Date: September 1980

PRINCIPAL INVESTIGATOR: Paul W. Schmidt

AFFILIATION/ADDRESS: Physics Department, University of Missouri, Columbia, MO 65211

MASTER

TELEPHONE NO: 314-882-8241

PROJECT TITLE: Small Angle X-Ray Scattering Studies of the Porosity of Coals and Chars - Contract No. ET-78-S-01-3169

QUARTERLY PROGRESS REPORT FOR THE PERIOD

JULY 1, 1980 THROUGH SEPTEMBER 30, 1980

SUMMARY

Considerable effort during the past quarter has been devoted to checking and verifying some of the preliminary data reported previously. The technique employed in the past for measuring the x-ray transmission of the samples has been modified to provide more accurate values of the transmission. These transmission measurements are important for quantitative interpretation of the scattering data both because they are needed to determine the amount of background scattering that must be subtracted from a measured scattering curve and also because the value of the transmission is required for calculating the specific surface from the scattering data. Previous determinations of the specific surface have been checked and modified when corrected transmission values made recalculation necessary. Evaluation of the specific surface from the scattering data also requires a measurement of the "absolute scattered intensity", or scattering cross section. In other words, the fraction of the incident radiation which is scattered must be known. For this scattering investigation of coals, the absolute intensity for the scattering system at the University of Missouri was determined by measurement of the scattering from a colloidal silica suspension. The details of this technique are described by I. S. Patel and P. W. Schmidt, J. Appl. Cryst. 4, 50-55. (1971).

To extend the previous estimates of the contribution of mineral matter to the scattering from coals, a series of PSOC coal samples, selected to have both low, normal, and high mineral contents, are being studied. The first results are now being analyzed.

A manuscript has been prepared to describe the small-angle x-ray scattering studies of porosity in coals. This paper has been submitted to the Symposium on New Approaches in Coal Chemistry, organized by Bernard D. Blaustein for the November, 1980 American Chemical Society regional meeting in Pittsburgh. The manuscript constitutes this quarterly progress report.

DISCLAIMER

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

DISCLAIMER

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

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

SMALL-ANGLE X-RAY INVESTIGATION OF THE POROSITY IN COALS*

M. Kalliat, C. Y. Kwak, and P. W. Schmidt

Physics Department, University of Missouri, Columbia, Mo. 65211 USA

*Work supported by the U. S. Department of Energy.

ABSTRACT

Small-angle x-ray scattering measurements are reported for 15 coal samples in the PSOC series of coals. The rank of the coal was found to be the main factor determining the form of the small-angle scattering curves. One type of scattering curve was characteristic of anthracites, while a somewhat different curve was obtained for low-volatile bituminous coals. In the scattering curves from many high-volatile bituminous and some sub-bituminous coals, a shoulder was observed. A fourth kind of curve was found to be typical of other high-volatile bituminous and sub-bituminous coals and also of lignites. Analysis of the scattering curves provides evidence for the presence of three classes of pores-- (1) large pores, with dimensions of at least 300 Å, (2) intermediate sized pores, with average dimensions of the order of 100 or 200 Å, and (3) very small pores, which with dimensions no greater than about 30 Å. These three types of pores are referred to as macropores, transition pores, and micropores, respectively. The system of three kinds of pores suggested by the x-ray scattering data is in good agreement with the three-class pore structure developed by other workers' investigations employing techniques besides small-angle x-ray scattering. The specific surfaces of the coals were calculated from the scattering curves. A method was developed for estimating the fractions of the total specific surface which should be assigned to the macropores and transition pores under the assumption that the specific surface computed from the scattering curves did not include any contribution from the micropores. The specific surfaces calculated from the scattering data have been compared with the specific surfaces obtained by adsorption of nitrogen at low temperatures and by carbon dioxide at room temperature. The x-ray data are not consistent

with the suggestion that many pores have dimensions of some hundreds of Ångströms but have restricted openings which exclude nitrogen at low temperatures. Instead, the high values of surface area obtained by carbon dioxide adsorption must be the result of the contribution of a large number of pores with minimum pore dimensions which are not greater than about 30 Å.

I. Introduction

Small-angle x-ray scattering is a technique which provides information about structures which, though larger than the normal interatomic distances in solids and liquids, are too small to be visible in the optical microscope. Since the interval of dimensions which can be conveniently studied by small-angle scattering thus includes those of many of the pores in coals, we have used small-angle scattering to investigate the porosity of a number of coal samples. Before presenting our results, however, we will review some techniques and concepts employed in the measurement and interpretation of the scattering data.

In our small-angle x-ray scattering studies of coals, x-rays (wavelength $1.54\text{\AA}$) from a copper-target diffraction tube were formed into a well-defined beam and struck the coal sample, which was in powdered form and which had a thickness of about 1 mm. Figure 1 shows a schematic diagram of the scattering apparatus.

Although most of the x-rays were either absorbed in the sample or passed through it without being affected, a small fraction of the radiation, called the scattered radiation, was emitted in directions other than that of the incoming beam. One of the quantities which determines the intensity of these scattered rays is the scattering angle θ , which is the angle between the incident and scattered rays, as shown in Fig. 1. (In many discussions of large-angle x-ray diffraction, the scattering angle is called 2θ , rather than θ). The scattered intensity also depends on the structure of the scattering sample. The object of most scattering experiments is to obtain information about the structure of the sample by analyzing measurements of the scattered intensity at a series of

scattering angles.

