Surface Properties of Photo-Oxidized Bituminous Coals

Final Report
September 1, 1993 - February 28, 1997

Work Performed Under Contract No.: DE-FG22-93PC93223

For
U.S. Department of Energy
Office of Fossil Energy
Federal Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

By
The Pennsylvania State University
Coal and Organic Petrology Laboratory
105 Academic Projects
University Park, Pennsylvania 16802

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

Natural weathering has a detrimental effect on the hydrophobic nature of coal, which in turn can influence clean-coal recovery during flotation. Few techniques are available that can establish the quality of coal surfaces and that have a short analysis time to provide input for process control. Luminescence emissions which can be quantified with an optical microscope and photometer system, are measurably influenced by degree of weathering as well as by mild storage deterioration. In addition, it has been shown that when vitrinite is irradiated with a relatively high intensity flux of violet- or ultraviolet- light in the presence of air, photo-oxidation of the surface occurs. The combination of measuring the change in luminescence emission intensity with degree of surface oxidation provided the impetus for the current investigation.

The principal aim of this research was to determine whether clear correlations could be established among surface oxygen functionality, hydrophobicity induced by photo-oxidation, and measurements of luminescence intensity and alteration. If successful, the project would result in quantitative luminescence technique(s) based on optical microscopy that would provide a measure of the changes in surface properties as a function of oxidation and relate them to coal cleanability. Two analytical techniques were designed to achieve these goals. Polished surfaces of vitrain bands or a narrow size fraction of powdered vitrain concentrates were photo-oxidized using violet or ultraviolet light fluxes and then changes in surface properties and chemistry were measured using a variety of near-surface analytical techniques.

Results from this investigation demonstrate that quantitative luminescence intensity measurements can be performed on fracture surfaces of bituminous rank coals (vittrains) and that the data obtained do reveal significant variations depending upon the level of surface oxidation. Photo-oxidation induced by violet or ultraviolet light fluxes does result in a progressive and significant increase in the amount of near-surface oxygen concentration at about the same level regardless of bituminous coal rank. These incremental changes in oxygen concentration appear to lower the hydrophobicity as shown by contact angle measurements on polished surfaces. Although this influence diminished as coal rank increased, the level of oxygen uptake was about the same, suggesting that the type of oxygen functionality formed during oxidation may be of great importance in modifying surface hydrophobicity. Changes in functional-group chemistry, measured by a variety of near-surface techniques, showed a general increase in the concentration of carbonyl-containing groups while those of CH_2 groups decreased. All of these observations follow the trends observed in previous investigations of naturally weathered coals.

The photo-oxidation technique also resulted in the development of phenolic, ester and anhydride moieties instead of the expected emplacement of carboxylic acid groups which are normally associated with naturally weathered coals. The importance of this observation is that esters and anhydrides would result in a more hydrophobic surface in comparison to the more hydrophilic surface resulting from acid functionality. This observation is consistent with the results of film flotation of UV-irradiated powdered vitrain in which floatability was generally observed to increase with increasing photo-oxidation.

TABLE OF CONTENTS

	<u>Page</u>
DISCLAIMER	ii
ABSTRACT	iii
LIST OF TABLES	vi
LIST OF FIGURES	vii
ACKNOWLEDGEMENTS	xii
EXECUTIVE SUMMARY	xiii
INTRODUCTION	1
Background	1
Scientific Approach	4
EXPERIMENTAL TECHNIQUES	5
<u>Coal Selection, Preparation and Analysis</u>	5
<u>Luminescence Analysis and Photo-Oxidation Techniques</u>	8
<u>Surface Property Measurements on Polished Vitrain Bands</u>	12
Reflectivity	12
Electron Microprobe	13
Contact Angles	13
Secondary Ion Mass Spectrometry (SIMS)	15
Scanning Transmission X-Ray Microscopy and Carbon-Near Edge X-Ray Absorption of Fine Structures	15
Reflectance-mode Fourier Transform Infrared Spectroscopy	16
<u>Film Flotation on Vitrain Concentrates</u>	16

TABLE OF CONTENTS (continued)

	<u>Page</u>
<u>Pyrolysis Gas Chromatography/Mass Spectrometry</u>	17
RESULTS AND DISCUSSION	18
<u>Surface Properties of Photo-Oxidized Polished Vitrain Bands</u>	18
<u>Contact Angle Measurements</u>	22
<u>Luminescence Intensity and Alteration of Vitrain</u>	26
<u>Luminescence Properties of Model Compounds</u>	41
<u>Change in Surface Chemistry with Irradiation</u>	41
<u>Infrared Microspectroscopy</u>	44
<u>Surface Properties of Photo-Oxidized Powdered Vitrains</u>	57
CONCLUSIONS	76
REFERENCES	80
APPENDIX A - Lower Kittanning Seam Survey	83
Lower Kittanning Samples	87
References	87
APPENDIX B - Irradiation of Powdered Vitrains	89
Experimental Procedure	89
Results and Discussion	89
APPENDIX C - Luminescence of Some Model Compounds	94
Experimental Procedures	94
Results and Discussion	95
Conclusions	101

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Comparison of Coal Quality of Whole Seam Channel Samples	6
2	Comparison of Characteristics of Vitrain Concentrate Samples	9
3	Relative Difference in Peak Intensity for Oxygen-Bearing Molecular Fragments From SIMS Analysis	42
4	Location of Major Absorption Bands From Second Derivative FTIR Plots; Irradiated and Non-irradiated Vitrains	55
5	Structural Parameters Determined by Pyrolysis GC/MS From Vitrain Concentrates	74
6	Structural Parameters Determined by Pyrolysis GC/MS From Vitrain Concentrates	75
1A	Assessment of Environments of Deposition From Mine Survey of the Lower Kittanning Seam in Northwestern Pennsylvania	86
1C	Spectral Luminescence, Intensity and Alteration Behavior in Air of Selected Model Compounds	96

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Schematic of the Contact Angle Measurement Equipment	14
2	Measurement of Contact Angle at the Air/Coal/Water Interface as Water Droplet Advances Across an Irradiated Area	14
3	Photomicrographs in Reflected Light and Oil Immersion of Areas of the Ohio #4a Seam Polished Vitrain Irradiated for 10 min	19
4	Difference in Random Reflectance Between Irradiated and Non-irradiated Regions of Vitrain with Time of Blue-Light Exposure	20
5	Change in Near-Surface Oxygen Concentration with Time of Blue-Light Irradiation as Measured by Electron Probe Microanalysis	21
6	Advancing-Drop Contact Angles Measured on Polished Surface of Vitrain Photo-Oxidized for Different Time Intervals	23
7	Advancing-Drop Contact Angles Measured on Polished Surface of Vitrain Photo-Oxidized for Different Time Intervals	24
8	Advancing-Drop Contact Angles Measured on Polished Surface of Vitrain Photo-Oxidized for Different Time Intervals	25
9	Maximum Change in Contact Angle with Irradiation Time of Six Bituminous Rank Vitrains	27
10	Luminescence Alteration Patterns From the hvCb Illinois #6 Seam (DECS-24) Comparing Whole Seam Channel Sample and Vitrain Concentrate	28
11	Luminescence Alteration Patterns From the hvBb Ohio #4a Seam (DECS-33) Comparing Whole Seam Channel Sample and Vitrain Concentrate	29
12	Luminescence Alteration Patterns From the hvAb Pittsburgh Seam (DECS-23) Comparing Whole Seam Channel Sample and Vitrain Concentrate	30

LIST OF FIGURES (continued)

<u>Figure</u>		<u>Page</u>
13	Luminescence Alteration Patterns From the hvAb Lower Kittanning Seam (PSOC-1562) Comparing Whole Seam Channel Sample and Vitrain Concentrate	31
14	Luminescence Alteration Patterns From the hvAb Lower Kittanning Seam (PSOC-1563) Comparing Whole Seam Channel Sample and Vitrain Concentrate	32
15	Luminescence Alteration Patterns From the mvb Splash Dam Seam (DECS-30) Comparing Whole Seam Channel Sample and Vitrain Concentrate	33
16	Luminescence Alteration Patterns From Irradiated Areas of the hvCb Illinois #6 Vitrain Bands, DECS-24	35
17	Luminescence Alteration Patterns From Irradiated Areas of the hvBb Ohio #4a Vitrain Bands, DECS-33	36
18	Luminescence Alteration Patterns From Irradiated Areas of the hvAb Pittsburgh Vitrain Bands, DECS-23	37
19	Luminescence Alteration Patterns From Irradiated Areas of the hvAb Lower Kittanning Vitrain Bands, PSOC-1562	38
20	Luminescence Alteration Patterns From Irradiated Areas of the hvAb Lower Kittanning Vitrain Bands, PSOC-1563	39
21	Luminescence Alteration Patterns From Irradiated Areas of the mvb Splash Dam Vitrain Bands, DECS-30	40
22	Carbon X-ray Absorption Spectra of Fresh and Photo-Oxidized Pittsburgh Seam Vitrain	43
23	Change in Absorption Intensity at Specific Energy Bands with Photo-Oxidation as Measured on Pittsburgh Seam Vitrain by STXM and C-NEXAFS	45
24	FTIR Spectra From Adjacent Areas of Illinois #6 Seam (DECS-24) Vitrain for Fresh and Irradiated (10 min) Surfaces	47

LIST OF FIGURES (continued)

<u>Figure</u>		<u>Page</u>
25	Comparison of FTIR Spectral Regions for Fresh and Irradiated Surfaces (1, 5 and 10 min) of the hvCb Illinois #6, DECS-24	48
26	Comparison of FTIR Spectral Regions for Fresh and Irradiated Surfaces (1, 5 and 10 min) of the hvBb Ohio #4a Seam, DECS-33	49
27	Comparison of FTIR Spectral Regions for Fresh and Irradiated Surfaces (1, 5 and 10 min) of the hvAb Pittsburgh Seam, DECS-23	50
28	Comparison of FTIR Spectral Regions for Fresh and Irradiated Surfaces (1, 5 and 10 min) of the hvAb Lower Kittanning Seam, PSOC-1562	51
29	Comparison of FTIR Spectral Regions for Fresh and Irradiated Surfaces (1, 5 and 10 min) of the hvAb Lower Kittanning Seam, PSOC-1563	52
30	Comparison of FTIR Spectral Regions for Fresh and Irradiated Surfaces (1, 5 and 10 min) of the mvb Splash Dam Seam, DECS-30	53
31	Film Flotation of hvCb Illinois #6 Vitrain Concentrate (DECS-24-Vit) Following 0, 10, 50 and 100 min UV Irradiation	58
32	Film Flotation of hvBb Ohio #4a Vitrain Concentrate (DECS-33-Vit) Following 0, 10, 50 and 100 min UV Irradiation	59
33	Film Flotation of hvAb Pittsburgh Vitrain Concentrate (DECS-23-Vit) Following 0, 10, 50 and 100 min UV Irradiation	60
34	Film Flotation of hvAb Lower Kittanning Vitrain Concentrate (PSOC-1562-Vit) Following 0, 10, 50 and 100 min UV Irradiation	61
35	Film Flotation of hvAb Lower Kittanning Vitrain Concentrate (PSOC-1563-Vit) Following 0, 10, 50 and 100 min UV Irradiation	62
36	Film Flotation of mvb Splash Dam Vitrain Concentrate (DECS-30-Vit) Following 0, 10, 50 and 100 min UV Irradiation	63
37	Repeatability of Film Flotation for Selected Illinois #6 and Splash Dam Seam Samples	65

LIST OF FIGURES (continued)

<u>Figure</u>		<u>Page</u>
38	Change in Surface Luminescence Intensity of Particulate Vitrain Following UV Irradiation at 366 nm	66
39	Total Ion Chromatograms of Pyrolyzates from Fresh and 10 min Irradiated Illinois #6 Vitrain Concentrate, DECS-24-Vit	68
40	Total Ion Chromatograms of Pyrolyzates from 50 and 100 min Irradiated Illinois #6 Vitrain Concentrate, DECS-24-Vit	69
41	Total Ion Chromatograms of Pyrolyzates from Fresh and 10 min Irradiated Lower Kittanning Vitrain Concentrate, PSOC-1562-Vit	70
42	Total Ion Chromatograms of Pyrolyzates from 50 and 100 min Irradiated Lower Kittanning Vitrain Concentrate, PSOC-1562-Vit	71
43	Total Ion Chromatograms of Pyrolyzates from Fresh and 10 min Irradiated Splash Dam Vitrain Concentrate, DECS-30-Vit	72
44	Total Ion Chromatograms of Pyrolyzates from 50 and 100 min Irradiated Splash Dam Vitrain Concentrate, DECS-30-Vit	73
1A	Mine and Sample Locations for the Lower Kittanning Seam Survey in Pennsylvania with Respect to Marine and Freshwater Overburden	84
2A	Pyrolysis-GC/MS Peak Intensities Measured on Vitrinite Concentrates from Pittsburgh and Lower Kittanning Seam Samples	85
1B	Influence of Exposing Various Coals to 366 nm Light From 5.7 cm on Luminescence Intensity Measured at 600 nm	90
2B	Influence of Exposing Various Coals to 366 nm Light From 3.2 cm on Luminescence Intensity Measured at 600 nm	92
3B	Temperature Increase Measured on Coal Surfaces During Irradiation with the BLAK-RAY Longwave (366 nm) Ultraviolet Spot Light	93
1C	Comparison of Spectral Luminescence of Model Compounds Following Blue-Light Irradiation	98

LIST OF FIGURES (continued)

<u>Figure</u>		<u>Page</u>
2C	Comparison of the Alteration of Luminescence Emission in Air of Selected Model Compounds During Blue-Light Irradiation	99

ACKNOWLEDGMENTS

A number of individuals and organizations provided valuable technical and analytical input into this research project and, therefore should be acknowledged for their efforts. First and foremost among them are Dr. Subhash Chander who directed the activities of three students who received financial support as a result of the project. Ms. Hurriyet Polat, Mr. Sundar Subbarayan and Mr. Daniel Werner of the Mineral Processing Section performed all of the surface hydrophobicity and film flotation measurements. Their analytical skills and useful suggestions and interpretations were integral to the successful conclusion of this project. Furthermore, two former students, Drs. Etuan Zhang and George Cody, provided support through many useful discussions and collaborations.

The authors are indebted to those organizations and individuals who provided analytical capabilities at no cost to this project. In particular, Dr. Paul Pigram formerly of the University of New South Wales, Australia who provided analyses using Secondary Ion Mass Spectrometry (SIMS); Dr. George Cody formerly of Argonne National Laboratories who performed analyses using Scanning Transmission X-ray Microscopy at Brookhaven National Laboratory and preliminary interpretations involving Carbon Near-Edge Absorption of Fine Structures; and, Drs. Rui Lin and Pradeep Iyre of UNOCAL Corporation for their luminescence reflectance-mode FTIR analyses of photo-oxidized vitrains. These associations, although short lived, provided valuable preliminary information regarding the photo-oxidation technique and surface chemistry.

In addition, the authors are indebted to Drs. Paul Painter and Maria Sobkowiak, of the Department of Materials Science and Engineering for their assistance in performing reflectance-mode FTIR analyses and to Dr. Patrick Hatcher for pyrolysis GC/MS determinations.

EXECUTIVE SUMMARY

It is known that surface oxidation induced by natural weathering has a detrimental effect on the hydrophobic nature of coal, which in turn could influence clean-coal recovery during flotation. If anticipated by the preparation plant engineer, recovery of partially oxidized coal can be improved by adjustments in process conditions, i.e., reagent concentration. Unfortunately, few techniques are available that can determine and quantify the quality of coal surfaces with respect to oxidation and fewer still that have a sufficiently short analysis time to provide practical input for process control.

Research involving the violet and ultraviolet luminescence from the coal maceral vitrinite conducted in these laboratories over the past ten years has demonstrated that luminescence emissions are measurably influenced by degree of weathering as well as by even mild storage deterioration. In addition, it has been shown that when vitrinite is irradiated with relatively high intensity violet- or ultraviolet- light in the presence of air, photo-oxidation of the surface occurs. An optical microscope and photometer system, when properly standardized, can provide measurements of relative luminescence intensity under a nitrogen atmosphere and of the alteration of intensity with time of irradiation in an air atmosphere (i.e., patterns of photo-oxidation).

The ability to measure the degree of surface oxidation by change in luminescence emission provided the impetus for the current investigation. The principal aim of this research has been to determine whether a clear correlation could be established among surface oxygen functionality, hydrophobicity induced by photo-oxidation, and measurements of luminescence intensity and alteration. If successful, the project would result in quantitative luminescence technique(s) based on optical microscopy that would provide a measure of the changes in surface properties as a function of oxidation and relate them to coal cleanability. Although optical microscopy does not represent a direct, on-line technique for unattended operation, it is likely that luminescence analysis can be performed on natural fracture surfaces of coal which would reduce analysis time into the range of process-control application.

To pursue these goals, two specific analytical approaches were employed; one involving the use of polished surfaces of vitrain and another using powdered vitrain concentrates. Coal blocks and associated channel samples from six bituminous coals ranging in rank from high volatile C bituminous (hvCb) to medium volatile bituminous (mvb) were carefully selected for this project by consideration of their geologic histories. From the blocks, small sections of coal containing 3-5 μm thick bands of vitrain were removed and polished surfaces prepared. The remainder of the block samples of each coal was hand-picked to provide about 40 g of vitrain particles and to establish the analytical characteristics of the vitrain relative to the respective whole-seam channel samples. Every effort was made to minimize exposure of these samples to atmospheric oxygen, direct sunlight and high humidity from the time of sampling, through preparation and analysis. This included preparation of vitrain concentrates under an inert atmosphere in a glovebox and intermediate storage of all samples in foil laminate bags under an inert atmosphere and refrigeration.

The experimental approach taken with the polished specimens was to use a blue-light (390-490 nm) flux to irradiate (photo-oxidize) selected areas of vitrain and measure the changes in luminescence emissions for periods of 1, 5 and 10 min. A variety of techniques was employed to measure the changes in surface properties in comparison to the fresh surface, including random reflectance, electron probe microanalysis, reflectance-mode Fourier Transform Infrared Spectroscopy, Secondary Ion Mass Spectroscopy and Scanning Transmission X-ray Microscopy with Carbon Near-Edge X-ray Absorption of Fine Structure analysis. Contact angle measurements were obtained as a means of identifying changes in surface hydrophobicity.

The other experimental approach used a narrow size fraction ($<420 \times >149 \mu\text{m}$) of the powdered concentrates to investigate the flotation characteristics of photo-oxidized vitrain under the assumption that broken particle surfaces may react differently than polished surfaces. Concentrates of the most predominant maceral component of coal, vitrinite, were used in an effort to reduce heterogeneous responses caused by inclusions of other macerals and minerals. A longwave (366 nm) ultraviolet spotlight was employed to irradiate the polished surfaces of these powdered samples. Based upon luminescence response, a technique for irradiating a monolayer of particles was developed which established UV-irradiation intervals of 10, 50 and 100 min as giving comparable exposures to the 1, 5 and 10 min, respectively, in the case of blue-light irradiation. Following irradiation, film flotation curves were generated from a 1 g sample of each photo-oxidized and fresh vitrain specimen. A small quantity of each specimen was set aside for luminescence intensity measurements and for analysis by pyrolysis Gas Chromatography/Mass Spectrometry (py-GC/MS).

Results from our investigation of polished surfaces showed that irradiation with blue light in air caused a reduction in the reflectivity of vitrinite and a significant increase in the near-surface oxygen concentration. Reflectivity changes appeared to be influenced by the particular vitrain band from which measurements were obtained, whereas the uptake of oxygen with irradiation time was fairly consistent regardless of vitrain band or rank. This result was unexpected considering the fact that the fresh hvCb vitrain tested had 2.5 times more oxygen than the fresh mvb vitrain.

