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CHANGES IN THE PORE STRUCTURE OF COAL WITH CHEMICAL PROCESSING

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CHANGES IN THE PORE STRUCTURE OF COAL WITH CHEMICAL PROCESSING

George Sam Booras* and E. E. Petersen

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CHANGES IN THE PORE STRUCTURE OF COAL

WITH CHEMICAL PROCESSING

by

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Energy Research and Development Administration.
Abstract ................................................................. v

I. Introduction .......................................................... 1
   A. Background ....................................................... 1
   B. Previous Work. .................................................. 1
      1. Internal Structure of Coal ................................. 1
      2. Measurement of Coal Surface Area ....................... 3
      3. Chemical Processing of Coal ............................... 8
   C. Objectives ....................................................... 9

II. Equipment and Procedures ......................................... 11
   A. Adsorption Equipment ......................................... 11
   B. Degassing, Adsorption and Calculation Procedures ...... 14

III. High vs Low Temperature Adsorption of CO₂ .................... 18
   A. Adsorption on Catalysts and Molecular Sieves ............ 18
   B. Adsorption on Coal ........................................... 19

IV. Surface Area Variations of Desulfurized Coal ................. 21
   A. Desulfurized Coal Samples ................................... 21
   B. Surface Areas of Desulfurized Coal ....................... 21

V. Surface Area Variations of Extracted Coal ..................... 29
   A. Extracted Coal Samples ...................................... 29
   B. Surface Areas of Extracted Coal ........................... 29
   C. Extracted Coal Pore Size ................................... 35

VI. Surface Area Variations of Reacted Coal ..................... 39
   A. Reacted Coal Samples ........................................ 39
   B. Surface Areas of Reacted Coal ............................. 39

VII. Conclusions and Suggestions for Future Work. ............... 41
ABSTRACT

Carbon dioxide adsorption experiments gave the same BET surface areas at room temperature and at dry ice temperature for a molecular sieve, an alumina catalyst, and a Wyoming subbituminous coal. This suggested that activated diffusion was not an important factor, even at 196°K. However, the adsorption of carbon dioxide on Illinois No. 6 coal decreased with increasing temperature.

Surface area variations of desulfurized coal, extracted coal, and reacted coal were examined by carbon dioxide adsorption at 196°K. The use of sodium hydroxide to remove sulfur from Illinois No. 6 coal appeared to cause partial blockage or collapsing of the pore structure. Subsequent extraction removed these obstructions somewhat. This conclusion was suggested by a minimum in the curve of surface area versus extraction time.

Pyridine extractions of Roland Seam coal appeared to open new areas that were previously inaccessible to carbon dioxide. The surface areas were nearly doubled, but the average pore diameter appeared to remain essentially unchanged as evidenced by neopentane adsorptions. Large solvent molecules such as benzene were able to penetrate the
coal pores, whereas a large, symmetrical molecule such as neopentane could not. These results suggest that the pores are slot shaped rather than cylindrical.
I. INTRODUCTION

A. Background

Coal has a highly complex internal pore system which possesses some characteristics similar to molecular sieves. In order for chemical reactions, gas adsorptions, and extractions to take place, reagents or vapors have to pass into the microporous structure of coal. Rates of mass transfer may be greatly restricted by the very small size of the openings in the coal structure.

The internal surface area of coal should be preserved during processing to allow the processing fluid (solvent, reactant, etc.) to be in contact with as much of the solid coal as possible. Therefore, the internal structure and area should be measured with progressive processing to determine if the high surface area is being utilized. If not, the processing variables should be modified to do this whenever possible.

To follow the changes in the pore structure of coal during chemical processing, reliable methods must be developed to measure the internal structure and surface area of coals. The area of surface available per unit mass is a fundamental property of porous solids. For heterogeneous systems this property is the interface where physical and chemical phenomena occur. Accordingly, a knowledge of the changes in the pore structure of coal should provide some insight into the mechanisms involved during the chemical processing of coal.

B. Previous Work

1. Internal Structure of Coal

The internal pore structure of coal can be divided into three
classifications. Generally pores in the size range below 12Å are described as micropores, those above about 200Å as macropores, and those in between as transitional or intermediate pores. Gan, Nandi, and Walker (1) measured the gross pore size distributions for a number of coals by nitrogen adsorption isotherms at 77°K. For an Illinois No. 6, high volatile C bituminous coal, 30.2% of the pore volume is smaller than about 12Å, 52.6% between about 12Å and 300Å, and 17.2% above 300Å. The pore size distribution varied greatly, depending on the rank of coal.

Medeiros and Petersen (2) have recast Walker's results in the form of surface areas versus pore diameter. The surface area distribution for the Illinois No. 6 coal then becomes:

<table>
<thead>
<tr>
<th>Pore Size</th>
<th>Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 12Å</td>
<td>156 m²/g</td>
</tr>
<tr>
<td>12 - 300Å</td>
<td>26 m²/g</td>
</tr>
<tr>
<td>&gt; 300Å</td>
<td>1 m²/g</td>
</tr>
</tbody>
</table>

The above surface area break downs show that the majority of the internal surface area of coals is contained in the very fine micropores.

The internal structure of coal has some characteristics like molecular sieves. Bond and Spencer (3) observed that the heat of wetting for any rank of coal decreases as the molecular volume of the wetting liquid increases. They obtained a relationship from the differential internal surface area as a function of the size of the ultrafine pores of coal. Their results show that the critical dimensions of the ultrafine pores are 5Å and 8Å in approximate diameters, corresponding to molecular diameters of wetting liquids whose molecular
volumes are around 50 and 150 cc/mole.

Lamond and Marsh (4) and later Medeiros and Petersen both used 4A and 5A molecular sieves to study the pore diameters of coal. Marsh observed that nitrogen at -196°C would penetrate a 5A sieve but not a 4A sieve, whereas carbon dioxide at -78°C had no difficulty penetrating either molecular sieve. Medeiros obtained results on coal that were similar to Marsh's molecular sieve results, thus leading to the conclusion that the average pore diameter of coals is roughly 4Å.

Medeiros made further use of the molecular sieve properties of coal to determine rough pore size distributions. He used the adsorption of four gases (CO₂, CF₄, N₂, and Ar) on Wyodak Roland Seam coal, Illinois No. 6 coal, and 4A and 5A Linde molecular sieves to study the microporous structure of coal. The reasoning was that the penetration depended upon the size of the adsorbate. Medeiros concluded that the Roland Seam coal resembles that 4A sieve in its microporous structure, whereas the Illinois No. 6 coal more closely resembles the 5A molecular sieve.

