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***Weathering effects on the structure
and reactivity of US coals: Final
report, July 15, 1984-July 14, 1987***

Meuzelaar, H.L.C.; Hill, G.R.; Yun, Yongseung; Jakab, E.;
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1987

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Department of Energy

entitled:

WEATHERING EFFECTS ON THE STRUCTURE AND REACTIVITY OF U.S. COALS

Grant No. DE-FG22-84PC70798

Project Period: July 15, 1984 - July 14, 1987

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EXECUTIVE SUMMARY

BACKGROUND

This report covers the work performed from July 1984 to July 1987 under the project entitled "Weathering Effects on Structure and Reactivity of U.S. Coals" (grant number DE-FG22-84PC70798). The main objectives of the study were to investigate the structural changes in coal during the weathering process as well as to develop a simple, reliable weathering index, which can monitor indirectly the weathering-induced changes in physical and chemical properties, using Argonne Premium Coal Sample Program (PCSP) coals. Since all eight PCSP coals were not available in the first year of the study, three non-PCSP coals were also used as samples for this study.

Although there have been numerous publications on structure and reactivity of coal, most data reported in the literature thus far have been obtained on coal samples of uncertain weathering status and therefore need to be interpreted with great caution. Weathering has a profound effect on many important coal properties such as heating value, caking characteristics, acidity, flotability and reactivity in liquefaction, combustion and gasification processes. The objective of developing a weathering index is to predict these coal property changes due to weathering without resorting to real-time measurements or pilot plant runs.

This report is comprised of four main chapters: I. Structural Changes due to Weathering; II. Material Balance in the Weathering Process; III. Development of a Reliable Weathering Index; and IV. Proposed Weathering Mechanisms. In the introduction to each chapter, the available literature has been summarized in order to document the current knowledge on the topic.

A battery of sophisticated analytical tools and techniques was employed during this study. Pyrolysis mass spectrometry in time-integrated, as well as in time-resolved modes with computer-aided data analysis techniques (such as factor and discriminant analysis), gas chromatography, thermogravimetry/mass spectrometry and solvent extraction were used for determining the role of oxygen during the weathering process. Pyrolysis mass spectrometry, Free Swelling Index and a novel slurry pH technique were employed as weathering indicators.

The main findings and conclusions are summarized in the following paragraphs.

STRUCTURAL CHANGES DUE TO WEATHERING

(Low Voltage Py-MS Experiments)

Low voltage pyrolysis mass spectra of artificially weathered (100°C for 170-212 hrs. in air) coals show that weathering-induced changes in pyrolysis patterns of subbituminous coals are dominated by a decreased yield of phenols and dihydroxybenzenes as opposed to decreased yields of phenols and naphthalenes from high volatile bituminous coals.

Comparison of weathering-induced structural changes in U.S. coals under controlled laboratory conditions (maximally 10 days at 100°C in air), indicates that rank-related differences in weathering behavior dominate over differences in depositional environment.

Subtracting spectra of the weathered coal samples from the corresponding fresh samples reveals that aromatic components of coal pyrolyzates have decreased markedly, whereas aliphatic signals thought to be primarily observed from alginite and cutinite appear to have remained constant.

When coal is weathered in air at 100°C for 170-212 hrs, polar, low molecular weight compounds such as CO^+ , CO_2^+ , CH_3COOH^+ increase and also the retention tendency of methanol solvent increases. The increased methanol retention is believed to be due to increased chemisorption on polar moieties in the weathered coal.

The loss of grafted (or trapped) aromatic molecules during weathering processes alone cannot fully explain the observed decrease in aromatic and hydroxy aromatic coal pyrolysis products. Apparently, some aromatic rings are destroyed by the oxidation process in spite of the relatively low temperature (100°C) used, resulting in the formation of the short chain aliphatic acids and ketones.

Resinite and semifusinite maceral concentrates undergo more severe oxidative changes at 100°C in air than vitrinite and sporinite concentrates. The sporinite concentrate shows the least severe weathering-induced degradation.

Structural changes induced by low temperature (100°C) air oxidation were shown to be detectable by Py-MS techniques after only 1 or 2 days.

(Time-Resolved Py-MS Experiments)

Time-resolved Py-MS is a very promising technique for obtaining chemical information on thermal decomposition mechanisms in fresh and weathered coals. It has all the advantages of vacuum micropyrolysis techniques, such as reduced mass transfer problems and lower probability of secondary reactions.

Several different stages of decomposition can be distinguished during the short (10 seconds) pyrolysis time employed in time-resolved Py-MS therefore thermal degradation mechanisms and kinetics can be studied in greater detail than by conventional, time-integrated Py-MS techniques.

The first decomposition step occurs around 300°C and is characterized by the evaporation of "mobile phase" components such as alkylnaphthalenes and alkyltetralins as well as the degradation of labile functional groups such as carboxylic acid moieties.

The second, main decomposition ("bulk pyrolysis") step is observed between 500° and 600°C.

The third stage consists of char forming reactions which occur at the equilibrium temperature of the ferromagnetic wire (610°C) during the final seconds of the pyrolysis process (pyrolysis of the network phase). These reactions are characterized by the evolution of small, stable pyrolysis products and aromatic hydrocarbon moieties.

Weathering influences all three decomposition steps. Low temperature yields of thermally extractable components (alkylnaphthalenes and alkyltetralins) are markedly reduced, probably through "grafting" reactions with the network phase. Yields of small, oxygen containing molecules, on the contrary, are increased in weathered coal. Bulk pyrolysis yields of Hiawatha coal decrease by 10-20%. Especially phenolic components show decreased abundances, possibly as a result of ether bridge formation with network components. Finally, char yields tend to increase slightly, as confirmed by thermogravimetry experiments.

Time-resolved desorption/pyrolysis curves of CH_3OH^+ (m/z 32) indicate differences in polarity of the three fresh coals as well as increased polarity upon weathering in the originally less polar Hiawatha coal. The increased abundance of polar groups in the weathered coals is also shown by the increased yield of polar compounds at lower temperatures, e.g., CH_3COOH^+ (m/z 60) and CO_2^+ (m/z 44).

(TG/MS Results Experiments)

The temperature of maximum rate of weight loss occurs at 520°C for Upper Freeport coal (mvb) and at 470°C for Anderson coal (subbituminous C).

The maximum rate of weight loss decreases significantly with the degree of weathering. This trend appears to be due to two separate weathering effects; namely (1) decreased total volatile matter yield, consequently an increased char yield, and (2) a broader distribution of activation energies in weathered coal.

Evolution profiles of each mass with temperature show the dramatic effect of weathering, confirming that kinetics in devolatilization and pyrolysis between fresh and weathered coals are quite different. Especially the evolution profile of carbon dioxide (m/z 44) shows significant formation of carboxylic functional groups as weathering proceeds.

TG/MS analyses indicate that both aromatic and aliphatic moieties in coal decrease with the degree of weathering. This trend was more profound in Upper Freeport coal (mvb) than Anderson coal (subbituminous).

The TG/MS technique is a valuable tool for investigating the kinetics of coal pyrolysis and combustion. More elaborate TG/MS studies are needed to examine the effect of weathering on kinetics and, thus, to determine the effect on variables in the real processes, such as combustion, liquefaction and gasification. This kind of study will give the sufficient information for the prevention of energy loss during coal usage from weathering.

(Isotope-Labelled Oxygen Weathering Experiments)

Isotopically (^{18}O) labeled oxygen was used to investigate the fate of ambient oxygen during low temperature (80°C) oxidation of a Wyoming lignite (Anderson). More than 50% of the CO_2 produced during weathering was found to contain one or two ^{18}O labeled oxygen atoms.

Oxygen from the ambient air participates in the formation of structural moieties producing CO_2 , CH_3COOH , and dihydroxybenzenes during subsequent pyrolysis. Py-MS data of weathered coal samples clearly establish that m/z 48 ($\text{HC}^{16}\text{O}^{18}\text{OH}$), m/z 112 and 126 (dihydroxybenzenes with one ^{18}O) are derived from oxygen containing moieties formed during low temperature oxidation with air.

Time-resolved pyrolysis MS studies of coals "weathered" in isotopically labeled atmospheric environments show great promise for elucidating the mechanisms and kinetics of highly complex weathering reactions in coals.

(Changes in Chemical Composition)

Upper Freeport Seam coal loses only 0.48% of its calorific value, but the volatile matter/fixed carbon ratio decreased from 0.48 to 0.38 during weathering at 100°C for 10 days. Since the measurement of oxygen consumption indicates only low reaction rates, the drastic changes in VM/FC ratio are thought to be due to the loss of "mobile phase" molecules by "grafting" reactions with the "network phase".

The reactivity of coals under oxidative conditions is indicated by the pronounced loss of calorific value, especially in the two lower rank coals (Anderson and Adaville #6). In contrast, the volatile matter/fixed carbon ratio is most strongly decreased in the weathered high volatile A bituminous Hiawatha coal.

Reaction rates are faster at the beginning of the weathering process as established by oxygen consumption measurements. This was also confirmed by the developed weathering index (FSI, slurry pH).

The higher the rank the lower the reactivity towards oxygen on the basis of oxygen uptake and calorific value loss.

After 10 days at 100°C in air, vacuum pyrolysis yields in Upper Freeport coal (as measured by Py-MS) were down 10%. Comparable losses were observed for Volatile Matter (3.4%) and for pyridine extractables (4.6%).

(Oxygen Mass Balance)

Coal weathering is accompanied by complex weight changes. Using control runs under N₂ the effect of moisture loss can be distinguished from that of weight gain due to the oxidation. However, measuring weight gain alone is not satisfactory for monitoring the reactivity of coals towards oxygen because of the concurrent loss of compounds (e.g. CO, CO₂, and H₂O) during weathering.

Complex mixtures of organic materials evolved with the gas even though the weathering temperature was only 100°C. Especially noteworthy was the fact that Wyodak coal produced relatively large quantities of sesquiterpenoids in the flue gas.

Dominant components accompanying the flue gas at 100°C were benzenes and alkenes as well as naphthalenes for the medium volatile bituminous Upper Freeport and high volatile bituminous Hiawatha coals. However, subbituminous Adaville coal produced phenols, alkenes, and ketones, whereas Wyodak subbituminous coal produced significant quantities of alicyclic sesquiterpenoids.

DEVELOPMENT OF A RELIABLE WEATHERING INDEX

The Free Swelling Index was not as sensitive to the initial stage of weathering as discriminant scores from Py-MS spectra and the slurry pH.

A simple pH titration method based on "rehydrating" coal slurries with water at 150°C was proven to be a successful way of monitoring weathering effects in all 8 Argonne National Laboratory Premium Coal Sample Program coals. For lower rank (e.g., subbituminous, lignite) coals, a direct measurement of slurry pH was good enough to used as a weathering index, which shows more than 2 pH units difference between fresh and 8 days weathered coal at 100°C.

As coal rank increases, the starting pH as well as the slope and shape of the titration curve (after rehydrating the coal slurry) change, as expected. Lower rank coals produce higher concentrations of acidic products.

The four high volatile bituminous coals from among PCSP coals showed different titration curves. This suggests that the surface characteristics of these coals are different as a result of differences in the original depositional environment.

Among the variables influencing the weathering in coal, temperature shows the most significant effect on the degree of weathering, whereas humidity level of gas atmosphere does not have any noticeable influence on the degree of weathering in terms of FSI and the slurry pH.

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I. STRUCTURAL CHANGES DUE TO WEATHERING

I.1. INTRODUCTION

According to recent views on coal structure, the organic matrix consists of a three-dimensional network of cross-linked macromolecules and relatively small molecules trapped within the macromolecular network [1,2]. Among heteroatoms, oxygen is the major constituent occurring in coal. Information about oxygen forms can be obtained by measuring the concentrations of the different types of oxygen-containing functional groups. Since the total oxygen content of coal is increased upon weathering, it is assumed that the distribution of oxygen is altered due to the formation of specific functional groups.

I.1.A. The Distribution of Absorbed Oxygen in Functional Groups

The early stages of oxidation are characterized by the formation of peroxides [3]. It is generally thought that the decomposition of peroxides, perhaps around 70°C [4], produces stable oxygen bearing functional groups in coal and volatiles such as water, carbon oxides, etc. At higher temperatures, the latter process is speeded up and only stable oxygen-containing functional groups are detected.

Due to the formation of new oxygen-containing functional groups the polarity of the coals increases. The changes in the polarity of coals can be studied by measuring the gas absorption properties. Weathered coals show decreased methane absorption but the absorption capacity with regard to carbon dioxide increases [5]. Increased methanol retention was observed in weathered samples [6] after the excess of methanol had been removed by evacuation. Apparently, the oxidized coal shows increased chemisorption of the methanol due to the increased polarity. Naturally weathered samples are reported as having higher moisture content than fresh coals [7] because advanced oxidation converts the coal to a more hydrophilic material.

Some of the organically bound oxygen in coal has a more or less pronounced acidic character. The formation of acidic groups can be detected by measuring the change in the acidity of a coal sample during the weathering process. Since the coal can not be dissolved without disrupting its cross-linked structure, the acidity of coal has to be measured in a slurry. Gray *et al.* have observed [8] that the slurry pH of the samples taken from the outcrop was about 5.5, whereas samples from freshly mined surfaces showed a pH around 7. The pH of the coal slurry decreased gradually as the distance from the freshly mined surface increased. Hill *et al.* [9] have reported a similar change in pH during the storage of subbituminous coals. Brooks and Maher [10] determined the acidity of several coals by titration in anhydrous ethylene diamine. The majority of titration curves showed two inflections, apparently due to the different strengths of acidic groups present in coal. Although substantial changes were not detected in coal oxidized at ambient temperature, a steady increase in acidity was observed for samples exposed to air at 105°C for several days.

Intensively weathered coals show a strongly acidic character due to the formation of humic acids [7,11]. Humic acids are chemically ill-defined complex mixtures with a wide molecular size range that are soluble in strong alkali solutions. They appear to be produced by oxidative cleavage of the "coal molecule" under severe conditions of weathering. Alkali-extraction has been proposed [12] as a reliable test method for detecting naturally oxidized coal in coking coal blends.

Several analytical techniques were developed for quantitative assessment of oxygen bearing functional groups. Wet chemical methods were reviewed by van Krevelen [13]. Recently, a compilation of methods for functional group analysis was made by Attar and Hendrickson [14]. Given summarized the results of wet chemical and instrumental analytical techniques on the functional group distribution in coal [1].

Although the reproducibility can be enhanced by thorough grinding and the use of long reaction periods, quantitative analysis of functional groups using selective reagents is a difficult task. In spite of the difficulties, several authors could detect changes in the quantity of functional groups upon weathering. However, the results sometimes contradict each other. As discussed above, the naturally weathered samples contain higher amounts of humic acids. It is in agreement with the results of functional group determinations that carboxylate and carboxylic acid contents decrease with increasing depth from the outcrop of the coal seam [15].

The less weathered coals prepared under laboratory conditions were reported to show varying changes in oxygen-containing groups due to the large variety of coals used and the different conditions of oxidation. Oxidation of a medium volatile and of a high volatile bituminous coal at 85°C did not produce a change in carbonylic group content [16]. Liotta established [17] that neither carbonylic nor acidic groups (COOH and OH) were formed in a bituminous coal oxidized at ambient temperature. It was concluded that ambient air oxidation leads to the formation of ether linkages only.

In contrast with this finding, however, several authors established that carboxylic, carbonylic and hydroxylic groups are all produced upon weathering [18, 19]. With increasing oxidation temperature the amount of carboxylic groups increases primarily [19, 20], although an increase in carbonylic content is generally observed as well [18, 20]. A considerable fraction of the oxygen taken up appears in unreactive functional groups, i.e., in oxygen-containing moieties other than carboxylic, carbonylic or hydroxylic groups [21-23]. It is likely that ether groups represent a significant portion of the unreactive moieties formed from hydroxylic groups present in coal or produced during weathering. Assuming the occurrence of two competing reactions (formation vs. reaction of hydroxylic groups) it can be explained that the amount of hydroxylic groups is either increased [18, 20] or decreased [22-24] depending upon the particular coal and its weathering conditions.

Although the total amount of oxygen added to functional groups upon oxidation increases with decreasing rank, Marinov detected similar tendencies in the variation of functional groups with oxidation for three coals of widely different rank [25]. On the other hand, Berkowitz et al.

[26] studied bituminous coals of similar rank and concluded that oxidation of Carboniferous bituminous coals leads to the formation of acidic functional groups (OH and COOH), whereas the younger Cretaceous coals develop carbonylic functional groups to a greater extent.

Among the more sophisticated instrumental techniques, infrared spectroscopy is especially suitable for determining the functional groups present in coal [27]. Nevertheless, detection of the relatively small changes occurring during weathering is not an easy task by conventional IR spectroscopic techniques. Naturally weathered samples [15] and coals oxidized at high temperatures [21, 28] or during long time periods [25] were studied by conventional IR spectroscopy in combination with wet chemical analysis. These strongly weathered samples showed similar tendencies in the functional group content as determined by wet chemical techniques; the intensity of carboxylic and carbonylic absorption bands was increased in the oxidized coals. It should be noted that carboxylic and carbonylic groups give particularly strong IR bands and can be detected at very low concentrations.

Fourier transform IR (FTIR) spectroscopy has the benefits of greater signal-to-noise ratio and the availability of more advanced data manipulation facilities. Difference methods can be used to detect subtle changes in the intensity of bands. However, the determination of the degree of subtraction is rather subjective because no band is available that can be unambiguously chosen as an internal standard. Some authors assume that no significant changes in the intensity of aromatic ring stretching [29,30] or aliphatic [31] bands occur and use these bands as references. Painter *et al.* [32, 33] determined the correct degree of subtraction so that certain clay mineral bands were eliminated.

Figure I-1 shows the IR spectra of a fresh and an oxidized high volatile bituminous coal as well as the difference spectrum obtained by Painter *et al.* [33]. Although the difference spectra recorded by different workers are more or less similar, the assignments are still different because the exact position of the bands is uncertain due to the overlapping of several bands. Rhoads *et al.* [30] used a derivative method to determine the peak position and to deconvolute the overlapping bands in the 1700 cm^{-1} region of the spectra. Carboxylic acids, highly conjugated carbonyls and carboxylate groups were assigned in the difference spectra. Quantitative evaluation of the band intensities showed an overall increase in carboxyl, carbonyl and carboxylate content of coal as oxidation proceeded as seen in Figure I.2. However, the relative proportion of the different carbonylic groups seems to vary with the extent of oxidation. It is suggested that carboxylate groups are formed from carboxylic groups produced initially during oxidation by exchange with cations. Finally, alkyl esters were also reported [32] to appear in the difference spectra of highly oxidized coals though formation of esters upon oxidation is not apparent.

The problem of the correct subtraction factor is eliminated by the use of in-situ oxidation. Thin sections of coal were applied by Gethner [34] instead of preparing KBr pellets. Thus the sample can be oxidized in a high temperature IR cell and changes in the surface layers can be detected. Vacuum drying at 100°C resulted in the decomposition of

Figure I-1. Infrared spectrum of oxidized coal (A) and of fresh coal (B) as well as difference spectrum (A-B). (Reprinted from ref. 33.)

