Small-Angle X-Ray-Scattering Investigation of Submicroscopic Porosity with Fractal Properties

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A method is developed for analyzing the outer part of the small-angle x-ray or neutron scattering curve for porous scatterers in which the pore boundaries can be described by fractals. When the results are applied to the scattering data from a lignite coal, the fractal dimension of the boundary surface of the pores in this coal is found to be 2.56 ± 0.03 .

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A recent small-angle x-ray-scattering study of the submicroscopic porosity in several lignite coals¹ showed that there was a broad region of the scattering curve in which the scattered intensity was proportional to a nonintegral negative power of

$$q = 4\pi\lambda^{-1}\sin(\theta/2), \tag{1}$$

where λ is the x-ray wavelength and θ is the scattering angle. This angular dependence was very unexpected, since according to the traditional theories of small-angle x-ray and neutron scattering,² which assume that the scatterers are bounded by a smooth surface, the limiting form of the scattered intensity should be proportional to q^{-4} . After remeasuring the scattering and finding that our first results were reproducible, we ascribed¹ this power-law scattering to independently scattering submicroscopic pores with a power-law dimension distribution.³

After we submitted the manuscript of Ref. 1, however, we learned about the application of fractals⁴ in studies of porosity.^{5,6} We therefore have reexamined our results for lignite coals and have found that our data can alternatively be considered to be the scattering from micron-sized pores with boundary surfaces which are fractals.

Below, we outline some equations which we have developed for this analysis of scattering data in terms of fractals and discuss the application of these equations to the lignites which we have studied.

In the model which we have developed, the coal is considered to be a three-dimensional porous solid with uniform electron density δ . (The assumption of uniform electron density is valid for *small*-angle x-ray and neutron scattering, since at scattering angles no greater than a few degrees, the scattering process cannot resolve the atomic structure.⁷) The scattered intensity for this model can be calculated by a modification of a procedure⁸ developed for analysis of the small-angle scattering from materials containing pores with smooth boundary surfaces. For a porous sample in which solid material with uniform electron density occupies a fraction c of the sample volume V, so that the pores take up a fraction 1-c of the sample volume, the scattered intensity I(q) is given by⁹

$$I(q) = 4\pi I_{e} \delta^{2} c (1-c) V \int_{0}^{\infty} r^{2} g(r) \frac{\sin qr}{qr} dr.$$
 (2)

In (2), I_e is the intensity scattered by a single electron; and g(r), the correlation function, is defined by the equation

$$g(r) = [Z(r) - c]/(1 - c),$$

where Z(r) is the probability, averaged over all points of the sample and over all sample orientations, that if a point lies in an occupied region (i.e., *not* in a pore), a second point a distance r from the first point also will be in an occupied part of the sample.

To approximate Z(r) for small r, we will use a technique similar to that employed by Guinier, Fournet, Walker, and Yudowitch,¹⁰ in their calculation of the small-r approximation for g(r) for a scatterer with uniform electron density and a smooth boundary surface. From the definition of the correlation function Z(r) given above, Z(r) = 1 at all occupied points except those located within a distance r of a pore boundary. According to the definition of the fractal or Hausdorff dimension D of the fractal boundary surface,¹¹ as r approaches zero, the number n of cubes with edge r needed to make a layer covering all points of the poreboundary surfaces can be expressed

$$n = N_0 r^{-D}, \tag{3}$$

where N_0 is a constant characteristic of the fractal boundaries. The layer of the occupied regions in which Z(r) < 1 thus has the volume

$$V_b = nr^3 = N_0 r^{3-D},$$
 (4)

while the volume of the sample in which Z(r) = 1 is equal to $cV - V_b$.

For $x \le r$, let p(r,x) be the probability, averaged over all orientations of r, that if a point in the occupied region is located at a distance x from a pore boundary surface, there is another occupied point a distance r from the first point. If in our approximate calculation of Z(r) for small r we assume that the boundary surface is a plane, then¹⁰

$$p(r,x) = (r+x)/2r.$$
 (5)

Since g(r) is defined to be the probability, averaged over both the inner region and the boundary layer, that two occupied points will be separated by a distance r, we find from (3), (4), and (5) that as r approaches zero,

$$Z(r) \simeq \frac{cV - V_b}{cV} + \frac{V_b}{cV} \frac{1}{r} \int_0^r p(r, x) dx$$

= 1 - N_0 r^{3-D}/4 cV

Thus, from the relation between g(r) and Z(r), we have

$$g(r) = 1 - N_0 r^{3-D/4} c(1-c) V.$$
(6)

Since we expect¹² that both g(r) and g'(r) approach zero as r becomes infinite, by two integrations of Eq. (2) by parts, I(q) can be written

$$I(q) = -4\pi\delta^2 I_e c (1-c) V q^{-3} \int_0^\infty [rg''(r) + 2g'(r)] \sin qr \, dr.$$
⁽⁷⁾

Erdélyi's theorem for asymptotic expansion of Fourier integrals¹³ can be used to calculate the limiting form of I(q) for large q. Thus

$$I(q) = -\frac{4\pi\delta^2}{q^{6-D}} I_e c (1-c) V \Gamma(3-D) \sin[\pi (D-1)/2] \lim_{r \to 0} \left\{ r^{D-2} \frac{d^2}{dr^2} [rg(r)] \right\}$$

From (6),

 $I(q) \simeq \pi N_0 \delta^2 I_e \Gamma(5-d) \sin[\pi (D-1)/2]/q^{6-D}.$

According to this approximation, I(q) is proportional to $q^{-(6-D)}$.