Contact angle values were obtained by advancing (growing) a droplet of distilled water across the fresh polished surfaces into the irradiated areas and by measuring the coal/water/air interfacial angle at various locations as it advanced. Contact angle values were stable across non-irradiated areas of individual vitrain bands. However, upon entering the irradiated regions values decreased by levels which were proportional to irradiation time. This effect diminished with increasing rank. The influence of rank and oxidation on hydrophobicity has been observed in previous studies; however, the fact that similar levels of oxygen were incorporated regardless of rank implies that the type of oxygen functionality may be more important in determining surface hydrophobicity than the total amount of oxygen emplaced.

Results from a variety of analytical techniques provided some expected and unexpected findings regarding changes in near-surface chemical functionality. SIMS analysis of a high volatile A bituminous (hvAb) vitrain irradiated for 10 min showed that considerably more mass

(molecular fragments) could be removed from the photo-oxidized regions compared to the non-irradiated areas; the size and relative composition of the ions suggests that a large part of the oxygen added is associated with the aromatic network. Thin sections prepared from this same hvAb vitrain and irradiated at 0, 1, 5 and 10 min time intervals were analyzed by STXM and C-NEXAFS. The results showed that most of the chemical changes were occurring at aromatic carbon sites. Systematic changes in the growth and intensity of carbon near-edge energy bands with irradiation time suggests that hydroxyl and carbonyl functionalities increased in concentration with increasing blue-light irradiation and is accompanied by an overall decrease in methyl group concentration. Except for the variation observed in hydroxyl concentration, the changes found for methyl and carbonyl functionalities have been observed before for naturally weathered and laboratory oxidized coals and vitrains.

Reflectance-mode FTIR analysis of all six vitrains and for all surface conditions (0, 1, 5 and 10 min irradiation), showed a significant and progressive increase in intensity of the carbonyl region and a decrease in the aliphatic C-H stretching region with increasing irradiation time. Also, in corroboration of the C-NEXAFS results, a broad increase in the intensity of the O-H region of the spectra was observed, but because of the diffuse nature of this absorption a positive assignment may not be justified. Thus, in very general terms reflectance FTIR analysis of blue-light irradiated vitrains demonstrated that the photo-oxidation technique caused a progressive oxidation of the near surface that resembled what has been reported in the literature for natural weathering and laboratory oxidation of coals.

Owing to the diffuse nature of some spectral regions, derivative spectroscopy was employed to better define the frequencies of important absorption bands. This technique provided a more detailed and less subjective assessment of the spectrograms and clearly revealed four prominent absorption bands for all of the samples analyzed, i.e., two bands assigned to the aliphatic stretching mode of CH_2 at 2939 and 2855 cm^{-1} , the carbon double bond stretch of the aromatic system at 1606 cm^{-1} , and the C- CH_3 deformation frequency at 1447 cm^{-1} . The intensity of absorption of these bands decreased and became more diffuse with increasing levels of oxidation, similar to what has been reported in the literature for naturally oxidized coals, suggesting that aliphatic CH_2 groups were involved in the formation of carbonyl-containing functional groups. Assessment of the absorption bands in the carbonyl region of the spectra (1850 - 1690 cm^{-1}) did not reveal the expected carboxylic acid frequencies, but instead showed absorption at much higher wavenumbers for nearly all of the irradiated specimens. Absorption in these regions increased in intensity with increasing degree of photo-oxidation. With minor variation, the lower rank vitrains (hvCb and hvBb) and one hvAb vitrain showed a pair of absorption bands that generally can be assigned to anhydrides, whereas two of the hvAb and the mvb vitrain showed a single characteristic absorption for carbonyl-containing cyclic esters (lactones).

The significance of these observations, in particular the lack of carboxylic acid absorption, was a clear departure from previous observations for coal oxidation and probably reflects differences imposed by the photo-oxidation and preservation techniques compared to the natural process. Functionalities that can involve hydrogen bonding like carboxylic acids, ketos

and enols logically would be responsible for a measurable decrease in the hydrophobic character (more hydrophilic) of the vitrain surface, whereas esters and anhydrides which lack this ability would tend to result in a more hydrophobic surface. Mechanisms for the formation of esters and anhydrides involve placement of more than one carbonyl group directly onto an aromatic unit or on an associated aryl group. Therefore, during the course of natural weathering the carbonyl moiety emplaced would be an acid site, but in a relatively high energy flux of blue-light multiple carbonyl groups may form in a way in which they interact together or perhaps with singlet oxygen resulting in the formation of esters and anhydrides. The fact that these moieties did not degrade to carboxylic acid groups may be a direct result of our preservation techniques. Further, secondary reactions involving peroxide intermediates also may result in the formation of phenols. An increase in aromatic OH concentration was suggested from C-NEXAFS and FTIR results, and because of its slightly acidic character could explain the observed decrease in surface hydrophobicity.

Regarding the temporal alteration of luminescence intensity measured during photo-oxidation, all of the high volatile bituminous (hvb) coals showed a dual response in which an early rapid decrease in intensity was followed by a sharp increase which becomes less rapid with increasing rank. The mvb coal generated a negative (decreasing) alteration response which was initially rapid and then slowed out to 10 min of irradiation. The general variations in alteration patterns corresponded well with contact angle results. However, because of the dual response for hvb coals, the actual intensity values measured at zero time and after 1, 5 and 10 min of irradiation did not correlate directly with contact angle. On the other hand, luminescence intensity measurements made on the broken surfaces of UV-irradiated powdered vitrains correlated well with irradiation time, mostly showing a significant decrease in intensity with increasing photo-oxidation. This observation agrees with published results on naturally weathered coals where luminescence intensity was typically much lower than for the corresponding fresh coal surface.

With an increase in irradiation time, all but the lowest rank particulate vitrains (hvCb and hvBb) showed an increase in floatability. In comparison to changes in contact angle obtained on polished surfaces these results were unexpected. One plausible explanation for these results involves the mobilization of aliphatic compounds (bitumens) which have been observed as thin films on the surface of bituminous coals exposed to direct sunlight. Such a material would act very much like a natural flotation collector by providing a more hydrophobic surface. However, exudations from coal are probably not uniform throughout the bituminous rank range and we would have expected to see more variation among the selected vitrains. Another explanation has been provided by our FTIR results which suggest that changes in oxygen functionality were due to the formation of ester and anhydrides. These moieties have less attraction to water than carboxylic acid groups, and if present in relatively high concentration, could provide a more hydrophobic surface than the fresh coal with regard to flotation. Unfortunately, results obtained from pyrolysis GC/MS were not sufficiently sensitive to detect the surface chemical changes which accompany UV-irradiation. Apparently the bulk chemistry of the $<74\ \mu\text{m}$ size particles overwhelms the changes in surface chemistry. Data from three vitrain oxidation series showed an expected change in concentration of phenols associated with the influence of rank, but were

not sufficiently sensitive to reveal the changes in n-alkane and alkene concentration that have been shown to accompany severe natural weathering.

In summary, results from this investigation demonstrate that quantitative luminescence intensity measurements can be performed on fracture surfaces of coal (vitrain) and that the data obtained do demonstrate significant variations with level of surface oxidation. Photo-oxidation induced by violet or ultraviolet light fluxes does result in a progressive and significant increase in the amount of near-surface oxygen concentration at about the same level regardless of the specific vitrain band or the rank of bituminous coal. These incremental changes in oxygen concentration appeared to decrease the hydrophobicity as shown by contact angle measurements on polished surfaces. This influence diminished as rank increased. Changes in functional-group chemistry, measured by a variety of near-surface techniques, showed a general increase in the concentration of carbonyl-containing groups while those of CH_2 decreased. These observations follow the trends expected from previous investigations of naturally weathered coals.

From our FTIR results, however, it appears that the photo-oxidation technique resulted in the development of ester and anhydride moieties instead of the expected emplacement of carboxylic acid groups which are normally associated with naturally weathered coals. The importance of this observation is that esters and anhydrides might result in a more hydrophobic surface in comparison to the more hydrophilic surface resulting from acid functionality. These observations are in line with the results of film flotation of UV-irradiated powdered vitrain in which floatability was generally observed to increase with increasing photo-oxidation.

The technique of luminescence analysis has been demonstrated to be an effective procedure for measuring the change in surface properties which results from oxidation. Further work to investigate the direct application of the technique in coal cleaning process control appears to be warranted.

INTRODUCTION

Operation of coal flotation units are influenced not only by control of process variables such as feed concentration, reagent levels and pH, but also by the quality of the feed materials, i.e., particle size distribution, mineral content and surface properties. Of these physical properties, the condition of the coal surface is the most difficult to characterize. It is known that coal surface oxidation (weathering) can have a major influence on hydrophobicity which, in turn can detrimentally affect clean-coal recovery during flotation. Coal surface oxidation may change daily (even hourly) due to mining operations, particularly where coal feed may be coming from multiple longwall panels and development headings within a mine. This fractional contribution of coal exposed for varying times to the atmosphere therefore may influence the yield of clean coal obtained during flotation. Changes in concentration of flotation reagents (frother and/or collector) can improve recovery of partially oxidized coal, if such a situation has been anticipated. Thus, the ability of the preparation engineer to predict coal surface quality and make process control adjustments may be fundamental to variations in recovery, lost production and to less than efficient separation of gangue (e.g., pyrite).

This document is the final report of an investigation, funded by the Department of Energy under the University Coal Research Core Program, that attempts to quantify the type and degree of surface oxidation that will adversely influence coal hydrophobicity. The technique employed to progressively photo-oxidize a coal surface can be monitored photometrically and, hence, may provide a valuable measure of surface quality. Therefore, the general objectives of this research are 1) to measure the changes in functional group concentration as a function of the duration of photo-oxidation using Fourier Transform Infrared Spectroscopy (FTIR) as well as other near-surface techniques, 2) to identify the influence of photo-oxidation on coal floatability by measuring contact angles from polished surfaces and powders as well as by microflotation, and 3) to correlate the changes in surface chemistry with measurements of luminescence intensity. The ultimate objective has been to develop new quantitative luminescence techniques that will measure changes in surface properties as a function of oxidation and relate them to coal cleanability.

Background

Gutierrez-Rodriguez and Aplan (1) and Gutierrez-Rodriguez et al. (2) demonstrated that the surface chemistry of coals can exert a profound influence on their response to cleaning. These investigations established a clear link between the natural oxygen content of a rank suite of coals and their surface oxidation on hydrophobicity (hydrophobicity decreases with increasing oxygen functionally) and floatability. Oxidation due to weathering at an exposed mine face or in a stockpile is the major means whereby the surface chemistry of coals undergoes post-coalification change. Natural weathering, involving processes of freeze-thaw action, alternating wet-dry periods, direct and indirect sunlight, free percolation of water, and perhaps the action of plants, animals and microbes, can be mild or severe with regard to its influence on industrial utilization. Studies over the past decade have led to the realization that weathering (3,4) and storage deterioration (5) can be detected and monitored by changes in luminescent emissions

obtained from vitrinite during ultraviolet- and violet-light irradiation under an optical microscope. The technique appears to be amenable to detecting very low levels of oxidation which otherwise can only be measured by small decreases in thermoplasticity.

Luminescence analysis of coals has been used to derive fundamental information about maceral chemistry and reactions involved in coal processing (6,7). Empirical relationships among luminescence characteristics and the chemistry and technological behaviors of coals with regard to weathering, cokemaking and thermoplasticity have been established. The analytical method involves the irradiation of the vitrinite component of coal with blue- or ultraviolet- light under an optical microscope. Absorption of light energy causes excitation of certain organic functional groups to various higher energy levels which, when returning to the ground state, emit energy at a longer wavelength as a luminescence response. The intensity of this emission can be measured with a calibrated photometric system using a narrow wavelength band or grating monochromator.

Quantitative photometric measurements of emission intensity from coal macerals using blue (390-490 nm) or ultraviolet light (340-380 nm) irradiation in air exhibits variations with exposure time that are characteristic of coal rank. This phenomenon, described as "fluorescence (luminescence) alteration" in the literature, has been shown to result from photochemical reactions at or near the surface of coal macerals that involve changes in both the peak emission frequency and peak emission intensity. Teichmüller (8) observed that individual macerals can have characteristic alteration behaviors. Later Ottenjann et al. (9) described three distinct classes of alteration behavior (i.e., positive, "ambivalent" (later referred to as "dual") and negative) which corresponds with the maturity level of sedimentary kerogen or coal maceral. Positive alteration refers to the progressive increase in intensity of luminescent emissions with time during continuous exposure to blue or UV light, negative alteration is the opposite trend and dual alteration describes an initial decrease in luminescence intensity followed by a later increase. Vitrinite from low-rank coals (lignite and subbituminous) exhibit exclusively positive alteration, intermediate-rank bituminous coals (h_vCb - h_vAb) exhibit dual alteration, and high-rank bituminous coals (m_{vb} - l_{vb}) exhibit negative alteration.

The influence of coal weathering on vitrinite luminescence was studied by Quick et al. (3) and Mitchell et al. (5) who showed that luminescence intensity and the pattern of luminescence alteration was measurably affected by the degree of weathering and/or storage deterioration. Qualitative analysis of this behavior has revealed that time-dependent luminescence analysis is a sensitive indicator of the weathering of bituminous coals. These authors noted that whereas high and medium volatile bituminous coals typically display a dual or negative alteration pattern, respectively, their weathered counterparts exhibit only a distinct luminescence increase during irradiation. It is interesting to note that the same positive alteration is obtained from low-rank coals which are composed of a crosslinked network of alkylated phenols and carboxylic acid groups.

Work by Davis et al. (10) on coals (vitrinites) of varying rank clearly demonstrated that the photochemical reactions observed under the optical microscope were in fact photo-oxidation.

This was done by contrasting time-dependent luminescence intensity obtained in air and nitrogen atmospheres under the optical microscope. In the absence of oxygen both the negative and positive component of alteration could be eliminated. Also, Davis et al. (10) surmised that the positive element of alteration was associated with a progressive increase in the concentration of carboxylic functional groups on or near the coal surface. This conclusion was reached from results obtained by staining the surface with a cationic dye, safranin-O, following photo-excitation. This dye is routinely used to detect coal oxidation (11), the degree of staining being proportional to the number of acidic adsorption sites available for interaction with the dye. The intensity of the staining of a high volatile bituminous coal particle surface was noted to increase in direct proportion with the length of time exposed to blue light.

The apparent increase in carboxylic acids groups during blue or UV irradiation is consistent with observation of Hayatsu et al. (12) who studied the macroscopic photochemical oxidation of a lignite and a bituminous coal as well as a large collection of aromatic and substituted aromatic "model" compounds. The products in both cases were dominantly benzene carboxylic acids, with minor amounts of other oxygen-substituted compounds, such as anthraquinone, fluorenone, and xanthone. Wilson (13), using X-ray photoelectron spectroscopy of UV irradiated coal particles, observed a progressive increase in the concentration of carboxylic functional groups with increasing irradiation time, along with a lesser increase in carbonyl concentration. Thus, the results of Davis et al. (10) are in accord with earlier macroscopic analyses of coal photo-oxidation.

In other work, Pradier et al. (14) observed a similar response using FTIR techniques to monitor the change in functional group concentration of photo-oxidized chromatographically separated fractions of a luminescent crude oil as a function of irradiation time. This study suggested that the molecular group responsible for the positive component of luminescence alteration was oxygen-substituted poly-aromatics. The fraction exhibiting significant negative alteration was composed of aromatic molecules. Furthermore, photo-oxidation of the oxygen-substituted aromatic compounds resulted in a loss in phenolic OH and a pronounced increase in both carbonyl content and aryl ethers. Photo-oxidation of the aromatic fraction resulted in a significant increase in the concentration of carboxylic acids and an increase in alkyl- and aryl-ethers.

Eberhardt et al. (15) used a 442 nm HeCd laser to irradiate various bituminous coals and aromatic compounds in a special cell which could be evacuated or charged with gas (room air or pure oxygen) to 1 Pa. The technique faithfully reproduced alteration patterns for bituminous rank coals that had been reported by earlier researchers. They concluded that the negative and positive components of alteration resulted from photo-oxidation, but by different mechanisms. The irreversible negative alteration observed in the first few seconds of irradiation may be caused by photo-oxidation of fresh coal with singlet oxygen generated from the quenching of fluorophores by triplet oxygen. The formation of epi-peroxide during the photo-oxidation of anthracene was invoked as the type of mechanism that could be responsible for decreased luminescence emissions during initial excitation of coal in the presence of oxygen. However, the development of slow positive alteration was found to be stable only when the atmosphere was

unchanged. Luminescence intensity was observed to decrease when the cell was evacuated and then to increase at an even faster rate when oxygen was re-admitted. Eberhardt et al. speculated that this response results from a photo-thermal production of a stable binary complex (coal and oxygen) which could be responsible for the formation of carbonyl-containing functional groups and a reversible intermediate complex formed in the presence of additional oxygen. The exact nature of and interrelationship between the stable binary complex and the intermediate complex are presently unknown.

It is evident from the foregoing that the alteration of emission intensity of vitrinite during continuous blue or UV irradiation is, at least in part, caused by photo-oxidation. Experimental results suggest that carboxylic acids, carbonyl and ether groups may be generated at the surface and that these groups increase in concentration at some rate as irradiation proceeds. Semi-quantitative results suggest that these functional groups also may be involved in intermediate reactions that are responsible for a slow increase in luminescence emissions. Elimination of gaseous oxygen from the system during this period results in a rapid and immediate decrease in emission intensity which can be restored if oxygen is re-admitted to the system. Presumably, the same observation could be made for naturally weathered coals and those of low rank (subbituminous and lignite) which have a high concentration of oxygen functional groups and that give positive alteration during irradiation.

Coal weathering influences the gross chemical, heating and thermoplastic properties of coal, reducing its quality for the production of steam and/or metallurgical coke. A minimal amount of surface oxidation accompanied by photo-oxidation may not be detected by the usual analytical techniques used to characterize coals, but may be extremely detrimental to the surface properties that are fundamental to cleaning a coal by froth flotation techniques. Knowing the amount and kind of oxygen-based functional groups responsible for reducing the hydrophobicity of coal surfaces and having a relatively simple technique to evaluate the changes may be of considerable benefit to the efficient operation of coal froth flotation cells.

In this regard, Death et al. (16,17) used a HeCd laser operating at 325 and 442 nm to demonstrate that luminescence emission intensity from pressed or powdered coal surfaces decreased with degree of thermal and chemical oxidation. Except for some difficulty in maintaining stability of their photomultiplier, they suggested that the method might be suitable for on-line discrimination of oxidized coal using run-of-mine particles.

Scientific Approach

The principal objective of the current project was to develop quantitative luminescence techniques based on optical microscopy that will measure the changes in surface properties as a function of oxidation and relate them to coal cleanability. The scientific or technical issues being addressed by this research are whether a clear correlation can be established among changes in surface oxygen functionality induced by violet or ultra-violet photo-oxidation, luminescence intensity, time-resolved alteration of luminescence intensity and surface hydrophobicity or flotation yield.

The experimental approach taken in this effort was to use a blue-light (390-490 nm) or ultraviolet (366 nm) flux to photo-oxidize fresh surfaces of vitrain (polished blocks and thinned sections) collected from a rank suite of coals (hvCb to mvb). Irradiation time intervals were varied in increments between 1 and 15 min depending upon the sensitivity of the analytical technique being employed; following this, surface or near-surface changes in oxygen functionality and concentration and surface hydrophobicity were measured. For each time interval, and for non-irradiated specimens, the chemical functionalities were determined using a variety of techniques. Reflectance-mode FTIR can provide near-surface chemical information from polished surfaces of vitrain. In addition, contact angle measurements can be made on these same irradiated surfaces, thus providing a correlation between surface chemical changes and a measure of hydrophobicity. By using relatively pure vitrain bands the variability resulting from maceral and mineral composition can be avoided. Other analytical techniques that were employed in this part of the study include Secondary Ion Mass Spectroscopy, electron microprobe analysis, and Scanning Transmission X-ray Microscopy with Carbon Near-Edge X-ray Absorption of Fine Structures. Each of these techniques has a different sensitivity and measuring area, and can provide information on surface chemical changes induced by photo-oxidation.