Figure I-2. Changes in relative intensity of IR bands versus time of oxidation at 140°C (○) and 60°C (●). a) 1690 cm⁻¹ band (carboxyl); b) 1655 cm⁻¹ band (highly conjugated carbonyl); c) 1575 cm⁻¹ (COO⁻). (Reprinted from ref.30)

carboxylic acid groups and subsequent oxidation at 100°C led to the formation of new carbonylic species. However, applying vacuum drying as a pretreatment may result in the cleavage of carboxylic groups to a greater extent than when using ambient pressure. Therefore, the net carboxylic content of the coal after drying and oxidation might even decrease depending on coal type, drying conditions and extent of oxidation. Furthermore, anhydride groups appear to be formed during dry oxidation [35], as indicated by the decreased pH of oxidized coals after hydrolysis in a Parr "digestion" bomb. In-situ monitoring of structural changes upon oxidation is possible in powdered coals by using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy as demonstrated by Fuller and Smyrl [36, 37]. The sensitivity of DRIFT spectroscopy to oxidation can be enhanced by applying the band ratio method [38].

Many researchers have attempted to use FTIR spectroscopy to determine hydroxylic functionalities in coals. Several problems arise with direct measurements using the KBr pellet technique, including variable water absorption in the KBr discs, water content of the coal and broadening of the OH bands due to hydrogen bonding. To eliminate these difficulties several authors [30, 39] used FTIR spectroscopy in combination with chemical derivatization techniques such as acetylation. The water adsorption problem can be avoided by grinding the coal in Fluorolube R using the glass plate technique [33]. Painter *et al.* [33] concluded that bands associated with carbon-oxygen single bonds (as in ethers or phenols) show increased intensities only at higher degrees of oxidation. Rhoads *et al.* [30] could differentiate between alkylic and phenolic OH groups using chemical derivatization techniques and curve-resolving procedures. Their results indicate that there is a decrease in the relative proportion of phenolic to alkyl OH groups during oxidation.

Pyrolysis methods are widely used for characterization of high molecular weight substances such as coals [40]. The volatile products formed during pyrolysis can be analyzed by chromatographic and spectroscopic methods (e.g., gas chromatography, mass spectrometry and combinations of these techniques). Ignasiak *et al.* demonstrated [41] that the degree of oxidation of coal can be measured by a pyrolysis method based upon analyzing the composition of the gas produced by pyrolysis. Low-temperature oxidation increases the yield of carbon oxides and water formed in the subsequent pyrolysis step [41-43]. The increased amounts of these products indicate that various oxygen-bearing functional groups were formed during oxidation. Several oxygen-containing groups decompose with evolution of carbon monoxide. However, the increased yield of pyrolytic water indicates the formation of hydroxylic groups in the weathered samples. Furthermore, it is likely that both aromatic and aliphatic carboxyl groups are formed during oxidation since the pyrolyzate is enriched in aliphatic acids and carbon dioxide [44].

I.1.B. Decreased Hydrocarbon Content

Oxygen-containing compounds such as aldehydes, alcohols and phenols appear to be more susceptible to oxidation than the corresponding aliphatic or aromatic hydrocarbons [45]. This suggests that some functional groups present in coal are further oxidized during weathering, thereby altering the functional group distribution. Since the total

amount of oxygen-containing groups appears to increase [22], new functional groups must be formed in hydrocarbon moieties resulting in an overall decrease of hydrocarbon content. Furthermore, some volatile products are evolved upon oxidation which may decrease the hydrogen and carbon content of the coal.

The hydrocarbon composition of coals is reflected by the optical properties. The vitrinite reflectivity is widely accepted as being related to the degree of aromatization and condensation of the molecular structure. It has been established [13,46] that the vitrinite reflectivity measured on oxidation edges of coal increases when the vitrinite is oxidized at high temperatures. Van Krevelen suggested [13] that oxygen first of all attacks the nonaromatic portion of the coal. Reflectance measurements are capable of revealing the increase of aromaticity in strongly weathered coals though conflicting results were reported regarding the effect of oxidation upon optical properties of macerals [11, 47-49].

The recent application of spectroscopic techniques allows the determination of aromatic/aliphatic hydrocarbon ratios in coal. Solid state ^{13}C NMR techniques with cross polarization and magic angle spinning enable the assessment of aromaticity because the spectrum consists of two resolved peaks corresponding to aromatic and aliphatic resonances. Studying the oxidation of a high volatile bituminous coal at 105°C MacPhee and Nandi established [50] that the aromatic to aliphatic carbon ratio decreased indicating that aromatic structures were modified primarily. On the contrary, other authors found [51, 52] the fractional aromaticity to increase with longer oxidation times indicating preferential attack on aliphatic structures. Nevertheless, Havens et al. [51] reported that some aromatic segments are also involved in the oxidation process at 140°C .

A reasonable chemical hypothesis could be that under low temperature oxidation conditions aliphatic structures are attacked first. This assumption is supported by several infrared spectroscopic studies. Rhoads et al. [30] calculated the integrated absorption of aromatic and aliphatic C-H groups on the basis of the C-H stretching region of the IR spectrum. It was established that the changes in the aromatic region were negligible at temperatures up to 140°C . The concentration of aliphatic C-H groups shows an initial sharp decrease followed by a more gradual decrease at longer oxidation times. At lower temperature (60°C) the loss of aliphatic C-H is not as great but still significant for the high volatile bituminous coal studied. Liotta et al. [17] detected the decrease of aliphatic C-H and methylene signals by FTIR spectroscopy in a coal oxidized at ambient temperature. It was concluded that the oxidation resulted in the formation of aliphatic ether linkages. Albers et al. established [53] that the methyl group content as measured by the intensity of the 1380 cm^{-1} band in the IR spectra remained almost unchanged but that the methylene content of the coal decreased upon oxidation. Similarly, the study of the IR spectra of benzene extracts indicated [15] that the terminal CH_3 groups are not significantly susceptible to oxidation even during natural weathering of the outcrop of a coal seam. A reasonable explanation of these results is that carbon

atoms in benzylic positions are the most easily oxidized of aliphatic side groups.

At temperatures below 150°C a slight increase in the aromatic carbon content of coals was observed by FTIR spectroscopy [39, 53]. Tooke and Grint concluded [39] that some of the aliphatic groups might have been in alicyclic structures that undergo dehydrogenation during oxidation. At elevated temperatures the aliphatic structures virtually disappear as indicated by the IR spectra of a vitrain oxidized at 170°C and 190°C for several days [21]. The intensity of the aliphatic band of a bituminous coal reaches a minimal value at about 250°C when applying short oxidation times [39]. Furthermore, above 200-250°C the intensity of the aromatic C-H stretching band also appears to decrease [37,39,54] indicating that the aromatic portion of the coal structure is also altered under severe oxidation conditions.

Experimental evidence [55, 56] supports the view that alkylaromatic and hydroaromatic moieties participate in oxidation reactions at low temperatures. Comparison of the reactivity of coal macerals shows that the highly aromatic fusinite is more susceptible to oxidation than the aliphatic-rich macerals [56, 57]. Pyrolysis mass spectrometric study of oxidized maceral concentrates indicates [56] that the hydroaromatic and alkylaromatic components in the resinite and semifusinite samples, respectively, undergo severe oxidative changes resulting in the formation of oxygen-containing aliphatic moieties. Aliphatic hydrocarbon-rich coal structures thought to be derived from cutinitic or algal sources show little chemical change under low-temperature oxidation. A possible explanation of the above results is that aliphatic side groups of aromatic moieties and saturated carbon atoms of hydroaromatic components are oxidized, however, the possibility of aromatic ring opening cannot be ruled out.

Pyrolysis methods yield quantitative information on the thermally volatilizable components of coal [58-62]. Marked increases in carbon oxides and water contents of pyrolyzates of weathered coals are accompanied by decreased production of hydrogen and light hydrocarbons as observed by laser pyrolysis [43]. This result is consistent with the view that the hydrocarbon portion of coal is chemically modified during oxidation.

Weathering causes a reduction in the extractable fraction of coal [44]. Proximate analysis data show that the volatile matter content is decreased and that the fixed carbon content is increased in oxidized coals [63]. Furthermore, the amount of pyrolytic coal tar decreases with oxidation [64]. Analysis of the pyrolysis products shows that there are significant differences in the quantitative composition of the pyrolyzate of fresh and weathered coals.

Pyrolysis mass spectrometry combined with computerized data processing [65, 66] provides a powerful tool for studying changes accompanying weathering [44, 63]. Figure 1-3 shows the low voltage pyrolysis mass spectra of fresh and oxidized hvb Hiawatha coal. Tentative chemical identifications of the mass peaks are based on Py-GC/MS experiments.

However, most mass peaks are likely to have contributions from more than one compound. The mass spectrum of the vacuum pyrolyzate shows prominent peak series at m/z 142, 156, 170, 184, 198 ("naphthalenes"), at m/z 94, 108, 122, 136 ("phenols"), at m/z 92, 106, 120, 134, 148 ("benzenes") and at m/z 42, 56, 70, 84 ("alkenes" and $C_nH_{2n}^+$ fragment ions). In order to study the weathering-induced changes in more detail, the Py-MS data set of fresh and weathered samples was evaluated by factor and discriminant analysis [66, 67]. The resulting different spectrum associated with the main weathering trend [63] is shown in Figure I-3c. The positive component of the spectrum represents peaks showing a decreased abundance in the spectra of the weathered coal whereas peaks of the negative component increase during weathering. Increased relative abundances of oxygen-containing pyrolysis products such as carbon monoxide (m/z 28), carbon dioxide (m/z 44) and short chain fatty acids (m/z 46, 60, 74) are observed. Naphthalenes, tetralins, phenols and benzenes show decreased yields in weathered coal. Time-resolved recording of the ion signals during the pyrolysis process [6] demonstrates that the Hiawatha coal has thermally extractable alkyl naphthalene and -tetralin components that evaporate from the coal at about 300°C in vacuum. These thermally extractable components markedly decrease in the weathered coal, presumably as a result of "grafting" reactions with the coal matrix although contributions from evaporation losses during the weathering procedure at 100°C cannot be completely ruled out.

The results of several studies cited in this section would indicate that the loss of aliphatic C-H content and the decrease of volatile alkyl substituted aromatic components can be linked with the loss of fluid properties of coking and caking coals. Some authors [68, 69] explain the loss of thermoplastic properties with the decreased transferable hydrogen on the aliphatic carbon atoms resulting in the decrease of volatile products upon carbonization. A different explanation [17] correlates the loss of aliphatic C-H groups with the formation of ether bridges. According to this hypothesis the development of ether linkages takes place on the aliphatic groups through hydroperoxide formation.

I.1.C. Cross-link Formation

It is well-established that weathering of coking and caking coals during storage or transportation can effectively destroy their thermoplastic properties [70, 71,]. In many studies the degree of oxidation has been determined by swelling measurements [32, 38,] because thermoplastic properties are often extensively altered before changes can be detected in the chemical composition of coal. Rapid decrease of the free swelling index (FSI) [38, 72-74] and reduction in the Gieseler plastometer fluidity values [30, 38, 75] are observed during oxidation. Decreased swelling properties result in a decrease in coke strength and yield [8, 70, 76]. The loss of thermoplastic properties suggests that a more highly cross-linked macromolecular structure is formed during weathering which does not easily melt and flow upon heating.

The decreased swelling characteristics are related to the decreased volatiles production during heating, as indicated by proximate analysis data [63] and thermogravimetric experiments [44]. Pyrolytic tar yields

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The decreased swelling characteristics are related to the decreased volatiles production during heating, as indicated by proximate analysis data [63] and thermogravimetric experiments [44]. Pyrolytic tar yields

Figure I-3. Pyrolysis mass spectra of fresh (a) and weathered (b) Hiawatha seam (hvb) coal as well as the corresponding difference spectrum (c). Weathering condition was at 100°C for 212 hrs with dry air 80 ml/min.

Figure I-4. Pyrolysis mass spectrum of fresh Anderson seam lignite (a) and difference spectrum (b) obtained by subtracting the spectrum of weathered Anderson lignite (not shown) from (a). Weathering condition was at 80°C for 232 hrs with dry air 80 ml/min.

are reduced whereas the molecular weight of the tar from oxidized coals is increased [20]. All this experimental evidence supports the concept that the cross-links density of coal is increased during weathering. A relatively small number of cross-links produced in a macromolecular system can dramatically alter the molecular mass of the macromolecules, therefore small structural changes can result in greatly modified physical properties. Intermolecular bonds are likely to be formed between various components of coal.

According to the binary phase model of coal structure, recently summarized by Given [1], coal appears to be a mixture of cross-linked macromolecules and relatively small molecules trapped in the macromolecular network. The decreased volatiles production during heating suggest that the so called "mobile phase" component participates in oxidation reactions. The increased molecular mass of the extracts [71] indicates the involvement of condensation reactions between the mobile constituents. However, as discussed by Meuzelaar *et al.* [44] it is more likely that the mobile phase molecules react with the network molecules by grafting reactions thereby resulting in strongly reduced extraction yields of weathered coals. Chemical identification of the low concentrations of newly formed cross-links is not an easy task. Therefore, the issue of cross-link formation is perhaps the most controversial subject of the structural changes caused by weathering.

Several workers have observed the formation of carboxyl, carbonyl and hydroxyl groups [18-20] as discussed in the previous sections. However, Wachowska *et al.* established [16] that the formation of these functional groups is not related to the decrease of thermoplastic properties because removing and blocking these functional groups does not have an obvious influence on restoring the swelling characteristics. Pyridine solvent swelling experiments indicate [68] that changes in the cross-link density are quite small during the initial stages of oxidation although the FSI decreases rapidly. On the other hand, lithium aluminium hydride reduction restores the lost plasticity of mildly oxidized coals [77]. On the basis of the above results Larsen *et al.* concluded [68] that it is not the presence of oxygen that destroys the thermoplastic properties but the loss of easily donating hydrogen atoms upon oxidation. This assumption is supported by the observation [78] that hydrogen addition is capable of restoring the lost swelling properties of weathered coals. Larsen *et al.* pointed out [68] that different mechanisms can result in the loss of plasticity. Besides the loss of readily donating hydrogen, the involvement of cross-linking reactions is indicated by the increase in molecular mass of pyrolysis tar [20].

Wachowska *et al.* established [16] that no significant polymerization through carbon-carbon bonds occurred. The treatment of a medium volatile bituminous coal with potassium in tetrahydrofuran resulted in a restoration of dilatation properties. Thus, it was concluded that ether type cross-links are produced during oxidation at 100°C. It should be noted, however, that this reagent cleaves C-O bonds as opposed to C-C bonds and it seems likely that ester linkages would react in a similar way. On the basis of FTIR results Painter *et al.* [32] suggested the involvement of carboxyl groups in the loss of coking properties.

According to their assumption, these groups represent initial oxidation products which subsequently react with hydroxyl groups thereby forming esters. However, ester bonds do not seem to be so thermally stable as to cause drastic reduction in coal swelling behavior when heated up to 800-900°C temperatures. In a follow-up paper [33] their observation was explained by the formation of ionic cross-links between the carboxylic acid groups and divalent cations or basic structures within the coal. However, production of ionic cross-links would not explain the decrease of volatile products from weathered coals, since it was observed [79] that the carboxylate groups yield more carbon dioxide than the carboxylic acids upon pyrolysis.

The production of ether cross-links was suggested by Liotta [17] in a study of ether cleavage reactions with hydrobromic acid in the presence of a phase transfer catalyst. Using chemical reactions and spectroscopic techniques it was concluded that the ethers produced were both aliphatic and aromatic in nature.

FTIR spectroscopic investigations confirmed the enhancement of C-O bands in oxidized coals. It should be noted that ethers have low extinction coefficients and are difficult to detect in the IR spectrum. Bands near 1100 cm^{-1} in the IR spectra are assigned to ethers and several authors have observed a more intensive absorption in weathered coals in this region [17, 31, 38]. Recording the spectra of the low temperature ash it was concluded [30], however, that the band near 1100 cm^{-1} can be due to clay minerals present in coal and that this band can be eliminated by choosing suitable subtraction factors. However, carrying out in-situ oxidation in an FTIR instrument [34] and assuming no change in the clay structure, the band assigned to ethers also appears in the difference spectrum. In summary, it seems that ethers as cross-linking functional groups are produced during weathering.

Pyrolysis experiments also indicate the formation of oxygen containing cross-links. Ignasiak *et al.* [80, 81] used isotope-labelled oxygen ($^{18}\text{O}_2$) to oxidize a high volatile bituminous coal at 100°C. When pyrolyzing this coal at 800°C, 40 percent of the labelled oxygen taken up by the coal remained in the char. It is likely that the residual oxygen forms cross-links and can not be driven off by pyrolysis. The authors tentatively concluded that weathering leads to the formation of ether bridges resulting in the loss of swelling properties.

It seems likely that ether cross-links are formed from hydroxyl groups. Hydroxyl groups are the only oxygen-containing groups that are reported to be decreased during weathering [24, 31] indicating the involvement of these groups in certain weathering reactions. Although the oxidation of phenols to quinones was also proposed in the literature [22] it is more likely that reactions of hydroxyl groups leads to the formation of ether bridges.

Low rank coals contain large amounts of hydroxyl groups as indicated by the pyrolysis mass spectrum of the Anderson seam lignite [63] shown in Figure 1.4a. The low voltage mass spectrum is dominated by homologous ion series representing hydroxyaromatic pyrolysis products (phenols and

dihydroxybenzenes) besides the aliphatic peak series. Multivariate analysis of the Py-MS data set of fresh and oxidized lignite samples resulted in the difference spectrum shown in Figure 1.4b. The phenols (at m/z 94, 108, 122, 136) and dihydroxybenzenes (at m/z 110, 124, 138) show strongly decreased intensities in the pyrolyzate of the weathered coal (positive component of the discriminant spectrum). As discussed before, the difference spectrum of the high volatile bituminous Hiawatha coal shows also the decrease of phenol signals during oxidation indicating that aromatic hydroxyl groups are affected by weathering.

The Anderson lignite sample was subjected to oxidation in isotope labelled oxygen ($^{18}O_2$) [82]. Comparison of the pyrolysis mass spectra of one fresh and two oxidized (heated at 80°C in $^{16}O_2$ and in $^{18}O_2$) samples reveals that the dihydroxybenzenes decreased in both oxidized coals. That isotope-labelled dihydroxybenzenes appeared in the spectra of the coal exposed to $^{18}O_2$ indicates that new hydroxyl groups were produced during oxidation. That isotope-labelled water was also produced upon pyrolysis suggests that not only aromatic but also aliphatic hydroxyl groups were formed during weathering. This experimental evidence supports the view that two competing reactions occur involving hydroxyl groups. On the one hand, they are produced upon oxidation and on the other hand, hydroxyl groups possibly take part in condensation reactions. It is likely that phenolic groups are more prone to react than aliphatic OH groups because the decrease of the phenolic OH groups is greater than the decrease of the total hydroxyl groups [30]. The reactivity of phenolic OH groups is confirmed by stability studies of coal-derived liquids [83, 84] indicating that hydroxyaromatic compounds (e.g. phenols and naphthols) are involved in retrograde reactions of coal tars under oxidative conditions.

I.1.D. The Role of Mineral Matter

Although oxidation of organic constituents may often be the most striking weathering effect from the standpoint of deterioration of coals upon weathering, changes in the inorganic part of coals were also extensively studied. Generally, the term mineral matter refers to all forms of inorganic constituents present in coal and includes metals and anions associated with the organic matrix as well as optically identifiable mineral phases. The major inorganic constituents of coal are clay minerals, silica, carbonate minerals and sulphides. The clay minerals and silica appear to be completely unaffected by weathering [17, 38].

Though oxidation of organic and inorganic coal constituents respectively is generally regarded as two separate processes, there are some indications that certain organically bound cations are able to catalyze oxidation. Schafer observed [24] that the exchange of acidic groups with barium ions promotes the oxidation during air drying of Yallourn brown coal. This observation indicates that brown coals containing high levels of organically bound cations (e.g. carboxylate salts) would oxidize more rapidly.

