chars are shown in Table III along with the results for total organic oxygen based on XPS analysis. For Illinois the level of organic oxygen drops nearly in half during hydrolysis. Less organic oxygen is lost during pyrolysis. There is only a slight increase in the relative level of total nitrogen after pyrolysis and hydrolysis. For Wyodak coal the organic oxygen level drops in half after pyrolysis and to one third of its initial value after hydrolysis. In contrast the relative level of nitrogen remain close to the initial value. The loss of organic oxygen after mild pyrolysis and hydrolysis conditions employed here is likely a result of loss of organic oxygen functionalities as CO₂, H₂O and CO [19, 20]. The loss of nitrogen as small gaseous molecules (i.e. NH₃, HCN, etc.) does not occur at low temperature (T < 450°C) [21] prior to the devolatilization of hydrocarbons. Since some carbon is lost with CO₂ and CO as well as through formation of small quantities of methane or other small hydrocarbon gases a slight increase in the level of nitrogen relative to carbon would be expected if nearly all of the initial nitrogen is retained in the pyrolysis and

hydropyrolysis chars.

The changes in the XPS nitrogen (1s) line shape following mild pyrolysis and hydropyrolysis of Illinois #6 and Wyodak coal have been studied. Figure 3 shows the The XPS nitrogen (1s) signals following hydropyrolysis. Included in Figure 3 are the results of the curve resolution analysis for nitrogen forms. In each case the individual peaks and the total simulated spectrum is shown with the actual spectrum. The anticipated pyrrolic (402.2 eV) and pyridinic (398.7 eV) nitrogen forms were the dominant species present. The two forms could describe the nitrogen (1s) spectrum following hydropyrolysis of Illinois #6 coal, however it was still necessary to include a small peak at the position expected for the quaternary nitrogen species.

The numerical results of the curve resolution analysis for nitrogen forms after pyrolysis and hydropyrolysis are shown in Table IV. There is a decline in the relative level of quaternary nitrogen for both coals after reaction. The decline is greater following hydropyrolysis. There is a significant increase in the relative level of pyridinic nitrogen for both coals after hydropyrolysis.

IV. Discussion

Detailed analysis of the XPS nitrogen (1s) signal has been used to determine the relative level of nitrogen forms in fresh Argonne premium coal samples. In agreement with previous investigations of other coals [10-14] pyrrolic and pyridinic species were the dominant nitrogen forms. In all cases it was necessary to include a peak found at the position expected for quaternary nitrogen ion. The relative level quaternary nitrogen decreases with increasing coal rank. It seems plausible that the quaternary nitrogen ion is associated with oxygen and the observed functional trend is caused by the loss of organic oxygen functionalities during coal metamorphism.

Quaternary nitrogen species have been identified in the XPS nitrogen spectrum of derived products of coal quaternarized with methyl iodide and examples shown where quaternary nitrogen is the most abundant species [12, 13]. The presence of quaternary nitrogen forms in fresh coal samples has not been reported before. The estimated experimental precision in the present study Argonne premium coal samples is estimated at (\pm) 3 mole %. It is possible that quaternary nitrogen species in lower rank coals was not measured in previous studies because the confidence level in the curve resolution process was substantially poorer on the order of (\pm) 10 mole %.

The XPS analysis for nitrogen forms in pyrolysis and hydropyrolysis chars showed that the relative level of quaternary nitrogen declines following reaction and is accompanied by a decline in the relative level of organic oxygen. There is ample reason to believe that nearly all of the nitrogen initially present is retained in the coal chars after reaction. The preferential retention of nitrogen [22] compared to sulfur and oxygen [2, 19, 20, 22] has been noted before. In the case of hydropyrolysis chars the relative level of pyridinic nitrogen increases substantially. It is concluded that the quaternary nitrogen species present in Illinois #6 and Wyodak coal are associated with oxygen and that the associations are broken during reaction. Furthermore, it appears likely that the quaternary nitrogen species is transformed during reaction and is largely retained in the coal char as a pyridinic nitrogen form. The appearance of quaternary nitrogen in fresh lower rank coal and the partial retention of these forms after mild pyrolysis indicates that these represent a significant class of strong non-covalent interactions present in the macromolecular structure of coal.