While the general relationship between the scattered intensity and the structure is so complicated that there is no general procedure applicable for the analysis of data from all kinds of samples, relatively simple methods can be used to interpret the scattering curves from the coals.

First, a general principle from scattering theory states that most of the information about the sample which can be obtained from scattering data is contained in the measurements at scattering angles which satisfy the condition

$$0 \leq hD \leq 10 \quad (1)$$

where D is a dimension characterizing the structure producing the scattering;

$$h = 4\pi\lambda^{-1} \sin(\theta/2); \quad (2)$$

and λ is the x-ray wavelength. According to (1), there is a more-or-less inverse relationship between the size of the structure producing the scattering and the angle at which the most useful scattering is observed. By convention, "small-angle" scattering has come to mean scattering at angles θ no greater than about 5 degrees. At these angles, h is essentially proportional to θ .

X-ray scattering occurs only when there are differences in the number of electrons per unit volume in different regions of the sample. Coals thus scatter x-rays because there are inhomogeneities in their electron

density. According to (1), this scattering occurs at small angles because an appreciable fraction of these inhomogeneities have maximum dimensions no greater than about $1000 \text{ \AA}$. When $hD_{\min}$ is large, where $D_{\min}$ is the smallest dimension appreciably affecting the scattering in a given interval of scattering angles¹, the scattered intensity $I(h)$ can be approximated by the relation

$$I(h) \approx 2\pi I_e d^2 S h^{-4}, \quad (3)$$

where I_e is the intensity scattered by a single electron; d is the difference in the electron densities of the two phases which the sample is considered to be composed of; and S is the value of the total surface area separating these two phases in the sample. (In the small-angle region, I_e can normally be considered to be a constant, and within each phase the electron density also can be assumed to be constant².) Equation (3) has been found to be quite well satisfied when

$$hD_{\min} \geq 3.5. \quad (4)$$

In the coal samples, usually one of the two phases is coal, and the other is pores, which are considered to contain air. Sometimes, however, the effects of the mineral matter in the coal must be considered. The system then contains three phases. Our scattering data from the coals suggest that the pores and mineral matter scatter independently of each other, so that when the contribution of the minerals to the scattering must be considered, the coals can be taken to be two independent systems--one made up of coal and air, and the other consisting of coal and mineral

matter. As we will explain in more detail in Section 4, we have estimated the contribution of the mineral matter to the scattering from several of the coals and have concluded that this scattering is small and often can be completely neglected.

According to (3), when $I(h)$ is proportional to h^{-4} and thus to θ^{-4} , the magnitude of the scattered intensity is proportional to the surface area dividing the two phases. The scattering data thus provide information about the specific surface of the coal samples. It is important to note, however, that meaningful results about the specific surface can be obtained only when there is an interval of scattering angles for which the intensity is at least approximately proportional to θ^{-4} .

When

$$hD_{\max} \leq 0.5, \quad (5)$$

where $D_{\max}$ is the largest dimension characterizing the structure³,

$$I(\theta) \approx I_e d^2 F_0. \quad (6)$$

In (6), F_0 is a constant. The scattered intensity from relatively small inhomogeneities thus is independent of the scattering angle but is proportional to d^2 .

2. Results

The scattering data were recorded with a Kratky small-angle scattering system⁴ (Fig. 1) and a stationary-anode x-ray tube operated at about 30 ma average current and at a peak voltage of about 45 KV. A proportional

counter was employed to detect the scattered radiation, and the x-rays scattered at the copper K- α wavelength of $1.54 \text{ \AA}$ were selected by a linear amplifier and a pulse-height analyzer. An electronic programmer was used to set the system at the desired scattering angles.

Each scattering curve was measured six times. After the results were averaged and corrected for the day-to-day fluctuations in the incident intensity, the curves were corrected for the background scattering from the scattering system and the 0.005 inch Mylar[®] plastic windows of the sample cell. Corrections were also made for the length⁵ and width⁶ of the collimating slits.

Scattering data were recorded for about 50 coal samples, most of which were obtained from the Pennsylvania State University PSOC set of coals. We will discuss the scattering from 15 of these coals. The results from the other samples were quite similar to those reported here.

We found that the form of the curve of the scattered intensity as a function of the scattering angle depends primarily on the rank of the coal. The scattering curves can be conveniently grouped into four classes. An example of each of these four types of curves is shown in Figure 2.

Curve 1 is the scattered intensity for Washington No. 4 Queen high-volatile A bituminous coal (PSOC 095). The inner part of this curve is nearly proportional to θ^{-4} , while the outer portion approaches a constant value. (In the logarithmic plot employed in Fig. 2, a straight line means that the intensity is proportional to some power of θ , and a straight line with slope -4 is obtained when $I(h)$ is proportional to θ^{-4} .) The form of this curve suggests that in this coal, there are two types of inhomogeneities, which have greatly different average dimensions. Since $I(h)$ is proportional to θ^{-4} even at the smallest scattering angles

accessible with the scattering system, in this coal there are inhomogeneities so large that inequality (4) is satisfied at all scattering angles at which data were recorded. Since the scattering was not measured at angles smaller than 0.003 radian, (4) implies that for the larger inhomogeneities $D_{\min} > 300 \text{ \AA}$. Although the scattering from these large inhomogeneities predominates in the inner part of the scattering curve, the scattering from them decays rapidly as the scattering angle increases. However, the scattering from the small inhomogeneities will be considered to satisfy (5) and thus will be essentially independent of the scattering angle. Because the scattering from the large inhomogeneities decreases so rapidly with increasing scattering angle, in the outer part of the scattering curve, only the relatively weak but constant scattering from the small inhomogeneities will be observed. The scattering from PSOC 095 coal thus can be considered to be produced primarily by two types of inhomogeneities, which, as in the terminology employed by M. M. Dubinin⁷, will be referred to as macropores and micropores.

