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STUDIES ON THE ULTRA- FINE STRUCTURE OF SOME ILLINOIS COALS

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ABSTRACT

By means of the nitrogen adsorption (BET) method, surface area and pore size measurements have been made on a number of Illinois high-volatile bituminous coals. These measurements are compared with similar data on a limited number of other coals of lower and higher ranks. Surface areas for Illinois samples averaged 3.2 square meters per gram for 3 high-volatile A bituminous coals, 11.8 square meters per gram for 6 high-volatile B bituminous coals, and 68.4 square meters per gram for 5 high-volatile C bituminous coals. Irreversible changes during evacuation caused results for a lignite to be unreliable; anthracitic coals gave surface area measurements between those for the high-volatile B and C bituminous coals.

In studies of the banded ingredients of several coals, vitrains showed the highest specific surfaces, clarain was lower, and fusain gave the lowest values.

All samples studied showed a predominance of pore diameters near the value of 40 angstrom units.

The nitrogen adsorption (BET) method is described briefly.

INTRODUCTION

During a period roughly limited to the years between 1933 and 1955, a number of papers were published in this country and abroad dealing with the problem of ultrafine structure of coals. The interest generated by the earliest of these communications was pointed up by a conference held in England on the Ultrafine Structure of Coals and Cokes. The proceedings of this conference were published in book form by the British Coal Utilisation Research Association (1944).

In this country, the problem was attacked by the use of gas adsorption (BET) methods (Brunauer, Emmett, and Teller, 1938). In England a method based on measurements of the heat of wetting of pulverized coal in methyl alcohol was

favored, partly because it was capable of quickly producing results that were believed to be sufficiently accurate for many purposes. However, it soon became apparent that the two methods gave results which disagreed seriously, sometimes by as much as three hundred or four hundred percent.

Many investigators seriously doubted whether the heat of wetting method could be used properly to measure the surface area of any porous material. These doubts were particularly strong in studying coal with methyl alcohol, which was known to dissolve some material from coal (methyl alcohol takes on a slight brownish color when left in contact with coal) and to cause some swelling of the coal. However, the method has been used often with considerable confidence in applying various liquids to the measurement of the surface areas of nonporous, powdered solids. On the other hand, some people considered that the discrepancies were unexpectedly large.

These doubts led to a reexamination of the gas adsorption method as applied to coal. The most obvious weakness in the method is that the temperature at which the measurements are made is at, or reasonably near, the boiling point of the gas being adsorbed. The most frequently used gases are nitrogen and argon at the boiling point of liquid nitrogen (about 77.5° Kelvin) or of liquid oxygen (about 90° Kelvin).

Coal, like other adsorbents containing ultrafine pores, acts as a molecular sieve; that is, small molecules can penetrate coal particles while larger ones cannot. From this fact, one might suspect that at higher temperatures than those mentioned in the preceding paragraph coal might adsorb more molecules because the expansion resulting from warming up would decrease the density and, consequently, increase the pore volume. That this actually happens was shown by Maggs (1952), although the precise mechanisms involved are a matter of conjecture. It might be that constrictions in the pores are opened enough to make available for adsorption surface which is inaccessible at temperatures below 100° Kelvin.

The net result of the controversy was not, as one might hope, a clearcut decision in favor of one method or the other, but a conclusion that the results obtained by the BET method were too low by an unknown amount (probably averaging about 15 percent) and that the methyl alcohol method gave results that were considerably too high. However, interest in the ultrafine structure of coal languished because industry found no application for the data.

At the Illinois State Geological Survey, work on the surface area and pore size distribution of midcontinent coals was carried on intermittently during the decade 1945 to 1955. These coals were not included in studies reported by the U. S. Bureau of Mines, which dealt mainly with eastern coals of rank higher than most coals found in Illinois.

EXPERIMENTAL METHODS

Two types of apparatus were used. The first was similar to that described by Harkins and Jura (1944). The second was a more elaborate and versatile setup, in many respects similar to one illustrated by Barr and Anhorn (1949, p. 277).

