Application of X-Ray Photoelectron Spectroscopy to Coal Oxidation Kinetics

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Abstract

Several aspects of the oxidation kinetics of Illinois # 6 bituminous and Wyoming Powder River Basin subbituminous coal were quantified between 295 -398K. XPS was used to determine the changes in the amount of surface organic oxygen and provide an oxygen functional group distribution. GC analysis of the gas phase products and weight changes from TGA experiments were used to place the XPS results in the context of bulk oxidation. The oxidation of Illinois # 6 coal produced mostly solid oxidation products. The rate of increase exhibited Arrhenius behavior with an apparent activation energy of 11.4 kcal/mole. Oxidation of Wyoming Powder River Basin coal at 398K gave mainly gaseous products and a slightly faster total oxidation rate relative to Illinois #6 coal. The amount of oxidized organic sulfur determined by XPS can be used to evaluate the total extent of coal oxidation.

I. Introduction

Oxidation reactions of coal which occur in air near room temperature contribute to the self heating of coal and produce detrimental changes to many coal properties. Both solid and gaseous species are produced as oxidation products.(1) After oxidation many aspects of the solid coal have been investigated and several properties can be used to gauge the extent of oxidation. These include the determination of the changes in the amount of oxygen by difference, by neutron activation analysis(2) and by XPS analysis of the coal surface.(3,4) Relative changes in the properties of coal have also been used to measure oxidation. These include free swelling index,(5) Gieseler fluidity,(6,7) PH,(8) FTIR signatures(9) and changes in pyrolysis response.(10,11)

Despite the many available approaches it is very difficult to quantify the kinetics of low temperature oxidation, T < 350K. The total amount of solid oxidation products after several days near room temperature can be small.(12,13,23-25) There has been a greater number of oxidation studies performed at higher temperatures, T > 350K. The connection between high and low temperature oxidation reactivity is not well established and few have adopted a unified approach to characterize both solid and gaseous oxidation products.

We have quantified several aspects of the oxidation of Illinois # 6 coal and Powder River Basin coal between 295-398K. XPS was used to determine the changes in surface organic oxygen. GC analysis of gas phase products was carried out in conjunction with XPS measurements in order to provide a more complete description of the oxidation process. Thermal Gravimetric Analysis (TGA) results help place the XPS information in the context of bulk oxidation.

II. Experimental

Illinois # 6 coal and Powder River Basin coal were obtained from the Exxon Research and Engineering Company Baytown Texas coal sample library.[26] Upon receipt, the sealed consignment was transferred to a nitrogen drybox. 100-200 mesh cuts were prepared and stored in the drybox for later use.

XPS spectra were obtained with an ion pumped Vacuum Generators ESCALAB instrument using non-monochromatic MgKα radiation. The source was operated at 300W, 20ma, 15KV. A complete XPS analysis took approximately 4 hours. The coal samples were mounted to a metallic sample block by means of double-sided Scotch nonconducting tape. An energy correction was made due to sample charging based on the C(1S) peak at 284.8 (eV) and the unoxidized organic sulfur 2p peak at 164.0 (eV). Samples were introduced using the standard diffusion pumped VG ESCALAB fast entry air lock. As previously observed with other coal samples[3,4,27,28] the elemental composition of the sample remained nearly constant during the measurement period; however, longer-term exposure to the X-ray beam produced damage as evidenced by decreases in the initial amount of carboxyl carbon and by subsequent increased vulnerability to surface oxidation at ambient conditions. New samples were obtained for measurement at every point in the oxidation sequence.

Data acquisition and processing were by means of a VGS 2000 software package using multi-scan averaging. The spectra were obtained at 0.9 eV resolution. Elemental concentrations were obtained relative to carbon calculated from the areas of the XPS peaks corrected for atomic sensitivity. The sensitivity factors relative to C(1s) were determined from VG sensitivity tables and experimentally measured standards.

The organic composition of the starting coal derived from an XPS measurement was compared to a standard bulk determination. The comparison for Illinois #6 coal is shown in table I and for Powder River Basin coal in table II. Both coals have XPS derived organic nitrogen and organic sulfur values in very good agreement with bulk values. The amount of surface organic oxygen also compares favorably with bulk derived values. The amount of organic oxygen was derived from XPS results by taking into account inorganic contributions. The amount of oxygen associated with silicon and aluminum were taken as SiO_2 and $AlO_{1.5}$. With recognition of the surface oxidation of pyrite, the amount of oxygen associated with the inorganic sulfate (2p) signal was taken as SO_4. The difference between the pyrite iron (2p) signal and sulfate sulfur (2p) signal was associated with oxygen as $FeO_{1.5}$.

