493 STATE OF ILLINOIS DEPARTMENT OF REGISTRATION AND EDUCATION Internal Surface Area, Moisture Content, and Porosity of Illinois Coals: Variations with Coal Rank Josephus Thomas, Jr. Heinz H. Damberger ILLINOIS STATE GEOLOGICAL SURVEY Jack A. Simon, Chief Urbana, IL 61801 **CIRCULAR 493** 1976

INTERNAL SURFACE AREA, MOISTURE CONTENT, AND POROSITY OF ILLINOIS COALS: VARIATIONS WITH COAL RANK

Josephus Thomas, Jr., and Heinz H. Damberger

CONTENTS

Page

Abstract
Introduction
Historical Background 2
Surface Area by Gas Adsorption 5
Carbon Dioxide as an Adsorbate on Coals 7
Experimental Investigation 9
Apparatus for Surface Area Measurements. 9
Experimental Conditions for Surface Area
Studies on Coals 9
Reflectance (R _o) Measurements
Selection of Samples
Results and Discussion
Range of ISA in Illinois Coals16
Influence of Coal Petrographic
Composition on ISA
ISA of Illinois Coals in Relation to That
of Other Coals

-

Influence of Porosity and Coal Rank		
on ISA	•	.20
Pore-Size Information from Mercury		
Porosimetry	•	.22
Porosity Information from Moisture		
Content of Coal		.23
Pore-Size Information from		
Nitrogen Adsorption	•	.27
Increasing the ISA by Heating		.27
Interrelation of Porosity, ISA, and		
Reflectance in Illinois Coals	•	.29
Geological Implications from ISA and		
Porosity Evaluations	•	.33
Summary and Conclusions	•	.35
Acknowledgments	•	.35
References	•	.36

Page

FIGURES

l – Time of passage of a gas molecule as a function of the reduced differential heat
of adsorption
2 - Schematic diagram of apparatus for surface area measurements
3 - Sample locations and stratigraphic distribution of samples
4 - Map of Illinois with isoranks of Herrin (No. 6) Coal Member depicted by inherent
moisture content; table of correlations between inherent moisture and ranges for
internal surface area values for both whole-coal and vitrain samples; and curve
depicting the average change of the inherent moisture content with relative depth
in the Illinois Basin
5 - Internal surface areas of whole-coal and vitrain samples from Illinois as they relate
to coal rank
6 - Correlation between coal rank and internal surface area based on a heat-of-wetting
method as published by Griffith and Hirst (1944)
7 - Correlation between coal rank and internal surface area based on data from the
xenon adsorption method as published by Kini (1964)
8 - Mercury penetration of two Illinois vitrain samples of different rank
9 - Correlation between calorinic values on moist and dry mineral-matter-iree bases and
innerent moisture content in high-volatile bituminous coals
10 - Correlation between natural (innerent) and equilibrium moisture contents of high-
Volatile bituminous dia subbituminous coals
11 - Relation between inherent more the content and volume-percent policity in filmions coars25
This pair a strategy pole diameters of whole coars and vitarits from the
11 - Comparison of mean "apparent" average pore diameter with "true" average pore
diameter of whole-coal samples from Illinois
4 - Correlation between "wet" and "dry" reflectance under oil immersion and the internal
surface area of whole-roal samples from Illinois
15 - Correlation between "wet" and "drv" reflectance under oil immersion and the inherent
moisture content of whole-coal samples from Illinois

(Continued on next page)

TABLES

1 - Surface Areas, Reflectivities, and Analyses of Various Whole-Coal Samples	•	 •	٠	•		14
2 - Internal Surface Areas of Coal Constituents (Herrin (No. 6) Coal Member,						
Jefferson Co., Illinois)	•	 •	•		•	18
3 - Surface Areas, Reflectivities, and Analyses of Vitrain Samples	•			•	•	19
4 - The Effect of Volatile-Matter Removal on Internal Surface Area		 ٠	•	•		28

INTERNAL SURFACE AREA, MOISTURE CONTENT, AND POROSITY OF ILLINOIS COALS: VARIATIONS WITH COAL RANK

Josephus Thomas, Jr., and Heinz H. Damberger

ABSTRACT

The efficiency of coal gasification, liquefaction, or solubilization processes probably depends, among other factors, upon the internal surface area of the coal used and the accessibility of that area to reactants in these processes. In addition, the yields of desired components from these processes may depend upon the porosity and the internal surface area of the coal.

In this report, we have discussed methods of measuring the surface area of coal, evaluated the internal surface area of Illinois coals on the basis of our studies, and shown the correlations of internal surface area with such coal rank parameters as calorific value, inherent moisture content, and vitrinite reflectance.

Illinois whole coals of high-volatile A, B, and C bituminous rank (hvAb, hvBb, and hvCb of ASTM classification) were evaluated by a gas adsorption method with carbon dioxide as the adsorbate at -78° C. Values ranging from 46 to 292 square meters per gram (m²/g) were obtained, the hvAb coals having the lowest values and the hvCb coals the highest. Values as much as $60 \text{ m}^2/\text{g}$ higher than those for whole-coal samples were obtained for vitrain concentrates of the same coals. Internal surface area correlated well with inherent seam moisture content and, thus, coal rank.

Mercury porosimetry data for an hvAb coal and for an hvCb coal revealed a significant difference in the pore-size distribution between the two ranks. The hvCb coal contained a number of pores with diameters in the range from 35 to 220 Å, whereas the hvAb coal contained relatively few pores greater than 35 Å in diameter, the lower limit of the pore-size measurements. This difference in pore-size distribution is thought to be a result of differences in the former depths of burial of the coals.

The pore-size distribution appears to have a significant influence on reflectance measurements of polished coal samples. Depending upon the sample preparation history, the pores in the polished surfaces are filled with either air or water, thus leading to appreciable differences in the measured reflectance values; that is, under oil immersion, "wet" samples reflect less light than "dry" samples. The difference between reflectance values of "wet" and "dry" samples is greatest with hvCb coals and decreases toward the hvAb coals, apparently because of the lack of larger pores in the surfaces of the latter coals. Studies were also made of the increase in internal surface areas of Illinois coals after the removal of small percentages of volatile matter at elevated temperatures under controlled conditions. It is apparent from these studies that Illinois coals, particularly the hvAb coals, are far more porous initially than the adsorption measurements with carbon dioxide would indicate. It is thought that these coals contain many pores that are plugged with relatively low-boiling organic constituents. The removal of these constituents at moderate temperatures ($\sim 200^{\circ}$ to 300° C) in a helium stream opens the pore structure, thus bringing about a large increase in the internal surface area.

INTRODUCTION

The surface area of a solid is an important physical parameter, which can generally be correlated with the solid's rate of reactivity. In general, the greater the surface area, the higher the rate of reactivity in such processes as solubilization, catalysis, ion exchange, thermal decomposition, and corrosion; for coals, combustion and weathering also can be included.

It is likely that reactivity rates of coal gasification, liquefaction, and solubilization depend, among other factors, upon the internal surface area of the coal used and the accessibility of that area to the reactants in these processes. In addition, the nature of the components released in these processes may be influenced by variations in porosity and internal surface area. To our knowledge, such relationships have been studied to only a limited extent.

Physically, coal may be considered as essentially a compacted colloidal substance, or hardened gel. It is interspersed with various-sized interconnecting pores and capillaries, which produce a large internal surface. An earlier, pre-liminary study by Thomas, Benson, and Hieftje (1966), for example, showed that the internal surface areas of Illinois whole coals range from 46 to 292 square meters per gram (m^2/g) .

A clearer understanding of the nature of the pore structure of coals has emerged only within the past 15 to 20 years. It is now generally accepted that the majority of pores in coals are less than 5 Å in diameter. Coals have molecularsieve properties that permit certain molecules to penetrate the pore structure while excluding other, larger molecules. Temperature plays an important role in the diffusion of gases within this type of pore structure. The recognition that coal possesses such an ultrafine structure has been of considerable help in the use of classical gas adsorption methods for estimations of surface area.

In view of the increased interest in gasification and liquefaction processes and in their future impact on the coal industry, it is the object of this report to present a more detailed evaluation of the internal surface area of Illinois coals than was presented in the earlier study, and to show the correlations of internal surface area with such coal rank parameters as calorific value, inherent moisture content, and vitrinite reflectance.

HISTORICAL BACKGROUND

Although it has been recognized for many years that coal has a porous structure, only since the middle 1950's has general agreement been reached

concerning the true nature of the pore structure and the related internal surface area.* The controversy that existed to that time was largely the result of marked differences between internal surface areas determined from nitrogen (N_2) gas adsorption data and those determined from heat-of-immersion (heat-of-wetting) data. In the classical BET gas adsorption method (Brunauer, Emmett, and Teller, 1938), N_2 is adsorbed on a solid at a temperature near that of liquid N_2 (-196° C). Typically, this method yields low surface area values for coals, ranging from about 0.5 to 100 m²/g. In the heat-of-immersion method, a calorimeter is used to determine the heat evolved (which is related to surface area) when a finely divided or porous substance is immersed in a polar liquid such as methyl alcohol. This method yields much higher surface area values for coals, ranging from about 20 to more than 300 m²/g.

Adherents of the BET gas adsorption method (Lecky, Hall, and Anderson, 1951; Malherbe, 1951; Malherbe and Carman, 1952) insisted that their values were correct and that the greater sorption of polar molecules with the heat-of-wetting method resulted from weak chemical bonding with the coal. The opposition, equally adamant in their views, thought that surface areas determined from the sorption of polar molecules, particularly methyl alcohol, were correct and that the low sorption of inert, nonpolar gas molecules with the BET method was due either to the presence of methane in the pores (Griffith and Hirst, 1944) or to the slow rate of diffusion of nonpolar molecules into the pores (Maggs, 1952; Maggs and Dryden, 1952; Zwietering, Oele, and van Krevelen, 1951).

A report by Maggs (1952) generated much research over the next few years to account for the differences. His study, which we and others have verified, showed that more N_2 is adsorbed on the same coal sample at -78° C than is adsorbed at the much lower temperature of liquid oxygen (-183° C). This behavior is contrary to that which normally occurs in physical adsorption, that is, a lower temperature brings about a decrease in the vapor pressure of the adsorbate (and a consequent greater adsorption) in accordance with the well-known Clausius-Clapeyron equation, the integrated expression being

$$\log (P_2/P_1) = L (T_2 - T_1)/2.303 RT_2 T_1$$

where P_2 and P_1 are the vapor pressures at temperatures T_2 and T_1 , L is the molar heat of vaporization, and R is the gas constant. Maggs suggested that closure of pores by thermal contraction was a possible explanation for the inverse behavior, but Zwietering and van Krevelen (1954) did not believe that pore closure accounted completely for the reduced accessibility of the internal surface at the lower temperature.

From mercury intrusion measurements on coal and from measurements of density by helium displacement, van Krevelen (1954) concluded that coal possesses a fine pore structure into which N_2 molecules at very low temperatures cannot diffuse unless they are provided with a sufficient energy of activation. Anderson et al. (1956) reached similar conclusions. They thought that in most coals an appreciable fraction of the pores have openings (diameters) of 4.9 to 5.6 Å at 0° C and about 4 Å at -196° C. They believed that low-temperature N_2 adsorption isotherms provide a measure of the areas only within pores having diameters greater than about 5 Å.

^{*}The external surface area of coal is an insignificant fraction $(< 1 m^2/g)$ of the total measured surface area. The emphasis throughout this report is on the internal surface area (ISA).

4 ILLINOIS STATE GEOLOGICAL SURVEY CIRCULAR 493

The diffusion of gases in small pores can be described without going into mathematical detail. For extensive treatments of the subject the reader is referred to three good texts: Barrer (1951); Carman (1956); and de Boer (1968). Briefly, when the molecular size of the diffusing gaseous species closely approaches the size of the pore opening, or aperture, through which it passes, there is a physical interaction between the gaseous molecule and the aperture. This interaction is the sum of dispersive and repulsive forces. The repulsive force is predominant when the pore opening is sufficiently small relative to the size of the gas molecule that the gas molecule requires a certain activation energy to pass through the aperture. Small differences in the sizes of diffusing gas molecules can result in large differences in the activation energy necessary for diffusion through a given aperture. As we shall emphasize later, in addition to size differences, the temperature of the gas molecules plays an important role in the diffusion process.

The technology of molecular sieves (zeolites) and the commercial use of these sieves for selective gas adsorption are based on these differences in the diffusion rates of different gas molecules. Synthetic zeolites are produced with closely controlled pore sizes to permit the diffusion and sorption of certain gas molecules while not allowing the sorption of others. Studies with molecular sieves of different pore sizes have provided further insight into the nature of the pore structure of coals. Breck et al. (1956) found that the sorption of N₂ on a 4A sieve (pores about 4 Å in diameter) increases with temperature from -195° C to -78° C, a phenomenon similar to that observed with coals. This effect was not observed with a 5A sieve. With the latter sieve the volume of N₂ adsorbed decreased predictably with increasing temperature between -195° C and 0° C.