The first step in the determination of the surface area of a powder sample by nitrogen adsorption is carried out by attaching a glass capsule containing a weighed sample of the powder to a vacuum system, pumping the system down to a pressure of the order of 10^{-5} millimeters of mercury, and continuing to pump until

the pressure in the system no longer increases when the system is closed off.

The second step is to cool the sample to some temperature in the neighborhood of the boiling point of liquid nitrogen by surrounding the sample capsule with liquid nitrogen or liquid air.

The third step is to admit gaseous nitrogen to the cooled sample capsule at a known pressure in the neighborhood of 0.05 atmospheres and measure the maximum volume of nitrogen that the sample will adsorb at this temperature and pressure. This is repeated at two or three other pressures, the highest of which should be about 0.3 atmosphere. From these volumes and pressures, the surface area may be calculated by means of one of the limiting forms of an equation derived by Brunauer, Emmett, and Teller (1938). This equation in its most general form is

$$V = \frac{V_m CX}{(1 - X)} \left[\frac{1 - (N + 1) X^N + NX^{N+1}}{1 + (C - 1) X - CX^{N+1}} \right] \quad (1)$$

where V is the total volume of gas adsorbed at any given pressure P , V_m is the volume of gas required to cover the surface of the sample with a layer one molecule deep, C is a constant, $X = P/P_0$ where P_0 is the pressure at which the gas being adsorbed would begin to condense to a liquid at the temperature of the measurement and P is the pressure at which the measurement is made, and N is the number of molecular layers that V cubic centimeters of gas would make on the sample if it were evenly distributed.

The equation in the above form is not convenient for determining the area of the sample. However, as N increases without limit, equation (1) approaches a simplified form:

$$V = \frac{V_m CX}{1 - X} \cdot \frac{1}{1 + (C - 1)X} \quad (2)$$

On replacement of X by its value P/P_0 and an algebraic rearrangement this becomes

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \cdot \frac{P}{P_0} \quad (3)$$

Equation (3) is in the form of a straight line equation, analagous to $y = b + ax$, where the variables $P/[V(P_0 - P)]$ and P/P_0 correspond to y and x respectively; $1/V_m C$ is the intercept corresponding to the constant b ; and $(C - 1)/V_m C$ is the slope corresponding to constant a . V_m and C are constant for any given adsorbent, such as a coal sample, and a given adsorbate, such as nitrogen. V and P are measurable, and P_0 is known when the temperature is known. If a graph is drawn using values of P/P_0 as abscissae and values of $P/[V(P_0 - P)]$ as ordinates, a straight line will result. Its slope, $(C - 1)/V_m C$, and its intercept on the vertical axis, $1/V_m C$, can be measured with satisfactory precision from a large-scale plot. From these it can be calculated that

$$C = \frac{\text{slope}}{\text{intercept}} + 1$$

and

$$V_m = \frac{1}{\text{slope} + \text{intercept}}$$

The determination of V_m is the main object of the experiment. Once it is

known, the total number of nitrogen molecules it contains may be calculated, and multiplication of this number by the area effectively covered by one nitrogen molecule when adsorbed on a surface gives the total area of the surface. The area occupied by one nitrogen molecule is taken as 16.2 \AA^2 (Emmett and Brunauer, 1937) for purposes of this report although some workers prefer slightly different values.

It will readily be seen by examination of table 1 that the whole coals of high-volatile C, B, and A bituminous rank from Illinois show a trend in surface area that is strongly downward with increasing rank. If the high-volatile B bituminous rank coals from Indiana are included, the trend, as might be expected, is not changed much.

A few coals from other areas are included, but because the number of samples is so small, the results must be accepted with caution in so far as making generalizations is concerned. It is, however, of interest to note that the surface areas of the anthracite and meta-anthracite samples are much higher than those of the high-volatile A bituminous coals. This may be of interest in connection with theories concerning the final stages in the coalification process, and it should merit more extensive study.

In the case of the lignite sample the very low surface area value is probably not a property of the untreated sample. The lignite sample on evacuation undergoes irreversible changes of uncertain character such that surface area determinations on the resulting product are meaningless. Another interesting fact about this lignite was that the heat of wetting by water of an evacuated sample was about 28.5 calories per gram, which is several times the average for some two dozen other coals on which such measurements were made.