2. Measurement of Coal Surface Area

The determination of the surface areas of coals is not straightforward. No method has so far been described which can be applied to all coals without some degree of criticism.

The method of heat of wetting has been in use for many years and is based on a measurement of the amount of heat liberated when the internal surface is completely wetted by either methanol or water. Griffith and Hirst (5) and Maggs (6) initially determined the total internal surface area of coal by this method. The heat of wetting method suffers from two main disadvantages. First, it is necessary
to have a conversion factor to obtain units of area from units of energy. This factor is only constant if one assumes that all coals have energetically similar surfaces. Secondly, some of the heat being liberated is actually due to solution and not adsorption. Using a conversion factor of 400 ergs/cm², Bond and Maggs (7) found surface areas of coal between 20 and 200 m²/g depending on the rank of coal.

The best known method for determining the specific surface area of porous solids obtains from the work of Brunauer, Emmett, and Teller (BET) (8,9,10). The method is based on the determination of the number of molecules of gas which, when adsorbed on the surface of a solid, completely cover the solid with a monolayer of the gas. This value multiplied by the cross-sectional area per molecule gives directly the surface area. The BET method involves measuring the adsorption isotherms of gases near their condensation points. The required data may be obtained by either volumetric or gravimetric measurements.

The specific surface area, S, in square meters per gram is given by the following equation:

\[
S = \frac{V_m \cdot A_m \cdot N}{V_0 \cdot W}
\]  

(1)

where \(V_m\) = the gas uptake for monolayer coverage corrected to STP, 
\(N\) = Avogadro's number \((6.023 \times 10^{23})\), \(V_0\) = the ideal gas volume, \((22,410 \text{ cm}^3)\), \(W\) = the mass of the sample in grams, and \(A_m\) = the average area occupied by the adsorbed gas molecule in angstroms squared. \(V_m\) is obtained by determining the volume of gas adsorbed (at STP) at a number of equilibrium relative pressures by use of the BET equation:
where \( V_a \) = the volume of gas adsorbed at STP, \( P_2 \) = the equilibrium pressure of the adsorbate, \( P_0 \) = the saturation pressure of the adsorbate at the temperature of adsorption, and \( C \) = a constant related to the energy of adsorption. A plot of \( P_2/V_a(P_0-P_2) \) versus \( P_2/P_0 \) gives a straight line with an intercept of \( 1/V_mC \) and a slope of \( (C-1)/V_mC \). From this plot \( C \) and \( V_mC \) are obtained and thus \( V_m \) can be calculated. Usually at least four points with relative pressures in the range 0.05 - 0.30 are utilized.

Average molecular areas were obtained by Medeiros (2) from several gases. He measured the surface areas of two Harshaw catalysts using nitrogen at \( 77^\circ K \). For nitrogen, \( A_m = 16.2 \, \AA^2 \). For all other gases, \( A_m \) values were chosen such that the calculated areas were the same as the nitrogen surface areas. Values of 17.0, 23.4 and 17.3\( \, \AA^2 \) were obtained from the argon, carbon dioxide, and carbon tetrafluoride molecules, respectively.

Maggs (11,12,13) showed that the equilibrium amount of nitrogen adsorbed on coal reaches a maximum at \( 195^\circ K \); below this temperature the rate of adsorption is very low and equilibrium is not reached in any reasonable length of time. This work confirmed earlier results that the low temperature nitrogen BET surface areas of coal are very small. Maggs concluded that either some temperature dependent physical change in the coal such as thermal contraction of the pores was occurring, or the diffusion of nitrogen into the very fine pores of
coal is an activated process whereby the rate of diffusion into the micropores would become sufficiently rapid above about 100°K.

Zwietering and Van Krevelen (14) measured the density of a coal sample in helium over a temperature range from 100°C to -196°C and observed no contraction of the internal volume of the coal. Therefore, it appears that the low surface areas calculated from nitrogen adsorption at low temperature are a result of the inability of the molecules to diffuse into the ultrafine pore structure of coal and not due to the thermal contraction of coal.

The adsorption of rare gases on coal also has been measured. Lahiri et al. (15) studied the adsorption of argon at -183°C, and Kini (16) studied the adsorption of xenon at 0°C on several coals and cokes. Lahiri obtained BET surface areas ranging from 13 to 51 m²/g for briquetted coal and a surface area of 7 m²/g for a British anthracite coal. Kini obtained surface areas from 140 to 200 m²/g depending on the coal studied.

Carbon dioxide has been used extensively in recent years to measure the internal surface area of coal. Anderson et al. (17) obtained surface areas for a low volatile bituminous Pittsburgh coal of 114 and 140 m²/g from carbon dioxide adsorption at -78°C. Walker and Geller (18) also used carbon dioxide to obtain an area of 175 m²/g for an anthracite coal. Czerski, Korla, and Lason (19) compared surface areas calculated by carbon dioxide adsorption and by the heat of wetting method for several different coals. The carbon dioxide areas were lower than the heat of wetting values on all samples.

Lamond, Marsh, and Wynne-Jones (4,20,21) studied the adsorption
of carbon dioxide on many carbonaceous materials. They concluded that carbon dioxide can be used satisfactorily at -78°C as an adsorbate to determine surface areas of coal. Anderson et al. (22) stated that the true value of the total surface area of coal probably lies between the value obtained from carbon dioxide adsorption at -78°C and heat of wetting values using methanol.

Walker and Nandi (1) compared carbon dioxide adsorption at -78°C and nitrogen adsorption at -196°C on several types of coal. On all of their samples, the areas obtained using nitrogen are lower than those obtained using carbon dioxide. For some coals the nitrogen surface areas were less than 1 m²/g while for other coal samples the nitrogen surface area was as high as 90 m²/g depending on the coal.