A detailed analysis of the XPS nitrogen (1s) line shape indicates the presence of quaternary type nitrogen species in addition to the anticipated pyrrolic and pyridinic forms. A trend of decreasing level of quaternary type

nitrogen with increasing coal rank is observed. The quaternary nitrogen species is lost with the loss of oxygen functionalities during pyrolysis. The ratio of pyridinic to pyrrolic nitrogen increases after pyrolysis. These observations suggest that the quaternary nitrogen species is associated with oxygen and that the association is broken as a result of thermal reactions. Furthermore, it appears that the quaternary nitrogen is transformed and remains in the coal char as a pyridinic nitrogen form.

V. Summary

Curve resolution analysis of the XPS nitrogen (1s) spectra of Argonne Premium coal showed that pyrrolic and pyridinic nitrogen are the most abundant forms. Quaternary nitrogen species are a significant fraction in lower rank coals and the trend is toward decreasing level of this species with increasing coal rank. Most nitrogen is retained in the remaining coal after mild hydrolysis. The relative amount of pyridinic nitrogen increases and while the level of quaternary nitrogen decreases after hydrolysis of Wyodak and Illinois #6 coal.

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Table I

Coal	Nitrogen/Carbon Atom Ratio (x100)	
	Total XPS	Total Bulk
Beulah Zap	1.5	1.5
Wyodak	1.3	1.4
Illinois #6	1.2	1.7
Blind Canyon	1.6	1.7
Pittsburgh #8	1.2	1.3
Lewiston	1.0	1.7
Upper Freeport	1.5	1.6
Pocahontas	1.2	1.3

Table II

Coal	XPS Pyridinic	Mole Percent Pyrrolic	(± 3.0) Quaternary
Beulah Zap	26	58	16
Wyodak	25	60	15
Illinois #6	26	62	12
Blind Canyon	31	55	14
Pittsburgh #8	32	61	7
Lewiston	31	60	9
Upper Freeport	28	65	7
Pocahontas	33	64	3

Table III

Coal	XPS Atom Ratio (x100)	
	Organic Oxygen/C	Organic Nitrogen/C
Illinois #6 (Initial)	9.0	1.2
Illinois #6 (Pyrolysis)	6.7	1.3
Illinois #6 (Hydropyrolysis)	4.8	1.5
Wyodak (initial)	16.9	1.3
Wyodak (Pyrolysis)	8.8	1.3
Wyodak (Hydropyrolysis)	5.6	1.4

Table IV

Coal	XPS	Mole Percent	(± 3.0)
	Pyridinic	Pyrolic	Quaternary
Illinois #6 (Initial)	26	62	12
Illinois #6 (Pyrolysis)	30	64	6
Illinois #6 (Hydropyrolysis)	35	65	0
Wyodak (initial)	25	60	15
Wyodak (Pyrolysis)	29	62	9
Wyodak (Hydropyrolysis)	35	65	3