From the scattering data alone, there is no way to determine that the inhomogeneities are pores--that is, that the electron density is smaller in the inhomogeneities producing the scattering than in the rest of the coal. A similar scattering would be produced by inclusions of mineral matter with the proper dimensions. Nevertheless, the information about coals obtained by adsorption measurements and other techniques besides x-ray scattering effectively rules out the possibility that the largest part of the scattering is due to anything except pores.

We have found that scattering patterns like Curve 1 in Fig. 2 are typical of lignites and of some sub-bituminous and high-volatile bituminous coals.

For other high-volatile bituminous, medium-volatile bituminous, and sub-bituminous coals, the scattering patterns, in addition to the features

of Curve 1 already discussed, have a shoulder at intermediate scattering angles. Curve 2 in Fig. 2 is an example of this type of scattering curve and was obtained for an Illinois No. 6 high-volatile bituminous coal (PSOC 022). We have interpreted the shoulder on this curve as evidence for the presence of a third type of inhomogeneity, with average dimensions between those of the macropores and micropores. To explain the scattering from these intermediate-sized inhomogeneities, which we consider to be the transition pores discussed by Dubinin, we assume that these pores are so large that at the largest scattering angles at which we recorded data, (4) is fulfilled for the transition pores, and so the scattering from these pores is proportional to θ^{-4} . To produce a shoulder on the scattering curve, however, the transition pores must also be small enough that at the smallest angles at which we measured the scattering, these pores satisfy (5) and thus give an essentially constant scattering. In the inner part of the scattering curve from this coal, we consider this constant intensity to be essentially negligible compared to the scattering from the macropores. In this region of the scattering curve, the scattering from this coal then is very nearly proportional to θ^{-4} and is caused almost entirely by the macropores. As the scattering angle becomes larger, the fraction of the scattering that is due to the macropores rapidly decreases, and so at intermediate scattering angles, most of the scattering will be produced by the transition pores, since the scattered intensity from these pores, though initially much weaker than that from the macropores, decays less rapidly with increasing scattering angle.

For there to be a shoulder on the scattering curve, the transition

pores must be small enough that the intensity scattered by these pores is constant in the inner part of the scattering curve and remains essentially constant even at scattering angles large enough that the contribution from the macropores has decayed so much that it is much weaker than the scattering from the transition pores. However, transition pores with suitable dimensions can explain the shoulder on scattering curves like Curve 2 in Fig. 2.

In this curve there are two regions of scattering angles in which the intensity is proportional to θ^{-4} . The inverse-fourth-power scattering in the innermost part of the curve can be ascribed to the macropores, and the magnitude of the scattered intensity at these angles is proportional to the surface area of these pores. The scattered intensity is also proportional to θ^{-4} in the part of the curve on the right of the shoulder--i.e., at scattering angles larger than those where the shoulder is observed. The magnitude of the scattered intensity in this interval of scattering angles is proportional to the sum of the surface areas of the macropores and transition pores. When there is a shoulder on a scattering curve, the inverse-fourth-power scattering must be appreciably greater from the transition pores than from the macropores.

In low-volatile bituminous coals, such as Pennsylvania E. Lower Kittanning coal (PSOC 127), a rather broad peak is found in the outer part of the scattering curve, as is illustrated by Curve 3 in Fig. 1. For this coal, the inner portion of the scattering curve, as in Curves 1 and 2, is proportional to θ^{-4} . The macropore structure can thus be considered to be quite similar to that in the lower-rank coals. The peak, which corresponds to a Bragg spacing of about $20 \text{ \AA}$, has previously been reported by Hirsch⁸, who interpreted it as being due to interactions between the fundamental

scattering units in these coals, which were made up of a few layers of planar aggregates containing aromatic rings. Because of the presence of this peak, the magnitude of the scattering from the micropores cannot be easily assessed, but the presence of micropores certainly cannot be excluded. According to the interpretation given for Curve 2 in Fig. 1, however, the contribution of the transition pores in PSOC 127 to the scattering must be quite small.

Curve 4 of Fig. 1 shows the scattered intensity for Pennsylvania Buck Mountain anthracite (PSOC 081). Quite similar scattering curves were recorded for several other anthracites.

The inner part of the scattering curves for the anthracites is very similar to the corresponding region of Curve 3 in Fig. 1. The macropore structure in anthracites thus is probably quite similar to that in low-volatile bituminous coals.

The distinguishing characteristic of the scattering curves for the anthracites is the outer part of the scattering curve, where the intensity is usually higher than for the lower-rank coals, and, though sometimes nearly constant, usually decreases smoothly.