Lamond (1962) studied the adsorption of N_2 at -195° C and carbon dioxide (CO_2) at -78° C on 4A and 5A molecular sieves. With the 5A sieve he found that the surface areas determined from N_2 and CO_2 adsorption were 770 and 695 m²/g, respectively. With the 4A sieve, however, the N_2 surface area value was only $1 \text{ m}^2/\text{g}$, whereas the value from CO_2 adsorption, 610 m²/g, remained large. It is significant that both the 4A and 5A sieves were found to have large sorption capacities for CO_2 at -78° C. Walker and Geller (1956) found that coals also possess large sorption capacities for CO_2 at -78° C. They reported that surface area values from N_2 adsorption at -195° C, and were more nearly equivalent to surface area values from heat-of-immersion data. They concluded, as did Anderson et al. (1962), that CO_2 at -78° C reaches most of the internal surface of a coal and thus is superior to N_2 as an adsorbate for the determination of the internal surface area of this microporous substance.

From these studies and others (Kini et al., 1956; Nandi, Kini, and Lahiri, 1956), it is now generally accepted that coals possess molecular-sieve properties. By analogy, it appears that coal has a large number of pores of sizes close to those in the 4A molecular sieve. Nitrogen, normally used as the standard adsorbate in the classical BET method, fails to reach most of the internal surface of coals at -195° C because it is not sufficiently activated at that temperature to diffuse, in a reasonable time, into pores having diameters less than about 4 to 5 Å.

The phenomenon of activated diffusion in coals has been discussed by Zwietering, Overeem, and van Krevelen (1956), Nandi and Walker (1964, 1966), Anderson and Hofer (1965), and Walker, Austin, and Nandi (1966). Although there is general agreement as to the nature of activated diffusion, there is some disagreement as to the actual activation energy values that are calculated for various adsorbate molecules. It is recognized, however, that CO_2 as an adsorbate at -78° C is more highly activated for diffusion than N_2 at -195° C and, thus, is able to diffuse into smaller-diameter pores than can nitrogen.

There is an apparent paradox here that needs further explanation. Because the CO_2 molecule is larger than the N_2 molecule, one would be inclined to predict, strictly from size differences, that CO₂ would diffuse more slowly rather than more quickly into the smaller pores than N_2 would. This prediction would be accurate if the two gases were compared at the same diffusion temperature. However, as was pointed out earlier, temperature plays a significant role in the diffusion process, and it is primarily for this reason that we have consistently included the temperature during our discussion of the diffusion or adsorption of the two gases. In surface area studies by the BET gas adsorption method, gases normally are adsorbed near their boiling points to insure monolayer coverage of the solid surface at increasing relative pressures of the adsorbate. Carbon dioxide as an adsorbate cannot be compared with N_2 at -195° C since the former is a solid below about -78° C; on the other hand, surface area measurements normally are not conducted with N₂ at -78° C since monolayer coverage is not even closely approached at this temperature. It is this large difference between the adsorption temperatures of CO₂ and N₂ that accounts for the greater diffusion rate of the larger CO₂ molecule at its necessarily higher adsorption temperature.

This difference in diffusion rates is depicted in figure 1, which is reproduced from a report by Thomas, Bohor, and Frost (1970) and is based on calculations from de Boer (1968) on the diffusion of gas in capillaries. Figure 1 shows the time of passage (t) of a gas molecule through a cylindrical pore, with the dimensions shown, as a function of Q_{diff}, the differential heat of adsorption. The values chosen for Q_{diff} are reasonably close to the accepted values for adsorption on clay minerals, and they should not differ markedly for adsorption on coals. In fact, the Q_{diff} values could even be reversed for the two gases depicted in the figure without



Fig. 1 - Plot showing time of passage (t) of a gas molecule as a function of the reduced differential heat of adsorption (Q_{diff}).

significantly changing the relative times of passage of the two gases. It is apparent that the time of passage for N₂ at -196° C is more than 10⁵ times that for CO₂ at -78° C. If the two gases were compared at -78° C, the time of passage for N₂ would be less than that for CO₂ on the basis of the relative sizes of the gas molecules.

Surface Area by Gas Adsorption

Until the late 1930's there was no satisfactory method for measuring the surface area of both porous and nonporous adsorbents. Apart from the aforementioned heat-of-immersion method that was commonly used, a number of other

5

methods were (and are) used successfully for nonporous solids. These include direct microscopic measurements; adsorption of suitable solutes, such as fatty acids, from solution (Harkins and Gans, 1931); measurement of rate of fluid flow through packed beds of the adsorbent (Carman, 1937, 1938, 1939); and radio-active exchange, where this technique is applicable (Paneth, 1922).

Gas adsorption methods have evolved since the middle 1930's. At present, the Brunauer-Emmett-Teller (BET) method is generally considered to be the "standard" method despite the fact that it, too, suffers from some shortcomings.

The BET equation may be written

$$\frac{P}{V(P_{o} - P)} = \frac{1}{V_{m}C} + \frac{(C - 1)}{V_{m}C} \cdot \frac{P}{P_{o}}$$

where V is the volume (at standard temperature and pressure) of gas adsorbed at pressure P, P_o is the liquefaction pressure of the adsorbate used at the temperature of experiments, C is a constant related to the energy of adsorption, and V_m is the volume of gas required to form a monolayer on the solid surface. The value for V_m is sought from the experimental data. A plot of the left-hand side of the equation against P/P_o (in the range from 0.05 to about 0.35) is linear, with the intercept and slope being $1/V_mC$ and $(C - 1)/V_mC$, respectively. By substitution, $V_m = 1/(\text{slope} + \text{intercept})$. The relative pressure (P/P_o) range of 0.05 to 0.35 corresponds to a coverage of a little less than a monolayer to about 1.5 layers, and data gathering generally is restricted to this range (unless the whole isotherm is desired for pore-size evaluations) since higher P/P_o values lead to condensation of the adsorbate.

The surface area of the adsorbent is calculated from $V_{\!m}$, from the area occupied by a single gas molecule, from Avogadro's number, and from the molar volume of the gas.

A value of 16.2 ${\rm \AA}^2$ is generally accepted as the cross-sectional area (σ) of an adsorbed nitrogen molecule. One of the uncertainties of the gas adsorption method in the determination of the "absolute" surface area of a finely divided or porous solid lies in the σ value assigned to the adsorbed gas molecule. The σ value is dependent to some extent upon the nature of the adsorbent—that is, its structural characteristics—which influences the packing of the adsorbate molecules on the surface of the adsorbent.

During the development of the gas adsorption method, Emmett and Brunauer (1937) emphasized the use of N_2 as an adsorbate. This gas has proved to be an excellent choice for surface area determinations because of its inertness and also because of the ready availability of liquid nitrogen as a constant-temperature bath.

Emmett and Brunauer computed the σ value of 16.2 Å² for N₂ from the liquid molecular volume. Evidence that this value is close to the absolute value is that surface areas calculated by using this value are in close agreement with those from an "absolute" heat-of-immersion method described by Harkins and Jura (1944).

Other σ values for N₂ have been suggested. According to Livingston (1949), a value of 15.4 Å² yields surface area values that are in close agreement with those obtained from electron micrographs (values which in themselves are questionable). Pierce and Ewing (1964), from their studies on graphite, stated that a value of 20 Å² was close to the absolute σ value with this particular adsorbent. When this uncertainty in the σ value is coupled with the inability of N₂ to penetrate cracks or crevices with dimensions of less than 5 Å on the surface of

ISA, MOISTURE, AND POROSITY OF ILLINOIS COALS

the adsorbent, it is apparent that the "absolute" surface area is not readily measurable. Brunauer (1943) pointed out that "absolute" surface area values determined for certain adsorbents may be in error by as much as 20 percent. However, there is no better method for determining surface area than the gas adsorption method, and the real value of the method lies in its excellent reproducibility. From an analytical standpoint, this permits one to obtain meaningful numbers with similar type samples and to place these samples in their proper order for correlation with those phenomena dependent upon surface area. We are in agreement with Pierce and Ewing (1964), who stated that "in view of these uncertainties we feel that as of today there is no better choice of standard for area measurements than N₂, that the value 16.2 Å² for normal packing is not absolute but is as good a relative standard as we now have, and that if vapors other than N₂ are to be used for area measurements, they should first be standardized by comparison with N₂ on the same type of surface as that of the sample to be measured."

Carbon Dioxide as an Adsorbate on Coals

Because CO_2 at -78° C diffuses into smaller pores (less than 5 A in diameter) than does N_2 at -196° C, CO_2 has been used advantageously by several workers in surface area studies on coals. In addition to the previously mentioned study by Thomas, Benson, and Hieftje (1966), other studies include those by Walker and Kini (1965); Anderson, Bayer, and Hofer (1965); Marsh and Siemieniewska (1965); Marsh and O'Hair (1966); Chiche, Marsh, and Prégermain (1967); Walker, Cariaso, and Patel (1968 a and b); and Walker and Patel (1970). Surface area values from these studies on coals do not differ greatly. Although there are differences in methodology and, in some cases, differences in the equations applied, it is not possible, in view of the uncertainties involved, to state that the surface area values obtained by one procedure are "more correct" than those by another.

With CO_2 , as with N_2 , one of the major uncertainties is the σ value assigned to the absorbate molecule. This will be discussed in greater detail later. Additionally, it has been argued that the BET equation, or for that matter any other equation, does not adequately represent the phenomena that occur in the diffusion and adsorption of gases in pores of molecular dimensions. This argument is well taken since, for example, there is not room to accommodate more than one molecular layer on each wall between parallel plates 5 Å apart. With a cylindrical pore 5 Å in diameter, there are additional wall forces, which restrict buildup of layers. Thus, the BET theory, which is based on multilayer buildup, would not appear applicable. However, Mikhail, Brunauer, and Bodor (1968) have recently come to the conclusion from pore-structure analyses that the BET theory is correct for all of the surface that is accessible to the adsorbate.

We do not wish to get too involved in this controversy in the present report. We believe that the surface area values obtained on porous substances by the BET method, although in error on an absolute basis, are meaningful on a relative basis in the comparison of similar samples.

There is little agreement at present on the value of σ for CO₂ at temperatures near -78° C. As pointed out earlier, there is disagreement on σ values assigned to different adsorbates since the exact nature of the molecular packing in the adsorbed monolayer is not known. CO₂ appears to be among the most puzzling of adsorbates in this regard. Published σ values for CO₂ range from

7



Fig. 2 - Schematic diagram of apparatus for surface area measurements.

17.0 Å², calculated by Emmett and Brunauer (1937) on the basis of liquid density, to 24.4 Å² reported by Pickering and Eckstrom (1952). From the literature it appears that the majority of investigators using CO₂ as an adsorbate, not only on coals but on other adsorbents as well, base their calculations on a σ value of 17.0 Å². We find, however, that the use of 17.0 Å² in our calculations gives surface area values that are much too low for "standard" materials in comparison with surface area values obtained on the same materials from N₂ adsorption (Thomas, Benson, and Hieftje, 1966). To obtain surface areas equivalent to those from N₂ adsorption, a σ value of 22.1 Å² for CO₂ is necessary in our calculations. Similarly, Anderson, Bayer, and Hofer (1965), in studies of CO₂ adsorption on silica gel, high-temperature carbon, and porous glass, found that σ values of 21.9, 19.5, and 21.1 Å², respectively, were necessary to give surface area values equivalent to those obtained from N₂ adsorption.

EXPERIMENTAL INVESTIGATION

Apparatus for Surface Area Measurements

Data for our study were obtained by a dynamic-sorption method. This method is more commonly called the gas chromatographic method, as the principles involved in the measurements are similar to those used in gas chromatography. Figure 2 is a schematic diagram of our apparatus, which is basically the same in design and use as that first described by Nelsen and Eggertsen (1958) and later refined by Daeschner and Stross (1962). We have converted this basic apparatus into more versatile equipment for a number of studies—in addition to surface area determinations—in which gases are either adsorbed or evolved (Thomas and Frost, 1971).

The general operational details for the apparatus in surface area determinations and the treatment of the experimental data are clearly outlined by Nelsen and Eggertsen (1958). There is little need here to elaborate on these particulars. Suffice it to say that the adsorbate gas is adsorbed near its boiling point at different relative pressures established by changing the flow rate of the adsorbate gas in a mixed-gas stream ($CO_2 + He$), with helium acting as both the carrier gas and the diluent gas. Adsorption or desorption of the adsorbate by the sample produces a peak on the recorder chart as the thermal conductivity detector responds to differing proportions of gases in the mixed-gas stream during the adsorption or desorption curve relating peak areas to known volumes of the adsorbate. The thermal conductivity detector response differs for the same volume of different gases (just as in gas chromatography); therefore, calibration is necessary for each gas that is to be used as an adsorbate.

Experimental Conditions for Surface Area Studies on Coals

Coal samples were crushed and screened, and the 40- by 120-mesh (about 425 to 125 μ m) sieve fractions were selected for the internal surface area measurements. A description of a typical experimental "run," with a discussion of the conditions employed, follows:

Approximately 0.200 g coal is weighed into the sample tube, which is then attached to the apparatus. A small heating mantle is placed around the base of the sample tube, and the sample is degassed in a stream of dry He for one hour at a temperature of 105° C.