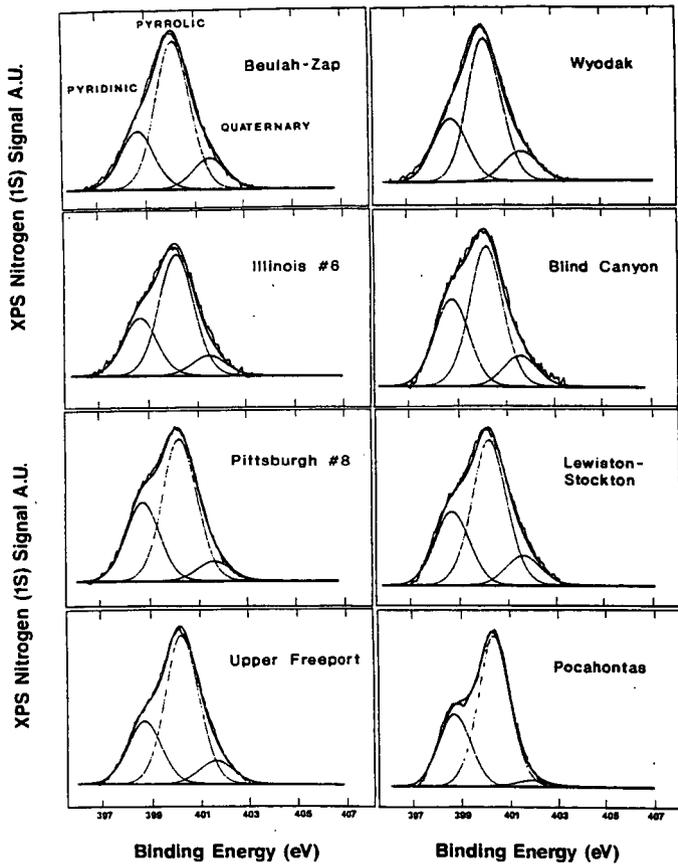


Figure 1. XPS Nitrogen (1s) Curve Resolution of Argonne Premium Coals

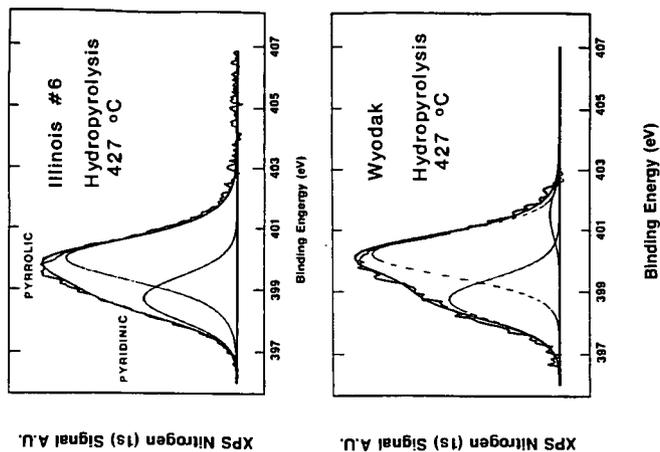


Figure 3. XPS Nitrogen (1s) Curve Resolution of Hydrolyzed Coals

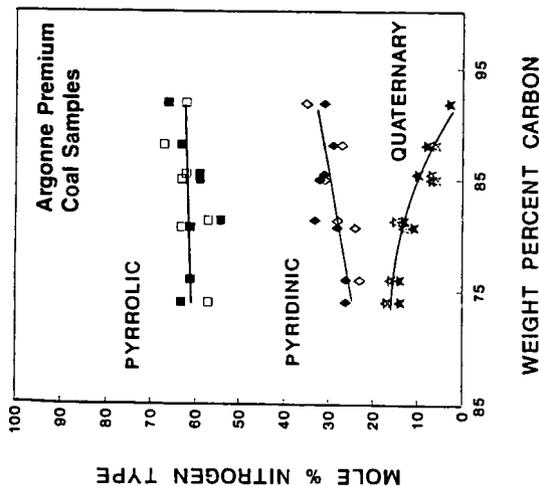


Figure 2. Nitrogen Functional Groups By XPS Curve Resolution Analysis

A PERSONAL VIEW OF COAL SCIENCE: PAST, PRESENT AND FUTURE

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INTRODUCTION

Coal is our most abundant fossil fuel resource. Its major commercial use today is for electric power generation through combustion, and to a lesser extent as a feed for the manufacture of metallurgical coke. The potential uses for coal are broader, such as feeds for producing liquid fuels and chemicals; technologies are available, but are not economically competitive. New, more efficient and environmentally sound technologies for coal utilization will be required in the future, and these will arise from more detailed fundamental knowledge of coal structure and reactivity. What follows is a personal assessment of the state of the art in several areas of coal science, some critical opportunities for new chemistry in these areas, and some guesses about the impact such new information might have. Taken together, these suggested research areas could provide the scientific bases from which the required technologies of the future could emerge.

It should be noted that significant progress in basic understanding of coal structure and reactivity has been made in the last decade. In order to assess the extent of this progress, it is instructive to review what were considered to be key research needs at that time. In 1979 the writer and his colleagues detailed such needs (1), and in this paper they will be referred to as starting points for assessing current state of the art.

COAL CHARACTERIZATION

Today, as in the past (2,3), coal is thought of as a complex heterogeneous "organic rock", made up of fossilized remnants of primordial plant matter and incorporated inorganics. Coal is also a porous rock. Thus coals have organic, inorganic and physical structures. Because of the inherent heterogeneity of coals, and limitations in analytical instrumentation, systematic studies of these structures were limited in 1979. With the advancement of many modern characterization approaches, not available in 1979, clearer, more precise and in-depth knowledge of each of these structures has been attained, and understanding the ways in which they affect coal reactivity becomes possible.

