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FOSSIL ENERGY

A DATA BASE FOR THE ANALYSIS OF COMPOSITIONAL CHARACTERISTICS OF COAL SEAMS AND MACERALS

Quarterly Technical Progress Report for the Period November–January 1981

By
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MASTER

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The Pennsylvania State University
Coal Research Section
University Park, Pennsylvania

U. S. DEPARTMENT OF ENERGY

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ABSTRACT

The basic objectives of this program are, first, to understand the systematic relationships between the properties of coals, and, second, to determine the nature of the lateral and vertical variability in the properties of a single seam.

Five coal samples were collected during the quarter, all from Pennsylvania. One hundred thirty eight coal samples and 216 printouts were provided on request to the coal research community.

Modification of the Fisher Coal Analyser program is giving volatile matter and ash values which are in better agreement with those obtained by the ASTM methods.

Multivariate statistical analyses applied to the Coal Data Base confirm a number of known trends for coal properties. In addition, nitrogen and some components of the ash analysis bear interesting relationships to rank.

The macroscopic petrography of column samples of the Lower Kittanning seam reveals a significant difference between the sample from a "marine-influenced environment" and those from toward the margins of the basin where conditions were non-marine.

The various methods of determining the amount and mineralogy of the inorganic fraction of coals are reviewed.

General trends in seam thickness, ash, sulfur, volatile matter yield, and vitrinite reflectance of the Lower Kittanning seam of western Pennsylvania are presented. Controls of sedimentation are discussed in relation to the areal variability which has been observed. Differential subsidence and paleotopography appear to have played a major role during the deposition of the coal. The same controls may have maintained some influence upon the coalification process after deposition, especially along the eastern margin of the Lower Kittanning basin.

The experimental procedure for measuring the optical properties of different wavelengths of light has been set up. Sources of error have been reviewed, and procedures for overcoming errors established. Thirty measurements each in air and oil media were used to calculate mean maximum reflectance, standard deviation, and 95% confidence limits after each reading. By examining the curves of 95% confidence limits versus number of readings, the number of readings required for accurate measurement were calculated for air and oil reflectance. Ten and twenty were the numbers chosen for air and oil immersion, respectively.

Extinction coefficients for aliphatic and aromatic C-H, NH, alkyl and phenolic OH, and COOH groups in the Fourier transform infrared spectra of vitrinite concentrates will be determined by a novel approach. In this the hydrogen contents of a suite of samples with varying hydrogen

contents will be equated to the sum of the intensities x extinction values of the relevant bands. A program to solve the large number of simultaneous equations has been written.

Apparent densities of several coals and macerals in methanol at 25°C, and the pore volumes accessible to the solvent are reported. The percentage swelling of coals and macerals in methanol is calculated from the volume uptake of methanol measured gravimetrically at a relative vapor pressure of 0.95 and 25°C and from the accessible pore volumes. Some results showing an appreciable swelling of coal in various pressures of CO_2 (up to 4.8 MPa) at 25°C are also presented.

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OBJECTIVES AND SCOPE OF WORK

The major objective of the program is to use the Penn State Coal Data Base to investigate the systematic relationships between the properties of U.S. coals.

To do this, we will build on the data base established for over 1000 coals during prior OCR, ERDA and DOE programs. A program to obtain a limited number of additional samples will be entailed so that specific investigations may be undertaken. The intent is to gain better understanding of the basic nature of coal interrelationships and the variability of its properties.

The following studies are included in the program:

a) A statistical study of the interrelationships between the properties of the organic fraction of coals. The extent to which natural groupings of U.S. coals might exist will be investigated by cluster analysis. Cause for the groupings will be sought in such factors as age of coal, source material and thermal/burial history.

b) A statistical study of the interrelationships between the properties of the inorganic fraction of coals. Correlations will be sought between the major, minor, trace element and mineralogical analyses of coals in the data base.

c) Studies of the lateral and vertical variability of properties within a single coal seam in response to changes in depositional environments and post-depositional metamorphic changes. The Lower Kittanning seam has been selected because of its broad extent and the range in environments by which it is thought to have been affected. Properties which will be studied include the petrographic characteristics, the minerals and the fluid characteristics.

An additional factor analysis will be performed on a range of compositional data together with fluid characteristics and conversion in tubing bomb reactions with tetralin; in this way the possibility that plasticity and liquefaction involve some common mechanisms will be investigated.

Oxidation can result in severe deterioration of the plastic behavior of coals. Because any parallel reduction in the liquefaction potential of coals could be critical to the economics of a process, we will study the relationship between the fluid and liquefaction properties of coals which have been exposed to varying degrees of natural and laboratory oxidation.

d) The basic physical and chemical properties of pure coal macerals. Detailed analyses of vitrinite concentrates will be made to determine what significant differences in functional group content, aromaticity, density, porosity, and optical properties arise from variation in the environmental conditions during peat deposition and in the thermal histories of coals. To the extent possible the same determinations will be made on concentrates of other macerals. One emphasis will be placed on comparisons between

vitrinite macerals thought to be representative of different environments existing during deposition of the Lower Kittanning seam. Another particular subject for investigation will be the nature and extent of differences between vitrinite macerals from the Eastern Province and those of equivalent rank from the Interior Province. The significance of our findings to industrial processes will be reported.

e) Feed coals and the solid residues of liquefaction experiments conducted or co-ordinated by Pittsburgh Energy Technology Center will be subjected to mineralogic and petrographic analysis. The possible influence of the mineralogic and maceral compositions on the experimental results, will be sought.

1. SAMPLE COLLECTION

During this quarter, five samples were collected, all in Pennsylvania. These were numbers PSOC-1336 through PSOC-1340 and included two full seam channel samples, two subsections and one grab sample of a cannel-like coal.

(C.P.D.)

2. BASIC COAL CHARACTERIZATION

Proximate Analysis by Means of Fisher Coal Analyser

During the last quarter, a procedure for the determination of moisture, volatile matter, and ash yield was established, using a Fisher Coal Analyzer, Model 490, complete with printer and digital balance. In the previous quarterly technical progress report (DOE-30013-3) it was noted that there seemed to be a systematic negative bias in the determination of volatile matter by means of the Fisher Coal Analyzer. This bias was substantiated and a modification of the recommended procedure adapted in order to provide acceptable agreement between values.

Probably the main difference between volatile matter values determined by ASTM method D 3175 and the Fisher Coal Analyzer (besides the sample containers) is the time taken to bring the sample up to 950°C. By the ASTM method, the sample is placed directly in the furnace at 950°C, left for 7 minutes, removed and weighed when cool. For sparking coals the sample is given a "preliminary gradual heating such that a temperature of 600 $\pm$ 50°C is reached in 6 minutes." After this the sample is put into a furnace set at 950°C for exactly 6 minutes, removed and weighed when cool. The Fisher method, as called for in the Instruction Manual, starts with the sample in a cold furnace. The temperature is raised to 950°C at a rate of 30-35°C/minute, maintained at 950°C for 7 minutes, after which the sample is removed, cooled and weighed. The total time that the sample is in the furnace is about 45 minutes.

Table 1 illustrates the variation of volatile matter with changing initial Fisher furnace temperatures. The drop-off in volatile matter values at starting temperatures over 750°C is due to deposition of carbon on the crucible walls and lid. At 750°C and lower, very little of the volatile matter is retained as carbon on the containers. The 750°C starting temperature gives values quite close to the mean value obtained by several laboratories using the ASTM procedures. As a result, our procedure has been modified such that samples are placed into the muffle furnace at 750°C, rapidly bringing the furnace to 950°C, maintaining the samples at 950°C for 7 minutes, removing and cooling before weighing. The total furnace time is about 22 minutes as compared to 12 minutes for sparking coals by the ASTM method. However, 20 samples are processed at one time with the Fisher Coal Analyzer compared to one by the ASTM method.

Sparking coals do not seem to be a problem with the Fisher method, although sparking normally would not be observed since the muffle furnace does not have a window in it and one should not open the door for observation

Table 1. Volatile Matter by Fisher Coal Analyzer

Starting Temp., °C / Sample	25	550	750	850	950	"SCV"*
TD 356	32.30%	33.07%	33.56%	33.22%	33.13%	34.00%
TD 357	36.84	37.83	38.24	38.73	38.01	38.11
TD 358	24.84	24.92	25.37	25.20	24.62	25.58
TD 361	38.37	38.90	39.68	39.70	39.22	40.02
TD 404	25.53	26.08	26.90	26.64	26.15	26.59
TD 407			37.71			38.12
TD 411			18.93			19.08
PSOC-1225	36.55	37.35	38.43		37.93	
PSOC-1228	31.62	32.08	33.68		33.43	
PSOC-1319	35.05	34.72	36.27		34.75	
Total Furnace Time, Min.	45	30	22	15	12	

Note: Volatile Matter values are averages of two determinations. The average range of the duplicates is 0.32%.

*"Statistically correct value" as determined from the results of several laboratories using the ASTM procedures.

during a determination. However, there is some problem with coals that swell and dislodge the lids during heating. This causes sample oxidation and loss, and consequently erroneously high volatile matter values. Fortunately, this swelling has occurred in only 5-10% of the coals we have analyzed, and it is quite obvious from the appearance of the button at the conclusion of the test. To overcome the problem, the normal sample size of 1.0g is reduced to 0.8 or 0.6g. As shown in Figure 1, in most instances there is a gradual slight increase in volatile matter down to about 0.4g. Sample sizes less than 0.4g give unacceptably high volatile matter values. In the coals processed so far, most of the deleterious swelling has been eliminated by using a sample size of 0.8 grams. For only three or four samples has it been necessary to go down to 0.6 or 0.5g.

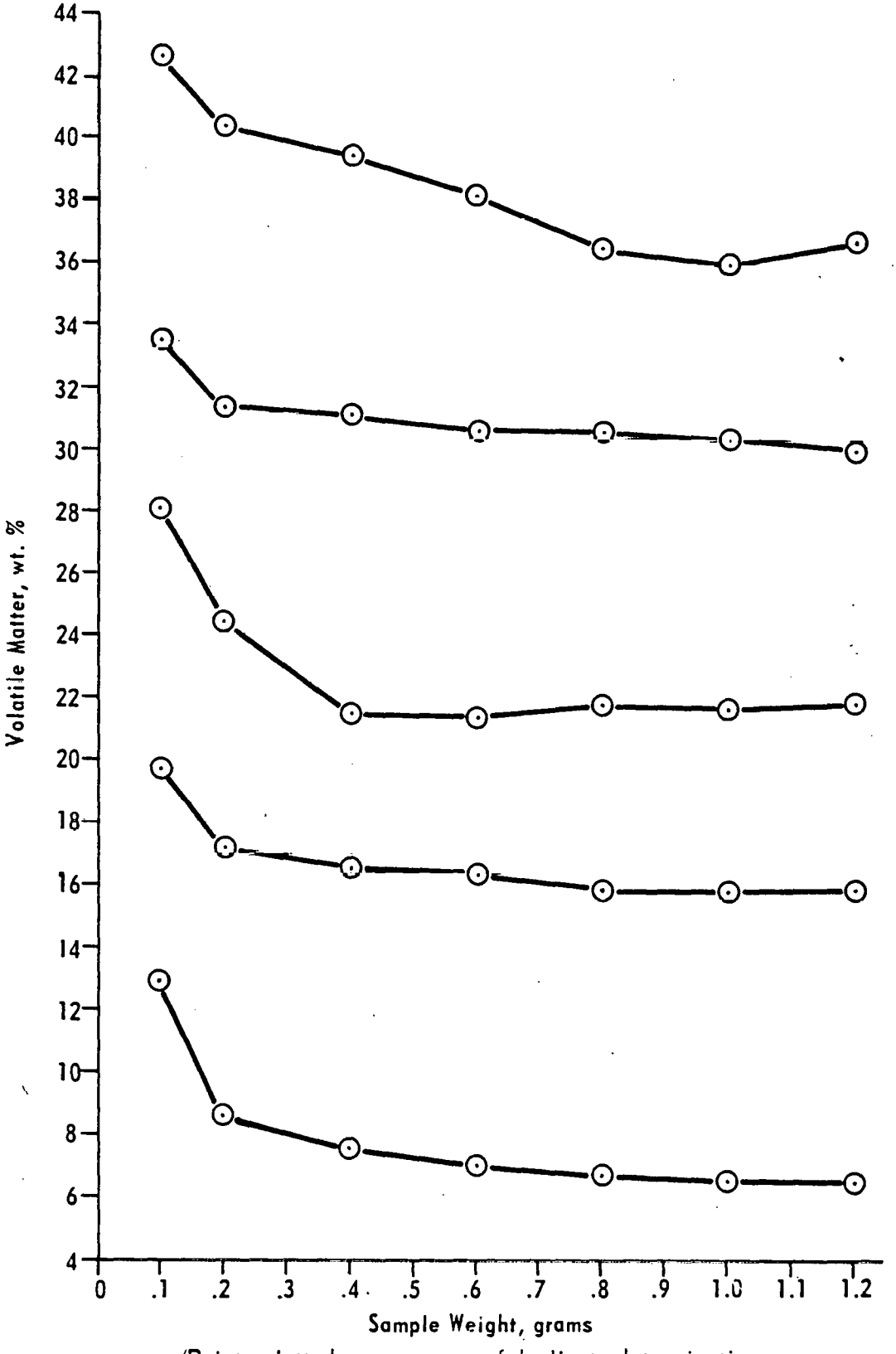
In the ASTM method for the determination of ash (D 3174) a difficulty is noted with coals containing high pyrite and calcite. In the normal procedure of heating, pyrite and calcite may decompose simultaneously with consequent fixation of sulfur dioxide by the calcium oxide to form $CaSO_4$. This is overcome by heating such coals slowly so that the sulfur dioxide from the pyrite and other constituents is expelled before the calcite is decomposed. In the Fisher technique, the ash sample is that which has gone through the volatile matter cycle. Initially we thought that there could be some sulfate fixation during this cycle and that the ash values would be too high. Table 2 is a comparison of values obtained by using the sample already used for volatile matter and by using a separate sample and a much slower heating cycle. The two sets of results compare well, although it should be noted that all of the samples are bituminous coals from the Lower Kittanning seam, and contain very little calcite.

Status of Other Analyses

Table 3 is a status report of chemical analyses submitted and performed since the commencement of this project.

Maceral analyses were completed on 20 PSOC coals. The free-swelling index was determined on nineteen coals, and the Gray-King coke type on one.

(N.S. and C.P.D.)



Points plotted are averages of duplicate determinations.

Figure 1. VARIATION OF VOLATILE MATTER WITH SAMPLE SIZE (DRY BASIS)

Table 2. Ash Content Comparisons

Sample PSOC No.	Fisher Ash	"ASTM" Ash
1214	10.20%	10.36%
1221	13.76	13.90
1229	10.30	10.74
1238	22.55	22.08
1239	12.42	12.64
1243	10.90	10.98
1269	24.46	24.52
1270	10.03	9.95
1272	9.70	9.65
1273	7.45	7.45

Note: Fisher ash program uses the sample previously used for volatile matter. The sample is heated as rapidly as possible to 750°C, maintained at 750°C overnight, cooled and then weighed. The "ASTM" ash program uses a fresh sample (dried). The sample is heated at 8°C/min. to 500°C, at 4°C/min. to 750°C (total time about 2 hours), and then maintained at 750°C overnight, cooled and weighed.

Table 3. Analyses Requested and Completed Since February 1, 1980

	Number Requested	Number Completed
Proximate Analyses	140	122
Ultimate Analyses	81	78
Forms of Sulfur	168	162
Low Temperature Ash	105	69
High Temperature Ash	112	109
Elemental Ash Analyses	110	107
Mineralogical Analyses	3	2

3. SERVICE TO OTHER AGENCIES

A total of 216 selected printouts of coal data and 138 coal samples were supplied to other agencies involved in coal research.

The agencies requesting the samples and data include: The University of Tennessee, Pittsburgh Energy Technology Center, Amoco Research, The Department of Physics at Florida State University, The Physics Department at the University of Missouri, Physical Sciences Incorporated, The Department of Chemistry at the University of Pittsburgh, Cities Service Research and Development Company, E.I. DuPont DeNemours, Gulf Research and Development, Howard University, Western Kentucky University, Perkin-Elmer Company, Iowa State University, The University of Southern California, The Chemistry Department at the University of Arizona, Exxon Research & Engineering, Southern Illinois University, Skidaway Institute of Oceanography; Spectron Laboratories, University of Michigan, Jet Propulsion Laboratories, Fluor Mining and Metals, Inc., and Battelle Pacific N.W. Laboratories.

(C.P.D.)

4. DATA BASE MANAGEMENT

As of February 12, 1981, the Penn State Coal Data Base maintained on the IBM 370/3033 computer represents samples through PSOC-999, a total of 925 coals.

All data for coals beyond PSOC-999 have been transferred from the PDP-8 based system to the 370, an addition of 305 samples. The information has not yet been added to the master data tape, so printouts are not yet available. When added to the tape the samples will run through PSOC-1304. Data exist for at least 30 samples beyond PSOC-1304, but this information has not been entered into the PDP-8 and will have to be added to the 370 data base by other means.

Changes were necessary in the program which does various calculations on the raw data and prints the results under specified formats. Two new files were specified, for a total of ten. These files allow for the printing of predetermined ranges of coals.

Corrections and additions are being made to coals between PSOC-780 and PSOC-999, as new or updated data have become available, or as previously unnoticed errors have shown up. Changes will continue to be made when necessary.

(D.W.)

5. STATISTICAL STUDY OF ORGANIC DATA ON COALS IN THE DATA BASE

Multivariate statistical techniques are applied to study the interactions of 12 variables within a set of 277 United States' coals. These coals represent whole seam samples obtained from each of the 6 coal provindes of the United States and vary in rank from lignite to anthracite. The data are maintained on the IBM-370 computer. The variables selected are components of the ultimate analysis (carbon, oxygen, hydrogen, nitrogen, and organic sulfur), selected components of the proximate analysis (volatile matter and moisture), calorific value, reflectance of the vitrinite macerals, and the relative proportion of the three maceral groups (total vitrinite, inertinite, and liptinite group macerals).

A factor analysis performed on all the data together, and the data divided into smaller sets on the basis of rank and geographic location, indicates that rank is the most important factor in determining the amount of variation of each data set. The variables which vary with rank include carbon, oxygen, calorific value, moisture, volatile matter, reflectance, and nitrogen.

The variables which vary strongly with rank for the entire data set are carbon, oxygen, volatile matter, calorific value, moisture, and reflectance. Hydrogen also varies with rank, but not nearly as strongly as the other variables because its response is curvilinear; slight early hydrogen gains are offset by later large hydrogen losses. The variation of nitrogen with rank in this factor analysis is not apparent for the entire data set because its rank relationship is also curvilinear. The maceral gorups account for the next greatest source of variation. Organic sulfur is independent of the first two factors. A cluster analysis indicates the data set forms a continuum, but the grouping arrangement which results in the most significant partitioning produces 4 groups which are differentiated from each other primarily on the basis of rank, maceral content, and sulfur content. Factor analysis of the individual groups provide insights into the coalification processes of these more homogeneous associations of coals. Carbon, oxygen, reflectance, and calorific value vary together and are strongly affected by the processes of coalification within each of the groups. At about mvb rank, moisture no longer responds to rank increase, but volatile matter and hydrogen do respond. Modest nitrogen enrichment in the low ranks is offset by modest nitrogen depletion in the high ranks.