While there is little inorganic sulfur in Powder River Basin coal it is known from bulk analysis that nearly $^1/_3$ of the total sulfur in this Illinois # 6 coal exists as inorganic forms with the majority as pyrite. Table I also shows that there is a large discrepancy between the surface and bulk values of pyritic and sulfate sulfur for Illinois # 6 coal. The value for surface pyritic sulfur is based on the absence of the pyritic iron (2p) signal. These differences are most likely a result of the surface oxidation of pyrite. The XPS sulfur spectrum from I # 6 coal showed a sulfur 2p peak centered about 171.3 eV. This peak was substantially reduced by a brief water wash at room temperature. The broad peak is interpreted to arise from ferrous and ferric sulfates. The reactivity of coal following the water wash was

identical to the untreated coal. The sulfate peak and the associated iron (2p) signal is shifted by ~-1.5 eV to higher binding energy than the reported literature value.[29,30] This discrepancy is most likely due to a slightly enhanced sample charging of these inorganic components in our samples. We could not observe the iron (2p) signal due to iron pyrite.

We deconvoluted the sulfur (2p) spectrum using a single peak to represent the unresolved 2p spin doublet. We used a mixed Gaussian-Lorentzian line shape and a peak width at half maximum of 2.60 eV for each sulfur species. The organic part of the sulfur 2p spectrum showed two main peaks that occur at 164.0 eV and 168.3 eV. The 164.0 eV peak is characteristic of a variety of unoxidized organic species which includes thiophenes, sulfides and mercaptans. While oxidation to produce sulfoxides (166.0 eV)[31] and sulfonic acid (169.2 eV)[32] will contribute to the development of the main 168.3 eV sulphur (2p) peak, the dominant oxidation products appear as sulfones(168.0).[31-34]

XPS difference curves were made using the C(1s) lines whose areas were normalized to the value of the clean starting spectrum. The following methodology was used to deconvolute the positive peak in each carbon (1s) difference spectrum. We use a mixed Gaussian-Lorentzian line shape and a peak width of 1.80 eV at half maximum for each peak. Four peaks are used in the deconvolution that occur at 286.3 eV, 287.5 eV, 289.0 eV, and 285.2 eV. The 286.3 eV represents carbon bound to a single oxygen bond (i.e. ethers, hydroxyls, hydroperoxides), the 289.5 eV peak to carbon bound to two oxygen bonds (i.e. carbonyl) and the 289.0 eV peak to carbon bound to three oxygen bonds (i.e. carboxyl).[35-40] The intensity of the 285.2 eV peak is fixed to the 289.0 eV peak intensity and represents the carbon adjacent to carboxyl carbon and is referred to as a β peak.

Oxidation experiments for XPS kinetic studies were done in air with <25% relative humidity. Oxidation experiments with gas phase analysis were done in a quartz reactor contained within a furnace. The outlet of the dead-ended reactor was connected to a Bellows pump and a recirculation loop. A gas sample could be taken from the recirculation loop for GC analysis via an evacuated 2 cc gas sample valve. The gas chromatograph used for product analysis was a Hewlett Packard 5840 equipped with a thermal conductivity and a FID detector. The separation column was Porapack Q. Samples were introduced into the quartz reactor vessel and evacuated to $1x10^{-3}$ Torr. The sample size was 100 mg. The reactor volume was then pressurized to 200 kPa with helium. Prior to oxidation the fresh coal samples were heated at the appropriate reaction temperature in He for 18 hours; thereafter the amount of thermal decomposition products were negligible compared to those produced in oxidizing environments. The samples were evacuated to $1x10^{-3}$ Torr before being pressurized to 200 kPa with the reactant gas mixture which consisted of ~6.7% oxygen in Helium. Periodic evacuation and pressurization with new reactant gas was done in order to avoid the build-up of excessive amounts of products and to keep the reactant O_2 partial pressure nearly constant. The closed recirculation reactor arrangement enabled the build-up of products over

long times. The loss of the portion of product gas due to gas sampling was corrected in the product analysis. TGA experiments were done by flowing dry air in a Dupont model 951 thermogravimetric analyzer.

