

X-RAY DESCRIPTORS OF THE "NEAR" DIFFRACTION PEAK IN SOME ARGONNE PREMIUM COALS.

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INTRODUCTION

The Argonne Premium Coals are being thoroughly characterized by many research groups.

Four of the bituminous coals in the Argonne Premium Coal Program samples have been utilized to determine the ability of x-ray diffraction methodology to define several of the non-crystalline features of these coals.

Three of the subject coals, Pocahontas #3 (APC 501), Pittsburgh #8 (APC 401), and Upper Freeport (APC 101), reportedly have very low moisture contents, 0.5-1.5 %. The fourth coal, Lewiston-Stockton, has a higher moisture content, 4.6 %. Three of the subject coals reportedly contain ca. 75 % carbon, of which at least 75 % has been classified as aromatic. Both the carbon percentage and its aromatic fraction are reportedly much higher in Pocahontas #3.¹⁻⁴

The subject coals differ in considerably in inorganic content, producing from 4.5% - 13.0% high temperature ash.¹ Furthermore, the coals differ considerably in volatile matter, ranging from 43.7 % for the Lewiston coal (high volatile bituminous) to 18.5% in Pocahontas #3 (low volatile bituminous). The coals also differ considerably in the reported volatile matter content.¹

The extent to which diffraction may be used to measure the crystalline entities in coals has been established.⁵ The effects of important other features on the diffractogram of a coal have not been so well established.⁶ The purpose of this study is to determine which parameters that are important to coal scientists and/or environmental scientists may be measured by x-ray diffraction methods.

EXPERIMENTAL

COALS. The Argonne Premium Coals, well defined in numerous references, were provided as finely powdered samples sealed into an inert atmosphere. For these samples, the particle diameter < 0.15 mm.

A more detailed description of these subject coals is presented in Table One.

Division of carbon into aromatic and aliphatic fractions is based on the average of values reported by two different groups who analyzed these coals by MAS ¹³C nmr methods.^{2,3} Except for Pittsburgh #8, the aromatic (and aliphatic) fraction reported by each group differ by less than the experimental uncertainty of their results. The difference between the aromatic fraction reported by the two groups is ca. 0.10, which exceeds the

experimental uncertainty suggested by each of the nmr groups.

X-RAY EXPERIMENTS. A 0.5 gram sample of each finely powdered coal was mounted into our θ - 2θ x-ray diffractometer which is equipped with a theta-compensating slit, a sample spinner, and a LiF crystal monochromator in the secondary x-ray beam. A diffractogram of each coal was obtained over the region from $2\theta = 5.00^\circ$ to 50.00° by measuring the secondary intensity for five seconds at angular increments of 0.02° . Diffractograms acquired over a much wider angular range but using a much shorter count time at each angle have already been presented.^{5,6}

TABLE ONE. PARTIAL COMPOSITIONS OF THE HIGHEST RANK COALS IN THE ARGONNE PREMIUM COAL PROGRAM SAMPLES¹

<u>COAL_DESCRIPTOR</u>	<u>COAL DESIGNATION</u>			
	A	A	A	A
	P	P	P	P
	C	C	C	C
	1	4	5	6
	0	0	0	0
	1	1	1	1
A. Rank	mvb	hvb	lvb	hvb
B. Volatile Matter	27.14%	37.20%	18.48%	43.72%
C. Moisture	1.13%	1.65%	0.65%	4.63%
D. High Temperature Ash	13.03%	9.10%	4.74%	4.49%
E. Carbon Content	73.34%	74.25%	86.15%	73.32%
E.1. Aromatic Fraction ^{2,3}	0.83	0.77	0.87	0.75
E.2. Aliphatic Fraction ^{2,3}	0.17	0.23	0.13	0.25

RESULTS

The abbreviated diffractograms of the four Argonne Premium Coals are presented in Figure One. Diffractograms of these four (and the other) Argonne Premium Coals obtained over a considerably wider angular range have been previously presented. The mass absorption coefficient (previously determined for these coals for Cu K α x-rays⁶) was used to calculate the absorption corrected intensity. These diffractograms were partitioned into diffraction peaks (due to crystalline species in the coals) and a residual intensity which describes the amorphous scattering, as shown in Figure Two. Included in Figure Two is experimentally measured curve (2.A), the diffraction intensity due to the minerals (2.C), and the residual intensity (2.B). The latter is due to non-crystalline scattering, including the amorphous scattering due to the average poly-cyclic aromatic structural unit in each coal as well as other structural features.

The residual intensity curve, due to non-crystalline scattering, is shown for each of the four coals in Figure Three.