Of the three high-volatile A bituminous coals listed in table 1, the range of surface areas was 1.8 to 4.5 square meters per gram with an average value 3.2.

Six high-volatile B bituminous coals from various Illinois counties ranged from a low of 7.2 to a high of 16.3 square meters per gram with an average of 11.8. For comparison, the area of a sample of Pocahontas (low volatile) coal that happened to be available was found to be 3.2 square meters per gram.

Five Illinois high-volatile C bituminous coals studied ranged from 46.8 to 91.8 square meters per gram. The average was 68.4.

SURFACE AREAS OF BANDED INGREDIENTS

In table 2 surface area measurements on the banded ingredients of samples of Illinois high-volatile A, B, and C bituminous coals are recorded. For all of these samples (except the A rank coal) and various other samples that we have studied, the vitrain always proved to have the highest specific surface. The clarain surface area was less than that of the vitrain and the fusain surface area was least.

In the case of the high-volatile A bituminous coal, the whole coal surface areas were small and, furthermore, it proved difficult to pick out amounts of fusain or clarain of sufficient size to make measurements. For these reasons it was not possible to get more conclusive data on A rank coals of the state.

Adsorption Isotherms on Coal

If adsorption data are plotted according to equation (3) using values of P/P_0 very much greater than 0.35, the points fall below the continuation of the straight line due to the fact that the amounts of gas adsorbed are greater than

TABLE 1 - SURFACE AREAS OF WHOLE COALS

Sample number	Coal rank	Source	Surface area, square meters per gram	Moisture-free volatile matter
C-8652	A ^a	Gallatin Co., Ill.	1.8	40.6
C-7959	A	do.	4.5	37.3
C-5637	A	do.	3.3	37.2
C-6669	B	Franklin Co., Ill.	16.3	—
C-7440	B	do.	9.9	40.0
C-8786	B	Jefferson Co., Ill.	11.6	38.2
C-6668	B	Saline Co., Ill.	7.2	—
C-5593	B	Williamson Co., Ill.	13.2	36.0
C-5598	B	do.	12.7	35.9
C-6452	B	Vigo Co., Indiana	25.8	40.3
C-6448	B	do.	22.4	43.6
C-5651	C	Henry Co., Ill.	66.3	45.4
C-8293	C	do.	58.4	46.8
C-5619	C	Macoupin Co., Ill.	46.8	40.5
C-7052	C	Sangamon Co., Ill.	78.7	42.1
C-9543	C	do.	91.8	—
Miscellaneous Samples				
C-5686	Lignite	Velva, N. Dakota	2.8 ^b	44.1
C-5707	C ^c	Colorado	4.1 ^b	45.0
C-5744	B ^c	do.	31.3	41.1
C-8835	Low-volatile	West Virginia ^d	3.2	16.3
C-5766	Anthracite	Pennsylvania	21.1	3.0
C-8859	Meta-anthracite ^e	Iron River, Michigan	41.8	4.0

a High-volatile bituminous rank in first 16 samples given.

b These two values are probably meaningless because the structure of the samples was radically changed by the removal of so much water during evacuation.

c Sub-bituminous

d Pocahontas

e Precambrian

TABLE 2 - SURFACE AREAS OF BANDED INGREDIENTS
(High-volatile bituminous coals)

Sample number	Coal rank	Coal	Source	Surface area, square meters per gram
C-7959	A	Whole coal	Gallatin Co.	4.5
C-7961	A	Vitrain	do.	3.2
C-7440	B	Whole coal	Franklin Co.	9.9
C-7441	B	Vitrain	do.	11.8
C-7442	B	Clarain	do.	6.6
C-7443	B	Fusain	do.	5.9
C-7052	C	Whole coal	Sangamon Co.	78.7
C-7053	C	Vitrain	do.	139
C-7054	C	Clarain	do.	67.6
C-7055	C	Fusain	do.	15.5
C-8293	C	Whole coal	Henry Co.	58.4
C-8294	C	Vitrain	do.	81.7
C-8296	C	Clarain	do.	40.6
C-8295	C	Fusain	do.	11.7

those predicted by equation (3). That is, the equation fits the experimental facts if the pressure is not greater than about one-third of the saturation pressure of nitrogen being adsorbed.