High temperature carbon dioxide adsorption has received much attention lately. Researchers believe that even carbon dioxide adsorption at -78°C may be somewhat inhibited by activated diffusion. The disadvantage of this method is that it requires high pressure adsorption equipment. Marsh and Siemieniewska (23) compared carbon dioxide surface areas at 195°, 273°, and 293°K for several coals using the Dubinin-Polanyi equation. They observed a slight increase in surface areas as the adsorption temperature increased for several coals. On other coals there was little or no change in area. Walker and Kini (24) obtained similar results using the BET equation with carbon dioxide at 195° and 298°K. An anthracite coal actually showed a slight decrease from 246 m²/g to 224 m²/g as the adsorption temperature was raised from 195° to 298°K. All other samples had either no change or a slight increase in surface area. Walker and Patel (25) compared
the BET and Dubinin-Polanyi equations for calculating the surface areas of coal with carbon dioxide at 298°K as the adsorbate. They found excellent agreement in all cases. It is generally concluded that the surface areas of coals calculated from carbon dioxide adsorption isotherms measured at 298°K represent the total surface area more closely than any other approach yet used.

3. Chemical Processing of Coal

New chemical processes must be developed in order to make full use of our vast reserves of coal to help supply our increasing need for energy and hydrocarbons. Coal research in the Department of Chemical Engineering at the University of California is proceeding along two main lines. First is the removal of sulfur from coal without appreciably altering the coal matrix. Second is the production of liquid hydrocarbons from coal by solvent extraction.

Sulfur is present in coal in two main forms: inorganic and organic sulfur. Inorganic sulfur as pyrites can occur in lenses and bands, balls or nodules, joints or cleats, and as finely dispersed particles. Coarse crushing may release much of the pyrites in the lenses, bands, cleats, and joints for subsequent removal by mechanical cleaning. Removal of the fine particles is more difficult since extremely fine grinding is impractical. Organic sulfur is distributed throughout the coal matrix as an integral part of the coal molecular structure and accordingly it can not be removed by conventional cleaning or preparation processes, but requires chemical treatment.

Several approaches to achieve the desulfurization of coal have been proposed. Among these are hydrogenation, oxidation, and sodium
hydroxide leaching. The effect of sodium hydroxide leaching on the coal pore structure and surface area was examined in this paper.

In the conversion of coal to liquid products, there are four general conceptual approaches. These approaches are: the production of H₂/CO mixtures from coal followed by a catalytic synthesis of higher hydrocarbons from this synthesis gas; partial dissolution with solvents without significant hydrogenation; partial dissolution with solvents with catalyzed or uncatalyzed hydrogenation; and staged pyrolysis.

There has been much research recently on the interaction of coal with various solvents, since many processes use a solvent to liquify coal partially either by simple dissolution or decomposition and solution with or without hydrogen transfer. Benzene, tetralin, and pyridine have all been tried as coal solvents. The changes in the pore structure of coal due to pyridine extraction have been studied in this paper.

A better understanding of the internal structure of coal would be very helpful in studying the action of prospective coal solvents or new desulfurization procedures. A knowledge of the chemical and physical processes involved may suggest new or improved processes.

C. Objectives

The objective of this research was to characterize the internal structure of raw coal and to follow the changes in the surface areas of coal with chemical processing. A reliable method was developed to measure the total internal surface area of coal. Some researchers have felt that carbon dioxide adsorption at 196°K may give low BET surface areas due to activated diffusion. Room temperature carbon dioxide adsorption was used to test this hypothesis.
Surface area variations of desulfurized coal, extracted coal, and reacted coal were examined by carbon dioxide adsorption at 196\degree K. An attempt was made to determine the chemical or physical mechanisms involved in the desulfurization and extraction processes. Neopentane adsorption was used to look for any pore enlargement due to extraction.
II. EQUIPMENT AND PROCEDURES

A. Adsorption Equipment

The adsorption apparatus used in this research was designed by Medeiros and Petersen* and constructed in the University of California, College of Chemistry, machine shop. Two volumetric apparatuses were used to measure the internal surface areas of porous materials, one for pressures below atmospheric and one for moderate to high pressures (to 1200 psig). Although the wall thicknesses of the 304 stainless steel tubing used are different for the low and high pressure systems, the linear dimensions of the two systems are identical so that each is interchangeable when mounting on the adsorption apparatus frame. The system is capable of handling up to four different samples in any one day, either for degassing or for surface area determinations. The assembled adsorption manifold is shown in Figure 2-1.

When degassing, the samples are heated with a temperature controlled aluminum heating block. The vacuum is produced by an oil diffusion pump in series with a mechanical vacuum pump.

The degassing pressure is read by ionization and thermocouple gauges. Three interchangeable pressure gauges (0–800 mm Hg abs; 0–80 psig; and 0–800 psig) are used for reading the manifold pressure during an adsorption experiment.

A 0–15 psid differential pressure transducer (National Semiconductor

*Medeiros and Petersen describe the adsorption apparatus in detail (2).
Fig. 2-1. Assembled adsorption manifold.
Corp. Model #LX1702D) was mounted on the manifold for the high pressure adsorption experiments. (See Figure 2-1.) This allowed more accurate readings of the small pressure changes due to adsorption at high system pressures. The pressure transducer output was read on a Fairchild Model #320759 digital voltmeter. The 0-80 psig gauge was used to calibrate the pressure transducer output voltage.

The addition of the differential pressure transducer required the recalibration of the high pressure manifold and reference volumes. The adsorption apparatus was calibrated using the same procedure as Medeiros and Petersen. A 515 cc calibrated volume was connected to a flange on the high pressure manifold through a Hoke needle valve. The calibrations were all constant temperature expansions from one volume into another volume. The calibration results from the high pressure manifold with the pressure transducer attached are as follows:

\[
\begin{align*}
V_{mc} &= 171.6 \pm 0.2 \text{ cc} \\
V_r &= 556.8 \pm 0.5 \text{ cc} \\
V_{m1} &= 170.1 \pm 0.1 \text{ cc} \\
V_m &= 95.5 \pm 0.1 \text{ cc} \\
V_{m2} &= 137.2 \pm 0.2 \text{ cc}
\end{align*}
\]

where: \( V_{mc} \) = Volume of manifold and 0-800 mm Hg gauge with calibrated volume attached.

\( V_r \) = Reference volume.

\( V_{m1} \) = Volume of manifold and 0-800 mm Hg gauge.

\( V_m \) = Volume of manifold only.

\( V_{m2} \) = Volume of manifold and 0-800 psig gauge.
B. Degassing, Adsorption, and Calculation Procedures

Approximately 1.0 grams of coal, or 0.8 grams of pelleted catalysts or molecular sieves, were weighed to 0.0001 grams on a microbalance. The sample was then placed into the sample holder and the weight of the sample and sample holder was recorded. The sample holder spacers were then inserted and the sample holder assemblies were attached to the manifold.