For a smooth pore-boundary surface, D=2, and from (3), $n = N_0 a^{-2}$. Comparison of (8) with the usual approximation² for I(q) in the outer part of the small-angle scattering curve for samples containing scatterers with a smooth boundary surface shows that for D=2, N_0 can be shown to be equal to the total surface area S separating the two phases in the sample when D=2.

For a sample with mass M, the quantity N_0/M thus can be considered to be analogous to the specific surface S/M for pores with smooth boundaries. As

$$I_e N_0 = (I_e A) (M/A) (N_0/M),$$
(9)

and the quantities $I_e A$ and M/A can be evaluated by scattering measurements,¹⁴ N_0/M can be calculated from the scattering data.

As (8) neglects the short-range atomic structure in the sample, this equation does not apply when qis large enough to permit resolution of structures with atomic dimensions. (The same restriction is true for most equations employed in the analysis of small-angle x-ray or neutron scattering.)

At least a rough estimate of the average pore dimension R can be obtained from q_{\min} , the smallest value of q at which Eq. (8) describes the scattering, since when this power-law scattering is observed, one expects $q_{\min}R >> 1$. If as a conserva-

tive estimate we assume that
$$q_{\min}R > 3.5$$
, the average dimension of the pores must be at least

age dimension of the pores must be at least $3.5/q_{\min}$. Figure 1 shows the scattering curve which we obtained¹ for Beulah lignite. Information about the experimental conditions and data corrections is given in Ref. 1. For a wide interval of q, the intensity is proportional to $q^{-(3.44 \pm 0.03)}$. (The uncertainty in the exponent was estimated from the

reproducibility of the scattering curve.) While, as we have mentioned, this kind of curve can be explained as being the result of the scattering from spherical pores with a power-law dimension distribution,³ the scattering data can also be described by Eq. (8), which implies that the lignite contains pores which are bounded by surfaces with a fractal dimension $6 - (3.44 \pm 0.03) = 2.56 \pm 0.03$. As the dependence on $q^{-(3.44 \pm 0.03)}$ holds even at the smallest angles at which scattering data can be registered, the pore dimension R must be at least 1 micron. However, in the outer part of the curve in Fig. 1, the scattering approaches a relatively low but constant value. We have interpreted¹ this part of the scattering curve as the result of density fluctuations with dimensions of the same magnitude as those of atoms or small molecules. In the leastsquares fit from which we constructed the curve in Fig. 1, we used a fitting function of the form

$$I(q) = B + Cq^{-\alpha} \tag{10}$$

(8)



FIG. 1. The scattered intensity for Beulah lignite, measured with Bonse-Hart and Beeman collimation systems, as described in Ref. 1. The points show the corrected scattered intensities, and the curve was drawn by a least-squares fit of Eq. (10). [Reproduced by permission from "Chemistry of Low-Rank Coals," edited by H. D. Schobert, ACS Symposium Series (American Chemical Society, Washington, D.C., to be published).]

with the constants C, B, and α being determined in the fit. (The constant B was included in order to take account of the atomic-scale density fluctuations.) When $I_e A$ is evaluated from the x-ray scattering data by a technique similar to that employed in one of our previous small-angle scattering studies of coal porosity,¹⁴ we find that for Beulah lignite $N_0/M = 20 \pm 2 \text{ m}^{2.5}/\text{g}.$

We have obtained similar scattering curves for all

of the lignites which we have examined.¹ Although the apparatus did not allow the scattering to be measured over such a large interval of q as in the curve shown in Fig. 1, the scattered intensity for all the lignites and subbituminous coals which we studied was proportional to $q^{-\alpha}$ for a large interval of q, with $\alpha \simeq 3.5$. Kaiser and Gethner⁵ found that the small-angle neutron scattering from Rawhide coal followed a power law for q between about 0.01 and 0.1 Å⁻¹ and concluded¹⁶ that the pores in this coal may have fractal properties. We therefore believe that the fractal interpretation applies to many lignites and other coals and that the fractal dimension of the pore boundary surfaces in these lignites is about 2.5.

Sinha, Freltoft, and Kjems¹⁷ and Schaefer and Keefer¹⁸ developed equations for analyzing their small-angle scattering data from fractal aggregates of silica particles. In their power-law equations for the scattered intensity, the exponent of q is not the same as in (8). These differences are to be expected, since fractal *objects* need not scatter in the same way as pores with fractal boundaries.

Pfeifer has pointed out¹⁹ that systems of pores with fractal boundaries have many features similar to those of pore systems with a pore-dimension distribution function with the form of a power law. The *number* distribution corresponding to the *volume* distribution in Ref. 19 for the characteristic pore dimension *a* is proportional to $a^{-(D+1)}$, and the scattered intensity calculated³ from this powerlaw distribution is proportional to $q^{-(6-D)}$, as given by Eq. (8). Systems of pores with a power-law dimension distribution thus scatter in essentially the same way for large *q* as pores with boundaries so rough that they can be described by fractal surfaces.

Avnir, Farin, and Pfeifer^{5b} have shown that pores bounded by fractal surfaces can explain the adsorption data for several adsorbents. Their results suggest that such fractal-pore systems may be more common than was previously suspected. Perhaps much of published small-angle scattering data from porous samples can also be interpreted with Eq. (8). In the past, when we obtained a corrected scattering curve that in the outer portion was proportional to a negative power somewhat smaller in magnitude than 4, we assumed that the deviation was the result of some unidentified experimental effect. We now realize that there may be a more fundamental reason for these noninteger exponents.

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