In addition, powdered vitrain concentrates were prepared from each coal in such a way as to limit atmospheric exposure. These powders were irradiated using an ultraviolet spotlight (366 nm) and then were used for microflotation tests. Small portions of these irradiated vitrains were analyzed by pyrolysis GC/MS to determine changes in amount and kind of oxygen-bearing molecular fragments. Luminescence intensity measurements were made on the fresh and irradiated surfaces so that comparisons could be made with results from the polished surfaces.

EXPERIMENTAL TECHNIQUES

Coal Selection, Preparation and Analysis

The six coals listed in Table 1 were used for most of the experimental work performed during this project. The original plan was to collect eight coals ranging in rank from high volatile C bituminous through low volatile bituminous. However, the low volatile coal was eliminated from further consideration because such coals are usually fine and friable and typically have very low luminescence emissions. Seven coals were collected during this project, but following sample analysis it was apparent that the coal selected to represent the hvAb/mvb rank transition (Upper Banner, VA, DECS-29) showed signs of weathering and therefore did not fulfill our main objective of collecting only fresh coals.

A number of other criteria also were used during coal selection. From a practical standpoint, it was imperative that coals of high vitrain content be collected. Although, the sub-maceral desmocollinite typically provides a greater level of luminescence emission within any given coal compared with telocollinite, only the latter is found in relatively broad bands that are mostly free of other macerals. This was the primary reason that telocollinite was selected for this

Table 1 - Comparison of Coal Quality of Whole Seam Channel Samples

Seam Identification →	DECS-24 Illinois#6	DECS-33 Ohio #4a	DECS-23 Pittsburgh	PSOC-1562 L. Kitt.	PSOC-1563 L. Kitt.	DECS-30 Splash Dam
ASTM Rank	hVCb	hVBb	hVAb	hVAb	hVAb	mvb
<u>Proximate Analysis</u>						
% Moisture, as-received	13.20	5.97	2.00	1.88	3.49	2.06
% Ash, dry	13.39	12.02	9.44	13.04	6.62	3.89
% Volatile Matter, daf	47.15	48.94	43.53	43.95	41.50	31.35
% Fixed Carbon, daf	52.85	51.06	56.47	56.05	58.50	68.65
<u>Ultimate Analysis, daf</u>						
% Carbon	76.27	79.01	81.95	81.77	81.31	87.83
% Hydrogen	5.30	5.81	5.63	5.98	5.90	5.36
% Nitrogen	1.32	1.35	1.49	1.73	1.77	1.57
% Total Sulfur	6.38	4.25	4.27	4.45	4.08	0.82
% Oxygen (diff.)	10.73	9.58	6.66	6.07	7.94	4.42
<u>Forms of Sulfur, dry</u>						
% Pyritic Sulfur	3.05	1.41	2.23	3.54	3.32	0.14
% Sulfate Sulfur	0.29	0.01	0.01	0.02	0.03	0.00
% Organic Sulfur (diff.)	3.05	2.32	1.63	0.31	0.46	0.65
<u>Petrography</u>						
Vitrinite, % min.-free	90.2	76.7	79.4	83.6	85.5	76.8
Liptinite, % min.-free	3.0	8.3	6.9	6.6	5.7	3.6
Inertinite, % min.-free	6.8	15.0	13.7	9.8	8.8	19.6
Mean Max. Vitrinite Reflect., %	0.49	0.51	0.73	0.77	0.77	1.16
Vitrinite Luminescence Intensity in N ₂ (Uranyl Glass=10)	-	2.45	3.18	2.35	1.91	1.28

study.

Coals that are associated with marine-influenced deposition also tend to have lower vitrinite reflectance and sometimes higher luminescence emissions compared with those from non-marine or freshwater environments. Speculation as to the cause(s) of this phenomenon has centered on the hypothesis that "bitumens" or bacterial or algal lipids have accumulated in the vitrinite structure. The concentration of relatively low molecular weight materials from the degradation products of bacteria would have been favored under marine conditions. Recently Zhang et al. (18) have suggested that bacterially reduced sulfur species, more readily available in marine-influenced peats, promotes vitrinite luminescence by reacting with functionalized lipids, vulcanizing them into a macromolecular phase. For this reason, it was important to include coals from both marine and freshwater environments of deposition.

These considerations were factored into the process of selecting coal samples for this project. As reported by Edmunds et al. (19), Pennsylvanian age coals from the Monongahela Group are believed to be non-marine. One of these, the Pittsburgh seam, from southwestern Pennsylvania is an economically important coal that is being mined and benefited as a metallurgical product. It is also a coal that has been studied worldwide. Another aspect of our plan was to collect pairs of coals from seams of large lateral extent that may have been deposited under both marine and freshwater conditions in different areas. Two such pairs that were investigated included the Lower Kittanning seam of the Allegheny Group coals in Pennsylvania and the Illinois #5 or #6 coals of the Kewanee Group (Carbondale formation) in Illinois. A survey of mines and limestone quarries in Northwestern Pennsylvania was conducted to identify the environment of deposition of the Lower Kittanning seam. Details concerning this evaluation are provided in Appendix A. This survey identified two hvAb coals in operations nine miles apart that apparently represent coals of marine (PSOC-1562) and non-marine (PSOC-1563) origin. These two coals were collected separately. A further survey of the Illinois basin revealed no good prospects for obtaining a coal of non-marine origin within the time frame of the project and so only one Illinois coal (DECS-24) of marine origin was collected. The remaining samples collected for this project, the hvBb Ohio #4a (DECS-33) and the mvb Splash Dam (DECS-30), are coals of marine origin as well.

At each mine, large blocks of coal were removed to provide a source of vitrain. In addition, whole seam channel samples were collected at the same sites. All samples were placed under a positive pressure of argon shortly after sampling for transport and storage. The channel samples were subsequently reduced in particle size and divided into homogenized subsamples, and then returned to an argon atmosphere for refrigerated storage while awaiting analysis. The block samples used for this study were refrigerated under argon until they could be processed.

Vitrain concentrates were prepared in the following manner. Bags containing coal blocks were placed in a controlled atmosphere glovebox that was evacuated and purged with nitrogen. Then, under a positive pressure of constantly-flowing nitrogen, the bags were opened, and each block inspected for vitrain bands greater than 3 mm in thickness. Small particles of vitrain were removed, inspected for purity and rejected if other lithotypes or minerals could be detected. Fine

powder and particles were collected and placed into glass vials. The vitrain concentrate collected from each bag was sealed under nitrogen in a glass vial which itself was sealed in a small foil bag in the glovebox before being removed and placed in refrigerated storage. A total of about 40 g of powdered concentrate was collected from each set of blocks. Also, several small blocks containing $\approx 3\text{--}5$ mm thick vitrain bands were separated for preparation of polished surfaces. These were sealed in foil laminate bags under nitrogen before being removed from the glovebox.

The vitrain concentrates were processed and subdivided in the glovebox by combining the contents of all containers, crushing the oversize in a mortar to pass a 40 mesh ($420\ \mu\text{m}$) screen and homogenizing using a micro-riffler. All further subsamples were split using the micro-riffler. Approximately 2 g of each concentrate was set aside for the preparation of a petrographic briquette and an 8 g sample was separated for proximate and ultimate analyses. The remaining concentrate was divided into two parts. Because film flotation measurements required a 1 g sample of limited particle size distribution, half of the concentrate was screened to remove the -100 mesh ($<149\ \mu\text{m}$) fraction and then was subdivided into ≈ 1.5 g subsamples (40×100 mesh or $<420 >149\ \mu\text{m}$). The other half of the concentrate was divided into 2.0-2.5 g subsamples (-40 mesh). All subsamples were placed into separate glass vials, purged with nitrogen, sealed in nitrogen-filled foil laminate bags in the glovebox and stored under refrigeration until needed.

Table 2 provides the analytical properties of all vitrain concentrates prepared for this project. In comparison to whole seam channel samples (Table 1), concentrates had significantly lower ash, total sulfur and volatile matter yields. Petrographic analysis revealed that all samples were predominantly vitrinite, mostly $>96\%$. Only the Splash Dam concentrate had a lower amount of vitrinite (91%) owing to the presence of finely dispersed inertinite. The influence of vitrinite concentration on the ultimate analysis chemistry was a slight increase in percentage of carbon and oxygen (diff.).

Surface preparation techniques for the polished blocks of vitrain were designed for each specific analytical procedure. Basically, small particles of coal containing 3-5 mm thick vitrain bands were cut from the interior of relatively large blocks of each coal. One surface was ground by hand using 320, 400, 600 grit papers, and polished with $0.3\ \mu\text{m}$ and $0.05\ \mu\text{m}$ alumina slurries on cloth and silk, respectively. The samples were cleaned only with distilled water in an ultrasonic bath and then desiccated overnight under vacuum. If intermediate storage was required samples were sealed in foil laminate bags under argon and refrigerated. The exact size and shape of the particles and photo-oxidized areas was determined by the requirements of the particular analytical method being used to evaluate surface properties.

Luminescence Analysis and Photo-Oxidation Techniques

A Leitz Orthoplan MPV-II microscope photometer system was used for photo-oxidation of the coal as well as for the measurement of luminescence intensity. This system generates excitation energy from a 100-watt high-pressure mercury-arc lamp which is passed through a

Table 2 - Comparison of Characteristics of Vitrain Concentrate Samples

Seam Identification →	DECS-24 Illinois#6	DECS-33 Ohio #4a	DECS-23 Pittsburgh	PSOC-1562 L. Kitt.	PSOC-1563 L. Kitt.	DECS-30 Splash Dam
ASTM Rank	hvCb	hvBb	hvAb	hvAb	hvAb	mvb
<u>Proximate Analysis</u>						
% Moisture, as-received	12.87	6.03	1.58	1.99	3.57	0.94
% Ash, dry	2.77	2.97	3.33	3.60	1.27	1.64
% Volatile Matter, daf	42.98	45.02	41.38	40.31	37.88	31.50
% Fixed Carbon, daf	57.02	54.98	58.62	59.69	62.12	68.50
<u>Ultimate Analysis, daf</u>						
% Carbon	78.12	80.01	82.67	82.31	82.93	87.44
% Hydrogen	5.32	5.62	5.57	5.56	5.60	5.42
% Nitrogen	1.26	1.21	1.54	1.63	1.40	1.65
% Total Sulfur	3.36	2.29	2.49	1.61	0.69	0.76
% Oxygen (diff.)	11.94	10.88	7.73	8.89	9.38	4.73
<u>Forms of Sulfur, dry</u>						
% Pyritic Sulfur	0.50	0.30	NA	0.72	0.11	0.05
% Sulfate Sulfur	0.03	0.04	NA	0.08	0.04	0.00
% Organic Sulfur (diff.)	2.73	1.88	NA	0.75	0.53	0.70
<u>Petrography</u>						
Vitrinite, % min.-free	98.7	97.3	96.7	97.4	96.4	91.2
Liptinite, % min.-free	0.6	0.9	1.1	0.9	1.2	1.2
Inertinite, % min.-free	0.7	1.8	2.2	1.7	2.4	7.6
Mean Max. Vitrinite Reflect., %	0.44	0.56	0.77	0.80	0.81	1.09
Vitrinite Luminescence Intensity in N ₂ (Uranyl Glass=10)	2.21	2.13	2.78	2.01	1.12	1.26

heat filter (suppressing red and infrared wavelengths) and then through a series of interference filters. The excitation light of wavelengths between 390-490 nm is reflected by a 510 nm reflection short-pass dichromatic beam splitter and condensed onto the sample through a 50X NPL FLUOTAR air objective. Part of the absorbed excitation energy is released as luminescence emissions at longer wavelengths than the absorbed light. The luminescence emission is passed back through the dichromatic beam splitter, and a 515 nm long-pass barrier filter blocks any reflected excitation light. The emitted luminescence passes through the measurement filter of 600 nm with a 60 nm halfwidth. The optical signal is transformed into an electronic signal by an EMI 9558 photomultiplier and amplified. Calibration of the photoelectric system is accomplished using a masked uranyl glass standard and a neutral density filter of 9.3% transmittance to reduce the intensity of the standard to a level comparable to that of vitrinite. The photomultiplier reading obtained from the filtered uranyl glass emission is adjusted to a voltage output of 1.000 ± 0.002 v immediately prior to analysis.

Two types of measurements were made on each sample, i.e., mean luminescence intensity and alteration. To perform these measurements, an area of vitrinite is moved under the measuring spot using white-light illumination. Then, with all light blocked from the surface, the filter block and mercury-arc illumination is introduced into the light path. At the moment the surfaces are exposed, a photometric reading of emitted luminescence intensity is taken. Mean intensity values are determined by taking the mean of 100 such readings measured under a positive pressure of nitrogen in an environmental cell (5,10), whereas luminescence alteration represents the accumulation of readings from the same area at regular intervals when exposed to air over a period of time (generally 1-10 min) during which photo-oxidation occurs. Thus, intensity measurements result in a single value, whereas alteration yields a curve representing the change in intensity with time.

Measurement of luminescence intensity of the raw and irradiated (photo-oxidized) surfaces of powdered vitrain used the same microscope instrumentation and general procedure as employed for analysis of polished surfaces. However, to obtain particle surfaces oriented perpendicular to the axis of the microscope a small amount of the powdered vitrain was gently pressed into modeling clay using a leveling press. A glass cover slip was placed between the press and the sample to avoid contamination. The sample was placed in the environmental cell of the microscope under a rapid flow of dry nitrogen for 5 min before measurements commenced. The surface of individual particles was brought into focus in white light and then luminescence intensity was measured at 600 nm. The mean intensity of twenty different particles for each specimen is reported.

The use of an optical microscope as a means of photo-oxidizing the polished surface of vitrains required some testing before standard techniques were developed. The aim was to enable photo-oxidation of a region of sufficient dimension to allow for both the evaluation of surface properties (i.e., reflectance-mode FTIR, scanning ion mass spectrometry, contact angle measurements, etc.) and for the changes in luminescence properties to be recorded. One of the main concerns about using the optical microscope as a instrument to photo-oxidize coal surfaces, was the time that may be required to irradiate areas as large as 1 mm^2 and then to accurately

relocate that area for the other surface characterization determinations. All of the prior surface oxidation experiments conducted in this laboratory and the quantitative measurement of the alteration of luminescence emissions has been undertaken by exposing relatively small areas (<50 μm diameter) of vitrinite to blue-light irradiation.

Tests performed early in the project demonstrated that to maintain a suitable energy flux for photo-oxidation the maximum effective area of irradiation must be limited at or below 200 μm diameter. FTIR analyses of areas larger than this showed limited oxidation response over the same exposure period. However, using 200 μm diameter spacing required a total of 5 hours to photo-oxidize a 1 mm^2 area employing a 10 min irradiation interval. Because of this time constraint 10 minutes was selected as the maximum irradiation interval for this study.

The significance of the negative and positive components of alteration with regard to oxidation is of importance and was taken into account in our experimental design. For all of the coals selected in this study, the time required to reach the minimum intensity value during alteration measurements was in excess of 60 sec. Consequently, a 1 min irradiation interval was selected so that the significance of the negative component of alteration could be evaluated. A five minute irradiation interval was selected for an intermediate time as a means of monitoring the progressive nature of change. Therefore, irradiation intervals of 1, 5 and 10 min for vitrain photo-oxidation were established based on these considerations.

Before the photo-oxidation step, polished vitrain bands were inspected under an optical microscope using an air objective in white light to locate regions that were free of imperfections and contamination. Once these regions were located, the vitrain band was oriented using thin scribe marks cut into the polished surface. An arrow head was cut to identify the up or north position placement relative to the microscope. In some cases an east-west scribe mark was cut into each vitrain band so as to identify the location of irradiated areas by quadrant. A sketch of the surface including imperfections, minerals, fractures, etc. near the areas of irradiation was prepared. Irradiation, in all cases, was performed using blue light (390-490 nm) in air for periods of 1, 5 and 10 minutes for individual areas of between 100 or 200 μm as defined by the microscope field diaphragm. Enough of these areas were placed side-by-side and/or end-to-end to generate a photo-oxidized region that met the resolution requirements of the intended surface analytical technique. During the course of irradiation, alteration patterns were recorded for some of these individual areas. After irradiation, the small coal blocks were carefully packaged separately and returned to refrigerated storage in foil laminate bags under argon.

The powdered vitrain samples were photo-oxidized using a longwave UV spotlight. A comparison was made of the level of photo-oxidation achieved with this system relative to that obtainable with the optical microscope. This comparison, reported in Appendix B, shows that the BLAK-RAY UV spotlight could provide the same effective alteration of surface luminescence following 10 times the exposure obtained with the optical microscope. Therefore, exposures of 10, 50 and 100 min would be required of the UV spotlight to provide the same level of photo-oxidation that the microscope system gives in 1, 5 and 10 min, respectively.

The procedure followed for the irradiation of powdered vitrains was as follows. A warm-up period (1 hour) was allowed prior to each operation of the BLAK-RAY spotlight. A monolayer of powdered vitrain was spread on the outside bottom half of an upturned glass petri dish and exposed to the UV irradiation for the appropriate period of time (10, 50 or 100 mins) at a distance of ≈ 5.7 cm from the lamp. Then, the top half of the petri dish was placed over the bottom half so as to secure the particles while they were inverted. The bottom half was then removed and the undersides of the particles were irradiated for the same period. These steps were repeated on successive monolayers until approximately a gram of irradiated vitrain was produced. A few milligrams of the original sample and the irradiated materials were set aside for measurement of luminescence intensity of the surface as well as for pyrolysis GC/MS analysis.

Surface Property Measurements on Polished Vitrain Bands

This section describes a variety of surface or near-surface analytical procedures that were performed on the samples collected for this study and prepared as polished surfaces (or in one case thin sections). Because some of these analytical procedures may alter or destroy the surface, the order of their analysis had to be carefully planned so that the maximum amount of information could be obtained from the same surfaces used for multiple tests. Consequently, although our primary objective was to utilize reflectance-mode FTIR analysis to determine the changes in chemical functionality as a result of photo-oxidation and to correlate these results with contact angle measurements and luminescence intensity, other surface analyses such as change in reflectance and near-surface oxygen concentration had to be delayed until the end of the project.

A major effort was made in this project to characterize the chemical changes that occur at the surface of vitrain as a result of blue-light irradiation. All of the in-house analytical methods that were planned had the basic ability to measure near-surface (reflectance-mode FTIR and electron microprobe analysis) or bulk (pyrolysis GC/MS) chemical properties, in particular oxygen content and functionality. However, our expectation was that other techniques and instruments, employed by experienced technical staff could contribute to the characterization of photo-altered coal surfaces. In this regard we were able to interest several other researchers in our project and convinced them to use their equipment and expertise to evaluate our irradiated surfaces. Among them were Dr. Paul Pigram, then of the University of New South Wales in Australia, utilizing Secondary Ion Mass Spectrometry (SIMS), Dr. George Cody, then of Argonne National Laboratory, using Scanning Transmission X-ray Microscopy (STXM) and Carbon Near-Edge X-ray Absorption of Fine Structures (C-NEXAFS) microanalysis and imaging, and Drs. Rui Lin and Pradeep Iyer of UNOCAL Corporation using reflectance-mode FTIR microanalysis.

Reflectance Analysis

Random reflectance is an optical microscopic technique that measures the amount of light reflected from the surface of vitrinite, using non-polarized, white light under oil immersion. As described in ASTM method D2798 (20), analysis is performed without stage rotation. Following

calibration of the photoelectric system with standard optical glasses in the reflectance range of the vitrinite being measured, a statistically significant number of readings are taken. To properly characterize the reflectance of a typical coal, 100 readings are accumulated and the mean value of the gaussian distribution of readings obtained is reported. Such determinations are usually repeatable within the same laboratory to within 0.02%.