In the case of coal it is customary to explain this situation by attributing the increased adsorption to condensation of the gas to a liquid in small capillaries present in the coal particles. The classical Kelvin equation

$$D = \frac{-4 \sigma V \cos \theta}{RT 2.303 \log(P/P_0)} \quad (4)$$

gives the diameter of a capillary in which a gas or vapor will condense to a liquid and fill the capillary. For highly accurate work, this equation is an oversimplification and must be modified. Here D is the pore diameter; σ the surface tension; V the molal volume of the liquid; θ the angle of contact of the liquid with the capillary wall (for liquid nitrogen on coal the angle θ is assumed equal to zero); R the gas constant; and T the absolute temperature. Barrett, Joyner, and Halenda (1951) have worked out a method of computing pore volume and area distributions based on the Kelvin equation with certain modifications which need not be explained here, except to say that their modification makes allowance for the fact that the walls of the pores may hold one or several layers of adsorbed gas molecules before condensation begins; thus, the true pore diameter is greater than that calculated from the Kelvin equation by twice the thickness of the adsorbed layer. It is perhaps unnecessary to consider this with large pores, but it becomes a very important factor in the case where many of the pores are only a relatively few molecular diameters in width.

Because the contact angle appears in the equation, it is evident that we must consider that we are dealing with a meniscus. The question arises: how many molecular diameters wide must a pore be before a meniscus can form? Holmes and Emmett (1947) say: "It is generally agreed that capillary condensation will not occur at relative pressures lower than that corresponding to four molecular diameters as calculated by the Kelvin equation." This appears to be an understatement; the diameter usually assumed for the nitrogen molecule (N_2) is about 2 Å, and the effective area usually assumed to be covered by this molecule on a surface is about 16.2 Å². The area of the pore section for a four molecular diameter pore, therefore, is quite small. This area would be covered by very few molecules. Whether so few molecules, or even twice that many, could arrange into anything resembling a meniscus, would appear to be questionable.

Nitrogen Isotherms

If adsorption on coal is carried out using nitrogen at the temperature of liquid nitrogen for a series of values of P/P_0 ranging between zero and one, and if the total amounts adsorbed are plotted as ordinates and the corresponding P/P_0 values as abscissae, then for low values of P/P_0 the curve rises sharply. As P/P_0 increases, the curve is concave downward, passing through a point of inflection at a point averaging somewhere in the neighborhood of $P/P_0 = 0.45$; then it is concave upward until P/P_0 is about 0.7 or 0.8; from there it is usually, although not always, concave downward until $P = P_0$. At this point, the sample is saturated with liquid nitrogen and all open pores are assumed to be full.

For example, if the pressure of nitrogen on the sample is reduced by five percent, the modified Kelvin equation says that the liquid nitrogen will evaporate and empty all larger pores down to the specific size corresponding to $P/P_0 = 0.95$.

With proper apparatus we can measure the volume of this nitrogen gas and calculate the volume it would occupy as a liquid, which is obviously the volume of the pores that have been emptied. By repeating this process we can arrive at the volume of pores emptied in each interval, and by combining these volumes we can obtain the total volume of all pores larger than any given diameter to which the equation, with reasonable confidence, can be applied. From these data, an estimate of pore size distribution can be made for pores larger than the minimum size for which the equation is valid. For the above reasons, it is agreed generally that it is not safe to apply the method to pores much smaller than 18 or 20 Å diameter. In figure 1, typical nitrogen isotherms for high-volatile bituminous A, B, and C coals of Illinois are shown. The isotherm for coal C-7052 is often referred to as a type IV isotherm (Brunauer, 1945). Those for C-7440 and C-7959 are usually designated as type II. This type differs from type IV; while type IV becomes concave downward in the portion near the right hand end of the curve and thus has two points of inflection, type II has only one point of inflection and remains concave upward at the high relative pressure end.