III. Results

We have monitored the increases in the amount of organic oxygen as a function of time and temperature. The results for Illinois # 6 coal are shown in Figures 1 and 2. The curve through the data points at each different temperature is based on a theoretical first order expression with a common asymptote corresponding to 0.085 maximum surface $^{O}/_{C}$ atom ratio increase, or in other words an increase of 8.5 oxygens per 100 carbons. An Arrhenius plot using the XPS derived rate information is shown in Figure 3. The line through the data corresponds to an activation energy of 11.4 kcal/mole and pre-exponential of 4.9×10^{6} $(^{O}/_{C})$ $(day)^{-1}$.

We have measured the corresponding changes in weight as a function of time up to 7 days at 398K. A comparison of these results with the XPS data is shown in figure 4. The same theoretical first order curve is used to fit the TGA data as the XPS data but with an asymptote of 5.0 wt.% $^{O}/C$ increase. The same expression provides an excellent fit to the TGA data.

We have measured the changes in gas composition which occur under similiar experimental conditions following oxidation for 2 days at 398K. Table III shows the changes in the number of gaseous molecules expressed relative to carbon. The Illinois # 6 coal contains 70.87 wt% carbon. With this information we have determined the wt% increase and oxygen atom ratio increase relative to carbon expected on the basis of GC data. We compare the results in Table IV to other experimental information. There is good agreement between the GC and TGA results for the wt% increase. IR analysis of the gas phase shows the presence of a small amount of CO. We did not quantify the weight loss due to CO evolution. The total hydrocarbon production is three orders of magnitude below the levels of CO_2 and H_2O and therefore was not considered. The increase in the surface oxygen concentration is 1.4 times greater than the bulk oxygen increase predicted from an oxygen balance using gas phase data. The fact that the surface enhancement is actually rather small and the similarity of the TGA and XPS kinetics imply that oxidation occurs throughout the bulk and that the surface oxidation process is a reflection of the bulk phenomenon.

The changes that occur in the XPS Carbon (1s) line shape can be related to the changes in the nature of the oxygen functional groups. The use of a difference spectrum facilitates the observation of the changes induced by oxidation. Examples of a C (1s) difference spectrum are found in figure 5 and were obtained after air oxidation of Illinois # 6 coal at 398K. The negative peak in each spectrum occurs near 284.7 eV. A decrease in intensity at this energy is indicative of a decrease in the amount of unoxidized carbon atoms. The presence of positive peaks at higher binding energies is associated with increases in the amount of oxygen functionalities. The fact that the positive going features are different in each spectrum indicates that the functional group distribution changes during the course of oxidation at 398K. Table V

shows the increases in the number of functional groups following oxidation. The information was obtained from the results of the deconvolution of the C (1s) spectrum, the deconvolution of the sulfur (2p) spectrum and the increase of total organic oxygen. Increases in the amount of oxygen associated with carbonyl and carboxyl types are obtained directly from the C (1s) difference spectrum. The amount of oxygen associated with sulfur species comes from the intensity increase in the sulfur (2p) sulfone peak. The amount of oxygen associated with groups bound to carbon by a single bond (i.e. ether, hydroxyl and hydroperoxides etc.) is obtained from the difference between the amount of total organic oxygen and the amount of oxygen associated with carboxyl, carbonyl, and oxidized sulfur.

After approximately 10 days at 398K, the oxygen concentration reaches a plateau. There are, however, changes that happen at longer oxidation times. We find that the carboxyl and oxidized organic sulfur concentration increases while that of the other types decline. Analysis of the gas phase changes, contained in table III, confirm that there is little change in the bulk oxygen to carbon ratio over the same period. The results also show that the Illinois coal continues to participate in oxidation reactions at long times; however, O_2 is consumed at a much slower rate. CO_2 and H_2O are the main gaseous oxidation products. While there are significant changes in the surface oxygen functional group distribution, the total amount of bulk organic oxygen remains nearly constant.

Following oxidation at 294K for 170 days we find that the majority of oxygen increase is associated with the formation of carboxyl structures. Oxidized surfaces produced at slightly higher temperatures and shorter times also show that increases in carboxyl oxygen is responsible for the majority of oxygen increase.