The sample holder valves, V1 to V4, the vacuum gauge valve, V6, and the vacuum pump valve, V9, were opened while all other valves remained closed. The vacuum pump was then turned on to evacuate the system. The heating block was raised into position and the temperature controller was turned on. Coal samples were degassed at 130°C and the catalysts and molecular sieves were degassed at 240°C. After the pressure was below 0.1 torr, the diffusion pump and cooling water were turned on. Liquid nitrogen was poured into the cold trap to condense any oil vapors and prevent them from entering the system.

The samples were degassed for approximately 16 hours at a pressure near 10⁻⁵ torr. All valves were then closed. The temperature controller and diffusion pump were turned off. The cooling water and vacuum pump were turned off after the diffusion pump oil had cooled to room temperature.

The adsorption procedure for the low pressure manifold was the same as that used by Medeiros and Petersen. The sample holder was placed in a 250 cc Dewar flask containing either liquid nitrogen, dry ice/methanol, or distilled water in order to maintain the adsorption temperature. The pressure gauge valve, V7, was opened and the gauge
was evacuated. The adsorbate gas was admitted to the manifold through valve V8 until the desired pressure was read on the pressure gauge. Valve V8 was then closed and the manifold pressure and temperature were recorded. The sample holder valve was then opened to allow the gas to expand into the sample holder and be absorbed. An equilibration time of 30 minures was allowed for all samples before the final pressure and temperature were recorded. The sample holder valve was then closed and the procedure was repeated at a higher initial pressure. Four adsorption points in the relative pressure range of 0.05 to 0.30 were taken for each sample.

The adsorption procedure for the high pressure manifold was slightly different due to the addition of the differential pressure transducer. The reference volume valve, V5, was opened when the manifold was being filled with gas. The initial pressure was recorded and then the pressure gauge and reference volume valves were both closed. The initial pressure transducer voltage was recorded and then the sample holder valve was opened. After 30 minutes, the final transducer voltage was recorded. The sample holder valve was then closed and the pressure gauge and reference volume valves were opened. More gas was admitted to the manifold and the entire procedure was repeated until four adsorption points had been measured. The final pressures were calculated from a knowledge of the initial pressure and the transducer voltage charge during adsorption. The four points were measured in the same relative pressure range as was used for the low pressure adsorptions.

Once the initial and final pressures and temperatures were known, the volume of gas adsorbed at a given final pressure could be calculated.
The following equation for the volume of gas adsorbed at standard conditions was developed by Medeiros and Petersen:

\[
V = \frac{T_m V_m}{P_m} \left[ \frac{P_{1,n}}{T_{1,n}} - \frac{P_{2,n}}{T_{2,n}} + \frac{V_{sh1}}{V_m} \left( \frac{P_{2,n-1}}{T_{2,n-1}} - \frac{P_{2,n}}{T_{2,n}} \right) \right] \\
+ \frac{(V_{sh2} - V_s)}{V_m T_o} \left( P_{2,n-1} - P_{2,n} \right)
\]

where:

- \( n \) = adsorption point indicator; \( n = 1,2,3,4 \).
- \( m \) = weight of the porous solid less volatiles, grams.
- \( P_{1,n} \) = initial pressure in manifold before expanding the adsorbate into the sample holder for the \( n \)th adsorption point. When \( n-1 = 0 \), \( P_{n-1} \) is equal to 0.
- \( P_{2,n} \) = final pressure in manifold after expanding the adsorbate gas into the sample holder for the \( n \)th adsorption point.
- \( P_s \) = standard pressure, 1 atm.
- \( T_{1,n} \) = initial temperature of the manifold for the \( n \)th point, °K.
- \( T_{2,n} \) = final temperature of the manifold for the \( n \)th point, °K.
- \( T_o \) = adsorption temperature, °K.
- \( T_s \) = standard temperature, 273°K.
- \( V_m \) = manifold volume, cc.
- \( V_{sh} \) = sample holder volume, cc.
\( V_{sh1} \) = volume of the sample holder not immersed in the liquid bath, cc. This volume was considered to be at the same temperature as the manifold.

\( V_{sh2} \) = volume of the sample holder immersed in the liquid bath, cc. This volume was considered to be at temperature \( T_0 \).

\( V_s \) = volume of porous solid, cc.

\( V \) = volume of gas adsorbed at STP per gram of sample, cc/g.

Note: \( V_{sh} = V_{sh1} + V_{sh2} \)

The value of \( V \) obtained from this equation was then used to construct a BET plot. The volume of gas adsorbed for a monolayer on the surface \( V_m \), could then be calculated from the slope and intercept of the BET plot. The product of \( V_m \) and the cross sectional area per molecule, \( A_m \), gave the total surface area per gram of porous solid sample. Values for \( A_m \) were obtained from the paper by Medeiros and Petersen.
III. HIGH VS LOW TEMPERATURE ADSORPTION OF CO₂

A. Adsorption on Catalysts and Molecular Sieves

The surface areas of a Harshaw alumina catalyst and a Union Carbide sodium mordenite molecular sieve were determined by carbon dioxide adsorption at 196°K and 294°K in order to determine the importance of activated diffusion. If the carbon dioxide adsorption at 196°K is limited by activated diffusion, then the adsorption at 294°K should result in a much greater surface area.

The high temperature adsorption experiments were conducted in the high pressure manifold with a differential pressure transducer to follow the small pressure changes due to adsorption. A 30-minute equilibration time was allowed for all adsorption points. Four adsorption points were measured for each sample in the relative pressure range of 0.5 to 0.30. The BET method was used to calculate the surface areas obtained at both temperatures.

The cross sectional area of the carbon dioxide molecule at room temperature was assumed to be 23.4 Å². This value was determined by Medeiros and Petersen (2) for carbon dioxide adsorption at 196°K. At room temperature the true cross sectional area may be slightly higher due to the increased energy of the molecules.

BET plots for the high and low temperature adsorption of carbon dioxide on catalysts and molecular sieves are included in the Appendix on Figure A-1.

The surface areas of the catalyst and molecular sieve as determined by carbon dioxide adsorption at 196°K and 294°K are as follows:
The surface areas determined at room temperature are essentially the same as those determined at 196°K, considering the accuracy of the BET method. This means that even at 196°K the carbon dioxide molecules can penetrate all of the available pores in the catalyst or the molecular sieve in the 30-minute equilibration time. Accordingly it appears safe to conclude that activated diffusion is not an important factor to consider when using carbon dioxide as the adsorbate either at 196°K or at room temperature in samples having pore pore diameters as low as 6.7Å.