The isotherm for coal C-7052 is drawn with both the adsorption and desorption branches. That is, the coal was allowed to adsorb the gas at increasing values of P/P_0 from zero up to one; then the process was reversed and the gas allowed to desorb by steps as the pressure was reduced. It will be noted that there is a hysteresis loop between the adsorption and the desorption curves. The area enclosed by this loop decreases as the total pore volume of the sample decreases. For the Illinois high-volatile C bituminous coal, this area is relatively large. For the Illinois high-volatile A bituminous coal, there is only a relatively small loop.

From the points on the desorption branch, it is possible to calculate a pore volume distribution curve in terms of the average pore radius between short intervals. Figure 2 is such a curve for an Illinois high-volatile C bituminous coal (C-7052). In this figure the abscissae are values of the pore radii in Å units. The ordinates are the values of the total volume ΔV of all pores with radii in the interval ΔR , divided by the values of ΔR . ΔV is expressed as cubic centimeters per gram of sample. For correcting the pore diameters for layers of adsorbed gas (Barrett, Joyner, and Halenda, 1951), the value 1.94 Å was assumed for the diameter of the nitrogen molecule. This curve has a prominent peak in the neighborhood of pore radius 20 Å, which indicated that the greater part of the pore volume in this coal is contained in pores around 40 Å diameter. This value kept recurring in such calculations for the coals for which we made these estimates.

For the banded ingredients, the isotherms in general are similar in character to those of the whole coal but differ in the areas within the hysteresis loops. That is, if the ingredient has a larger surface area or a smaller surface area than the whole coal, the loop is correspondingly larger or smaller.

Water Isotherms

A number of isotherms were run on the water adsorption of coals because the moisture content and its variations with relative humidity and other weather factors is of interest in the marketing of coal on specification.