9

10 ILLINOIS STATE GEOLOGICAL SURVEY CIRCULAR 493

Conditions for degassing coals are difficult to establish. The complete removal of water from coals and other porous substances such as molecular sieves, cellulose, and clay minerals is nearly impossible without utilizing very high temperatures, because of the strong physical attraction between the last adsorbed water layer (layers) and the surface of the solid. For obvious reasons, the temperatures used to degas coals must be lower than those used to degas inorganic materials.

Degassing commonly is conducted under vacuum for long periods. However, from unpublished studies that we have made with a Cahn Electrobalance in the determination of the loss of moisture versus time at a given temperature, it appears that the degassing of porous samples in He is more rapid than degassing in a vacuum at the same temperature. This superiority apparently is the result of the small atomic size and high thermal conductivity of He, which permit it to enter micropores readily, transfer heat rapidly within a particle, and remove adsorbed water by displacement without being adsorbed to a significant extent itself. If degassing is conducted on a small quantity of sample at 105° C in a helium stream, very little residual water remains after one hour. We have found that surface area results are not significantly different if degassing is conducted at the same temperature for a much longer period (up to 16 hours) either in He or in a vacuum.

After the degassing operation is completed, the gas mixture of CO_2 and He in a desired ratio is permitted to flow over the sample. A Dewar flask containing a slush of dry ice-absolute ethanol (approximately -78° C) is then raised into position around the sample tube and adsorption is conducted for 16 hours. This adsorption period was selected for convenience (adsorption could begin in the late afternoon of one day and desorption be conducted the next morning) even though Thomas, Benson, and Hieftje (1966) found that somewhat less than 16 hours is required to essentially reach adsorption equilibrium with nearly all Illinois coals. Adsorption equilibrium is not even closely approached if adsorption is conducted for only 30 minutes (30% complete in one instance), or even two hours. Thus, certain studies reported in the literature in which these short adsorption periods were used no doubt produced low surface area values for the coals evaluated. With Illinois coals, the increase in uptake of CO_2 after 24 hours adsorption over that after 16 hours was insignificant. Higher-rank coals would not necessarily reach adsorption equilibrium in the same period of time as Illinois coals.

Walker and Kini (1965), recognizing that considerable time is required to approach adsorption equilibrium on coals at -78° C with CO₂, reported internal surface area values from adsorption isotherms obtained with CO₂ at 25° C rather than at -78° C, believing adsorption at the higher temperature to be superior to that at the lower temperature. It is true that at the higher temperature a much shorter time is required to reach adsorption equilibrium and, additionally, advantage may be gained by using multipoint BET plots. However, it is necessary at the higher temperature to use high-pressure apparatus in obtaining adsorption data. Insofar as the "correctness" of surface area values is concerned, because of the uncertainties previously discussed (σ , in particular), it is not likely that the surface area values obtained from the higher-temperature method necessarily are closer to the "absolute" values than those obtained when adsorption occurs for a longer period at -78° C.

We use single-point BET plots passing through the origin, recognizing that some error is introduced, producing slightly lower values (perhaps by 5%) than those that would be produced if the intercept from multipoint plots were used in the BET calculations.

ISA, MOISTURE, AND POROSITY OF ILLINOIS COALS 11

After the adsorption step is completed, the gas is desorbed from the sample by removing the dry ice-absolute ethanol bath and quickly replacing it with a hot water bath (~95° C). At this temperature the adsorbed CO_2 is driven rapidly from the sample, and the desorption peak, which shows surprisingly little "tailing," becomes the measure of the total gas adsorbed, as determined from calibration curves.

To allow for a very slightly higher temperature resulting from the flow of the gas over the sample, a saturation vapor pressure (P_o) of 1450 mm Hg is used in the calculations rather than the value (1413 mm Hg at -78° C) extrapolated from Bridgeman's data (1927). A value of 22.1 Å² is used for the area occupied by the CO_2 molecule on the coal surface under the existing experimental conditions.

For comparison, surface area determinations were made on a few coals with N_2 as the adsorbate. For these determinations, an adsorption period of 30 minutes was used with a liquid nitrogen bath, although it was found that 2 to 3 minutes is sufficient to essentially reach adsorption equilibrium. A saturation vapor pressure (P_0) of 800 mm Hg was used in the calculations, with a value of 16.3 Å² for the area occupied by an adsorbed N_2 molecule near the temperature of liquid nitrogen.

Reflectance (R_o) Measurements

The method for determining microscopically the reflectance of polished coal has recently been standardized on the national and international levels (ASTM, 1974 - Designation D 2798; ICCP, 1971). The differences between the two standards are very minor; the method used in our laboratory conforms to the standard methods. A brief description of our setup and procedure follows. For further details on the method, we refer to the two standards and to Schapiro and Gray (1960), Kötter (1960), Murchison (1964), and de Vries, Habets, and Bokhoven (1968).

We use a Leitz Ortholux microscope that is set up for observation under incident light. Observation under oil immersion, as opposed to observation in air, is used, not only because of the higher magnification achieved but primarily because of the increased contrast obtained between the different constituents of coal. Reflectance under oil immersion ($R_{\rm o}$) is about 1/5 to 1/12 lower than that under air (R_a). The 60× oil immersion objective, together with 10× oculars in the binocular viewing head and a tube factor of 1.25, provides a magnification of $750 \times$ for observation. The light is plane-polarized before it is directed to the reflecting coal surface. The green portion of the reflected light (546 nm wavelength) is filtered out and measured to avoid dispersion effects. With Illinois coals, only 1 percent or less of the incident light is reflected under these conditions. The effective field of measurement is 4 μm to 5 μm in diameter, which is achieved by the insertion of a limiting aperture into the straight tube below the photomultiplier window. The small area of measurement, the low reflectance, polarization, and filtering all reduce the amount of light that reaches the pickup surface of the photomultiplier tube. It is necessary to measure minute differences of about 0.01 percent in the intensity of the reflected light. This requires the use of a highly stabilized power supply for the light source together with a very sensitive photomultiplier tube (Photovolt M520 system). The power supply to the light source can be regulated with a constant-voltage transformer. At regular intervals during a measurement, the reflectance of any coal sample is compared to that of glass standards (Bausch & Lomb Optical Co.), the reflectances of which are known under the conditions of measurement. For the most part, Bausch & Lomb optical glasses No. 751278 and No. 827250, with reflectance

values under oil immersion of 0.533 and 0.895 percent, respectively, are used in the determination of the reflectances of Illinois coals.

Vitrinite is the most common and also the most homogeneous constituent of coal, and is therefore the most suitable constituent for such measurements in the comparison of coals. As is customary, the mean maximum reflectance of vitrinite is determined from at least 100 individual measurements. The circular stage is slowly rotated through 360 degrees, and the maximum reflectance is noted.

The method of preparing coal samples for reflectance measurements is described in detail in ASTM Designation D2797 (ASTM, 1974). The coal is ground until 100 percent passes through a No. 20 sieve (850 μ m). A representative subsample is embedded in a suitable epoxy in a standardized pellet form (1 or 1 1/2 inches diameter), and the surface of the pellet is ground and polished in several stages. The grains exposed in the polished surface presumably are representative of the whole original sample.

Selection of Samples

Since coal gasification, liquefaction, or solubilization proc-

esses no doubt will involve the whole coal, it was deemed desirable to tabulate internal surface area values for whole-coal samples from various seams. Most of the samples are from active mines. Only two samples are from outcrops; in addition, several boreholes were sampled. A large number of the samples in the present study are from the Herrin (No. 6) Coal Member, which is the most widely mined coal seam in Illinois. Figure 3 shows the areal and stratigraphic distribution of the samples. County and section locations are included in the data of table 1.

Whole-coal samples show considerable variation in mineral-matter content and in petrographic composition. Therefore a number of vitrain samples were handpicked from crushed vitrain-rich coal samples. All but one of these were from the Herrin (No. 6) Coal seam. Vitrain forms the shiny, black, brittle, vitreous, conchoidally-fracturing, homogeneous-looking bands and lenses in coal seams; it apparently was derived from the coalification of fragments of wood and bark. Vitrain samples have a low ash content of only up to a few percent and a vitrinite



Fig. 3 - See caption on facing page.



Fig. 3 - Map of Illinois with sample locations and stratigraphic distribution of samples. Number or letter abbreviation at each location refers to coal seam from which sample was taken (see stratigraphic column on facing page).

TABLE 1 - SURFACE AREAS, REFLECTIVITIES, AND ANALYSES (WHERE OBTAINED) OF VARIOUS WHOLE-COAL SAMPLES

14

[]		I	1	1			Derent							1		
			×			<i>"</i> " "			.mate analys		Colonifia		01010	ate alla	Tyses		A
Samp1e	Laboratory	Coal	Location	Surface	<u> </u>	% K ₀		% Voiatile matter,	% Ash,	% Moisture,	value, Btu/1b		Dry	, ash-f:	ree		% inherent
no.	designation	seam	SecTR.	area, m ² /g	Wet	Dry	% Diff.	As received Dry, ash-free	As received	As received Ash-free	Moist, mmf	с	н	76 N	0	S	moisture (from fig. 4)
1	<u>C 13775</u> A 807	7	Vermilion 3-19W-12W	184	0.507	0.570	11.1	<u>39.6</u> 50.1	9.2	$\frac{11.6}{13.1}$	12733	79.36	5,94	1.48	9.46	3.76	14.5
2	<u>C 12570</u> A 955	6	Bureau	220	0.447	0.551	18.9	$\frac{34.0}{46.9}$	8.4	$\frac{19.0}{21.5}$	11169						19
3	C 12399	6	Christian	214				$\frac{34.8}{48.2}$	13.7	$\frac{14.2}{17.1}$	11912					6.05	
4	C 13056 A 430	6	Douglas 36-16N-10W	213	0.532	0.651	18.2	$\frac{34.6}{44.7}$	6.7	$\frac{16.0}{17.4}$	12162					2.27	15
5	<u>C 12834</u> A 804	6	Franklin 8-55-2E	205	0.631	0.740	14.7	$\frac{33.4}{40.4}$	7.8	$\frac{9.5}{10.4}$	13115					1,11	9.5
6	<u>C 11744</u> A 5	6	Franklin 34-65-3E	116	0.618	0.693	10.8	$\frac{36.9}{45.0}$	10.7	7.5	13726					4.42	9
7	C 13971	6	Franklin 11-6S-2E	155				$\frac{36.6}{44.1}$	9.9	7.1 8.1	13468	80.45	5.88	1.61	8.56	3.50	9.5
8	<u>C 12828</u> A 813	6	Franklin 20-7S-3E	135	0.593	0.622	4.8	$\frac{37.7}{45.2}$	9.9	6.7	13609					3.77	9
9	<u>C 9714</u> A 822	6	Gallatin 15-105-9E	46	0.669	0.677	1.2	$\frac{39.4}{46.3}$	11.9	$\frac{3.1}{3.5}$	14804					5.22	3
10	<u>C 13973</u> A 812	6	Jackson 25-75-2W	218	0.611	0.655	6.7	$\frac{34.4}{43.2}$	10.5	$\frac{9.8}{11.2}$	13036					3.46	9.5
11	C 13650 A 816	6	Jefferson 12-45-1E	196	0.627	0.718	12.7	$\frac{34.1}{41.2}$	8.3	$\frac{9.0}{10.0}$	13223					1.44	10
12	C 10807 A 827	6	Madison 9-4N-7W	292	0.529	0.591	10.5	$\frac{32.6}{43.8}$	9.7	$\frac{(16.0)}{(18.0)}$	(11665)					1,17	14
13	C 12539	6	Marion 31-2N-1E	151				$\frac{37.3}{47.2}$	11.8	$\frac{9.2}{10.8}$	13027					5.48	11.5
14	<u>C 14024</u> A 829	6	Montgomery 12-12N-5W	245	0.481	0.526	8.6	$\frac{37.2}{47.6}$	9.0	$\frac{12.7}{14.4}$	12356					4.61	15.5
15	C 13976 A 806	6	Perry 28-65-4W	189	0.525	0.617	14.9	$\frac{37.5}{46.3}$	9.5	9.5	12942					3.77	10.5
16	<u>C 13604</u> A 640	6	Saline 13-95-5E	83	0.702	0.747	6.1	$\frac{34.6}{42.9}$	13.8	5.6	13724					4.78	7
17	C 13893 A 823	6	St. Clair 15-1S-7W	194	0.468	0.536	12.7	$\frac{37.9}{48.4}$	11.2	$\frac{10.5}{12.3}$	12565					5.07	13.5
18	<u>C 13198</u> A 499	6	Vermilion 36-19N-11W	230	0.457	0.560	18.4	$\frac{37.2}{47.9}$	7.7	$\frac{14.6}{16.1}$	12168					2.62	15
19	<u>C 11213</u> A 794	6	Williamson 28-85-3E	115	0.628	0.729	13.9	$\frac{36.9}{43.9}$	9.3	$\frac{6.7}{7.6}$	13510					3.42	8.5
20	<u>C 13399</u> A 588	5A	Gallatin 19-105-9E	59	0.712	0.726	1.9	$\frac{38.1}{44.7}$	12.1	<u>2.8</u> 3.3	14546	81.56	6.01	1.59	7.35	3.49	4
21	C 13400 A 589	5A	Gallatin 19-105-9E	50	0.697	0.711	2.0	$\frac{37.6}{44.6}$	12.9	$\frac{2.7}{3.2}$	14607	81.43	5.84	1.52	6.65	4.56	4