Factor analyses performed on 5 classifications of coals grouped by only the rank criterion indicate that oxygen, carbon, and calorific value vary together and are sensitive rank indicators throughout the entire rank range. Reflectance is a more sensitive rank indicator for high-rank coals than for low-rank coals. Moisture is depleted and nitrogen enriched in the low-rank coals. The depletion of volatile matter with rank becomes significant in the hvBb coals; the depletion of hydrogen becomes significant in the hvAb coals; and the depletion of nitrogen becomes significant at mvb rank. The high-sulfur Interior Province coals which are of hvB and Cb ranks complicate the analyses of these rank groupings.

Analysis of variance on Eastern Province coals grouped according to stratigraphic position indicate that they differ significantly in only 4 variables: carbon, hydrogen, volatile matter, and nitrogen. Not surprisingly, these differences indicate that coals lower in the stratigraphic section have attained a higher rank than coal higher in the section. Coals from Rocky Mountain, Gulf Coast, Northern Great Plains, and Pacific Provinces are younger and lower in rank than Eastern Province coals. Interior Province coals are of intermediate rank and contain the highest organic sulfur contents. Analysis of variance indicates Interior Province coals of the hvBb rank range are significantly higher in moisture and lower in reflectivity than coals of similar rank from the other provinces. Within the mvb rank range, Interior Province coals have normal moisture contents but are still significantly lower in reflectivity. Analysis of variance of post-Pennsylvanian coals grouped by age indicates that Paleocene age coals are significantly lower in rank than both Cretaceous and Eocene age coals.

Analysis of variance applied to coals from the Eastern Interior, and Rocky Mountain Provinces obtained as multiple samples from individual mines indicates that the variance within the mines is inhomogeneous when measured by selected variables which are independent in the factor analysis. The lack of homogeneity at the lowest level precludes pooling the data to investigate sources of variation at higher levels. The sources of variation are not consistent for the different variables over the different provinces.

A reconnaissance study of selected ash components and a subdivision of the inertinite maceral group reveals that calcium oxide decreases strongly with rank. Magnesium oxide decreases moderately with rank, but is also inversely related to the organic sulfur content of a coal. In the analysis, iron oxide bears a very strong relationship to organic sulfur content. Sodium oxide is insensitive to both sulfur and rank. Macrinite displays a strong inverse relationship to organic sulfur; no immedate explanation can be offered for this result.

(J.G. and A.D.)

6. STATISTICAL STUDY OF INORGANIC DATA ON COALS IN THE DATA BASE

A literature review of previous coal mineral characterization studies continued during the report period. Further correlations of mineral and inorganic elements in coal have been noted. When the results of the current study are obtained, they will be compared with those previously described correlations.

The specific samples from the Penn State Coal Data Base to be included in the statistical study must now be selected. Criteria will include consistency of sample type, geographic distribution, and frequency distribution of variables concerned, as required for statistical validity.

(D.G. and A.D.)

7. STUDIES OF THE LATERAL AND VERTICAL VARIABILITY OF CHARACTERISTICS OF COAL SEAMS

A. Petrographic Characteristics of the Lower Kittanning Seam

One of the objectives of this research is to provide a description and classification of the coal types which occur as part of the Lower Kittanning coal seam in western Pennsylvania. An additional goal is to utilize the petrographic data to delineate vertical and lateral changes within the Lower Kittanning coal seam and to determine relationships between these changes and the depositional setting of the coal swamp.

The geologic setting, depositional environments and previous studies on the petrography of the Lower Kittanning coal have been discussed in the preceeding quarterly technical progress reports.

Sampling

A total of 5 column samples of the Lower Kittanning seam have been collected and prepared for analysis. The technique of colum sampling consists of collecting a series of oriented blocks of the coal which represent the entire seam from top to bottom. Each block was labelled at the sampling site to record the orientation and vertical position within the seam. In the laboratory these blocks were cut into a series of slabs approximately 6 cm x 8-10 cm x 1 cm and mounted in an epoxy resin for polishing. The exposed surface (perpendicular to the bedding plane) was then polished for megascopic and microscopic analysis.

Of the five columns collected, four are from locations within the so-called fresh-water environment of the Lower Kittanning. The fifth is from the area of supposed marine-influence. Sample numbers, their location by county and their determined paleoenvironmental settings are shown in Table 4.

Table 4. Sample Numbers, Locations and Environments of Column Samples Collected

Sample No.	Location	Paleo-environment
PSOC-1197	Somerset County	"Fresh-water"
PSOC-1325	Somerset County	"Fresh-water"
PSOC-1330	Somerset County	"Fresh-water"
PSOC-1335	Cambria County	"Fresh-water"
PSOC-1340	Jefferson County	"Marine"

Petrographic Analysis

Megascopic Petrography

Megascopic descriptions of the coal were conducted using the coal lithotype terminology defined by Stopes and described in the International Handbook of Coal Petrography (1963) with some modification and modifiers. The four lithotypes recognized in the Stopes system are Vitrain, Clarain, Durain, and Fusain. In order to more adequately describe the Lower Kittanning seam, the terms "clarodurain", "duroclarain", and "boney coal" were added. Clarodurain and duroclarain represent transition types between clarains and durains. Boney coal is a term used in describing impure coal layers, usually clay-rich. A minimum thickness of 3 mm was required for a layer to be identified as a discrete lithotype.

Lithotypes were identified by examination of the polished surfaces of the coal blocks. The thickness of each lithotype was determined, and any distinguishing characteristics (such as pyrite lenses or exceptionally bright or dull appearance) were noted. Microscopic profiles were constructed to illustrate the lithotypes present in each column. Two examples are shown in Figure 2.

The two columns descriptions shown in Figure 2 show that PSOC-1340 consists of two principal zones or coal types. The upper 29 cm of the coal consists almost entirely of clarodurain and durains, while the bottom 50 cms, except for a shale parting near the top, is composed of a bright clarain with no durains or duller layers present. The other four columns, while containing some durain and/or dull layers are not as markedly zoned as is PSOC-1340; and are more uniformly bright. The profile of PSOC-1335 is included in Figure 2 as an example.

The megascopic character of the 5 Lower Kittanning samples are summarized in Table 5 which displays the percent of each lithotype for the different columns. For three of the samples, portions of the seam were not collected owing to the extremely friable nature of the coals at their locality. However, in all these cases the missing portions were identified in the field as clarain and therefore were included in the total clarain in parentheses.

The data shown in Table 5 demonstrate the significant difference in lithotype composition between PSOC-1340 and the other four samples. This may indicate a different environment of formation for this area of the Lower Kittanning. This hypothesis is supported by the fact that PSOC-1340 was collected in that area of the seam which was influenced by a marine incursion during or immediately following deposition of the peat. The other 4 are from localities where the seam was influenced by non-marine and fresh-water conditions as determined from the paleoenvironmental studies of the overlying rock units (see previous quarterly technical progress reports for discussion).

The megascopic profiles are being used as guidelines for conducting the microscopic petrographic analysis.

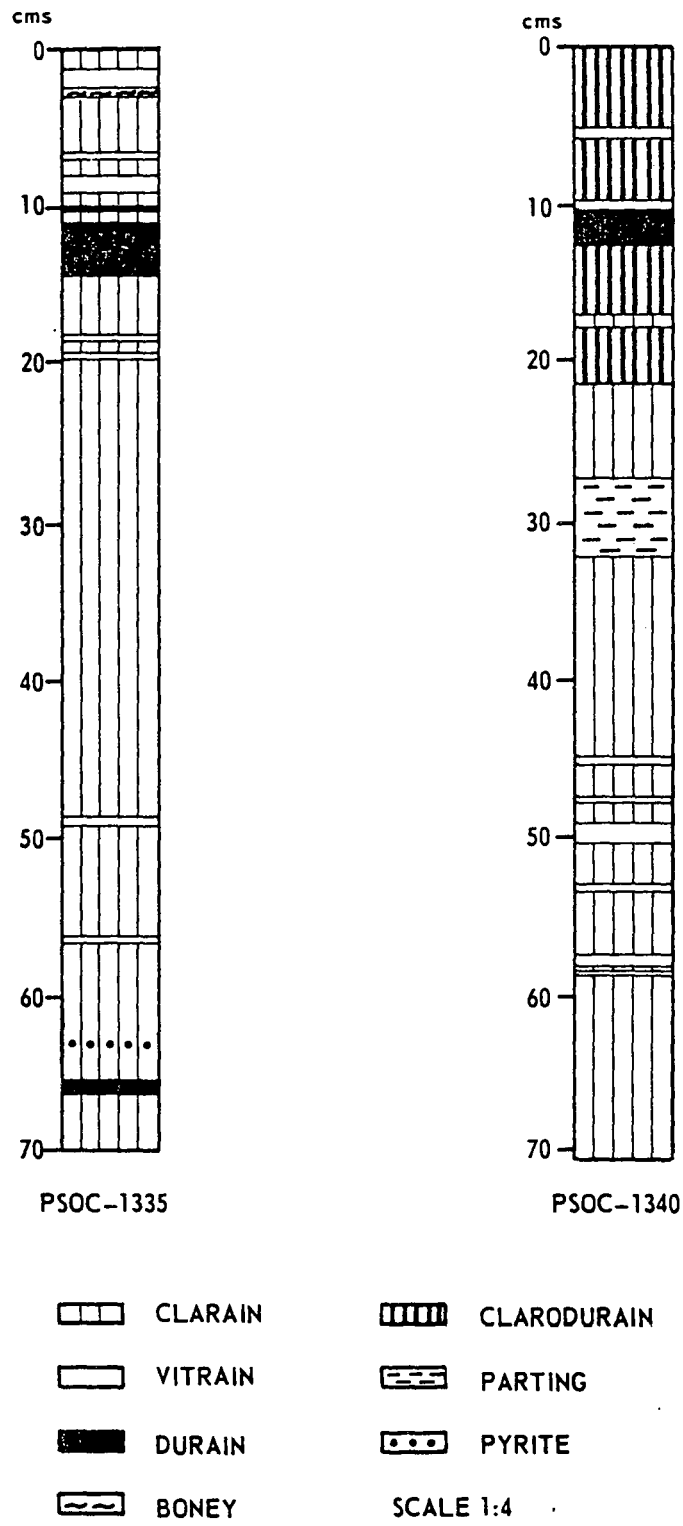


Figure 2. LITHOTYPE PROFILES – COLUMN SAMPLES OF LOWER KITTANNING SEAM

Table 5. Lithotype Percentages for 5 Column Samples of Lower Kittanning. EX: 83.3% of PSOC-1197 is Clarain.

	PSOC-1197	PSOC-1325	PSOC-1330	PSOC-1335	PSOC-1340
Clarain	83.3(90.2)*	92.4(95.4)*	72.3(78.1)*	84.7	58.7
Vitrain	6.8	2.9	9.1	5.9	6.9
Durain	0	0.6	3.7	7.4	3.1
Fusain	0	0	0	0	0
Claro-Durain/ Duro-Clarain	3.0	1.1	0	1.0	24.1
Boney Coal	0	0	1.3	1.0	0
Partings	0	0	7.8	0	7.1
Missing	6.9	3.0	5.8	0	0
	100%	100%	100%	100%	100%

*Numbers in parentheses are % clarain with missing portions added in. See text for explanation.

Microscopic Petrography

The microscopic petrographic analyses which are being conducted will reveal whether the differences observed megascopically exist on the microscopic level. These analyses will be conducted in such a way as to determine if factors such as compositional or textural variations, maceral association or a combination of factors are responsible for the observed lithotype differences. Two columns, PSOC-1335 and PSOC-1340, have been selected for detailed microscopic analysis. The overall goal is to discern any petrographic similarities or differences between lithotypes within a single column and between columns. The results will be compared with those obtained in previous studies, and interpreted to see how the samples fit the model of Lower Kittanning deposition by other workers.

Analysis will be performed using point counting techniques modified to suit the particle character of the samples. Different analytical procedures are being tested to determine which is best suited for the study.

(S.D.A. and A.D.)

B. The Mineralogy of the Lower Kittanning Seam: Review of Analytical Procedures Used for Coal

The nature of the mineral content is one of the properties under investigation in the study of the lateral and vertical variability within the Lower Kittanning seam. There are many different techniques which have been employed to study the mineralogy of coals, but they are complicated by the need to consider the several problems with which they are associated.

Mineral Matter Content

Of the two basic ways by which total mineral matter may be determined, one approach involves calculation from the percentage high temperature ash, using formulas such as the Parr formula, and the second approach involves separation of the minerals from the organic fraction prior to identification.

Indirect Methods

To use the Parr formula (1), high temperature ash and pyritic sulfur values are required as follows:

$$mm = 1.08\ A + 0.55\ Sp \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where mm = mineral matter,
A = percent high temperature ash, and
Sp = percent pyritic sulfur.

This calculation allows for an 8% water loss from the dehydration of clays and the weight loss incurred in the oxidation of pyrite. Such a formula would hold if indeed the coal contained only pyrite and clay. However, this is an oversimplification because carbonates, quartz and minor amounts of other silicates, oxides and sulfates may also be present.

The King, Maries and Crossley (MKC) formula, King, et al. (2) attempts to correct for some of the other changes that occur during high temperature ashing:

$$mm = 1.13\ A + 0.8\ CO_2 + 0.5\ Sp - 2.8\ (S_{ash} - S_{SO_4}) + 0.5\ CL \quad \ldots (2)$$

In addition to correcting for oxidation of pyrite and dehydration of clays, this formula also allows for loss of carbon dioxide from carborates, loss of chlorine and sulfur fixation (S_{ash} and S_{SO_4} referring to sulfate in the ash and coal, respectively).

Given et al., (3) have further modified the Parr formula to:

$$mm = 1.13\ A + 0.47\ Sp + 0.5\ CL \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where only pyritic sulfur, and not organic sulfur, is considered. A detailed discussion of the problems encountered with mineral matter determinations and their importance in relation to coal analysis is presented in Given and Yarzab (4).

The methods discussed so far allow for the indirect determination of the total amount of mineral present in the coal but provide no information on the nature and abundances of these minerals. Pollack (5) described a method by which a normative analysis was applied to chemical data on high temperature ashes. A similar approach was used by Given et al., (6). A potential source of error is the assumption of average compositions for the minerals present. This method also fails to differentiate between some of the more complex clays, including smectites and mixed-layer clays. Given et al., (6) also indicated that this form of analysis would not be appropriate for lignites and subbituminous coals due to the presence of cations as exchangeable ions on carboxyl groups or in chelate complexes.

A modified type of normative analysis is used routinely at the Minerals Constitution Laboratory at Penn State. X-ray diffraction, infrared spectroscopy and chemical analyses of high temperature ashes are used to determine the various amounts of minerals present.

A more direct approach is that developed by Radmacher and Mohrhauer (7) and later modified by Bishop and Ward (8). This procedure involves washing the coal with HCL, HF and then HCL again at 50°C. After washing, drying and weighing the residue, percent mineral matter may be determined after allowing for changes in moisture content, adsorption of HCL, and the presence of some unreacted pyrite. This method provides good agreement with values calculated by the KMC formula (8).

Direct Methods

These methods involve isolation of the minerals from the coal. Early attempts utilized density separations which did not remove the organics and merely concentrated mineral-rich material. Organic material may be removed by peroxidation (9, 10) or the more commonly used method of low temperature ashing (11). Peroxidation has the advantage over low-temperature ashing in that dehydration of clays and hydrated minerals does not occur, but the disadvantage in that oxidation of sulfide minerals does occur (9).

In low temperature ashing, activated oxygen is passed over the coal at low pressures (1-3 torr), oxidizing the organic material at relatively low temperatures (about 150°C) (12, 13). Under these conditions little alteration of the mineral species takes place. Kaolinite, illite, quartz and calcite are unaltered while expandable clays (smectites and mixed-layer clays) may temporarily lose some interlayer water. Gypsum ($CaSO_4 \cdot 2H_2O$) is altered to hemihydrate ($CaSO_4 \cdot 1/2H_2O$) and γ-$CaSO_4$ (11, 12). Under high oxygen flow rates (14) and extended ashing times (15, 16) some oxidation of pyrite can occur. It has also been shown that organic sulfur may be fixed during low temperature ashing (15, 16).

Once the minerals have been isolated from the coal, analyses may be performed by x-ray diffraction, infrared spectroscopy or Fourier-Transform infrared spectroscopy (as discussed below). Other analytical methods that have been applied to coal include Mössbauer spectroscopy, scanning electron microscopy, differential thermal analysis and electron probe microanalysis. These techniques will not be discussed at this time.

X-ray Diffraction Analysis of Coal Minerals

Qualitative data on non-clay minerals may be obtained by making a smear of the low temperature ash (LTA). O'Gorman and Walker (13) hand ground the LTA in alcohol, and following evaporation of the alcohol, dispersed the ash in distilled water onto a glass slide. Grinding in alcohol was recommended because dry grinding may destroy crystal structure. Given et al., (6) described a similar method where alcohol was used to disperse the LTA onto the glass slide. Rao and Gluskoter (12) compared the use of water smears, alcohol smears and cavity mounts and found the latter to be preferable. Results indicated that water reacted with iron sulfate and sulfide minerals to form sulfuric acid which converted calcite to gypsum. Similar effects were seen when 95% alcohol was used, due to small amounts of water present in the alcohol. However, if purer alcohol (99%) is used this effect is negligible, and some authors recommend the use of alcohol smears for qualitative work (17). Use of a cavity mount introduces no liquid and thus no alteration and is preferred by other workers (12, 18, 19). One objection to the use of a cavity mount is the danger of enhanced orientations of certain minerals due to improper packing of the cavity. If certain precautions are taken, as suggested by Russell and Rimmer (19), this effect is minimized.

Samples are usually x-rayed, using CuKα radiation (λ = 1.5418 Å), between 2 and 60°2θ in order to include all major diffraction peaks of the minerals. Diffraction spacings, d(Å), are then calculated from peak positions (°2θ) and the mineral phases are identified.

Most quantitative analyses of minerals in coal are based on the internal standard method (12, 20, 18 and others), details of which are described by Jenkins and Walker (17) and Russell and Rimmer (19). This method involves x-ray diffraction analysis of standards containing various amounts of minerals similar to those found in LTA's, followed by the construction of calibration curves. Although the minerals selected as standards should be crystallographically similar to those minerals seen in the LTA's, finding suitable samples can be difficult. Quartz, pyrite and calcite and selected other minerals are routinely quantified by this method. This technique is not suitable for clay minerals due to the difficulties encountered in the selection of standard clay minerals and the low peak intensities observed when random powder mounts are used (19).

Aspects of this type of analysis that require special consideration include the choice of internal standards, grinding procedure, choice of sample holder, use of peak heights versus peak areas, and the selection of peaks used for quantification. Estimates of the precision of this form of analysis range from ± 10% (17) to ± 5-7% (19). Greater precision is unlikely due to equipment limitations, sample heterogeneity, availability of suitable standard minerals, and human error.

Despite the success of the internal standard method in the analysis of non-clay minerals, it is of questionable application to the analysis of clays. One question that may be raised is whether or not clays should be determined in the whole LTA or in the < 2 μm fraction. Clay mineralogists and soil scientists widely accept the use of the < 2 μm fraction. Not only do clay minerals tend to concentrate in this size fraction, thus facilitating

the preparation of well-oriented mounts, but also this fraction tends to be free of most non-clay minerals (21). The type of analysis used should reflect the objectives of the study at hand. As a key to the environment of deposition, analysis of the clay-size fraction may be very important. However, if the effect of clays in various types of coal utilization is to be evaluated, not only should the clays be characterized (using analysis of the < 2 μm fraction) but also the total amount of clay present in the coal should be determined from the whole LTA.