To obtain data for water isotherms, the technique is necessarily somewhat

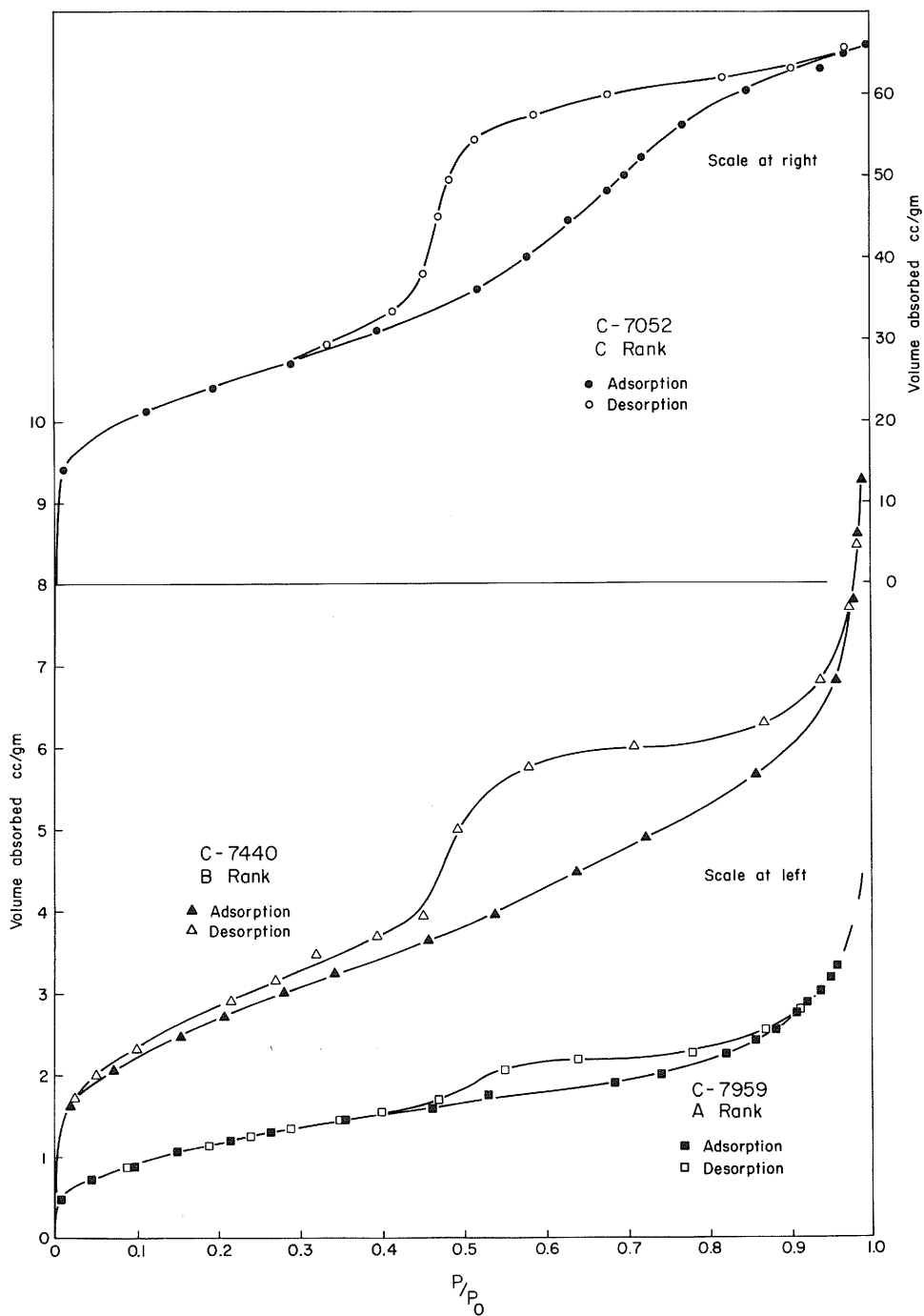


Fig. 1 - Nitrogen isotherms for coals of A, B, and C rank.

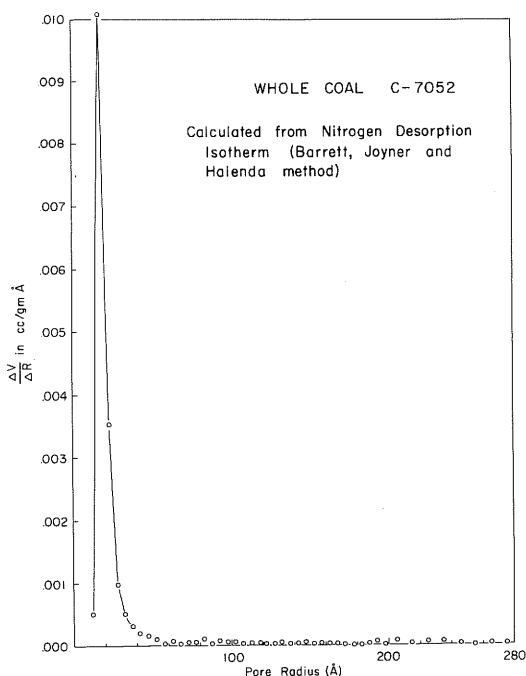


Fig. 2 - Pore volume distribution curve

are of largest area for the vitrain, of intermediate area for the clarain, and of smallest area for the fusain. The isotherm for the whole coal is plotted on the same figure for comparison.

There are at least two obvious reasons for this difference in behavior between nitrogen and water at the lower pressures. First, the nitrogen isotherms are measured at a temperature very near the boiling point of liquid nitrogen, while the water isotherms are measured at room temperature. Second, the size of the water molecule is considerable less than that of the nitrogen molecule. It is probable that the first reason is much more important than the second.

CONCLUSIONS

Illinois high-volatile C bituminous coals are much more porous than the Illinois high-volatile A and B bituminous coals and, consequently, have much greater specific surface. The high-volatile B bituminous coals have greater specific surfaces than do the Illinois high-volatile A bituminous coals.

The pore size distribution computations indicate that for all coals entering into this study, there is a high peak in the region of 40 Å diameter. The position of this peak does not appear to vary much with coal rank.

An interesting feature of the surface area studies is that the surface areas of the small number of anthracites studied were considerably greater than those of the high-volatile A and the low-volatile bituminous coals studied.

different from that used for nitrogen. For one thing, the total pressure range involved is from zero to 30 millimeters of mercury, which necessitates the use of more refined techniques of measurement in order to get reliable data. For another, varying ambient temperature in the laboratory makes it difficult, if not impossible, to obtain accurate pressure-volume measurements of the total amounts of water taken up by the sample. However, if weight methods are used, good data can be obtained.