**B. Adsorption on Coal**

The surface areas of a Wyodak Roland Seam coal and an Illinois No. 6 coal were determined by using the BET method with carbon dioxide at room temperature as the adsorbate. The procedure was the same as that used in the previous section for adsorption on catalysts and molecular sieves.

BET plots of the high and low temperature adsorption of carbon dioxide on Wyodak Roland Seam coal and Illinois No. 6 coal are included in the Appendix on Figures A-2 and A-3.

The surface areas of the two coals as measured by carbon dioxide adsorption at 196°K and at room temperature are as follows:
The BET surface areas of the Wyodak Roland Seam coal do not vary with the adsorption temperature. This behavior is very similar to that observed for the high and low temperature adsorptions on catalysts and molecular sieves. All of the available pores appear to be penetrated in the 30-minute equilibration time. These results suggest that activated diffusion is not an important factor for carbon dioxide adsorption on Roland Seam coal, even at 196°K.

The surface areas of the Illinois No. 6 coal as calculated by the BET method show a definite temperature dependence. The amount of carbon dioxide adsorbed at a given relative pressure decreases as the adsorption temperature is increased. These results are reproducible, but we can give no satisfactory explanation for the observed temperature dependence.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature</th>
<th>BET Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wyodak Roland Seam</td>
<td>196°K</td>
<td>101</td>
</tr>
<tr>
<td>(-28 + 150 mesh)</td>
<td>298°K</td>
<td>105</td>
</tr>
<tr>
<td>Illinois No. 6</td>
<td>196°K</td>
<td>181</td>
</tr>
<tr>
<td>(-200 mesh)</td>
<td>273°K</td>
<td>175</td>
</tr>
<tr>
<td></td>
<td>294°K</td>
<td>145</td>
</tr>
<tr>
<td></td>
<td>295°K</td>
<td>128</td>
</tr>
</tbody>
</table>
IV. SURFACE AREA VARIATIONS OF DESULFURIZED COAL

A. Desulfurized Coal Samples

The desulfurized coal samples used for this research were obtained from Mendizabal and Petersen. The detailed desulfurization procedures and results are presented by Mendizabal and Petersen (26). They used an Illinois No. 6 bituminous coal, obtained from the Illinois State Geological Survey. The analysis of this coal is presented in Table 4-1.

The coal samples were treated with sodium hydroxide or oxygen for two hours in a pressurized reaction vessel. The temperatures varied between 150°C and 250°C. In one series of experiments, the coal samples were treated with 10% sodium hydroxide at 250°C for 15 minutes, 30 minutes, 1 hour and 2 hours. The coal samples were all -200 mesh.

B. Surface Areas of Desulfurized Coal

The surface areas of the desulfurized coal samples were determined by using the BET method with carbon dioxide at 196°K as the adsorbate gas \( (A_m = 23.4A^2) \). The samples were degassed at 130°C for 16 hours to a pressure of about \( 10^{-5} \) torr prior to the adsorption experiment. The adsorption temperature was maintained with a dry ice/methanol bath. A 30-minute equilibration time was allowed for each adsorption point.

BET plots of the desulfurized Illinois No. 6 coal samples are included in the Appendix on Figure A-4. The BET surface areas of the desulfurized coal samples are presented in Table 4-2 along with the results of the treatment by Mendizabal and Petersen. The surface
Table 4-1
Analysis of Illinois No. 6 Coal

<table>
<thead>
<tr>
<th></th>
<th>Proximate Analysis</th>
<th>Ultimate Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>as received</td>
<td>dry basis</td>
</tr>
<tr>
<td>% Moisture</td>
<td>12.62-12.67</td>
<td>16.63-16.73</td>
</tr>
<tr>
<td>% Ash</td>
<td>14.53-14.61</td>
<td>16.63-16.73</td>
</tr>
<tr>
<td>% Volatile</td>
<td>32.54-33.39</td>
<td>37.24-38.23</td>
</tr>
<tr>
<td>% Fixed Carbon</td>
<td>39.33-40.31</td>
<td>45.04-46.13</td>
</tr>
<tr>
<td>BTU</td>
<td>9988-10001</td>
<td>11431-11452</td>
</tr>
<tr>
<td>% Sulfur</td>
<td>3.64-3.95</td>
<td>4.17-4.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Carbon</td>
<td>56.03-56.31</td>
<td>64.16-64.44</td>
</tr>
<tr>
<td>% Hydrogen</td>
<td>3.89-3.92</td>
<td>4.45-4.49</td>
</tr>
<tr>
<td>% Nitrogen</td>
<td>1.15-1.17</td>
<td>1.32-1.34</td>
</tr>
<tr>
<td>% Chlorine</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>% Sulfur</td>
<td>3.64-3.95</td>
<td>4.17-4.52</td>
</tr>
<tr>
<td>% Ash</td>
<td>14.53-14.61</td>
<td>16.63-16.73</td>
</tr>
<tr>
<td>% Oxygen (difference)</td>
<td>7.42-7.85</td>
<td>8.49-8.98</td>
</tr>
</tbody>
</table>
Table 4-2. Surface Areas of Desulfurized Illinois No. 6 Coal