Clay minerals may be identified in the whole ash by x-ray analysis of water smears (13) or alcohol smears (17). Analysis of air-dried and ethylene glycol-treated samples permits identification of kaolinite, illite and expandables. Heating to 350°C allows comparison of the amount of expandables to the amount of illite.

Attempts to quantify clay minerals in the whole LTA involved the use of talc as an internal standard (22, 12). In these studies on Illinois coals, 5 percent by weight of talc was added to each coal ash before making alcohol smears. Ratios of clay mineral peak areas to that of talc were calculated. This ratio was then multiplied by an empirically determined "R" factor and by the amount of talc added. Based on runs in air, after ethylene glycol treatment and after heating to 330°C for one hour, percentages of kaolinite, illite, and expandables were determined.

Analysis of the < 2 μm fraction requires that clay-size material must first be separated. This is achieved by dispersing the clays and isolating them either by centrifuge or gravity settling (as described by Tanner and Jackson (23)). Disperson may be achieved by adding sodium hexametaphosphate or similar dispersing agents (24). It is important to note however that these dispersants can produce extraneous peaks which may interfere with those produced by clay minerals.

A more complicated method of clay dispersion is that described by Ward (18) adapted from Jackson (25). This sodium dithionite-citrate-bicarbonate method involves the removal of carbonates, soluble ions, and soluble ferrous iron following reduction from the ferric state. Ferric iron (Fe^{3+}) is reduced by the sodium dithionite ($Na_2S_2O_4$) to ferrous iron (Fe^{2+}). Sodium dithionite has a high reducing power in a basic or neutral system, but not in an acid system, therefore, a buffer (sodium bicarbonate $Na\text{-}HCO_3$) is used. Equations for this reaction (25) are:

in a basic or neutral system (high reducing power):

$$4OH^- + S_2O_4^{=} \rightarrow 2SO_3^{=} + 2H_2O + 2e^- \qquad E_{OX} = 1.12\ V \quad \ldots\ldots\ldots(4)$$

in an acid system

$$2H_2O + HS_2O_4^- \rightarrow 2H_2SO_3 + H^+ + 2e^- \qquad E_{OX} = 0.08\ V \quad \ldots\ldots\ldots(5)$$

The use of HCO_3^- to raise the pH also prevents sulfur precipitation. Precipitation of iron sulfide is prevented by sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) which is a strong complexing agent for iron (25).

Once dispersion has been achieved slides may be prepared. There are many techniques for doing this and their application to the analysis of low temperature ashes is discussed at length in Russell and Rimmer (19).

Various methods exist for calculating the percentages of clays in the < 2 μm fraction, each devised for a particular study and usually based on the method described by Johns et al., (26). Gluskoter (24) measured the intensity of the (001) peaks of kaolinite and illite, and summed a series of values taken every 1/2° 2θ beneath the broad (001) peak of the mixed-layer clay. These intensites were then used to calculate the relative amount of each type of clay present.

Gluskoter (24) also used the diffraction effect (D.E.) ratio, which was determined from the ratios of peak intensities for illite and illite plus expandable clays.

In recent studies (18, 27) certain empirical formulas (modified from Griffin, (28)) have been used to determine the percentages of kaolinite plus chlorite, illite and expandables in the < 2 μm fraction. These calculations were based on the intensities of the 7 Å and 10 Å peaks obtained following glycol treatment and heat treatment.

Analysis of Minerals by Infrared Spectroscopy

Because of the many difficulties encountered in quantitative x-ray diffraction analysis of clays, various researchers have utilized infrared spectroscopy. X-ray diffraction and infrared spectroscopy differ in that the former is sensitive to long range order and the periodic arrangement of atoms in crystalline structures, while the latter is extremely sensitive to short range ordering (13). Infrared spectroscopy (29, 30, 31 and others) and far-infrared spectroscopy (32, 33) have been successfully applied to the identification of minerals. However, the presence of broad bands from organic material conceals inorganic bands in the infrared spectra of coals. Following the development of low temperature ashing as a method to remove organics without affecting the mineral matter, infrared analysis was used to study LTA's (34, 35). Recently, this method has been used for quantitative analysis of kaolinite and gypsum (13, 20).

The most widely used method is the pressed alkali halide (potassium bromide) pellet technique (36), the procedures and applications of which have been discussed by Tuddenham and Lyon (31). In the analysis of low temperature ashes, 1 mg of ash is mixed with 200-300 mg of pure KBr. At this concentration, the requirements of the Beer-Lambert law are met and absorbance is a linear function of concentration. Even lower concentrations (0.75 mg ash and 300 mg KBr) may be used (13). Potassium bromide is a suitable matrix since few minerals interact with it, no interfering adsorption bands are produced, and reproducible dispersions of the unknown can be achieved (31). Mixing and grinding the unknown and matrix is of critical importance (37, 31, 35, 38). According to van der Maas (39), the particle size of the sample must be less than that of the wavelength of the incident light used in the analysis. If this is not the case, the Christiansen effect is observed whereby distortions in the band shape occur due to the difference between the refractive index of the unknown and that of the KBr.

Large particle size also produces unwanted scattering (31). However, the actual grinding process introduces further problems. Excessive hand grinding can destroy mineral structures, particularly those of the clays and thus alter the infrared spectrum (40, 41). Wet grinding in alcohol is suggested by these authors to minimize this problem. Hand grinding of samples is not recommended for multicomponent samples as it may result in poor reproducibility (31). Painter et al., (38) have shown that 30 minutes grinding in a Wig-L-Bug produces the desired particle size and hence maximum absorbance. Differential grinding in multicomponent samples, resulting from hardness differences, may produce non-linear relationships between absorbance and concentration (31).

After the sample has been ground, an optically pure pellet is produced in a vacuum die using 40 tons/in^2 pressure (13). Infrared scans over the 4000 to 200 cm^{-1} region are made for each pellet, using a blank KBr pellet as a reference.

Qualitative identification of minerals is based on the positions of absorption bands. Kaolinite and gypsum have been determined quantitatively (13, 20, and others). In this procedure standards containing various known amounts of the mineral to be quantified are prepared by the method described above, and calibration curves are constructed using specific absorption bands (e.g., 910 cm^{-1} for kaolinite). Gypsum is determined after heating the LTA to 500°C to convert the gypsum to anhydrite. The absorption band at 670 cm^{-1} is used for quantification (17). While detection limits are very good for some minerals, such as 1% for quartz and 2% for carbonates (30), there are some problems encountered with clay minerals. Kaolinite is easily identifiable but exhibits such sharp absorption bands that the diffuse bands of more poorly ordered minerals cannot be detected (13). Not only are there some difficulties in distinguishing between montmorillonite and illite (29), but also the spectrum of montmorillonite lacks strong diagnostic bands and thus low concentrations (less than 20 percent) may only be detected in the absence of kaolinite and illite (30). Despite these problems, various researchers (30, 42) have developed procedures facilitating clay identification by infrared.

Far infrared, defined as the 200 to 650 cm^{-1} region, complements the higher frequency region and contains absorption bands suitable for analytical purposes which are well resolved even in mixtures. This is particularly true of carbonates, pyrite and quartz (32). Thus, it should be of particular interest to those studying mineral matter in coal. Procedures for analysis of coal by far infrared, developed by Karr et al., (34) enable certain minerals (kaolinite, quartz, and gypsum) to be determined directly using the 650 - 200 cm^{-1} region without first removing the organic material. This is possible because there is no significant interference from absorption bands of organics in this region. The same procedures may be applied to low temperature ashes. The far infrared region is especially important in the analysis of pyrite, which has no absorption bands in the 5000 to 650 cm^{-1} region (34). In this type of analysis, cesium iodide (CsI) is used as a matrix rather than KBr. Detection limits by this method are good, particularly for carbonates. Gypsum may be detected down to 1-2% by weight, calcite down to 0.5-1%, kaolinite as low as 1-2% and quartz down to 1-2%. Pyrite, in the absence of kaolinite, may be detected down to 2% (34). Due to the almost ubiquitous nature of kaolinite in coal, however, detection limits of pyrite are not this low in reality. Other minerals detectable by far

infrared which shows no bands in the 5000 to 650 cm^{-1} region include marcasite (FeS_2), pyrrhotite ($Fe_{1-x}S$), halite (NaCl), fluorite (CaF_2), haematite (Fe_2O_3) and magnetite (Fe_3O_4) (34).

Analysis of Minerals by Fourier Transform Infrared Spectroscopy

Recently it has been shown that Fourier transform infrared (FTIR) spectroscopy can be applied successfully to the analysis of mineral matter in coals and coal products (38, 43, 44). Analysis by conventional infrared is hindered by the relatively small amount of energy throughput and the complex mineralogy of coal which produces overlapping absorption bands. FTIR overcomes the former problem by utilizing an interferometer rather than dispersive slits, thus energy throughput is 80-100 times greater than with the dispersive unit (45). Utilizing minicomputers and the Fourier transform, the interferogram is converted to a total spectrum from which subtractions of identified minerals can be made (38). Procedures for sample preparation are similar to those for conventional infrared. The unknown (usually as a low temperature ash) is mixed with either KBr or CsI and ground for at least 20 minutes. Large numbers of scans (400) are taken and co-added to produce a high signal-to-noise ratio spectrum (38). Spectra of standard minerals are obtained and for multicomponent systems, such as coal, these individual spectra may be subtracted from that of the coal. Quantitative analysis by this method is based on knowing the weight of the sample in the standard and the fraction of the spectrum that is subtracted (38).

One of the main problems with dispersive infrared analysis is the strong absorption by kaolinite which masks the presence of other minerals. Because the kaolinite spectrum may be subtracted, the use of FTIR tends to eliminate this masking problem. Another problem is the choice of absorption bands. Painter et al., (46) have shown that contributions from other clay minerals to the 910 cm^{-1} band, commonly used for kaolinite determinations by dispersive infrared, can result in overestimating the amount of kaolinite present. If the 910 cm^{-1} absorption band is attributed solely to kaolinite and subtractions are made to the spectrum to eliminate this peak, negative dips in the spectrum appear at 1010 and 1035 cm^{-1} (other kaolinite absorption bands) suggesting too much subtraction for kaolinite.

Painter et al., (47) have shown that the use of a least squares curve-fitting program greatly enhanced the accuracy of quantitative analyses of minerals in coal. Not only did this new program correctly identify and quantify a variety of clay minerals present in a sample, it also differentiated between kaolinites of different crystallinites and source. The ability of this equipment to discern minor differences between samples of a mineral such as kaolinite emphasizes the importance of careful selection of standard minerals. (S.M.R.)

C. Vertical and Lateral Variations of the IL Herrin (No. 6) Coal in Northwestern and West Central Illinois

The purpose of this study is to examine the vertical and lateral variability with respect to petrography and mineral partings of the Illinois Herrin (No. 6) coal for the areas of northwestern and west central Illinois. The depositional environments of the No. 6 coal in these two areas will be inferred mainly from the coal petrography and the two areas will be compared. The study should also elucidate the history of the development of the No. 6 coal swamp.

Sample Collection for the Summer of 1981

Planning is under way for the collection of additional coal column samples for the summer of 1981. Collection is being planned for 4 to 6 mines with from 6 to 10 columns to be collected. Samples will be obtained from mines located in west central and northwestern Illinois. It is intended to acquire samples from the Herrin No. 6 coal with the widest distribution possible in the two geographic areas under study. However, sampling also will depend upon accessibility of mines to our personnel.

(S.J.R. and A.D.)

D. Analysis of the Factors Controlling the Fluid Behavior of Lower Kittanning Seam Samples, Their Response to Oxidation, and Relationship to Liquefaction Behavior

Introduction

Understanding of the lateral variation in composition of coal seams of the Lower Kittanning can assist the ability to predict responses to various industrial processes. Interpolation between data points provides an interpretation of the general geological pattern existing within the coal bed. If this geological pattern can be explained, the powers of coal property prediction are greatly increased. In order to characterize and explain geological trends within an area, one should attempt to limit the number of natural possibilities by drawing upon previously established relationships.

Williams and Bragonier (48) have outlined the effects of four factors upon the patterns of sedimentation in basins of the Early Pennsylvanian of western Pennsylvania. These factors should affect the deposition of the coal as well as associated sediments. The first-order control was differential subsidence within the coal basin (Pittsburgh-Huntington Synclinorium) whereby the margin of the basin is topographically higher. The greatest subsidence occurred where the basement is now deepest, in the southwestern parts of western Pennsylvania. The second-order control was the existence of intermittent basement highs which are located around the margins of the basin and therefore modify the first order pattern. Third-order controls were growing folds and lineaments. The locations of these structures are shown in Figure 3. Williams and Bragonier (48) demonstrated that present-day folds were probably active during Pennsylvanian time. Lineaments such as those reported by Gwinn (49) and shown in

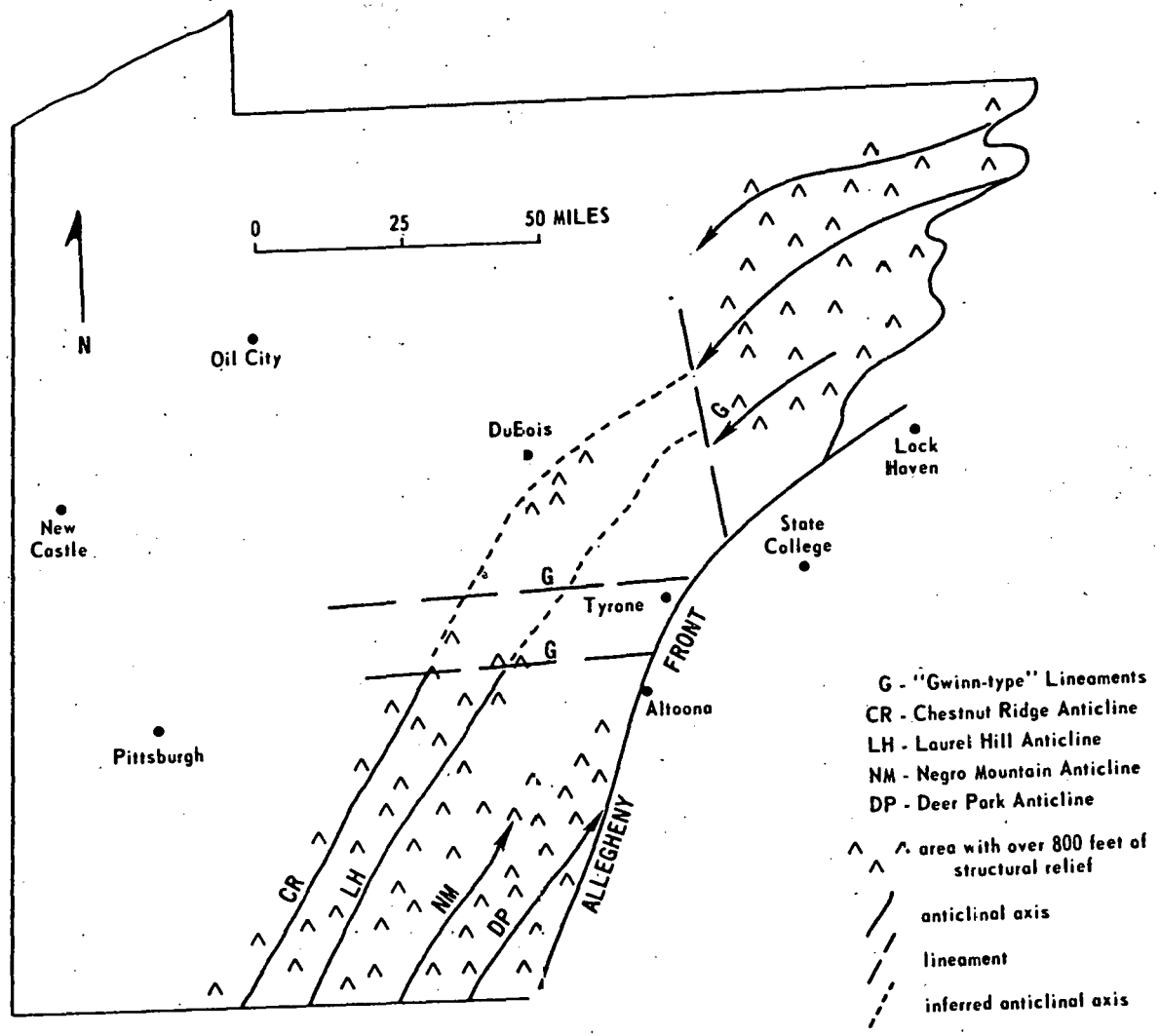


Figure 3. STRUCTURAL MAP OF THE ALLEGHENY PLATEAU (adapted from Gwinn, 1964)

Figure 3 have been interpreted by Williams and Bragonier (48) as commencing development in the Pennsylvanian and exerting controls on subsequent sedimentation. The fourth-order controls were local paleotopography caused by erosion, differential sedimentation and compaction. These factors provided only limited control of general geological trends because their effects were of relatively small scale.

The controls on deposition are complex and it may be impossible to derive a full and accurate interpretation of the controls affecting the deposition of a coal bed. Superimposed upon the controls of deposition, one must consider post-deposition alteration and metamorphism of the coal. Chemical composition of both the organic and inorganic fractions of the coal changes systemmatically with rank.

Using the previously established relationships outlined above, an attempt has been made to explain the geological trends in the Lower Kittanning seam.

Experimental

In this study a total of 123 coal samples from the Lower Kittanning seam were used to determine the geological and compositional trends in Western Pennsylvania. The sample set included data for 42 coal samples included in the Penn State Sample Bank and for 81 samples from the Pennsylvania Geological Survey (50, 51, 52). The locations of the samples are shown in Figure 4.

In order to objectively illustrate the geological patterns in the study area, the data was contoured using the Surface II Graphics system, a spatial analysis computer program written at the Kansas Geological Survey for the IBM 370 computer (53)..

The variables used in the regional study were coal seam thickness, sulfur, ash and volatile matter. In addition, trends in the mean maximum reflectance were illustrated using only the 42 coals from the Penn State Sample Bank. The results of these analyses are presented in Figures 5-9.