We have used XPS to monitor the changes in the amount of organic oxygen after oxidation of Powder River Basin coal between 294K and 398K, Figure 6. There is very little increase in oxygen concentration even after 170 days at 298K. There is also very little change in the oxygen functional group distribution. Higher temperature oxidation resulted in the build-up of surface products but at much lower levels than that previously observed with Illinois # 6 coal. The changes in surface oxygen concentration were not amenable to a simple kinetic description. The lines in Figure 6 represent a linear connection of data points.

Despite the small or negligible increases in total organic oxygen near room temperature, the relative increase in the amount of oxidized organic sulfur can be substantial. Figure 7 shows the sulfur 2p spectrum of fresh Powder River Basin coal and a spectrum following air oxidation at 295K. The 164 eV peak is due to unoxidized organic sulfur. A peak develops near 168 eV following oxidation and is attributed to the presence of oxidized organic sulfur.

Analysis of the changes in the gas phase composition, Table VI, show that the oxidation of Powder River Basin coal is dominated by gaseous products. These results also support the XPS finding that there are only slight changes in the amount of organic oxygen during the initial oxidation period at 398K.

Discussion

We have found that the oxidation of Illinois # 6 coal produces mainly solid oxidation products. A single kinetic expression was used to model the surface oxidation kinetics between 398K and 295K. TGA and GC gas phase analysis showed that the surface oxidation kinetics reflected bulk oxidation behavior.

Recent FTIR work on thin sections of Illinois # 6 coal indicated the presence of two kinetically distinct oxidative reaction sequences.[23-25] A slow oxidation process was extensively characterized at 393K but was difficult to measure below 343K.[23-25] A fast oxidation process was found to occur over two days at 295K but was complete after 30 minutes at 343K. This reaction is believed to result in a very small net decrease in the amount of organic oxygen. Both the fast and slow oxidation processes can contribute to the observed oxidation response of coal. We were unable to identify the fast oxidation process using XPS. This failure places an upper limit of 0.01 O/C change associated with this process. In another study[12] of Illinois # 6 coal, an increase of 2.4 oxygens per 100 carbons was observed after oxidation for 56 days under external ambient conditions. Nonalkylatable oxygen was the main product, presumably ether oxygen. In the present study near room temperature carboxyl was the main oxygen surface species.

The rate of increase of total oxidation products of Illinois # 6 coal exhibits Arrhenius behavior with an apparent activation energy of 11.4 kcal/mole. Non-isothermal studies[18] of bituminous and subbituminous oxidation, at a heating schedule of 5°C min^{-1}, demonstrate Arrhenius behavior for O_2 consumption above 413K. The apparent activation energy is between 10.0 and 13.2 kcal/mole. Lower temperature oxidation was characterized by much lower activation energies attributed to the influences of diffusion-controlled processes or to physical absorption.[18] A study[22] of subbituminous coal oxidation kinetics demonstrated Arrhenius behavior between 303K-343K with activation energies between 15 to 20 kcal/mole. Apparent global activation activation energies between 12.6 and 24.5 kcal/mole were found based on calorimetric data for a variety of coals of different rank.[46] The energies were determined from data obtained between 373K-423K so as to minimize contributions due to the heat of wetting.

It is generally believed that the oxidation of coal proceeds by way of a free radical oxidation mechanism.[12,14,16-18,21,23-25,41-45] E.S.R. work provides experimental evidence for the changes in free radical population during coal oxidation.[41,42] The variety of oxygen functionalities that we have observed can be accounted for within the framework of a free radical mechanism.[14,16,44,45] It is known that mineral oxidation reactions occur simultaneously with organic oxidation in coal.[6,29,47-53] The catalytic participation of inorganic components toward low temperature organic oxidation has been considered[52,53] but not confirmed. Low temperature inorganic reactions are generally regarded as separate processes. Nevertheless, the presence of inorganic matter complicates the interpretation of the oxidation kinetics based solely on gas phase oxygen uptake or heat release.

Most agree that a radical chain oxidation mechanism, involving decomposition of hydroperoxides, explains coal oxidation behavior at moderate temperatures. The dominant reactions that take place near room temperature are less certain. We find that our XPS results fit a single kinetic expression. The oxygen functional group distribution observed at 295K after long times is similiar to that found after shorter oxidation periods at 398K. We therefore conclude that under our experimental conditions the same basic chemistry occurs over the temperature range. Consideration of the errors associated with the XPS measurement enables us to place an upper limit of 0.01 $^{O}/_{C}$ surface increase that can be associated with faster oxidation processes.