In the current study we were interested in quantifying the difference in reflectance of the irradiated and non-irradiated surface of vitrain bands. To obtain the comparison, the standard procedure was modified to collect reflectance pairs (50 readings), that is, reflectance readings were taken along bedding planes within the vitrain, 50 - 100 μm from one another in both non-irradiated and irradiated (1, 5 and 10 min) regions. To reduce the influence of the normal variation in vitrinite reflectance from place to place within vitrain bands, the difference between these readings was reported. The magnification employed was 625 X.

Electron Microprobe Analysis

Electron probe microanalysis was employed to determine whether there was a measurable increase in the surface oxygen concentration after irradiation. In this procedure, two sample sets were prepared that included all irradiation sequences for the hvCb Illinois #6 seam (DECS-24) and the mvb Splash Dam seam (DECS-30). After carbon-coating, samples were placed in a Cameca Camebax SX50 electron microprobe under a high operating vacuum for quantitative analyses. A PC2 synthetic nickel-carbon pseudocrystal spectrometer was used for oxygen analysis, whereas other elements were monitored with an attached Energy Dispersive System (EDS). Spectrometer wavelengths were calibrated for oxygen using a Pyrex glass standard. The accelerating voltage of the beam was set at 10 keV which yields a spot size of $\approx 10 \mu\text{m}$ and an approximate depth of penetration of $2 \mu\text{m}$. The $K\alpha$ peak of oxygen ($25.511\text{\AA}$) was used for all analyses, background values were measured and subtracted for each new vitrain band or sample.

Contact Angle Measurements

An initial evaluation of contact angle measurements using different techniques was performed to establish whether the placement of a stationary water droplet could be used effectively to measure contact angles in the present study. However, because it was difficult to simultaneously observe both the surface and the interfacial angle, it was difficult to determine placement relative to the irradiated region and the results were somewhat erratic. A technique that provided much improved control involved growing or advancing the water droplet across the polished surface of vitrain. The experimental set-up, shown in Figure 1, used a high-resolution video camera connected to a microscope to record the profile of a water droplet at the coal/water/air interface. A Gilmont syringe coupled to an adjustable speed syringe pump was used to grow the water droplet. The droplet was initially placed on an unoxidized area of the coal and allowed to grow across the irradiated area. A schematic representation of the droplet growth and the change in the contact angle as it reached and entered the irradiated area is shown in Figure 2. The entire sequence of growth was recorded on video tape. Contact angle values were measured at different positions as the droplet advanced from the fresh through the photo-

Figure 1 - Schematic of the Contact Angle Measurement Equipment

1: High-resolution camera; 2: Microscope; 3: Coal sample; 4: Syringe;
5: Syringe pump; 6: Movable stage; 7: Vibration-free table; 8: Light
source

Figure 2 - Measurement of Contact Angle at the Air/Coal/Water Interface as Water Droplet Advances Across an Irradiated Area

γ_{AW} , γ_{CW} and γ_{CA} : air-water, coal-water and coal-air interfacial energies; θ contact angle.

oxidized surface.

Secondary Ion Mass Spectrometry (SIMS)

As a surface analysis technique, Secondary Ion Mass Spectrometry (SIMS) has an analysis depth of $<10 \text{ \AA}$ with a spatial resolution of $10 \text{ }\mu\text{m}$ and sensitivity of about 0.2 ppm. The technique requires a thin wafer of coal (2 mm thick), $\approx 10 \text{ mm}$ square, attached to a metal sheet for support and for improved electrical conductivity between the sample and instrument sample holder. In our initial preparation, a block of the Pittsburgh seam coal (DECS-23) was cut and glued to a 10 mm square of 1 mm thick copper sheeting. The coal was oriented so that a 4 mm band of vitrinite was exposed on the surface, and the sample was ground and polished by hand to less than a total thickness of 3 mm using our standard technique. North-south and east-west scribe marks were cut into the polished surface and each quadrant inspected for cleanliness. In one quadrant a matrix of 25 adjacent $100\text{-}\mu\text{m}$ diameter areas was irradiated for 10 min with blue light to give a $500 \times 500 \text{ }\mu\text{m}$ photo-oxidized region for analysis.

The instrument used was a PRISM Time-Of-Flight SIMS manufactured by Kratos. The system employed a FEI 69Ga ion gun at 25 keV and 1 nAmp continuous ion current with a pulse width of 100 nS and pulse rate of 10 kHz. The technique involved focusing a stream of Ga^+ ions at the sample surface under high vacuum (1×10^{-8} Torr). Depending upon the scan rate and the material, molecular fragments (ions) are removed from the first several atomic layers of the surface. These fragments are collected and analyzed by a time-of-flight mass spectrometer.

A limited number of tests were originally planned using this technique in collaboration with Dr. Pigram of the University of New South Wales. After the initial evaluation further attempts at defining the change in concentration of oxygen-bearing fragments with photo-oxidation time (at 1, 5 and 10 min) with this same coal were unsuccessful because of difficulties in locating the irradiated areas. Shortly thereafter, Dr. Pigram left the University of New South Wales and the collaborative effort ended.

Scanning Transmission X-Ray Microscopy and Carbon-Near Edge Absorption of Fine Structures

In another study, results were obtained by Dr. George Cody then of Argonne National Laboratory using the Scanning Transmission X-ray Microscopy (STXM) and Carbon-Near Edge X-ray Absorption Fine Structure (C-NEXAFS) techniques. This work was conducted at the National Synchrotron Light Source, Brookhaven National Laboratory. The approach employed a spherical monochromator capable of a maximum 0.3 eV energy resolution at a spatial resolution limit of $550 \text{ \AA}$. Transmission is measured using a gas-filled detector which counts X-ray photons passing through the sample and provides high-resolution energy images. Images have been acquired by Dr. Cody at energies near the carbon absorption edge ($E < 282 \text{ eV}$) which allow for the distinction of vitrinite, cutinite and sporinite based on the relative intensities of several absorption bands (21), one which correlates with the concentration of aromatic carbon, another of which correlates with the concentration of aliphatic carbon, and others assigned to oxygen-containing functionalities. In an effort to test these assignments and to provide base information

on our photo-oxidation technique, a series of samples were prepared for STXM analysis. Fresh coal blocks of the hvAb Pittsburgh seam (DECS-23), subbituminous Wyodak seam (DECS-26), and medium volatile Sewell seam (DECS-13) containing visible vitrain bands, were selected for the experiment and shipped to Dr. Cody for the preparation of ultra-thinned sections (<800 nm thick). Very small particles of vitrain were mounted in epoxy resin and a microtome used to cut the thinned sections. Sections were placed between grid plates to facilitate the location of regions suitable for irradiation. Samples were returned to this laboratory where different areas of the thin sections were identified as vitrinite and irradiated using blue light for periods of 1, 5, 10 and 15 min.

Reflectance-mode Fourier Transform Infrared Spectroscopy (FTIR)

The reflectance-mode FTIR equipment, a Bio-Rad/Digilab spectrometer with a UMA 300A infrared microscope accessory, originally planned for use in this investigation had many alignment problems in the early going and eventually was destroyed in an electrical fire in March 1995. Before replacement equipment could be acquired, our initial evaluation of the reflectance-FTIR and sample preparation techniques were conducted in collaboration with Drs Rui Lin and Pradeep Iyre of UNOCAL Corporation. Their instrument was not only a much newer model, but was equipped with both white- and blue-light capabilities so that photo-oxidation of the polished surface could be undertaken just prior to infrared analysis. Using two different Pittsburgh seam samples (DECS-12 and DECS-23), this work involved initial evaluation of surface preparation and irradiation techniques as well as a determination of the sensitivity of the FTIR technique.

For the in-house work, specular reflectance FTIR spectra were obtained from the new FTS 175 spectrometer with a Bio-Rad UMA 500 infrared microscope accessory fitted with a 250 μm diameter narrow-band MCT (mercury-cadmium-telluride) detector cooled to 77°K. The polished specimens of vitrain were leveled on a slide with modeling clay. An area on the surface was identified in white light (40 X total magnification in air) and masked to include only the irradiated area. Then, the infrared objective (150 X total magnification) was moved into the optical path. Before measurements were made an environmental chamber was placed around the sample and a rapid flow of nitrogen was begun. The flow of nitrogen helped to reduce moisture levels within the chamber and at the coal surface. Preliminary interferograms were taken to monitor moisture levels; depending upon the coal, 10-60 min were required before analysis could commence. The analytical conditions used were: single beam accumulation of 2000 scans; 4000-650 cm^{-1} spectral range; spectral resolution of 2-4 cm^{-1} . An infrared background spectrum was collected from a gold-coated plate at the beginning of each session and was subtracted from spectra derived from the coal surfaces. Correction of the reflectance spectra for distortions caused by specular reflection and refractive index was carried out using a Kramers-Krönig transformation provided with the Bio-Rad software.

Film Flotation Using Vitrain Concentrates

Film flotation was conducted on the powdered samples by placing a monolayer of about 0.2 g of vitrain on the surface of a liquid in a shallow vessel (a funnel was used in this case) of

about 75 mm diameter at the top and a height of about 20 to 30 mm. In general, the particles either remained on the liquid surface (lyophobic) or were imbibed into the liquid (lyophilic). Thus, the flotation procedure involves separating the material into lyophilic and lyophobic fractions which are then dried and weighed to provide a distribution of wettable coal particles in a technique that is analogous to a density distribution (22). The surface tension of the liquid used was varied from 30 to 50 dynes/cm by the addition of anhydrous methanol (22.6 dyne/cm at 20°C) to twice-distilled water (72.8 dynes/cm at 20°C).

Pyrolysis Gas Chromatography/Mass Spectrometry

Flash pyrolysis gas chromatography and mass spectrometry was performed using a Varian 2700 gas chromatograph and a DuPont 21-490B mass spectrometer equipped with a Chemical Data Systems Pyroprobe 1000 according to the method outlined by Hatcher et al. (23). The pyroprobe pyrolyzes samples at any fixed heating rate ranging from 10 to 20,000°C/s to a desired final temperature (max. 1400°C), and holds at that temperature for a given time (0.01 - 99.99 s). In this project a flash pyrolysis temperature of 610°C was employed. Lower temperatures produce smaller fragments of low molecular weight which would provide little structural detail and obscure the information on the exact structural features present in the sample. A heating rate of 10°C/sec was used because this relatively rapid heating minimizes the potential for secondary reactions and enhances the detection of pyrolysis fragments characteristic of the original macromolecular nature of the vitrain. The time of pyrolysis was 10 sec to ensure complete expulsion of the volatile pyrolyzates from the capillary tube into the gas chromatograph - mass spectrometer.

It is important to carefully prepare the finely powdered sample and properly select the sample weight to minimize the effects of thermal gradients in the sample and to ensure that the representative sample was completely pyrolyzed. A sample weight of about 0.5 mg was used. Samples were weighed with a microbalance and loaded into a quartz capillary tube as evenly as possible to minimize thermal gradients. The quartz tube was placed inside the platinum heating coil of the pyroprobe; this assembly was then inserted into the injection port (temperature maintained at 280°C) of a Varian 2700 gas chromatograph and the sample pyrolyzed. The pyrolyzate was cryotrapped with liquid nitrogen prior to being subjected to gas chromatography in a J&W DB-17 capillary column (25 m in length, 0.25 mm in diameter, made of 50% phenyl methyl silicone). The chromatograph temperature was programmed from 30°C (0 min) to 280°C (20 min) at a rate of 4°C/min. The effluent was swept into the source of a DuPont 21-490B mass spectrometer fitted with a Teknivent Vector/One data system for detection and compound identification. Groups of compounds were identified by a combination of methods including comparison of mass spectra to the NBS/Wiley library and other published mass spectra and to authentic standards. This Py-GC/MS technique has been found to be very reproducible for repetitive analysis of the same sample.

RESULTS AND DISCUSSION

Surface Properties of Photo-Oxidized Polished Vitrain Bands

Most of the samples employed in this part of the study were prepared with the restrictions of measuring contact angle in mind. In a modification of the general irradiation technique, the light flux of the microscope was focused into a 200 μm diameter area. As a guide, a single scribe mark was placed through the entire thickness of the vitrain bands. Approximately 200 μm from the scribe mark, successive areas of vitrinite were irradiated in a line parallel with the mark until the full thickness of the vitrain band was traversed. A second line of irradiated areas placed immediately adjacent to the first provided a photo-oxidized area about 400 μm wide for the full thickness of the vitrain band. This procedure was followed for each period of irradiation, i.e., 1, 5 and 10 minutes. Usually, different vitrain bands in different blocks were irradiated for each time period. Also, luminescence alteration patterns were recorded at various locations during the course of irradiation. Following irradiation, the samples were returned to storage in foil laminate bags under argon gas and refrigerated until measurements could be made.

As seen in Figure 3, irradiation of vitrain resulted in a darkening of the exposed surface. Figure 3a clearly shows the adjacent lines of irradiated areas composed of dark nine-sided regions following photo-oxidation of the Ohio #4a (DECS-33) for 10 min. The shape of the irradiated areas was defined by the iris field diaphragm of the microscope. Viewed at higher magnification, Figure 3b shows the uniform change in the individual irradiated regions. In an effort to determine whether the surface properties of vitrinite were altered uniformly by duration of exposure to blue light, mean random reflectance was measured for three sets of vitrain, i.e., Lower Kittanning (PSOC-1563), Pittsburgh (DECS-23) and Ohio #4a (DECS-33) exposed for 1, 5 and 10 min. Figure 4 shows the difference in mean random reflectance between these regions of vitrains from three coals. The results show that vitrains from different rank coals are influenced differently by exposure to blue light. For the two hvAb coals (Pittsburgh and Lower Kittanning) a steady increase in this difference is measured with duration of exposure, although the magnitude of change after 1 min exposure may not be significant. The hvBb Ohio #4a on the other hand, shows significant changes in reflectance at 1 and 5 min exposures, but the difference diminishes after 10 min. This observation could be a function of the material (i.e., very different rank or type of vitrain) or of the irradiation procedure. In comparison to the hvAb samples where irradiation of the 1 and 10 min regions was performed on the same vitrain band, the Ohio #4a was performed on three different bands which increases the likelihood that the observed reflectance difference results from variations in the characteristics of the vitrain.

To determine the amount of oxygen that may be emplaced near the surface of vitrain during blue-light irradiation, electron microprobe readings were taken on non-irradiated and irradiated areas in pairs parallel with the bedding direction for two of the vitrains, i.e., the hvCb Illinois #6 (DECS-24) and the mvb Splash Dam (DECS-30). Four to six pairs of readings were taken from each irradiation interval; the mean weight percent concentration of oxygen in these regions is plotted for both coals in Figure 5. Note that the measured oxygen values of the non-irradiated vitrains (time 0) are very close to the ultimate oxygen values reported in Table 2 for

Figure 3 - Photomicrographs in Reflected Light and Oil Immersion of Areas of the Ohio #4a Seam Polished Vitreous Irradiated for 10 min.

Figure 4 - Difference in Random Reflectance Between Irradiated and Non-irradiated Regions of Vitrain with Time of Blue-light Exposure

Figure 5 - Change in Near-surface Oxygen Concentration with Time of Blue-light Irradiation as Measured by Electron Probe Microanalysis

both vitrains. This level of agreement also was obtained in an electron microprobe analysis of oxygen for vitrinite reported by Mastalerz and Bustin (24). The present results show a significant increase in the near-surface oxygen concentration with increasing blue-light irradiation. An unexpected result, however, is that regardless of the coal rank and difference in original oxygen content of the coals, the level of increase in oxygen concentration was nearly identical for each irradiation interval. These results clearly demonstrate that exposure to blue light results in a significant photo-oxidation of vitrinite, not only at the surface, but possibly also to a depth of 2 μm . For the lower rank Illinois #6 seam sample some buckling of the irradiated surface was perceived for the areas irradiated for 10 min.

Contact Angle Measurements

The principal objective of coal flotation is the attachment of an air bubble to the surface of the organic fraction of coal as a means of separating (by flotation) organic materials from the inorganic fraction. The technique depends on the more hydrophobic character of the organic fraction compared to the more hydrophilic character of most inorganic compounds. Contact angle measurements represent a very direct method of determining the relative affinity of a liquid or gas for a solid surface. One technique often employed with coals is to place a droplet of distilled water onto a polished surface and then measure the angle the droplet makes at the coal/water/air interface. The more hydrophobic the coal surface, the greater will be the interfacial angle. As simple as this approach seems, the results can be greatly influenced by the nature and quality of the prepared surface. Surface imperfections caused by polishing artifacts (scratches and pits), component heterogeneity (inclusions of different macerals and minerals) and fractures or cleats, can have a profound influence on the contact angle. In the current study great care was taken to ensure that the areas of vitrain selected for irradiation and contact angle measurements were free of such imperfections.

Contact angle measurements are shown for all of the vitrains and conditions of photo-oxidation used in this study in Figures 6 - 8. These data show that contact angle values are influenced significantly by irradiation time as well as by coal rank. Generally, contact angle values were relatively stable when measured through areas that were not irradiated and photo-oxidized. Major differences in contact angle values on non-irradiated surfaces resulted from measurements made on vitrain bands from different coal blocks; those that are similar were measured on the same band (Figures 6 - 8). Regardless of the initial contact angle, the relative changes resulting from photo-oxidation were found to be significant. Note too, that there was considerable variation in the measured contact angles within the irradiated areas. Some of this variation can be explained by our inability to completely photo-oxidize the entire region (see Figure 3a) as well as by some buckling of the surface upon oxidation.

In general, a decrease in contact angle occurred when the droplet advanced into an irradiated area and the value remained lower than the initial value (un-oxidized surface) throughout the 400 μm (0.4 mm) wide zone. This decrease is clearly related to photo-oxidation of the vitrain surface. In all but one case (Lower Kittanning, PSOC-1563), one minute of irradiation resulted in only a minor decrease in contact angle. A progressively greater decrease in

Figure 6 - Advancing-Drop Contact Angles Measured on Polished Surfaces of Vitrain Photo-Oxidized for Different Time Intervals

Figure 7 - Advancing-Drop Contact Angles Measured on Polished Surfaces of Vitrain Photo-Oxidized for Different Time Intervals

Figure 8 - Advancing-Drop Contact Angles Measured on Polished Surfaces of Vitrain Photo-Oxidized for Different Time Intervals

contact angle was observed from surfaces irradiated for 5 and 10 min, resulting in a maximum decrease of 5-10 degrees for all coals. Greater levels of maximum decrease were observed for vitrains of lower rank (Figure 6), but contact angle values fluctuated more within the irradiated area. For the mvb Splash Dam vitrain (Figure 8), the contact angle reached its minimum value after one minute of irradiation and did not change with longer irradiation times.

Figure 9 uses the maximum change in contact angle (i.e., $\Delta CA = CA_{\text{fresh}} - CA_{\text{min}}$), to illustrate the effect of both rank and irradiation time for the six vitrains employed in this study. A linear decrease is observed in the change in contact angle with increasing rank resulting from 5 and 10 minute irradiations, with the change upon 10 min irradiation being significantly greater, particularly at lower rank. In summary, these results from polished surfaces show that photo-oxidation decreases the hydrophobic character of bituminous rank vitrains and suggest that their floatability would be reduced. This effect is less apparent at lower levels of oxidation (1 and 5 min irradiation times) and at higher rank levels. These same conclusions were arrived at by Gutierrez-Rodriguez and Aplan (1) in their study of aqueous oxidation of whole coals.

It is interesting that the present work and that of Gutierrez-Rodriguez and Aplan (1) showed a major influence of rank even though our measurements of oxygen uptake (electron probe results) for the lowest (Illinois #6) and highest (Splash Dam) rank coals in this study were essentially the same (6.2 and 6.8% after 10 min irradiation, respectively). This suggests that the type of oxygen functionality that forms during surface oxidation has a more important influence upon hydrophobicity than the total oxygen emplaced. The fact that Gutierrez-Rodriguez and Aplan also determined that the progressive oxidation of anthracites led to an initial increase in hydrophobicity (as measured by captive-bubble contact angles) before decreasing, suggests to us that development of the necessary oxygen functionality may be delayed during oxidation of higher rank coals and is dependent upon secondary reactions involving the surface and oxygen already emplaced.