Although there were no peaks in any of the scattering curves from the anthracites, the outer portion of the scattering pattern for these coals could be a vestige of a maximum like that in the curves for the low-volatile bituminous coals. An alternative explanation of the form of this part of the scattering curve for anthracites is that the average dimensions of the micropores in these coals are so large that inequality (5) is not satisfied, and so the scattering from the micropores is not independent of the scattering angle. Then, if the micropores scatter independently of each other, the scattering in this part of the curve can be approximated by

the expression⁹

$$I(h) = I_0 e^{-(1/3)h^2 R^2}, \quad (7)$$

where I_0 is a constant, and R , the average radius of gyration⁹ of the inhomogeneities, is a measure of the average size of the inhomogeneity. Equation (7) is a good approximation when hR is not much larger than 1. For spheres¹⁰ with radius a , $R = (3/5)^{1/2}a$. With (7), a radius of gyration $2.4 \pm 0.2 \text{ \AA}$ was calculated for the micropores in anthracite PSOC 081.

The scattering in the outer region of the intensity curves for the anthracites could also be the result of a combination of all these effects. In other words, the scattering could be due to three kinds of structures: (1) the tail of the inverse-fourth-power scattering from the macropores and transition pores, (2) the structure which is responsible for the peak corresponding to a Bragg distance of about $20 \text{ \AA}$, and (3) micropores for which the scattering is described by (7). In different coals, the relative magnitudes of these three effects would differ, and as a result there would be some differences in the form of the outer part of the scattering curve.

We wish to point out the outer part of the scattering curve for PSOC Coal 135, which is a medium-rank medium-volatile bituminous coal, is quite similar to the corresponding curves for the anthracites. The fact that the outer portion of the scattering curves from both a medium-volatile bituminous coal and also from anthracites have the same form can be quite naturally explained if the scattering at these angles is the result of superposition of the three structures mentioned above.

Further study, however, is necessary before a detailed and quantitative explanation of the outer part of the scattering curves from these

coals is possible.

3. Determination of Specific Surfaces

To obtain an equation describing the scattering from the pores in the coals, we assumed that

$$I(h) = I_{oo} I_e A \left[\frac{S_{ma}^0}{h^4} + \frac{S_{tr}^0}{(h^2 + a^2)^2} + \frac{C_{mi}}{(1 + b^2 h^2)^2} \right], \quad (8)$$

where

$$I_{oo} = \frac{2\pi d^2}{T} \frac{M}{A}. \quad (9)$$

In (8) and (9), I_e is the intensity scattered by one electron, S_{ma}^0 and S_{tr}^0 are the specific surfaces, or surface areas per unit mass of coal, of the macropores and transition pores, respectively; the constant C_{mi} is proportional to the weak but constant scattering from the micropores; b is a constant characterizing the micropore dimensions; M and A are respectively the mass of the sample and its cross-section area perpendicular to the incident beam; T is the x-ray transmission; and a is a constant inversely proportional to the average dimensions of the transition pores. The factor $1/T$ is included in (9) to take account of the absorption of x-ray in the samples, since (3) was developed under the assumption that the samples were non-absorbing. The transmission T can be expressed¹¹

$$T = \frac{I}{I_0} = \exp(-\mu \frac{M}{A}); \quad (10)$$

where I_0 is the x-ray intensity striking the sample; I is the intensity transmitted through the sample; and μ is the mass absorption coefficient.

The term proportional to S_{ma}^0 in (8) describes the scattering from the macropores and was obtained by rewriting (3), while the middle term was selected to give a reasonable and convenient approximation to the contribution from the transition pores. An intensity with this form is expected¹² from pores randomly distributed in a material with uniform electron density. This expression has the desired properties of approaching a constant value of small h and of being proportional to h^{-4} for large h .

The term $C_{mi}(1 + b^2h^2)^{-2}$ in (8) allows for the scattering from the micropores. For the relatively small scattering angles included in our curves, this expression is essentially equivalent to (7). The form of the term was chosen for convenience in the calculations. If (7) and the expression $C_{mi}(1 + h^2b^2)^{-2}$ are to be equivalent to terms of order h^2 --that is, if to terms of order h^2

$$(1 + b^2h^2)^{-2} \approx e^{-(1/3)h^2R^2},$$

b must satisfy the relation

$$b = (1/6)^{1/2}R.$$

From (9)

$$\frac{M}{A} = \frac{1}{\mu} \log_e(1/T). \quad (11)$$

Thus, from (9), (11), and the measured value of the T , we could evaluate the quantity I_{00} . For this calculation we assumed that the coal consisted entirely of carbon, that¹³ $\mu = 4.60 \text{ cm}^2/\text{gm}$, and that the mass density of the coal 1.30 gm/cm^3 . This density is a compromise between the helium densities determined for coals of different rank and origin¹⁴.

We made non-linear least-squares fits¹⁵ of (8) to the corrected scattering curves of each of the 15 coal samples. For all coals except PSOC 135 and PSOC 081, we assumed that b was zero, since except for these two coals, the data suggested that the scattering from the micropores did not depend on the scattering angle. For PSOC 081 and PSOC 135, from the least-squares fits we calculated that $b = 1.44 \pm 0.01 \text{ \AA}$ and $1.06 \pm 0.02 \text{ \AA}$, respectively. These values correspond to micropore radii of gyration of $3.5 \pm 0.1 \text{ \AA}$ and $2.6 \pm 0.1 \text{ \AA}$, respectively. The result $3.5 \pm 0.1 \text{ \AA}$ for PSOC 081 is in fair agreement with the radius of gyration $2.4 \pm 0.2 \text{ \AA}$ calculated for this coal by use of (7).