From the maxima and minima observed in each diffractogram, the molecular scattering associated with the average poly-cyclic aromatic hydrocarbon unit in each coal was calculated and then removed from the amorphous scattering intensity, as shown in Figure Four for APC 501. A well define peak results. Shown in Figure Five is the resulting "diffraction" peak, which (a) dominates the diffractogram, (b) is much broader than a typical diffraction peak, and (c) is asymmetrical.

In graphite, an ideal poly-cyclic aromatic compound (PAC), a corresponding diffraction peak, much more intense and much less broad, occurs at 3.35 Å and describes the stacking of its [00L] planes.

This unusually broad diffraction peak is due to imperfect diffraction from the [00L] planes present in each of the coals. As noted in Figure Five the shapes of the [00L] peak differ considerably, although each appears to be composed a symmetrical peak and a broad maximum. The symmetrical peak was simulated by the method of Kurita⁸, i.e.

$$I(2\theta) = Q \cdot \exp(-a' \Delta s^2) = Q \cdot \exp(-a' \cdot HW^2) \quad (1)$$

where Q is the maximum peak intensity and s is the half width at half maximum (HW) measured for the diffraction peak in reciprocal space. A summary of the symmetrical peak simulated for each coal is presented in Table Two.

TABLE TWO. SUMMARY OF SOME X-RAY DESCRIPTORS OF THE NEAR DIFFRACTION PEAK.

COAL	dmax	I*max (CPS)	HW (rad)	s (Å ⁻¹)
APC 501	3.541 Å	1,880	0.0332	0.0210
APC 101	3.578 Å	1,471	0.0387	0.0244
APC 401	3.749 Å	1,328	0.0707	0.0447
APC 601	3.755 Å	1,271	0.0775	0.0490
*GRAPHITE	3.354 Å	75,466	0.0174	0.0027

PEAK MAXIMUM. The intensity of the broad [00L] peak, as measured by the peak height in the absorption corrected diffractograms, is related to the % aromatic character by:

$I_{max} = m'(\% C_{ar}) + b$; where m and b are coefficients determined by linear least squares methods. For this analysis, R = 0.9989.

The [00L] maximum shifts, from 3.54 Å in APC 501 (the low volatile bituminous) to ca. 3.75 Å in the two high volatile bituminous coals -- APC 401 AND APC 601. This increase in the average inter-planar spacing parallels decreasing aromatic (and concomitant increasing aliphatic) content in the coals, suggesting that the aromatic PAC lamellae become further separated, on the average, as the rank of the coal decreases.

PEAK WIDTH. The width of a diffraction peak may be affected by several factors. However, to a first approximation, $\Delta 2\theta$ (in radians) = $ef + \{0.9\lambda/T\cos\theta\} + \{2\cdot(\Delta d/d)\cdot\tan\theta\}$; (2) where ef is a characteristic function of the diffractometer, λ is the x-ray wavelength, T is the particle size of the diffracting material(s), $\Delta d/d$ is the deviation (strain) in the inter-planar spacing that cause diffraction peak characterized by the inter-planar spacing d .

(1) The Diffractometer Contribution. $\Delta d/d \rightarrow 0$ for graphite, as evidenced by the very intense and very narrow diffraction peak observed from the finely powdered graphite used as the reference in this study. As a consequence, the observed peak width ($0.25^\circ = 0.0174$ rad) has been attributed to our diffractometer.

(2) Effect of Particle Size. The coal particles provided via the Argonne Premium Coal Sample Program and the graphite particles are 10^4 - 10^6 Å in diameter. Since $\lambda = 1.5404$ Å, $\lambda/T \rightarrow 10^{-4}$, which is considerably smaller than experimental uncertainty in these diffraction experiments. Consequently, for neither the coals nor the graphite is peak broadening due to particle size effects important.

(3) Effect of Inter-Planar Strain due to Distortions ($\Delta d/d$). For these coals, the peak broadening due to distortions in the distance between the PAH planes is given by:

$$\Delta 2\theta = 2\cdot\Delta d/d\cdot\tan\theta. \quad (3)$$

(4) Approximate Solution to the Peak Broadening Effect for the Argonne Premium Coals. Since $\lambda/t \rightarrow 0$, the observed peak broadening, $\Delta 2\theta$, may be related only to $\Delta d/d$ by:

$$\Delta d/d = (\text{HW} - 0.0174)/\tan\theta \quad (4)$$

Shown in Table Three in the strain associated with the [00L] planes for these coals.