Figure 3 presents water adsorption and desorption isotherms for high-volatile A, B, and C bituminous coals. It will be observed that the desorption isotherm with water does not rejoin the adsorption branch until the pressure reaches a value of zero, whereas in the case of the nitrogen isotherms the adsorption and desorption are superposed, or nearly so, at low values of P/P_0 .

Figure 4 presents water adsorption isotherms for banded ingredients of a high-volatile C bituminous coal (C-7052). The hysteresis loops, as might be expected,

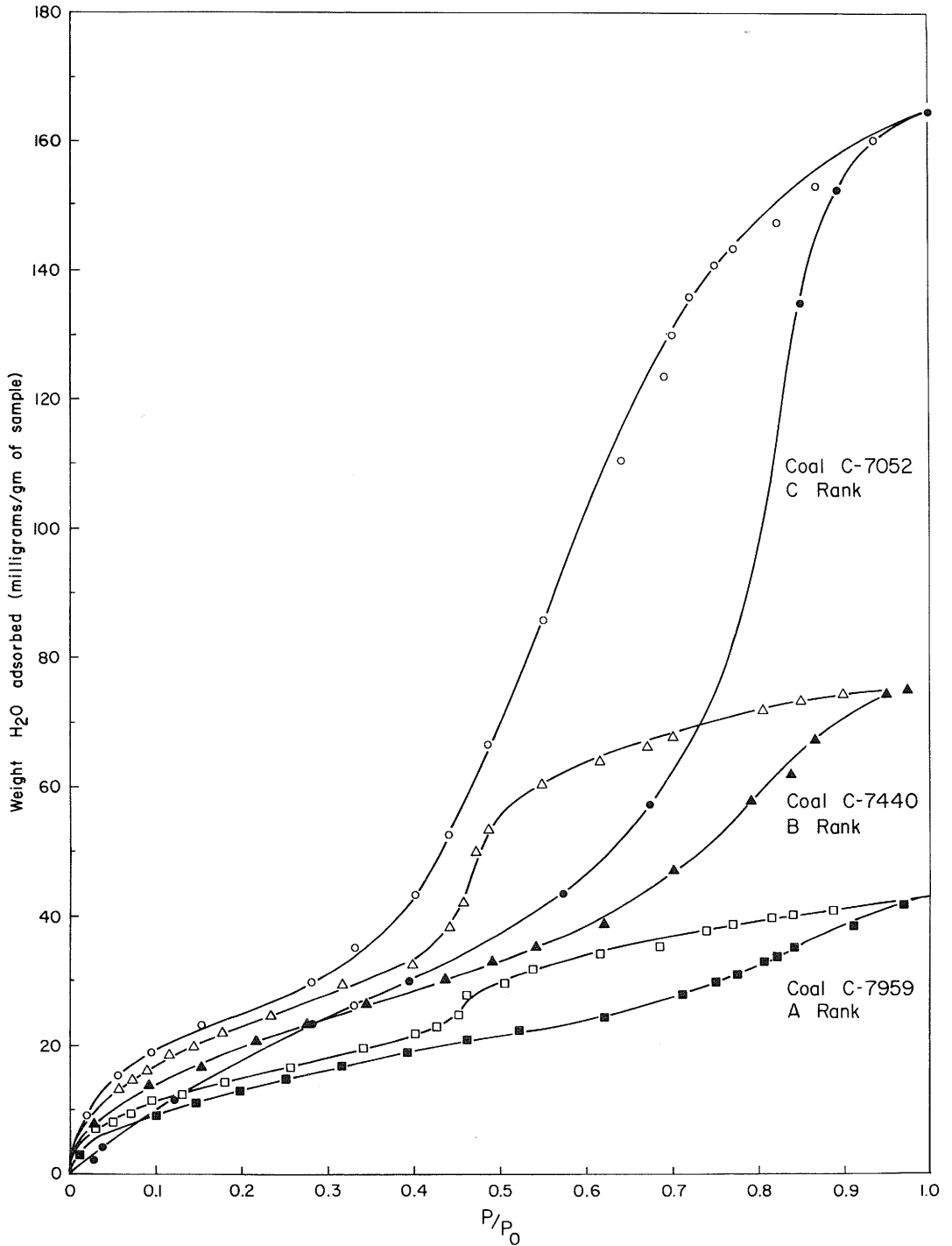


Fig. 3 - Water isotherms whole coals.