Among the major inorganic constituents of coal only iron disulphide appears to react with oxygen during weathering. Iron disulphide occurs in

coal in two crystalline forms [85]; pyrite has a cubic crystal structure and the orthorhombic structure is called marcasite. Since the two dimorphs are similar in terms of chemical reactivity and pyrite is more abundant in the coal, many investigators use the term pyrites for both forms of iron disulphide. We will follow this practice.

There has been considerable controversy on the subject of the role of pyrites in the self-heating and spontaneous ignition of coal. There is no doubt that pyrites undergo oxidation and evolve heat during weathering. Differences of opinion arise in evaluating the magnitude and importance of the heat released by pyrite oxidation [86]. By now it is accepted that even though the oxidation of pyrites is an exothermic reaction, the contribution of pyrites to the self-heating of coal is only of secondary importance and the role of pyrites has been overemphasized in the past.

In spite of the fact that pyrite oxidation has been extensively investigated for many years, little agreement exists on the mechanisms and products of the process. In general, it is assumed that at low temperatures the reaction requires both oxygen and water [87]. In several publications [76] pyrite oxidation is described by the following reaction:

Sulphur determinations support the above chemical reaction [17]. The distribution of sulphur in pyrites and sulphates is altered in weathered coal samples; i.e. the decrease of pyrites is accompanied by an increase in the sulphate content of oxidized samples. Huffman et al. [38], using Mossbauer spectroscopy, established the formation of ferrous sulphate ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$) in samples treated in an oven at 50°C. However, iron oxyhydroxide ($\alpha\text{-FeOOH}$, goethite) was reported as the principal oxidation product of pyrite in naturally weathered samples from strip mines [88] and in coal samples stockpiled outdoors [38]. Huffman et al. found [38] that the percentage of pyrite converted to iron oxyhydroxide correlates well with other measurements of the degree of oxidation.

Shyu et al. [89] using Mossbauer spectroscopy concluded that the oxidation of pyrites in bituminous Illinois No.6 coal occurs in three steps: (1) to iron sulphates between 25 and 310°C, (2) to $\gamma\text{-Fe}_2\text{O}_3$ between 310 and 325°C and (3) to $\alpha\text{-Fe}_2\text{O}_3$ between 325 and 400°C. The formation of Fe_2O_3 is generally described by the following reaction [89, 90]:

The conversion rates of pyrites in coal appear to be one order of magnitude higher than those of mineral pyrites under identical experimental conditions [89] indicating that the oxidation of pyrites in coal is highly influenced by the organic coal constituents. Apparently, the organic matrix promotes the oxidation reaction.

The oxidation of pyrites in oxygen depleted atmospheres leads to the formation of magnetite (Fe_3O_4) [91]. The partial conversion of pyrites to a more magnetic form has been studied in view of pyrite removal from coal by the use of magnetic fields [91, 92].

Besides the major products of pyrite oxidation such as iron sulphates, iron oxyhydroxides, iron oxides and sulphur dioxide, the formation of FeS, SO₃ and sulphur polymers were also reported [89, 93]. The product distribution strongly depends on the oxygen partial pressure in addition to temperature and particle size [89, 91].

The oxidation of pyrites may lead to secondary reactions in the mineral phase of coal. Pearson and Kwong have reported [94] that the extent of oxidation can be quantitatively estimated by the mineral bassanite content in the low-temperature ash as measured by X-ray diffraction. The sulphate anions formed during oxidation of pyrites could react with the calcite (calcium carbonate) content of coal forming gypsum (CaSO₄.H₂O). During the ashing process the gypsum undergoes partial dehydration producing bassanite (CaSO₄.1/2H₂O). This relationship is limited to weakly pyritic, non-marine coal samples, although the partial conversion of calcite to gypsum was also observed in other coals [38]. The drastic changes in the calcium phases, however, were reported in coals subjected to very extended natural weathering [38, 94] or oxidation at high temperatures [90].

I.2 EXPERIMENTAL

I.2.A. Fresh Coal Samples

One to two pound aliquots of 2-4" sized PCSP (Premium Coal Sample Program) coals were obtained, submersed under water and sealed in metal cans. Coals were dried with Drierite in a nitrogen atmosphere overnight and then ground to -60 mesh in a ball mill under nitrogen. Ground coals were transferred to 25 ml polyethylene vials in a glove box filled with nitrogen and stored at -90°C (Figure I-5).

It should be noted that the PCSP coals used in this report are slightly different from the standard ampule samples under Argon, since the former was received from ANL (Dr. Vorres) as a pound of lump-sized fragments which were crushed, milled and aliquotted in our laboratory. When the ampule samples under Argon are used, it will be specified as such in the following content of the report.

Anderson seam coal (used in TG/MS and time-resolved Py-MS experiments) was a drill core sample from the Gillette area, Wyoming provided by Phillips Petroleum, and had very similar characteristics to the Wyodak coal in the Argonne Premium Coal Sample Program. Two more western coals were used in time-resolved Py-MS experiments: Adaville #6 seam (Kemmerer field, Wyoming) coal and Hiawatha seam (Emery county, Utah) coal. The original locations of the coal samples are shown in Figure I-6.

Table I-1 shows the ultimate analyses of PCSP ampule samples under Argon. To illustrate the differences between the samples used in the report and the original PCSP ampule samples, a comparison is shown in Table I-2 for two coals.

Table I-3 shows the proximate analysis results of 7 samples used in this report. Since all the analysis results on eight PCSP coals should be available from ANL, proximate analyses were performed only on 4 coal samples prepared in our laboratory after being received as a pound of lump-sized fragments from ANL for comparison.

I.2.B. Laboratory Coal Weathering

A schematic diagram of the experimental apparatus is shown in Figure I-7. The equipment used for carrying out the weathering experiments consisted of a glass reactor (104 mm in length and 37 mm o.d.) fitted with Swagelok fittings at each end and an effluent line connected to a bubble flow meter to check the flow rate. A sintered glass frit distributor at the bottom of the reactor was used to prevent channeling inside the reacting coal. Glass wool was used inside the reactor to prevent entrainment of coal particles. 14-16 g of sieved (-60 mesh) coal in the reactor produced a bed height of approximately 3 cm. The reactor was then placed in a convection oven which was controlled to within $\pm 1.0^\circ\text{C}$ and heated to 100°C in less than 2 minutes. The weight of the coal sample was monitored at regular intervals during each run to calculate the weight corrected calorific value.

Figure I-5. Fresh coal sample preparation procedure.

SOURCE: P. Averitt, *Coal Resources of the United States, Jan. 1, 1974*, U.S. Geological Survey Bull. 1412, at 5 (1975).

Figure I-6. Sampling locations of coals described in this report. (*) coals represented in Argonne Premium Coal Sample Program (PCSP).

TABLE I-1
ULTIMATE ANALYSIS RESULTS ON PCSP AMPULE SAMPLES UNDER ARGON

Seam	Rank	C	H	O	S	Ash
Upper Freeport	MVB	87	5.5	4	2.8	13
Wyodak	Subbit.	74	5.1	19	0.5	8
Illinois #6	HVB	77	5.7	10	5.4	16
Pittsburg #8	HVB	83	5.8	8	1.6	9
Pocahontas #3	LVB	91	4.7	3	0.9	5
Blind Canyon	HVB	79	6.0	13	0.5	8
Lewiston-Stockton	HVB	81	5.5	11	0.6	20
Beulah-Zap	Lignite	73	5.3	21	0.8	6

LVB: low volatile bituminous
MVB: medium volatile bituminous
HVB: high volatile bituminous

Ref: Vorres, K.S., "The preparation and distribution of Argonne Premium Coal Sample," ACS Preprints (Div. of Fuel Chem.), 32(4), 221-226, 1987.

TABLE I-2

COMPARISON OF ULTIMATE ANALYSIS RESULTS BETWEEN TYPICAL PCSP AMPULE
SAMPLES AND THE SAMPLES PREPARED AT THE UNIVERSITY OF UTAH
BIOMATERIALS PROFILING CENTER (BPC).

Seam	Sample	C	H	O	S	Ash
Illinois #6	PCSP ampule**	77	5.7	10	5.4	16
	BPC*	68.72	4.95	9.48	2.48	12.44
Blind Canyon	PCSP ampule**	79	6.0	13	0.5	5
	BPC*	78.62	5.85	11.91	0.50	1.52

*Analysis performed by Standard Labs. Inc., Huntington, Utah

**data supplied by Dr. Vorres

TABLE I-3.

COMPLETE PROXIMATE ANALYSIS RESULT ON 5 COAL SAMPLES
(AS RECEIVED BASIS)

Seam	Moisture (%)	Volatile Matter (%)	Fixed Carbon (%)	Ash (%)	Sulfur (%)	Calorific Value (Btu/lb)
Upper Freeport	0.7	29.03	60.15	10.10	1.93	13853
Wyodak	24.56	37.05	31.88	6.51	0.78	8993
Illinois #6	7.10	40.05	41.29	11.56	2.65	11619
Blind Canyon	5.06	44.82	48.68	1.44	0.47	13595
Anderson	30.16	30.70	33.66	5.48	0.43	8099
Adaville #6	18.29	33.39	43.00	5.32	0.33	9988
Hiawatha	3.45	41.42	42.38	12.75	0.48	13786

Analyses performed by Standard Labs. Inc., Huntington, Utah

Figure I-7. Schematic of laboratory weathering system when using dry air.

Gas (air or pre-purified nitrogen) was passed through a moisture trap (silica gel) and the reactor at a constant flow rate of 10 ml/min via a rotameter for Py-MS samples, 80 ml/min for TG/MS samples. The gas flow rate in each experiment was checked with a soap bubble flow meter placed at the reactor outlet. A stable pressure of 15-20 psig was maintained on the up-stream side of the moisture trap by a standard two-stage pressure regulator. Gas lines inside the weathering oven were all 1/8" teflon tubing.

Weathered coal samples from each run were transferred to two 25 ml polyethylene vials, flushed with nitrogen and stored at -20°C until they were used as samples for Py-MS and TG/MS.

I.2.C. Laboratory Macerals Weathering and Pyridine Extraction

In order to examine the effects of weathering on different maceral components, three separate experiments were performed: (a) oxidation under dynamic reactor flow conditions; (b) oxidation under static conditions; and (c) pyridine extraction of fresh and oxidized coal.

Under dynamic conditions, 20-24 g aliquots (-60 mesh) of four coals (Wyodak, Adaville #6, Hiawatha, Upper Freeport) were exposed to an air flow of 5-10 ml/min in a 100 ml glass reactor at 100°C for 170-212 hours. Under static conditions, four maceral concentrates were oxidized with air (viz. vitrinite and semi-fusinite fractions prepared by density gradient centrifugation of Dakota seam coal (New Mexico, PSOC 858), sporinite prepared by density gradient centrifugation, from the Brazil block seam (Indiana PSOC 107) and a hand-picked resinite sample from the Wattis seam (Utah)). Twenty five mg aliquots of these macerals were exposed to air at 100°C for 100 hours in sealed 2 l flasks.

Pyridine extraction was performed on Hiawatha coal in a regular Soxhlet extractor for 24 hours. A weathered coal sample for pyridine extraction was prepared by exposing a 15 g aliquot (-60 mesh) to air at 100°C for 212 hours [12] under dynamic flow conditions. Solvents were removed from the residue by vacuum drying at 10^{-2} torr.

I.2.D. Pyrolysis Mass Spectrometry and Data Processing

Pyrolysis experiments were performed using an Extranuclear 5000-1 Curie-point Py-MS system as shown in Figure I-8.

All whole coal samples as well as insoluble extraction residue were hand ground into a fine, uniform suspension in Spectrograde methanol (5 mg of sample per ml of methanol). The pyridine-extracted fraction was dissolved in a mixture of benzene and methanol (3:1, v/v) at a concentration of 2 mg/ml. Five microliter drops of the above suspensions and the solutions were coated on the ferromagnetic filaments used in Curie-point pyrolysis and air-dried under continuous rotation, resulting in approximately 20 ug of dry sample on the filament.

The wires were inserted into borosilicate glass reaction tubes and introduced into the vacuum system of the mass spectrometer. The

Figure I-8. Curie-point pyrolysis mass spectrometry system. Time-resolved signal recording mode is indicated in the figure.

ferromagnetic wires were inductively heated at a rate of approx. 100°C/s to an equilibrium temperature of 610°C (as determined by the Curie-point temperature of the wire). Total heating time was 10 s. The temperature time profile of the wire was measured by means of a 0.003" dia. chromel/alumel thermocouple and shown in Figure I-9.

Two different analysis modes were used. In the so-called "time-integrated" analysis mode spectra were taken under the following conditions: electron ionization source operated at 12 eV (set value); scanning rate 1000 amu/s; total scanning time 20 s. The spectra were summed into a single, "time-integrated" spectrum.

In the time-resolved analysis mode the same pyrolysis conditions were used. However, electron energy was set at 20 eV to increase overall signal intensity. The mass range of m/z 50-200 was scanned for 8 s starting 0.5/s after the start of the sample heating cycle. Several interesting mass peaks in the lower mass range below m/z 50 were scanned during separate pyrolysis runs.

After spectrum calibration and normalization the time-integrated spectra of the fresh and weathered coal samples were evaluated by factor and discriminant analysis using the SPSS program package [95] and additional multivariate analysis programs as described by Windig et al. [96, 97]. The results are presented in the form of discriminant spectra.

The time-resolved data sets were subjected to factor analysis after spectrum calibration. The variance diagram (VARDIA) technique [96] was used to determine the major components showing different time profiles. The major chemical components were visualized in the form of so-called "factor spectra" using the procedure described by Windig et al. [97].

I.2.E. Thermogravimetry-Mass Spectrometry (TG/MS)

A Perkin-Elmer TGS-7 system was connected to the all glass reactors (containing approximately 30 g of coal) and a Balzers QMM 611 quadrupole MS through an interface. The TG/MS interface used has been described elsewhere [61]. Sample aliquots 6.6-6.7 mg (Anderson coal) and 8.1-8.3 mg (Upper Freeport coal) respectively were pyrolyzed in the TG system under an inert atmosphere of Argon flowing at 140 ml/min. The temperature was programmed from 25°C to 950°C at 20°C/min. Thermogravimetry (TG) and differential thermogravimetry (DTG) curves were normalized for the original sample weight (after being under Argon flow for one hour) and for the intensity of the Ar^+ mass peak at m/z 40. All TG/MS experiments were performed at the Institute for Inorganic Chemistry of the Hungarian Academy of Sciences (Budapest Hungary).

The weathering conditions employed for obtaining the weathered coal samples were as follows: 100°C for Upper Freeport coal, 80°C for the low-rank Anderson coal; dry air at 80 ml/min.

Figure I-9. Measured temperature/time profile of a ferromagnetic wire with 610°C Curie-point temperature (T_c) and corresponding time-resolved Py-MS (total ion current) profile of standard mixture containing 3 polymers, namely nitrocellulose (a), polymethylstyrene (b), and polystyrene (c).

1.2.F. Isotope-Labeled Oxygen Weathering

In order to determine this value and to measure subtle structural changes, Anderson lignite was weathered at 80°C under two different atmospheres composed of (21% $^{16}\text{O}_2$ + 79% N_2) in closed 2 l flasks and the oxidized coal samples subsequently analyzed by means of pyrolysis mass spectrometry (Py-MS). Two different Py-MS methods were used; namely time-integrated Py-MS and time-resolved Py-MS. Furthermore, computerized multivariate analysis methods such as factor and discriminant analysis were used for data reduction as well as for the numerical extraction of underlying chemical tendencies in the data.

I.3. RESULTS AND DISCUSSION

I.3.A. Pyrolysis-Mass Spectrometry (Py-MS) Studies of Coals and Maceral Concentrates

Pyrolysis mass spectra of fresh and weathered Hiawatha coal, averaged from three replicate analyses of each sample, are shown in Figure I-10. Pyrolysis mass spectra of coals are generally dominated by homologous ion series [58, 59, 65]. It has to be pointed out that the chemical identification of the mass peaks is tentative only and that the chemical labels used throughout this article are meant to identify the main underlying compound series based on available literature data on coal pyrolyzates, e.g., obtained by GC/MS [62, 98] or MS/MS [99] techniques. However, it should be kept in mind that most mass peaks are likely to have contributions from more than one chemical compound. The low voltage mass spectrum of the vacuum pyrolyzate of fresh Hiawatha coal (Figure I-10a) shows prominent peak series at m/z 142, 156, 170, 184, 198 ("naphthalenes"), at m/z 94, 108, 122, 136 ("phenols") at m/z 92, 106, 120, 134, 148 ("benzenes") and at m/z 42, 56, 70, 84 (alkenes and $C_nH_{2n}^+$ fragment ions). Furthermore, some typical sulfur-containing ion signals are seen at m/z 34 (H_2S^+) and at m/z 64 (SO_2^+).

The weathering process has strong effects on the structure of coals as described in the introduction of this chapter. The yield of volatile pyrolysis products is decreased as reflected by a 20% lower total ion current of the pyrolysis mass spectra of Hiawatha coal weathered for 10 days at 100°C in air (Figure I-11). However, not only the yield but also the composition of the volatile pyrolyzate is changed by weathering as in Figure I-10b.

In order to study the complex weathering-induced changes in as much detail as possible, the Py-MS data set was evaluated by factor and discriminant analysis. The resulting "difference spectrum" associated with the main weathering trend [63] is seen in Figure I-10c. The positive component of the spectrum represents peaks showing decreased abundance in the spectra of the weathered coal whereas peaks of the negative component are increased. The decreased yield of naphthalenes, tetralins, phenols and benzenes is accompanied by an increased abundance of small oxygen containing pyrolysis products such as carbon monoxide (m/z 28), carbon dioxide (m/z 44) and short chain fatty acids (m/z 46, 60, 74) as well as a markedly increased retention of the methanol solvent (peak at m/z 32) in the weathered sample [63].

Low voltage pyrolysis mass spectra of 8 fresh and weathered ANL coals, as well as those of two fresh and weathered non-ANL coals are shown in Figures I-12 through I-21. Comparison of the spectra of 10 fresh coal samples in Figures I-12a through I-21a shows the obvious effects of rank differences. The spectra of lower rank coals are dominated by dihydroxybenzenes and phenols of various degrees of alkylsubstitution, whereas those of higher rank coals show a dramatic decrease in dihydroxybenzene signals coupled with a markedly higher abundance of aromatic hydrocarbon series such as naphthalenes and benzenes. The effects of low temperature oxidation on the eight coals also can be examined by "subtracting" the

Figure I-10. Pyrolysis mass spectra of (a) fresh and (b) weathered Hiawatha seam coal (hvb) obtained at 12 eV electron energy and (c) the corresponding difference spectrum.

Figure I-11. Total ion current profiles of fresh and weathered Hiawatha seam coal. Note a 20% decrease in total yield and change in shape after weathering. Weathering condition was at 100°C for 212 hrs with dry air 80 ml/min.

Figure I-12. Curie-point pyrolysis mass spectra of (a) fresh, (b) weathered Pocahontas #3 seam coal, and (c) difference spectra. (s) denotes peak originating from solvent.

Figure I-13. Curie-point pyrolysis mass spectra of (a) fresh, (b) weathered Upper Freeport seam coal, and (c) difference spectra. (s) denotes peak originating from solvent.

Figure I-14. Curie-point pyrolysis mass spectra of (a) fresh, (b) weathered Lewiston-Stockton seam coal, and (c) difference spectra. (s) denotes peaks originating from solvent.

Figure I-15. Curie-point pyrolysis mass spectra of (a) fresh, (b) weathered Pittsburgh #8 seam coal, and (c) difference spectra. (s) denotes peak originating from solvent.