In the least-squares fits of (8) to the scattering curves for the coal samples, when there was a peak on the scattering curve, we made the fit only for angles smaller than those at which the maximum was observed. For all the other coals, we were able to fit the entire scattering curve.

The constants a^{-1} obtained from the fits provide an estimate of the average dimensions of the transition pores. From the fits we obtained values a^{-1} ranging from about 28 through $54 \text{ \AA}$. We could observe no pattern to the variation of a^{-1} from sample to sample. Just as for the parameter b which characterizes the dimension average dimension of the micropores, the radius of gyration of the transition pores is $6^{\frac{1}{2}}a^{-1}$, and if the pores can be considered spherical, the sphere radius is $6^{\frac{1}{2}}(3/5)^{-\frac{1}{2}}a^{-1}$. Thus if the transition pores are considered to be spherical, the least-squares fits showed that the average pore radii varied from about 90 to $170 \text{ \AA}$.

To find the product $I_e A$, we measured the scattering from a concentrated Ludox[®] colloidal silica suspension and evaluated the integral Q in the

equation¹⁶

$$Q = \int_0^{\infty} h^2 I_{\text{corr}}(h) dh = 2\pi^2 I_e (d_{Si})^2 c(1 - c) V, \quad (12)$$

where d_{Si} is the difference of the electron densities of the spherical silica particles and the water in which these particles are suspended; and c is the fraction of the volume V of the suspension that is occupied by the silica particles. In the integral Q , $I_{\text{corr}}(h)$ is the part of the corrected scattered intensity from the silica suspension which is proportional to h^{-4} in the outer part of the scattering curve. (In other words, $I_{\text{corr}}(h)$ is the corrected intensity after the slowly-varying or constant scattering from the solvent and any other relatively short-range structure has been subtracted.) Since the scattering from the suspension and the coals were measured under the same conditions, the value of $I_e A$ calculated for the suspension could be used with all of the coals.

From (12) and (11)

$$Q D_{Si} = 2\pi^2 I_e A d^2 c(1 - c) \frac{M}{A} = 2\pi^2 I_e A d^2 c(1 - c) \frac{\log_e(1/T_{Si})}{\mu_{Si}} \quad (13)$$

where D_{Si} is the mass density of the silica suspensions; A is the cross-section area of the sample; and T_{Si} and μ_{Si} are the transmission and mass absorption coefficient of the suspension. To find $I_{\text{corr}}(h)$ from the corrected scattering curve for the suspension, we made a least-squares fit of an equation like (8) to the corrected scattering curve from the suspension. We evaluated the integral Q by a technique¹⁷ previously developed in our laboratory. As given by the manufacturer and verified¹⁷

from scattering measurements, $D_{Si} = 2.28 \text{ gm/cm}^3$. We used this mass density to calculate the electron density and employed the measured concentration k gm of silica per gm of suspension to compute the mass absorption coefficient μ_{Si} and the volume fraction c , with the assumption that one gram of suspension consisted of k gm of SiO_2 with density D_{Si} and $(1 - k)$ gm of water.

After we had determined $I_e A$ and calculated I_{oo} for the coal samples, we evaluated the specific surfaces S_{ma}^0 and S_{tr}^0 for the macropores and transition pores in the 15 coals. These specific surfaces are listed in Table 1. We estimate that the uncertainty in the specific surfaces is about $\pm 25\%$.

4. The Contribution of Mineral Matter to the Scattering

To estimate the scattering by the mineral matter in the coals, we prepared four ash samples by low-temperature ashing.

The scattering from these samples was assumed to be proportional to the scattering that would have been produced by the mineral matter when it was in the coals. Allowance was made for the fact that the intensity from the ash differed from that scattered by the minerals in the coals because of the fact that in the ash samples, the minerals were surrounded by air, rather than embedded in the coal. The size of the particles of the mineral matter, however, was considered to be unaffected by the ashing process.

The scattered intensity from the ash samples was proportional to h^{-4} over almost all of the interval of scattering angles at which data were recorded, although in the outer part of the curve, the intensity approached a weak but constant value. To estimate the specific surface associated with the mineral matter, the mineral densities were approximated by considering that the mineral matter was either pyrite or kaolinite--that

is, that mineral matter which was not pyrite had a density and chemical composition enough like those of kaolinite that the scattering from the minerals would be essentially the same as if they were composed of kaolinite. The pyrite and total mineral matter concentrations were taken from the data in the PSOC analyses. Our estimates showed that in the inner part of the scattering curves, the mineral matter contributed from about 10% to 25% of the total surface area. In other words, the specific surface values in Table 1 which are considered to be due only to the surface of the macropores should be reduced by 10 to 25 per cent. As this change does not exceed the uncertainty in the determination of the specific surfaces, the contribution of the mineral matter can, at least in these preliminary evaluations of the specific surface, be neglected.