22	<u>C 11744</u> A 5	5	Franklin 34-65-3E	144	0.618	0.693	10.8	$\frac{36.9}{45.0}$	10.7	$\frac{7.5}{8.7}$	13726					4.42	9
23	C A 805	5	Gallatin 13-95-8E	86	0.631	0.669	5.7	31.4 37,5	12.4	$\frac{3.0}{4.3}$	14526						6.5
24	<u>C 13401</u> A 592	5	Gallatin 19-105-9E	65	0.601	0.638	5.8	$\frac{37.1}{43.2}$	11.4	$\frac{2.7}{3.2}$	14608	81.59	5.86	1.43	6.51	4.61	4
25	<u>C 13979</u> A 807	5	Perry 21-6S-4W	200	0,529	0.587	9.9	$\frac{36.7}{45.8}$	10.3	$\frac{9.5}{10.9}$	12865	78.39	5.77	1.43	9.93	4.48	10
26	C 13602 A 640	5	Saline 14-95-5E	158	0.702	0.747	6.0	$\frac{33.3}{40.1}$	9.1	$\frac{7.6}{8.5}$	13555	83.04	5.46	1.20	8.07	2.23	7
27	<u>C 12464</u> A 239	5	Williamson 35-9S-4E	100	0.665	0.733	9.3	$\frac{33.7}{40.4}$	9.8	6.8	13543					3.56	8
28	A 595	4	Gallatin 19-105-9E	77	0.661	0.687	3.8										3.5
29	<u>C 13402</u> A 593	Shawnee- town	Gallatin 19-105-5E	51	0.701	0.706	0.7	$\frac{37.7}{45.6}$	14.7	$\frac{2.5}{3.0}$	14687	82.19	6.05	1.56	6.22	3.98	3
30	<u>C 12630</u> A 311	2	Fulton 2-3N-1E	209				$\frac{37.1}{47.9}$	7.5	$\frac{15.0}{16.6}$	12301					4.02	18
31	A 594	2	Gallatin 19-105-9E	57	0.523	0.546	4.2										3
32	<u>C 10683</u> A 174	2	Kankakee 19-31N-9E	250	0.457	0.543	15.8	$\frac{36.3}{50.1}$	15.1	$\frac{12.4}{15.2}$	12286	64.17	4.79	1.18	8.53	4.11	16
33	C 12901	2	La Salle 15-30N-2E	180				$\frac{41.8}{49.0}$	5.2	(9.3) (10.0)	(13553)	****				2.14	15
34	C 12422 A 220	2	Peoria 7-6N-6E	183				42.6	6.7	$\frac{(11.5)}{(12.7)}$	(12833)	79.48	6.01	1.42	8.78	4.31	16
35	<u>C 13403</u> A 590	DeKoven	Gallatin 19-105-9E	58	0.700	0.740	\$.4	$\frac{37.5}{43.4}$	11.0	$\frac{2.6}{3.0}$	14698	82.03	6.03	1.50	5.63	4.81	2.5
36	<u>C 13404</u> A 591	Davis	Gallatin 19-105-9E	74	0.718	0.743	3.4	$\frac{38.4}{43.1}$	8.2	$\frac{2.6}{2.9}$	14701	82.07	5.85	1.41	8.12	2.55	2.5
37	C 10482	1	Mercer 26-14N-1W	184				$\frac{38.2}{49.9}$	8.5	$\frac{15.0}{17.0}$	11794	78.43	5.66	1.28	8.91	5.72	17
38	C 13184 A 371	Willis	Gallatin 30-105-9E	57	0.863	0.857	0.7	$\frac{35.3}{38.8}$	6.9	$\frac{2.1}{2.3}$	14904	84.36	5.58	1.25	5.37	3.44	3
39	C 14770	Coal in lower part of Abbott Formation	Pope 32-128-6E	59				$\frac{27.1}{31.6}$	12.8	$\frac{1.5}{1.8}$	15199					6.68	2
40	C 13852	Reynolds- burg	Johnson 32-115-4E	66				$\frac{38.9}{42.3}$	4.3	$\frac{3.8}{4.0}$	14623					2.06	2

content of well over 90 volume percent, in most cases more than 95 percent. Such relative homogeneity makes vitrain samples somewhat superior to wholecoal samples for comparative studies—for example, studies to show systematic changes of properties of coals within the Illinois Basin.

RESULTS AND DISCUSSION

Table 1 summarizes our data on internal surface area (ISA), vitrinite reflectance, and chemical composition of the whole-coal samples. The data in table 1 (and similar data for vitrain petrographic fractions in table 3) need some clarifying comments. Column 1 lists the sample numbers used in this paper for convenient reference. Column 2 lists the laboratory numbers assigned to the samples by our chemical (C) and coal petrographic (A) laboratories. These numbers are listed primarily for future reference. Column 3 identifies the coal seam from which the sample was taken. The samples are listed in stratigraphic order (see fig. 3). Column 4 gives the location from which the sample was taken, first by county, then by the section location within the county. Within each seam, the samples are listed alphabetically by county. The CO_2 surface area values are tabulated in column 5. Reflectance (R_o) values are given in columns 6 and 7. The meaning of "wet" and "dry" reflectance values and the percent difference shown in column 8 will be discussed later. The results of the proximate analyses (columns 9, 10, and 11) are listed on both "as received" and "ash-free" bases. Calorific values (column 12) are on a moist, mineral-matter-free (unit coal) basis. The ultimate analyses (columns 13 through 17), where obtained, are shown on a dry, ash-free basis. The moisture values (column 11) and the corresponding calorific values, listed on a moist, mineral-matter-free basis (column 12), are enclosed in parentheses if a significant portion of the original inherent seam moisture appeared to have been lost before the moisture analysis or if the moisture content appeared too high, as with sample 12; loss of moisture occurred in all of the vitrain samples of table 3 and in several of the whole-coal samples of table 1.

Calorific values on a moist, mineral-matter-free basis are normally used to classify Illinois coals by rank. Only calorific values that are not in parentheses can be considered to indicate rank. The moisture value in column 18 was not determined from the sample itself; it is the inherent seam moisture content (ashfree basis) that we would have expected for that particular sample on the basis of the isoranks on the map in figure 4, which will be discussed in greater detail later.

Range of ISA in Illinois Coals

Coals in the Illinois Basin are high-volatile A, B, and C bituminous in rank (hvAb, hvBb, and hvCb of ASTM classification). The ISA values of wholecoal samples range from 46 to 292 m^2/g (table 1). The lowest values found are for hvAb coals from southern Illinois, in particular those from the Eagle Valley area in Gallatin County. ISA values increase rather regularly towards the north, the highest values having been found for the hvCb coals in the extreme northern and northwestern counties of the Illinois coal basin. This variation coincides quite well with the long-recognized decrease in rank of Illinois coals in progressing from the southern part to the northern part of the Illinois coal basin (fig. 4; Damberger, 1971; Cady, 1935).



Fig. 4 - Map of Illinois with isoranks of Herrin (No. 6) Coal Member depicted by inherent moisture content; table of correlations between inherent moisture and ranges for internal surface area values for both whole-coal and vitrain samples; and curve depicting the average change of the inherent moisture content with relative depth in the Illinois Basin.

18 ILLINOIS STATE GEOLOGICAL SURVEY CIRCULAR 493

Differences in ISA between adjoining coal seams in a particular area are small, varying only about as much as ISA values for samples taken from the same coal seam in that area. As shown in the next section, some variation in ISA is expected from different parts of the same coal seam owing to differences in petrographic composition.

Influence of Coal Petrographic Composition on ISA

Whereas the major differences in ISA for coals within the Illinois Basin are related to coal rank, smaller differences within a given coal rank can be attributed in part to variations in the petrographic composition of the samples measured. Table 2 gives the ISA and the petrographic composition of samples of a vitrain, a clarain, and a fusain that were handpicked from the same whole-coal sample (sample no. 11 in table 1).

	Petr	CO2 surface			
Sample type	Vitrinite	Exinite	Inertinite	Mineral matter	area, m²/g
Whole coal	79	7	8	6	196
Vitrain	91	4	4	1	204
Clarain	72	12	9	7	179
Fusain*			90+	-	36

TABLE 2 - INTERNAL SURFACE AREAS OF COAL CONSTITUENTS (HERRIN (NO. 6) COAL MEMBER, JEFFERSON CO., ILLINOIS)

*No analysis. Inertinite content is an estimate.

Vitrain, clarain, and whole coals, which in Illinois are made up predominantly of vitrinite macerals, yield the largest ISA values. Vitrinites include collinite and telinite. Exinites embrace sporinite, cutinite, alginite, and resinite. The inertinites include fusinite, semifusinite, micrinite, and sclerotinite. Mineral matter, for the most part, is clastic material (clay minerals, quartz) and pyrite.

The greater part of the ISA of whole-coal samples certainly stems from their vitrinite content. The whole coals of Illinois normally contain 70 to 85 volume percent vitrinite and the vitrinite has a large surface area, particularly in comparison with the surface areas of inertinite (mostly fusinite and semifusinite in Illinois coals) and mineral matter. Exinite probably is close to vitrinite in ISA. The vitrain samples are characterized in table 3. Vitrinite-enriched handpicked vitrain samples consistently yield higher ISA values—as much as $60 \text{ m}^2/\text{g}$ higher than corresponding whole-coal samples. These differences are shown in figure 5, a plot of ISA values as related to rank in Illinois coals. A certain proportion of the scatter in ISA values for the whole-coal samples in figure 5 can be attributed to variations in the petrographic compositions of the coals.

ISA of Illinois Coals in Relation to That of Other Coals

In published studies relating surface area to coal rank, a minimum in surface area is observed in the region of hvAb coal to medium-volatile bituminous (mvb) coal. Figures 6 and 7 include data from two such studies, the former from

					Proximate analyses			0.1		Ultimate analyses						
Sample no.	Laboratory designation	Coal seam	Location County SecTR.	CO ₂ surface area, m ² /g	% Volatile matter, <u>As received</u> Dry, ash-free	% Ash, As received	% Moisture, <u>As received</u> Ash-free	Calorific value, Btu/lb <u>As received</u> Moist, mmf	с	<u>As</u> Dry, H	receiv ash-f % N	ree 0	S	Average % inherent moisture (from fig. 4)		
41	<u>C 16110</u> A 1163	7	Vermilion 2-19N-12N	269	$\frac{43.8}{46.0}$	0.4	$\frac{(4.4)}{(4.5)}$	(<u>13630</u>) (<u>13730</u>)	$\frac{75.8}{79.7}$	$\frac{6.0}{5.8}$	$\frac{1.3}{1.3}$	$\tfrac{14.9}{11.6}$	$\frac{1.57}{1.65}$	14.5		
42	A 1173	6	Franklin 13-65-2E	220										9.5		
43	<u>C 16109</u> A 1164	6	Gallatin 8-105-9E	63	<u>39.0</u> 40.9	2.3	$\frac{(2.2)}{(2.3)}$	(<u>14160</u>) (<u>14580</u>)	$\tfrac{80.2}{84.0}$	$\frac{5.5}{5.5}$	$\frac{1.4}{1.5}$	$\frac{8.9}{7.3}$	$\frac{1.7}{1.8}$	3		
44	A 1171	6	Gallatin 4-105-9E	47										3		
45	A 821	6	Jefferson 11-45 - 1E	204										10		
46	<u>C 16146</u> A 1168	6	Montgomery 34-12N-5W	288	40.5	2.0	<u>(9.9)</u> (10.3)	(12360) (12680)	$\frac{69.9}{79.3}$	$\frac{5.7}{5.2}$	$\frac{1.2}{1.4}$	$\frac{18.7}{11.2}$	$\frac{2.5}{2.9}$	15.5		
47	<u>C 16112</u> A 1161	6	Peoria 24-9N-5E	290	$\frac{39.0}{42.1}$	2.9	$\frac{(4.4)}{(4.6)}$	(<u>13120</u>) (13610)	$\frac{75.9}{82.0}$	$\frac{5.2}{5.2}$	$\frac{1.1}{1.2}$	$\frac{12.2}{8.9}$	$\frac{2.59}{2.80}$	17		
48	<u>C 16144</u> A 1166	6	Peoria 25-9N-6E	278 & 299	$\frac{38.8}{42.7}$	1.1	<u>(8.1)</u> (8.3)	(<u>12980</u>) (<u>13182</u>)	72.7 80.1	$\frac{5.4}{4.9}$	$\frac{1.1}{1.2}$	$\frac{17.7}{11.6}$	$\frac{2.0}{2.2}$	17		
49	<u>C 16111</u> A 1162 & A 1170	6	Saline 23-95-5E	176 & 149	<u>37.7</u> 40.6	3.6	$\frac{(3.6)}{(3.8)}$	(<u>13510</u>) (<u>14110</u>)	75.5 81.4	<u>5.4</u> 5.4	$\frac{1.4}{1.5}$	$\frac{12.1}{9.6}$	$\frac{2.0}{2.1}$	6.5		
50	<u>C 16113</u> A 1160	6	Stark 13-13N-6E	304	40.6	1.1	$\frac{(5.4)}{(5.5)}$	(<u>12990</u>) (<u>13180</u>)	<u>73.9</u> 79.0	$\frac{5.2}{4.9}$	$\frac{1.1}{1.1}$	$\tfrac{17.1}{13.2}$	$\frac{1.68}{1.80}$	18.5		
51	<u>C 16145</u> A 1167	6	Stark 13-13N-6E	293	<u>39.5</u> 43.7	0.8	<u>(8.9)</u> (9.0)							18.5		

TABLE 3 - SURFACE AREAS, REFLECTIVITIES, AND ANALYSES (WHERE OBTAINED) OF VITRAIN SAMPLES



Fig. 5 - Internal surface areas of whole-coal and vitrain samples from Illinois as they relate to coal rank, expressed by average inherent moisture content and calorific value on the moist, mineral-matter-free basis. Only samples from the No. 5, No. 6, and No. 7 Coals are plotted. No drill-hole samples are included.