Luminescence Intensity and Alteration of Vitrain

Mean luminescence intensity values for whole-seam channel samples and vitrain concentrates are shown in Tables 1 and 2, respectively. These results show the expected trends of lower mean intensity values from vitrain concentrates owing to the higher concentration of telocollinite. Also, luminescence intensity was found to be much higher for the Lower Kittanning sample (PSOC-1562) from marine-influenced deposition compared with the non-marine sample (PSOC-1563). Also as expected, the lowest intensity values were obtained for the medium volatile Splash Dam (DECS-30). Figures 10 - 15 compare alteration curves obtained from 10-min irradiations and derived from one or more vitrain particles for each of the samples. These patterns exhibit the dual alteration anticipated from vitrinite of lower rank bituminous coals and the single negative alteration from the medium volatile Splash Dam (DECS-30). As seen in these figures, the positive component of the dual alteration patterns diminishes as rank increases so that by medium volatile rank only negative alteration occurs during exposure.

Figure 9 - Maximum Change in Contact Angle with Irradiation Time
of Six Bituminous Rank Vitrains

Figure 10 - Luminescence Alteration Patterns from the hvCb Illinois #6 (DECS-24)
Comparing Whole Seam Channel Sample and Vitrain Concentrate

Figure 11 - Luminescence Alteration Patterns from the hvBb Ohio #4a (DECS-33)
Comparing Whole Seam Channel Sample and Vitrain Concentrate

Figure 12 - Luminescence Alteration Patterns from the hvAb Pittsburgh Seam (DECS-23)
Comparing Whole Seam Channel Sample and Vitrain Concentrate

Figure 13 - Luminescence Alteration Patterns from the hvAb Lower Kittanning (PSOC-1562)
Comparing Whole Seam Channel Sample and Vitrain Concentrate

Figure 14 - Luminescence Alteration Patterns from the hvAb Lower Kittanning (PSOC-1563)
Comparing Whole Seam Channel Sample and Vitrain Concentrate

Figure 15 - Luminescence Alteration Patterns from the mvb Splash Dam (DECS-30)
Comparing Whole Seam Channel Sample and Vitrinite Concentrate

Luminescence alteration patterns also were collected during the course of photo-oxidation for each time interval and vitrain prepared for contact angle measurements. Figures 16 - 21 shows the individual patterns, identified as Area1, Area2, etc. on the graphs, which are keyed to maps of the irradiated regions (not shown). These patterns demonstrate the greater variability of alteration response from place to place within the same vitrain band of the lower rank vitrains (Illinois #6, Figure 16 and Ohio #4a, Figure 17) compared with those of higher rank (Figures 18 - 21). They also show that 1 min of irradiation was sufficient duration to isolate the negative component of alteration. The positive component of alteration observed for the polished vitrain bands of the Lower Kittanning (PSOC-1562, Figure 19) samples was somewhat diminished compared to that of the whole-seam channel (Figure 13).

These alteration patterns provide important insight into the contact angle response. For example, the alteration patterns for the hvAb, non-marine influenced coals (Pittsburgh, Figure 18 and Lower Kittanning, Figure 20) are very similar. Both vitrains showed an initial rapid decrease in intensity to some minimum value, followed by a slow, regular increase. After 10 minutes of irradiation, luminescence intensity had not returned to initial value measured at time zero. Because of this slow positive response, little difference was recorded between the intensity values measured at 5 and 10 minutes of irradiation. This corresponds to the relatively small difference observed in contact angle values for these two times of irradiation (Figures 7 and 8, respectively). For the Illinois #6 (Figure 16) and Ohio #4a (Figure 17) vitrains, on the other hand, luminescence intensity diminished to a minimum and then increased quite rapidly, eventually exceeding the initial value (time zero) after 10 min of irradiation. Thus, with a greater luminescence alteration response, we expected and in fact did see a comparably greater change in contact angle (Figure 6) at 5 and 10 min of irradiation for these vitrains compared to the hvAb vitrains. Also, there was more variability in the apparent rate of increase in luminescence intensity from place to place within individual vitrain bands (Figures 16 and 17). For the Illinois #6 and Ohio #4a, contact angles dropped sharply then increased slightly within the irradiated area, suggesting that photo-oxidation of these lower rank vitrains may be more heterogeneous (Figure 6).

In contrast to the coals discussed above, the alteration pattern of the mvb Splash Dam sample (Figure 21) was negative out to 10 min, i.e., a rapid initial decrease followed by a uniform, very slow decline. As already noted, the contact angles for this coal decrease by the same amount whether irradiated for 1, 5 or 10 minutes; however, total oxygen emplacement near the surface has been noted to occur at the same rate as in vitrain of lower rank (Figure 5). These results in combination suggest that a fundamentally different mechanism of surface oxidation of this high-rank coal has less influence on wettability.

In the process of evaluating the use of luminescence alteration patterns as a means of measuring the quality of the vitrain surface with respect to hydrophobicity, a number of correlations tested were performed. Because of the dual nature of alteration, the actual intensity values measured after 1, 5 and 10 min of irradiation were found to be unsuitable for comparison with measured contact angles. Furthermore, no relationship was found between the initial luminescence intensity of the vitrain bands (at time zero) and contact angle values. Therefore,

Figure 16 - Luminescence Alteration Patterns from Irradiated Areas
of the hvCb Illinois #6 Vitrain Bands, DECS-24

Figure 17 - Luminescence Alteration Patterns from Irradiated Areas
of the hvBb Ohio #4a Vitrain Bands, DECS-33

Figure 18 - Luminescence Alteration Patterns from Irradiated Areas
of the hvAb Pittsburgh Vitrain Bands, DECS-23

Figure 19 - Luminescence Alteration Patterns from Irradiated Areas
of the Lower Kittanning Vitrain Bands, PSOC-1562

Figure 20 - Luminescence Alteration Patterns from Irradiated Areas
of the hvAb Lower Kittanning Vitrain Bands, PSOC-1563

Figure 21 - Luminescence Alteration Patterns from Irradiated Areas
of the mvb Splash Dam Vitrain Bands, DECS-30

although alteration patterns represent a good guide to the differences in photo-oxidation experienced by different vitrains, they appear to be less useful for expressing the relative quality of the hydrophobicity of the surface. This is contrary to observations made on naturally weathered coals (vitrains) where the initial luminescence intensity is generally much lower than that of the fresh surface and the alteration patterns are only positive (3,4,5,17).

Luminescence Properties of Model Compounds

In an effort to generate some basic chemical information on luminescence, 16 solid aromatic model compounds were evaluated in terms of luminescence intensity, alteration and spectral range resulting from blue-light irradiation. The analytical procedures and results of this investigation are discussed separately in Appendix C, but can be summarized as follows. The results show that luminescence intensity values increased in response to increasing numbers of aromatic rings, that molecular shape and placement of substituents (O, N and S) within an aromatic structure influenced emissions as did the atomic size and weight of heteroatoms. Furthermore, most of the oxygen-bearing compounds, particularly those containing carbonyl and carboxylic acid groups, had relatively high initial luminescence emissions and possessed positive or dual alteration patterns when photo-oxidized. Similar luminescence results are obtained from low-rank coals and, although naturally weathered coals typically show lower levels of luminescence, they too give positive alteration when photo-oxidized.

Change in Surface Chemistry with Irradiation

In a collaborative effort with Dr. Pigram of the University of New South Wales, SIMS analysis of photo-oxidized vitrain showed that a greater number of ions were generated from the irradiated area on the Pittsburgh seam sample (DECS-23) compared to the fresh surface. The effect was such that the matrix of irradiated areas was clearly visible in an image of total ion content compared to the surrounding non-irradiated surface. A higher total ion count has been observed in previous pyrolysis GC/MS studies of naturally weathered coals which were leaner in aliphatic and aromatic hydrocarbons and richer in oxygenated species (25). Interpretation of the mass spectra from photo-irradiated and non-irradiated areas in this study also gave a variety of possible oxygen-containing ions, all of which were found in significantly higher concentration in the photo-oxidized region as is shown in Table 3. These early results gave us confidence that our irradiation technique was indeed causing a photo-oxidation of the vitrain surface. Because of the size (amu) and relative concentration of the molecular fragments the results suggest that a large part of the oxygen was associated with the aromatic network and not necessarily with aliphatic side chains.

In another collaborative effort, thinned sections of various photo-irradiated vitrains were evaluated by Dr. George Cody at Argonne National Laboratory using the Scanning Transmission X-ray Microscopy (STXM) and Carbon-Near Edge X-ray Absorption of Fine Structure (C-NEXAFS) techniques. The results from this study are currently being prepared for publication (26). C-NEXAFS spectra obtained in the region of 280 to 300 eV from the Pittsburgh vitrain are described here. Figure 22 shows the changes in the spectra between the non-irradiated surface

Table 3 - Relative Difference in Peak Intensity for Oxygen-Bearing Molecular Fragments From SIMS Analysis

Molecular Fragments	amu	Relative Peak Intensity	
		Photo-Oxidized	Fresh Surface
CH_3O^+	31	625	135
$\text{C}_2\text{H}_4\text{O}^+$	44	667	176
$\text{C}_2\text{H}_5\text{O}^+$	45	917	205
$\text{C}_3\text{H}_6\text{O}^+$	58	583	189
$\text{C}_3\text{H}_7\text{O}^+$	59	917	100
$\text{C}_5\text{H}_7\text{O}_3^+$	115	293	44

Figure 22 - Carbon X-ray Absorption Spectra of Fresh and Photo-Oxidized Pittsburgh Seam Vitrain, DECS-23

and that irradiated for 10 min, along with preliminary energy band assignments. Peak intensities at "A" and "C" decrease, whereas peaks at "B" and "D" increase. Together with the spectra at 1 and 5 min irradiation (not shown), the results demonstrate a progressive decrease or increase in these intensities with irradiation time. Variations in the intensity of energy bands tentatively assigned to protonated/alkyl substituted aromatic carbon (A=285.5 eV), hydroxylated aromatic carbon (B=287 eV) and carboxylated aromatic carbon (D=289.5 eV) are summarized in Figure 23. These results suggest that hydroxyl and carbonyl functionalities increase in concentration with increasing time of blue-light irradiation accompanied by an overall decrease in methyl group concentration. Changes in concentration of methyl and carbonyl groups agree well with published results from weathered bituminous coals; both Wu et al. (27) and Valia (28) observed similar results in careful laboratory and coal-pile investigations of weathering using FTIR. However the identification of an increasing concentration of hydroxyl groups attached to aromatic structures in the STXM results was unexpected. Variation in the hydroxyl concentration may have been overlooked in previous FTIR coal oxidation and weathering studies or may be an artifact specific to our photo-oxidation techniques.

Infrared Microspectroscopy

Specular-reflectance Fourier Transform Infrared Spectroscopy (reflectance-FTIR) has become an important analytical technique for the characterization of functional group chemistry of heterogeneous materials. By combining the power of an optical reflectance microscope for coal maceral identification with the ability to focus an infrared beam within the range of 250 - 20 μm , it is possible to measure the functional group chemistry of coal macerals free of contamination. Furthermore, Mastalerz and Bustin (24) showed good agreement when comparing results from the more traditional methods of FTIR analysis of coal macerals (i.e., transmission-mode from thin sections and KBr pellets of maceral concentrates) with the reflectance technique. Consequently, the technique was employed for the characterization of photo-oxidized vitrains in the current study. However, as a means of measuring changes in surface properties, reflectance-mode FTIR may not provide the needed level of sensitivity. Depth of penetration of the infrared beam during the analysis has been reported to be as little as 2 and as great as 5 μm . This translates into relatively large sampling volumes which could potentially obscure any minor changes in the surface properties of interest.

In the early phase of this research a collaborative effort with Drs. Lin and Iyre of UNOCAL was undertaken to evaluate surface preparation and irradiation techniques. In these studies, a polished section of DECS-12 vitrain (Pittsburgh seam) was used to investigate the duration of irradiation (in air) necessary to induce changes in surface chemistry. Measurable changes in surface functionality were not observed for areas of vitrinite irradiated for less than one hour in UNOCAL's system. However, after 1.5 h of irradiation significant changes in absorbance were seen in the aliphatic C-H stretching region around 2960 cm^{-1} and in the carbonyl (C=O) region between 1800-1700 cm^{-1} . A decrease in absorbance in the C-H stretching and a large increase in the C=O region resulted from their photo-oxidation technique. The magnitude of the observed changes became more exaggerated with further increases in irradiation time. Also, the change in surface chemistry was determined to be irreversible; similar FTIR spectra

Figure 23 - Change in Absorption Intensity at Specific Energy Bands with Time of Photo-Oxidation as Measured on Pittsburgh Seam Vitrain by STXM and C-NEXAFS

were obtained from an irradiated area after a 24 h period of storage.

In another experiment, a vitrain band of the DECS-23 (Pittsburgh seam) sample was irradiated in a 3 by 3 square matrix of 100 μm diameter areas for 10 min each at Penn State and supplied to UNOCAL for analysis. This test was performed to establish whether use of smaller areas of irradiation than employed by UNOCAL (300 μm) would improve the FTIR spectra. This was of interest because decreases in the irradiation area will concentrate the energy flux, potentially leading to higher levels of photo-oxidation. The UNOCAL group was able to locate and obtain FTIR spectra from several regions within the 3 by 3 matrix. Their results showed that changes in the aliphatic C-H stretch and C=O spectral regions were more intense than in the larger area they had irradiated for 2 h on the DECS-12 polished surface. These results demonstrate that control of the relative light flux is very important to the photo-oxidation effect and, therefore must be addressed in establishing and following an irradiation procedure.

With these preliminary results and following the acquisition of our new reflectance-mode FTIR equipment, analysis of the entire sample set were performed. An example of complete infrared spectra for fresh and irradiated (10 min) surfaces of the Illinois #6 seam (DECS-24) is given in Figure 24 for comparison. The diffuse nature and relative absorbance of reflectance-mode spectra shown in this figure are fairly characteristic of most FTIR spectra collected in this study. For more detailed comparisons, specific regions of spectra (between 2000 - 1200 cm^{-1} and 3800 - 2700 cm^{-1}) collected from each irradiated area are plotted in Figures 25 - 30 together with spectra from the non-irradiated areas of the six vitrains.

In most cases the spectra were smoothed and their baselines rotated for better comparison of relative absorbance with wavenumber. The quality of these spectra are comparable with those published by Mastalerz and Bustin (24) for vitrinite from different rank coals. However, the presence of water caused distortion of spectra collected from the surface of the Ohio #4a (DECS-33) and Lower Kittanning (PSOC-1562) specimens irradiated for 1 and 5 min, as indicated by the periodic noise in the 3800 - 3600 cm^{-1} regions of Figures 26 and 28, respectively. Also, the apparent lack of change in the carbonyl region (1800 - 1650 cm^{-1}) of the Pittsburgh seam (DECS-23) vitrain following 10 min of irradiation (Figure 27) contrasts to the strong change observed following 5 min irradiation suggesting that the irradiated area may not have been located properly. Attempts at recollecting these spectra using the same specimens did not improve upon the results shown.

Comparison of the spectra within groups demonstrates that as irradiation time increased there was a significant and progressive increase in intensity of the carbonyl region located between 1775 - 1650 cm^{-1} and a decrease in the aliphatic C-H stretching region between 3030 - 2850 cm^{-1} . The magnitude of these changes, although variable among the vitrains, appeared to decrease with increasing rank. Also, there was some indication of a broad increase in the intensity of the O-H band near 3450 cm^{-1} with increasing irradiation time, and although this region is observed to be rather diffuse, these results may corroborate the observation reported by Dr. Cody using the C-NEXAFS analyses. These results show that as time of exposure to blue light increased there was an increasing level of photo-oxidation manifested as an increase in the

Figure 24 - FTIR Spectra From Adjacent Areas of Illinois #6 Seam (DECS-24)
Vitrain for Fresh and 10 min Irradiated Surfaces

Figure 25 - Comparison of FTIR Spectral Regions for Fresh and Irradiated Surfaces (1, 5 and 10 min) of the hvCb Illinois #6 Seam Vitrain, DECS-24

Figure 26 - Comparison of FTIR Spectral Regions for Fresh and Irradiated Surfaces (1, 5 and 10 min) of the hvBb Ohio #4a Seam Vitrain, DECS-33

Figure 27 - Comparison of FTIR Spectral Regions for Fresh and Irradiated Surfaces (1, 5 and 10 min) of the hvAb Pittsburgh Seam Vitrain, DECS-23

Figure 28 - Comparison of FTIR Spectral Regions for Fresh and Irradiated Surfaces (1,5 and 10 min) of the hvAb Lower Kittanning Seam Vitrain, PSOC-1562

Figure 29 - Comparison of FTIR Spectral Regions for Fresh and Irradiated Surfaces (1, 5 and 10 min) of the hvAb Lower Kittanning Seam Vitrain, PSOC-1563

Figure 30 - Comparison of FTIR Spectral Regions for Fresh and Irradiated Surfaces (1, 5 and 10 min) of the mvb Splash Dam Seam Vitrain, DECS-30

carbonyl region and a concomitant decrease in the aliphatic region of the spectra. In general, this is very similar to what has been reported in the literature for natural weathering and laboratory oxidation of coals (27,28).

To better elucidate the changes that have occurred as a result of irradiation, second derivative plots of each spectra were generated. Derivative spectroscopy has been used extensively to enhance the appearance of minute shoulders in spectra (29). However, our application has been to provide values for the major absorption band positions and to eliminate those bands that are of the same order of magnitude as the noise level.

Table 4 provides the wavenumber locations of the prominent bands obtained from all vitrains and irradiation conditions. This table along with the scale-expanded spectrographs in Figures 25-30 shows that four prominent absorption bands are consistently identified for all of the samples, i.e. those around 2939, 2855, 1606 and 1447 cm^{-1} . The bands at approximately 2939 and 2855 cm^{-1} (the mean values of those given in Table 4) are very close to those assigned in the literature for the characteristic absorbance of the aliphatic stretching modes of predominantly CH_2 (2926 and 2853 cm^{-1} , 30) and to a lesser degree for CH_3 groups directly attached to aromatic units. The band at $\approx 1606 \text{ cm}^{-1}$ is typically assigned to the carbon double bond stretch of the aromatic system, which may be influenced by the presence of phenolic O-H and/or conjugated carbonyl structures (29,30). Finally, the consistent absorption at about 1447 cm^{-1} generally has been assigned to a C- CH_3 deformation frequency. It is of interest to note that the band intensities of all these frequencies decrease and/or become more diffuse with extent of irradiation (Figures 25 - 30). All of these effects have been noted in the literature to occur as a result of natural weathering or thermal oxidation of coals (27,28,31,32), so their appearance in this investigation was not unexpected. The implication is that aliphatic CH_2 groups are prone to oxidation and result in the formation of carbonyl-containing functional groups.

Another expected result of photo-oxidation would be the growth with increasing exposure time to blue light of a diffuse absorption band in the 1775 to 1710 cm^{-1} region of the spectra as seen in Figures 25 - 30. Characteristic bands in the 1850 to 1690 cm^{-1} region are typically assigned to carbonyl stretching modes for the various carbonyl-bearing functional groups (carboxylic acids, ketones, aryl aldehydes, esters and lactones), as well as to conjugated anhydrides and aryl peroxides (30). Band assignments in this region are particularly complicated for coal because of the potential fractional contribution of any number of these functional groups and the influence of chemical substitution and conjugation imposed by oxidation.