ORGANIC STRUCTURE

Many average molecular models representative of the organic material in coals have been and continue to be proposed (4-8), and as expected, become more refined as new information is obtained. An excellent review of this area, published in 1981, is still relevant (9). These models are useful to guide thinking, but must be used with care, since they are average structures meant to represent functional group distributions and may not be completely accurate. All recent model structures may be viewed as "islands" of aromatic ring clusters, many of which contain substituents, held together by largely aliphatic, or aliphatic-heteroatomic "bridges". The relative sizes of the islands, bridges and substituents vary depending on rank.

About a decade ago, major unknowns of coal structure included the types and amounts of oxygen, nitrogen and sulfur functionalities, carbon aromaticities, the ring size distributions, and bridging structures for coals of different rank. Since then characterization techniques have been developed which allow much of this information to be obtained:

Organically bound oxygen functionalities (hydroxyl, carboxyl, and ethers by difference) may now be accurately determined by the O-alkylation method (10). This knowledge makes possible the understanding of the role of oxygen functionalities during coal reactivity. For example, the effect of hydroxyl group hydrogen bonding on the caking properties of bituminous coals has been demonstrated (11).

An X-Ray Photoelectron Spectroscopy (XPS) method has been developed to accurately speciate and quantify forms of organically bound nitrogen (12), including the basic pyridines and quinolines and the weakly acidic or neutral indoles and carbazoles. It is necessary to know how nitrogen is incorporated in the organic matrix, since it has been apparent for some time that nitrogen species play a role in coal asphaltene behavior (13) and in coal conversion chemistry (14).

Since 1979 major advances have been made in speciating and approximately quantifying forms of organically bound sulfur, involving reactive and direct measurements. The reactive method uses flash pyrolysis (15), while the direct measurements involve XPS (16) and X-ray Absorption Near Edge Structure Spectroscopy (XANES) (17, 18). The latter methods were applied to the suite Argonne Premium coals (19), and it was shown that aromatic sulfur forms increased directly with increasing rank of the coals studied (17). In addition these methods are now being used to follow the chemistry of organically bound sulfur under mild oxidation (20) and pyrolysis conditions (21).

Knowledge of ring size distributions has grown significantly in the last several years. In 1979, solid state ^{13}C nuclear magnetic resonance (nmr) held real potential for this purpose, which has since been fulfilled. Aromatic ring cluster sizes have been estimated for the Argonne Premium coal samples based on some very elegant nmr experiments (22). For this sample suite varying from lignite to low volatile bituminous, the striking result is that the average ring cluster ranged between 9 (lignite) and 20 carbons (lvb), with most subbituminous and bituminous coals of this suite containing 14. This indicates an average size of 2-3 rings per cluster.

Another indicator of ring size distribution comes from coal depolymerization experiments (23). High levels of naphtha and distillate yields from a number of coals treated by this method indicate that average ring size distributions in the coals studied range from 1-3.

While methods are available today to get detailed information of the important coal structural features, they have not been uniformly applied to a standard suite of coals, and this represents an important research opportunity. Only the sulfur, nitrogen and nmr work described above have been done on the exact same suite of coals. This is necessary in order to get an idea of the parametric variations as a function of coal rank. Also, major opportunities now exist for using these methods to characterize starting and reacted coals and their products in order to be able to provide a basis for elucidating and understanding the detailed the chemistry taking place during conversion procedures.

INORGANIC STRUCTURE

Although the amounts of mineral matter in coals vary considerably, most contain about 10% (24). Mineral matter is inorganic material deposited before, during or after coalification of partially decayed biomass, and is largely in a reduced chemical state. Mineral matter is not necessarily inert during coal conversion processes, and has been reported to act beneficially in some cases as a catalyst for

gasification (25) and liquefaction (26) or detrimentally (27, 28). Therefore, a knowledge of the structures of the minerals present and their reactivities is important. Unfortunately, not much progress has been made in this type of characterization. Furthermore, the ways in which the inorganic matter is bound to the organic matter is not well understood. When coal is burned, the remaining inorganic mixture of oxides is called ash. Techniques to characterize the chemical compounds in ash, many of which are non-stoichiometric, are required. Sensitive probes to determine the compounds in which trace elements exist in native coals and in ash are being developed (29).