Griffith and Hirst (1944), who used the heat-of-wetting method, and the latter from Kini (1964), who used the gas adsorption method. Our averaged data are superimposed on their data in each of the two figures. In both cases the agreement is excellent in the regions of comparison.

It is also apparent from figures 6 and 7 that the ISA values for Illinois coals practically cover the whole range of values reported for coals of all ranks from different parts of the world. To account for the considerable decrease in ISA in proceeding from the hvCb coals to the hvAb coals requires a further understanding of the differences in total porosity and of the variations in pore size that exist among these coals. (These differences are treated in sections which follow.) In turn, an understanding of the porosity variations, together with ISA values, helps explain the apparent minimum in ISA that exists in the region of the hvAb coals.

Influence of Porosity and Coal Rank on ISA

The hvCb coals of northern Illinois contain a greater proportion of larger pores than the hvAb coals of southern Illinois. This difference is apparent not only from their relative moisture contents but also from mercury porosimetry data. It is not apparent from ISA values alone, because extensive surface area can be present within an ultrafine pore structure, in which the total pore volume (as determined from moisture content) is relatively small.



Fig. 6 -

Correlation between coal rank (expressed in % volatile matter, V.M., in higher-rank coals and % moisture content in lower-rank coals) and internal surface area based on a heat-of-wetting method, as published by Griffith and Hirst (1944). Our data for Illinois whole coal and vitrain samples are superimposed (heavy dashed lines) and show good agreement with Griffith and Hirst's data in the region of comparison.

Fig. 7 -

Correlation between coal rank, expressed by % carbon content (dry, ash-free basis), and internal surface area based on data from the xenon adsorption method, as published by Kini (1964). Our data for Illinois coals are superimposed and show good agreement with Kini's data in the region of comparison.



Pore-Size Information from Mercury Porosimetry

The sizes and relative amounts of pores in porous materials can be determined by the intrusion of mercury into these pores under increasing pressure. The method is based on the fact that increasing pressure is necessary to force the mercury into successively smaller pores. The method is applicable with commercial instrumentation for determinations of pore sizes from 350 μ m to about 0.0035 μ m (35 Å), the lower limit of measurement at present. A pressure of about 50,000 psia (about 3500 kg/cm²) is required to penetrate pores at the lower limit. It is obvious that only an open-pore structure can be penetrated. It is also obvious that rather large pores cannot be penetrated if the entrances to the pores are very small (ink-bottle structure).

As we have already pointed out, a large proportion of the pores in coals are much smaller in diameter than 35 Å. Thus, it might appear that the data from mercury intrusion would be quite limited for interpretive purposes. Actually, the technique does yield valuable supplemental information about the larger pores in coals.

Without going into great detail here about the instrumentation and test procedures, the principle of the method simply involves the determination of the amount of mercury that can be forced into the pores of a material at known increasing pressures. Mercury will penetrate crevices and pore openings with a strict dependence upon the force applied as given by the equation

$PD = -4\gamma \cos \theta$

where P is the applied pressure, D is the diameter of the pore, γ is the surface tension of mercury, and θ is the contact angle between the mercury and the surface. Instrumentation is designed to permit the pressure on the mercury to be adjusted to a known value and to permit the determination of the amount of mercury forced into the pores at that pressure. Only pores of a given size are intruded and filled at a given pressure. Pressure-volume curves are plotted from the experimental data. Two such curves are shown in figure 8 for two different vitrain samples, one from northern Illinois, the other from southern Illinois. The ISA values for these two samples, determined with CO_2 , were 304 m²/g and 47 m²/g, respectively.

The steep rise of the two curves at the low-pressure end indicates only a filling of the void spaces between the sample particles. A gradual increase in



Fig. 8 - Mercury penetration of two Illinois vitrain samples of different rank.

slope over the middle segments of the two curves indicates some compression of the samples. It is at the high-pressure end of the curves that differences in pore filling are manifested, and it is readily apparent that there is a greater proportion of larger pores (larger than 35 A) present in the northern Illinois hvCb coal than in the hvAb coal from southern Illinois. The increase in penetration volume $(0.158 \text{ cm}^3/\text{g})$ of mercury is appreciable for the hvCb coal for pores between 35 and 220 A (in the pressure region greater than 8000 psia, or about 550 kg/cm²). There is only a slight increase in penetration volume

 $(0.022 \text{ cm}^3/\text{g})$, on the other hand, for the hvAb coal, amounting to approximately one-seventh of the pore volume of the hvCb sample; this increase is associated only with pores 90 Å in diameter and smaller. The pressure-volume data show that there are essentially no pores greater than 90 Å in diameter present in the hvAb coal and that, in fact, only a small proportion of pores are intruded in the size range from 90 to 35 Å, that is, down to the lower limit of the measurement.

Porosity Information from Moisture Content of Coal

Rank in Illinois coals, as in other high-volatile bituminous coals, is expressed by calorific values on a moist, mineral-matter-free or a moist, ash-free basis (ASTM, 1974; United Nations, 1956). It can be shown that most of the variation in calorific value (moist, mmf) is actually due to the inherent moisture content of the coal (fig. 9): calorific value on a dry basis varies only slightly and within a broad band between 5 and 20 percent inherent moisture contents, which are typical for Illinois coals, whereas a nearly linear correlation exists between calorific value (moist basis) and inherent moisture content for Illinois coals.

In this paper, we use moisture content and calorific value (moist, mmf basis) as equivalent and equally suitable rank parameters. Conversion of one into the other can be made easily by using the "moist" band of figure 9.

Since there is considerable confusion about the meaning of "moisture in coal," particularly with regard to the comparison and significance of analytical data, some detailed discussion of this subject is in order here.

A "moist" sample, according to ASTM (1974, p. 55), is a sample that "shall be taken in a manner most likely to preserve inherent moisture for purposes of analysis." The ASTM "Classification of Coals by Rank" (Designation D388) theoretically is based on the natural, or inherent, moisture of the coal seam before it is sampled or mined. It is assumed that coal occurs in nature in a moisture-



Fig. 9 - Correlation between calorific values on moist and dry mineral-matter-free bases and inherent moisture content in high-volatile bituminous coals.

saturated condition. It should be readily apparent that high-moisture coals, in particular, can lose appreciable amounts of water before sampling, in transit from the sampling location to the laboratory, or during other handling procedures (crushing, sieving, etc.). Samples that may have lost moisture before sampling, or after sampling but before analysis, "shall not be used for classification on a moist basis unless brought to a standard condition of moisture equilibrium at 30° C in a vacuum desiccator containing a saturated solution of potassium sulfate (97 percent humidity) as specified in the Method of Test for Equilibrium Moisture of Coal at 96 to 97 Percent Relative Humidity and 30° C" (ASTM Designation D1412, ASTM, 1974, p. 250-252). It has been shown for the coals of high-volatile

bituminous (hvb) rank that we have in Illinois that equilibrium moisture and inherent seam or bed moisture are essentially identical (Ode and Gibson, 1960; Hückel, 1967). In figure 10, we have combined the data from Ode and Gibson, from Hückel, and from a few samples of Illinois coals for which equilibrium moisture values were determined by Dr. Marlies Teichmüller (Geologisches Landesamt NW, Krefeld, West Germany) and by investigators at the Central Laboratory, Peabody Coal Company, Freeburg, Illinois. The data points are about equally scattered on each side of the 1:1 ratio line, an indication that the two moisture contents are virtually interchangeable.

Because of the uncertainties involved in the determination of the inherent (natural) moisture of coal, equilibrium moisture data are generally more reliable than inherent moisture data. However, ASTM does not normally require the



Fig. 10 - Correlation between natural (inherent) and equilibrium moisture contents of highvolatile bituminous and subbituminous coals. Samples from various coal basins in U.S.A. and Europe.

determination of equilibrium moisture if proper precautions are taken to preserve the inherent seam moisture. Equilibrium moisture is not routinely determined in the Illinois State Geological Survey laboratories.

The inherent coal seam moisture changes quite regularly within the Illinois Basin, both regionally and with depth. Figure 4 gives the main results of a systematic study of several thousand analyses carried out over several years on coals from the entire Illinois coal field. The lines of equal inherent seam moisture for Herrin (No. 6) Coal shown in the map are the result of an averaging process. Thus, moisture values taken from this map are averages from many samples and are probably more representative than any single moisture determination would be. The moisture-depth curve of figure 4 permits the inference of moisture values for seams both below and above the Herrin (No. 6) Coal if the distance between the two seams is known. We have determined the average inherent seam moisture for each of our samples using both the map and the depth curve of figure 4 and have listed these values in tables 1 and 3 as "average inherent moisture (from fig. 4)." Single moisture evaluations and corresponding calorific values (moist basis) that deviated by more than about 10 to 15 percent (relative) from this "map moisture" were put in parentheses since it can be assumed that these samples either had lost some of their natural moisture or, in one case, contained excessive moisture. In the discussion of the relationship between rank and internal surface areas and pore sizes (see figs. 5, 12, and 13), map-moisture values from figure 4 have been used to establish our coal rank parameter.

The "as received" moisture contents of all the vitrain samples are much lower than anticipated from the values given by the isorank lines in figure 4 (see table 3). Several factors contributed to these low moisture contents. These samples were taken during the summer. The original samples were spread out on a laboratory bench and crushed with a hammer to permit the handpicking of bright

vitrain pieces. In addition, a number of the samples were stored for a considerable period of time before they were submitted for chemical analysis. The vitrain samples from southern Illinois (Pope, Saline, and Gallatin Counties) yielded somewhat lower equilibrium moisture contents (table 3) than we would have expected from the map (fig. 4) and from the plot showing the correlation between natural seam moisture and equilibrium moisture (fig. 10). We are not sure about the significance of this difference at this time.

If all pores were filled with water in nature, the inherent (natural) seam moisture would give direct information on the pore volume, as shown in figure 11. Pores in coal usually contain, in addition to water, small amounts of gaseous and liquid hydrocarbons and CO_2 , but as a first approximation, the natural moisture



Fig. 11 - Relation between inherent moisture content and volume-percent porosity in Illinois coals.

content can be assumed to fill most of the pore space of a coal. Thus, pore volume in Illinois coals ranges from about 5 to about 25 percent (fig. 11).

Pore volume combined with the ISA permits the calculation of the size of an average pore. If we assume that all pores are spherical in shape and have equal diameters, d (in angstroms), and if N is the number of pores present in 1 gram of coal having a surface area, A (in m^2/g), and a moisture content of P/100 gram (in cm³), then:

(N)
$$(S_v) (10^{-24}) = P/100 \text{ and } (N) (S_a) (10^{-20}) = A$$

where S_v is the volume (in Å³), S_a is the surface area (in Å²) of each one of these idealized spherical pores, and P is the moisture content of coal in weight percent. By elimination of N and use of the proper equations regarding a sphere, the diameter, d (in angstroms), of an average pore can be determined by the following equation:

$$d = 600 P/A.$$

Spherical pores are not actually representative of the tortuous pore system that exists in coals, but the relative change in d is of interest here for comparative purposes. In figure 12 we have plotted the "apparent" average pore diameters of whole coals and vitrain fractions by using the above equation with the experimental data, assuming spherical pores.

The pore diameters of the whole coals shown are somewhat large because these coals contain mineral matter, which does not contribute much to the total measured surface area. We do not have enough data to calculate internal surface areas on a mineral-matter-free basis: the internal surface areas on a mineralmatter-free basis would be somewhat larger and the "apparent" average diameters smaller, thus moving the whole-coal curves closer to the vitrain curves in figures 5 and 12.



Fig. 12 - Range of "apparent" average pore diameters (calculated from inherent moisture contents and ISA values) of whole coals and vitrains from the Illinois Basin.

The surprising result of this manipulation of the porosity and internal surface area data (fig. 12), in view of our knowledge of pore-size differences from mercury intrusion and from relative moisture contents, is the small change of the "apparent" average pore size over most of the range of coal rank in Illinois coals. A maximum is even indicated in the hvAb region. Then, as rank increases in the direction of the mvb coals, the "apparent" average pore diameter decreases to about 20 Å in the higher-rank coals from the southernmost part of the Illinois Basin. Probably an even further decrease in the average pore diameter would be observed in mvb coals.