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Time (hr)</th>
<th>Temperature (°C)</th>
<th>Organic Sulfur (wt. %)*</th>
<th>Inorganic Sulfur (wt. %)*</th>
<th>Total Sulfur (wt. %)*</th>
<th>Percent Weight Loss</th>
<th>BET Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dry Basis gram of raw coal</td>
<td>Dry Basis, per gram of raw coal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw Illinois No. 6</td>
<td>--</td>
<td>--</td>
<td>2.60</td>
<td>2.86</td>
<td>5.46</td>
<td>--</td>
<td>181</td>
</tr>
<tr>
<td>10% NaOH</td>
<td>0.25</td>
<td>250</td>
<td>2.22</td>
<td>.67</td>
<td>2.89</td>
<td>15.3</td>
<td>160†</td>
</tr>
<tr>
<td>10% NaOH</td>
<td>0.50</td>
<td>250</td>
<td>2.04</td>
<td>.70</td>
<td>2.74</td>
<td>16.0</td>
<td>166†</td>
</tr>
<tr>
<td>10% NaOH</td>
<td>1.0</td>
<td>250</td>
<td>1.99</td>
<td>.68</td>
<td>2.67</td>
<td>16.0</td>
<td>170†</td>
</tr>
<tr>
<td>10% NaOH</td>
<td>2.0</td>
<td>250</td>
<td>1.92</td>
<td>.64</td>
<td>2.56</td>
<td>16.0</td>
<td>169</td>
</tr>
<tr>
<td>10% NaOH</td>
<td>2.0</td>
<td>200</td>
<td>2.27</td>
<td>1.02</td>
<td>3.29</td>
<td>6.0</td>
<td>126</td>
</tr>
<tr>
<td>H₂O, O₂</td>
<td>2.0</td>
<td>250</td>
<td>--</td>
<td>--</td>
<td>2.48</td>
<td>2.4</td>
<td>233</td>
</tr>
<tr>
<td>H₂O, O₂</td>
<td>2.0</td>
<td>150</td>
<td>2.12</td>
<td>1.39</td>
<td>3.51</td>
<td>1.7</td>
<td>182</td>
</tr>
</tbody>
</table>

*DAF Basis
†Duplicate run
area and sulfur content of the raw -200 mesh Illinois No. 6 coal also have been included for comparison.

Two different surface areas are reported for each sample. The first value listed is the specific surface area of the coal residue after treatment. Any increase in the specific surface area would mean that either the average diameter of the micropores has increased, or new areas have been opened up that were previously inaccessible to carbon dioxide. The second value takes into account the fact that there is some loss in weight due to extraction. The value is the surface area per gram of untreated coal.

The changes in surface area with extraction time for the coal samples treated with sodium hydroxide are shown in Figure 4-1. The surface area decreases from an initial value of 181 m²/g to a minimum area of 155 m²/g in 15 minutes. The area then increases and levels off at 170 m²/g in 2 hours. A minimum in the curve suggests that two separate mechanisms of sulfur removal are occurring simultaneously.

Figure 4-2 shows the percent sulfur in the coal samples as a function of treatment time. Separate curves are drawn for organic, inorganic, and total sulfur. The inorganic sulfur drops off very rapidly to its steady state value, whereas the organic sulfur is decreased more slowly. In general inorganic sulfur occurs in coal as a phase heterogeneous to the coal matrix. It is composed of fine particles of micro sizes and hence probably has low specific surface area. The sodium hydroxide is known to soften the coal matrix (27). As the inorganic sulfur is removed, the coal structure is partially collapsed or blocked thus preventing access of the adsorbate molecules
Illinois No. 6 Coal (-200 mesh)
Extracted with 10% NaOH at 250°C

Fig. 4-1. Surface area vs extraction time for sodium hydroxide treated Illinois No. 6 coal.
Illinois No. 6 Coal (-200 mesh)
Extracted with 10% NaOH at 250°C

Fig. 4-2. Sulfur content vs extraction time for sodium hydroxide treated Illinois No. 6 coal.
used to determine the BET surface area. Subsequent extraction removes these obstructions somewhat.

Figure 4-3 shows the variation in surface area with temperature for both the sodium hydroxide and oxygen treatments. The surface areas are significantly increased in both cases as the temperature is increased. These larger surface areas are due to the removal of additional sulfur from the micropores at high temperature.
Fig. 4-3. Surface area vs treatment temperature for desulfurized Illinois No. 6 coal.
V. SURFACE AREA VARIATIONS OF EXTRACTED COAL

A. Extracted Coal Samples

The extracted Coal samples used in these adsorption studies were obtained from Dorighi and Grens. The detailed extraction procedures and results are presented by Dorighi and Grens (28). They used a Wyoming subbituminous coal from the Roland seam of the Wyodak Mine at Gillette, Wyoming. The analysis of this coal is presented in Table 5-1.

The coal was extracted with pyridine for four hours at temperatures varying from 100°C to 300°C in a pressurized refluxed extraction apparatus. One sample was extracted for 100 hours at 250°C. Extractions were made on -28 + 150 mesh coal.*

The extracted coal was dried at 130°C and 200 mm Hg for 24 hours, while N₂ was swept over the samples at 60 - 80 cc/minute. The dried extracted coal was then stored in a desiccator under vacuum.

B. Surface Areas of Extracted Coal

The extracted coal samples were weighed and placed in the adsorption apparatus. The samples were then degassed at 130°C for 16 hours to a pressure of about 10^-5 torr. Carbon dioxide at 196°K was used as the adsorbate gas. The adsorption temperature was maintained with a dry ice/methanol bath. An equilibration time of 30 minutes was allowed for each adsorption point. The cross sectional area of the CO₂ molecule was taken to be 23.4Å².

* -28 + 60 mesh coal was used for the 300°C extraction.
Table 5-1
Analysis of Roland Seam Coal

<table>
<thead>
<tr>
<th></th>
<th>Proximate Analysis</th>
<th>Ultimate Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>as received</td>
<td>dry basis</td>
</tr>
<tr>
<td>% Moisture</td>
<td>23.43-23.83</td>
<td>----</td>
</tr>
<tr>
<td>% Ash</td>
<td>10.40-11.49</td>
<td>13.64-15.08</td>
</tr>
<tr>
<td>% Volatile</td>
<td>29.04-35.52</td>
<td>37.93-47.23</td>
</tr>
<tr>
<td>% Fixed Carbon</td>
<td>30.16-36.17</td>
<td>39.60-47.23</td>
</tr>
<tr>
<td>BTU</td>
<td>8226-8372</td>
<td>10800-10934</td>
</tr>
<tr>
<td>% Sulfur</td>
<td>0.70-0.94</td>
<td>0.92-1.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Moisture</td>
<td>23.43-23.83</td>
<td>----</td>
</tr>
<tr>
<td>% Carbon</td>
<td>47.02-47.37</td>
<td>61.67-62.19</td>
</tr>
<tr>
<td>% Hydrogen</td>
<td>3.79-4.04</td>
<td>4.97-5.30</td>
</tr>
<tr>
<td>% Nitrogen</td>
<td>0.73-0.87</td>
<td>0.96-1.13</td>
</tr>
<tr>
<td>% Chlorine</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>% Sulfur</td>
<td>0.70-0.94</td>
<td>0.92-1.23</td>
</tr>
<tr>
<td>% Ash</td>
<td>10.40-11.49</td>
<td>13.64-15.08</td>
</tr>
<tr>
<td>% Oxygen (difference)</td>
<td>11.72-13.35</td>
<td>15.40-17.51</td>
</tr>
</tbody>
</table>
BET plots of the pyridine extracted coal samples are included in the Appendix on Figure A-5. The BET surface areas of the extracted coal samples are presented in Table 5-2 along with the yield data obtained by Dorighi and Grens. Three different values for the surface area are reported for each sample. The first value is the specific surface area of the coal residue after extraction. The second value is the surface area of the coal residue on a dry and ash free basis. (Based on the ash content of the unextracted coal). The last value accounts for the weight loss in the coal sample due to extraction. This value is the surface area per gram of unextracted coal.