Figure I-16. Curie-point pyrolysis mass spectra of (a) fresh, (b) weathered Illinois #6 seam coal, and (c) difference spectra. (s) denotes peak originating from solvent.

Figure I-17. Curie-point pyrolysis mass spectra of (a) fresh, (b) weathered Utah Blind Canyon seam coal, and (c) difference spectra. (s) denotes peak originating from solvent.

Figure I-18. Curie-point pyrolysis mass spectra of (a) fresh, (b) weathered Wyodak seam coal, and (c) difference spectra. (s) denotes peak originating from solvent.

Figure I-19. Curie-point pyrolysis mass spectra of (a) fresh, (b) weathered Beulah-Zap seam coal, and (c) difference spectra. (s) denotes peak originating from solvent.

Figure I-20. Curie-point pyrolysis mass spectra of (a) fresh, (b) weathered Hiawatha seam coal, and (c) difference spectra. Positive components (DI⁺) represent mass peaks decreased in weathered sample and negative components (DI⁻) represent compounds increased in weathered sample. (s) denotes peak originating from solvent.

Figure I-21. Curie-point pyrolysis mass spectra of (a) fresh, (b) weathered Adaville #6 seam coal, and (c) difference spectra. Positive components (DI⁺) represent mass peaks decreased in weathered sample and negative components (DI⁻) represent compounds increased in weathered sample. (s) denotes peak originating from solvent.

spectra of the weathered coal samples in Figures I-12b through I-21b from those of the corresponding fresh samples (Figures I-12a through I-21a) using a discriminant analysis procedure [63] as described above for Hiawatha coal. This results in the difference spectra shown in Figures I-12c through I-21c. Comparison of the latter reveals an intriguing, generalized trend. The aromatic components of the eight coal pyrolyzates have decreased markedly, whereas the strong aliphatic signals (e.g., corresponding to C_nH_{2n+1} , C_nH_{2n} , C_nH_{2n-1} , and C_nH_{2n-2} ; $n \leq 10$) in each spectrum appear to have remained constant. This apparently reflects a difference in susceptibility to weathering effects between those structural moieties producing the above mentioned aliphatic peak series and those moieties giving rise to the aromatic hydrocarbon and hydroaromatic peak series.

A second, intriguing observation from Figures I-12c through I-21c is the qualitative similarity between the low molecular weight ion signals found to increase upon weathering. In all eight coals, especially lower rank coals than medium volatile bituminous, these peak series appear to represent highly polar short chain aliphatic compounds such as CO_2^+ (m/z 44) and CH_3COOH^+ (m/z 60). Furthermore, it is interesting to note the high intensity of m/z 32, thought to represent increased retention of the methanol solvent (used to prepare coal suspensions for Py-MS analysis) in the more polar, weathered coals.

A third, intriguing observation is that weathered Pocahontas #3 and Pittsburgh #8 coals produced different pyrolyzates compared to the other six coals; the former produced a big signal in m/z 178 (unfortunately, the exact nature of m/z 178 has not been identified yet) and the latter shows that the structural moieties producing benzenes and naphthalenes are changed to the moieties producing phenols and dihydroxybenzenes, suggesting the following mechanism of weathering might be possible for the Pittsburgh #8 coal:

The different behavior of Pittsburgh #8 and the higher rank Pocahontas #3 coals might give us a clue to the underlying mechanism of weathering. Here, it has to be pointed out that the normalization technique in the discriminant analysis might be responsible for the noticeably different behavior of Pittsburgh #8 coal. In order to confirm the different behavior of these two coals on weathering, one more series of Py-MS runs were performed on the same weathered coals, resulting in the same discriminant spectra.

First, let us concentrate on the differential loss of aromatic vs. aliphatic pyrolyzate components. It is tempting to try to explain this on the basis of possible differences in the susceptibility of the different

coal maceral components. As evident from the averaged pyrolysis mass spectra of maceral concentrates in Figure I-22, marked differences exist between the relative aliphaticity and aromaticity of pyrolyzates from fusinites (highly aromatic), vitrinites and sporinites (primarily aliphatic). Other liptinitic macerals such as alginite and cutinite provide even stronger aliphatic Py-MS patterns than sporinite [100], whereas resinites from Western U.S. coals are characterized by alicyclic and hydroaromatic series [101]. Thus, in principle, it would be possible that low temperature oxidation could effect primarily the more highly aromatic vitrinitic and/or fusinitic macerals while leaving the more aliphatic macerals relatively unaffected.

This brings up the interesting question which of the various liptinites are primarily responsible for the remarkably similar aliphatic patterns observed in all ten coals in Figures I-12 through I-21. Although sporinite is likely to contribute to the Py-MS pattern of the Carboniferous Upper Freeport coal, Cretaceous (Adaville, Hiawatha; Figures I-20, I-21) and Tertiary (Wyodak) Western coals generally contain only minor amounts of sporinite. Many Western coals, however, are known to contain marked amounts (e.g., 5-10%) of resinite [101]. Nevertheless, typical Py-MS patterns of resinites are quite different from the prominent aliphatic hydrocarbon patterns in Figures I-12 through I-21. Consequently, the authors believe that two ubiquitous liptinitic macerals, namely alginite (or detrital forms such as bituminite) and cutinite are primarily responsible for the observed aliphatic Py-MS patterns and may well be present in much larger quantities than estimated by micropetrographic techniques. Evidence supporting the potentially important contributions of algal coal components has been presented (though not completely interpreted) in previous Py-MS studies of over 130 U.S. coals [58, 102], whereas the grossly underestimated role of cutinitic macerals has recently been highlighted in several studies by de Leeuw and co-workers [103].

Pyridine extraction of Hiawatha coal before and after low temperature oxidation (Figure I-23) not only shows a dramatic decrease in extraction yield (22% vs. 4%) but also reveals a nearly complete separation between aromatic peak series (dominant in the extract) and aliphatic peak series (retained in the residue). Although it should be pointed out that the residue is likely to contain more or less highly condensed aromatic components as well (which may well have remained "invisible" to the Py-MS procedure), the apparent insolubility of the aliphatic hydrocarbon components is in line with the previous contention that alginite and/or cutinite derived macerals are likely to be responsible for the bulk of the observed aliphatic hydrocarbon signals in Py-MS patterns of whole coal. Both types of macerals are notoriously difficult to dissolve (cutinites and algal kerogens can be purified by means of strong acids!).

Careful examination of Figure I-23 also provides an important clue with regard to the possible fate of the disappearing aromatic moieties during low temperature weathering. Py-MS analysis of the pyridine residue of the weathered coal sample reveals a clear series of alkyl-naphthalenes, apparently liberated by the vacuum pyrolysis conditions. It is tempting to speculate that these aromatic moieties became linked ("grafted") to the macromolecular network during the weathering process. However, the possibility of physical entrapment (clathration) cannot be ruled out.

b) Vitrinite (averaged spectrum)

c) Fusinite (averaged spectrum)

b) Fresh Coal Pyridine Residue (78% yield)

c) Weathered Coal Pyridine Residue (96% yield)

Figure I-22. Typical pyrolysis mass spectra of three different maceral types obtained by averaging spectra of several different maceral concentrate samples, as obtained in an earlier study (25).

Figure I-23. Low voltage desorption/pyrolysis mass spectra of pyridine extract and residues from Hiawatha seam coal (s) denotes solvent peaks (pyridine solvent signals are indicated by dashed lines). Coal was weathered at 100°C 212 hrs with dry air 80 ml/min.

Present indications are that the grafted (or trapped) aromatic molecules alone cannot fully explain the marked loss of aromatic and hydroxyaromatic moieties but that some aromatic rings are destroyed by the oxidation process (in spite of the relatively low temperatures used), resulting in the formation of short chain aliphatic acids and ketones seen in Figures I-12 through I-21. Further support for this explanation is found in the results of low temperature oxidation studies on selected maceral concentrates of similar rank shown in Figures I-24 and I-25.

The factor score plot in Figure I-24 reveals that the resinite and semifusinite concentrates underwent more severe oxidative changes, which resulted in the formation of oxygen containing aliphatic moieties, than did the vitrinite concentrate. The sporinite concentrate showed the least severe weathering-induced degradation. The semifusinite samples provide the most likely source for the short chain, carboxyl- and carbonyl-containing, aliphatic compounds observed in the Py-MS patterns of weathered coal.

In short, aliphatic, hydrocarbon-rich coal structures thought to be derived from cutinitic or algal sources show little or no chemical changes under low oxidation temperatures. Further oxidation experiments with coals and maceral concentrates from different sources will have to be carried out in order to determine the general validity of the observed phenomena for coals of different rank and depositional history.

I.3.B. Results From Time-resolved Py-MS Studies

To obtain better insight into the underlying mechanisms of weathering-induced change in the pyrolysis patterns, time-resolved pyrolysis experiments were performed. The temperature of the Curie-point wire as a function of pyrolysis time was shown in Figure I-9. A relatively slow heating rate (approx. 100°K/s) was used compared to the maximum possible heating rate (approx. 5,000°K/s) of the Curie-point pyrolyzer in order to achieve better time resolution. As seen in Figure I-9, the heating rate is not linear over the whole temperature-rise period.

Time-integrated spectra, obtained by summing the 40 spectra recorded during the time-resolved pyrolysis experiments on Hiawatha coal, are shown in Figure I-26. As mentioned under "Experimental" these spectra were taken at 20 eV electron energy (set value) in order to increase signal intensity. Comparison of the spectra recorded at 12 eV and 20 eV, as shown in Figures I-20 and I-26 respectively, reveals that at 12 eV the aromatic ion signals dominate the ion signals of aliphatic hydrocarbons. As demonstrated by Nip *et al.* [62] aliphatic and aromatic compound series tend to give roughly similar signal intensities around 20 eV. However, as seen in Figure I-26, pyrolysis mass spectra taken at 20 eV are dominated by fragment ions. Even aromatic compound series such as alkylphenols and alkylnaphthalenes produce high intensity fragment ion signals thereby complicating the interpretation of the pyrolysis mass spectra. Because of the very high relative intensity of some ion signals in the lower mass range at 20 eV (e.g., at m/z 28, 32 and 44) only the m/z 50-200 mass range was scanned for the time-resolved analyses.

Figure I-24. Factor score plot from Py-MS data sets on fresh and weathered macerals. 100° rotation clearly shows the weathering effect. Macerals were weathered in sealed 2 l flasks containing dry air at 100°C for 100 hrs.

Figure I-25. Discriminant spectra of macerals. 100° rotation is weathering direction and 280° rotation is resinite direction when compared with Figure I-24.

Figure I-26. Pyrolysis mass spectra of (a) fresh, and (b) weathered Hiawatha seam coal obtained at 20 eV (compare with 12 eV spectra in Figure I-25.)

The time-resolved total ion current (TIC) curves of the Hiawatha coals (Figure I-11) indicate that the decomposition of this coal takes place primarily in a single stage. It should be noted, however, that the influence of potential low temperature products such as H_2O and CO_2 is eliminated because of the mass range selected.

Nevertheless, the first part of the TIC curves in Figure I-11 indicates the presence of some minor early components. Moreover, the intensity of the TIC curve is decreased by 20% in the weathered coal, although only slight weathering effects are visible on the shape of the curve. By looking at selected individual ion curves (e.g. at m/z 18 (H_2O^+), 32 (CH_3OH^+), 44 (largely CO_2^+), 60 (CH_3COOH^+) and 156 (mainly C_2 alkylnaphthalenes) (Figures I-27)) differences in the evolution profiles of some ion signals are readily observable. The m/z 60 (CH_3COOH^+) and m/z 156 (C_2 -alkylnaphthalenes) curves show strong weathering effects.

The profiles of three ions in the lower mass range were recorded at 12 eV electron energy. Methanol (m/z 32), used as solvent for preparing coal suspensions, is adsorbed into the pore structure of the coal and released during heating. The strongly increased methanol retention would seem to reflect the higher polarity of the weathered coal resulting in increased chemisorption. Obviously, a contribution by pyrolytic formation of CH_3OH cannot be ruled out. Water is formed during the entire pyrolysis process as seen in Figure I-27d. The first peak seems to belong to the chemisorbed water and shows decreased intensity in the weathered sample due to the drying effect of weathering. However, the second peak - appearing to be pyrolytic water - is increased, possibly reflecting the formation of hydroxyl groups during the weathering process. The ion signal at m/z 44 is mainly carbon dioxide since the propane contribution is only about 10% according to Py-GC measurements on the same coal [104]. Carbon dioxide has an increased early component showing that carboxylic groups were formed during weathering.

Of course, it is highly impractical to perform a visual comparison of the more than 150 ion signals scanned. Therefore, a multivariate analysis approach was chosen. Factor analysis was performed on both time-resolved data sets obtained during pyrolysis of the fresh and weathered samples. Factor analysis produced 3 factors with eigenvalues ≥ 1 from both data sets. Since Factor III explained only 1.2% and 1.5% of the total variances in the fresh and weathered coal spectra, respectively, only Factors I and II will be discussed here.

The scores of the first two factors of the fresh coal are plotted in Figure I-28. Each pair of two consecutive spectra was summed to improve signal-to-noise ratios. Thus, each point in the plot represents two spectra and spectrum sequence numbers increase linearly with pyrolysis time. The first factor (FI) represents 92.5% of the total variance showing that strong correlations exist between the evolution behavior of many pyrolysis products. The second factor (FII) represents only 3.8% of the total variance but indicates the presence of an early component (positive part) around spectrum #17, as well as a steadily increasing late component (negatively part of FII). These late components (e.g., phenols) are released more slowly during pyrolysis resulting in broader evolution curves

Figure I-27. Time-resolved intensity profiles of selected mass peaks at m/z 60 (a), m/z 156 (b), m/z 32 (c), m/z 18 (d) and m/z 44 (e) from fresh (—) and weathered (---) Hiawatha seam coal. For discussion see text. Note that all curves have been normalized to 100% relative ion intensities and, thus, do not reflect absolute abundances. Weathering condition was at 100°C for 212 hrs. with dry air 80 ml/min.

Figure I-28. Score plot of the first two factors showing the occurrence of several correlated trends in the time-resolved spectral patterns on Hiawatha seam coal. Plot numbers correspond with spectral sequence numbers. Compare with Figures I-29 and I-30.

Figure I-29. Variance diagrams depicting the behavior of correlated peak series in the two-dimensional space defined by Factors I and II revealing the evolution of "early components" during pyrolysis of both fresh and weathered Hiawatha seam coals. Compare with Figures I-28 and I-30.

The variance diagram technique [96] was applied to the data sets in order to numerically extract components with different evolution shapes. The variance diagram displays the total variance contribution of all mass variables found within consecutive 10°C windows in the space described by two factors. The variance diagrams of the fresh and weathered coals in the space of Factors I and II are shown in Figure I-29. The loadings (= correlation coefficients) on the second factors are multiplied by 2 in order to help bring out the salient aspects of FII in spite of the relatively low variance contribution.

Both variance diagrams in Figure I-29 reveal two clear component axes. The chemical components represented by these component axes are shown in the form of so-called "factor spectra" [97] in Figure 30. According to the variance diagram the early component is a linear combination of the first and second factors which can be obtained through a simple rotation. However, the rotated spectra would be entirely dominated by the first factor since the first factor represents more than 92% of the total variance in the data. Therefore, a better representation of the early component can be obtained by looking at the unrotated second factor.

Factor I represents components produced in the main degradation step. Comparison of the spectra of Factor I of the fresh (Figure I-30a) and weathered (Figure I-30c) coal, respectively, reveals that the "bulk pyrolyzate" is very similar in both coals. Only the phenols show decreased intensities in the weathered coal.

Weathering does have major effects, however, on the composition of the early components. The factor spectrum of FII is dominated by naphthalene and tetralin series in the fresh coal (see Figure I-30b) whereas the factor spectrum of FII in the weathered coal (see Figure I-30d) shows prominent sulfur dioxide (m/z 64), aliphatic acids (m/z 60, 74) and ketones or aldehydes (m/z 58, 72). The high SO_2^+ signals at m/z 64 indicates that some sulfur moieties in this low sulfur Western coal are oxidized during the weathering process.

On the basis of the factor analysis results, the TIC curves can be deconvoluted into three basic curves showing different evolution shapes. The deconvoluted curves are obtained by summing the ion intensities of the naphthalene series and of the main oxygen compounds as displayed in the spectra of the second factors in Figure I-30b and I-30d, respectively, as well as by plotting the scores of the first factors (the "bulk" components). As seen in Figure I-31, two different types of reactions take place both of which reach maximum rates at about 300°C. Naphthalenes and tetralins evaporating from the "mobile phase" [44], as well as small oxygen-containing molecules produced by pyrolytic pathways are produced. Weathering has opposite effects on the relative abundances of these components. Therefore only minor changes are detectable in the TIC curves shown in Figure I-11.

Figures I-32 and I-33 show total ion current profiles and each ion signal profiles on fresh and air weathered Upper Freeport seam coal. The total ion current curve has two noticeable maxima in Upper Freeport seam

Figure I-30. Numerically extracted "factor spectra" corresponding to the component axis identified in the variance diagrams (Figure I-29 on Hiawatha seam coal). Note the marked differences between the "low temperature components" before and after weathering as opposed to the clear similarity in "bulk component" patterns. Weathering condition was at 100°C for 212 hrs with dry air 80 ml/min.

Figure I-31. Time-resolved intensity profiles (Hiawatha seam coal) of the low temperature components as well as bulk components identified in Figures I-29 and I-30 showing the effective deconvolution of the total ion current profiles in Figure 11 into several component profiles by means of factor rotation methods. Weathering condition was at 100°C for 212 hrs with dry air 80 ml/min.

Figure I-32. Time-resolved recording of the total ion current during pyrolysis of fresh and air weathered Upper Freeport Seam coals. Weathering condition was at 100°C for 227 hrs with dry air 80 ml/min.

Figure I-33. Time-resolved recording of ion signals on Upper Freeport seam coal at (a) m/z 170 (C_3 -naphthalenes), (b) m/z 32 (methanol), (c) m/z 18 (water) and m/z 44 (mainly carbon dioxide). Each curve normalized to its own maximum intensity. Solid lines indicate fresh coal and dashed lines represent weathered coal. Weathering condition was at $100^{\circ}C$ for 227 hrs with dry air 80 ml/min.

coal whereas Hiawatha seam coal showed only one prominent maximum and an initial negligible maximum.

The second maximum is the main decomposition stage while the first maximum is caused by volatile naphthalenes and acids as well as to the carbon dioxide peak (e.g., representing decarboxylation reactions) as illustrated in Figure I-31. The detail evolution steps at two different electron energies are illustrated in Figure I-34. At both electron energies the main peak is broader in the weathered coal, similar to the DTG curves (Figure I-35). At 12 eV electron energy the peak at about 350°C appears to represent the increase amount of carbon dioxide.

Five major product evolution steps can be distinguished according to the time profile curves: (1) at the lowest temperatures water and solvent molecules (MeOH) evaporate from the coal; (2) at about 350°C "mobile phase" components (such as alkyl naphthalenes are released); (3) the degradation of functional groups starts at approx. 400°C (CO₂, H₂O formation); and (4) the thermal decomposition rate of the coal reaches a maximum at about 550°C. The last maximum (5) on the fresh coal curve (Figure I-27 and I-33) appears to be due to the combined effects of stabilization of the wire temperature at 610°C and the occurrence of further charring reactions.

Figure I-35 shows the DTG curves of the fresh and weathered Hiawatha seam coals illustrating the main stages of degradation (as established by TG-MS experiments). These measurements were performed at atmospheric pressure (in Argon), so the "mobile phase" evaporation starts at higher temperatures than under vacuum conditions. Since the coal samples were heated up to 900°C in the thermobalance, noticeable degradation of the inorganic components of coal also commences at about 800°C.