With decreasing rank in the direction of subbituminous and lignitic coals, the average pore diameters increase rapidly. As we shall explain

ISA, MOISTURE, AND POROSITY OF ILLINOIS COALS 27

more fully later, we believe that the surprising cessation of a decrease in the "apparent" average pore diameter with increasing rank among the hvb coals is the result of a clogging of pores and pore entrances by relatively low-boiling organic matter that evolves from coal during coalification, particularly within the hvb coals. Such clogging makes a part of the ISA inaccessible even to CO_2 ; thus ISA values from CO_2 adsorption do not represent the complete surface area of all the pores that contribute to the natural moisture content of coal. The "apparent" average pore diameters in figure 12 therefore are somewhat greater than they should be throughout the full moisture range, but are markedly greater for the coals containing about 3 to 11 percent inherent moisture.

Pore-Size Information from Nitrogen Adsorption

As emphasized earlier in this report, N_2 at -195° C cannot diffuse in a practical time into pores smaller than about 4 to 5 Å in diameter. In spite of the lower surface area values obtained with N_2 as the adsorbate, however, valuable supplemental information about the relative sizes of pores in coals can be gleaned from comparing N_2 adsorption data with CO_2 adsorption data. Machin, Staplin, and Deadmore (1963) studied a number of Illinois coals and reported N_2 surface area values of 47 to 92 m²/g for hvCb coals, 7 to 16 m²/g for hvBb coals, and 1.8 to 4.5 m²/g for hvAb coals. In a similar study with N_2 as the adsorbate, we obtained a value of 99 m²/g for the Colchester (No. 2) Coal Member in Kankakee County (hvCb), 15 m²/g for the Herrin (No. 6) Coal in Jefferson County (hvBb), and 0.6 m²/g for the coal in the lower part of the Abbott Formation in Pope County (hvAb). These coals had yielded surface area values of 250 m²/g, 198 m²/g, and 59 m²/g, respectively, with CO_2 as the adsorbate.

An examination of the ISA values from N_2 adsorption data alone shows that the hvCb coals have much larger internal surface areas than the hvAb coals. The surface area values from N_2 adsorption fall off markedly in proceeding from the HvCb coals through the hvBb coals to the hvAb coals; the latter yield values two magnitudes smaller than those from the hvCb coals. Clearly, the hvCb coals from northern and western Illinois contain a much larger proportion of pores with pore entrances larger than 4 to 5 Å than do the higher-rank coals from southern Illinois.

Increasing the ISA by Heating

Controlled-temperature experiments were carried out using a Cahn Electrobalance, with which weight loss of a sample at given temperatures can readily be studied as a function of time. A known quantity of volatile matter was removed from a given coal sample, and the surface area of the sample was then redetermined. The samples were heated in a He gas stream. Water was removed at a temperature of about 120° C until no further weight loss occurred. The temperature then was increased to remove a small percentage of the volatile matter. The temperature was kept below 330° C (200° C was sufficient for low-percentage removal), which is considerably below the softening temperature of the coals (\sim 380° C). Results are shown in table 4 for three different whole coals (one hvAb, two hvBb).

The increase in internal surface area as a function of the removal of volatile matter is readily apparent with either CO_2 or N_2 used as the adsorbate. The percentage increase in surface area is greatest for the hvAb coal at the same level of volatile-matter removal. For example, after the removal of only 3.87 percent

Coal member	% Volatile matter, dry basis	Volatile matter removed (as % of total volatile matter, dry basis)	Volatile matter removed (as % of total coal sample, dry basis)	CO ₂ surface area, m ² /g	N ₂ surface area, m ² /g
Briar Hill (No. 5A)	38.7	. 0	0	50	0.8
Coal Member, Gallatin County		2.48	0.96	110	2.9
(hvAb)		5.34	2.07	153	4.5
		10.00	3.87	200	6.0
		15.08	6.32	220	34.9
		19.92	7.73	244	40.0
Harrisburg (No. 5)	39.8	0	0	144	8.0
Coal Member, Franklin County		2.39	0.95	182	8.4
(hvBb)		5.01	2.00	215	17.9
		10.21	4.06	284	58.2
Herrin (No. 6)	35.5	0	0	205	9.2
Coal Member, Franklin County		3.05	1.08	256	10.8
(hvBb)		5.22	1.86	273	19.3
		9.74	3.46	295	34.7

TABLE 4 - THE EFFECT OF VOLATILE-MATTER REMOVAL ON INTERNAL SURFACE AREA

volatile matter, or 10 percent of the total volatile matter present, the surface area, with CO_2 as the adsorbate, increased from 50 to 200 m²/g for the hvAb coal, a fourfold increase in surface area from that of the original dried sample. At the same level of volatile-matter removal, one of the hvBb coals doubled in surface area (from 144 to 284 m²/g) and the other hvBb coal increased by almost 50 percent (from 205 to 295 m²/g). Surface area values with N₂ as the adsorbate also increased markedly. It is significant in light of the discussion which follows, however, that after the volatile-matter removal the N₂ surface areas are still not as large as N₂ values for hvCb coals, whereas the CO_2 values are equal to those for hvCb coals.

The increase in internal surface area is surprisingly large in view of the small quantity of relatively low-boiling organic material removed during heating. The generation of such a large surface with such little weight loss is unknown, for example, in numerous studies involving the thermal decomposition of inorganic carbonates, oxalates, and hydroxides. Thus, it would appear that the increased surface area of the heated coal samples can be associated only with the unplugging of an already existing pore structure that, in the original unheated sample, was inaccessible even to CO_2 at -78° C. As the data also indicate, the pores in the hvAb coals of southern Illinois, being smaller on the average than those in hvBb coals or hvCb coals, are more easily plugged and, thus, a greater proportion of the pore structure in the unheated hvAb coal samples is not penetrated by CO_2 .

We do not know the exact nature of the relatively low-boiling organic material that is removed at temperatures up to 330° C. However, a series of papers, "The Smaller Molecules Obtainable from Coal and Their Significance" (Palmer and Vahrman, 1972; Rahman and Vahrman, 1971; Spence and Vahrman, 1970; Vahrman, 1970), lends support to our interpretation. The authors of these papers concluded that much larger quantities of lower-boiling hydrocarbons exist in coal than had previously been suspected. These hydrocarbons are adsorbed on the internal surfaces of the micropores and, thus, have been overlooked simply because they are difficult to reach with solvents in extraction studies. In one of their experiments, Palmer and Vahrman (1972) used superheated steam to heat coal and remove these lower-boiling hydrocarbons. At 300° C they removed about 2 to 5 percent volatile material, which is quite comparable to the weight percent of material that we removed under helium. Analysis of their extracted material showed that it consists almost solely of hydrocarbons—aliphatic gases, for the most part, together with small amounts of tar oil, the bulk of which was soluble in light petroleum.

The inability of CO₂ to penetrate all pores results in the relatively large "apparent" average pore diameters of about 30 to 50 Å, as calculated from pore volume (from inherent moisture content) and CO₂ internal surface area data (fig. 12). The anticipated decrease in "apparent" average pore diameters in proceeding from hvCb rank coals to hvAb rank coals is not realized from these calculations. In view of the data from the controlled-heating experiments, this lack of significant change in the "apparent" average pore diameters over most of the coal ranks represented among Illinois coals (fig. 12), is, with little doubt, indicative of the inaccessibility of pore spaces to CO, due to plugging. However, if surface areas were larger, as they are made to be by the controlled-heating experiments, the calculated "apparent" average pore diameters would decrease (see equation on page 26) if the pore volume is assumed to remain essentially constant. A fourfold increase in surface area, which occurs in an hvAb coal after removal of 10 percent of the available volatile matter. in recalculation would result in a reduction of the "apparent" average pore diameter to one-fourth that of the initial calculated value used in figure 12.

The internal surface area data from the controlled-heating experiments (using ISA values after 10% total volatile-matter removal) were used for recalculating the average pore diameters. The limited data from the three coals studied are depicted linearly in figure 13 as "true" ("T") average pore diameters for whole coals. The data show the expected decrease in average pore sizes in progressing to the hvAb coals. The mean values within the range of "apparent" average pore diameters calculated for the whole coals of Illinois (shown in fig. 12) are replotted in figure 13 as "A" whole coal for comparison. The area between curve "A" whole coal and curve "T" whole coal is indicative of the degree of plugging that occurs in Illinois coals, with the larger area in the region of the hvAb coals indicating greater plugging. Although the "true" average pore diameters, represented by curve "T" in figure 13, no doubt are still somewhat large (owing to the use of a spherical-pore model), the rate of decrease (slope of "T") of the average pore sizes from hvCb coals probably reflects rather closely the actual rate of change of the average pore sizes.

Thus, it would appear that the well-known minimum in data plots of surface area versus coal rank in the region of the hvAb coals (figs. 6 and 7) should not be nearly as steep or as extensive as studies published thus far would indicate. Carbon dioxide as an adsorbate gas cannot enter the compressed and plugged pore system, nor can liquids, such as methanol, in the heat-of-wetting method.

Interrelation of Porosity, ISA, and Reflectance in Illinois Coals

In recent years the reflectance of polished coal has become increasingly accepted as a rank parameter throughout much of the coalification series. Generally, the maceral vitrinite is used as the reference material because of its relative homogeneity and its abundance, both in normal coal and as finely disseminated coaly particles ("phytoclasts," Bostick, 1970; "organoliths," Alpern, 1970) in sedimentary rocks.



Fig. 13 - Comparison of mean "apparent" ("A") average pore diameter (fig. 12) with "true" ("T") average pore diameter of whole-coal samples from Illinois. The latter was calculated from porosity (fig. 11) and from increased ISA after removal of relatively low-boiling hydrocarbons during controlled heating. The difference between the mean "apparent" average pore diameter and the "true" average pore diameter is probably indicative of the degree of plugging of pores that are not accessible to CO₂ in ISA determinations without prior heat treatment of the coal samples.

Reflectance increases over the whole coalification series. In lignite, R_o may be as low as 0.3 percent. In high-volatile bituminous coals, R_o ranges from about 0.4 to about 1.2 percent, which is the range for Illinois coals. The highest-rank coals, semianthracites and anthracites, reflect about 2.0 to 6.0 percent (and higher in certain cases) of the incident light from a polished surface under oil immersion.

Most of the studies on coal reflectance have been done in connection with efforts to find simple petrographic methods for the prediction of coking properties of single coals and of coal blends with R_o above 0.7 percent (that is, high-volatile B and A and medium- and low-volatile bituminous coals). It has been only relatively recently that the reflectances of high-volatile C bituminous, subbituminous, and lignific coals have been studied to any great extent. Teichmüller and Teichmüller (1968, table 1, p. 248) and M. Teichmüller (1971) indicate that R_o of vitrinite is a good rank parameter only above about 0.7 percent. It would appear that R_o is fairly closely related to the volatile matter content, even in high-volatile bituminous coals, for which the volatile matter content is not a reliable rank parameter. At present there is some doubt as to the reliability of R_o as a rank parameter in the lower-rank coals.

ISA, MOISTURE, AND POROSITY OF ILLINOIS COALS 31

Harrison (1965) reported the effect of moisture content on reflectance values for Illinois coals. He noted that "moist" samples, that is, those prepared from moist coals, yielded lower reflectance values than samples prepared from well-dried coals. The effect was most pronounced among the hvCb coals of northern and western Illinois. The effect also was noted when measurements were made on samples soon after they had been wet polished. Harrison recommended that coal samples be air dried for at least 15 hours before a briquette is made, and that the briquette, after it is wet polished, be placed in a desiccator for at least 15 hours before reflectance analysis measurements are made. This proposal was included in the recently adopted ASTM Designation D2797, "Preparing Coal Samples for Microscopical Analysis by Reflected Light" (ASTM, 1974, p. 551-555), and it has also been adopted for the corresponding international standard method for coals that might be affected by moisture absorption in the 1971 Supplement (ICCP, 1971) to the second edition of the International Handbook of Coal Petrography.

Harrison and Thomas (1966) compared the differences between the reflectance values of "wet" and "dry" samples with ISA values and found a good correlation. A greater disparity existed between "wet" and "dry" reflectance values for the high-porosity hvCb coals (higher ISA values) than between those reflectance values for the hvBb and hvAb coals (lower ISA values). Additional samples have since been analyzed (table 1 lists both "wet" and "dry" reflectance values and percentage differences), and the data have been plotted as functions of ISA (fig. 14), and of moisture content as taken from the map in figure 4 (fig. 15). There is appreciable scatter in the data; nevertheless, the trend established in the earlier study is reconfirmed. Scattering is to be expected because of the difficulty in replicating moisture content under nonequilibrium conditions.

As Harrison and Thomas (1966) pointed out, the noted differences in reflectance probably are dependent upon the number of macropores into which water can reenter. As we have shown in preceding sections, there is a greater proportion of larger pores (>100 Å) present in hvCb coals than in hvAb coals. Thus, strictly speaking, porosity rather than internal surface area is the parameter that is responsible for variations in reflectance between "wet" and "dry" samples. However, since internal surface area also has been shown to correlate with porosity in Illinois coals, it is a satisfactory substitute for porosity for correlation with reflectance differences. It should be realized that such a correlation with internal surface area would not be obtained for higher-rank coals of lower porosity.

How do the differences in macroporosity account for the observed differences in reflectance for "wet" and "dry" samples, with the latter samples producing the higher reflectance values? Although we do not have unequivocal proof at this time, one explanation that we find plausible follows.