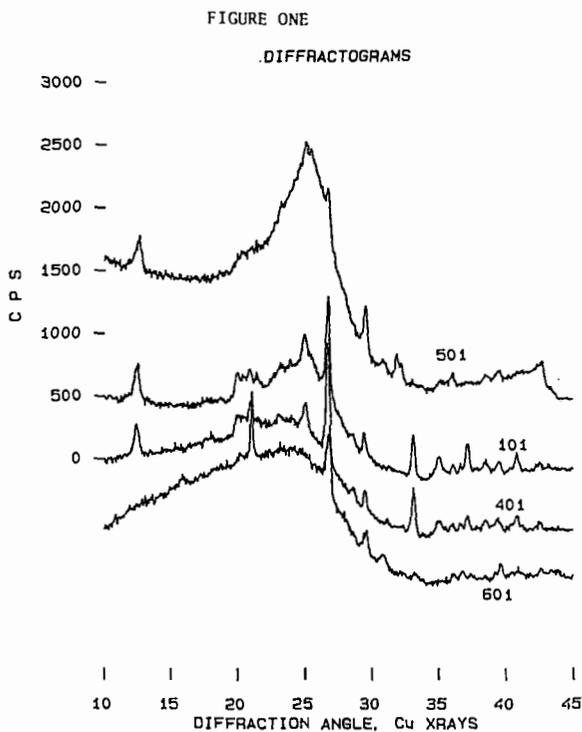
TABLE THREE. ESTIMATE OF THE STRAIN IN THE [00L] PEAK.

COAL	$\Delta d/d \cdot 100$
APC 101	9.6 %
APC 401	23.7 %
APC 501	7.1 %
APC 601	27.1 %

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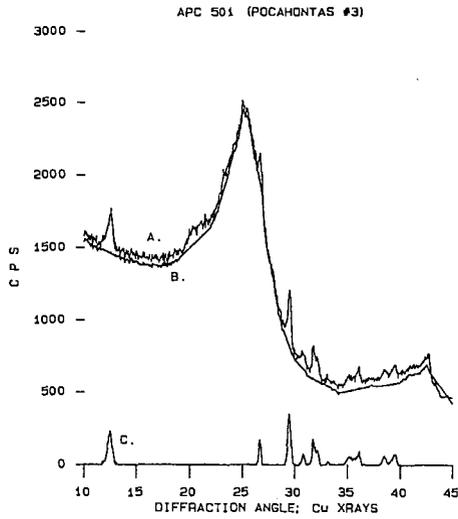


FIGURE TWO

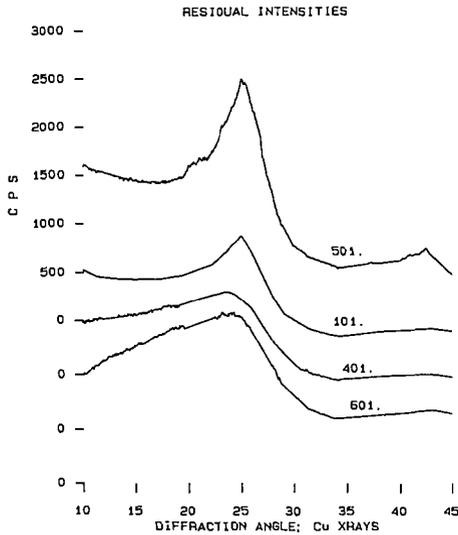


FIGURE THREE

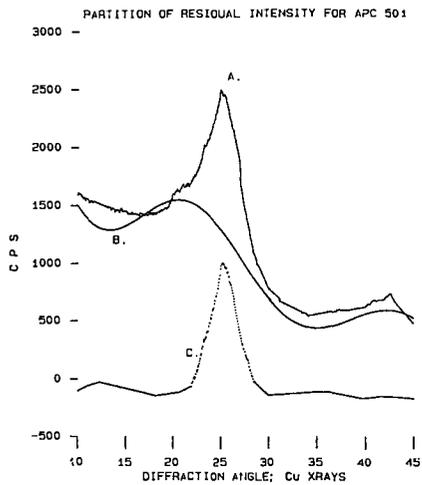


FIGURE FOUR

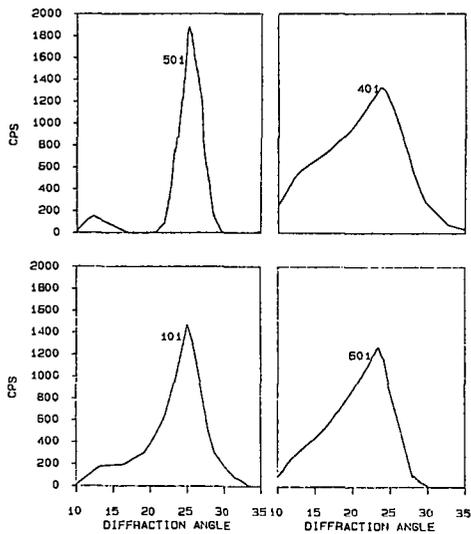


FIGURE FIVE