I.3.C. Results from Thermogravimetry/Mass Spectrometry (TG/MS) Experiments

Thermogravimetry (TG) is the technique of measuring changes in sample weight as a function of temperature, usually employing a linearly increasing temperature profile [105] whereas derivative thermogravimetry (DTG) is the technique of measuring the rate of weight loss (the first derivative of the TG profile). The importance of the DTG curve is that the temperature of maximum rate of weight loss in the DTG curve can be correlated to the relative reactivity of coal samples [106, 107]. For anthracite, this temperature occurs at the region of 750-870°C, whereas for high volatile bituminous coals it occurs at 490-600°C [105]. In general, low rank coal is more reactive than high rank coal because of its high content of functional groups. Figure I-36 shows TG and DTG curves for two coal samples. The temperature of maximum rate of weight loss occurs at 520°C for Upper Freeport coal (mvb) and at 470°C for Anderson coal (subbituminous C) respectively, confirming the general trend.

The TG and DTG curves in Figure I-36 also show the effects of weathering. As weathering proceeds, the slope of the weight loss curve decreases, which is clear in DTG curves. This trend is more dominant in Upper Freeport coal than in Anderson coal. The decreased slope appears to

Figure I-34. Time-resolved recording of total ion current during Py-MS on Hiawatha seam coal run at a) 12 eV and b) 70 eV electron energy. Fresh coal is indicated by solid lines and weathered coal by dashed lines.

- 1 = evaporation of moisture and solvent;
- 2 = mobile phase evaporation (e.g., alkylnaphthalenes)
- 3 = functional group decomposition (e.g., formation of CO_2)
- 4 = mobile phase decomposition (tar formation)
- 5 = network phase decomposition (char formation)

Figure I-35. DTG curves of fresh (-) and weathered (---) Hiawatha seam coal in argon atmosphere (heating rate 20°C/min.). Weathering condition was at 100°C for 212 hrs with dry air 80 ml/min.

Figure I-36. TG/DTG curves for Upper Freeport seam coal (hvAb) and Anderson seam coal (subbituminous C) coals at a heating rate of 20°C/min under a flowing argon atmosphere (140 ml/min.). Dry air 80 ml/min was applied for coal weathering.

be due to two separate weathering effects, namely (a) a decreased total volatile matter yield (and thus increased char yield); and (b) a broader distribution of activation energies in weathered coal. The latter effect appears to be explainable by a broader range of bond energies in weathered coal, encompassing weak noncovalent (hydrogen, ionic) bonds as well as covalent oxygen-containing bonds (e.g., anhydrides and esters) and highly stable covalent (e.g., arylether) bonds. The evidence for these new bond types in weathered coal has been discussed in earlier reports and publications [44, 108].

Earlier reported [6, 109] time-resolved Py-MS results for Hiawatha coal (hvb) showed that the evolution patterns of carbon dioxide (m/z 44), methanol solvent (m/z 32, used to prepare coal suspensions for Py-MS analysis), water (m/z 18), etc., become quite different as weathering proceeds. Figure I-33 shows the evolution profile of H_2O^+ (m/z 18) for Upper Freeport and Anderson coals. Upper Freeport coal shows a much more marked effect of weathering than the high moisture (30.2 wt%) containing Anderson coal. The first H_2O peak belonging to the "bulk" water and/or physically adsorbed (e.g., capillary) H_2O , shows decreased intensity in the weathered sample, thus reflecting the drying effect of the laboratory weathering conditions employed. The second and the other peaks are mainly due to chemically absorbed water and to pyrolytic water formed during pyrolysis [6]. For the Upper Freeport coal the time-resolved Py-MS results in Figure I-37 show that the pyrolytic water is increased, apparently reflecting the formation of hydroxyl groups during the weathering process. However, the Anderson coal does not show this trend, possibly due to its high initial moisture content. Significant quantities of strongly chemisorbed water in low rank Anderson coal must contribute to the second peak.

The characteristic weathering effect can be found in the evolution profile of m/z 44 as shown in Figure I-38. Pyrolysis GC data for Hiawatha coal showed that the ion signal at m/z 44 came mainly from carbon dioxide, only about 10% came from propane [6,109]. It is presently generally accepted that carboxyl, carbonyl and ether groups are increased when coal is weathered. Therefore, it is not surprising that CO_2^+ peaks are increased in Figure I-38. Especially the Upper Freeport coal shows dramatic changes in profile due to weathering. Normally fresh low rank coal contains more carboxylic functional groups. Comparing the area below the profiles (which is representative of the relative amount of the components measured) fresh Anderson coal contains more carboxylic groups than higher rank Upper Freeport coal. As weathering proceeds, however, the relative amount of these groups in Upper Freeport coal exceeds that of the lower rank Anderson coal. This suggests that in this respect Upper Freeport coal may be more susceptible to weathering than Anderson coal. Alternatively, newly formed carboxylic groups in Anderson coal may be lost more readily by decarboxylation during the weathering process (CO_2 production in Anderson coal during weathering is several times higher than in Upper Freeport coal [110]). Finally, the higher weathering temperature (100°C; Anderson coal: 80°C) of the Upper Freeport coal may be responsible for the observed discrepancy. For the peak profiles at m/z 28 (shown in Figure I-39) the effect of weathering is less obvious. The ion signal at m/z 28 may originate from CO_2^+ as well as from $C_2H_4^+$. Without information on which proportion of the signal comes from CO^+ or $C_2H_4^+$, it is difficult to draw any conclusions.

Figure I-37. Evolution profiles of m/z 18 (H_2O^+). Dry air 80 ml/min was applied for coal weathering.

Figure I-38. Evolution profiles of m/z 44 (CO_2^+). Dry air 80 ml/min was applied for coal weathering.

Figure I-39. Evolution profiles of m/z 28 (CO^+ and C_2H_4^+).
Dry air 80 ml/min was applied for coal weathering.

Figures I-40 and I-41 show the evolution profiles of aliphatic components such as m/z 42 ($C_3H_6^+$), m/z 41 (e.g., $C_3H_5^+$), m/z 43 (e.g., $C_3H_7^+$), m/z 56 (e.g., $C_4H_8^+$), and m/z 54 (e.g., $C_4H_6^+$). As weathering proceeds, the relative ion intensity of each aliphatic component decreases and the TG curve becomes broadened in 440-600°C region. Moreover Figure I-40 shows that the area below curve, representing the relative amount of each component, decreases with weathering. This result may be interpreted to mean that the aliphatic portion of the coal matrix is attacked by oxygen while being weathered. Generally, Fourier Transform Infrared (FTIR) analysis results and some NMR data [51] support this finding whereas other NMR [50] and Py-MS data [56] are contradictory.

Another interesting observation from Figures I-40 and I-41 is the difference in weathering rate. For Upper Freeport coal (mvb), the TG/MS differences between 10 days weathered coal and 1 day weathered coal are more profound than between the fresh and the 1 day weathered coal. For Anderson coal (subbituminous C), however, the changes during the first day almost equal the changes during the subsequent 8 days.

In the case of aromatics such as alkylbenzenes, alkylnaphthalenes, alkylphenols, and dihydroxybenzenes, several analytical methods generally agree on the effect of weathering. Volborth summarized the effect of weathering on structural changes of aromatic components in coal [111]. According to this summary, oxidation reactions of coal with air, oxygen, or some oxidizing agent such as hydrogen peroxide, nitric acid, potassium permanganate, sulfuric acid produce a mixture of water-soluble acids. Chromatographic and MS studies of these acids obtained from oxidation of bituminous coal, have detected mainly benzoic acid, phthalic acid, (+ isomers), mellitic acid, and trimellitic acid and its isomers.

The presence of phthalic acid suggests that naphthalene, anthracene, and phenanthrene type polycyclic aromatic nuclei are oxidized according to the following scheme:

Tronov has proposed an oxidation sequence of coal starting with the formation of polyhydric phenols and proceeding through carbonyl compounds (quinones) to acid anhydrides and carboxylic acids [111], as shown below:

Relative Ion Intensity

Figure I-40. Evolution profiles of aliphatic fragments from Upper Freeport seam coal (hvAb). Dry air 80 ml/min was applied for coal weathering.

a) Fresh Anderson Coal

b) 1 day weathered at 80°C

c) 9 days weathered at 80°C

Figure I-41. Evolution profile of aliphatic fragments from Anderson seam coal (subbituminous C). Dry air 80 ml/min was applied for coal weathering.

Jensen et al. [111] also proposed a scheme for coal oxidation similar to Tronov's:

Figures I-42 through I-44 show the trend of decreasing aromatic peak signals with weathering. Higher rank coals contain more aromatic compounds such as benzenes and naphthalenes, whereas oxygen-substituted aromatics such as dihydroxybenzene are more abundant in low rank coals. Therefore, alkylbenzenes and alkylnaphthalenes were chosen to represent the aromatic components of Upper Freeport coal and alkylphenols and dihydroxybenzenes were chosen as the representative moieties for Anderson coal. It should be noted that after each TG run tar deposits were cleaned off with benzene before the next run. Therefore the benzene peak (m/z 78) appearing at temperatures below 300°C is due to the benzene used for cleaning.

The benzene peak (m/z 78) in Figure I-42 shows another interesting phenomenon. As coal is being weathered at 100°C, the maximum peak temperature increases from 520°C for fresh coal to 640°C after 10 days weathering. This can be interpreted as a consequence of the "grafting reaction" proposed and discussed in earlier publications [44, 108].

I.3.D. Results from Isotope-Labeled Weathering Experiments

Structural changes due to different weathering atmospheres can be seen in Figure I-45. Fresh Anderson lignite is characterized by dominant dihydroxybenzene and phenol series. In samples oxidized in $^{16}\text{O}_2 + \text{N}_2$ as well as $^{18}\text{O}_2 + \text{N}_2$ atmospheres dihydroxybenzenes are decreased. Even though the main structural changes due to weathering appear to be almost identical for these two conditions, some noticeable differences in Py-MS patterns occur, as shown in Figure I-45.

First, the intensity differences between phenols and dihydroxybenzenes can be easily recognized in Figures I-45b and I-45c. The intensity of the dihydroxybenzene peaks at m/z 110 and 124 when the coal was oxidized in $^{18}\text{O}_2$ is lower than when it oxidized in $^{16}\text{O}_2$. Also m/z 112, 126, 140 are increased in the $^{18}\text{O}_2$ containing atmosphere. This means that some portion of the dihydroxybenzene molecules has incorporated ^{18}O and consequently the m/z values are increased by two. This is a clear indication that some of the dihydroxybenzene precursor molecules have reacted with ambient air (as simulated by $^{18}\text{O}_2 + \text{N}_2$). In addition, the peaks at m/z 46 ($\text{C}^{16}\text{O}^{18}\text{O}^+$), and m/z 62 ($\text{CH}_3\text{C}^{16}\text{O}^{18}\text{OH}^+$) also increased when $^{18}\text{O}_2$ was used. The same explanation applies to these components.

Multivariate analysis such as factor and discriminant analysis is a powerful tool to test the above mentioned explanation in a further logical

Relative Ion Intensity

Figure I-42. Evolution profile of alkylbenzenes from Upper Freeport seam coal (hvAb). Dry air 80 ml/min was applied for coal weathering.

Figure I-43. Evolution profile of alkynaphthalenes from Upper Freeport seam coal (hvAb). Dry air 80 ml/min was applied for coal weathering.

Figure I-44. Evolution profile of alkylphenol and dihydroxybenzenes from Anderson seam coal (subbituminous C). Dry air 80 ml/min was applied for coal weathering.

Figure I-45. Low voltage (12 eV) pyrolysis spectra of fresh, $^{16}\text{O}_2$ weathered, and $^{18}\text{O}_2$ weathered Anderson seam coal samples. (s) denotes solvent peak.

way. Figure I-46 shows the discriminant scores and the Variance Diagram obtained by discriminant analysis, which reveals a clear distinction between three groups. The discriminant score and Variance Diagram plots in Figure I-46 may be compared directly in order to explain the meaning of the Variance Diagram. This clearly shows that the main $^{18}\text{O}_2$ "weathering" direction explains structural changes induced by oxidation. Similarly, the 120° and 300° vectors appear to represent the $^{16}\text{O}_2$ weathering direction as well as the fresh coal direction respectively.

The chemical changes underlying the overall weathering trend can be visualized by plotting the discriminant spectrum corresponding to the 300° direction (Figure I-47a). This reveals decreased intensities of phenols and dihydroxybenzenes and increased intensities of alkenes and small polar molecules such as CO , CO_2 , CH_3COOH when the coal is weathered in either the $^{16}\text{O}_2 + \text{N}_2$ or the $^{18}\text{O}_2 + \text{N}_2$ atmosphere.

Figures I-47b and I-47c show the discriminant spectra corresponding to the $^{16}\text{O}_2$ weathering (120°) and the $^{18}\text{O}_2$ weathering (30°) directions, respectively. Mass peaks shown on the positive side of the spectra increased during oxidation. These figures clearly show that part of the CO_2 , CH_3COOH , and alkyl-dihydroxybenzenes signals is derived from newly formed oxygen functionalities during oxidation, whereas the remainder appears to represent oxygen containing structural moieties which were already present in the original fresh coal.

A semiquantitative impression of the component fractions derived from ambient oxygen can be obtained from the bivariate mass intensity plots in Figure I-48 and I-49.

According to the results shown in Figure I-44, the ratio between three kinds of CO_2 molecules ($\text{C}^{16}\text{O}^{18}\text{O}$, $\text{C}^{16}\text{O}^{16}\text{O}$, $\text{C}^{18}\text{O}^{18}\text{O}$) is approximately 3.5:3.5:1.0 after 200 hours of weathering. This shows that over 50% of the CO_2 represents oxygen functionalities produced by reactions with oxygen from ambient air; whereas less than 50% of the CO_2 produced comes from pre-existing structural moieties, e.g., carboxylic groups in coal.

Also, Figure I-49 clearly shows that m/z 48 ($\text{C}^{18}\text{O}^{18}\text{O}$), m/z 62 ($\text{CH}_3\text{C}^{18}\text{OH}^+$), and m/z 112, 126 (^{18}O labeled dihydroxybenzenes) increased in the oxygen isotope ($^{18}\text{O}_2$) environment, which agrees with the discriminant analysis results shown in Figure I-47.

Figure I-50 shows that H_2O produced by oxidative reactions with ambient air (m/z 20, H_2^{18}O) evolves at higher temperatures during pyrolysis than unlabeled H_2O (m/z 18, H_2^{16}O) representing moisture present in the original coal or formed during pyrolysis of pre-existing oxygen containing moieties, e.g., carboxylic acids. Apparently, ^{18}O labeled water molecules are primarily formed by pyrolytic mechanisms and little or no ^{18}O labeled water is found in the moisture fraction.

Figure I-46. Discriminant score plot and Variance diagram obtained from Py-MS data sets on fresh, $^{16}\text{O}_2$ weathered, and $^{18}\text{O}_2$ weathered Anderson seam coal samples.

Figure I-47. Discriminant spectra of Anderson seam coal (fresh, $^{16}\text{O}_2$ weathered, and $^{18}\text{O}_2$ weathered). Weathering condition was at 80°C for 214 hrs.

Figure I-48. CO₂ isotopes produced from the weathering of Anderson seam coal.

Figure I-49. Relations between intensities of ions containing ^{16}O and ions containing ^{18}O and representing aliphatic as well as aromatic oxygen containing components.

Figure I-50. Time-resolved curves of Anderson seam coal weathered in $^{18}\text{O}_2$ (21%) + N_2 . Weathering condition was at 80°C for 214 hrs.

II. MATERIAL BALANCE IN THE WEATHERING PROCESS

II.1. INTRODUCTION

II.1.A. Oxygen Uptake and Loss of Volatile Components

When coal is exposed to air, complex physical and chemical processes take place. At low temperatures the changes may occur very slowly, but the reactions often proceed over long time periods. From the standpoint of coal storage the temperature range of 0°C to 100°C is of the greatest interest. However, it was established that chemisorption of oxygen on the coal surface occurs even below 0°C [112]. Studying the type of oxygen adsorption as a function of temperature gives information about the interaction between oxygen and the coal surface. Adsorption isobars (Figure II-1) indicate the occurrence of three stages of oxygen adsorption. At very low temperatures the increase in the amount of adsorbed gas with increasing temperature is explained by activated diffusion [112]. The minima in the amount of adsorbed oxygen are ascribed to the change from physical adsorption to chemisorption occurring below 0°C. The magnitude of the heat of adsorption confirms that the adsorption is of a chemical nature even at about 0°C. The amount of oxygen recoverable from the adsorption decreases with rising temperature showing that chemical reactions are responsible for increasing oxygen consumption.

The occurrence of chemical reactions is indicated by the formation of volatile compounds evolved at temperatures as low as 10°C [4]. However, determination of the temperature at which these reactions start seems to depend on the detection limits of the instrument applied.

Using the term "oxycoal" for the weathered coal [13] the chemical reaction can be expressed as follows:

Coal consumes large quantities of oxygen. As a result, the concentration of oxygen in a coal storage pile rapidly diminishes and the amount of gases produced during weathering increases with increasing time as shown in Figure II-2 [29]. The reaction liberates heat and the accumulated heat accelerates the oxidation reaction leading often to spontaneous ignition [76, 113]. This aspect of weathering has been investigated in previous studies sponsored by Utah Power and Light Co. [114].

Since the temperature and gas composition as well as other affecting factors can not be controlled in a coal pile, laboratory scale experiments are widely used to study the mechanism and kinetics of low temperature oxidation of coal where each condition can be varied separately and its effect can be determined.

Several parameters have proved to be useful to describe the extent of oxidation of a particular coal (e.g. weight gain [115] and oxygen content [21]). Since the first oxidation reactions take place on the surface of a solid material, the reaction rate can be expressed by the rate of oxygen

Figure II-1. Absorption isobars obtained at constant oxygen pressure with two coals. (Reprinted from ref. 112).

Figure II-2. Gas composition and temperature inside a coal pile. o, oxygen; Δ , carbon monoxide $\times 100$; ∇ , carbon dioxide; $\bullet$, temperature. (Reprinted from ref. 4.)

uptake. This oxygen consumption parameter appears to be among the most reliable indicators for characterizing the reactivity of coals towards oxygen.

The experimental methods applied to the determination of oxygen uptake are generally based on measuring the amount of gaseous oxygen that disappears from the gas phase over a given time interval. The coal sample is maintained at constant temperature in a closed vessel or in a gas flowing at a measured rate through the coal. Manometric [116, 117] and volumetric [118, 119] techniques are used to calculate the oxygen consumption from the pressure drop or decreased volume of the weathering gas. Since coals release gaseous products during oxidation, these compounds should be removed before detecting pressure or volume changes. Direct analysis of the weathering gas composition provides information about both the oxygen consumed and the oxidation products. The accuracy of the gas analysis can be enhanced by using mixtures of gases (like air) instead of pure oxygen, in this case the inert component of the gas mixture serves as an internal standard. Nowadays the classical Orsat gas analysis [120] is replaced by sophisticated gas analysis techniques. Especially gas chromatography is applied for the analysis of gas components associated with coal weathering because of its high sensitivity and accuracy [121].

When coal is exposed to oxygen, the oxygen uptake proceeds at a high rate, but the rate of absorption declines with time [76]. In spite of the fact that stepwise changes in the rate of oxygen consumption were also reported [116, 117] it is generally accepted that the decrease of the rate of oxidation is continuous [119, 122]. Several rate equations were determined to describe the oxidation process [122-131], but it is not the purpose of this chapter to enter into the details of oxidation kinetics. It is interesting to note, however, that at low temperatures the oxidation of coals is slow but very persistent. The longest period over which the oxygen consumption was monitored at ambient temperature was 22 years [132] as seen in Figure II-3. This Figure shows the oxygen consumption of three coals in comparison with some other substances and indicates that coals exceed machine oil and cellulose in reactivity towards oxygen. However, coals appear to be less reactive than wood.