The effect of mineral matter is so small that it is completely negligible compared to the combined specific surface of the macropores and transition pores in coals with scattering curves which have a shoulder.

5. Discussion

Although the magnitude of the scattered intensity in the outer part of the scattering curve can be taken as a rough measure of the extent of the micropore structure, as yet we have found no way really reliable to obtain quantitative information from this part of the curve. Interpretation of this region of the curve is complicated by the fact that peaks like the $20 \text{ \AA}$ maximum in POSC Coal 127 can mask the scattering from the micropores and also because in this interval of angles, the part of the "small-angle" scattering curve that gives information about the micropores may not be separable from the "small-angle tail" of the large-angle diffraction pattern. For example, the small-angle tail of the first maximum in the large-angle diffraction pattern may not

be negligible in the angular region sensitive to the micropores. Further study is therefore necessary before quantitative information about the micropores can be obtained from the small-angle scattering data.

In Table 1 we list the sum of the specific surfaces of the macropores and transition pores and also the specific surfaces obtained by low temperature nitrogen adsorption and by adsorption of carbon dioxide at room temperatures. The nitrogen and carbon dioxide specific surfaces are taken from the PSOC data bank, except for coal PSOC 105. Since the specific surfaces in the data bank for this coal appeared questionable, they were remeasured by R. G. Jenkins at Pennsylvania State University.

Information about the pore structure in the coals can be obtained by comparison of the specific surfaces determined by the three techniques. Before discussing the detailed results, however, we would like to point out some general properties of the different methods of determining specific surfaces.

For a surface to be detected in adsorption measurements, the adsorbed gas must be able to penetrate the pores. Adsorption methods thus will not detect closed pores. Also, nitrogen at low temperatures may not penetrate pores as small as those which carbon dioxide can enter at room temperature.

While x-ray scattering detects both open and closed pores, only pores for which the minimum dimension satisfies (4) will contribute to the specific surface calculated from the scattering curves. The properties of the x-ray and adsorption techniques must be kept in mind during comparison of the specific surfaces obtained by these techniques.

The differences between specific surfaces determined by low-temperature nitrogen and room-temperature carbon dioxide adsorption have been ascribed¹⁸

to the fact that many of the pores in the coals are accessible only through small, constricted openings which cannot be penetrated by nitrogen molecules at liquid nitrogen temperatures, while carbon dioxide molecules at room temperature have sufficient energy to go into the pores. On the other hand, if the pore dimensions are large enough that (4) is satisfied in a given interval of scattering angles, the scattering will be proportional of h^{-4} regardless of the size of the entrances to the pores. Moreover, as we have mentioned, the scattering process will detect completely closed pores. On the other hand, unless the minimum pore dimensions are large enough to satisfy (4), the scattered intensity will not be proportional to h^{-4} , and so these pores will not be included in the surface calculated from the scattering curves.

All of the differences between the specific surfaces obtained by adsorption and small-angle scattering therefore cannot be explained by the existence of pores with restricted entrances. Instead, since the specific surfaces from adsorption of carbon dioxide at room temperature are always much greater than those obtained from the scattering data, there must be a large number of pores for which smallest pore dimensions do not satisfy (4).

As can be seen from the scattering curves in Fig. 2, the scattered intensity for coals PSOC 081 and PSOC 127 begins to deviate from a θ^{-4} dependence for scattering angles greater than 0.02 radians, while this deviation starts at about 0.03 and 0.04 radians for coals 095 and 022, respectively. Since (4) is not satisfied at larger scattering angles, the minimum dimensions of the pores which contribute to the specific surfaces calculated from the scattering data cannot be less than about 45 Å in coals 081 and 127, 30 Å in coal 095, and 22 Å in coal 022.

These minimum pore dimensions are so large that both carbon dioxide at room temperature and nitrogen at low temperature can penetrate pores smaller than those contributing which contribute to the x-ray scattering specific surface. Thus, when the specific surface calculated from the scattering curves exceeds the specific surface from low temperature nitrogen adsorption, there must be closed pores inaccessible to nitrogen at low temperature, while if the latter specific surface is greater than the former, there will be many pores penetrable by nitrogen but not detected by small-angle scattering.

Since the specific surfaces from the x-ray scattering curves thus is due to the relatively large pores, it is not surprising that the adsorption techniques, which are capable of detecting surface areas of much smaller structures, often give specific surfaces considerably larger than those calculated from the scattering curves.

For the Coals 318, 127, 130, 135, 134, and 095, all of which are of relatively high rank, the nitrogen specific surfaces are very small, while the carbon dioxide surfaces range from about 180 through 250 m^2/gm . The specific surfaces from the x-ray data vary from 2.4 through 5.7 m^2/gm . Since the nitrogen specific surfaces are smaller than those from the scattering curves, we can conclude, at least tentatively, that there are an appreciable number of pores large enough to be detectable by scattering but impenetrable to nitrogen at low temperatures. These pores, for example, could be completely sealed. On the other hand, since the carbon dioxide specific surfaces are always much larger, there must be many pores with minimum dimensions less than about 20 $\text{\AA}$ which are accessible to carbon dioxide at room temperature.