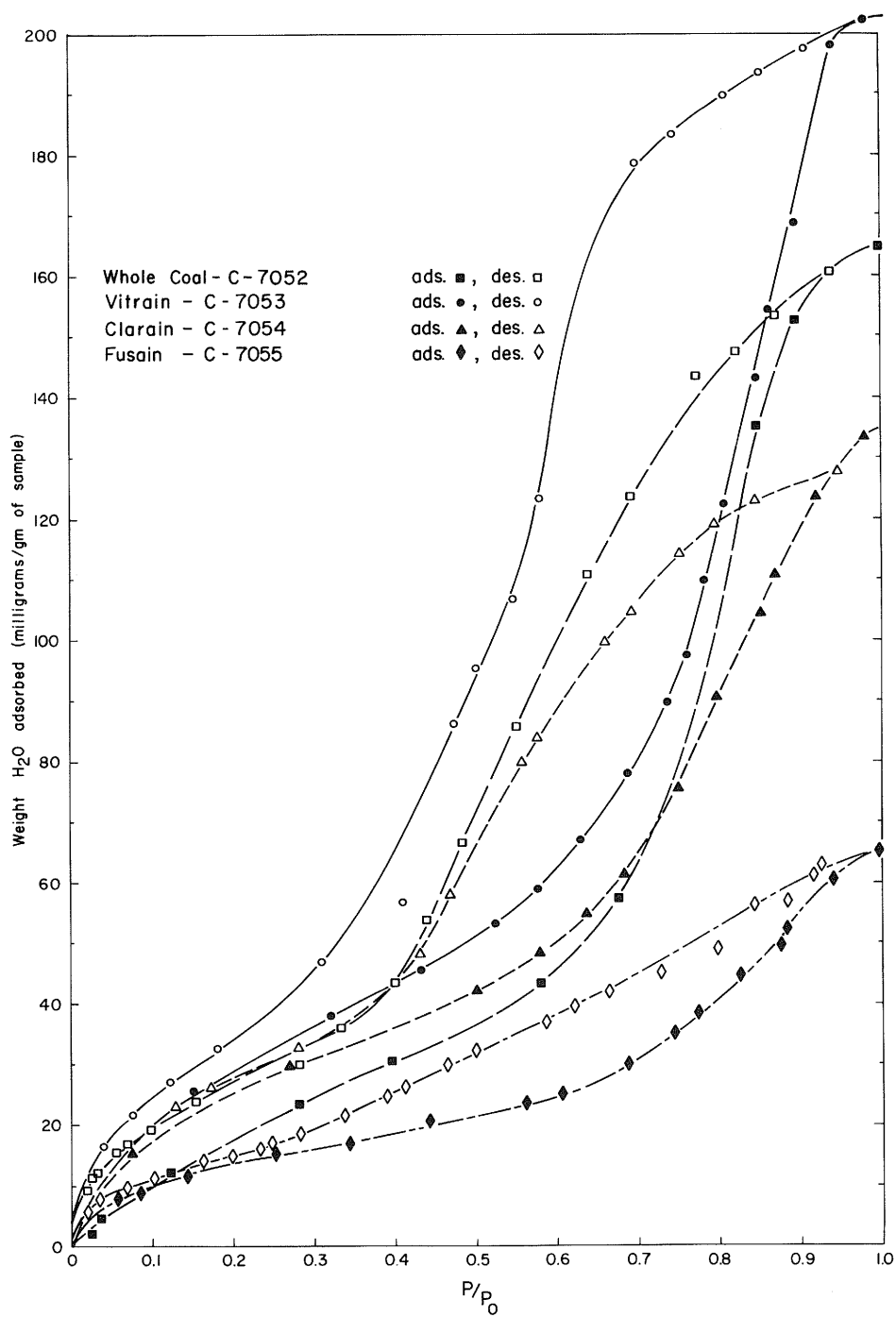


Fig. 4 - Water isotherms, banded ingredients.

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