The oxidation behavior of Illinois # 6 coal changes at long times at 398K. The surface and bulk oxygen concentration remains nearly constant but CO_2 and H_2O are still being produced. The total oxidation rate is much slower than the well defined kinetic process found at earlier times. The surface functional group distribution changes. The amount of oxidized organic sulfur continues to rise along with carboxyl oxygen, while other species decline.

We have made a limited study of Powder River Basin Coal. The initial oxidation at 398K gives mainly gaseous products. The total extent of oxidation after 2 days is 1.3 times that found with Illinois # 6 coal. We have monitored the changes in the surface composition at lower temperatures and find only small changes in the amount of organic oxygen. An earlier study indicated a high selectivity toward gaseous products for a low rank coal.[1] Previous work on this coal[13] at room temperature indicated that the change in bulk oxygen content was small. Chemical decarboxylation was offset by increases in the amount of nonalkylatable organic oxygen. Despite the small changes in total organic oxygen, we have found a substantial relative increase in the amount of oxidized organic sulfur.

Conclusions

1) A single kinetic expression can be used to describe the surface oxidation of Illinois # 6 coal from 398K to 295K.

2) The surface oxidation kinetics observed at 398K reflects bulk oxidation behavior. We were unable to identify any faster oxidation process for Illinos # 6 coal. This failure places an upper limit of 0.01 O/C on the amount of surface oxygen change that can be associated with faster oxidation processes.

3) A much slower oxidation process was identified at 398K after reacting Illinois # 6 coal for long times. The total surface oxygen concentration remains nearly constant but the oxygen functional group distribution shifts towards carboxyl and oxidized sulfur. CO_2 is the main gaseous product.

4) The initial oxidation of Powder River Basin coal at 398K produces mainly gas. The total oxidation after 2 days is 1.3 times greater than observed with Illinois # 6 coal.

5) There is a significant relative increase in the amount of oxidized organic sulfur during 295K oxidation of Powder River Basin coal. The total amount of organic oxygen remains almost constant.

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Table I

Atom ratio relative to carbon x 100	I #6 coal Fresh XPS	I #6 coal Fresh Bulk Analysis	I #6 coal Water Wash XPS
Organic Sulfur	1.68	1.45	1.65
Sulfate Sulfur	1.19	0.02	0.32
Pyritic Sulfur	0.00	0.62	0.00
Organic Oxygen	10.3	9.9	11.6
Nitrogen	1.4	1.4	1.4

Table II

Atom ratio relative to carbon x 100	Powder River Basin Fresh XPS	Powder River Basin Fresh Bulk Analysis
Organic Sulfur	0.42	0.47
Sulfate Sulfur	0.03	0.027
Pyritic Sulfur	0.00	0.005
Organic Oxygen	19.3	20.1
Nitrogen	1.1	1.0

Table III

Changes in the gas composition after oxidation of Illinois #6 coal at 398K

Time	2 Days	13 Days	48 Days
O_2/carbon (x100)	-1.74	-5.48	-8.73
CO_2/carbon (x100)	0.33	1.68	4.46
H_2O/carbon (x100)	0.16	0.45	1.06
Change in Bulk oxygen/carbon (x100) based on GC data	2.7	7.1	6.9

Table IV

Comparison of the Changes found after oxidation of I #6 coal at 398K for 2 days

	Wt% Increase	Oxygen atom ratio increase relative to carbon x100
From GC Experiment	2.3	2.7
From TGA Experiment	2.7	---
From XPS Experiment	---	3.9

Table V

Amount of oxygen increase per 100 carbons Associated with Various Functional Types Following Air oxidation of Illinois #6 coal

Oxidation Temperature	Oxidation Time	Total Organic Oxygen increase	Carboxyl	Oxidized Sulfur	Carbonyl	Ether hydro-peroxide Alcohol
295K	170 days	3.8	2.1	0.3	0.7	0.7
398K	15 days	8.2	4.2	0.7	2.6	0.7
398K	41 days	8.1	4.9	1.0	1.4	0.8
398K	54 days	8.6	6.4	1.3	0.4	0.5

Table VI

Changes in the gas composition after oxidation of Powder River Basin coal at 398K

Time	2 Days	13 Days
O_2/carbon (x100)	-2.32	-6.33
CO_2/carbon (x100)	2.10	5.37
H_2O/carbon (x100	0.47	1.45
Change in bulk oxygen/carbon (x100) based on GC data	-0.03	0.47