The relative tendency of coals to oxidize is different for various coals as seen in Figure II-3. Oxygen consumption rates reported for various coals under similar conditions differ by more than one order of magnitude. Low-rank coals react more readily with oxygen than high-rank coals. This can be related to the changes in the chemical composition and porosity of coals with rank. The lower the rank of coal, the higher its content of oxygen functional groups [13] which are more readily oxidized than saturated and aromatic hydrocarbons [45]. As rank increases from subbituminous to high volatile B or A bituminous coal, the porosity of coal decreases [133]. Thus, the internal surface area available for oxygen attack is higher in the low-rank coals.

The rate of oxidation increases with decreasing particle size, with increasing temperature and with increasing oxygen concentration. The influence of these factors has been studied by a number of investigators

[76, 116, 117, 130] and reviewed by Frost et al. [86]. Water plays an important role in the weathering of coals [134]. The effect of moisture is discussed in a separate chapter [135].

As already noted, volatile products are released from coal during weathering. Water and carbon dioxide constitute the major volatile components produced by every coal [18, 19]. By comparison, the amount of carbon monoxide evolved at ambient temperature is one order of magnitude less [132]. However, its rate of production increases to a greater extent with temperature than that of other gases [4]. The evolution of carbon monoxide together with the oxygen uptake appears to be related to the spontaneous heating tendency of coals [121]. Especially bituminous and subbituminous coals produce methane and other light hydrocarbons. Furthermore, traces of alcohols, aldehydes, ketones and carboxylic acids can be detected at oxidation temperatures of about 100°C [4, 136].

Figure II-4 [137] compares the carbon dioxide production rates of four U.S. coals to their respective oxygen consumption rates. The above discussed rank effect is reflected in the increased oxygen uptake with decreasing coal rank. The carbon dioxide formation varies similarly with rank but is not closely proportional to the amount of oxygen consumed. Carbon dioxide production appears to depend on the structure of coal as well as the rate of oxidation (as measured by oxygen consumption). However, the amount of CO₂ produced in inert atmosphere at the same temperature (80°C) is much less [137] indicating that CO₂ is not primarily formed by thermal decomposition of the carboxylic groups present in the fresh coal.

The amount of volatile products depends on the weathering conditions as well as the composition of the coal. The total amount of volatiles relative to the oxygen uptake increases with the rise of temperature [18, 19]. As seen in Table II-1, the water production predominates at lower temperature. However, at higher temperature the evolution of carbon oxides increases more rapidly. The production of CO₂ relative to the O₂ uptake increases as rank decreases [137]. Thus, coals of high oxygen content produce carbon dioxide to a greater extent than those of low oxygen content.

TABLE II.1.

Oxygen consumption, volatile products and mass gain (percent of original dry coal) during oxidation of a brown coal. (The data were taken from ref. 19.)

T	O ₂ uptake	CO ₂	CO	H ₂ O	Mass gain
°C	%	%	%	%	%
35	7.7	1.3	0.1	4.9	1.4
70	10.8	5.0	0.5	3.8	1.5

Figure II-3. Oxygen consumption of various substances as a function of time. a, pine tree; b, brown coal; c, hard coal (VM: 35.1%); d, hard coal (VM: 23.0%); e, cellulose; f, machine oil. (Reprinted from ref. 132).

Figure II-4. Integrated oxygen consumption (a) and carbon dioxide production of coals oxidized at 80°C in air. ∇, Anderson lignite; ●, Adaville subbituminous coal; Δ, Hiawatha seam coal (hvb); ○, Upper Freeport seam coal (mvb). Dry air 5 ml/min was applied for coal weathering.

II.1.B. Changes in Mass and Elemental Composition

The mass of the coals continuously changes during weathering. The observed change in mass is a balance between the mass gain due to the oxygen uptake and the mass loss due to the evolution of volatile products. The ratio of the oxygen consumption to the volatile production depends on the coal constitution and the weathering conditions (mainly on the weathering temperature).

The mass changes can be studied as a function of temperature by thermogravimetry. The TG curve and measurements of the main volatile products reveal that several stages of oxidation can be distinguished by applying slow heating rates [138], as shown in Figure II-5. At low temperatures (up to 70°C) chemisorption takes place and the resulting measurable increase in mass was detected by Oreshko [139]. The mass loss in the second stage can be explained by the decomposition of the coal-oxygen complex [139]. It is more likely, however, that the mass loss can be attributed to the release of moisture, as measured by a mass spectrometer coupled to the thermobalance (Figure II-5). During the third stage (about 200-300°C) a rapid increase in mass is observed due to the formation of stable oxygen functional groups. At higher temperatures a sharp decrease in mass is observed which is accompanied by the rapid evolution of volatile products indicating that thermal decomposition of coal occurs. As seen in Figure II-5, the evolution of water is dominant at lower oxidation temperatures, but the amount of carbon dioxide increases rapidly with the rise of temperature. It is likely that the oxidation stages overlap each other and that the rates of the various steps change continuously with temperature. It is evident that chemisorption precedes chemical reaction. However, chemical reaction occurs already at ambient temperatures [4, 112]. It is generally accepted that less stable compounds such as peroxides are formed in the first stage of chemical reaction [3]. Stable oxygen containing functional groups are produced after longer oxidation times or at higher temperatures [17, 18, 53].

In order to eliminate the disturbing effect of the continuous moisture loss on the mass determination, isothermal measurements are required. Before weathering experiments are performed, moisture is generally removed by evacuating the sample or by heating the sample while flushing with inert gas. Care must be taken to avoid contact with air, otherwise the mass of the fresh coal (reference point) will be uncertain. Figure II-6 shows the mass gain of a medium volatile bituminous coal oxidized at coal oxidized in a TG system at constant temperature [138]. The samples oxidized at lower temperatures (150, 210 and 260°C) show continuous gain in mass up to several hours. At higher temperature (285°C), however, after a rapid increase in mass the mass curve passes through a maximum. The temperature at which the decline of mass occurs appears to be dependent on coal rank. The mass of the subbituminous coal produced a maximum curve at 175°C [140], while the decline in mass takes place at 250°C using a high volatile bituminous coal [141]. In these experiments the decrease in mass occurs within a few hours. When applying lower oxidation temperatures the decline occurs only after longer periods of time, e.g. Swann and Evans [19] reported no further increase in mass after

Figure II-5. Mass changes (a) as well as water and carbon dioxide production (b) during oxidation of a medium volatile bituminous coal when using a 4°C/min heating rate. (Reprinted from ref 138)

Figure II-6. Mass changes of a medium volatile bituminous coal oxidized at constant temperatures. (a) 150°C; (b) 210°C; (c) 260°C (d) 285°C. (Reprinted from ref. 138)

about 45 days at 70°C for a brown coal. According to the previously discussed gas analysis results [132] the oxidation does not cease at this point, but the mass of oxygen consumed equals the mass of volatile products evolved from the coal.

The results of the previously discussed studies can be rationalized as follows. During weathering the coal consumes oxygen, causing the concentration of oxygen containing groups to increase with time and the apparent rank of the coal to decrease. However, the "lower rank coal" releases relatively large amounts of volatile products and eventually the volatiles production exceeds the oxygen uptake. At high temperatures the rate of oxidation is very high and the structure of the coal is altering rapidly. Therefore, the decline in mass occurs within a short time.

Thermogravimetric methods of recording sample masses are capable of maintaining the sample at constant temperature only for a limited time. Therefore, TG studies were carried out at higher temperatures (above 120°C) to detect measurable changes within a few hours [140, 141]. However, studying the temperature range 0 to 100°C is more important from the standpoint of coal storage. The mass changes can be monitored over long time periods by weighing the samples regularly. Figure II-7 [137] shows the mass changes of three U.S. coals at 100°C in flowing air and nitrogen. The reference runs in nitrogen show the amount of moisture evolved under the same conditions (temperature, flow rate, time) as the oxidation was carried out. The advantage of this method is that the samples were not previously subjected to a drying procedure, thereby avoiding possible oxidation. As reflected by the mass differences, the oxidation accompanying the drying of coal in air is very rapid during the first hours. It reveals that the moisture content of coals is underestimated under oxidative conditions because of the concomitant oxidation reactions. Nevertheless standard ASTM drying procedures are carried out in air atmosphere [142]. As seen in Figure II-7, the rate of mass gain does not show a simple relationship to the rank of the coal. Thus, it should be noted that the relative oxidation tendency is determined more precisely by measuring the oxygen uptake.

That oxygen is consumed and mainly carbon oxides and water are released during the oxidation of coal suggests that the weathering is accompanied by changes in the elemental composition of coal. Procedures for determining the elemental composition of coals ("ultimate analysis") are based on combustion methods for quantitative assessment of carbon, hydrogen, nitrogen and sulphur [143]. The amount of oxygen is routinely estimated by difference. The measured elemental composition is generally normalized to a "dry, mineral matter free" or "dry, ash free" basis. Therefore the calculated value of the oxygen content accumulates not only the analytical errors, but also errors in determination of mineral matter content [144]. Notwithstanding all these uncertainties, ultimate analysis is widely used in addition to proximate analysis to characterize the rank of a coal [13].

Since ultimate analysis is not suitable to detect subtle variations in coal composition, significant changes in elemental composition are generally reported only for severely weathered samples. Most outcrops of

coal seams have been exposed to air for many thousands of years and they show a high degree of weathering in every respect. Fissures and oxidation rims can be detected by microscopic examination [8, 13] and the chemical composition of the surface coal differs markedly from that of the coal at greater depths. The oxidation gradient decreases sharply from the surface and the physical and chemical characteristics are reasonably constant after about 20 m depth [8, 15]. In general, outcrop samples have 3-5 times higher oxygen content than the fresh coal which is accompanied by a significant decrease in carbon and hydrogen content [8, 42]. Although the observed weathering trends appear to be generally similar for naturally oxidized coals and for samples oxidized under laboratory conditions, it is difficult to explain the apparently weathering related, fine structural differences among the layers of a coal seam [8]. The nature of the coalified "input" materials and the conditions of coalification may differ considerably across a seam. On the other hand, leaching of soluble organic and inorganic components by percolating surface water may be expected to contribute to natural weathering processes.

In laboratory experiments, the weathering process can be speeded up considerably by applying higher temperatures. Figure II-8 shows the distribution of carbon, hydrogen and oxygen of a vitrain oxidized at 170°C for periods of up to ten days [21]. The changes are very rapid during the first hours and eventually the oxygen content increases to about 29%. The hydrogen concentration is reduced to half its original value, while the loss of carbon is relatively small. It should be noted that these data are calculated on a 100% mass basis and not corrected for the changes in mass during oxidation.

The disturbing effect of the mass changes can be eliminated by calculating the ratios of the element concentrations. H/C vs. O/C diagrams (so-called Van Krevelen plots) are useful for detecting tendencies in a series of coal samples [13]. Plotting Marinov's data [25] in this type of diagram (Figure II-9) reveals that low-temperature oxidation (60°C) is accompanied by detectable changes in elemental composition if oxidation is carried out for long periods of time. The H/C ratio is decreased with increasing O/C ratio for the three coals of various rank. In other words, more hydrogen is evolved probably in the form of water than as carbon oxides during oxidation. According to gas analysis data [18, 19], at low temperatures, indeed more water is produced than carbon oxides on a molar basis. However, at higher temperature the formation of light hydrocarbons might contribute to the decrease in H/C ratios.

In the first period of oxidation the increase in the oxygen content appears to be the most important change in elemental composition because the yield of volatile products is low in comparison with the oxygen uptake. Therefore, the precise determination of oxygen content might contribute to the detection of incipient oxidation. The only direct method available for oxygen determination is activation analysis. Neutron activation [145-147] and charged particle activation [31] analysis are sensitive to total oxygen and do not differentiate between the oxygen combined with various minerals and organically bound oxygen. Though both the organic constituents and minerals (pyrites) are affected by

Figure II-7. Mass changes of coals oxidized at 100°C in air (●, ▲, ▼) and heated in nitrogen at 100°C (○, △, ▽). ●, ○, Upper Freeport seam coal (mvb); ▲, △, Hiawatha seam coal (hvb); ▼, ▽, Adaville subbituminous coal. Dry air and nitrogen 80 ml/min were applied for coal weathering.

Figure II-8. Changes in elemental composition of vitrain oxidized at 170°C. (Reprinted from ref. 21).

Figure II-9. Diagram showing H/C ratio versus O/C ratio in coals oxidized at 60°C. Carbon content of original samples: o, 87.6%; ▽, 76.1%; Δ, 67.6%. (The data were taken from ref. 25).

weathering, changes in total oxygen content can be monitored by activation analysis. The sensitivity of the charged particle activation analysis was demonstrated by Cronauer *et al.* [8]. An increase in the O/C ratio was already detected during the oxidation of a bituminous coal at 125°C for only one hour. The distribution of oxygen within the coal particle appeared to be homogeneous as determined by the oxygen depth profiles on a coal oxidized at 150°C. Neutron activation analysis data were compared with "oxygen by difference" values for naturally weathered samples by Gray *et al.* [8]. The use of activation analysis is promising with respect to coal weathering especially when combined with other techniques. For example, inorganic oxygen can be determined in the low-temperature ash and the organically bound oxygen can be calculated from the difference between inorganic oxygen content and total oxygen content as determined by activation analysis [111, 148].

Besides the major elemental constituents (C,H,O) the sulphur content of coal also appears to be affected by weathering. Sulphur occurs in coal in both organic and inorganic forms. Changes in the pyrite and sulphate moieties phases have been studied by a number of investigators as discussed in Chapter I.1.D. However, little is known about the effect of weathering on the organic sulphur groups. Liotta *et al.* [17] have reported that the organic sulphur content decreases in a high sulphur coal during oxidation. Thermogravimetry mass spectrometry studies [138] showed that the amount of hydrogen sulphide produced from organic sulphur moieties during thermal decomposition decreases markedly in weathered coals. This experiment indicates that sulphide groups are likely to be involved in oxidation processes.

II.2. EXPERIMENTAL

Four coal samples (Upper Freeport, Hiawatha, Adaville #6, Wydak), the proximate analysis data of which were given in Table I-3, were oxidized at 100°C to examine the effect of coal rank on the mass balance during air weathering. Samples were crushed and milled to -60 mesh in nitrogen atmosphere and stored under nitrogen atmosphere in hermetically closed glass bottles at -20°C in the dark.

A schematic diagram of the experimental apparatus is shown in Figure II-10. The reactor used for carrying out the weathering runs was a glass reactor, 104 mm in length and 37 mm o.d., fitted with Swagelok fittings at each end and an effluent line connected to a GC. A sintered glass disc distributor at the bottom of the reactor was used to prevent channeling inside the reacting coal. Also glass wool was used inside of the reactor to prevent entrainment of coal particles. A charge of 19-24 g of sieved (-60 mesh) coal to the reactor produced a bed height of approximately 5 cm. The reactor was then placed in a weathering oven which was controlled to within $\pm 1.0^\circ\text{C}$ and heated to 100°C in less than 2 minutes. The coal sample was not dried before the experiment.

Gas (dry air or pre-purified nitrogen) was passed through the reactor at a constant flow rate via a rotameter. The gas flow rate in each experiment was also checked with a soap bubble flowmeter set at the reactor outlet. A stable pressure of 10 psig was maintained on the up-stream side of the rotameter by a standard two-stage gas cylinder pressure regulator.

To prevent the condensation of water vapor inside the teflon tubes connecting the reactor with the GC inlet, all tubes were properly heated. Special care was given to the tube connecting the oven for weathering and the GC oven. The teflon tube was kept inside of a 3/8" copper tube which was also kept inside of a heated aluminum rods (3.7 cm o.d., 1.0 cm i.d.). The aluminum rod was always kept above 200°C during the run.

Organic substances from the reactor were collected in a cold trap using acetone and dry ice at the outlet from the weathering reactor for pyrolysis mass spectroscopy. The teflon tube to the trap was kept inside a 3/8" copper tube which was wrapped with an insulating wool.

The cold trap was carefully rinsed with 1 ml methanol to dissolve the organic substances which were condensed on the wall of the trap. Five microliters of methanol suspension which contained the organics were then dropped and adsorbed on the 610°C Curie-point wire which was coated with water glass and activated carbon and was prepyrolyzed 3 or 5 times to get rid of impurities. Curie-point pyrolysis conditions for coal samples and organic samples were identical, that is, electron energy 12 eV, scanning mass range 20-260 m/z, scanning rate 1000 amu/s, temperature rise time about 6 s, equilibrium temperature 610°C, total heating time 10 s.

The experiment was performed in a semi-batch operation mode. Gas samples were taken from the reactor through a 6-way valve to GC for the analysis of O₂, CO₂, H₂O, CO, CH₄, etc. (Figure II-11). For this

Figure II-10. Schematic of weathering system with on-line GC analyses of evolved gases and trapping of organic volatiles.

Figure II-11. Schematic of flow system for coal weathering.

report, only one 4-way valve in the GC oven, one 6-way valve for collecting gas samples (250 μ l), and a thermal conductivity detector (TCD) were used. Molecular sieve 5-A and Porapak-Q were used as adsorbents at 80°C (isothermal) in the GC. The carrier gas was helium.

The gas analysis results were interpolated polynomially by least squares approximation and then the interpolated polynomials were numerically integrated using the Romberg algorithm to get the cumulative values.

The operating conditions for the individual runs are given in Table II-2 and proximate analyses were done by the ASTM method.

Pyridine extractions were performed in a regular Soxhlet extractor for 24 hours at room temperature. An attempt was made to remove the pyridine from the extracts and residues by evaporation under vacuum at 10^{-2} torr.

TABLE II-2.

OPERATING CONDITIONS OF WEATHERING RUNS FOR OXYGEN MATERIAL BALANCE

COAL	UPPER FREEPORT	HIAWATHA	ADAVILLE	WYODAK
<u>EXPERIMENTAL CONDITION</u>				
Temperature (°C)	100	100	100	100
Gas Flowrate (ml/min)				
Air Weathering	5.0	5.0	10.0	10.0
Nitrogen Weathering	5.0	5.0	10.0	10.0
Sample Weight (g)				
Air Weathering	19.86232	23.78598	20.55001	20.44268
Nitrogen Weathering	19.95502	22.75909	20.68243	19.48719
Weathering Time for the Weathered Py-MS sample (hrs)	203	170	212	186
<u>CHROMATOGRAPH CONDITION</u>				
Oven Temperature (°C)		80 isothermal		
TCD Temperature (°C)		150		
TCD Current (mA)		150		

II.3. RESULTS AND DISCUSSION

II.3.A. Changes in Chemical Composition

The qualitative information on changes in chemical composition in coal due to weathering was already illustrated in Chapter I. In this section, the quantitative results will be shown and discussed in terms of changes in proximate analysis values and extraction yields.

The effects of weathering on proximate analysis values are shown in Table II-3. Although interpretation of the subbituminous data is complicated by some unforeseen idiosyncrasies of the ASTM proximate analysis methods, it is clear that the Hiawatha coal undergoes the most pronounced changes. The strong increase in fixed carbon content (3.9% after 96 hrs at 100°C in air) would seem to be understandable in light of the drastic decrease in vacuum (5% → 1%) and pyridine extractable (22% → 4%) components exhibited by this coal (Table II-4). Although no data are available on the loss of extractable components in the Adaville coal, the Anderson lignite showed only an insignificant change (12.8% → 11.5%) in pyridine extractables after weathering at 80°C in air for 232 hours. In general, the weathered coals show a pronounced decrease in volatile matter content and an increase in fixed carbon content, thus an increase in fuel ratio, especially for higher rank coals than lower rank coals.