Results and Discussion

Thickness of Coal Seam

The isopach map of the Lower Kittanning seam is presented in Figure 5. The seam is thinnest at the northwestern region of the study area and thickens toward the east-southeast. The coal thickens in three areas; the northeast margin, the southeast margin and the southwest portion of the study area. The area of thickening in the southwest coincides with the center of the depositional basin but the contouring for this area is based on a very limited number of samples and requires confirmation with additional information. There is a relative thinning of the coal along the eastern margin (Altoona-Tyrone Area) between the two areas of thickening to the northeast and southeast. This area of relatively thin coal coincides with the area in which Gwinn has found sets of east-west and a north-south trending lineaments (49). Such lineaments represent zones

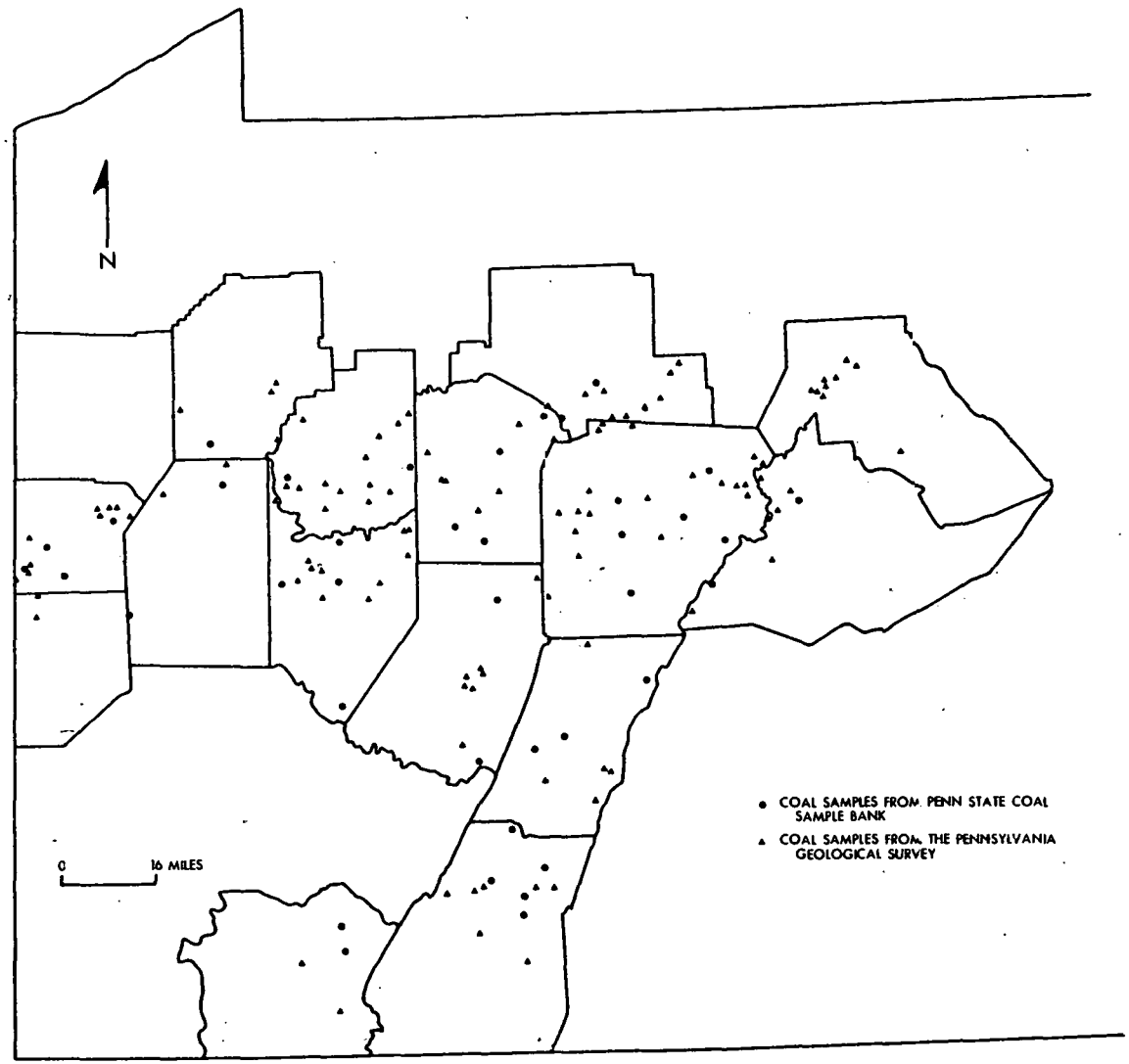


Figure 4. SAMPLE LOCATION MAP

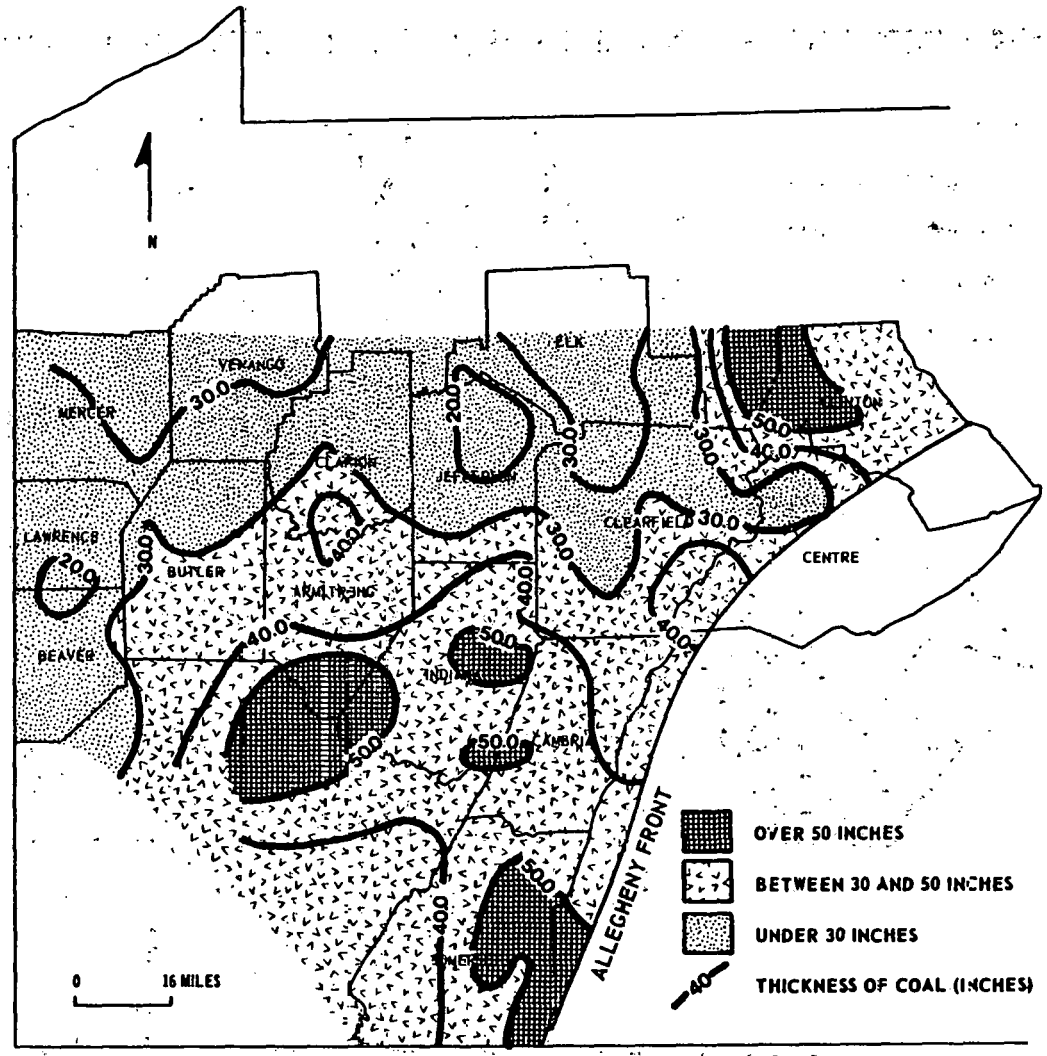


Figure 5. GENERALIZED THICKNESS MAP OF THE LOWER KITTANNING SEAM

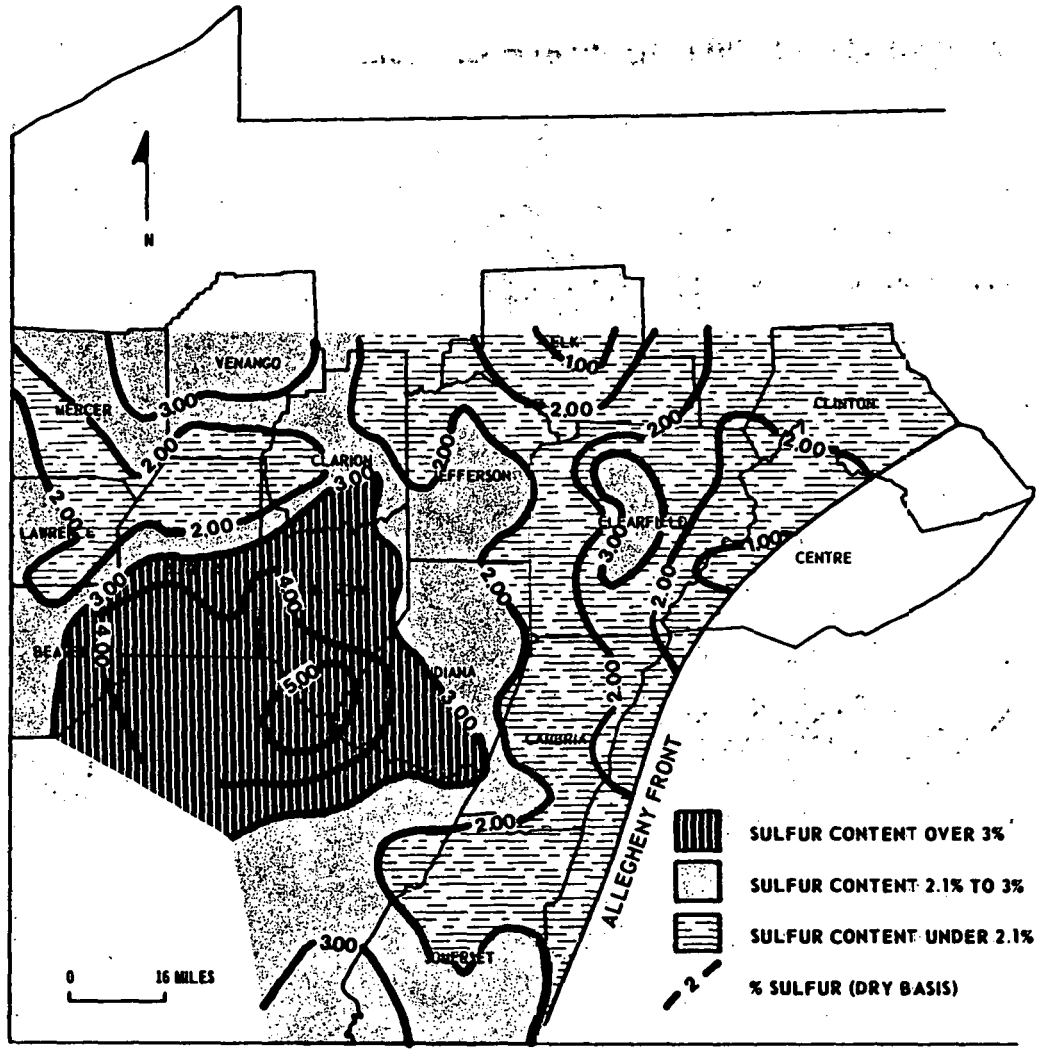


Figure 6. GENERALIZED SULFUR CONTENT OF THE LOWER KITTANNING SEAM

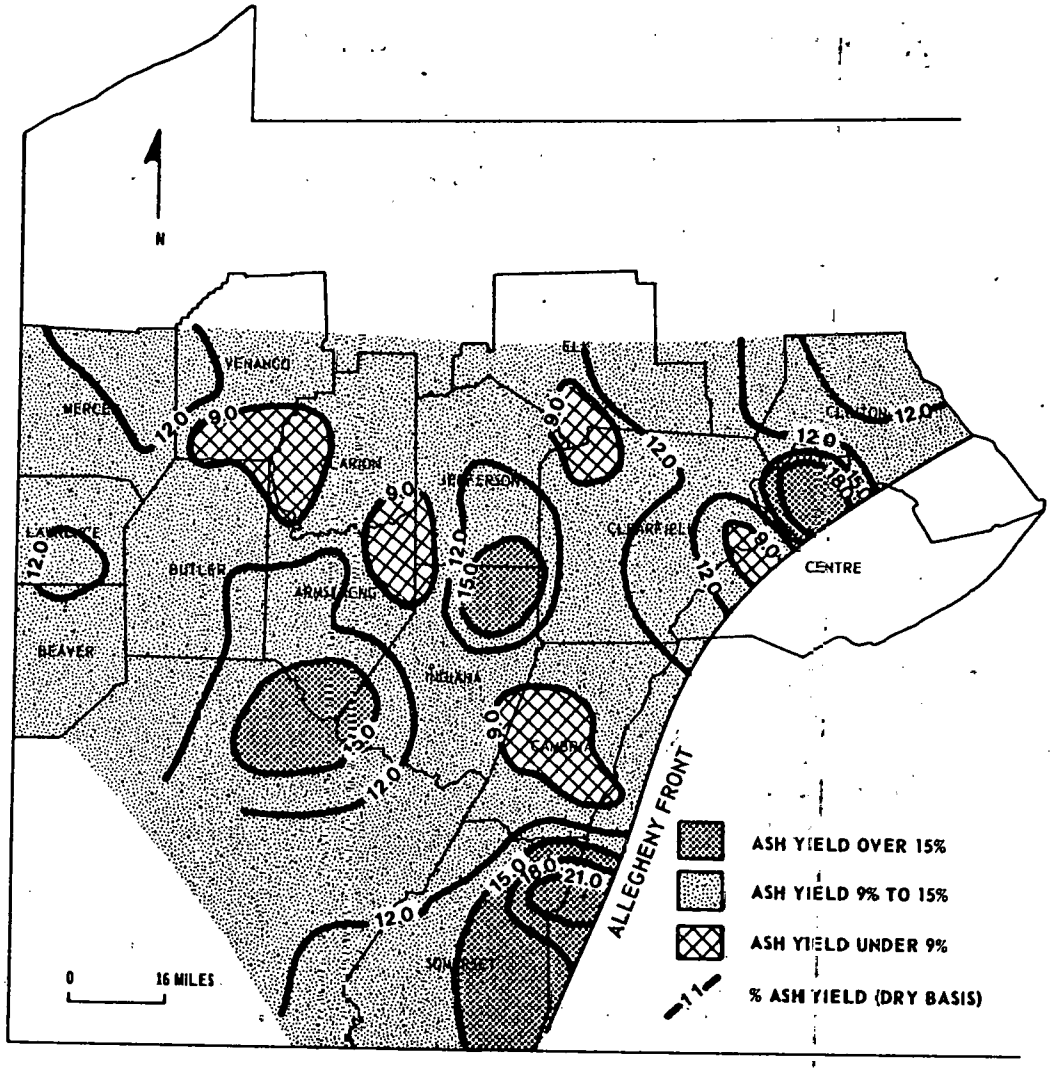


Figure 7. GENERALIZED ASH YIELD OF THE LOWER KITTANNING SEAM

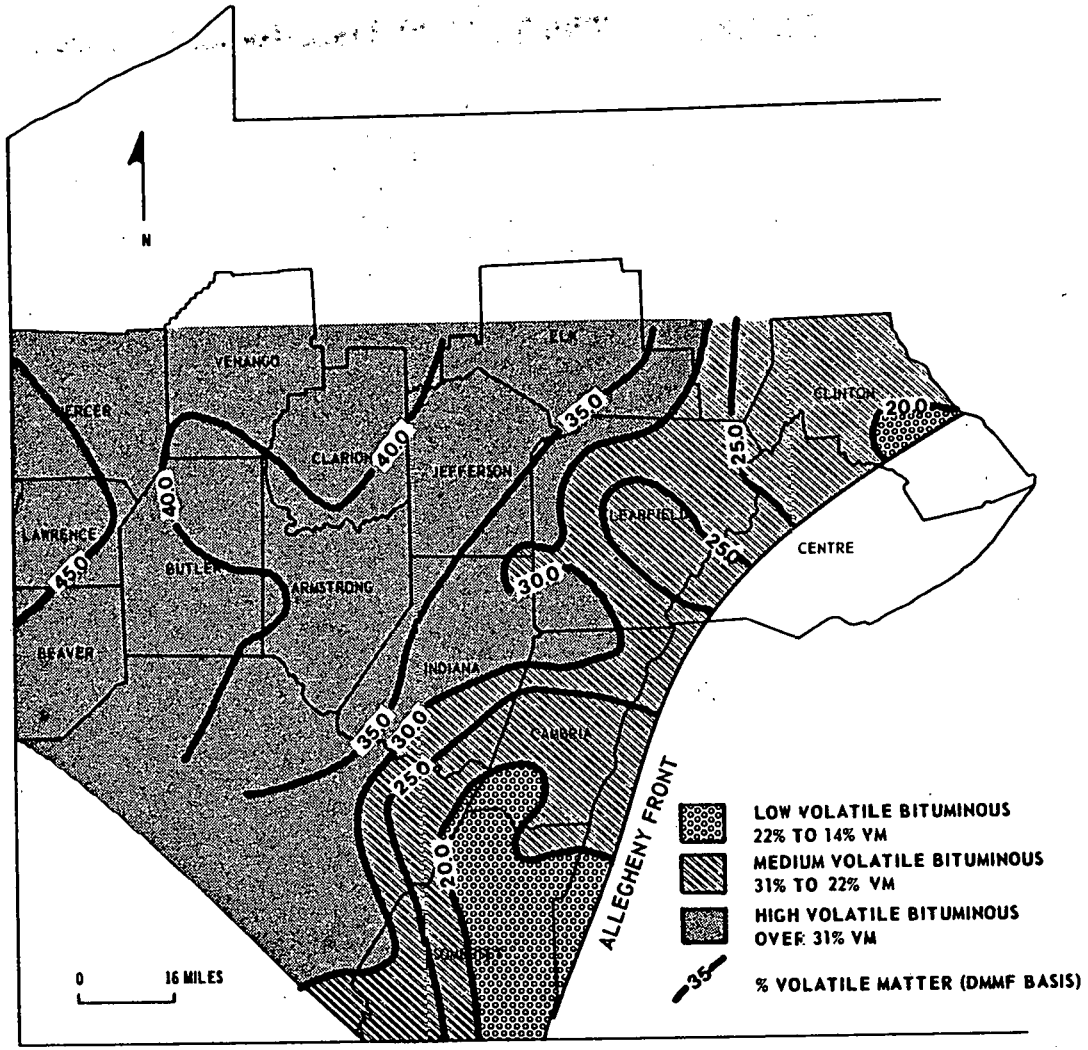


Figure 8. VOLATILE MATTER AND COAL RANK OF THE LOWER KITTANNING SEAM

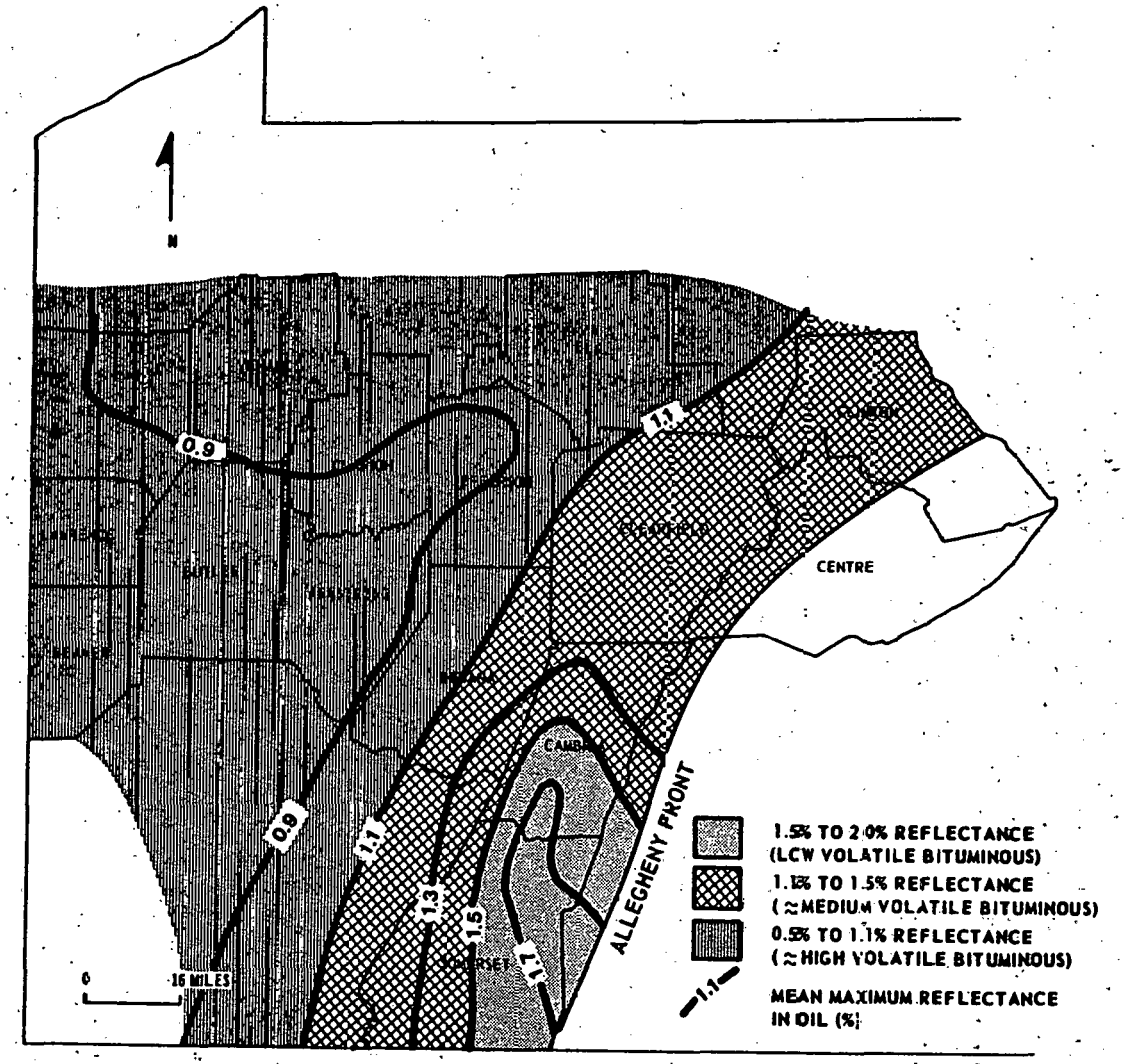


Figure 9. REFLECTANCE VARIATION OF THE LOWER KITTANNING SEAM

of structural offset and marked structural relief, tectonic factors which controlled sedimentation in the Pennsylvanian.