For the four of the last eight coals listed in Table 1, the carbon

dioxide specific surfaces vary from 100 to 255 m²/gm. There thus must be an appreciable number of micropores in these coals, just as in the higher-rank coals discussed previously. However, for the last 8 coals in Table 1, both the x-ray and nitrogen specific surfaces are larger than for the first 8 coals in the table. The specific surfaces calculated from the x-ray scattering curves for these 8 coals are sometimes larger and sometimes smaller than the surfaces determined by low-temperature nitrogen adsorption. When the x-ray specific surface exceeds surface area measured by low-temperature nitrogen adsorption, there must, as we have mentioned, be an appreciable number of pores large enough to be detected by scattering but closed to nitrogen. On the other hand, when the low-temperature nitrogen specific surface is larger than that from the x-ray data, there must be a significant fraction of the pores which are too small to be included in the x-ray specific surface.

There are pronounced shoulders on the scattering curves for PSOC Coals 105, 022, and 188, while there are no shoulders on the curves for Coals 197 and 138. The shoulders in the scattering curves from Coals 185 and 181 are less evident, and a shoulder can be seen for Coal 212 only after careful inspection. These results suggest that there will be well-defined shoulders in the scattering curves only when the specific surface of the transition pores is at least ten times as great as that of the macropores.

For the first seven coals in Table 1, the surface area from the transition pores is only one to two times as great as the specific surface from the macropores. There are no inflections in the scattering curves for any of these coals, in agreement with the above criterion for the presence of an inflection in the scattering curve.

The fraction of the volume associated with a given type of pore can be described as the product of an average dimension and the specific surface for this pores class. When, as is true for many of the coals listed in Table 1, the specific surface contributions from the macropores and transition pores are roughly equal, the specific volume occupied by the macropores therefore will be, in general, considerably larger than the volume of the transition pores, for which the average dimension is much smaller than that of the macropores. Gan, Nandi, and Walker¹⁴ have combined measurements by mercury porosimetry and low-temperature nitrogen adsorption at 77 K to find the fractions of the pore volume associated with the macropores, transition pores, and micropores. Among the coals for which they calculated pore-volume distributions were PSOC Coals 127, 135, and 197 which we have examined by small-angle x-ray scattering. They also studied PSOC Coal 105A, which probably is very similar to the coal PSOC 105 which we investigated. In Coals 127 and 135, they found that the volume occupied by the transition pores was very small, and that over half the pore volume was taken up by micropores. These conclusions are quite consistent with the specific surface results in Table 1, according to which the transition pores make a relatively small contribution to the specific surface, and the specific surface from room-temperature carbon dioxide adsorption is much larger than the surface area obtained by other techniques. Similarly, Gan, Nandi, and Walker found that the fraction of the pore volume occupied by the transition pores is about four times as great in PSOC Coal 105A as in PSOC Coal 197. This result is in at least qualitative agreement with our calculation that in PSOC Coal 105, for which the small-angle x-ray scattering curve has a pronounced inflection, the specific surface associated with the transition pores is much larger than in PSOC Coal 197, for which there is no inflection in the scattering curve.

The PSOC coals were especially convenient samples for our x-ray studies, because in the data bank, there is a considerable amount of information about these coals obtained by techniques other than x-ray scattering. Without these other results we would not have been able to make such a detailed interpretation of the scattering data. Moreover, since we had studied PSOC coals, we could compare our porosity studies with the work of others, such as that of Gan, Nandi, and Walker¹⁴. On the other hand, as the other small-angle x-ray scattering studies of coals¹⁹⁻²² which we are aware of did not investigate PSOC coals, we could not make a quantitative comparison of our scattering results with those previously published.

It is natural to ask whether the least-squares fits of (8) to the scattering curves for these 15 coals are merely exercises in curve fitting or whether the fact that quite good fits can be obtained, in many cases over the whole scattering curve at which data were recorded, means that the pore structure used in developing (8) really has some connection with the pore structure in the coals. This point is especially important because in principle, more than one sample can produce the same small-angle x-ray scattering pattern.

As is true almost all small-angle scattering studies, the final decision about interpretation of the scattering data must be made from other information about the sample besides the scattering data. Since other studies of coal have suggested a pore structure which consists of three classes of pores--macropores, transition pores, and micropores, and as this structure provides a useful way of analyzing the scattering data, we feel that at least the general features of our interpretation of the scattering curves are essentially correct.

We therefore suggest that the x-ray scattering method can be useful in studies of the pore structure of coals. In particular, the scattering curves from medium-rank and low-rank coals can provide an estimate of the specific surfaces associated with the macropores and the transition pores. This information is difficult to obtain by other techniques.

ACKNOWLEDGMENTS

We would like to express our sincere gratitude and appreciation to S. R. Koirtyohann for assistance with the preparation of the ash samples by low-temperature ashing, to Robert G. Jenkins for measuring the specific surfaces of PSOC Coal 105, and to S. S. Pollack, D. W. Houseknecht, B. E. Cutter, Robert G. Jenkins, and Phillip L. Walker, Jr. for advice and assistance during parts of the investigation.

Captions for Figures

Figure 1. A diagram of the Kratky collimation system used to obtain the scattering curves.

Figure 2. Typical scattering curves for the coal samples. Curve 1 (circles): PSOC Coal 095. Curve 2 (squares): PSOC Coal 022. Curve 3 (plus signs): PSOC Coal 127. Curve 4. (triangles): PSOC Coal 081. The curves drawn through the points were obtained from the least-squares fits of (8).