It can be concluded that weathering, even at relatively low temperature (100°C) compared to the practical operating conditions, makes coal lose a fair amount of volatile matter as shown in Table II-3 so that it can be easily expected that the weathered coal will lose its heating value. The change in heating value due to weathering is shown in Table II-5. From this table, it is obvious that the direct use of heating value by the standard ASTM method can greatly mislead the conclusion such that weathering makes coal increase its heating value. When heating value is not corrected for weight change, heating value appears to be increased by weathering. As will be discussed in detail in the next section, weathering is a complex, dynamic process involving concomittant moisture loss, oxygen gain and loss of carbon and hydrogen through CO, CO₂, CH₄, H₂O, etc., and thus the weight of coal during weathering changes continuously. Since the heating value is based on unit mass of coal, without the information on weight changes the comparison of heating value between fresh and weathered coal does not represent the real situation, especially in weathering accompanying a fair amount of weight change (i.e., dry air weathering experiment at the laboratory). The weight change curves for three coals are shown in Figures II-12.

II.3.B. Oxygen Material Balance

The material balance equation can be set up at time t as follows if the initial portion of water produced due to drying can be ignored:

TABLE II-3.

EFFECT OF WEATHERING ON THE VOLATILE MATTER AND FIXED CARBON CONTENT OF COALS

(Data corrected for weathering reduced weight changes and calculated as an "as received" basis)

COAL	SAMPLE TREATMENT*	F.C.(%)	V.M.(%)	FUEL RATIO (F.C./V.M.)
Upper Freeport (mvb)	fresh	60.15	29.03	2.07
	air weathered at 100°C for 10 days	66.63	25.64	2.60
Hiawatha (hvab)	fresh	42.38	41.42	1.02
	N ₂ exposed at 80°C for 120 hrs.	42.86	40.02	1.07
	air weathered at 80°C for 96 hrs.	44.48	39.57	1.12
	air weathered at 100°C for 96 hrs.	46.29	38.67	1.20
Adaville #6 (subbit.)	fresh	43.00	33.39	1.29
	N ₂ exposed at 100°C for 120 hrs.	39.55	32.47	1.22
	air weathered at 100°C for 120 hrs.	43.44	33.82	1.28
Anderson (lignite)	fresh	33.66	30.70	1.10
	N ₂ exposed at 80°C for 232 hrs.	33.69	29.91	1.13
	air weathered at 80°C for 232 hrs.	34.36	30.74	1.12

* 80 ml/min N₂ or dry air was used for weathering

TABLE II-4.

PYRIDINE EXTRACTION YIELDS ON FRESH AND WEATHERED COALS

COAL	SAMPLE TREATMENT	PYRIDINE EXTRACTION YIELD (%)
Upper Freeport (mvb)	fresh	28.7
	air 80 ml/min weathered at 100°C for 10 days	24.1
Hiawatha (hvab)	fresh	22.
	air 80 ml/min weathered at 100°C for 212 hrs.	4.
Anderson	fresh	12.8
	air 80 ml/min weathered at 80°C for 232 hrs.	11.5

TABLE II-5.

EFFECT OF WEATHERING ON CALORIFIC VALUE (Btu/lb)

Coal	Calculation Basis	Fresh	80°C, N ₂ *	%**	80°C, air*	% **	100°C, air*	%**
Anderson (lignite)	as received	8099	11629	+43.6	10982	+35.6	n.d.	
	dry	11597	11626	+0.3	10985	-5.3	n.d.	
	weight corrected***	8099	8019	-1.0	7747	-4.3	n.d.	
Adaville #6 (subbit.)	as received	9988	n.d.		n.d.		11393	+14.1
	dry	12225	n.d.		n.d.		11480	-6.1
	weight corrected***	9988	n.d.		n.d.		9343	-6.5
Hiawatha (hvAb)	as received	12028	12556	+4.4	12299	+2.3	12063	+0.3
	dry	12457	12575	+0.9	12318	1.1	12078	-3.0
	weight corrected***	12028	12003	-0.2	11893	-1.1	11773	-2.1

n.d. = not determined

* weathering time: Anderson coal 232 hrs, Adaville #6 coal 120 hrs, Hiawatha coal 96 hrs.

** difference with corresponding "fresh" value.

*** corrected for weight changes due to incorporation of oxygen during weathering; BTU values calculated on and "as received" basis.

Figure II-12. Effect of weathering on weight of (a) Hiawatha seam (b) Adaville #6 seam and (c) Anderson coals. Dry air and nitrogen 80 ml/min were applied for coal weathering.

$$O_{2in} + W_{N_2} = W_{O_2} + O_{2out} + H_2O_{loss} + CO_2 + Volatiles_{loss} \dots (1)$$

where: W_{O_2} : weight of coal sample at time t in air atmosphere
 W_{N_2} : weight of coal sample at time t in nitrogen atmosphere
 O_{2in} : cumulative oxygen weight at reactor inlet until time t
 O_{2out} : cumulative oxygen weight at reactor outlet until time t
 H_2O_{loss} : cumulative water weight at reactor outlet until time t
 CO_{2loss} : cumulative carbon dioxide weight at reactor outlet until time t
 $Volatiles_{loss}$: cumulative weight of other substances at reactor outlet until time t

In fact, O_{2in} minus O_{2out} and W_{O_2} minus W_{N_2} are identical to cumulative oxygen uptake and overall weight gain, respectively. Then eq. (1) can be arranged to give:

$$W_{gain} = O_{2uptake} - H_2O_{loss} - CO_{2loss} - Volatiles_{loss} \quad (2)$$

Weight gain in eq. 2 can be measured from the result shown in Figure II-13, which shows weight changes due to weathering by air and nitrogen for each coal sample studied. Usually the first weight gain was measured after 20 hours of weathering so the data curves were not drawn at this initial stage in Figures II-14 through II-17. The first two terms in the right hand side of eq. (2) can be calculated from the gas analysis results. The integrated values for these two terms until time t are shown in Figure II-14 through II-17.

The weight change curve using nitrogen was used as a basis to calculate the weight gain mainly due to oxygen uptake. The weight gain of the coal matrix until time t was calculated as follows:

$$\frac{[(\text{weight \% using } O_2 \text{ at time } t) - (\text{weight \% using } N_2 \text{ at time } t)]}{(100) (\text{weight of the initial coal sample, g})}$$

$$\times (\text{weight of the initial coal sample, g}) \times (1000), \text{ mg weight gain/g-coal} \quad (3)$$

H_2O and CO_2 loss in the right hand side of eq. (2) can be calculated from the gas analysis results. The integrated values for these two terms until time t were shown in Figure II-14 through II-17.

The main components of the flue gas were carbon dioxide and water. These products may be produced from the desorption from coal matrix and/or the reaction with oxygen. According to the $^{18}O_2$ isotope experiment in the closed reactor, approximately 56 percent of carbon dioxide produced comes from the reaction with oxygen from air [82].

Figure II-13. Effect of weathering on weight of four different rank coals. Weathering conditions are given in Table II-2.

Figure II-14. Cumulative mass change vs. weathering time for Upper Freeport seam coal; notice large contribution of lost organic volatiles.

Figure II-15. Cumulative mass change vs. weathering time for Hiawatha seam coal.

Figure II-16. Cumulative mass change vs. weathering time for Adaville #6 seam coal.

Figure II-17. Cumulative mass change vs. weathering time for Wyodak seam coal.

Carbon monoxide was not detected at the 100°C experiments. According to the result of Kaji et al. [130] who used Wyoming coal with similar properties as Wyodak coal, the carbon dioxide production rate at 100°C was approximately 5 percent of the carbon dioxide production rate. This means about 300 ppm of carbon monoxide are produced after 20 hours of weathering with air. Since Wyodak Coal (lignite) may release more carbon dioxide than the other coals studied as shown in Figures II-14 through II-17 the detection of carbon monoxide from the other three coals should be even more difficult than that from Wyodak coal. Methane concentrations were also negligible.

As shown in Figures II-14 through II-17, the material balance could not be closed only with CO₂, H₂O and weight gain. There is still a big discrepancy which needs to be accounted for. This portion is expressed in eq. (2) as volatile loss which comprises in fact many volatile organic substances as shown in Figures II-18 through II-21.

According to the results which are shown in Figures II-14 and II-15, Upper Freeport coal consumed almost identical amounts of oxygen as Hiawatha coal, but produced much less CO₂ and H₂O. It is very interesting to compare this result with that of Adaville and Wyodak coals, which consumed almost identical amounts of oxygen and also produced nearly identical amounts of CO₂ and H₂O.

Analysis of the condensable flue gas components revealed major differences between the four coal samples. The higher rank coals (Upper Freeport and Hiawatha) produced mainly aromatic (benzenes, naphthalenes) and aliphatic hydrocarbons, as shown in Figures II-18 and II-19. For Adaville coal, phenol and alkenes were the main flue gas components (Figure II-20). The most interesting observation was made for Wyodak coal, which produced abundant quantities of a sesquiterpenoid resin (see Figure II-21). Nearly all peaks appearing in the spectrum of organics in the Wyodak flue gas (Figure II-21) are electron ionization fragments of sesquiterpenoid molecular ions at m/z 206. Finally, it should be mentioned that the weathered Upper Freeport and Adaville coals showed increased SO₂⁺ abundance in the pyrolyzate but not in the flue gas.

Figure II-18. Curie-point pyrolysis mass spectra of condensable volatiles accompanying the flue gas for Upper Freeport seam coal.

Figure II-19. Curie-point pyrolysis mass spectra of condensable volatiles accompanying the flue gas for Hiawatha coal.

Figure II-20. Curie-point pyrolysis mass spectra of condensable volatiles accompanying the flue gas for Adaville #6 seam coal.

Figure II-21. Curie-point pyrolysis mass spectra of condensable volatiles accompanying the flue gas for Wyodak coal.

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III. DEVELOPMENT OF A RELIABLE WEATHERING INDEX

III.1. INTRODUCTION

It is well known that weathering has a profound effect on many important coal properties such as coking characteristics, slurry pH, flotability, tar yield, extractability, etc., as well as on coal utilization processes such as combustion, pyrolysis, gasification and liquefaction. However, since coal is a very heterogeneous material and its properties differ according to rank and seam, it is very difficult to define reliable standard values for the degree of weathering. Therefore, most methods for determining the degree of weathering provide relative values and have practical usefulness only if measured values can be calibrated against coal samples weathered under carefully standardized conditions. Since fresh samples from several standard coals are now available from the Argonne Premium Coal Sample Program (PCSP) systematic studies of the weathering behavior of these coals have become practical as well as timely.

One of the main goals of the research reported here is to develop a reliable "weathering index". For the purpose of this report "weathering index" can be defined as a combination of several weathering sensitive tests (weathering indicators) which together provide a more sensitive and reliable measurement of the weathering status of a given coal than can be obtained by each individual test.

In the past, many different attempts have been made to measure the degree of weathering of given coal sample. One of the more obvious approaches is perhaps to determine the oxygen content by oxidative [149, 150], reductive [151, 152], or pyrolytic methods [153]. Alternatively, oxygen content can be measured directly by neutron activation analysis [144]. However, the uptake of oxygen by a given coal can be offset to a significant degree by the concomitant loss of CO_2 , CO and H_2O [110], thus making the new increase in oxygen content far from easily predictable. Moreover, most oxygen measurement techniques are notoriously time-consuming and unreliable.

Workers in the coke producing industry have known for a long time that caking properties of coal change dramatically upon weathering. consequently, they have tried to develop simple and practical methods for determining the degree of weathering. Gray *et al.* [8] suggested an alkali-extraction method as one of several candidates. Lowenhaupt and Gray [12] applied this alkali-extraction method using light transmittance as an index of weathering for high to low volatile bituminous coals. The fact that coal swelling properties change dramatically when a caking coal is weathered presents many potential opportunities for determining the weathering status. Swelling properties of coal can be measured by means of Free Swelling Index (FSI), dialation, Gieseler fluidity or gas flow resistance tests [154, 155]. For strongly caking coals FSI is not as sensitive as the other three methods [38, 156]. However, Gieseler values tend to drop to zero after some oxidation time. Under moderate and severe weathering conditions, however, FSI is a good index of weathering, especially in the FSI range between 1 and 4 [73].

Fourier Transform Infrared Spectroscopy is known to show an increase in carbonylic, carboxylic and phenolic groups as well as a decrease of aromatic and aliphatic moieties. Huggins et al. [72] proposed the ratio of reflectance in the carbonyl band region to that in the region of the aromatic and aliphatic C-H stretch bands as a possible weathering index.

Thermal analysis methods, e.g., thermogravimetry (TG), as well as analytical pyrolysis techniques (e.g., pyrolysis MS (Py-MS)) also show a strong response to weathering. Izuhara et al. used the change of maximum weight loss rate in TG as a weathering parameter, whereas Jakab et al. [6] used time-resolved Py-MS to show that the evolution profiles of several components (carboxylic acids, naphthalenes, methanol, water, etc.) were quite different when coal was weathered.

The Zeta potential of coal particle suspensions in H₂O can also be a good indicator of weathering. Since weathered coal shows poor flotation characteristics, several studies were undertaken to understand this phenomenon in more detail [158-160]. In general, weathered coal shows lower Zeta potential values than fresh coal.

Another important feature of weathered coal is its acidic character. Thus, Gray et al. [8] suggested coal slurry pH measurement method as one of several candidate techniques for determining weathering status. They reported slurry pH changes from 7.1 to 5.5 for fresh and severely weathered Pocahontas #3 coal, respectively. Hill et al. [9] applied this idea to subbituminous (Adaville #6) coal, but added 0.01 wt% surfactant to the slurry in order to enhance the wetting of coal with water. For fresh and moderately weathered (1 to 6 days at 100°C) coals, they reported pH changes from 7.2 to 5.0 and applied this result to coal samples obtained from coal storage piles in order to estimate concomittant btu losses. When coal is exposed to air, oxygen, hydrogen peroxide, nitric acid, potassium permanganate, and other oxidizing agents, mixtures of water soluble acids are formed. For bituminous coal, chromatographic and mass spectrometric studies show that these acids consist mainly of benzoic, phthalic, mellitic and trimellitic acids and their isomers [111]. Py-MS results also show an increase of short chain carboxylic acids, e.g., acetic acid, during weathering [56].

Moreover, in some cases phthalic anhydrides can be detected by FTIR [33, 57] as well as by time-resolved Py-MS [35]. If these phthalic anhydrides formed due to weathering can be hydrated to the free acid form, then simple slurry pH measurements can be used as a method of detecting the degree of weathering, as will be shown in this report.

Also, results obtained by other weathering sensitive tests, e.g., FSI as well as Py-MS data, which may be used in combination with pH measurement techniques in order to obtain a more reliable "weathering index", will be shown.

III.2. EXPERIMENTAL

III.2.A. Free Swelling Index (FSI) Determination

The Free Swelling Index of the weathered and non-weathered (fresh) coal was determined according to the ASTM standard method D-720. Briefly the method involves heating one gram of 60 mesh coal powder contained in a special crucible in an oven at 800°C and then comparing the resulting coke button with a series of standard profiles to which indices are assigned (Figure III-1). The slightly modified experimental set up used in these experiments has been reported in more detail elsewhere [73].

III.2.B. Pyrolysis MS Tests and Data Processing

Spectrum calibration and normalization were carried out on the Py-MS data sets using numerical techniques described by Harper *et al.* [66]. Subsequently, factor and discriminant analysis were performed using the SPSS (Statistical Package for the Social Sciences) program as described by Windig *et al.* [96, 97]. After factor analysis, discriminant analysis was applied on all factors with eigenvalues ≥ 1 using each group of triplicate analyses of a single sample as a separate category. Thus, the discriminant analysis approach used here should be regarded as a "nonsupervised" form of multivariate data analysis aimed at improving the signal-to-noise ratio of the data while avoiding the creation of artificial clustering. The results are presented in the form of discriminant score plots which provide a quantitative measure for the differences between the pyrolysis mass spectra of the fresh and weathered coal samples, and in the form of rotated "discriminant spectra" [97] which provide insight into the major underlying chemical tendencies.

III.2.C. pH Titration

Twenty gram aliquots (-60 mesh) of all eight PCSP coals were exposed to dry air flow (10 ml/min in a 100 ml glass reactor, at 100°C for 8 days. The Blind Canyon seam coal was weathered for 2, 4, 6 and 8 days in separate glass reactors at 100°C and the Pittsburgh #8 seam coal was weathered at 150°C for 1 and 3 days in order to determine the effects of weathering time and temperature, respectively.

Weathered coal samples were then transferred to a Parr 4745 general purpose digestion bomb. 2.0 g of coal were mixed with 20 ml deionized water, put in a 23 ml Teflon container and heated to 150°C for 2 hours. Subsequently, the bomb was cooled under tap water for 10 minutes. Next the coal slurry was transferred to a polystyrene beaker for pH measurements. 20 ml of deionized water was used to rinse the remaining coal from the teflon container. Resistivity of the deionized water used was more than 16 megohm-cm. pH titrations were performed with a Mettler DL40RC titrator using a 20 ml burette with 0.01 M titrant (0.01N NaOH) increments. This procedure is summarized in Figure III-2 and the schematic of the titration system is shown in Figure III-3.

Figure III-1. ASTM standard FSI profiles.

Figure III-2. Modified coal slurry pH measurement procedure.

Figure III-3. Schematic of automatic titration system.

III.3. RESULTS AND DISCUSSION

III.3.A. Free Swelling Index (FSI) [73]

The results of FSI determination (ASTM method) on freshly mined Wasatch Plateau coals, as listed in Table III-1, show that FSI values of 3.5 to 4.0 are common in these coals if care is taken to minimize exposure to air. The FSI values in Table III-1 are probably the highest FSI values reported for Wasatch Plateau Field coals. The values for "fresh" Wasatch Plateau Field coals in the Penn State Coal Data Bank are in the 2.0 - 3.0 range. However, after 5-7 years storage in the Penn State Coal Bank under Argon (but not submerged in water), several of these coals examined by us now have FSI values as low as 1.0 -1.5. Although it is possible that some of these FSI losses occurred during sub-aliquotting, grinding and mixing of the "mother" samples in the Penn State Coal Bank, the occurrence of markedly decreased FSI values in samples distributed by the Penn State Coal Bank provides further arguments in favor of the "Premium Coal Bank" project currently underway at Argonne National Laboratories. Several other observations can be made upon inspection of Table III-1. First of all several of the top seam samples show lower FSI values. The cause of these lower values has not been investigated yet. However, it is well known that the composition of the inorganic as well as organic constituents of coals can fluctuate widely as a function of depth and that such fluctuations can be especially pronounced near the upper and lower seam boundaries.

The observed differences in FSI values between samples from the same seam channels highlight the notoriously difficult problem of obtaining representative samples of any given channel, mine or seam.

Each of the 11 samples in Table III-1 were analyzed by pyrolysis mass spectrometry in order to obtain an impression of the heterogeneity of the samples with regard to organic composition. These analyses revealed no major systematic differences between the different mines or seams. Moreover, no obvious correlation existed between the Py-MS patterns and the FSI values. Marked differences were found, however, between a few individual samples, e.g. Deer Creek (top) or Desbedove, (bottom) and most of the remaining samples. Since the middle portions of the Desbedove, Wilberg and Deer Creek mines showed very similar Py-MS patterns and also showed relatively small differences in FSI values, these middle portions were selected for further weathering studies. The samples from the Beehive mine were totally excluded from further study since the relatively low FSI values of the two Beefive samples pointed to possible weathering e.g., as a result of the long term exposure of the channel faces in the (inactive) Beehive mine to air. Proximate analyses of composite samples of coal from these four mines are given in Table III-2.