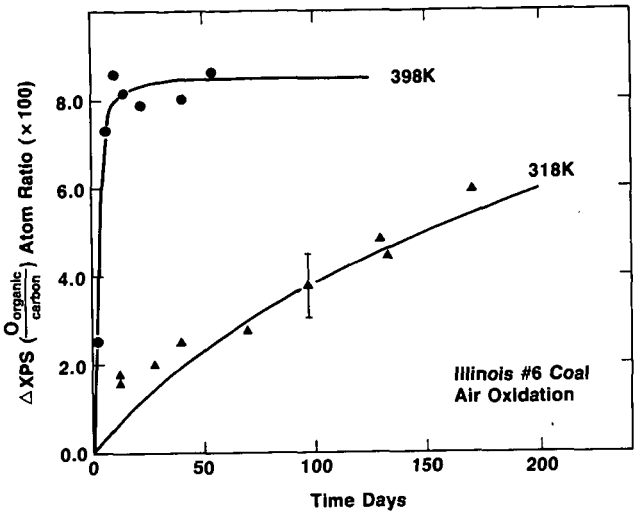

Figure 1. Change in the organic oxygen (1s) to carbon (1s) XPS atom ratio as a function of exposure time at 398K and 318K in air for Illinois # 6 coal

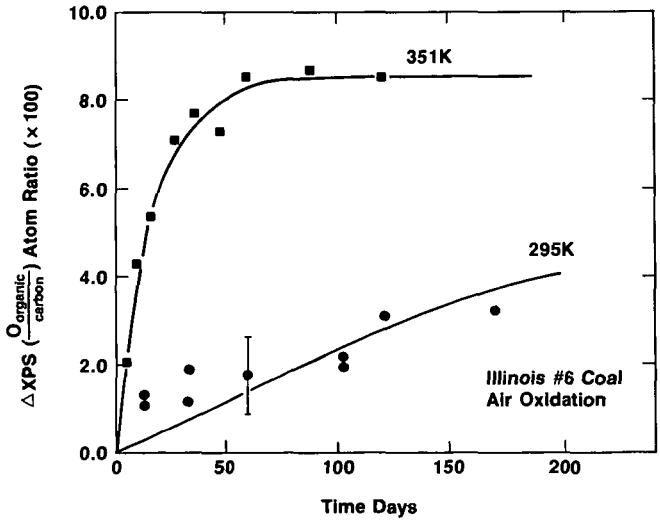

Figure 2. Change in the organic oxygen (1s) to carbon (1s) XPS atom ratio as a function of exposure time at 351K and 295K in air for Illinois # 6 coal

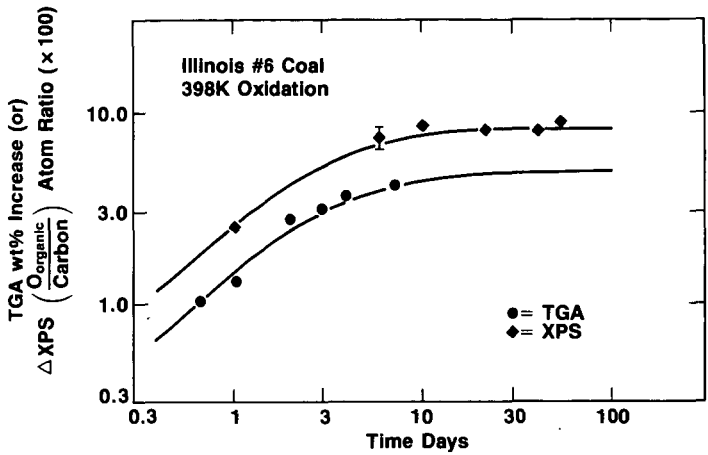

Figure 3. Comparison of the TGA wt% increase and the XPS oxygen (1s) to carbon (1s) atom ratio increase as a function time at 398K for Illinois # 6 coal