Holbrook (54) studied the mineralogy of the Lower Kittanning underclay in western Pennsylvania and he demonstrated that the real variability of the underclay is closely related to the paleotopography. His results (Figure 10) show high kaolinite contents in the northeast and southeast regions of coal thickening. It is logical to suggest that the variation in the composition of the underclay was controlled by those same processes controlling the deposition of the coal. High kaolinite contents are associated with documented paleotopographic highs (54). This suggests that the thinning of the coal may be related to a deepening of the water in the peat swamp in the Tyrone-Altoona area. Consequently, it is suggested that the area around the "Gwinn-type" lineaments was an area of higher subsidence relative to adjacent areas.

Distribution of Sulfur

The distribution of sulfur is presented in Figure 6. Apparently sulfur values above 3 percent are restricted to the southwest, along the axis of the depositional basin.

Williams (55) described the character and distribution of invertebrate fossils in the shales overlying the Lower Kittanning seam of western Pennsylvania. He found areas of marine fossils which extended in a belt trending east-west and northeast-southwest across the central part of the Lower Kittanning basin. This belt was bounded on the northwest and southeast by areas of brackish or restricted marine fossils. The southeast was further bounded by fresh-water fossils. This study has given direct indication of the sedimentary environments existing during deposition of the shale, and somewhat indirect indication of the depositional environments of the underlying Lower Kittanning coal.

Williams and Keith (56) demonstrated a regional correlation between the pyritic sulfur content in the Lower Kittanning seam and the facies of the overlying shale. They noted that the pyritic sulfur content is higher under the marine facies and lower under the freshwater facies. The sulfur data presented in Figure 6 corresponds in a general way with the observations of Williams and Keith (56). The sulfur distribution suggests that the basin was more marine along the axis and progressively more non-marine toward the margins of the basin. Further support of this hypothesis is presented by Holbrook (54) who found a low kaolinite/mica trend in the underclay directly beneath the Lower Kittanning seam in a zone approximately between DuBois and Butler (Figure 10). This trend directly corresponds to the most marine fossils within the root shales, suggesting that a paleotopographic low and a marine environment existed in this area during and after the formation of the Lower Kittanning underclay.

Distribution of Ash

Figure 7 shows the areal distribution of ash values for the Lower Kittanning seam of western Pennsylvania. The ash is fairly uniform throughout the western portion of the study area. Along the eastern

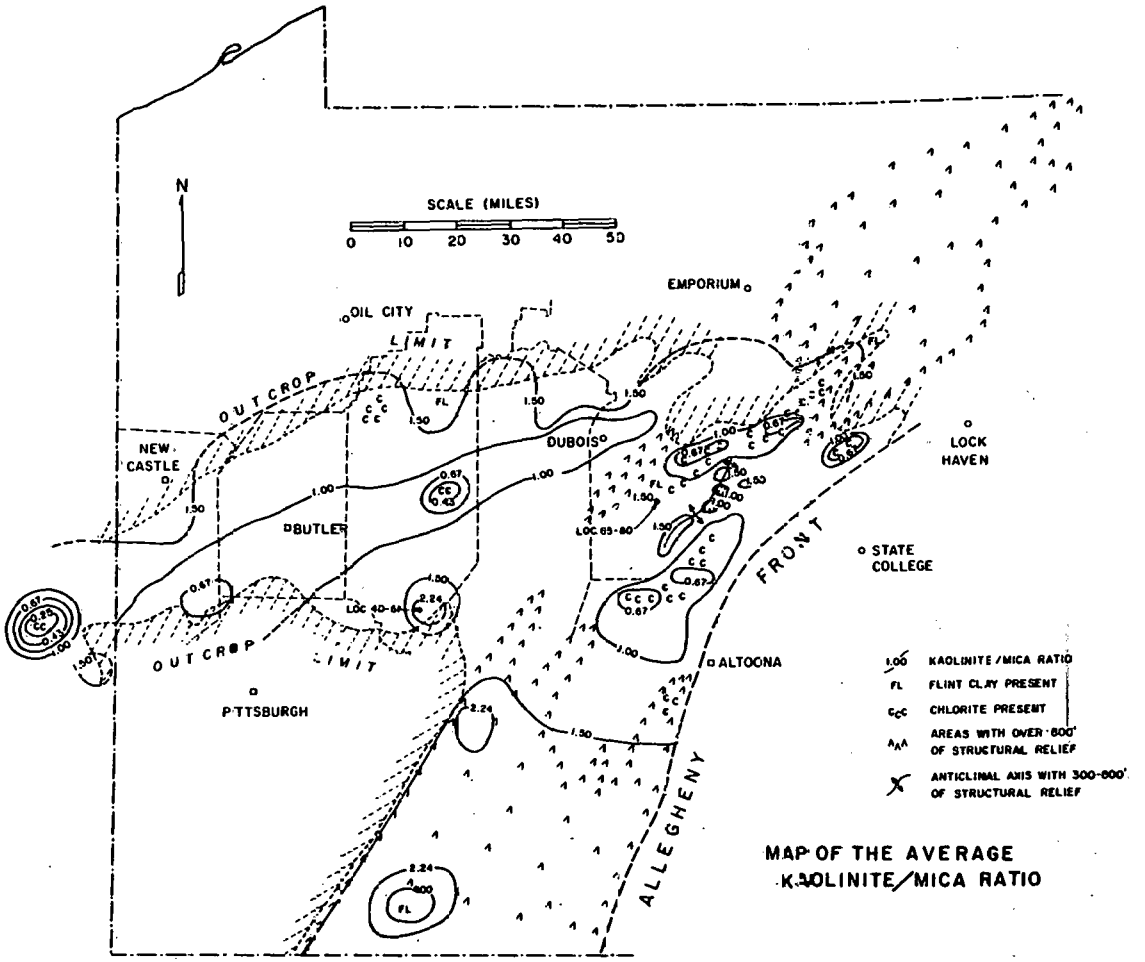


Figure 10. CONTOUR MAP OF THE AVERAGE KAOLINITE/MICA RATIO FOR THE LOWER KITTANNING UNDERCLAY (from Holbrook, 1973)

margin of the basin, the values are high in the southeast and northeast, and there is a low in ash content in the Tyrone-Altoona area.

The mineral matter which comprises the ash may originate in three ways. Firstly, it can be derived from the vegetable material of the original plants. Secondly, it can form during deposition of the peat (syngenetic), and thirdly, it can be deposited after the consolidation of the coal from migrating groundwater (epigenetic). Minerals deposited by any of these three means may subsequently undergo alteration to a secondary mineral.

The distinction between syngenetic and epigenetic materials may be difficult. The frequency of deposition of cleat pyrite, assumed to be epigenetic, tends to be greatest along the axis of the basin (corresponding to the marine facies of the overlying shales). The anomolous high ash areas along the eastern margin of the basin appear to be related to syngenetic mineralization. Cleat pyrite was rarely observed in these areas, and actually the sulfur content is relatively low (possibly a reflection of the freshwater facies in the overlying shales).

The two major factors which influence the amount and distribution of sediment into a basin are:

1) amount of sediment available
2) relief (energy) of the hinterland

The two anomolous ash highs may be due to proximity to the areas of sediment source. Conversely, the ash low in the Tyrone-Altoona area could result from the presence of a barrier to sediment migration, possibly in the form of a paleotopographic high. Holbrook (54), however, has suggested that this area was probably a paleotopographic low, basing his conclusion on the kaolinite content of the underclays.

It is proposed here that depositional centers were present in the areas of high ash content. It is in these areas that the amplitude of folding in the Appalachian mountains is most severe (Figure 3).

Distribution of Volatile Matter

The areal distribution of volatile matter is illustrated in Figure 6. It increases from 45% at the western border of Pennsylvania to less than 20% at the eastern margin of the basin. Volatile matter lows occur to the northeast and southeast, and an anomolous high occurs in the Tyrone-Altoona area. Similar trends were observed by Stadnichenko (57).

The data suggest that the controls which influence the pattern of deposition in the Lower Kittanning coal basin may also have influenced the metamorphic (rank) changes in the area.

Variation of Reflectance

The areal distribution of mean maximum reflectance of Lower Kittanning seam samples across western Pennsylvania are given in Figure 9. Overall

the reflectances increase from 0.8% at the western border of the state to 1.3% at the eastern margin of the basin. A distinct reflectance high is seen to the southeast (Somerset and Cambria County) with reflectances up to 1.7%. This area corresponds to a volatile matter low present in Figure 8.

Hower (58) studied the variation in reflectance in western Pennsylvania. He also observed an increase in reflectance in the Somerset and Cambria county area. Using reflectance data he calculated that a geothermal gradient difference of 10°C/km existed between the area of high rank and western Pennsylvania. He concluded that the eastwardly increase in rank is due to an elevated geothermal gradient rather than to depth of burial.

Conclusions

The purpose of this work was to elucidate some of the general geologic trends present within the Lower Kittanning coal seam as a means of interpreting some of the principal controls of coal sedimentation. Further, reflectance and volatile matter were examined for trends in the coalification rates within the basin.

The strongest controls to sedimentation appear to have occurred along the eastern margin of the basin in the form of differential subsidence. A break in this control occurred in the vicinity of the "Gwinn-type" lineaments where the coal tends to thin and the ash value is low relative to the adjacent areas; a paleotopographic high in this area is proposed to have controlled the sedimentation here. Holbrook (54), however, has presented data on the Lower Kittanning underclay which suggest that the area was a paleotopographic low at the time of coal deposition. Regardless, the "Gwinn-type" lineaments appear to have created changes in the structural relief through structural offsetting in this area.

The rank of the Lower Kittanning seam increases from west to east. Volatile matter variation illustrates that the degree of coalification in the area of the "Gwinn-type" lineaments was relatively lower than the areas to the north and south. This suggests the possibility that the controls which influenced sedimentation may also have effected coalification in these areas.

Future Work

General trends in carbon, hydrogen, nitrogen and oxygen content of the Lower Kittanning seam are currently being studied.

(J.T.S. and A.D.)

8. OPTICAL PROPERTIES OF COALS

Introduction

The goal of this research is to compare the optical properties of vitrain concentrates from the Eastern Interior coal region with vitrains of similar rank from the Lower Kittanning seam in the Appalachian basin. Reflectance will be measured at five wavelengths (402, 475, 546, 625, 701 nm) in the visible spectrum in both air and oil. From these the absorption and refractive indices can be calculated and their dispersion curves plotted.

Sources of Error in the Measurement of Reflectance

Before commencing to make reflectance measurements on vitrain samples it is advisable to examine the optical system and the standards for sources of error that could detract from the accuracy of the measurements. The following is a summary of possible sources of error and an enumeration of procedures that should allow these to be measured or minimized before data collection begins.

Instrument Error

Instrumental error includes errors originating the source of illumination, the optical system and the photomultiplier. Some of these can be controlled by adjustment of the system while others must be measured and subtracted from subsequent measurements.

Before examining the effects of other factors in the system, the optical system should be checked for proper alignment. Procedures for accomplishing this are outlined by Davis (59), Galopin and Henry (60) and Piller (61). Light should be allowed to pass through to illuminate the specimen without adding effects due to scattering or glare.

Even in the absence of a source of illumination a certain amount of current may be produced by the measuring system. This is dark current which is mainly the result of thermionic emissions from the photomultiplier tube (61). Cooling the photomultiplier decreases the amount of dark current produced. Dark current values can be eliminated from measuring results by setting the voltmeter to zero while the dark current is being registered, or by including dark current in the correction for back reflectance.

Noise can be detected as variations in the measured value of an unchanging object. It is caused by fluctuations in the electrical supply or intensity of the light source, mechanical vibrations, and variations in the performances of the various electronic components of the system including photomultiplier noise (61). The effect of noise is greatest on reflectance measurements when the sampling time (time in which a measurement is made) is short with respect to the periodicity of the noise.

Back reflectance or primary glare is the amount of incident light that is reflected back to the photomultiplier from the surfaces of lenses in

the system. Because this light never reaches the specimen it is a spurious addition to the measured reflectance of the specimen and must be subtracted for accurate measurement. The combined effects of back reflectance and dark current for a particular wavelength can be measured by focussing the objective into a non-reflecting void containing air or oil (depending on the medium to be used). The measured value of this non-reflecting object is the amount of back reflectance in the system which may then be subtracted from all measurements at that wavelength providing the experimental conditions are not varied (60, 61).

The photomultiplier may not react linearly to changes in radiant flux across its range of sensitivity. One way to test the linearity of the system is to vary the radiant flux a known amount by inserting a neutral density filter of known transmittance and observe if the quantity measured by the photomultiplier changes by a proportional amount (61). The entire range of sensitivity of the apparatus may be tested by performing this test with filters of different transmittances at a number of voltages across the range of sensitivity of the photomultiplier.

A second test of linearity employs a set of standards of known reflectance. Each standard in succession is used as the primary standard and the reflectances of the other standards are measured with respect to the primary standard. When the measured reflectance values are plotted versus the calculated values any systematic deviation from a line at 45° to the axes may be assumed to be the result of nonlinearity of the photomultiplier. Random deviations from the described line may be attributed to imperfection of the set of standards used. Once again the amplification of the photocurrent may be changed to look at the full range of sensitivity of the instrument.

Monochromator Error

The monochromatic filters to be used for this study are precision band interference filters manufactured by the Schott Optical Glass Company. According to the manufacturer (62) these have maximum transmittances of 0.45 to 0.58% and pass band widths of 20 to 22 nm at one-half maximum transmittance. The manufacturer's specifications note that tilting of the filter with respect to the optical axis of the microscope will cause the transmitted beam to be displaced toward lower wavelengths. The displacement observed is minimal (at most 2 nm) for angles of less than 10°, but becomes more significant as the angle of tilting is increased. In addition, tilting causes the beam to be split into two overlapping pass bands polarized perpendicularly to one another. Splitting increases the width of the pass band transmitted by the filter and is more pronounced at higher angles of tilt.

The observer needs to be concerned only with the spreading and displacement effects of tilting. Splitting of the pass band should not change the results because the filter is located adjacent to the photomultiplier and does therefore not affect light incident on the stage object. In addition, the photomultiplier is not sensitive to changes in polarization direction versus phase so changes in these should not affect reflectance values.

Standardization Errors

Standards used for reflectance measurement should be chemically stable, mechanically resistant, homogeneous, isotropic and should display a fairly linear reflectance curve in the range of wavelengths at which measurements will be made. A clean, scratch-free, level surface gives the most consistent, reliable values of reflectance. Deviations from these ideal conditions will introduce error into the reflectance measurements.

Standard reflectances are calculated from the refractive index reported by the manufacturer for each wavelength. When measuring the reflectance of coals, standards are selected whose calculated reflectance values bracket the expected reflectance values of the coal at that wavelength. Choosing standards as close as possible to the actual reflectance of the coal minimizes errors due to nonlinearity of the system and secondary glare (see below).

Secondary glare is a function of the relative reflectances of the standard and the specimen. It is the result of multiple reflections between the stage object, whether standard or sample, and the objective before the high is transmitted back to the photomultiplier. The effect of secondary glare may be to increase or diminish the apparent reflectance of the specimen relative to the primary standard depending on whether the specimen is of higher or lower reflectance than the standard. If the reflectance of the specimen is less than the standard, an incorrectly low reflectance will be measured for the specimen, whereas an incorrectly high value will be recorded when the standard is of lower reflectance than the specimen. Galopin and Henry (60) explain the phenomenon in detail and suggest several procedures, both calculated and graphical, for determining the actual value of secondary glare effects. In general, secondary glare may be minimized by reducing the illuminated field of the specimen to no more than two times the measuring area.

Procedural Errors

It is important that the standards and specimens be properly levelled when they are measured. A tilted surface will cause scattering of the reflected beam and result in incorrect measurements. One means of checking the levelling uses the Bertrand lens to view the conoscopic image of the aperture diaphram while the stage is rotated (60, 61). Movement of the image indicates that the surface is not level. Piller (61) enumerated a number of types of levelling equipment that may be employed if levelling with the hand press is insufficient.

Correct focussing is also very important during reflectance readings. Galopin and Henry (60) have noted that within the range of the depth of focus of a microscope the measured reflectance value changes very little, but outside the depth of focus a small change in focussing height will cause a large change in reflectance. Consequently, it is important to focus the microscope each time a measurement is made.

Errors due to the influence of temperature variation in the measurement of oil reflectance may be considerable only if the standard and unknown have significantly different reflectance values. Providing the standard and coal specimen are close in reflectance, it is valid to consider the refractive index of the immersion oil as being that at its 23°C reference value.

Finally, stray light from the room may cause fluctuations in reflectance measurements. Therefore, it is best to perform the measurements in a darkened room and to block any parts of the microscope through which stray light is likely to enter the measuring system.

Preliminary Testing and Procedures

In view of the sources of error described above, a number of testing procedures and precautionary measures will be carried out before data collection begins. Those to be performed include:

1) Alignment of the system, including filters. This check should be performed periodically.

2) Determination of back reflectance and dark current contributions to measured values at each wavelength by recording the reflectance of a non-reflecting void filled with air or oil.

3) Estimation of the linearity of the system by its response to

   a) changes in transmittance using a set of neutral density filters

   b) changes in reflectivity of a set of standards with each used as the primary standard in succession.