First, consider that the polished coal surface contains a large number of openings which, for the most part, are less than 200 Å in diameter. Since these openings are considerably smaller in diameter than the wavelength of visible light, light cannot enter the pores (as black boxes) and be scattered from beneath the surface. Thus, the only scattering and reflection of the incident light occur at the surface, where the pores, either water-filled or air-filled, are considered part of the continuum of the coal surface. To account for the observations then, it is necessary to show only that an immersion oil-air interface has a higher reflectance than an immersion oil-water interface. These reflectances can be calculated from Beer's equation

$$R = \frac{(n' - n'')^2 + (n'k)^2}{(n' + n'')^2 + (n'k)^2}$$



Fig. 14 - Correlation between "wet" and "dry" reflectance under oil immersion (R_o) and the internal surface area of whole-coal samples from Illinois.



Fig. 15 - Correlation between "wet" and "dry" reflectance under oil immersion (R_o) and the inherent moisture content of whole-coal samples from Illinois.

where R = reflectance, n' = index of refraction of first medium, n'' = index of refraction of second medium, and k = absorptivity. We define R_1 as a "dry" (airfilled) pore and R₂ as a "wet" (water-filled) pore. The experimentally observed relationship is $R_1 > R_2$.

Rewriting Beer's equation,

$$R_{1} = \frac{(1 - [n_{1}/n_{2}])^{2} + k_{1}^{2}}{(1 + [n_{1}/n_{2}])^{2} + k_{1}^{2}} ; \qquad R_{2} = \frac{(1 - [n_{1}/n_{3}])^{2} + k_{2}^{2}}{(1 + [n_{1}/n_{3}])^{2} + k_{2}^{2}}$$

and solving for R_1 and R_2 by using the values

 $n_1 = index of refraction of oil of cedar (1.515)$

 $n_2 = index of refraction of air (~1.0)$

 $n_3 = index \text{ of refraction of water (1.333)}$

and neglecting the absorptivity (which is small and does not change significantly for hvb coals), then

$R_1 = \frac{(1 - 1.515)^2}{(1 + 1.515)^2}$;	$R_{2} = \frac{\left(1 - \frac{1.515}{1.333}\right)^{2}}{\left(1 + \frac{1.515}{1.333}\right)^{2}};$
$R_{i} = 41.93 \times 10^{-3}$;	$R_2 = 4.08 \times 10^{-3}$.

Thus, it is clear that reflectance from a "dry" (air-filled) pore is nearly 10 times greater than that from a "wet" (water-filled) pore when using oil of cedar as an immersion medium.

Coal is relatively low in reflectance. If 15 to 20 percent of the coal surface is void space (a reasonable figure for the hvCb coals of Illinois in view of the moisture contents), it should be apparent that the presence of "dry" or "wet" pores can significantly alter the total reflectance from the coal surface. On the other hand, if a solid (other than coal) with relatively high reflectance were under evaluation, the presence of "wet" pores or "dry" pores would make little difference in total reflection, although the density of the solid would certainly be an important factor influencing the reflectance.

Geological Implications from ISA and Porosity Evaluations

The relatively high porosity of the Illinois hvCb coals and of some of the hvBb coals makes these coals unusual in comparison with similar coals of the same rank from other coal fields. Illinois coals tend to have appreciably higher freeswelling indices, higher contents of hydrogen and volatile matter, and lower contents of carbon and oxygen than other coals with comparable inherent or equilibrium moisture contents; in addition, Illinois coals are relatively rich in organic sulfur and finely disseminated syngenetic pyrite. These characteristics are, of course, typical of coal seams that were laid down under marine influence.

Petrascheck (1952) mentions a "coking coal" that occurred in a sequence of noncoking high-volatile bituminous coals of the Ostrava Coal Basin, eastern Czechoslovakia. The coking coal was overlain by marine beds and had a higher than normal sulfur content. Teichmüller (1955) and Mackowsky (1947, 1949) discuss the unusual properties of the Katharina seam of the Ruhr Basin, West Germany. Not only do the roof rocks reflect marine conditions by the presence of marine

33

fossils, but the coal itself is also unusual in comparison with adjacent seams not having marine roof sediments. The seam is characterized by a special kind of clarite that has few spores and other protobitumina, is exceptionally rich in finegrained micrinite, and has much fine-grained syngenetic pyrite disseminated through it. Vitrinite of this seam possesses less cell structure and reflects less light than do other coal macerals. The coal is rich in organic sulfur, has higher than normal H/C and H/O ratios, and tends to swell more than adjacent coals. Apparently, it is this type of coal that we have in Illinois.

Hilt's rule (1873) that coal rank in any given area increases with depth is manifested in the Illinois Basin by the decrease of inherent moisture—and thus also porosity—with depth, approximately as shown by the rank versus depth curve in figure 4.

Coals now at or near the surface have attained appreciably higher coal rank in southern Illinois than in northern and western Illinois (fig. 4). Thus it would seem that the coals of southern Illinois were once more deeply buried than the coals of northern Illinois, probably by more than 6,000 feet, judging from the rank versus depth curve in figure 4. Since the former depth of burial of northern Illinois coals was possibly 4,000 to 5,000 feet (Altschaeffl and Harrison, 1959), the total depth of burial of coals in southern Illinois was probably some 10,000 feet. Such a pattern of southward-increasing sediment thickness within the Illinois Basin throughout Paleozoic time is well documented (Buschbach, 1971; Bond et al., 1971).

However, the difference in burial depth may have been much less than the full 6,000 feet. The somewhat unusual coalification pattern of southern Illinois, discussed elsewhere by Damberger (1971, 1974), may have resulted from increased heat flow above deep-seated igneous intrusions sometime after coal formation, and burial may therefore not have been that much deeper in southern Illinois than in the north. Such heating at relatively shallow depths might help explain the marked increase of internal surface area after the removal of only small percentages of volatile matter during controlled heating well below the softening temperature of the coal (see page 27). The geothermal heating and the sweating out of relatively low-boiling organic matter from the coal occurred at a time when porosity was still quite high and many pore spaces and connections were open, allowing the migration and deposition in pores of these relatively low-boiling hydrocarbons. Many of the pores could have become blocked during this stage, or during further compression of the coal.

Although the influence of such deposited organic materials in pores on porosity and internal surface area may be quite pronounced in Illinois coals, we believe that the minimum in the parabolic curves of rank versus porosity and internal surface area in the region of high-volatile A bituminous to medium-volatile bituminous coals (Kini, 1964; Marsh and Siemieniewska, 1965; Toda et al., 1971) is the result of both the presence of a smaller-diameter pore system and the presence of pores clogged with relatively low-boiling organic components (fig. 13). With further increase in temperature during coalification, this volatile organic matter is removed, along with other volatile matter formed by slow decomposition of coal at elevated temperatures. With increase in rank there is a regeneration of an open-pore system, even under overburden pressure, as gaseous products are released from the interior of the coal. The internal surface area, as measured by CO_2 adsorption, changes with increase in rank through the higher-rank coals by increasing from a minimal value of 25 to 40 m^2/g for mvb coals to more than 300 m²/g for anthracites (Thomas, Benson, and Hieftje, 1966). Nitrogen surface area values, however, remain small because the average pore diameters remain small, for the most part less than 4 to 5 Å.

SUMMARY AND CONCLUSIONS

Internal surface area measurements on coals by a single-point BET method with CO_2 as the adsorbate provide useful data for the comparison of coals of different rank. In Illinois coals, the internal surface areas correlate well with moisture contents. In these coals, both of these parameters also correlate well with porosities.

Internal surface areas of whole coals range from $46 \text{ m}^2/\text{g}$ for hvAb coals to 292 m²/g for hvCb coals. Most of the large ISA values are derived from the vitrinite portion of coals: handpicked vitrains containing well over 90 volume percent vitrinite produced ISA values up to $60 \text{ m}^2/\text{g}$ greater than the values from the whole coals from which the vitrains were obtained.

Illinois hvCb coals have greater porosity than hvBb coals, which in turn have greater porosity than hvAb coals. Mercury-intrusion data show that in Illinois hvCb coals, there is a large number of pores having diameters in the range of 90 to 220 Å, whereas in hvAb coals there are virtually no pores in this size range. Most pores in the latter coals appear to be smaller than 35 Å. These differences may be indicative of a progressive increase in depth of burial from the northern to the southerm part of the Illinois Basin.

The hvAb coals of southern Illinois actually are more porous than ISA measurements with CO_2 indicate. This is borne out by the large increase in ISA that accompanies the loss of only small quantities of volatile organic matter during controlled-heating conditions. It would appear that, in addition to having a smaller-diameter pore structure, the hvAb coals have much of their internal pore structure plugged by relatively low-boiling organic constituents. In plots of ISA versus various rank parameters, reported by several workers, there is a minimum in ISA in the curve near the hvAb and mvb coal ranks, followed by an increase in ISA as rank increases through the low-volatile bituminous (lvb) coals, the semi-anthracites, and the anthracites. The increase in ISA in the higher-rank coals may be a result of natural removal of relatively low-boiling organic constituents from pores, which reopened an already existing internal pore structure in the course of coalification as burial depth and temperature increased.

Differences that have been observed in reflectance measurements on Illinois coals probably can also be attributed to the marked differences in the porosities of these coals. Differences between reflectance values of "wet" and "dry" prepared briquettes of hvCb coals are large; differences between reflectance values of "wet" and "dry" briquettes of hvAb coals are much smaller. This phenomenon is likely associated with the larger pores (35 to 220 Å) that are present in hvCb coals (but virtually absent in hvAb coals) and into which water can readily reenter during briquette preparation. We have shown that reflectance under oil immersion is lower from "wet" (water-filled) pores that from "dry" (air-filled)/pores.

ACKNOWLEDGMENTS

We are pleased to acknowledge the assistance of Mr. Larry Spears, a former member of the Coal Section of the Illinois State Geological Survey, for his coal-reflectance calculations and also the assistance of Mr. Evan Johnson in work in the controlled-heating experiments. Special thanks are due to Miss Susan Richardson of the Micromeritics Instrument Corporation, Norcross, Georgia, for obtaining the mercury porosimetry data. We also thank Dr. Marlies Teichmüller of the Geologisches Landesamt Nordrhein-Westfalen, Krefeld, West Germany, and the Peabody Coal Company, Freeburg, Illinois, for supplying us with some inherent moisture data on Illinois coals.

REFERENCES

- Alpern, Boris, 1970, Classification pétrographique des constituants organiques fossiles des roches sédimentaires: Revue de l'institut français du pétrole et Annales des combustibles liquides, v. 25, p. 1233-1266.
- Altschaeffl, A. G., and W. Harrison, 1959, Estimation of the minimum depth of burial for a Pennsylvanian underclay: Journal of Sedimentary Petrology, v. 29, p. 178-185.
- Anderson, R. B., J. L. Bayer, and L. J. E. Hofer, 1965, Determining surface areas from CO₂ isotherms: Fuel, v. 44, p. 443-452.

Anderson, R. B., W. K. Hall, J. A. Lecky, and K. C. Stein, 1956, Sorption studies on American coals: Journal of Physical Chemistry, v. 60, p. 1548-1558.

Anderson, R. B., and L. J. E. Hofer, 1965, Activation energy for diffusion-controlled adsorption processes: Fuel, v. 44, p. 303-306.

Anderson, R. B., L. J. E. Hofer, and J. L. Bayer, 1962, Surface area of coal: Fuel, v. 41, p. 559-560.

ASTM, 1974, Annual book of ASTM standards, Part 26, Gaseous fuels; coal and coke; atmospheric analysis: Philadelphia: American Society for Testing and Materials, 828 p.

Barrer, R. M., 1951, Diffusion in and through solids: Cambridge: Cambridge University Press, 464 p.

Bond, D. C., et al., 1971, Possible future petroleum potential of Region 9—Illinois Basin, Cincinnati Arch, and Northern Mississippi Embayment, in Cram, I. H., ed., Future petroleum provinces of the United States—their geology and potential: American Association of Petroleum Geologists Memoir 15, v. 2, p. 1165-1218.

Bostick, N. H., 1970, Thermal alteration of clastic organic particles (phytoclasts) as an indicator of contact and burial metamorphism in sedimentary rocks: Ph.D. thesis, Stanford University, 220 p.

Breck, D. W., W. G. Eversole, R. M. Milton, T. B. Reed, and T. L. Thomas, 1956, Crystalline zeolites. I. The properties of a new synthetic zeolite, Type A: Journal of the American Chemical Society, v. 78, p. 5963-5977.

Bridgeman, O. C., 1927, A fixed point for the calibration of pressure gauges; the vapor pressure of liquid carbon dioxide at O⁰: Journal of the American Chemical Society, v. 49, p. 1174-1183.

Brunauer, Stephen, 1943, The adsorption of gases and vapors: Princeton, N. J.: Princeton University Press, 511 p.

Brunauer, Stephen, P. H. Emmett, and Edward Teller, 1938, Adsorption of gases in multimolecular layers: Journal of the American Chemical Society, v. 60, p. 309-319.