As seen in Table 4, for most of the vitrains two discrete bands (mean values of 1764 and 1731 cm^{-1}) were identified from the derivative plots; these appear to develop and grow in intensity with increasing blue-light irradiation (see Figures 25 - 30). These are clearly different from the 1700 - 1690 cm^{-1} absorption frequency normally observed in naturally weathered coals (27,28,31,32) and which is the frequency range assigned to solid-state carboxylic acid carbonyl vibrations described by Bellamy (30). In addition most ketonic carbonyl vibrations, particularly those associated with aromatic rings, also occur at lower frequencies. Although normal unconjugated alkyl aldehydes may result in carbonyl bands in the approximate range of 1740 to

Table 4 - Location of Major Absorption Bands From Second Derivative FTIR Plots; Irradiated and Non-Irradiated Vitrains

Vitrain	Irradiation Time (min)	Band Locations Wavenumber, cm ⁻¹											
Illinois#6 DECS-24	0	-			3052	2939	2856	-	-	1605	1448		1268
	1	-			3052	2939	2856	-	-	1605	1448		1268
	5	3597			3064	2939	2856	-	1710	1605	1448		1268
	10	3597			3064	2939	2856	1763	1710	1605	1442		1268
Ohio#4a DECS-33	0					2957	2860	-	-	1616	1449	1368	1329
	1					-	2860	-	-	1603	1445	1368	1329
	5					2944	-	1773	1728	1603	1449	1368	1329
	10					2944	2852	1773	1728	1603	1445	1368	1329
Pittsburgh DECS-2	0			3524	3055	2942	2854	-		1609	1446	1368	1268
	1			3524	3055	2942	2854	1750		1603	1446	1368	1268
	5			3524	3055	2942	2844	1750		1603	1446	-	-
	10			3524	3055	2942	2844	1750		1603	1446	1368	1268
L. Kittanning PSOC-1562	0					2955	2861	-	1729	1613	1453	1370	
	1					2955	2861	1774	1729	1613	1446	1370	
	5					2950	2866	1774	1729	1613	1450	1370	
	10					-	-	1774	1729	1602	1446	1370	
L. Kittanning PSOC-1563	0	3684	3545		3072	2931	2863		-	1611	1455	-	
	1	-	3545		-	2931	2863		1736	1603	1440	1352	
	5	3684	3545		3072	2931	2863		1736	1603	1440	1352	
	10	3684	3504		3072	2919	-		1736	1603	1440	1352	
Splash Dam DECS-30	0	3683	3567		3051	2931	2848		1744	1607	1448	1359	1253
	1	3683	3560		3051	2931	2848		1739	1604	1448	-	-
	5	3683	3542		3051	2931	2848		1739	1604	1448	1359	1253
	10	3683	3542		3051	2931	2848		1739	1604	1448	1359	1253

1730 cm^{-1} , aryl aldehydes associated in conjugation with aromatic rings absorb in the range of 1710-1695 cm^{-1} . From this consideration it may be possible to eliminate these individual functional groups as contributors to the band frequency observed from the blue-light photo-oxidation of vitrains.

Of the remaining functional groups involving carbonyl vibrations, esters, lactones, anhydrides and peroxides all exhibit absorption at higher frequencies principally as a result of the influence of an adjoining oxygen atom. Absorption frequencies obtained from complex, unsaturated esters are found around 1738 cm^{-1} , whereas methyl esters of naphthalene and phenanthrene absorb at 1724 cm^{-1} (30). Band absorption of six-member ring lactones, cyclic esters resulting from the esterification of carboxylic acids, generally falls into the 1750 to 1735 cm^{-1} range unless the lactone has two carbonyl groups in the same six-member ring which increases the frequency into the 1767 - 1757 cm^{-1} range (30). Unsaturated five-member lactones and aromatic lactols have been found to absorb around 1750 cm^{-1} . Anhydrides exhibit two carbonyl absorption bands which are usually about 60 cm^{-1} apart in the 1810 and 1750 cm^{-1} range. However, in the case of cyclic six-member ring anhydrides condensed to aromatic systems, the separation has been observed to be smaller ($\approx 30 \text{ cm}^{-1}$), giving characteristic absorptions at 1770 and 1736 cm^{-1} . Absorption frequencies of peroxides are similar to those of anhydrides except that separation of the two characteristic frequencies are rarely more than 30 cm^{-1} apart (1815 and 1790 cm^{-1}). The presence of two aryl groups lower both frequencies into the ranges of 1790 and 1770 cm^{-1} . Limited investigations of peroxy acids and esters show only a single carbonyl absorption in the range of 1790 - 1740 cm^{-1} with a number of peroxy acids absorbing at 1748 - 1747 cm^{-1} (30).

Close inspection of the FTIR spectra from each vitrain suggests that for the freshly polished surface (0 min, Figures 25-30) there was minimal absorption in the carbonyl region typically assigned to carboxylic acids (1700 cm^{-1}) except perhaps a broadening in this area for the lower rank coals (hvCb, Illinois #6 and hvBb, Ohio #4a). With increasing exposure to blue light the significant increase in absorption that was expected in this region did not occur. Instead, a fairly uniform increase in diffuse absorption was observed at higher frequencies with greater exposure to blue light. Table 4 shows that two high frequency carbonyl absorption bands form and grow in intensity as a result of the extent of blue-light irradiation, i.e., 1764 and 1731 cm^{-1} . With some variation, one or both of these frequencies may be found in all of the photo-oxidized vitrains. From consideration of classical infrared absorption discussed above, these frequencies are generally associated with esters, lactones and anhydrides attached to aromatic systems. Evaluation of the specific data given in Table 4 for the Illinois #6, Ohio #4a and Lower Kittanning (PSOC-1562) shows the pair of absorption bands generally assigned to six-member ring anhydrides develop and grow in intensity as a result of progressive photo-oxidation. Individual absorption bands in the range of 1750 to 1735 cm^{-1} are found for the Pittsburgh, Lower Kittanning (PSOC-1563) and Splash Dam vitrains and may correspond to six-member ring lactones. It is interesting that the two non-marine influenced hvAb vitrains and the high rank mvb Splash Dam did not develop the pair of absorption bands characteristic of anhydrides.

The formation of these types of functional groups are difficult to reconcile with regard to

chemical changes of large and complex solid-state aromatic systems (such as are present in vitrain) under ambient conditions. At best, these chemical species should be relatively unstable and degrade rapidly to carboxylic acid groups. Presently, we can only attribute their observation to our techniques of photo-oxidation and sample preservation. Furthermore, from a very basic point of view, organic molecules containing oxygen atoms are generally capable of forming strong hydrogen bonds which, in the case of carboxylic acids, means a greater attraction to water (hydrophilic). Esters and anhydrides, however, are polar compounds lacking a hydrogen attached to oxygen and therefore do not form strong hydrogen bonds (more hydrophobic). With this in mind, the functional group chemistry revealed by our FTIR analyses suggests that the irradiated surface of vitrain should be more hydrophobic in nature, which is in conflict with contact angle measurements showing a progressively more hydrophilic surface with increased photo-oxidation.

Mechanisms for the formation of ester and anhydride functionality must involve the placement of more than one carbonyl group directly adjacent on an aromatic unit or on an associated aryl group. Consequently, during the course of natural weathering the carbonyl moiety emplaced would be an acid site, but in a relatively high energy flux of blue light, multiple carbonyl groups may form in a way in which they interact together or perhaps with singlet oxygen resulting in the formation of esters and anhydrides. Secondary reactions of carbonyl groups (carboxylic acids) emplaced by photo-oxidation with additional oxygen was suggested as a possible mechanism to explain positive luminescence alteration by Eberhardt et al. (15). Carboxylic acid groups may indeed form at the surface of vitrain during photo-irradiation until all readily accessible sites have reacted. However, as more reactive (singlet) oxygen becomes available and interacts with these groups, secondary reactions involving peroxides may result in the formation of phenols. An increase in the concentration of aromatic OH groups, which has been suggested from C-NEXAFS and FTIR results, as well as their slightly acidic character could explain the observed decrease in surface hydrophobicity. Moreover, as the concentration and proximity (adjacent carbon atoms) of carbonyl or carboxylic acid groups increases, conditions for the formation of esters and anhydrides would be met.

Surface Properties of Photo-Oxidized Powdered Vitrains

In another approach to establishing the influence of photo-oxidation on the flotation characteristics of coals, powdered vitrain concentrates having a narrow particle size distribution ($<0.42\text{ mm} > 0.15\text{ mm}$) were irradiated using a BLAK-RAY 100-watt long-wavelength ultraviolet spotlight. The purpose for this line of research was to evaluate the influence of photo-oxidation on surface wettability of particulate samples of vitrain instead of single polished surfaces. The procedure followed was to compare results from film flotation experiments with surface luminescence intensity and a limited number of pyrolysis gas chromatography and mass spectroscopy analyses. It was hoped that this series of procedures would parallel those made on the polished surfaces.

Film flotation distribution curves are shown in Figures 31 - 36 for the six vitrain concentrate samples prepared during this study and for all conditions of UV irradiation (0, 10, 50 and 100 min). Each curve shows the decrease in percent float as the surface tension of the liquid

Figure 31 - Film Flotation of hvCb Illinois #6 Vitrain Concentrate (DECS-24-Vit)
Following 0, 10, 50 and 100 min UV Irradiation

Figure 32 - Film Flotation of hvBb Ohio #4a Vitrain Concentrate (DECS-33-Vit)
Following 0, 10, 50 and 100 min UV Irradiation

Figure 33 - Film Flotation of hvAb Pittsburgh Vitrain Concentrate (DECS-23-Vit)
Following 0, 10, 50 and 100 min UV Irradiation

Figure 34 - Film Flotation of hvAb Lower Kittanning Vitrain Concentrate (PSOC-1562-Vit)
Following 0, 10, 50 and 100 min UV Irradiation

Figure 35 - Film Flotation of hvAb Lower Kittanning Vitrain Concentrate (PSOC-1563-Vit)
Following 0, 10, 50 and 100 min UV Irradiation

Figure 36 - Film Flotation of mvb Splash Dam Vitrain Concentrate (DECS-30-Vit)
Following 0, 10, 50 and 100 min UV Irradiation

is progressively lowered. Upon initial examination these flotation curves suggested erratic behavior with respect to anticipated results, i.e., some of the more strongly photo-oxidized powders appeared to exhibit greater hydrophobicity. This contrasts with the results of contact angle measurements on polished surfaces which showed diminished hydrophobicity with increasing photo-oxidation. Duplicate film flotation analyses performed on two of the concentrates (Figure 37) suggests some moderate variability in the results, but generally the technique was repeatable within 5 percent float.

Of the film flotation tests performed, only those obtained from the lowest rank coal, the hvCb, Illinois #6 (DECS-24-Vit), showed a decrease in floatability with increasing photo-oxidation (Figure 31), but only for powders irradiated for 0, 10 and 50 min. Following 100 min of photo-oxidation, floatability increased to a point intermediate between the raw flotation curve and those of particles irradiated for 10 and 50 min. With some variation, the hvBb Ohio #4a (DECS-33-Vit) exhibited a similar relationship but only at higher surface tension (>40 dynes/cm, Figure 32); at lower surface tensions little variability in percent float was observed. For the powdered vitrains from hvAb and mvb coals (Figures 33 - 36), increased levels of hydrophobicity were recorded for all of the 100 min irradiated concentrate samples and even for some of the 10 and 50 min irradiated samples.

Clearly, UV irradiation of powdered samples does not produce results in accord with those obtained from photo-oxidation of polished surfaces. However, it can not be argued that irradiation has had no effect because significant changes in surface hydrophobicity are observed, although in an unexpected direction. In addition, measurements of surface luminescence (Figure 38) demonstrate that some change in surface properties has occurred that results in a decrease in luminescence intensity, although the degree of change was quite variable among the vitrains. The Pittsburgh and Ohio #4a seam vitrains showed the greatest loss in luminescence intensity with irradiation time, whereas the Illinois #6 and Splash Dam showed the least. The two Lower Kittanning samples gave intermediate responses. However, the important observation is that luminescence intensity in all cases decreased with exposure time to UV light. This differs from our observations on blue-light irradiated surfaces (Figures 10 - 21), which for all but the mvb Splash Dam showed dual alteration, and is more in line with what occurs as a result of natural weathering, i.e., decreased luminescence intensity with severity of oxidation (3,5).

One explanation for these results is that aliphatic compounds (oils) within the coals have been mobilized as a result of irradiation. Mobile "bitumens" can be observed as surface films on the mined faces of coal exposed to sunlight and have been observed during blue-light irradiation under the optical microscope (33). If oils are exuded from the fracture surfaces during UV irradiation of powdered vitrains they would act very much like a natural flotation collector by providing a more hydrophobic surface and may, to some extent, counter any surface oxidation. Because most aliphatic compounds have little or no blue-light induced luminescence, these exudations could also reduce the surface luminescence (see Figure 38). Presumably, the longer the exposure, the greater would be the amount of exudation and the lower the luminescence intensity. The natural fracture surfaces present in the powdered vitrain samples are different from those of polished surfaces which have been closed or obscured during the polishing process,

Figure 37 - Repeatability of Film Flotation for Selected Illinois #6 and Splash Dam Samples

Figure 38 - Change in Surface Luminescence Intensity of Particulate Vitrain Following UV Irradiation at 366 nm

possibly explaining the different observations between polished and natural fracture surfaces.

Another explanation for the observed results suggests that more may be involved at or near the vitrain surface than a simple increase in oxygen concentration and functionality during photo-oxidation. It may be more important to consider also the type of oxygen functionality (i.e., alcohols, ketones, aldehydes, esters, carboxylic acid, or anhydrides) created at the surface and changes in their relative concentrations with irradiation time. In other words, although oxygen content may increase with increasing severity of irradiation, some oxygen functionalities may inhibit whereas others may promote or have no influence on hydrophobicity. As often reported in the literature, carboxylic acid functionality has been identified prominently by infrared spectroscopy from natural and laboratory oxidized coals. The current FTIR investigation of blue-light irradiated polished vitrains did not reveal any acid functionality, but rather suggested the presence of esters and anhydrides. These groups have a lower attraction to water than carboxylic acids and so could be the reason UV-irradiated vitrain appear to be more hydrophobic with regard to flotation.

It is possible that one or both of these mechanisms has operated. However, it was uncertain at the outset whether the pyrolysis GC/MS analyses undertaken as part of this project would be able to prove or disprove them. The likelihood of this approach providing an answer is low because it is a bulk analytical technique. Surface oxidation would have to be relatively severe with respect to the total mass for significant changes to be detected. However, samples of three of the powdered vitrains [Illinois #6 (DECS-24-Vit), Lower Kittanning (PSOC-1562-Vit) and Splash Dam (DECS-30-Vit)] were set aside from materials irradiated for film flotation. These samples were crushed with an agate mortar and pestle to a fine powder (<200 mesh or <74 μm) and irradiated for periods of 10, 50 and 100 min using the UV spot light.

Total ion chromatograms of pyrolyzates are given for each vitrain and surface condition in Figures 39 - 44 and the structural parameters determined from the total area of GC-amenable products are listed in groups by percentage in Tables 5 and 6. As seen in Table 5, up to 21% of the molecular fragments reporting to mass units were unidentified, whereas the remaining material could be assigned to the broad categories shown, i.e., n-alkanes and alkenes, phenols, non-oxygenated aromatics and furans. For a better comparison, Table 6 lists data on an "unidentified"-free basis. These results show that regardless of irradiation time values for an individual vitrain are relatively similar, but comparisons among the vitrains revealed some influence of rank. As has been reported (34), the concentration of phenols in vitrinite pyrolyzates generally decrease with increasing rank as they do for the hvCb Illinois #6 to mvb Splash Dam in this study. Beyond this, there was very little significant difference or trend that correlated with irradiation time. In a pyrolysis GC/MS study of fresh and outcrop coals, Pisupati et al. (25) found a significant decrease in the total amount of alkanes and alkenes and a slight decrease in phenols as a result of severe weathering. Because of the very consistent nature of our results and the fact that neither trend was observed (Tables 5 or 6), we must conclude that the relatively minor amount of surface oxidation resulting from irradiation was overwhelmed by the total mass of material being pyrolyzed.

Figure 39 - Total Ion Chromatograms of Pyrolyzates From Fresh and 10 min Irradiated Illinois #6 Vitrain Concentrate, DECS-24-Vit

Figure 40 - Total Ion Chromatograms of Pyrolyzates From 50 and 100 min
Irradiated Illinois #6 Vitrain Concentrate, DECS-24-Vit

Figure 41 - Total Ion Chromatograms of Pyrolyzates From Fresh and 10 min Irradiated Lower Kittanning Vitrain Concentrate, PSOC-1562-Vit

Figure 42 - Total Ion Chromatograms of Pyrolyzates From 50 and 100 min
Irradiated Lower Kittanning Vitrain Concentrate, PSOC-1562-Vit

Figure 43 - Total Ion Chromatograms of Pyrolyzates From Fresh and 10 min Irradiated Splash Dam Vitrain Concentrate, DECS-30-Vit

Figure 44 - Total Ion Chromatograms of Pyrolyzates From 50 and 100 min Irradiated Splash Dam Vitrain Concentrate, DECS-30-Vit

Table 5 - Structural Parameters Determined by Pyrolysis GC/MS From Vitrain Concentrates

Vitrain	Irradiation Time (min)	% Total Area of GC-Amenable Products				
		% n-Alkanes and Alkenes	% Phenols	% Non-Oxygenated Aromatic Hydrocarbons	% Furans	% Unident.
Illinois#6 DECS-24	0	13.6	40.3	25.7		20.4
	10	18.4	35.0	25.7		20.9
	50	14.7	37.3	26.3		21.7
	100	14.7	25.7	40.3	0.6	18.7
L. Kittanning PSOC-1562	0	11.5	28.4	45.0	5.1	9.9
	10	13.3	26.1	43.2	4.3	13.0
	50	15.0	17.9	47.6	2.6	16.8
	100	16.8	30.0	41.3	4.4	7.5
Splash Dam DECS-30	0	43.0	8.2	28.6	0.4	19.9
	10	47.3	7.9	32.2	2.4	10.2
	50	42.0	11.9	27.1	0.1	18.5
	100	45.4	11.9	31.9	0.2	10.6

Table 6 - Identified Structural Parameters Determined by Pyrolysis GC/MS
From Vitrain Concentrates

Vitrain	Irradiation Time (min)	% Total Area of GC-Amenable Products			
		% n- Alkanes and Alkenes	% Phenols	% Non- Oxygenated Aromatic Hydrocarbons	% Furans
Illinois#6 DECS-24	0	17.1	50.6	32.3	-
	10	23.3	44.2	32.5	-
	50	18.8	47.6	33.6	
	100	18.1	31.6	49.6	0.7
L. Kittanning PSOC-1562	0	12.8	31.5	50.0	5.7
	10	15.3	30.0	49.7	5.0
	50	18.0	21.6	57.3	3.1
	100	18.2	32.4	44.6	4.8
Splash Dam DECS-30	0	53.6	10.2	35.7	0.5
	10	52.7	8.8	35.8	2.7
	50	51.5	14.6	33.2	0.1
	100	50.8	13.3	35.7	0.2

CONCLUSIONS

The influence of photo-oxidation on surface hydrophobicity as measured by contact angle decreases proportionally with irradiation time, being greater at the 5 and 10 min irradiation levels, but diminishing with increasing rank. These changes with irradiation time are accompanied by a progressive decrease in reflectivity and increase in oxygen concentration as measured by reflectance and electron microprobe analyses regardless of the rank or the vitrain band analyzed. The influence of rank and level of oxidation on hydrophobicity has been observed in other studies; however, considering that similar levels of oxygen were incorporated in all instances, it implied that the type of oxygen functionality may be much more important to surface hydrophobicity than the total amount of oxygen emplaced.