This information can impact on all forms of coal utilization including beneficiation, combustion, gasification, and liquefaction. For example, if mineral matter has catalytic effects during liquefaction, identification of the chemical species involved could lead to ways of enhancing its catalytic behavior. Better understanding of organic-inorganic interactions is needed to improve current coal cleaning procedures, and the determination of the compounds that make up slags found in furnaces might lead to ways of controlling the slagging phenomenon.

PHYSICAL STRUCTURE

The physical structure of coal has been described as a porous macromolecular gel (30). From the "porous rock" point of view, methods for determining surface areas and pore volumes on coals are needed. Depending on the coal, the adsorbing gas, the procedures used to acquire adsorption data and the equation used for the calculation, values of from 2-200 m²-g have been reported for the same sample (31). The difficulty in making these measurements is compounded because pore structures of subbituminous and lower rank coals collapse upon drying (32). Knowledge of surface areas and pore volumes are needed in order to help establish correlations between surface areas and chemical reactivity, particularly regarding access of gases and liquids to the interior of a coal particle.

From the "macromolecular network" point of view, much progress has been made in recent years in characterizing coals, and some reviews are available (33). It is well known that coals imbibe solvents, swell appreciably, and in some ways swollen coal networks take on elastomeric properties (35). Much work in recent years has focussed on adapting solvent swelling as applied to polymers to defining coal macromolecular structure in terms of M_c , the molecular weight between cross-links. There are many difficulties with translating polymer science techniques to coal (34), and the opportunities remain for finding reliable methods to determine M_c . This vital parameter could be used to follow the extent of coal network "depolymerization" during processing and for determining how many bonds need to be cleaved to reduce the "molecular weight" of coal from a solid macromolecular network to desired liquid products.

In recent years, another view of coal physical structure has been proposed (36), based on observed rapid and slow proton relaxation rates in nmr experiments. In this view, the macromolecular network is an "immobile phase" and is "host" to a number of many presumably smaller, mobile molecules, the "mobile phase", called by some "guests". As yet it has not been possible to distinguish between a long chain mobile molecule which exists independent of the network, and a similar molecule bound at a point to the network. Evidence to date suggests this model of unbound materials embedded in a rigid network may be valid for lignites and brown coals (37), but may not be for bituminous coals (38, 45). Regardless, this model has spawned some very important new work which addresses the true nature of

the bonding in coals.

If one assumes the host-guest, or two-phase model to be correct, then one would assume that a solvent or set of solvents could be found which would be able to dissolve large portions of the coal structure under mild solvent extraction conditions. Indeed recent reports suggest that N-methyl pyrrolidone (NMP) alone (39), or in combination with carbon disulfide (40) is capable of extracting up to 70% of some bituminous coals. The phenomenon is rank dependent, and appears to be most effective for low and medium volatile bituminous coals (40). Further understanding of this could help provide a basis for a low temperature procedure for obtaining liquid products from coals.

These observations, along with many others have called into question the nature of the bonding interactions in coals. It is fair to state that in 1979, most researchers believed that coal networks were held together almost entirely by covalent bonds, with minor contributions of ionic bonding in low rank coals (1). Perhaps the most important development in the last ten years and also the greatest opportunity for more research has been the realization that other bonding forms exist and exert major influences. The effect of aromatic-aromatic (π - π) interactions have been proposed and discussed (41, 42), as has charge transfer interactions (43). These interactions appear to contribute more and more to binding of coal structures as coals increase in rank and develop more aromaticity. Proton nmr relaxation experiments have differentiated between mobilities caused by heat and solvent swelling (44, 45) and confirm that non-covalent polar linkages become increasingly important with increasing rank. Computer modeling studies of proposed coal structures are consistent with this idea (46), and a qualitative representation of the types of bonding in coals as a function of rank has been proposed (47).