Both tests will be performed at various voltages through the range of sensitivity of the photomultiplier.

4) Comparison of the sampling time with the periodicity of noise in the system to ensure that the sampling time is sufficient to average out noise.

5) Determination of the amount of secondary glare produced for various differences in reflectance between the standards and the specimens.

6) Verification of standard reflectance values obtained from dispersion curves of refractive index versus wavelength.

7) Checking of levelling devices and addition of more sophisticated levelling techniques if necessary.

8) Elimination of stray light from outside sources.

Experimental Method

Equipment

Mean maximum reflectance measurements will be carried out on a Leitz Orthoplan MPV-2 microscope equipped with a rotating stage. A Digital Equipment Corporation model PDP-8/A computer is being used to create the reflectance program and record the data. Details of the microscope equipment and computer facility can be found in Kuehn and Davis (63) and Hoover and Davis (64)

A 50X immersion oil objective and a 20X air objective will be used to measure reflectance. The photomultiplier aperture will be adjusted so that at each magnification a 16 μm^2 area will be measured.

Four Schott and Gen. light filters with wavelengths of 402, 475, 625, and 701 μm will be used for this study in addition to the standard wavelength filter of 546 nm.

A Leitz hand press will be used to level the coal pellets for microscopic examination. To check the levelling, the pellet will be placed on the microscope and a vertical and horizontal traverse will be made across it. If the pellet does not remain in focus, it will be levelled again. Other tests of levelling will be performed as outlined above.

A set of five Schott glass standards will be used to calibrate the system. A dispersion curve was constructed for each of these glasses to determine the refractive index values in air and oil at the five wavelengths mentioned above. The reflectance values were determined by the Fresnel equation where absorption (k) is negligible:

$$R = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

R = reflectance of the standard
n_2 = refractive index of the standard
n_1 = refractive index of the medium (air or oil)

Leitz 500 immersion oil will be used, and a dispersion curve has been constructed for it to determine its refractive index at the five wavelengths. The refractive index and reflectance values for the glass standards as well as the refractive index of the immersion oil at these wavelengths are included in Table 6. Since the refractive indices of the immersion oil were determined at 23°C, a temperature versus refractive index chart was constructed to adjust for temperature variation, if necessary.

Determining the Number of Sample Points

Before the study commenced, the most efficient number of sample points for mean maximum reflectance in air and oil has been determined. A concentrate with a good range of reflectance values was chosen for this study. Thirty readings were taken with the standard 546 nm filter in both air and oil immersion. Mean maximum reflectance, standard deviation and 95% confidence limits were calculated for each sample point. The 95% confidence

Table 6. Refractive Index and Reflectance of the Glass Standards and Refractive Index of the Immersion Oil at Specified Wavelengths

		WAVELENGTH (nm)									
Refractive Index of the Glass Standards		402		475		546		625		701	
Glass Number	Schott Catalogue Number										
2	SF13-741276	1.7945		1.7638		1.7477		1.7365		1.7298	
3	LaF12-836423	1.8708		1.8508		1.8400		1.8319		1.8267	
4	LaSF9-850322	1.9013		1.8717		1.8567		1.8461		1.8390	
6	LaSF6-961349	2.0113		1.9830		1.9670		1.9557		1.9485	
Reflectance of the Glass Standards, %		air	oil	air	oil	air	oil	air	oil	air	oil
2		8.083	0.595	7.637	0.529	7.405	0.495	7.244	0.451	7.147	0.425
3		9.201	0.956	8.907	0.933	8.748	0.919	8.630	0.908	8.553	0.901
4		9.650	1.119	9.214	1.044	8.993	1.007	8.838	0.982	8.734	0.966
6		11.278	1.782	10.859	1.707	10.622	1.660	10.455	1.627	10.348	1.608
Refractive Index of the Leitz 500 Immersion oil at 23°C		----	1.5375	----	1.5247	----	1.5130	----	1.5132	----	1.5099

limits were plotted agains the number of sample points for each medium (Figures 11 and 12) as recommended by Griffiths (65). The curve for oil reflectance falls within the ASTM accepted limits of $\pm$ .02% reproducibility at 14 sample points. Three times as many measurements would be needed to cut this error in half again. For practical purposes, the number of measurements chosen for oil immersion is 20, the point where the curve becomes shallow. The curve for air reflectance shows an inflection point at 6 sample points with a confidence interval of $\pm$ .08%. In order to reduce this confidence interval to half, 4 times the number of points would be required. The accepted ASTM standard error would not be reached until a very large number of points had been measured. However, when the coefficient of variation (standard deviation divided by the mean) is determined for each of the points, it is observed that the reflectance readings in oil are over twice as variable as those taken in air:

oil - .032/1.484 = .022

air - .095/10.266 - .009

This is probably due to the relatively larger effect of electronic noise on the smaller reflectance values in oil. The variability of the air measurements never approaches that of the oil even when the number of sample points is reduced to 2. Ten has been chosen as the number of measurements for reflectance in air.

Hower (58) did a similar study to determine the effective number of sample points using a rank suite of coals and calculating a mean maximum reflectance in oil and standard deviation every 10 readings (5 readings per pellet). He found that the mean maximum reflectance in oil can be determined from 25-30 sample points. In most cases the standard deviation did not improve after 10 readings.

Calculations

Reflectance of an absorbing medium such as coal can be determined from Beer's equation:

$$R = \frac{(n_2 - n_1)^2 + n_2^2 k_2^2}{(n_2 + n_1)^2 + n_2^2 k_2^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

where n_2 = refractive index of the coal
n_1 = refractive index of the medium used (air or oil)
k_2 = absorptive index of the coal

When reflectance is measured directly against glasses of known reflectance, a modification of Beer's equation can be used to determine the refractive and absorptive indices of the coal:

$$n = \frac{1/2\ (n_o^2 - 1)}{n_o \left(\frac{1 + R_o}{1 - R_o}\right) - \left(\frac{1 + R_a}{1 - R_a}\right)} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

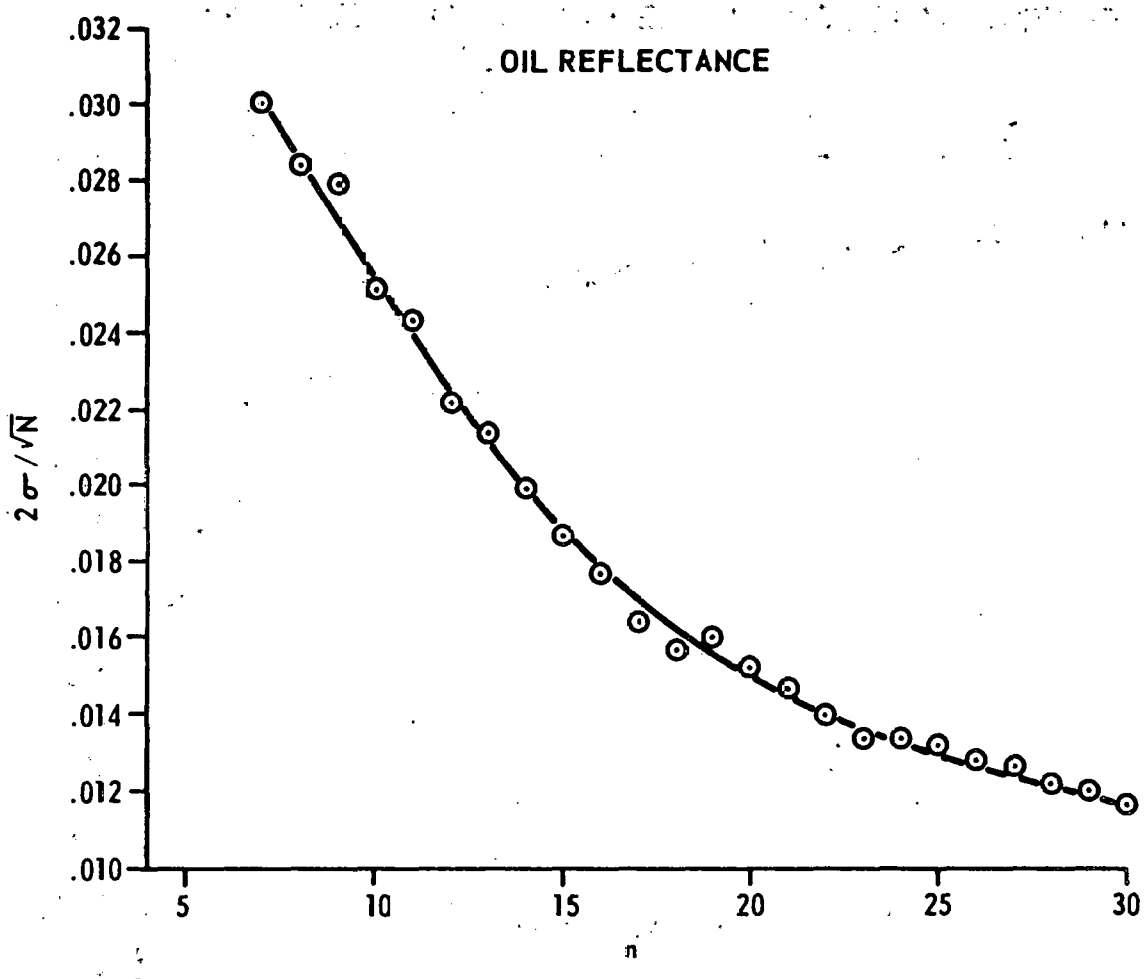


Figure 11. RELATIONSHIP BETWEEN STANDARD ERROR AND SAMPLE SIZE FOR PSMC-52

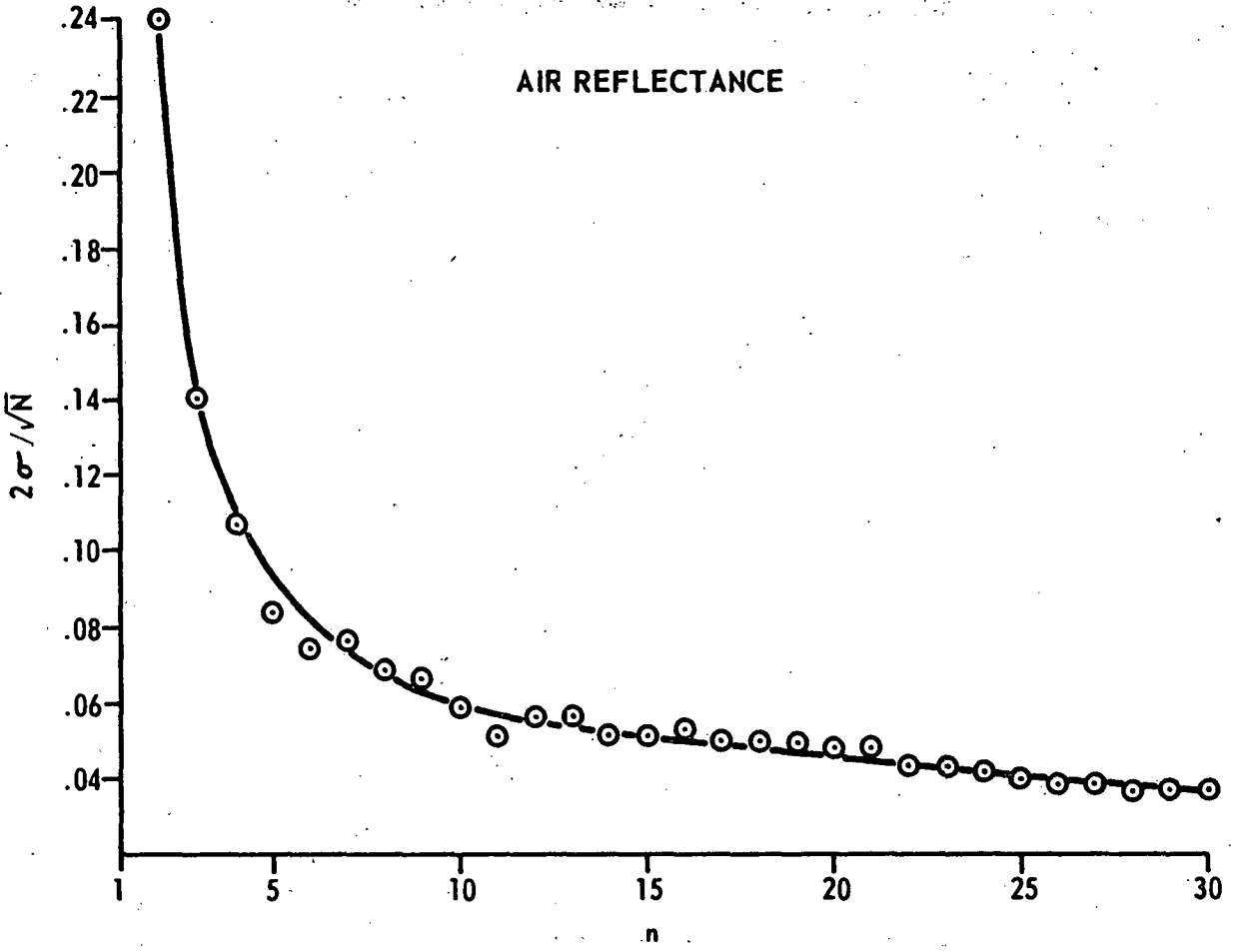


Figure 12. RELATIONSHIP BETWEEN STANDARD ERROR AND SAMPLE SIZE FOR PSMC-52

where n_o = refractive index of the immersion oil
R_o = reflectance of the coal in oil
R_a = reflectance of the coal in air

$$k^2 = \frac{R_a (n + 1)^2 - (n - 1)^2}{n^2(1 - R_a)} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

Most of the authors discussed in the previous quarterly technical progress report (DOE-30013-3) determined the refractive and absorptive indices of their coal samples from paired reflectance readings. That is, the exact spot in the coal maceral was measured in 2 different media. Jakeman and Cook (66) felt that this was the only correct procedure because refractive index is not a linear function of reflectance. Therefore, they claimed, an accurate refractive index value could not be obtained simply by taking a number of reflectance readings in air, then in oil, and using the mean reflectance values in the determination. To see how much the 2 methods differ, the refractive index was determined both ways using the reflectance data of Jakeman and Cook (66). At each wavelength the results were identical to the hundredth decimal place. A more precise comparison could not be made. In order to determine the amount of variation that might be found in the 2 procedures, 10 paired readings were taken on a vitrinite concentrate and the refractive index as calculated for each pair of readings then averaged, and from the two mean reflectance values. The results are contained in Table 7. The two refractive indices were identical to the thousandth decimal place. The conclusion reached here is that theoretically Jakeman and Cook (66) are correct in saying that refractive index is not a linear function of reflectance, but when dealing with such a small range of reflectance values from a single coal sample, the error in calculating refractive index from mean reflectance values is not significant. Therefore, for practical purposes, the study will be done in this simpler way.

Procedure

The procedure employs an interactive computer program giving the user control of the system. Several operator input variables, such as sample name, glass standards, wavelength, number of readings, and air or oil medium, are available. An automated calibration routine, where the computer reads back the standard reflectance value, will also be used. The reflectance data and operating parameters will be stored on disk for subsequent data manipulation.

Reflectance in air will be performed first. Using the 546 nm filter, the glass standards will first be checked for linearity. The 402 nm filter will then be placed in the microscope and the system recalibrated using the automated routine. A 0.5 nm grid system will be employed in the selection of vitrinite particles for maximum reflectance. After ten readings, the 475 nm filter will be inserted, the system will be recalibrated and ten more readings will be taken with different grid coordinates to ensure that the measurements are independent. This procedure will be repeated for the remaining three wavelengths.

Table 7. A Comparison of Two Methods for Determining Refractive Index

Reflectance in air	Reflectance in oil	Reflectance Index for paired readings
10.166	1.575	1.917
10.205	1.537	1.929
9.945	1.491	1.901
10.114	1.519	1.919
9.880	1.449	1.899
9.938	1.456	1.906
10.108	1.541	1.915
9.737	1.456	1.879
9.867	1.497	1.889
9.828	1.438	1.894
Mean Values		
9.979	1.496	1.905
Refractive Index of mean reflectance values:		
1.905		

For reflectance in oil, back reflectance will be checked and corrections made if necessary. Other than increasing the number of readings to 20, the procedure will be the same as that done for air.

Conclusions

In order to determine an efficient amount of sample points for this study, 30 reflectance readings were made on a vitrinite concentrate in both air and oil. From the curves of 95% confidence limits versus number of readings, 10 and 20 were the numbers decided upon for air and oil immersion, respectively.

Ten paired readings were taken on a vitrinite concentrate and the refractive index was determined from the average of 10 refractive indices and from the mean reflectance values in air and oil. Both were identical to the thousandth decimal place. Probably because of the small range of reflectance values for a single coal sample, the difference in the values were not significant.

(J.A.T., D.W.K. and A.D.)

9. THE CHARACTERIZATION OF COAL MACERALS BY FTIR

In a preceeding quarterly technical progress report (DOE-30013-2) we critically discussed the problems associated with the quantitative determination of functional groups by infrared spectroscopy. Particular attention was paid to the measurement of O-H and C-H groups. Our preliminary analysis can be summarized as follows:

1) The measurement of aliphatic and aromatic C-H groups is limited by the absence of good extinction coefficients. In part, this is because previous studies have relied on measuring the integrated area in a given region of the spectrum, for example between 3000 and 2800 cm^{-1} for aliphatic C-H. This procedure essentially assumes that the extinction coefficients of overlapping bands in this region are the same. A close examination of the literature reveals that this is not the case. Consequently, the differing values of extinction coefficients obtained by various researchers using different coals is not surprising.

2) Previous determinations of hydroxyl groups have relied on measuring the intensity of a band near 3450 cm^{-1}. Such measurements are complicated by the presence of water and effects due to hydrogen bonding. We demonstrated that a superior method for hydroxyl determination was by combining acetylation with FTIR procedures. This procedure allows us to distinguish between phenolic and alkyl OH groups with the added bonus of also measuring NH groups.

The key to using FTIR in these studies is to obtain appropriate extinction coefficients. We are proposing to accomplish this end in a novel fashion. Essentially total hydrogen content of each sample will be equated to the sum of the intensity of a number of bands, multiplied by a conversion factor (equivalent to an extinction coefficient converted to weight units);

$$H = \sum_n I_n e_n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

where H is the weight percent hydrogen content,
I_n is the intensity of the n^{th} band (e.g. a band assigned to CH_2 groups), and
e_n is a conversion factor relating band intensity to the weight percent hydrogen present as this specific functional group.

Curve-resolving methods have been established for deconvoluting overlapping bands. We have identified three separate bands associated with aromatic hydrogen, three bands associated with various aliphatic groups (CH, CH_2 and CH_3) and bands in the spectra of acetylated samples that can be assigned to NH, alkyl OH and phenolic OH. In low-rank coals bands near 1700 cm^{-1} can be readily assigned to COOH groups. Clearly, if we have sufficient maceral (or coal) samples chosen so as to cover a range of rank and hence hydrogen content, then theoretically the problem could be solved as a set of simultaneous equations. In fact, we should be able to "overdetermine" the problem by analyzing a sufficient number of samples.

This approach has a number of advantages. Model compounds will not be required to obtain extinction coefficients. If a sufficiently large data base is used, any systematic variations in extinction coefficients with rank and hence chemical structure should be apparent, providing that a method for determining variations in measured and calculated (by FTIR) hydrogen is included in the procedure.