The surface area of the raw coal used in these extractions was 119 m²/g (OAF basis). For the 300°C extraction, -28 + 60 mesh coal was used, which had a surface area of 84 m²/g (OAF basis).

The variation of surface area with extraction yield is shown in Figure 5-1. Results for other solvents have been taken from the paper by Medeiros and Petersen and are included here for comparison. The surface areas of the pyridine extracted coals increase rapidly with increasing yield. This same trend was observed by Medeiros and Petersen for tetralin extractions. At extraction yields of greater than 20 percent, the tetralin surface areas showed no further increase with increasing yield. This leveling off was not observed with the pyridine extracted coal.

Figure 5-2 shows the effect of extraction temperature on the coal surface areas. These coal samples were all extracted for 4 hours. The pyridine surface areas are a strong function of extraction temperature. The coal structure is more easily broken down at higher
Table 5-2. Surface Areas of Extracted Roland Seam Coal

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>Time (hr)</th>
<th>Extraction Yield (DAF, wt. %)</th>
<th>BET Surface Area ($m^2/g$)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>DAF Basis</td>
</tr>
<tr>
<td>Pyridine</td>
<td>100</td>
<td>4</td>
<td>9.33</td>
<td>140</td>
</tr>
<tr>
<td>Pyridine</td>
<td>150</td>
<td>4</td>
<td>10.3</td>
<td>154</td>
</tr>
<tr>
<td>Pyridine</td>
<td>200</td>
<td>4</td>
<td>12.9</td>
<td>184</td>
</tr>
<tr>
<td>Pyridine</td>
<td>250</td>
<td>4</td>
<td>17.0</td>
<td>204</td>
</tr>
<tr>
<td>Pyridine</td>
<td>250</td>
<td>100</td>
<td>21.3</td>
<td>142</td>
</tr>
<tr>
<td>Pyridine*</td>
<td>300</td>
<td>4</td>
<td>20.1</td>
<td>251</td>
</tr>
</tbody>
</table>

*Ash content (dry basis) = 15.08%

†Raw coal surface area (-28 + 150 mesh) = 119 $m^2/g$ (DAF basis, except as noted.

+Raw coal surface area (-28 + 60 mesh) = 84 $m^2/g$ (DAF basis).
Fig. 5-1. Surface area vs extraction yield for Roland seam coal.
Fig. 5-2. Surface area vs extraction temperature for Roland seam coal.
temperature, therefore giving greater extraction yields and larger surface areas.

The changes in the surface areas with extraction time are shown in Figure 5-3. The surface area of the pyridine extracted coal decreased from a high of 169 m²/g at 4 hours to a value of 112 m²/g after 100 hours of extraction. This result can be explained if one looks at the equipment and procedure used by Dorighi and Grens. They began with a -28 + 150 mesh coal sample which was placed in a 200 mesh wire basket. Fresh solvent was continuously refluxed and the condensate was contacted with the coal in the wire basket. This process gradually reduced the coal particle size to the point where very fine coal particles could pass through the wire mesh basket and become suspended in the solvent-extract solution. Medeiros and Petersen have determined that these fine Roland Seam coal particles contain up to 50 percent more surface area than the -28 + 150 mesh coal. The loss of very fine coal particles is much more severe during the 100-hour extraction and, thus, the extracted coal shows an apparent decrease with extraction time.

C. Extracted Coal Pore Size

Adsorption of neopentane on raw and extracted Wyodak Roland Seam coal was used to determine the effect of extraction on the average pore diameter. Medeiros and Petersen have determined that the majority of the pores in the Wyodak Roland Seam coal are approximately 4Å or less in diameter. Pyridine extraction at 250°C for 4 hours increased the surface area from 119 m²/g to 240 m²/g. This doubling of the surface area must be due to either increasing the average pore diameter
Fig. 5-3. Surface area vs extraction time for Roland seam coal.
by a factor of two, or opening up new areas that were previously inaccessible to carbon dioxide at 196°K.

Neopentane is a symmetrical molecule with a kinetic diameter of 6.2 Å(29). Its molecular area was taken to be 62 Å² at 0°C. Neopentane adsorption on a Union Carbide sodium mordenite molecular sieve gave a BET surface area of 168 m²/g, whereas the carbon dioxide surface area was 390 m²/g. This is evidence that there probably is significant penetration and also significant sieving action to restrict passage of the neopentant into the 6.7Å pores of this molecular sieve. Neopentane should therefore be able to penetrate into pores with diameters of 6.7Å or larger. Since considerable sieving was observed in the neopentane adsorption on sodium mordenite, it is unlikely that neopentane will absorb in pores of less than 6.7 Å.

Neopentane adsorption on unextracted Roland Seam coal gave a very low BET surface area, less than 2 m²/g. This was to be expected since the majority of the pores are less than 4Å in diameter.

Adsorption on the pyridine extracted coal also gave a very low BET surface area. With the existing equipment, there was no measurable increase in neopentane adsorption.

This result suggests that the extraction had opened up new areas that were previously inaccessible to carbon dioxide. The average pore diameter may be somewhat enlarged, but it is still considerably less than 6.7Å. This conclusion poses an interesting question. How are large solvent molecules such as benzene, pyridine, or tetralin able to penetrate the coal pore structure if neopentane cannot?