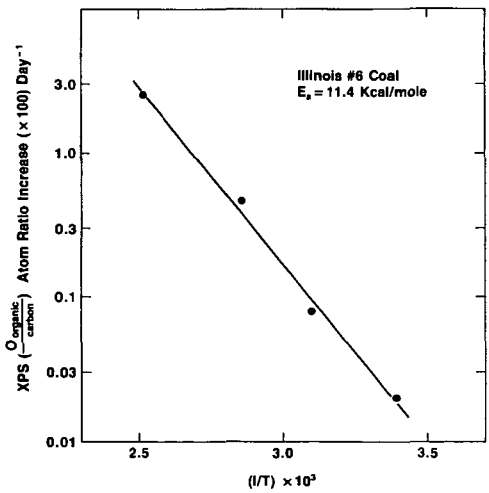

Figure 4. Arrhenius plot of the initial oxidation rate of Illinois # 6 coal based on the XPS data using a first order fit and common maximum $^{O}/_{C}$ increase of 0.085

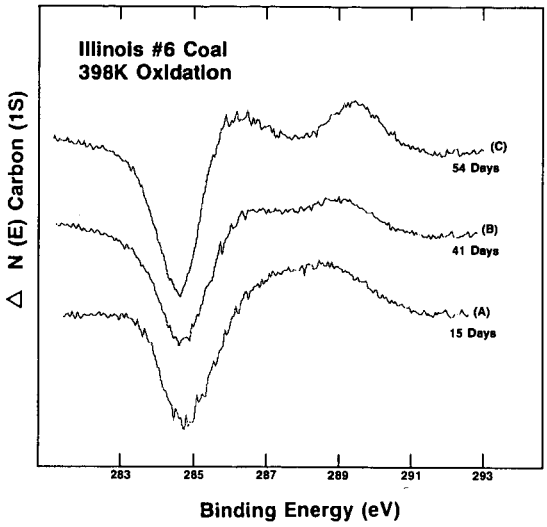

Figure 5. Change in the C (1s) spectrum following oxidation of Illinois # 6 coal for different times at 398K

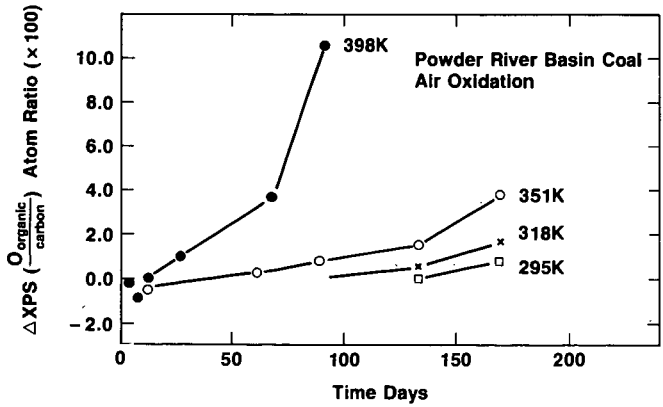

Figure 6. Changes in the Powder River Basin coal organic oxygen (1s) to carbon (1s) atom ratio as a function of exposure time in air at different temperatures.

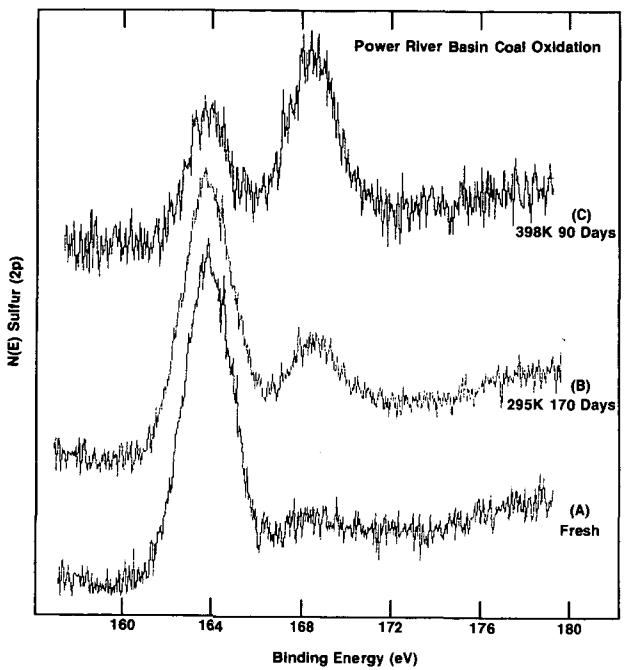

Figure 7. XPS sulfur (2P) spectrum from

A) fresh Powder River Basin coal
B) after oxidation for 170 days at 295K
C) after oxidation for 90 days at 398K