We have made considerable progress in applying this methodology. Elemental hydrogen has been measured for a large number of vitrinite concentrates. Approximately twelve of these samples (to date) have been acetylated. The tedious task of curve resolving these spectra remains but should be accomplished in the next few months. We have written a program for solving the large number of simultaneous equations we ultimately wish to include. This is described in the following section. We anticipate preliminary results will be published in the next quarterly report.

Program for Quantitatively Determining Functional Groups in a Number of Coal Samples by FTIR

Given the hydrogen wt. % of a set of samples determined from elemental analysis and the normalized peak intensities of hydrogen-related bands in the infrared, we need to solve for factors which will relate these intensities to the concentration of hydrogen involved in various functional groups. This problem may be set up as follows:

$$AX = H \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

where A is a matrix of peak intensities
H is a vector containing the hydrogen wt. %
X is a vector containing the desired conversion factors.

To obtain the best possible set of factors more samples will be used than there are peaks related to hydrogen-containing groups. This problem then is overdetermined and it will be necessary to optimize the X-vector. This may be done using Gauss' method of least squares which calls for a minimization of the sum of squares.

$$S = \Sigma(h_i - \hat{h}_i) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$

where h_i is the experimental hydrogen concentration, and
$\hat{h}_i$ is the calculated hydrogen concentration, or

$$\hat{H} = A\hat{X} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (13)$$

where X is the optimized $\hat{X}$ vector.

It has been shown by Hamilton that $\hat{X}$ may be determined by the following:

$$\hat{X} = (A^T M^{-1} A)^{-1} A^T M^{-1} H \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (14)$$

where M is a variance-covariance matrix of rank n,
A is the MXN matrix of intensities, and
H is the vector containing the hydrogen concentrations.

Therefore by setting up a computer program to simply multiply these matrices together in the given order the optimized solution may be solved for directly. (P.C. Painter)

10. SURFACE AREA AND DENSITY DETERMINATIONS ON COALS AND MACERALS

Densities and Pore Volumes

Apparent densities of several coals and macerals were determined at 25°C using methanol as the displacing fluid. Pycnometer bottles, 2-5 cc in volume, were used. About 0.8-1.0 g of sample, 110°C oven-dried for 15 h, was taken for each density measurement. The procedure, which allows the addition of the displacing liquid under vacuum so as to prevent the effect of air present in the bulk and the macropores, has been described in detail in a previous quarterly technical progress report (DOE-30013-2). The density of high purity natural graphite was determined in methanol, in the first instance, using different amounts of graphite and a methanol density of 0.7866 g/cc (67). It was found to be 2.260 $\pm$ 0.010 g/cc which appears in good agreement with the true density of graphite, that is, 2.268 g/cc. Alternatively, using the graphite density of 2.268 g/cc, an average density of methanol was calculated to be 0.7864 g/cc. In further measurements, the density of methanol was, therefore, taken as 0.7866 g/cc.

The effect of the presence of air on kinetics of uptake during density measurements was also studied. Essentially equal amounts of a coal (-20 mesh) were taken in two pycnometers and dried as usual. Methanol was added, in one case under vacuum in the manner described previously, and, in the second case, at ambient pressure. The densities at 25°C were determined after different intervals of time. Plots of apparent density versus time in the two cases are shown in Figure 13 for PSOC-1166. The density of the -20 mesh sample to which methanol was added under vacuum increases sharply and levels off after about 30 h, whereas the density of the sample to which methanol was added at ambient pressure increases asymptotically with time and tends to more slowly approach the equilibrium value attained for the outgassed sample. Thus, the presence of air hinders penetration of methanol into the pores and slows down the rate of absorption.

The densities, in methanol, of some coals and macerals were also determined using a smaller size fraction, that is -100 mesh. Results of a representative sample are depicted in Figure 13. Equilibrium in the case of the -100 mesh sample is more rapidly attained, that is, within 3-4 h. Further, equilibrium densities of -100 mesh samples were found to be slightly higher than those for -20 mesh size fractions. It is concluded that closed pores are increasingly opened on grinding to smaller sizes, thus reducing the displacement by methanol and increasing methanol densities. Densities in methanol of selected -20 mesh coals (PSOC samples) and macerals (PSMC samples) are given in Table 8. Densities are expressed on a dry, mineral matter containing (dmmc) basis.

Knowing the density in methanol (ρ_S) and the particle density (ρ_{Hg}), pore volumes (V_S) accessible to methanol can be calculated as follows.

$$V_S = \frac{1}{\rho_{Hg}} - \frac{1}{\rho_S} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

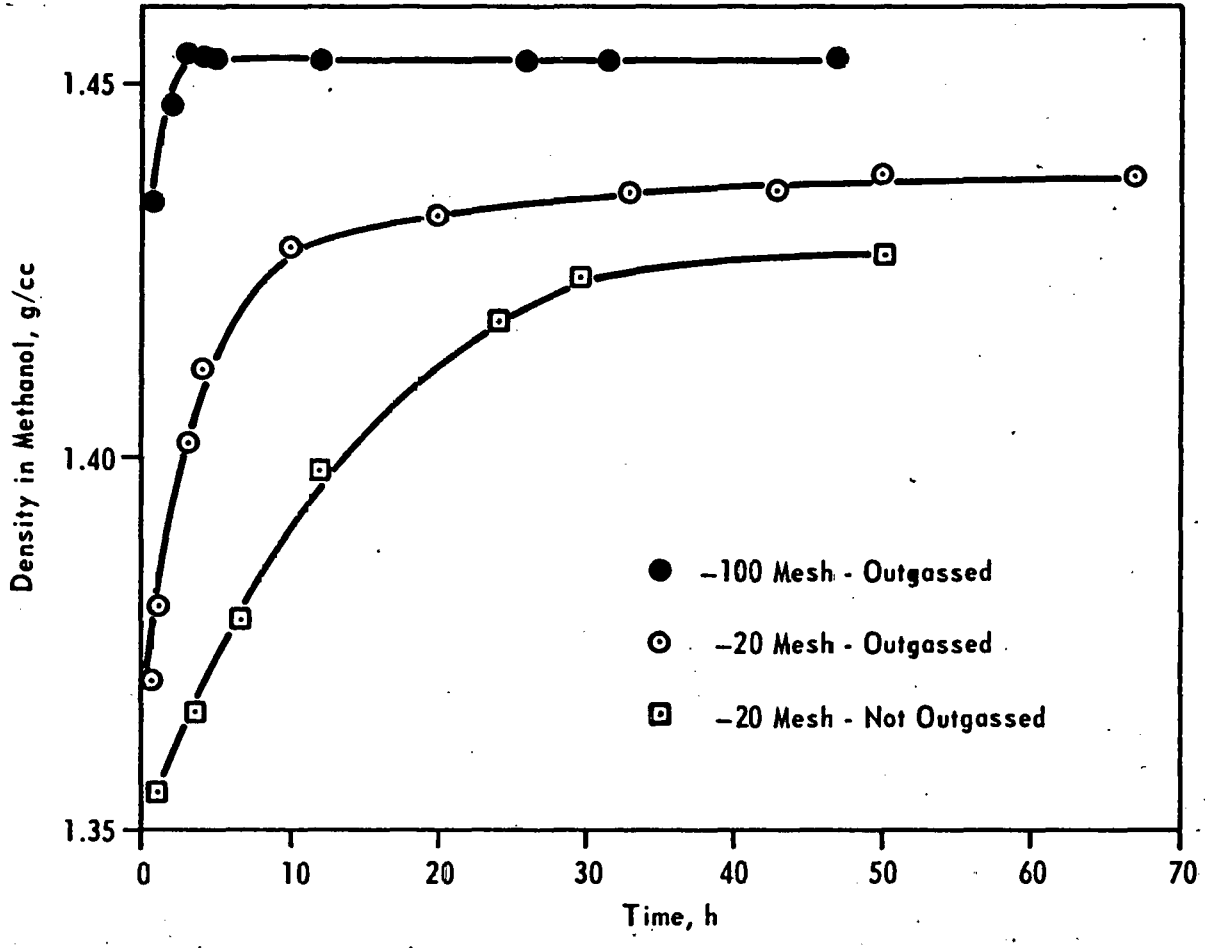


Figure 13. EFFECT OF PRIOR OUTGASSING AND DIFFERENT SIZE FRACTIONS ON DENSITY OF PSOC–1166 COAL IN METHANOL AT 25°C

Particle densities of coals and macerals were determined in the usual manner with a mercury porosimeter. The procedure has been described in a previous technical progress report (DOE-30013-3). Some earlier workers (68, 69) have reported particle densities of coals reflecting a random distribution of reported values, apparently due to different pressures at which densities were estimated. In the present study, particle densities on -20 mesh material were measured at 0.68 MPa, as the plots of mercury intrusion versus applied pressure were found to level off at this pressure in almost all the coals and macerals studied. These densities for selected samples are included in Table 8.

Pore volumes accessible to methanol in each case were calculated using equation number 15. Pore volumes of these samples were also calculated from Dubinin-Polanyi plots of CO_2 adsorption (see discussion of these plots in DOE-30013-1) at 25°C, assuming the density of CO_2 in the pore system to be 1.037 g/cc (70). Comparison of the two pore volumes shows that methanol can penetrate into the pore system in coals to a greater extent than CO_2. In some cases, pore volumes accessible to methanol are almost double volumes accessible to CO_2. Earlier, workers have shown that organic molecules can penetrate into some pores in coal which are closed to helium due to imbibition causing swelling of the coal (67, 69). The swelling in coals is believed to depend on the amount of crosslinking in the structure and the correspondence of the solubility parameters of the organic liquid and the coal (71, 72). The uptake of methanol on carbonaceous solids also has been shown to be related to specific interactions between the solvent and the oxygen-containing functional groups on the surface (73). Such possibilities will be investigated, after this study is extended to more coals and macerals.

Swelling of Coals in Methanol

The pycnometric density in methanol measures only the volume occupied by a unit weight of the sample. It has been previously suggested that the volume of methanol imbibed is offset equally by the extent to which the coal swells as a result of imbibing. The volume accessible to methanol, as calculated above, is, therefore, exclusive of the volume imbibed. A comparison of this volume with the volume uptake of methanol measured gravimetrically at a relative vapor pressure of 0.95 and 25°C provides a measure of solvent-induced swelling. It is estimated, using the Kelvin equation, that pores greater than about 500 Å in diameter are not filled by capillary condensation at a relative pressure of 0.95. Thus, depending on the extent that there are pores in coal above this size, uptake of methanol determined gravimetrically would be underestimated. This, in turn, would reduce the values calculated for methanol imbibing in coal, as will be seen.

The apparatus and procedure for sorption runs have been described in an earlier report (DOE-30013-2). Coal and maceral samples were outgassed for 15 h at 110°C before exposure to methanol vapor at 25°C and a relative vapor pressure of 0.95. The desired vapor pressure of methanol was generated by immersing a bulb containing the solvent in a Forma temperature bath filled with a water-antifreeze mixture. Rates of methanol uptake on a selected coal and a maceral are shown in Figure 14. Uptake is rapid in the first few hours and then gradually slows down with increasing sorption. After about 20 h, approach to equilibrium becomes

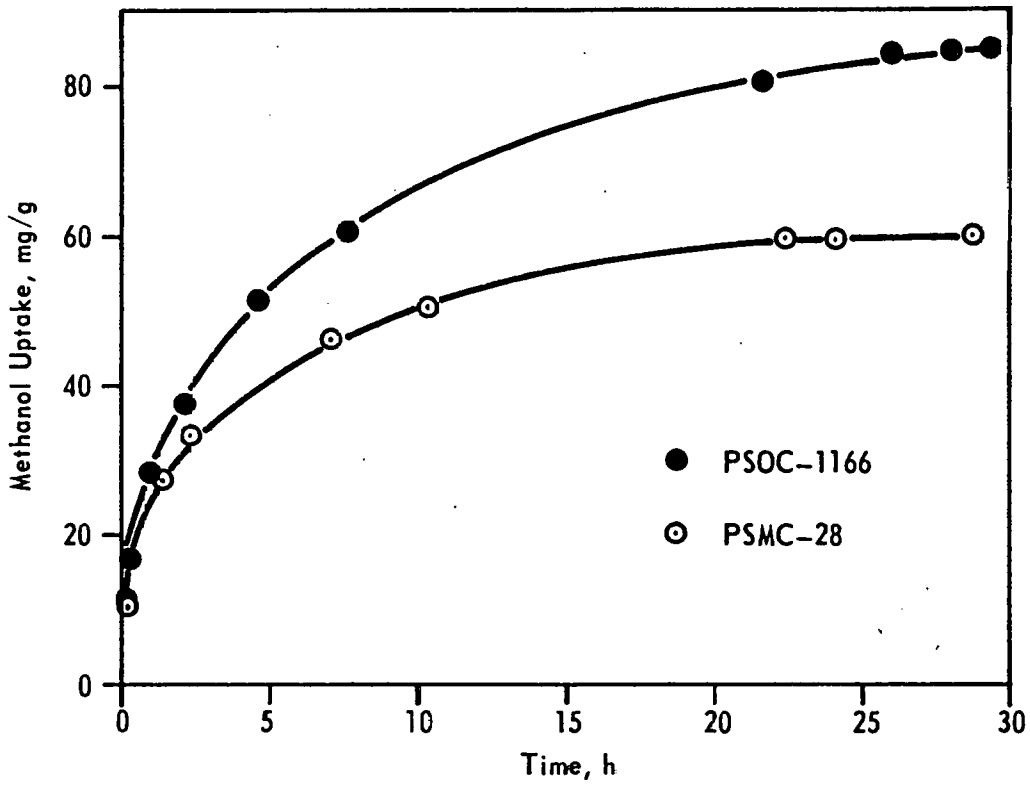


Figure 14. RATE OF METHANOL UPTAKE AT A RVP OF 0.95 AND 25°C

Table 8. Densities and Pore Volumes of -20 Mesh Coals and Macerals

Sample	Rank	Density g/cc (dmmc)		Pore Volume, cc/g	
		Mercury	Methanol	Accessible to Methanol (V_S)	From CO_2 Uptake at 25°C
PSOC-					
1141	MV	1.319	1.449	0.068	0.048
1142	HVA	1.364	1.477	0.065	0.027
1143	HVA	1.380	1.549	0.071	0.040
1167	HVA	1.332	1.471	0.077	0.053
1168	HVA	1.383	1.529	0.069	0.041
1169	HVA	1.326	1.459	0.069	0.037
1170	HVA	1.324	1.445	0.063	0.050
1171	HVA	1.322	1.434	0.059	0.024
1194	MV	1.323	1.413	0.048	0.045
1197	LV	1.334	1.487	0.077	0.050
PSOC-					
26	MVA	1.283	1.396	0.063	0.055
34	HVA	1.294	1.393	0.055	0.050
63	HVC	1.275	1.457	0.098	0.066
64	HVB	1.247	1.423	0.099	0.047
69	MV	1.281	1.374	0.053	0.043
71	MV	1.252	1.363	0.065	0.042

slow and the curves tend to level off. It was observed in many cases that extremely slow uptake of methanol continues even beyond 2 days. In some coals and macerals, methanol uptake was measured up to about 70 h, beyond which there was essentially no significant uptake. Volume uptake is calculated assuming that the density of methanol in the sorbed or imbibed state is equal to its bulk density. Nelson (67), while studying the sorption of organics on coals, carbons and polymers, showed that: (i) in the case of a Saran carbon with a known uniform porosity, the volume calculated from solvent and particle densities was in close agreement with the volume uptake measured gravimetrically according to the above assumption, and (ii) two differently crosslinked macroporous polystyrene samples showed identical densities in spite of varying degrees of swelling. These findings support the validity of the above assumption.

The percent solvent-induced swelling (S) was calculated from the following expression:

$$S = 100 \cdot \rho_S[(W_1/\rho_1) - V_S + V_M] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (16)$$

where W_l = solvent uptake measured gravimetrically, g/g.
ρ_l = bulk density of solvent, g/cc.
ρ_S = density of the sample in solvent, g/cc.
V_S = pore volume accessible to solvent, cc/g.
V_M = macropore volume of the coal sample, that is, volume contained in pores larger than 500 Å, cc/g.

Because the volume contained in the macropores of most coals is small (68), the V_M term is taken as zero. However, in future, efforts will be made to determine macropore volumes and their necessary inclusion will be considered.

Swelling of selected coals and macerals in methanol on a dmmc basis is given in Table 9. Considerable swelling is observed in the case of macerals PSMC-63 and 64. The effect of rank and other parameters of coals and macerals on their swelling will be summarized after measurements are completed on more samples.

Swelling of Coals in CO_2

Recently, it has been pointed out that micropore volumes obtained from Dubinin-Polany plots of CO_2 at 25°C on several coals are greater than the total pore volumes accessible to helium (74). Currently, the difference is believed to be due to some imbibing of CO_2, thus leading to consequent swelling of coal. Some preliminary work done on measuring the swelling of coals exposed to various pressures of CO_2 at 25°C is summarized in this report.

A sensitive high-pressure dilatometer built by the LECO Corporation was used for these measurements. The equipment is designed to measure the expansion of materials under controlled conditions of temperature and pressure. A schematic set-up of the apparatus is shown in Figure 15. The dilatometer is provided with a linear variable-differential transformer (LVDT). An integral furnace in the dilatometer can provide heating if required. The sample holder is enclosed in a pressure jacket which has two alternate quick-disconnect gas-input ports. A gas outflow connection is provided under the base of the pressure jacket. The LVDT is a large bore unit which allows installation outside the pressure jacket. The probe rod is made up from four separate pieces; a lower quartz piece, and the weight pan. The probe rod is positioned on top of the sample and can move up and down freely. The sample probe with the core on its top remains in the pressure chamber which extends to the top of the LVDT unit. This unit has a linear range $\pm$ 0.25 in., with linearity better than 0.5% and sensitivity of 0.8 mv/.001 in./V. The dilatometer is connected to a DuPont 990 thermal analyser (an X-Y recorder) through an electronic interface. This assembly enables the following of changes in the height of the coal bed.