A variety of analytical techniques were employed to evaluate changes in near-surface chemical functionality resulting from photo-oxidation. SIMS analysis of an hvAb vitrain irradiated for 10 min showed that a greater mass of molecular fragments was removed from the photo-oxidized regions compared to the non-irradiated areas. The size and relative composition of these fragments suggests that a large part of the oxygen was associated with the aromatic network. Thin sections prepared from the same hvAb vitrain and irradiated at 1, 5 and 10 min intervals for STXM and C-NEXAFS analysis also showed that most of the chemical changes were occurring at aromatic carbon sites. Growth and systematic changes in intensity of carbon near-edge energy bands with irradiation time suggests that hydroxyl and carbonyl functionalities increase in concentration with increasing blue-light irradiation accompanied by an overall decrease in methyl group concentration. Except for the variation observed for aromatic hydroxyls, these changes have been observed for naturally weathered and laboratory oxidized coals and vitrains.

Results from reflectance-mode FTIR analysis of all six vitrains and surface conditions (0, 1, 5 and 10 min irradiation) demonstrated a significant and progressive increase in intensity of the carbonyl region and a decrease in the aliphatic C-H stretching region with increasing irradiation time. Furthermore, in corroboration of the C-NEXAFS results, a broad increase in the absorption of the O-H region of the spectra was observed. Thus, in general terms FTIR analysis of blue-light irradiated vitrains showed that the photo-oxidation technique causes a progressive oxidation of the near surface resembling changes previously observed for natural weathering and laboratory oxidation of coals.

On further analysis of the FTIR spectra using derivative spectroscopy, four prominent absorption bands were identified for all of the samples analyzed, i.e., two bands assigned to the aliphatic stretching mode of CH_2 at 2939 and 2855 cm^{-1} , the carbon double bond stretch of the aromatic system at 1606 cm^{-1} , and the C- CH_3 deformation frequency at 1447 cm^{-1} . Absorption intensity of these bands decreased with increasing levels of oxidation, similar to what has been reported in the literature, and suggested that aliphatic CH_2 groups were involved in the formation of carbonyl-containing functional groups. Assessment of the absorption bands in the carbonyl region of the spectra (1850 - 1690 cm^{-1}) did not reveal the anticipated carboxylic acid frequencies, but instead showed absorption at much higher wavenumbers for nearly all of the

irradiated specimens. Absorption in these regions increased in intensity with increasing degree of photo-oxidation. With minor variation, the lower rank vitrains (hvCb and hvBb) and one hvAb vitrain showed a pair of absorption bands that generally could be assigned to anhydrides, whereas two of the hvAb and the mvb vitrain showed a single characteristic absorption for carbonyl-containing cyclic esters (lactones). The latter hvAb vitrains were derived from coals of non-marine influenced deposition.

The lack of carboxylic acid absorption in photo-oxidized vitrain was a significant departure from previous observations for coal oxidation and can only be explained by our techniques of photo-oxidation and sample preservation. Oxygen-containing functionalities that can involve hydrogen bonding like carboxylic acids, ketos and enols reasonably would be expected to account for a measurable decrease in the hydrophobic nature (more hydrophilic) of the vitrain surface. Ester and anhydride functionalities, which lack this ability, would tend to result in a more hydrophobic surface. Therefore, their presence on the vitrain surface could not explain the observed changes in hydrophobicity indicated by contact angle measurements.

Mechanisms for the formation of ester and anhydride functionality must involve the placement of more than one carbonyl group directly adjacent on an aromatic unit or on an associated aryl group. Consequently, during the course of natural weathering the carbonyl moiety emplaced would be an acid site, but in the relatively high energy flux of blue light multiple carbonyl groups may form in a way in which they interact together or perhaps with singlet oxygen resulting in the formation of esters and anhydrides. Secondary reactions of carbonyl groups (carboxylic acids) emplaced by photo-oxidation with additional oxygen has been suggested as a possible mechanism to explain positive luminescence alteration. Carboxylic acid groups may indeed form at the surface of vitrain during photo-irradiation until all readily accessible sites have reacted. However, as more reactive (singlet) oxygen becomes available and interacts with these groups, secondary reactions involving peroxides may result in the formation of phenols. An increase in the concentration of aromatic OH groups, which has been suggested from C-NEXAFS and FTIR results; also, their slightly acidic character could explain the observed decrease in surface hydrophobicity. Moreover, as the concentration and proximity (adjacent carbon atoms) of carbonyl or carboxylic acid groups increases, conditions for the formation of esters and anhydrides would be met.

The alteration of luminescence intensity measured during photo-oxidation showed a consistent dual response for all hvb vitrains in which an early rapid decrease in intensity was followed by a sharp increase which became less rapid with increasing rank. The mvb vitrain gave a negative alteration response which was initially rapid and then became a slow rate of decline out to 10 min of irradiation. The general variations in alteration patterns tended to correspond well with contact angle results from different rank vitrains, but because of their dual nature (for hvb vitrains) the actual intensity values measured initially and after 1, 5 and 10 min of irradiation do not correlate directly with contact angle. On the other hand, luminescence intensity measurements made on the natural surfaces of UV-irradiated powdered vitrains appear to correlate well with irradiation time, mostly showing a significant decrease in intensity with increasing photo-oxidation. This observation agrees with published results on naturally

weathered coals where luminescence intensity was typically much lower than for a corresponding fresh coal surface.

The expected response of decreasing flotation yield with increasing oxidation was not observed in the film flotation testing of photo-oxidized powdered vitrains. The lower rank vitrains (hvCb and hvBb) showed this trend at lower oxidation levels, but as irradiation time increased an increase in floatability was found. In comparison to the measured changes in contact angle from polished surfaces these results were unexpected. Nevertheless, because of the magnitude of changes in floatability and in luminescence intensity of the irradiated particles, the response is significant.

One explanation to account for these results involves the mobilization of aliphatic compounds (bitumens) which have been observed as thin films on the surface of bituminous coals exposed to direct sunlight. Such a material would act very much like a natural flotation collector by providing a more hydrophobic surface. However, exudations from coal are probably not uniform throughout the bituminous rank range and therefore we would have expected more variation among the selected vitrains. Another explanation is suggested by our FTIR results which show that changes in oxygen functionality are due to the formation of ester and anhydrides. These moieties have less attraction to water than carboxylic acid groups and if present in relatively high concentration, could provide a more hydrophobic. The results obtained by pyrolysis GC/MS were not sufficiently sensitive to detect the surface changes induced by UV-irradiation. Data from three vitrain oxidation series show an expected change in the concentration of phenols associated with the influence of rank, but were not sufficiently sensitive to detect the changes in n-alkanes and alkene concentration that have been shown to accompany severe natural weathering.

Results from this investigation demonstrate that quantitative luminescence intensity measurements can be performed on fracture surfaces of coal (vitrain) and that the data obtained do reveal significant variations with level of surface oxidation. Photo-oxidation induced by blue or ultraviolet light fluxes does result in a progressive and significant increase in the amount of near-surface oxygen concentration at about the same level regardless of the rank of bituminous coal. These incremental changes in oxygen concentration appear to reduce hydrophobicity as shown by contact angle measurements on polished surfaces. This influence diminishes as rank increases. Changes in functional-group chemistry, measured by a variety of near-surface techniques, revealed a general increase in the concentration of carbonyl-containing groups as those of CH_2 decreased. All of these observations follow expected trends from previous investigations of naturally weathered coals.

From our FTIR results, however, it is concluded that the photo-oxidation technique resulted in the development of phenolic, ester and anhydride moieties instead of the expected emplacement of carboxylic acid groups which are normally associated with naturally weathered coals. The importance of this observation is that esters and anhydrides might result in a more hydrophobic surface in comparison to the more hydrophilic surface resulting from acid functionality. These observations are in line with the results of film flotation of UV-irradiated

powdered vitrain in which floatability was generally observed to increase with increasing photo-oxidation. Attempts at measuring the chemical changes occurring to the powdered vitrain by py-GC/MS were unsuccessful because of mass limitations, i.e., mass oxidized to mass available was very small.

The technique of luminescence analysis has been demonstrated to be an effective method for measuring the changes in surface properties which result from oxidation. Further work to investigate the direct application of the technique in coal cleaning process control appears to be warranted.

REFERENCES

1. Gutierrez-Rodriguez, J.A. and Aplan, F.F. (1984), The Effect of Oxygen on the Hydrophobicity and Floatability of Coal, Colloids and Surfaces, 12, 27-51.
2. Gutierrez-Rodriguez, J.A., Purcell, Jr., R.J. and Aplan, F.F. (1984), Estimating the Hydrophobicity of Coal, Colloids and Surfaces, 12, 1-25.
3. Quick, J.C., Davis, A. and Lin, R. (1988), Recognition of Reactive Maceral Types by Combined Fluorescence and Reflectance Microscopy, Proc. Ironmaking Conf., 47, 331-337.
4. McHugh, E.A., Diessel, C.F.K. and Kutzner, R. (1991), Use of Fluorescence Microscopy in the Detection of Low Level Oxidation in Bituminous Coals, Fuel, 70, 647-653.
5. Mitchell, G.D., Davis, A. and Rathbone, R.F. (1991), The Use of Vitrinite Fluorescence as a Measure of Changes in Coal Thermoplasticity and Weathering, Proc. Ironmaking Conf., 50, 199-206.
6. Lin, R., Davis, A., Bensley, D.F. and Derbyshire, F.J. (1986), Vitrinite Secondary Fluorescence: Its Chemistry and Relation to the Development of a Mobile Phase and Thermoplasticity in Coal, Internat. Jour. Coal Geology, 6, 215-228.
7. Lin, R. and Davis, A. (1988), A Fluorogeochemical Model for Coal Macerals, Org. Geochem., 12, 363-374.
8. Teichmüller, M., (1974), Entstehung und Veränderung Bituminöser Substanzen in Kohlen in Beziehung zur Entstehung und Umwandlung des Erdöls, Fortschr. Geol. Rheinld. u. Westf., 24, 65-112.
9. Ottenjann, K., Wolf, M. and Wolff-Fischer, E., (1982), Das Fluoreszenverhalten der Vitrinit zur Kennzeichnung der Kokungseigenschaften von Steinkohlen, Glückauf-Forsch., 43, 173-179.
10. Davis, A., Rathbone, R.F., Lin, R. and Quick, J.C. (1990), Observations Concerning the Nature of Maceral Fluorescence Alteration with Time, Org. Geochem., 16, 897-906.
11. Gray, R.J., Rhoades, A.H. and King, D.T., (1976), Detection of Oxidized Coal and the Effect of Oxidation on the Technological Properties, Trans. Soc. Min. Eng., AIME, 260, 334-341.
12. Hayatsu, R., Winans, R.E., Scott, R.G., Moore, L.P. and Studier, M.H. (1978) in Organic Geochemistry of Coal, John W. Larsen, ed., ACS Symp. Series 71, Amer. Chem. Soc., Washington, D.C.

REFERENCES (continued)

13. Wilson, R. (1984), Surface and Bulk Characterization of Selected Coals, Bitumens, and Polymers as Revealed by ESCA and Other Analytical Techniques, Unpub. Ph.D. Thesis, University of Durham.
14. Pradier, B., Largeau, C., Derenne, E., Martinez, L., Bertrand, P. and Pouet, Y. (1990), Chemical Basis of Fluorescence Alteration of Crude Oils and Kerogens - I. Microfluorimetry of an Oil and Its Isolated Fractions; Relationships with Chemical Structure, Org. Geochem., 16, 451-460.
15. Eberhardt, J.E., Nguyen, T.H. and Read, R. (1992), Fluorescence Alteration of Coal and Polycyclic Aromatic Hydrocarbons, Org. Geochem., 18, 145-153.
16. Death, D.L., Eberhardt, J.E. and Read, R. (1991a), Laser-Induced Macrofluorescence of Coal: Oxidation and Spectral Effects, Fuel, 70, 1065-1071.
17. Death, D.L., Eberhardt, J.E. and Read, R. (1991b), Laser-Induced Macrofluorescence of Coal: Oxidation and Macroalteration, Fuel, 70, 1073-1077.
18. Zhang, E., Mitchell, G.D., Davis, A. and Hatcher, P.G. (1994), The Effect of Organic Sulfur Incorporation on Reflectance and Fluorescence Properties of Vitrinite in Western Pennsylvania Bituminous Coals, Amer. Chem Soc, Geochem, Div., Geochemistry Newsletter, Pap. 27.
19. Edmunds, W.E., Berg, T.M., Sevon, W.D., Piotrowski, R.C., Heyman, L. and Rickard, L.V. (1979), The Mississippian and Pennsylvanian (Carboniferous) System in the United State - Pennsylvania and New York, Geol. Survey Professional Paper 1110-B, B1-B33.
20. ASTM D 2798 (1996), Microscopical Determination of the Reflectance of Vitrinite in a Polished Specimen of Coal, Annual Book of ASTM Standards, 05.05, 274-278.
21. Cody, G.D., Botto, R.E., Ade, H., Behal, S., Disko, M. and Wirick, S. (1995), C-NEXAFS Microanalysis and Scanning X-ray Microscopy of Microheterogeneities in a High-Volatile A Bituminous Coal, Energy & Fuels, 9, 75-84.
22. Williams, M.C. and Fuerstenau, D.W. (1987), A Simple Flotation Method for Rapidly Assessing the Hydrophobicity of Coal Particles, Internat. Jour. Min. Processing, 20, 153-157.
23. Hatcher, P.G., Lerch, H.E., III, Kotra, R.K., and Verheyen, T.V. (1988), Pyrolysis/gc-ms of a Series of Degraded Woods and Coalified Logs that Increase in Rank from Peat to Subbituminous Coal, Fuel 67, 1069-1075.

REFERENCES (continued)

24. Mastalerz, M. and Bustin, R.M. (1993), Electron Microprobe and Micro-FTIR Analyses Applied to Maceral Chemistry, Internat. Jour. Coal Geol., 24, 333-345.
25. Pisupati, S., Scaroni, A.W. and Hatcher, P.G. (1993), Devolatilization Behaviour of Naturally Weathered and Laboratory Oxidized Bituminous Coals, Fuel, 72, 165-173.
26. Cody, G.D., Ade, H., Wirick, S., Mitchell, G.D. and Davis, A. (in prep.), Time Resolved C-NEXAFS Analysis of the Photo-Oxidation Chemistry Accompanying Luminescence Alteration of Vitrinite.
27. Wu, M.M., Robbins, G.A., Winschel, R.A. and Burke, F.P. (1988), Low-Temperature Coal Weathering: Its Chemical Nature and Effects on Coal Properties, Energy & Fuels, 2, 150-157.
28. Valia, H.S. (1990), Effects of Coal Oxidation on Cokemaking, Proc. Ironmaking Conf., 49, 199-209.
29. Painter, P.C., Snyder, R.W., Starsinic, M., Coleman, M.M., Kuehn, D.W. and Davis, A. (1981), Concerning the Application of FT-IR to the Study of Coal: A Critical Assessment of Band Assignments and the Application of Spectral Analysis Programs, Applied Spectroscopy, 35, 475-485.
30. Bellamy, L.J. (1975), The Infra-red Spectra of Complex Molecules, John Wiley & Sons, NY, 433p.
31. Vasallo, A.M., Liu, Y.L., Pang, L.S.K. and Wilson, M.A. (1991), Infrared Spectroscopy of Coal Maceral Concentrates at Elevated Temperatures, Fuel, 70, 635-639.
32. Rhoads, C.A., Senftle, J.T., Coleman, M.M., Davis, A. and Painter, P.C. (1983), Further Studies of Coal Oxidation, Fuel, 62, 1387-1392.
33. Spackman, W., Davis, A. and Mitchell, G.D. (1976), The Fluorescence of Liptinite Macerals, Brigham Young University Geology Studies, 22, 59-75.
34. Senftle, J.T., Larter, S.R., Bromley, B.W. and Brown, J.H. (1986), Quantitative Chemical Characterization of Vitrinite Concentrates Using Pyrolysis-Gas Chromatography, Org. Geochem., 9, 345-350.

APPENDIX A

Lower Kittanning Seam Survey

In order to identify pairs of similarly ranked coals of the same seam that were deposited under both marine and freshwater conditions, a survey of coal mines and limestone quarries in which the Lower Kittanning seam is exposed was conducted in northwestern Pennsylvania. These pairs are of interest because of the potential differences in chemistry and optical properties of their vitrinites that may influence photo-oxidation.

According to the maps of Ferm and Williams (1A) and Williams (2A), the Lower Kittanning seam of northwestern Pennsylvania should provide a suitable marine/freshwater pair. Within a relatively short distance the strata directly overlying the Lower Kittanning seam progresses from having an assemblage of marine invertebrate fossils to having a freshwater assemblage or no invertebrates at all. Figure 1A shows the approximate limits of the transition zone (established by Ferm and Williams (1A)) in Lawrence and Butler Counties, Pennsylvania. The location of this transition zone in northwestern Pennsylvania is important in that it determines our ability to collect pairs of coals from two depositional environments at the same rank level. Rank increases rapidly to the east and southeast.

With the assistance of Mr. Tim VanDyke of the Knox office of the Department of Environmental Resources, visits were planned to evaluate eight strip mines (coal and limestone quarries) shown in Figure 1A. The strata overlying the Lower Kittanning seam was inspected for their fossil content and, in most cases, a small grab sample of the coal was obtained for provisional laboratory evaluation. In addition, arrangements were made with each mine operator to collect a full-seam channel sample as close to the time the seam would be uncovered to ensure sample freshness.

During the course of this survey no invertebrate fossils were found in the immediately overlying strata in any of the mines. However, based upon published descriptions of rock types, grain size, associated plant fossils and/or size and shape of concretions (1A, 2A), a general assessment was made of the environments of deposition (EOD) of the Lower Kittanning seam at each site (Table 1A).

As a further aid in determining EOD, small coal samples were retrieved from most of these mines for determination of vitrinite reflectance (Table 1A) and analysis by pyrolysis GC/MS (Figure 2A). Recently published work (A3, A4) suggests that coals (vitrinite) deposited under marine conditions have lower levels of reflectance and higher luminescence intensities and concentrations of aliphatic biopolymers than coals of similar rank deposited under freshwater conditions. Evaluation of reflectance (Table 1A) and aliphatic peak intensities (Figure 2A) of vitrinite from a suite of coals supports our assessment of EOD made from field observations. From the GC/MS data, comparisons were made between four of the Lower Kittanning samples and two Pittsburgh seam samples (DECS- 12 and 23). The Pittsburgh seam provides a good comparison because it was deposited under freshwater conditions. Aliphatic intensities are lower

Figure 1A - Mine and Sample Locations for the Lower Kittanning Seam Survey in Pennsylvania with Respect to Marine and Freshwater Overburden

Figure 2A - Pyrolysis-GC/MS Peak Intensities Measured on Vitrinite Concentrates from Pittsburgh and Lower Kittanning Seam Samples

Table 1A
Assessment of Environments of Deposition from Mine Survey of the
Lower Kittanning Seam in Northwestern Pennsylvania

Mine Identification	Assessment of Environmental Deposition	% Mean Maximum Vitrinite Reflectance
Allegheny Minerals- Harrisville Pit	Freshwater	No Sample
Allegheny Minerals- Slippery Rock Pit	Freshwater	0.80
C&M Aggregates- Medure Pit	Lacustrine (Freshwater/Brackish)	0.77
Medusa Cement	Lacustrine (top) Restricted Marine	No Sample
McQuiston Coal Co., PSOC-1563	Freshwater	0.78
Ambrosia Coal Co.	Restricted Marine	0.76
East Fairfield Coal Co.	Restricted Marine	0.78
Kerry Mining Co., PSOC-1562	Marine	0.72

and the aromatic rings containing oxygen functionality are higher for the Pittsburgh seam and the Lower Kittanning seam sample from McQuiston Coal Co. In contrast, aliphatic intensity was higher for the Kerry Mining Co. sample, identified in the field as having been deposited under marine conditions. In addition, from the survey samples, vitrinite reflectance values were significantly lower for the Kerry Mining Co. sample compared with that of the McQuiston sample. From this evaluation, it was decided to collect full-seam channel samples, blocks and vitrain concentrates from the McQuiston and Kerry Mining Co. sites (Figure 1A) as being representative of freshwater- and marine- influenced coals, respectively.