One important implication of this new understanding of how coals are held together is that it may be possible to convert solid coal into liquids using milder approaches than thermolysis, since these other interacting bonds are of much lower energy than covalent links. Use of milder conditions also has the potential of increasing the selectivity of the conversion of solid coal to lower molecular weight products, by avoiding the retrogressive reactions common to high temperature treatments. This area needs to be investigated further.

COAL LIQUEFACTION

Ten years ago, a number of coal hydroliquefaction processes were being developed, all based on a thermal conversion step, but differed in how hydrogen was provided: either from organic donors or molecular hydrogen, with or without catalysts (48), and these development programs were accompanied by relatively short-term laboratory research programs. During this same period, there were no process developments for pyrolysis and laboratory research was limited. Many of the hydroliquefaction process developments were completed by the mid 1980's, and provided the basis for substantial technological progress. For example, equipment performance was demonstrated on a large scale, and scale up issues were addressed. It was also demonstrated that coal liquids could be upgraded to transportation fuels using standard petroleum refining operations. Finally, successful methods of dealing with potentially harmful plant emissions were developed.

Major advances have since been made in the technology of coal hydroliquefaction in terms of

significantly increased yields of lighter, cleaner liquids, along with higher conversion selectivities and process efficiencies and costs. These improvements have come about largely by use of process staging and by having catalysts present in each stage. The scope of this progress has been reviewed in a recent U. S. Department of Energy needs assessment study (49). The current estimated cost of liquid transportation fuels produced from coal hydroliquefaction is in the range of US\$ 35 per barrel (50).

It must also be mentioned that fundamental research also progressed during this period. Notable among the recent discoveries are the proposal of new mechanisms for hydrogen donation, involving solvent assisted processes (51), and new bond breaking chemistry, such as the use of water to cleave refractory diaryl ether covalent bonds (52). There is also new interest in pyrolysis as a result of the discovery that the catalyzed hydrolysis of bituminous coals can lead to liquid yields approaching 60% (53).

The study mentioned above lists many research opportunities in priority order, and the interested reader is referred to it for greater detail (49). In the writer's opinion, numerous research opportunities exist to gain understanding of the catalysis mechanisms involved in coal hydroliquefaction (54). For example, it is generally recognized that it may be relatively easy to affect the course of reactions after the primary products are out of the coal particle; by this time, however, the product distribution may already be determined (49). If a catalyst could be found which could influence the product distribution of the primary products as they are formed, entirely different types and quantities of products might be formed. Better understanding of catalysis mechanisms could lead to catalysts which use hydrogen more efficiently, and even to modification of naturally occurring mineral matter to improve its catalytic properties (26).

A more in depth understanding of the chemistry occurring as coal is heated to reaction temperature is a fertile area for new research (49). This would include the building of kinetic models containing intrinsic rate expressions for conversion of individual components, and include bond breaking, cross-linking, hydrogen donation, mass transport, and effects of solvents. This understanding can lead to methods to mitigate the retrogressive, i.e., molecular weight growth, reactions which are believed to take place at and even below presently used coal conversion temperatures. This might lead to pretreatment methods which would allow much lower temperatures to be used for the conversion process, presumably resulting in higher thermal efficiencies and greater selectivities to lighter products than now achievable. Finally, a coal structure-reactivity model needs to be developed, based on the coupling of the knowledge base of coal structure and kinetic models of its reactivity.

FUTURE OUTLOOK

By its nature, coal is a highly complex organic material, and many different approaches are required to gain the necessary scientific understanding. It is not at all certain that all of those have been mentioned in the above. In this context, the writer cannot help but remark that ten years ago the accomplishments of today's bio-science and technology, and specifically their application in coal science were not even thought of. Also, many environmental issues have not only surfaced, but been placed in the scientific and political forefront in the past ten years. To be applied, new science must have associated with it answers to any environmental concerns connected with it. Thus it is apparent that new research in coal science must be multi-disciplinary, including not only the familiar organic,

inorganic, physical and analytical chemistry, and chemical and mechanical engineering, but also solid state-condensed matter physics, geology, biology, and environmental science. No doubt, ten years from now, there will be others. As with recent advances in other fields involving complex materials, the greatest chance of success will come as a result of interactions among people specializing in these disciplines. The writer believes that the time for coal science to make major advances has arrived, and awaits the contributions of the scientific community.

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