A known weight of the sample is taken in the sample holder and placed in the LVDT unit. The pressure cap is replaced. The required mechanical and electrical adjustments are then made. The height of the sample bed is measured from the dilatometer output with and without a sample present. The pressure chamber is then purged with N_2 for about 5 min. It is then pressurized with CO_2 at a rate sufficiently slow to avoid jarring the sample

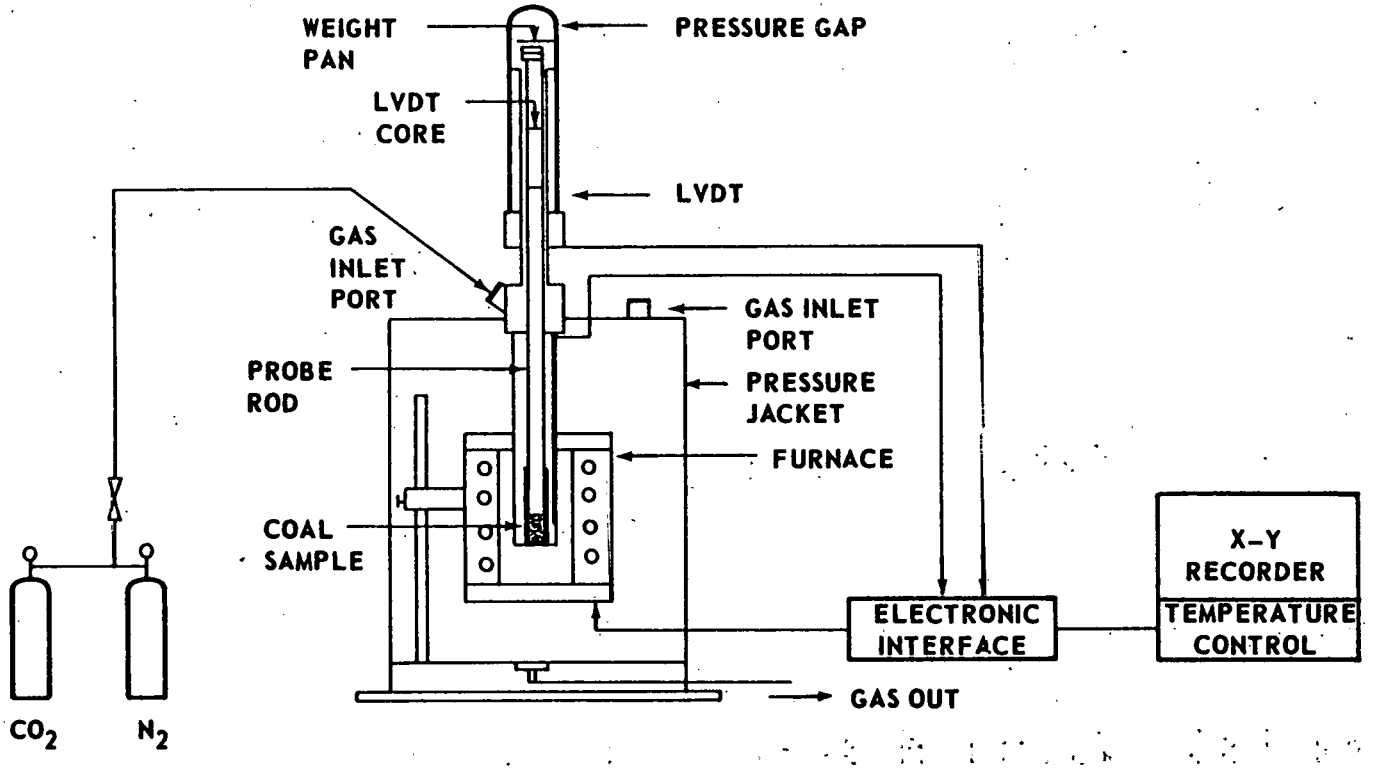


Figure 15. DILATOMER ASSEMBLY FOR HIGH PRESSURE SWELLING STUDIES

Table 9. Methanol-Induced Swelling of -20 Mesh Coal and Macerals at 25°C

Sample	Rank	Pore Volume Accessible to Methanol cc/g (dmmc)	Volume Uptake Of Methanol at rvp = 0.95 cc/g (dmmc)	Swelling %
PSOC-				
1167	HVA	0.077	0.095	2.6
1168	HVA	0.069	0.093	3.7
1170	HVA	0.063	0.098	5.1
PSMC-				
26	HVA	0.063	0.109	6.6
63	HVC	0.098	0.288	27.7
64	HVB	0.099	0.196	13.8

or breaking the sample holder. Usually a rate of 0.68 MPa per minute is used to increase or reduce the pressure. It was found in a few preliminary experiments that the time allowed to pressurize the dilatometer chamber to a desired level has no significant effect on swelling of coal in CO_2. Any expansion or contraction of the coal bed is recorded on the X-Y recorder as a function of time. In the present study, expansion was studied until equilibrium, that is until no further change in bed height was observed. Results are expressed as percent swelling.

$$\text{Swelling} = \frac{\Delta h}{h} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (17)$$

where Δh = change in height of the coal bed.
h = original height of the coal bed.

After the maximum pressure and swelling are attained, the gas pressure is released and the change in bed height is followed until the pressure inside the chamber is reduced to atmospheric.

Swelling of a -20 mesh coal at increasing pressures of CO_2 is shown in Figure 16 (dotted line). The CO_2 pressure was increased in steps, and sufficient time was allowed after each increment in pressure for the coal to swell to its maximum amount. A linear, sharp increase in swelling is seen up to about 3.4 MPa. The extent of swelling with further increases in pressure is, however, diminished. Swelling was also measured in the case of three coals (-20 mesh in size) at 0.1, 3.4, and 4.8 MPa CO_2 pressures. A fresh sample of coal was taken to measure swelling at each pressure. These results are also shown in Figure 16. Swelling is seen to increase linearly even up to 4.8 MPa for some coals.

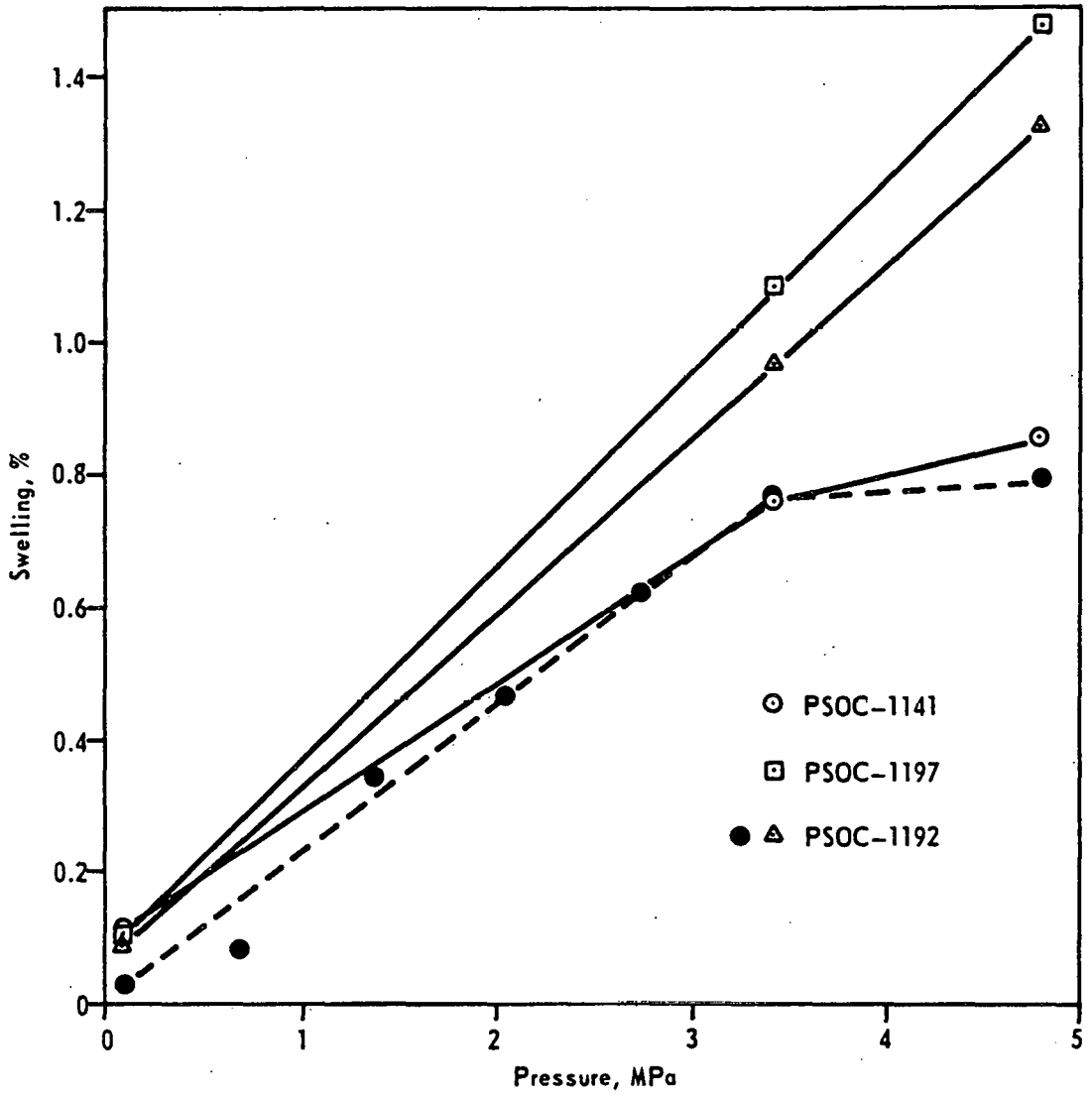


Figure 16. SWELLING AT DIFFERENT CO_2 PRESSURES AND 25°C FOR -20 MESH FRACTIONS OF THREE COALS

These results suggest that CO_2 is imbibed into the coal causing consequent swelling. Swelling has been related to the plastic properties of coal. In 1950 Berkowitz suggested that swelling relates to pressure of the gas forcing its way through the micropores in the coal (75). However, it appears from the present investigation that at high pressures CO_2 is forced into pores which are otherwise inaccessible. At increasing pressures increasing amounts of CO_2 are imbibed into the pore structure of coal and when the pressure is released the imbibed CO_2 is trapped in some of the pores with small constrictions resulting in some permanent swelling in coals. It was found that at atmospheric pressure of CO_2 swelling in coal was extremely small.

The effect of particle size on swelling was also studied. Two size fractions, -20 and -100 mesh, of two coals were exposed to 4.8 MPa CO_2 pressure and held at this pressure for about 3 h before releasing the pressure back to atmospheric. Plots of swelling (expressed in mils) versus time are shown in Figure 17. The -100 mesh samples are seen to swell to significantly greater extents than the -20 mesh material. Appreciable permanent swelling remains in each case upon releasing the pressure back to atmospheric. Immediately upon reducing the pressure below 4.8 MPa there is a small increase in expansion of the coal. This is attributed to the coal having been compressed under the CO_2 pressure, as discussed by Nelson et al. (67). For example, for the mvb coal PSOC-1141 such expansion would be about .07%, based on the compressibility data of Nelson et al.

Swelling of coals in CO_2 at 25°C was compared with that found for a Saran char before and after heating it at 1400°C in N_2. Saran char is similar in structure to chars derived from thermosetting coals. The results are summarized in Table 10. Significant swelling is seen in the original char, whereas the 1400°C-heated sample swelled much less. A second exposure to CO_2 pressure enhanced swelling in the original char, while no change was observed in the heated sample. The heated sample also did not show any permanent swelling on releasing the gas pressure back to atmospheric. Imbibing of CO_2 into the solid char structure is not expected. Thus these results suggest that some swelling also occurs as a result of penetration into the accessible pore volume of the solid. Since the surface area of the Saran char (as measured by CO_2 adsorption at 25°C) is expected to decrease sharply upon heating to 1400°C, it is not surprising that the heat-treated sample shows reduced swelling.

Experiments were also performed on measuring swelling of a cylindrical piece of coal 6.99 mm in length and 5.05 mm diameter (PSOC-1192) in CO_2 at 3.4 MPa. It is interesting to compare these results with those of the -20 mesh sample of the same coal. Similar weights of the piece and the sieved sample were subjected, separately, to 3.4 MPa pressure of CO_2 under identical conditions. After the sample attained maximum swelling, the system was depressurized back to atmospheric in each case. Three such cycles were carried out on both samples. Results expressed as percent swelling are given in Table 11. Swelling in the case of the single piece is greater than in the sieved sample, and it increased after every cycle. It is also seen that residual swelling after each depressurization increased in the case of the single piece, while no significant change was observed in the sieved sample. However, it is interesting to note that

Table 10. Swelling of Original and 1400°C-Heated Saran Char in CO_2 at 25°C

Sample	Cycle No.	CO_2 Pressure MPa	Swelling %
Saran	1	3.4	0.23
		4.8	0.36
		0.1	0.23
	2	3.4	0.43
		4.8	0.50
		0.1	0.30
1400°C-Saran	1	3.4	0.07
		4.8	0.07
		0.1	0.00
	2	3.4	0.07
		4.8	0.07
		0.1	0.00

Table 11. Swelling of Single Piece and -20 Mesh Coal (PSOC-1192) in CO_2 at 25°C

Sample Type	Cycle No.	CO Pressure MPa	Swelling %
Single Piece	1	3.4	1.11
		0.1	0.44
	2	3.4	1.16
		0.1	0.51
	3	3.4	1.27
		0.1	0.55
-20 Mesh	1	3.4	0.83
		0.1	0.65
	2	3.4	0.96
		0.1	0.65
	3	3.4	1.00
		0.1	0.69

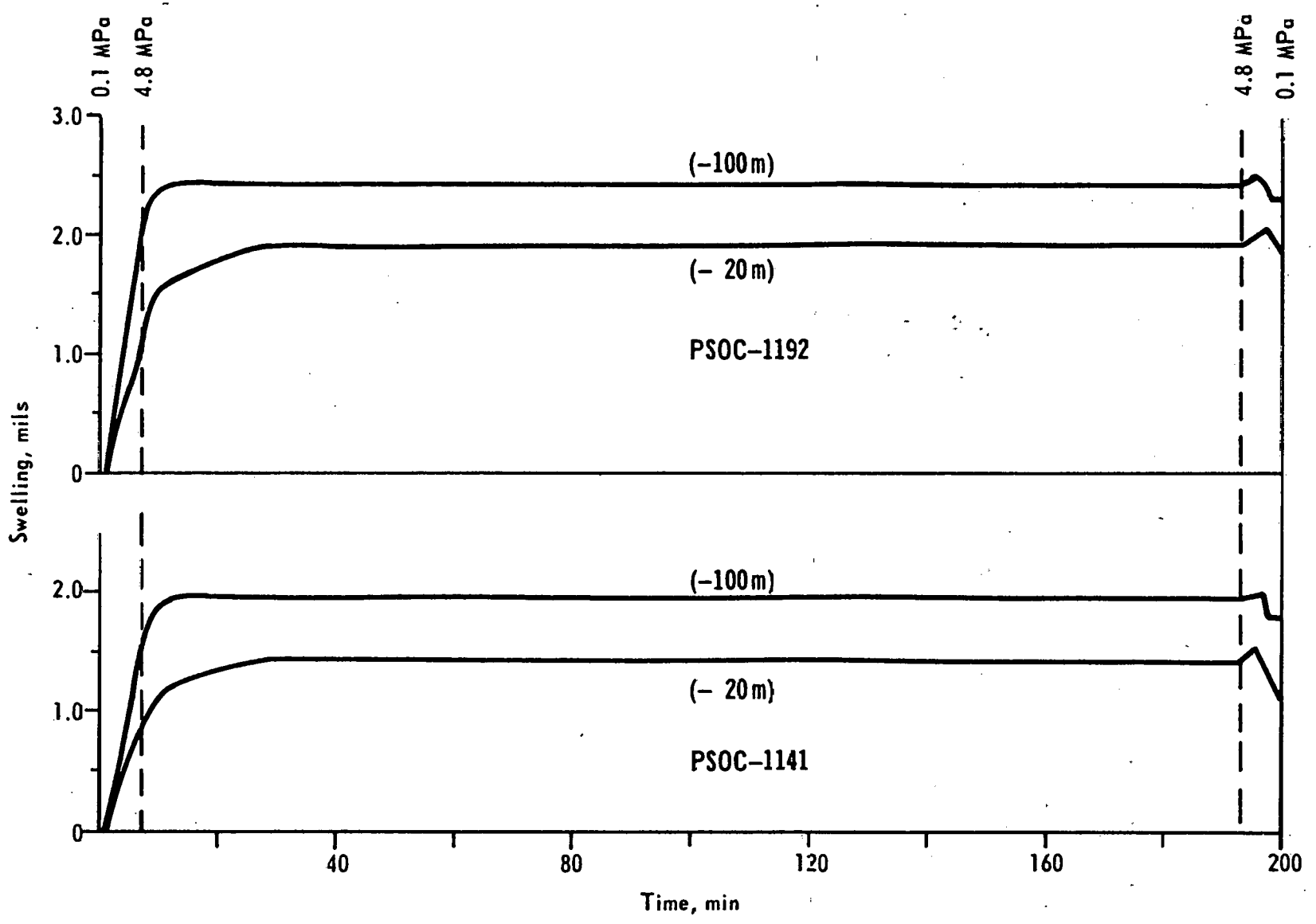


Figure 17. SWELLING IN –20 AND –100 MESH FRACTIONS OF TWO COALS IN 4.8 MPa CO_2 AND 25 °C

the permanent swelling left in the sieved sample at the end of first cycle is higher than the swelling left in the single piece even after the third cycle.

Further investigations are being carried out on more coals. Work has also commenced using the pressure adsorption apparatus where CO_2 uptake on coals will be measured at high pressures (i.e. up to about 3 MPa) and 25°C, volumetrically.

Acknowledgments

We greatly appreciate Dr. R.G. Jenkins making available to us the high-pressure dilatometer for our studies. We appreciate the preliminary runs which Mr. R. Khan carried out to show the feasibility of using the dilatometer apparatus.

(P.L.W., S.K.V. and J.R-U.)

11. CHARACTERIZATION OF COALS AND LIQUEFACTION RESIDUES FOR P.E.T.C.

During this quarter twenty three samples were received from the Pittsburgh Energy Technology Center for characterization. Samples numbered PETC 27, 28, 41, 42, 49 were coal samples, PETC 29-35 were liquefaction residues, PETC 36-37 were pyrites, PETC 38 was a flue dust sample and PETC 39-40 were sink portions from the gravity separation of coal. PETC 43 was a preasphaltene preparation and PETC 44 was the THF insolubles from a preasphaltene. PETC 45 was a NiMO H-coal catalyst and PETC 46 was a CoMo catalyst; both of these were used catalysts supported on Al_2O_3 after HF treatment. PETC 47 was a CoMo catalyst and PETC 48 was a NiMo catalyst. These catalysts were supported on Al_2O_3 without HF treatment.

Petrographic analyses were requested for the feed coal samples and the liquefaction residues. The initial requisition included major element and mineralogic analyses on PETC 29-40. Unfortunately, the size of the samples on which petrographic analyses were carried out (PETC 29-35) was small and will prevent the performance of all the requested analyses. Qualitative petrographic analyses and description will be performed on PETC 43-48. Results will be presented in the next quarterly technical progress report.

(J.T.S. and A.D.)

CONCLUSIONS

1. Placing coal samples in the Fisher Coal Analyser at 750°C instead of the manufacturer-recommended cold furnace gives volatile matter values which are close to those obtained by the ASTM method. A factor analysis of coal data reveals a modest nitrogen enrichment in low-rank coals and depletion at higher ranks. Calcium oxide decreases strongly and potassium oxide increases strongly with rank.

2. There is much greater vertical variability in the macroscopic petrography of a column sample of the Lower Kittanning seam from a so-called marine environment than in four others from an area where there was no marine influence.

3. It appears that differential subsidence and paleotopography may have played a major role in influencing the thickness, ash and sulfur contents of the Lower Kittanning seam throughout western Pennsylvania. The same control may have maintained some influence upon the coalification process after deposition, especially along the eastern margin of the basin, as indicated by trends in volatile matter and reflectance.

4. Previous workers have contended that refractive index cannot be determined from mean reflectance values because it is not a linear function of reflectance. Ten paired readings (an air and oil reading at the same location) were taken on a vitrinite concentrate. The refractive index was determined both from the average of 10 individual refractive indices and from the means of the reflectance values. The values were found to be identical.

5. For a number of coals and macerals, pore volumes accessible to liquid methanol at 25°C are greater than pore volumes measured by CO_2 adsorption. For -20 mesh coal, methanol uptake is slow, taking at least 30 h to reach equilibrium. Uptake is accompanied by the swelling of coal, the amount of swelling in methanol increasing with decrease in coal rank. Coals also swell in CO_2, the amount increasing with increasing pressures, at least up to 4.8 MPa at 25°C. However, the extent of swelling in CO_2 is much less marked than that found in methanol.

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