A possible answer to this question can be obtained if one considers
the pores in coal to be slot shaped rather than cylindrical. Solvent molecules such as benzene could easily penetrate the slots, whereas the large, symmetric neopentane molecule could not. The surface area would be increased by deepening the slots or by widening the long dimension of the slot. However, an increase in the short dimension of the slot would have little effect on the surface area, depending on the degree of slot elongation. Neopentane would still be unable to penetrate the pores if the short dimension of the slot was not significantly increased. The idea of slot shaped pores was first proposed by Bond in 1956 (30). He theorized that the macropores were slot shaped with very fine interconnecting, cylindrical micropores. Unlike the Bond model, the model deduced from this work has slot shaped micropores.
VI. SURFACE AREA VARIATIONS OF REACTED COAL

A. Reacted Coal Samples

The reacted coal samples for this portion of the research were obtained from Holten and Vermeulen. The detailed reaction procedures and results are presented by Holten and Vermeulen (31). The analysis of the Wyodak Roland Seam coal used in these experiments was presented in Table 5-1.

The coal samples were allowed to react with molten zinc chloride containing some catalytic additives (vide infra). The reactions were carried out in a pressurized reaction vessel at temperatures between 200°C and 300°C. All reactions were carried out under hydrogen pressure. The melt treated coal was then extracted with benzene and dried at 105°C under vacuum for 24 hours.

B. Surface Areas of Reacted Coal

The surface areas of the reacted coal samples were determined by using the BET method with carbon dioxide at 196°K as the adsorbate. The procedure was the same as that used for the desulfurized and extracted coal samples.

BET plots of the reacted coal samples are included in the Appendix on Figure A-6.

A mixture of zinc chloride, magnesium chloride, potassium iodide, and iodine was allowed to react with -28 + 150 mesh Wyodak Roland Seam coal for 2 hours at 200°C. The treated coal was then extracted with benzene at 80°C. The surface area increased from its initial
value of 101 m²/g to 121 m²/g.* The benzene extractables increased only slightly from 1.76% to 2.00%.

A sample of -28 + 100 mesh Roland Seam coal was allowed to react with zinc chloride at 300°C and 500 psig hydrogen for 15 minutes. This treatment increased the surface area of the coal to 140 m²/g.* The reacted coal sample was then extracted with benzene at 80°C for 3 hours. The benzene extractables had increased to 5.97% and the surface area was further increased to 176 m²/g.*

*dry basis.
VII. CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

Carbon dioxide adsorption experiments gave the same BET surface areas at room temperature and at dry ice temperature for a molecular sieve, an alumina catalyst, and a Wyoming subbituminous coal. This suggests that activated diffusion is not an important factor, even at 196°K. The results on the Illinois No. 6 coal are inconclusive in that the areas decreased with increasing temperature. In general, carbon dioxide at 196°K may be used as an adsorbate on porous solids having pore diameters as low as 4Å.

Neopentane was able to penetrate a 6.7Å sodium mordenite molecular sieve to give a significant BET surface area. However, since the area was low we can say that there is also significant sieving action to restrict the passage of the neopentane. Neopentane should, therefore, only measure the surface area of pores greater than 6.7Å. Neopentane adsorption on Wyodak Roland Seam coal gave a BET surface area of less than 2 m²/g. Since the average Roland Seam micropore diameter is about 4Å, we must conclude that most of this area is due to adsorption in the macropores or in micropores greater than 6.7Å in diameter.

The use of sodium hydroxide to remove sulfur from Illinois No. 6 coal appears to cause partial blockage or collapsing of the pore structure. Subsequent extraction removes these obstructions somewhat. This conclusion was suggested by a minimum in the curve of surface area versus extraction time.

Pyridine extraction of Roland Seam coal appears to be opening up new areas that were previously inaccessible to carbon dioxide.
The surface areas have nearly doubled, yet the average pore diameter appears to remain essentially unchanged as evidenced by neopentane adsorptions. Solvent molecules such as benzene could easily penetrate the pores, whereas a large, symmetrical molecule such as neopentane could not. These results suggest that the pores in the Roland Seam coal are slot shaped rather than cylindrical. This would explain the large increases in surface area with no apparent increase in pore diameter. The surface area of the pyridine extracted Roland Seam coal increases rapidly with increasing yield and increasing temperature.

Much information about the pore structure of coal is still missing. More work needs to be done on determining pore size distributions. This would help us determine where the extract comes from, how new surface areas are opened up, and how the solvent molecules are able to penetrate the coal structure.

One of the most promising methods of determining pore size distributions is the adsorption of various size molecules onto the porous solid. This takes advantage of the molecular sieve properties of coal. A given size molecule will only be able to penetrate to a given pore size. This will give the surface area of pores greater than the particular pore size in question.

The other missing piece of information is pore volumes. We would like to know the volume of the pores that are associated with each of the measurable pore diameters. Methods need to be developed to obtain these pore volumes. Total pore volumes can be determined by helium displacement. Mercury porosimetry gives the pore size distribution for pores greater than 200Å. Nitrogen adsorption isotherms have been
used to determine pore size distributions down to 12Å.

This additional information would help us to understand better the changes in the pore structure of coal as it undergoes chemical processing.

ACKNOWLEDGEMENT

This work was done under the auspices of the U. S. Energy Research and Development Administration.
REFERENCES

Fig. A-1. High and low temperature adsorption of CO₂ on an aluminum catalyst and a molecular sieve.
Fig. A-2. High and low temperature adsorption of CO₂ on Wyodak Roland seam coal.

1. Wyodak Roland Seam, 196°K, 101 m²/g*
2. Wyodak Roland Seam, 295°K, 105 m²/g*
3. Wyodak Roland Seam, 298°K, 105 m²/g*

*dry basis
Fig. A-3. High and low temperature adsorption of CO₂ on Illinois No. 6 coal.
Fig. A-4. Adsorption of CO₂ at 196°K on desulfurized Illinois No. 6 coal.
Pyridine Extractions

1. 100°C, 4 hr., 140 m²/g*
2. 150°C, 4 hr., 154 m²/g*
3. 200°C, 4 hr., 184 m²/g*
4. 250°C, 4 hr., 204 m²/g*
5. 300°C, 4 hr., 251 m²/g*
6. 250°C, 100 hr., 142 m²/g*

*dry basis

Fig. A-5. Adsorption of CO₂ at 196°C on pyridine extracted Roland seam coal.
Fig. A-6. Adsorption of CO₂ at 196°C on zinc chloride treated Roland seam coal.

1. ZnCl₂, MgCl₂, I, 200°C, 2 hr, Benzene Extracted, 121 m²/g*
2. ZnCl₂, 300°C, 15 min, 140 m²/g*
3. ZnCl₂, 300°C, 15 min, Benzene Extracted, 176 m²/g*

*dry basis
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