Buschbach, T. C., 1971, Stratigraphic setting of the Eastern Interior Region of the United States, <u>in</u> Bond, D. C., chairman, Background materials for symposium on future petroleum potential of NPC Region 9 (Illinois Basin, Cincinnati Arch, and northern part of Mississippi Embayment): Illinois State Geological Survey Illinois Petroleum 96, p. 3-20.

Cady, G. H., 1935, Classification and selection of Illinois coals: Illinois State Geological Survey Bulletin 62, 354 p.; 1948, Analysis of Illinois coals: Illinois State Geological Survey Bulletin 62 Supplement, 77 p.

Carman, P. C., 1937, Fluid flow through granular beds: Transactions of the Institute of Chemical Engineers (London), v. 15, p. 150-166.

Carman, P. C., 1938, The determination of the specific surface of powders. I.: Journal of the Society of Chemical Industry (London), v. 57, p. 225-234.

Carman, P. C., 1939, Determination of the specific surface of powders. II.: Journal of the Society of Chemical Industry (London), v. 58, p. 1-7.

Carman, P. C., 1956, Flow of gases through porous media: New York: Academic Press, Inc., 182 p.

Chiche, P., H. Marsh, and S. Prégermain, 1967, Adsorption of carbon dioxide, methanol, and water vapour on cokes-determination of micropore volume: Fuel, v. 46, p. 341-350.

Daeschner, H. W., and F. H. Stross, 1962, An efficient dynamic method for surface area determinations: Analytical Chemistry, v. 34, p. 1150-1155.

Damberger, H. H., 1971, Coalification pattern of the Illinois Basin: Economic Geology, v. 66, p. 488-494.

Damberger, H. H., 1974, Coalification patterns of Pennsylvanian coal basins of the eastern U.S.A., <u>in</u> Carbonaceous materials as indicators of metamorphism: Geological Society of America Special Paper No. 153, p. 53-74; Illinois State Geological Survey Reprint 1974-R.

de Boer, J. H., 1968, The dynamical character of adsorption, second edition: Oxford: Clarendon Press, 240 p.

de Vries, H. A. W., P. J. Habets, and C. Bokhoven, 1968, Das Reflexionsvermögen der Steinkohle: Brennstoff-Chemie, v. 49, p. 15-21, 47-52, 105-110.

Emmett, P. H., and Stephen Brunauer, 1937, The use of low temperature van der Waals adsorption isotherms in determining the surface area of iron-synthetic ammonia catalysts: Journal of the American Chemical Society, v. 59, p. 1553-1564. Griffith, M., and W. Hirst, 1944, The heat of wetting of coals in organic liquids: Proceedings of a conference on the ultra-fine structure of coals and cokes, BCURA: Banbury, England: Cheney & Sons, p. 80-94.

Harkins, W. D., and D. M. Gans, 1931, Adsorption method for the determination of the area of a powder: Journal of the American Chemical Society, v. 53, p. 2804-2806.

Harkins, W. D., and George Jura, 1944, An absolute method for the determination of the area of a finely divided crystalline solid: Journal of the American Chemical Society, v. 66, p. 1356-1373.

Harrison, J. A., 1965, Effect of moisture content on reflectance values of coal: Fuel, v. 44, p. 225-228. Harrison, J. A., and Josephus Thomas, Jr., 1966, Relation between moisture content, reflectance values

and internal surface area of coal: Fuel, v. 45, p. 501-503.

Hilt, Carl, 1873, Die Beziehungen zwischen der Zusammensetzung und den technischen Eigenschaften der Steinkohlen: Zeitschrift des Vereins deutscher Ingenieure, v. 17, H. 4, p. 195-202.

Hückel, Bernhard, 1967, Die natürliche Gebirgsfeuchte von Kohlenproben aus dem Saarkarbon (Report for research program on mine gas in Saar Coal District): Saarbrücken: Saarbergwerke A.G., Geologische Abteilung, 14 p.

ICCP (International Committee for Coal Petrology), 1971, Determination of rank by reflectance measurement of vitrinite (16 p.), <u>in</u> Supplement to the second edition of International handbook of coal petrography: Paris: Centre National de la Recherche Scientifique.

Kini, K. A., 1964, Measurements of the surface area of coals and cokes by adsorption of xenon, krypton, argon and methanol: Fuel, v. 43, p. 173-180.

Kini, K. A., S. P. Nandi, J. N. Sharma, M. S. Iyengar, and A. Lahiri, 1956, Surface area of coal: Fuel, v. 35, p. 71-76.

Kötter, Klaus, 1960, Die mikroskopische Reflexionsmessung mit dem Fotomultiplier und ihre Anwendung auf die Kohlenuntersuchung: Brennstoff-Chemie, v. 41, p. 263-272.

Lamond, T. G., 1962, The sorption of gases on carbons: Ph.D. thesis, University of Durham, Durham, England.

Lecky, J. A., W. K. Hall, and R. B. Anderson, 1951, Adsorption of water and methanol on coal: Nature, v. 168, p. 124-125.

Livingston, H. K., 1949, The cross-sectional areas of molecules adsorbed on solid surfaces: Journal of Colloid Science, v. 4, p. 447-458.

Machin, J. S., Frances Staplin, and D. L. Deadmore, 1963, Studies on the ultrafine structure of some Illinois coals: Illinois State Geological Survey Circular 350, 12 p.

Mackowsky, M. Th., 1947, Mineralogy and petrography as aids to qualitative coal research: Bergbau-Archiv, v. 5/6, special ed., 12 p.

Mackowsky, M. Th., 1949, Neuere Anschauungen über den Inkohlungsvorgang: Fortschritte der Mineralogie, v. 28, p. 38-46.

Maggs, F. A. P., 1952, Anomalous adsorption of nitrogen at 90° K: Nature, v. 169, p. 793-794.

Maggs, F. A. P., and I. G. C. Dryden, 1952, Accessible surface areas of coals: Nature, v. 169, p. 269-270. Malherbe, P. Le R., 1951, Microstructure of some South African coals: Fuel, v. 30, p. 97-109.

Malherbe, P. Le R., and P. C. Carman, 1952, Swelling of coals by methanol and its significance:

Fuel, v. 31, p. 210-219.

Marsh, H., and T. E. O'Hair, 1966, The adsorption of nitrous oxide on coals and carbons-considerations of surface area and microporosity. Fuel, v. 45, p. 301-309.

Marsh, H., and T. Siemieniewska, 1965, The surface areas of coals as evaluated from the adsorption isotherms of carbon dioxide using the Dubinin-Polyani equation: Fuel, v. 44, p. 355-367.

Mikhail, R. Sh., Stephen Brunauer, and E. E. Bodor, 1968, Investigations of a complete pore structure analysis: Journal of Colloid and Interface Science, v. 26, p. 45-61.

Murchison, D. G., 1964, Reflectance techniques in coal petrology and their possible application in ore mineralogy: Transactions of the Institution of Mining and Metallurgy, v. 73, p. 479-502.

Nandi, S. P., K. A. Kini, and A. Lahiri, 1956, Adsorption of polar gases by anthracite: Fuel, v. 35, p. 133-134.

Nandi, S. P., and P. L. Walker, Jr., 1964, The diffusion of nitrogen and carbon dioxide from coals of various rank: Fuel, v. 43, p. 385-393.

Nandi, S. P., and P. L. Walker, Jr., 1966, Diffusion of argon from coals of different rank, <u>in</u> Coal science, Advances in Chemistry Series 55 (R. F. Gould, ed.): Washington, D.C.: American Chemical Society, p. 379-385.

Nelsen, F. M., and F. T. Eggertsen, 1958, Determination of surface area: Adsorption measurements by a continuous flow method: Analytical Chemistry, v. 30, p. 1387-1390.

Ode, W. H., and F. H. Gibson, 1960, International system for classifying brown coals and lignites and its application to American coals: Report of Investigations 5695, U.S. Bureau of Mines, 20 p.

Palmer, T. J., and M. Vahrman, 1972, The smaller molecules obtainable from coal and their significance. Fart 3. Steaming/carbonization of a weakly caking coal at temperatures up to 600° C: Fuel, v. 51, p. 14-21. Palmer, T. J., and M. Vahrman, 1972, The smaller molecules obtainable from coal and their significance. Part 4. Composition of low-temperature tars: Fuel, v. 51, p. 22-26.

Paneth, F., 1922, Über eine Methode zur Bestimmung der Oberfläche adsorbierender Pulver: Zeitschrift Elektrochemie, v. 28, p. 113-115.

Petrascheck, W., 1952, Der Einfluss der Fazies der Flözablagerung auf die Eigenschaften der Kohle: Zeitschrift der deutschen geologischen Gesellschaft, v. 104, p. 1-9.

Pickering, H. L., and H. C. Eckstrom, 1952, Physical adsorption of gases on anatase: Journal of the American Chemical Society, v. 74, p. 4775-4777.

Pierce, Conway, and Bland Ewing, 1964, Area of uniform graphite surfaces: Journal of Physical Chemistry, v. 68, p. 2562-2568.

Rahman, M., and M. Vahrman, 1971, The smaller molecules obtainable from coal and their significance. Part 2. High pressure extraction at 200-300° C: Fuel, v. 50, p. 318-328.

Schapiro, N., and R. J. Gray, 1960, Petrographic classification applicable to coals of all ranks: Proceedings of the Illinois Mining Institute, v. 68, p. 83-97.

Spence, J. A., and M. Vahrman, 1970, The smaller molecules obtainable from coal and their significance. Part 1. Solvent extraction of a weakly caking coal at atmospheric pressure: Fuel, v. 49, p. 395-408.

Teichmüller, Marlies, 1955, Anzeichen mariner Beeinflussung bei der Kohle aus Flöz Katharina der Zeche Friedrich Heinrich: Neues Jahrbuch für Geologie und Paläontologie, Monatshefte, v. 1955, p. 193-201.

Teichmüller, Marlies, 1971, Anwendung kohlenpetrographischer Methoden bei der Erdöl- und Erdgasprospektion: Erdöl und Kohle/Brennstoff-Chemie, v. 24, p. 69-76.

Teichmüller, Marlies, and Rolf Teichmüller, 1968, Geological aspects of coal metamorphism, <u>in</u> Murchison, D. G., and T. S. Westoll, eds., Coal and coal-bearing strata: Edinburgh: Oliver and Boyd, p. 233-267.

Thomas, Josephus, Jr., G. S. Benson, and G. M. Hieftje, 1966, Measurement of the surface areas of coals from the dynamic sorption of carbon dioxide: American Chemical Society, Division of Fuel Chemistry Preprints 10 (3), p. 120-124; Illinois State Geological Survey Reprint 1966-N.

Thomas, Josephus, Jr., B. F. Bohor, and R. R. Frost, 1970, Surface area measurements on clays: Clays and Clay Minerals, v. 18, p. 405-407.

Thomas, Josephus, Jr., and R. R. Frost, 1971, Versatile apparatus for studying reactions involving gas adsorption or evolution: Transactions of the Illinois State Academy of Science, v. 64, p. 248-253.

Toda, Y., M. Hatami, S. Toyoda, Y. Yoshida, and H. Honda, 1971, Micropore structure of coal: Fuel, v. 50, p. 187-200.

United Nations, 1956, International classification of hard coals by type: United Nations Publications E/ECE/COAL/110, Sales No. 1956 II. E. 4, 52 p.

Vahrman, M., 1970, The smaller molecules derived from coal and their significance: Fuel, v. 49, p. 5-16.

van Krevelen, D. W., 1954, The problem of coal constitution: BCURA Quarterly Gazette, v. 24, p. 6-19.

Walker, P. L., Jr., L. G. Austin, and S. P. Nandi, 1966, Activated diffusion of gases in solids: Fuel, v. 45, p. 173-175.

Walker, P. L., Jr., O. Cariaso, and R. L. Patel, 1968a, Surface areas of coals: Fuel, v. 47, p. 322-324.

Walker, P. L., Jr., O. Cariaso, and R. L. Patel, 1968b, Surface areas and pore volumes of coal macerals: Fuel, v. 47, p. 331-332.

Walker, P. L., Jr., and Irwin Geller, 1956, Change in surface area of anthracite on heat treatment: Nature, v. 178, p. 1001.

Walker, P. L., Jr., and K. A. Kini, 1965, Measurement of the ultrafine surface area of coals: Fuel, v. 44, p. 453-459.

Walker, P. L., Jr., and R. L. Patel, 1970, Surface areas of coals from carbon dioxide adsorption at 298° K.: Fuel, v. 49, p. 91-94.

Zwietering, P., A. P. Oele, and D. W. van Krevelen, 1951, Pore structure and internal surface of coal: Fuel, v. 30, p. 203-204.

Zwietering, P., J. Overeem, and D. W. van Krevelen, 1956, Chemical structure and properties of coal. XIII. Activated diffusion of gases in coals: Fuel, v. 35, p. 66-70.

Zwietering, P., and D. W. van Krevelen, 1954, Chemical structure and properties of coal. IV. Pore structure: Fuel, v. 33, p. 331-337.

Illinois State Geological Circular 493 38 p., 15 figs., 4 tables, 2500 cop., 1976 Urbana, Illinois 61801

Printed by Authority of State of Illinois, Ch. 127, IRS, Par. 58.25.

CIRCULAR 493

ILLINOIS STATE GEOLOGICAL SURVEY URBANA, IL 61801