Figure 1

Figure 2

References

1. A. Guinier, G. Fournet, C.B. Walker, and K.L. Yudowitch, Small-Angle Scattering of X-Rays, Wiley, New York, 1955, Eq. (26), p. 17.
2. Ref. 1, pp. 3-4.
3. Ref. 1, Equations (6), and (21a), Chapter 2.
4. O. Kratky and Z. Skala, Zeits. Elektrochem.-Ber. Bunsenges. phys. Chemie 62, 73-77 (1958).
5. J.S. Lin, C.R. Von Bastian, and P.W. Schmidt, J. Appl. Cryst. 7, 439-442 (1974).
6. T.R. Taylor and P.W. Schmidt, Acta Phys. Austriaca 25, 293-296 (1967).
7. M.M. Dubinin, in Chemistry and Physics of Carbon, (P.L. Walker, Jr. ed.), Vol. II, pp. 51-59, Dekker, New York, 1956.
8. P.B. Hirsch, Proc. Roy. Soc. (London) 226A, 143-169 (1954).
9. Ref. 1, pp. 24-28.
10. Ref. 1, p. 26.
11. A. Guinier, X-Ray Diffraction in Crystals, Imperfect Crystals, and Amorphous Bodies, Freeman, San Francisco, 1963, pp. 3-4.
12. P. Debye, H.R. Anderson, Jr., and H. Brumberger, J. Appl. Phys. 28, 679-683 (1957); J. Goodisman and H. Brumberger, J. Appl. Cryst. 4, 347-351 (1971) and J. Appl. Cryst. 12, 398-399, (1979).
13. International Tables for X-Ray Crystallography, International Union of Crystallography, 1962.
14. H. Gan, S.P. Nandi, and P.L. Walker, Jr. Fuel 51, 272-277, (1972).
15. P.R. Bevington, Data Reduction and Error Analysis for the Physical Sciences (McGraw-Hill, New York, 1969), Program CURFIT, pp. 237-240.
16. Reference 1, p. 157, Equation (33).

17. I.S. Patel and P.W. Schmidt, J. Appl. Cryst. 4, 50-55 (1971)
18. S.J. Gregg and K.S.W. Sing, Adsorption, Surface Area, and Porosity, Academic Press, London and New York, 1967, pp. 211-217.
19. S. Durif, J. Chim. Physique 60, 816-24 (1963).
20. C. Kröger and G. Mues, Brennstoff-Chemie 42, 77-84 (1961).
21. Z. Spitzer and L. Ulicky, Fuel 55, 21-25 (1976).
22. J.S. Lin, R.W. Hendricks, L.A. Harris, and C.S. Yust, J. Appl. Cryst. 11, 621-625 (1978).

® Registered Trademark, E.I. du Pont de Nemours & Co., Inc.

Table 1

SPECIFIC SURFACES FOR THE COALS OBTAINED FROM THE SCATTERING CURVES AND FROM ADSORPTION DATA

PSOC-NO	RANK	STATE & SEAM NAME	SURFACE AREA (m ² /g)				
			ADSORPTION N ₂	CO ₂	TOTAL	X-RAY SCATTERING MACRO- PORES	TRANSITION PORES
PSOC-081	ANTHRACITE	PENNSYLVANIA	ND	ND	3.91	1.54	2.37
PSOC-318	LOW. VOL.	BUCK MOUNTAIN PENNSYLVANIA E. UPPER FREEPORT	<1.0	186	2.54	1.09	1.45
PSOC-127	LOW. VOL.	PENNSYLVANIA E. LOWER KITTANNING	<1.0	271	2.51	1.23	1.29
PSOC-130	MED. VOL.	W. VIRG. POCAHONTAS #3	<1.0	249	2.51	1.08	1.43
PSOC-135	MED. VOL.	ALABAMA PRATT	<1.0	227	2.42	1.33	1.09
PSOC-134	MED. VOL.	ALABAMA PRATT	<1.0	208	2.39	0.86	1.54
PSOC-095	HVA.	WASHINGTON #4 QUEEN	<1.0	220	5.66	1.6	4.08
PSOC-105	HVB.	INDIANA #1 BLOCK	16.0	105	46.58	2.06	44.5
PSOC-197	HVC.	OHIO #6 MIDDLE KITTANNING	11.0	ND	6.18	2.15	4.04
PSOC-185	HVB.	INDIANA #6	49.0	ND	8.72	0.85	7.87
PSOC-022	HVC.	ILLINOIS #6	99.0	189	18.4	0.84	17.6
PSOC-212	HVC.	OHIO #2 QUAKERTOWN	3.7	254	9.16	1.47	7.68
PSOC-181	SUBBIT. A.	INDIANA UPPERBLOCK	49	ND	24.01	4.41	19.6
PSOC-138	SUBBIT. C.	TEXAS DARCO LIGINITE	2.5	254	7.25	2.71	4.55
PSOC-188	HVB.	ILLINOIS #2 COLCHESTER	32	ND	15.95	0.48	15.5

ND: Not determined. The specific surfaces from adsorption measurements were taken from the PSOC data bank, except for coal 105, for which these specific surfaces were recently measured by R. G. Jenkins. The x-ray specific surfaces were calculated from the least-squares fits.