Lower Kittanning Samples

Full-seam channel and block samples were collected from Kerry Mining Co. on 5-19-94 and from McQuiston Coal Co. on 6-2-94. The coal had been uncovered for approximately 20 h at the Kerry Mine and was uncovered in our presence at the McQuiston Mine. The fresh coals were sealed in argon at the mines, transported back to Penn State and were processed and resealed in argon the following day.

Analytical information from the two channel samples is given in Table 1 (in the text of this report). These coals appear to be very similar in rank and overall chemistry and petrography. Small, but significant differences exist between volatile matter, total oxygen and fluorescence intensity. These differences may be related, in that coals with higher oxygen functionality tend to have lower luminescence intensity values. In the case of the freshwater Lower Kittanning coal (PSOC-1563) the question was raised as to whether the higher oxygen functionality results from environment of deposition or from weathering. The fact that the percentage sulfate sulfur was low (normally high in weathered coals) suggests that the coal was fresh at the time of collection. The luminescence alteration patterns (Figures 13 and 14, in the text of this report) provides further evidence that PSOC-1563 (freshwater sample) has not deteriorated in that, except for having a lower intensity, its pattern is comparable with that of PSOC-1562 (marine sample).

References

- 1A Ferm, J.C. and Williams, E.G. (1979), Characterization of a Carboniferous Marine Invasion in Western Pennsylvania, in "Carboniferous Depositional Environments in the Appalachian Region" (Eds. J.C. Ferm, J.C. Horne, G.A. Weisenfluh and J.R. Staub), University of South Carolina, 23-34.
- 2A Williams, E.G. (1979), Marine and Fresh Water Fossiliferous Beds in the Pottsville and Allegheny Groups of Western Pennsylvania, in "Carboniferous Depositional Environments in the Appalachian Region" (Eds. J.C. Ferm, J.C. Horne, G.A. Weisenfluh and J.R. Staub), University of South Carolina, 35-49.
- 3A Rathbone, R.F. and Davis, A. (1993), The Effect of Depositional Environment on Vitrinite Fluorescence Intensity, Org. Geochem., 2, 177-186.

- 4A Zhang, E., Hatcher, P.G. and Davis, A. (1993), Chemical Composition of Pseudo-phlobaphinite Precursors: Implications for the Presence of Aliphatic Biopolymers in Vitrinite for Coal, Org. Geochem., 20, 721-734.

APPENDIX B

Irradiation of Powdered Vitrains

The effort needed to photo-oxidize powdered vitrain using our optical microscope system would have been prohibitively time consuming. Consequently, we evaluated the use of a BLAK-RAY, 100 watt ultraviolet spotlight. This lamp generates a brilliant spot of long wavelength ultraviolet light (366 nm) which is slightly lower than the wavelength employed in our optical microscope system (390 - 490 nm). Because of the differences in luminous and thermal energies of these sources, a series of tests were conducted to establish the effects of this irradiation on the luminescence intensity of polished surfaces of vitrain with irradiation time.

Experimental Procedure

The spotlight was fixed in a ring stand and leveled so that the area of maximum incident luminescence could be determined visually at different focal lengths by illuminating paper containing a phosphor. Following a two hour warm-up period small, freshly polished blocks of coal containing vitrain bands were exposed to the light source for different time intervals up to a total of 40 min. After each exposure the luminescence intensity of the vitrain surface was measured under a nitrogen atmosphere using our standard microscope system and procedure (see p. 8). Two measurements were made on the surface, one from an irradiated area and the other from an adjacent area that had been masked from exposure to the ultraviolet light (control). These measurements were made $\approx 400 \mu\text{m}$ apart along bedding and following an east-west scribe mark. A piece of card stock was used to mask off half the area above or below the scribe mark, while the other half was exposed to the ultraviolet light. In this manner, the effect of the ultraviolet irradiation on vitrain luminescence intensity was determined.

Two experiments were conducted based on the distance between the coal surface and the UV lamp. Distances of 5.7 and 3.2 cm provided a surface area suitable for the irradiation of powdered vitrinite, with a minimum of light dispersion at the edges of the affected area. For each experiment, the coal blocks were mounted on a glass slide with modeling clay and the polished surface leveled to the same height in a mounting press. Luminescence intensity was measured in what were to be the masked and unmasked areas under a flow of nitrogen. Then, with the mask in place, each sample was exposed to the ultraviolet light for a set amount of time, following which new intensity measurements were taken. Repeated exposures and luminescence intensity measurements were made on adjacent areas of the surface for a total of 40 min. Exposure times are cumulative with the maximum duration of any irradiation being 10 min.

Results and Discussion

In an initial experiment with a distance of 5.7 cm between coal surface and the lamp, polished blocks of the Ohio #4a (hvBb, DECS-33), Lower Kittanning (hvAb, PSOC-1563) and Splash Dam (mvb, DECS-30) were used to establish differences imposed by coal rank. Figure 1B shows the measured difference in luminescence intensity between the masked (control) versus

Figure 1B - Influence of Exposing Various Coals to 366 nm Light from 5.7 cm on Luminescence Intensity Measured at 600 nm

irradiated surface for the three coals. Data points from the masked surface are provided with error bars based on the standard deviation about their mean. As can be seen, there was significant variation in the measurements made on the Ohio #4a vitrain and some instances where the control surface was inadvertently exposed to ultraviolet light, making it difficult to determine whether changes in luminescence intensity with time are statistically important. However, measurements made on the Lower Kittanning and Splash Dam vitrain samples demonstrate that for these vitrains ultraviolet irradiation using the BLAK-RAY spotlight progressively decreases the measured luminescence intensity at 600 nm, particularly after 10 min of exposure.

In a second experiment, where the distance between the coal surface and lamp was reduced to 3.2 cm, the Illinois #6 (hvCb, DECS-24) was substituted for the Ohio #4a vitrain in the analysis set. It was anticipated that by reducing the distance an increase in luminous flux might be obtained thereby intensifying the effect of photo-oxidation. However, as seen in Figure 2B, little effective difference in the level of change in the luminescence intensity was obtained compared with the earlier experiment (Figure 1B). A significant decrease in luminescence intensity over time is found for the Illinois #6 and Lower Kittanning samples, whereas only a slight decrease was observed for the Splash Dam.

More variation was observed in the luminescence intensity measured from the control surface (masked) at a closer distance for the three coals. This may be attributable to the experimental conditions. In the case of our microscope system, red and infrared wavelengths are filtered from the light source in order to reduce thermal damage. This is not the case with the ultraviolet lamp; the sample surface is close to the hot lamp and no wavelengths are filtered from the system. To determine the potential for thermal oxidation of the coal from the lamp, a fine unsheathed K-type thermocouple was fixed to the surface of coal and exposed to the ultraviolet light source at the two distances (i.e., 5.7 and 3.2 cm). Figure 3B shows that within the first 2 to 3 minutes there is a very rapid temperature rise, followed by a steady low rate of increase out to 10 minutes (the longest period of exposure). The important observation is that there is a significantly lower temperature rise and maximum temperature at a greater distance from the lamp and, therefore, from the viewpoint of avoiding the potential of thermal oxidation, an increased distance from the lamp is desirable.

The progressive decrease in luminescence intensity over time suggests that exposure to this ultraviolet light may indeed be photo-oxidizing the coal surface. Diminished luminescence intensity is a consequence of both natural weathering and storage deterioration of coals. However, for this study it was important to correlate the degree of photo-oxidation that is occurring from the spotlight with respect to our optical microscope system. By observing the maximum decrease in luminescence intensity obtained from both the optical microscope system and the UV lamp, it was determined that (on average) the microscope system induces approximately a factor of 10 greater change in intensity. Thus, to obtain a comparable level of surface photo-oxidation using the UV spotlight, irradiation times would need to be increased by a factor of ten. Furthermore, to guard against extensive thermal oxidation of the surface, the maximum distance between the light source and polished surface (5.7 cm) was maintained.

Figure 2B - Influence of Exposing Various Coals to 366 nm Light from 3.2 cm on Luminescence Intensity Measured at 600 nm

Figure 3B - Temperature Increase Measured on Coal Surfaces During Irradiation with the BLAK-RAY Longwave (366 nm) Spotlight

APPENDIX C

Luminescence of Some Model Compounds

In an effort to establish a better understanding of how aromatic compounds contribute to luminescence emissions upon blue-light irradiation, a series of sixteen, solid model compounds were selected for a preliminary investigation. Compounds were chosen to cover variation in the number of condensed aromatic rings, degree of saturation, inclusion of heteroatoms and variation in oxygen-containing functional groups. The compounds were prepared and analyzed in such a way as to allow measurement of luminescence intensity and spectral distribution under a nitrogen atmosphere, and to measure the degree of alteration during blue-light irradiation in air.

Experimental Procedures

All model compounds evaluated were solid-state, reagent-grade chemicals of 99.9% purity. Following a period of initial evaluation, a standard procedure was developed. For all compounds about 0.5 g of material was placed into a clean, steel cylindrical mold fitted with steel end caps. Samples were placed in a hydraulic press under 10 MPa (1500 psi) pressure for 2 min, then the sample was pushed to the surface of the cylindrical mold so that the steel end-cap could be removed. To minimize disturbance of the sample, measurements were made on this surface while still in the mold. No further surface preparation was involved.

Analysis of luminescence intensity and alteration at 600 nm and the measurement of spectral distribution between 510-750 nm were performed using modified Leitz MPV-II microscope photometer systems. For both methods light energy from a mercury-arc lamp was passed through a heat filter, suppressing red and infrared wavelengths, and then through a series of interference filters which defined the appropriate excitation and emission wavelengths. Analyses were performed with filter combinations utilizing 390-490 nm (blue-light) excitation, a 510 nm short-pass dichromatic beam splitter and a 515 nm long-pass barrier filter. The excitation light was reflected by the beam splitter and condensed onto the sample through a 50X NPL FLUOTAR dry objective. Intensity measurements were made using a dry nitrogen atmosphere to eliminate photo-oxidation, whereas alteration of fluorescence intensity was measured in air. The emitted light energy was transmitted back through the dichromatic beam splitter, and the 515 nm long-pass barrier filter blocked any residual reflected excitation light. From this point, the measuring system was varied depending upon the desired measurement, i.e., intensity at a single wavelength or spectral distribution. Different microscope systems were used for the two procedures.

For measurement of intensity, the luminescence emission passed through a filter centered around 600 nm (570-630 nm). The optical signal(s) was (were) transformed into electronic signals by an EMI 9558 photomultiplier and then amplified. Once the photoelectric system was calibrated to a uranyl glass standard of stable fluorescence intensity at 529 nm and arbitrarily set to 1.000, a statistically adequate number of intensity readings were accumulated. Provided readings were collected under dry nitrogen, the mean of 10 individual readings was found to be

sufficient to characterize the model compounds. For measurements of luminescence alteration in air, 50 intensity readings were taken from the same area at 6 sec intervals during a period of constant irradiation. Readings from two different areas were taken and the average value of the change in intensity was plotted with time.

For the measurement of relative intensity by wavelength (spectra), luminescence emissions were passed through an optical train similar to that just described. Here, however, a motor-driven Kratos GM200 double-grating monochromator with 20 nm bandwidth replaced the band filter. An RCA C31034A water-cooled photomultiplier, having a more consistent range of responsivity between 250 to 850 nm than the EMI 9558, was used for spectral measurements. With this instrumentation the relative emission intensities within the wavelength range from ≈ 510 - ≈ 760 nm were measured. Synchronization of the photomultiplier readings with the appropriate monochromatic wavelength was controlled initially by adjusting the speed of the monochromator motor drive and finally by computer software. Raw data was directed to a 386SX computer through an A/D control board.

The wavelength of the monochromator was synchronized using a uranyl glass standard with a peak fluorescence at 529 nm. Also, several light-emitting diodes with peak intensities at 590 and 705 nm were used to check a greater portion of the spectral range. In addition, all spectra were corrected with respect to a quartz halogen lamp with a stable color temperature at 3400°K.

Spectral information was collected in a controlled micro-environment of dry nitrogen. Five separate spectra were collected on different areas of each sample. Then the mean intensity at each wavelength was determined and used for the graphical representation reported here.

For some of the model compounds that exhibited extremely high luminescence intensity, neutral density filters were placed in the light path to reduce the light intensity into the voltage range of the photomultiplier. Following data collection, intensity values were corrected with respect to the calibrated transmittance values measured for the neutral density filters.

Results and Discussion

Table 1C summarizes the results of spectral luminescence, intensity and alteration measurements on the complete list of model compounds evaluated during this investigation. Spectral distributions obtained from blue-light irradiation are compared for most of the compounds in Figure 1C and the alteration patterns in response to photo-oxidation are given in Figure 2C. A number of observation can be made from these data with regard to chemical structure.

In general, most of the model compounds possess much higher luminescence emission intensity and narrower spectral distributions than vitrinite in response to blue-light irradiation. However, their response to photo-oxidation is as varied as that observed for coals, displaying all three alterations-pattern types (negative, positive and dual).

Table 1C - Spectral Luminescence, Intensity and Alteration Behavior in Air of Selected Model Compounds

Model Compounds	Measured Intensity at 600 nm (Uranyl=1.0)	Peak Luminescence (Blue), nm	Alteration Type in Air	Compounds
Naphthalene	0.23		≈Positive
Anthracene	131.90	559	Dual
Pyrene	684.70	550	Positive
1,2,4,5-Dibenzopyrene	5,384.00	555	Negative
Phenanthrene	7.93	548	Positive
Phenanthridine	0.49	554	Positive
Fluorene	1.38	550	Positive
Dibenzofuran	3.49	556	Positive

Table 1C Continued - Spectral Luminescence, Intensity and Alteration Behavior in Air of Selected Model Compounds

Model Compounds	Measured Intensity at 600 nm (Uranyl=1.0)	Peak Luminescence (Blue), nm	Alteration Type in Air	Compounds
Dibenzothiophene	7.60	549	Positive
Anthrone	19.90	563	Positive
Bibenzyl	8.32	597	Negative
Benzylphenylether	6.38	556	Dual
Benzophenone	3.86	553	Positive
2,3-Naphthalene-Dicarboxylic Acid	445.70	596	Dual
2,6-Dimethylphenol	0.20	None	None
Tannic Acid	65.06	606	Negative

Figure 1C - Comparison of Normalized Spectral Luminescence of Model Compounds Following Blue-Light Irradiation

Figure 2C - Comparison of the Alteration of Luminescence Emissions in Air of Selected Model Compounds During Blue-light Irradiation

The influence of the number of condensed aromatic rings on the fluorescence properties was pronounced. For the naphthalene- anthracene- pyrene- dibenzopyrene series (2,3,4,6 rings), luminescence intensity values increased by magnitudes as the number of aromatic rings increased (Table 1C). As shown in Figure 1Ca, very little difference in the peak luminescence and spectral distribution was observed among these compounds (naphthalene could not be measured because of the low signal). Some gross differences in alteration patterns were observed; naphthalene and pyrene gave positive and anthracene dual (first negative and then positive fluorescence emissions with irradiation time) responses, whereas 1,2,4,5-dibenzopyrene was negative. Interestingly, coals of medium volatile rank, having larger more condensed aromatic structures, also exhibit negative alteration. The luminescence intensity results were unexpected considering that the extensive π -bond network of the larger aromatic molecules might be expected to effectively transfer (i.e., re-absorb) the emission-energy, thereby reducing intensity. The luminescence intensity of coals decreases into the higher levels of rank, presumably because the aromatic structure becomes larger and more condensed.

To understand how molecular shape might influence luminescence emissions, phenanthrene was compared with anthracene (Table 1C). Luminescence intensity values were substantially lower and the alteration pattern varied from dual in anthracene to strongly positive for phenanthrene. The luminescence spectra of these compounds in blue light (compared in Figure 1Cb) are very similar. This observation suggests that the shape of condensed aromatic molecules has a profound influence on the luminescence emissions measured in our system. Considering that it is equally likely that molecular shape may enhance emissions as well as lowering them, this may contribute to the unexpectedly high intensity values measured from molecules with greater numbers of aromatic rings.

For phenanthridine, in which one of the carbon atoms in the phenanthrene structure has been replaced with nitrogen, a decrease in luminescence intensity was observed along with a positive alteration response (Figure 2Cb). This result was not unexpected, as more polar molecules containing heteroatoms with unpaired electrons have the ability to re-absorb or transfer luminescence emissions. Peak luminescence intensity measured in blue light for these compounds are very similar (Figure 1Cb), although phenanthridine has a somewhat narrower spectral distribution compared with anthracene and phenanthrene.

Molecules of similar structure but with different heteroatoms in the same position as occurs with fluorene, dibenzofuran and dibenzothiophene (C, O and S) shows a small, but significant increase in luminescence intensity with increasing atomic size and weight of heteroatom. As shown in Figure 2C, all these compounds possess a fairly weak positive alteration when irradiated in air. Although the peak luminescence was similar for these compounds (Figure 1Cc), spectral distribution broadens towards the red in the order fluorene-dibenzothiophene-dibenzofuran. The fact that these heteroatoms result in a much higher luminescence than was observed for phenanthridine, suggests that their position within the molecule also may be an important factor controlling luminescence emissions.

Substitution of a carbonyl group into the central ring of anthracene, as with anthrone

(Table 1C), resulted in a decrease in luminescence intensity and positive alteration. Other compounds with substituents between condensed aromatic rings gave relatively high fluorescence intensity (with some variation), as with the bibenzyl- benzylphenylether- benzophenone series. Also, these compounds exhibit three different alteration patterns when irradiated in air, with bibenzyl being slightly negative and benzylphenylether being slightly dual, and benzophenone showing a strong positive alteration in similar manner to the carbonyl-containing anthrone (Figure 2C). It is interesting to note that compounds containing oxygen functionality possessed a positive element to their alteration pattern. Similarities therefore exist with weathered and low-rank coals which also tend to have positive alteration and possess greater oxygen functionality. Bibenzyl shows a much broader spectral distribution and has a greater peak luminescence intensity compared with any of the other model compounds (Figure 1Cd). This, and the higher luminescence intensity may result from the fact that it is less polar and less rigid than the oxygen-containing compounds in this series.

Coals of low rank contain substantial carbonyl and carboxylic acid groups also possess relatively higher luminescence intensity and positive or dual alteration patterns. Consequently, it is no surprise that when carboxylic acid groups are incorporated into the naphthalene structure, as with 2,3-naphthalene dicarboxylic acid, the luminescence intensity was substantially increased and a dual alteration pattern was obtained.

When phenolic functional groups are incorporated into aromatic structures, as with 2,6-dimethylphenol, luminescence emissions were found to be extremely low (Table 1C), but in combination with carboxylic acid groups in tannic acid, luminescence intensity was high.

Conclusions

Luminescence emissions obtained from a suite of sixteen aromatic compounds were found to have considerably higher emissions than those obtained from coal (vitrinite). The main reason for this rests in the fact that coal is composed of a complex mixture of substituted and condensed aromatic molecules that can effectively transfer or re-absorb energy from adjacent molecules. Through this investigation a number of observations can be made regarding luminescence emissions measured using our particular technique and equipment. Results showed that luminescence intensity values increased in response to increasing numbers of aromatic rings, that molecular shape and placement of substituents within an aromatic structure influenced emissions as did the atomic size and weight of heteroatoms. Further, most of the oxygen-bearing compounds, particularly those containing carbonyl and carboxylic acid groups, had relatively high luminescence emissions and possessed positive or dual alteration patterns when photo-oxidized. Similar luminescence results are obtained from low-rank coals and, although naturally weathered coals typically show lower levels of luminescence, they too give positive alteration when photo-oxidized.