Figures III-4 and III-5 show the effect of variables (i.e., temperature, humidity, gas flow rate) on weathering in terms of FSI. There were the dramatic effects due to weathering by temperature and gas flow rate on FSI, however no noticeable effect on FSI by humidity level of weathering gas was found. As will be discussed in the next section, there was no effect of humidity level on the initial pH values, which is consistent with the result from FSI.

TABLE III-1

FREE SWELLING INDEX* OF FRESH MINED WASATCH PLATEAU COALS

Mine:	Desbedove	Wilberg	Deer Creek	Beehive
Seam:	Hiawatha (#1)	(Hiawatha #2)	(Blind Canyon)	(Blind Canyon)
Top	1.5 (1.5 + 1.5 + 1.0)	3.5 (3.0 + 3.5 + 3.5)	2.0 (2.0 + 2.0 + 1.5)	2.5 (2.5+2.5+3.0) 3.0 (3.0+3.0+3.0) these samples do not reflect top, middle or bottom of the seam
Middle	3.5 (3.5 + 3.5 + 3.5)	4.0 (4.0 + 4.0 + 4.0)	3.5 (3.0 + 3.5 + 3.5)	
Bottom	4.0 (4.0 + 4.0 + 4.5)	3.5 (3.5 + 3.0 + 3.5)	3.5 (4.0 + 3.5 + 3.5)	

* averages of three determinations (individual values given between parentheses).

TABLE III-2

PROXIMATE ANALYSIS OF FRESH MINED WASATCH PLATEAU COALS

Mine:	Desbedove	Wilberg	Deer Creek	Beehive
Seam:	Hiawatha (#1)	Hiawatha (#2)	Blind Canyon**	Blind Canyon**
% Ash	10.9	16.7	5.9	4.8
% Volatile Matter	42.6	41.3	45.2	46.0
% Moisture	3.0	2.0	2.4	3.0
% Fixed Carbon	43.5	40.0	46.5	46.2

* "as received" values for composite samples obtained by non-standardized aliquotting and mixing procedures and therefore not necessarily representative of mine output.

** non-ANL ampule sample

Figure III-4. Free Swelling Index value of Hiawatha #1 seam coal at different weathering conditions.

Figure III-5. Effect of weathering at 100°C in air on FSI of coal samples from Hiawatha and Upper Freeport seam mines. (*) Non-ANL ampule sample.

Figures III-6 through III-8 show the effect of weathering temperature on FSI for Blind Canyon and Hiawatha seam coals. Blind Canyon seam coal used for this experiment was not obtained from ANL.

III.3.B. Discriminant Analysis of Py-MS spectra

In order to follow the chemical changes occurring throughout the weathering process the Py-MS data were evaluated by factor and discriminant analysis. For discriminant analysis each set of three replicate spectra was assigned to a separate category. Discriminant analysis optimizes the differences between the categories ("between-category variance") relative to the differences within the categories ("within-category variance"). The discriminant scores provide a quantitative measure of the differences between the samples.

A scatter plot of the discriminant scores of the Upper Freeport coal samples in the space described by the first two discriminant functions (DI, DII) is seen in Figure III-9a (DI and DII represent 98.8% of the between-category variance). The score plot shows that the overall weathering trend appears to correlate negatively with both discriminant functions and thus is best represented by a (40-50°) rotated vector (W) which can be regarded as a simple linear combination of DI and DII. The corresponding "Variance Diagram" [96] in Figure III-9b confirms that the main correlations between changes in peak intensities are found in the 40-50° direction in DI/DII space. The DI and DII scores were projected orthogonally onto the weathering vector W and the new scores were plotted as a function of weathering time [Figure III-10]. As seen in Figure III-10 there is a gradual change in the pyrolysis pattern although the rate of change is slightly more pronounced at the beginning of the weathering process. This observation was supported by independent reaction rate measurements [104] and by the study on weathering index using the initial slurry pH [161].

The discriminant score obtained by discriminant analysis on Py-MS spectra was found to be more sensitive to weathering than FSI when compared to Figures III-5 and III-10.

III.3.C. pH titration

In earlier weathering studies involving a subbituminous Adaville coal [9], direct pH titration at ambient temperature showed a marked increase in acidity (more than 2 pH units) after exposure of the coal sample to air at 100°C for 6 days. However, subsequent pH titration experiments with coals of different rank, including Wyodak (subbit/lignite), Hiawatha (hbBb) and Freeport (mvb) coals gave negative or ambiguous results under the same weathering conditions. Nevertheless, Py-MS analyses of the same coals showed a distinct increase in carboxylic and carbonylic functional groups [56]. In subsequent Py-MS studies of the weathering behavior of individual macerals [35], strong signals were noted which appeared attributable to anhydrides of phthalic acid and/or other aromatic acids. This provided us with a possible clue to the observed lack of strong pH changes since anhydride formation would effectively remove the acidic protons. Therefore, an attempt was made to re-hydrate the weathered coal

Figure III-6. Free Swelling Index value of coals weathered at 50°C with air stream; 80 cm³ min⁻¹.

Figure III-7. Free Swelling Index value of coals weathered at 60°C with air stream; 80 cm³ min⁻¹.

Figure III-8. Free Swelling Index value of coals weathered at 80°C with air stream; 80 cm³ min⁻¹.

Figure III-9. (a) Score plot of the first two discriminant functions obtained from Py-MS data on fresh and weathered (100°C, 80 ml/min) Upper Freeport seam coal samples. Numbers denote the duration of weathering (in days). Note the direction of the rotated vector W corresponding to the weathering trend. (b) Variance diagram showing the direction of the major correlations of mass peak variables in the space of the first two discriminant functions. Compare with Figure III-9a.

Figure III-10. Weathering curve obtained by projecting the discriminant scores in Figure III-9a on the main weathering vector W. Note that changes in Py-MS patterns are detected before measurable FSI changes occur (see Figure III-5).

samples before carrying out pH titrations. As described under Experimental, rehydration was carried out at 150°C in teflon-lined Parr bombs. As shown in Figure III-11 and subsequent figures this procedure was found to be very simple as well as effective in "restoring" the acidity of all weathered coals investigated thus far. Figure III-11 further suggests that the initial pH can also be a good weathering index for Utah Blind Canyon coal, and in fact the initial slurry pH was successfully used to estimate heating value loss in the subbituminous coal pile [161].

Figure III-12 shows the effect of weathering duration on pH and repeatability of the method. Clearly, as coal is weathered, more acidic products are dissolved out and therefore lower pH values are obtained. The small differences between repeat analyses on the same weathered coal may be due to temperature variations of the solution. More precise standardization of the method is planned to overcome this problem.

Figure III-13 shows the effect of different coal rank, viz. low volatile bituminous (hvb) to lignite. As expected, low rank coals produce more acidic products during weathering. The difference in the amount of titrant needed to reach pH 8 between fresh and weathered coals reveals even more clearly the effect of rank. Difference spectra obtained by Py-MS analysis of coals of different rank confirmed this observation by showing that structural changes in mvb Upper Freeport coal were only about 30% of those observed in subbituminous Wyodak coal when weathered at 100°C [56].

Possible depositional effects for four coals of similar rank (hvb) are shown in Figure III-14. Profound differences in terms of the initial pH as well as the slope of the titration curve are found. Lewiston - Stockton coal has the highest initial pH. This is thought to be due to major differences in depositional environments. Although Lewiston-Stockton coal and Pittsburgh #8 coal show very similar titration curves the difference of the initial pH is most noticeable. In contrast to these coals, Illinois #6 coal produces the most acidic solution. This may be due to its higher sulfur content (and/or higher surface area) than other coals.

The effect of weathering temperature is shown in Figure III-15. Note the dramatic pH difference after only 1 day at 150°C as contrasted to up to 8 days weathering at 100°C. This suggests that the weathering temperature may be the most important variable in weathering.

Another important variable to weathering, air humidity, was found not to be dependant on the initial slurry pH as shown in Figure III-16, which is consistent with the FSI result. However, the titration curves show the effect of air humidity. This may be due to the fact that as titration proceeds, the difference in surface characteristics between weathered coals by dry air and humid air may start to play an important role. The coal used in Figure III-16 was Adaville #4 seam coal which has very similar properties to Adaville #6 seam coal. Also it should be pointed out that the sample used for titration in Figure III-16 was not water-treated like other coals in this report. For lower rank coals, the direct measurement of the initial slurry pH proved to be a good weathering indicator, although sometimes the wetting problem arises [161].

Figure III-11. Effect of water treatment at 150°C on pH titration curve.

Figure III-12. Effect of weathering duration on pH titration curve. Lower three curves show repeatability for 8 days weathered coal at 100°C. Sample were water-treated before titration and dry air 10 ml/min was applied for coal weathering.

Figure III-13. Effect of rank on pH titration curves. Samples were water-treated before titration and dry air 10 ml/min was applied for coal weathering.

Figure III-14. Effect of deposition on pH titration curves. Samples were water-treated before titration and dry air 10 ml/min was applied for coal weathering.

Figure III-15. Effect of weathering temperature on pH titration curves for Pittsburgh #8 seam coal. Samples were water-treated before titration and dry air 10 ml/min was applied for coal weathering.

Figure III-16. Effect of air humidity on the pH titration curves of fresh and weathered Adaville #4 seam coal. Note the absence of change in the initial slurry pH between dry air and humid air runs. Samples were not water-treated before titration and dry air 10 ml/min was applied for coal weathering.

In conclusion, a simple pH titration method based on rehydrating coal slurries at 150°C was proved to be a successful way of monitoring weathering effects in all 8 ANL-PCSP coals. For LVB and higher rank coals, however, slurry concentrations should perhaps be increased to compensate for the decreased susceptibility to low temperature weathering. Also, detailed characterization of the low MW components extracted by the rehydration procedure is expected to yield important information on the underlying mechanisms of the weathering process.

The difference in pH value between fresh and weathered Lewiston-Stockton seam coal was small when compared with other similar rank coals in Figure III-14. This is in contradiction to the weathering results on macerals discussed in Chapter I.3. Lewiston-Stockton seam coal is known to contain about 16% fusinite. Consequently, the pH difference would be expected to be at least as much as for other similar rank coals, since (semi)fusinite was the most sensitive maceral component to weathering [56, 57]. This suggested that the "fresh coal" prepared at BPC was weathered and prompted us to test the original PCSP coals received in ampules under Argon. The results of the comparison between fresh coals prepared at BPC and fresh ampule coals under Argon after water treatment are shown in Figures III-17 and III-18. These figures clearly show that the fresh coals prepared at BPC were weathered. It is not clear whether fresh coals prepared at BPC were originally weathered, and/or weathered during shipment under water from ANL, and/or weathered during drying and grinding under nitrogen at BPC. The nitrogen concentration for drying and grinding at BPC was above 99.%. However, the temperature while grinding in the ball mill was around 40-60°C approximately. Considering the earlier discussions of the observed, dramatic effects of temperature on the weathering process, the grinding step may well be the main reason for the difference.

Figure III-17. Effect of hydration treatment (2 hours at 150°C) pH titration curve for four fresh high volatile bituminous PCSP ANL coal samples. Comparison with Figure III-14 used BPC prepared ANL coals clearly shows that BPC prepared samples were weathered than ANL ampule samples.

Figure III-18. Effect hydration treatment (2 hours at 150°C) on pH titration curve for four fresh PCSP ANL coal samples ranging from low volatile bituminous coal to lignite coal. Comparison with Figure III-13 used BPC prepared ANL coals clearly shows that BPC prepared samples were weathered than ANL ampule samples.

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IV. PROPOSED WEATHERING MECHANISMS

Low-temperature air oxidation is a selective process and the most reactive structural moieties are oxidized first. Due to the complex structure of coal, different oxidation reactions are likely to proceed simultaneously. Moreover, low temperature oxidation of coal is, to some extent, reversible. It has been observed [3] that oxidized coals are able to oxidize solutions of ferrous thiocyanate and potassium iodide. This experiment indicates that less stable oxygen-containing groups, such as peroxides and hydroperoxides, are formed during the first stages of oxidation and then decompose to produce stable oxygen-containing groups. Involvement of organic free radicals in the oxidation processes has been established by electron spin resonance spectroscopy (ESR) [162]. Free radical concentrations are increased in coal after vacuum drying due to the breakdown of labile functional groups (e.g. carbon dioxide is evolved from carboxylic acid groups) [162, 163]. Subsequent exposure of dry coal to air leads to changes in free radical concentration indicating that on the one hand free radicals react with oxygen and on the other hand they are produced during oxidation [162]. These observations are consistent with the view that peroxides are formed by radical mechanisms in the first step of oxidation. It is thought [17] that aliphatic hydrocarbon moieties are oxidized through peroxide formation.

The autoxidation of hydrocarbons in the liquid phase is well known [164]. The results of these studies are the source of theories concerning the mechanisms of coal oxidation. Several routes have been proposed for the production of hydroperoxides in coal [4, 17, 165, 166]. It can be assumed that the oxidation starts with the generation of a carbon radical:

The oxygen as a diradical might contribute to the abstraction of hydrogen [4, 165]. Also, the breakdown of functional groups appears to be accompanied by radical formation [162, 163]. Assuming the existence of a chain reaction, the propagation step can be described as follows:

Coupling reactions of two radicals can terminate the chain reaction:

The hydroperoxide may then decompose to form stable oxygen-containing functional groups. Alkylperoxides produce a mixture of alcohol and carbonyl compounds and generally water is evolved during thermal decomposition of peroxides. Primary ($R' = H$) and secondary ($R' = \text{alkyl}$) hydroperoxides may undergo the following reaction:

Hydrogen abstraction from aliphatic side groups of aromatic rings or from saturated carbon atoms of hydroaromatic moieties requires less energy than hydrogen removal from saturated hydrocarbons due to the stabilization of the resulting radicals by resonance interaction with the aromatic rings. Thus, it seems reasonable that the autoxidation of coal develops from the aliphatic -groups of the aromatic rings through peroxide formation, analogous to the oxidation of model compounds [53]. The decomposition of primary and secondary alkylaromatic peroxides leads to the formation of alcohol and carbonyl groups, as described above. Tertiary alkylaromatic hydroperoxides may produce hydroxyaromatic moieties (e.g. phenols) by the following rearrangements:

The formation of acids can be explained by the subsequent oxidation of the primary oxidation products.

It should be pointed out that oxidation of coal occurs on the surface of a solid material where the movement of organic radicals is restricted. Thus, the rate of chain reaction must be reduced. Furthermore, convincing experimental evidence has not been reported to support the chain reaction mechanism of coal oxidation. If oxidation proceed by chain reactions we would expect to observe an induction period in the rate of oxidation. However, most of the studies could not detect any induction period [119]. On the other hand, introduction of antioxidants should have a retarding effect on the chain reaction. Phenols are known as radical inhibitors because the resulting free radicals are resonance stabilized and therefore less reactive to further oxidation. Especially the low-rank coals, which are most susceptible to oxidation, do contain appreciable concentrations of phenolic groups. Nevertheless, low-rank coals are readily oxidized in the presence of such potential inhibitors. Antioxidant tests show [119, 167, 168] that high dosages of inhibitors are necessary to produce a measurably decreased reactivity of coals towards oxygen. On the basis of these facts, the possibility of chain reactions can not be excluded. However, we can assume that easily donatable benzylic hydrogens are lost but that other mechanisms also play a role in coal oxidation.

From studies on the mechanisms of coal weathering one can conclude that the oxidation is almost exclusively restricted to the reactions of hydrocarbon species via peroxide formation. However, it is well-known [45] that saturated and aromatic hydrocarbons are not as susceptible to oxidation as some of their oxygen-containing derivatives. In other words, aliphatic hydrocarbons have to be activated first by the formation of peroxides. Certain oxygen-bearing functional groups are much more readily oxidized. Stability studies of coal-derived liquids indicate [84] that non-hydrocarbon components are more susceptible to oxidation and that the phenolic hydroxyl groups of the acidic fraction are directly involved in the oxidation process rather than in the role of inhibitor.

That the oxygen-containing groups are further oxidized was confirmed by experiments with isotope-labelled oxygen ($^{18}\text{O}_2$) [82]. A lignite was oxidized in $^{18}\text{O}_2$ at 80°C and subsequently pyrolyzed. Both kinds of isotope-labelled carbon dioxide ($\text{C}^{16}\text{O}^{18}\text{O}$ and C^{18}O_2) were evolved during pyrolysis, but the $\text{C}^{16}\text{O}^{18}\text{O}$ to C^{18}O_2 ratio was about 3:1. Similarly, acetic acids with one ^{18}O atom ($\text{CH}_3\text{C}^{16}\text{O}^{18}\text{OH}$) were detected in the pyrolyzate whereas the production of acetic acid with two ^{18}O atoms was not observed. Ignasiak et al. [80] oxidized a high volatile bituminous coal in $^{18}\text{O}_2$ and found the $\text{C}^{16}\text{O}^{18}\text{O}$ to C^{18}O_2 ratio in the pyrolyzate to approximately 2:1. These observations indicate that oxidation of oxygenated species to carboxylic groups is dominant over the oxidation of hydrocarbon moieties to carboxyl groups, especially in low rank coals. It seems reasonable that carboxyl groups are formed by oxidation of carbonyl groups. Especially aldehydes are susceptible to oxidation, therefore the following reaction can be proposed:

The thermal stability of carboxyl groups is strongly influenced by the neighboring groups. It can be assumed that thermally less stable carboxyl groups (e.g. -ketoacids) are also formed which then decompose producing carbon dioxide. This conception explains the evolution of carbon dioxide during low-temperature oxidation.

Several studies [17, 24, 31] indicate the involvement of phenolic OH groups in weathering reactions and the formation of ether cross-links. Condensation of two hydroxyl groups may result in the formation of ether bridges, however, the role of oxidative atmosphere in condensation reactions can not be explained. Furthermore, pyrolysis-mass spectrometric investigations showed [63] that the decrease of dihydroxybenzenes is more pronounced in the pyrolyzate of weathered coals than the decrease of phenols. A possible explanation is that the dihydroxybenzene moieties are first oxidized to quinonic structures:

The IR spectra of weathered coals show the enhancement of highly conjugated carbonyl groups [30], but other experimental evidence for the formation of quinones has not been reported. Since quinones are known as radical inhibitors, it is reasonable to assume that they react with radicals formed during oxidation of other moieties in coal:

The above reaction schemes provide an explanation for the formation of ether bridges as well as for the decrease of phenolic groups observed especially in low-rank coals.

Oxidation studies of model compounds [169] reveal that some condensed aromatic rings are as susceptible to oxidation as hydroaromatic

compounds. It was suggested [170] that oxidation of condensed aromatic systems produce phenols and quinones which are capable of retarding chain reactions as discussed above. Further oxidation of phenols and quinones may result in ring opening of aromatic structures, especially at elevated temperature. For example, the oxidation of anthracene moieties may lead to the formation of phthalic acid:

Pyrolysis-mass spectrometric experiments [56] indicate the production of aromatic and aliphatic carboxylic acids as well as the corresponding anhydrides during oxidation of coals at 100°C. The increased abundance of acids is accompanied by the decreased intensities of aromatic and hydroaromatic compounds in the pyrolyzate of weathered coals. These observations can be explained by the degradation of aromatic and hydroaromatic rings during oxidation.

In this section we attempted to outline the most likely reaction types which can explain the main experimental observations. However, it should be emphasized that probability of certain reactions strongly depends on the original structure of coal and the weathering conditions.

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