

X-RAY CHARACTERIZATION OF THE CRYSTALLINE INORGANIC SPECIES AND THE ORGANIC MATRIX IN WILSONVILLE RECYCLE RESID FROM RUN # 259.

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INTRODUCTION.

Products recovered from the two-stage direct liquefaction of a Pittsburgh seam coal (and several other coals) produced at the Wilsonville facility have been studied extensively as part of a global project sponsored by the U.S. Department of Energy.¹

An x-ray scattering-diffraction-fluorescence spectral study of the resids produced from processing Illinois # 6 coal at the Wilsonville facility has recently appeared. The effect(s) of the two-stage catalytic processes on the poly-cyclic aromatic character in the resids (as indirectly measured by the diffuse scattering caused by its graphitic layer stacking) and on the crystalline inorganic materials are reported.

Presented below are our preliminary finding from an x-ray study of the recycle resid produced during run # 259 at the Wilsonville facility. This study is a continuation of the group's efforts to utilize x-ray characterization methods to better understand the molecular structuring in coals and how various processes (such as liquefaction) affect that structuring.

EXPERIMENTAL.

Each sample was received (from Brandes) as a fine powder and was analyzed "as received."¹

Diffraction Experiments. A carefully weighed amount (ca. 0.5 grams) of each sample was deposited onto the sample holder (1.0 mm depth) and mounted into our θ - 2θ x-ray diffractometer. The sample was irradiated with copper x rays. Scattered x-ray intensities were accumulated by measuring the CuK_α wavelength (made monochromatic by use of a graphite crystal at $\Delta 2\theta \approx 0.01^\circ$ from $2\theta = 10.00^\circ$ to $2\theta = 90.00^\circ$ for 2 second intervals using the conventional step-scan procedure.³

Absorption Experiments. A carefully weighed amount of each sample (ca. 0.1 or 0.5 grams) was deposited onto the aluminum sample holder (which served as the substrate). The intensity of the (311) peak of the aluminum was measured both in the presence of and in the absence of the resid sample.⁴ For the recycle resid, an aluminum sample holder with depth of 1.0 mm was used. For its tetrahydrofuran insoluble fraction, a sample holder of 0.1 mm depth was used.

X-Ray Fluorescence Spectral Experiments. Approximately 1 gram of each resid was pressed into a pellet and then mounted into our wavelength dispersive x-ray spectrometer. Using chromium as the exciting radiation, both a soft x-ray spectrum (using a MOXTEK multi-layer as the monochromator) and a hard x-ray spectrum (using graphite as the monochromator) were obtained using the normal step-scan procedure.

RESULTS AND DISCUSSION.

X-Ray Fluorescence Experiments. The soft and hard x-ray spectra of the recycle resid and its THF-insoluble fraction are presented in Figures One and Two. After irradiation with the Cr x rays, large secondary x-ray peaks due to iron and calcium are observed, along with smaller peaks due to titanium, potassium, sulfur, and silicon are

observed in both spectra.

Mass Absorption Experiments. Shown in Figure Three are the intensities of the (311) diffraction peak from the aluminum sampleholder in the absence of and in the presence of the recycle resid sample. The mass absorption coefficient of each resid was calculated by:

$$\mu = [T \sin \theta / 2m] \ln [A_s / A_p] \quad (1)$$

In eq. 1, T is the irradiate surface area, $\theta = 0.52\theta$ for the (311) peak, and A_s and A_p are the areas measured under the (311) peak of aluminum in the absence of and in the presence of the finely powdered resid samples. The mass absorption coefficient of each sample is presented in Table I.

X-Ray Diffractograms. The measured secondary x-ray intensity, $I(2\theta)$ was converted to the absorption corrected intensity by:

$$I'(2\theta) = \mu m I(2\theta) / \{1 - \exp(-2\mu m / T \sin \theta)\} \quad (2)$$

The absorption corrected diffractograms of the recycle resid and its THF-fraction are shown in Figure Four. The absorption corrected diffractograms have been utilized throughout the remainder of this manuscript because peaks $I'(2\theta)$ are proportional to the abundances of the various analytes in the complicated resid matrices.

The diffraction peaks due to the crystalline mineral components present in the resid (B) and its THF-insoluble component (A) are shown in Figure Six. That the mineral peak intensities are much higher in the THF-insoluble fractions is consistent with its significantly higher ash content and its significantly higher x-ray mass absorption coefficient and substantiates that extraction by tetrahydrofuran increases the relative abundances of the crystalline minerals by preferentially removing carbonaceous materials from the resid.

Huffman, Huggins, et al.⁶ have recently reported that pyrrhotite ($Fe_{1-x}S$) is formed by reaction with H_2S during direct coal liquefaction processes using iron-based catalysts, with iron oxide(s) present only in the case of insufficient sulfur.⁶ Our best current correlation to date of the diffraction peaks with the crystalline components present in these samples involves pyrrhotite 11-T as well as α -quartz and other minerals but not iron oxide(s).⁷

REFERENCES

- * DOE EPSCoR Fellow. Funding of EPSCoR Fellowship is acknowledged.
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TABLE I. MASS ABSORPTION COEFFICIENT CALCULATIONS.

SAMPLE	MASS (g)	A_s (CPS)	A_p (CPS)	μ cm ₂ /g
recycle resid	0.3351	26,130	2,303	13.8
THF-insoluble	0.1036	23,886	1,215	54.8

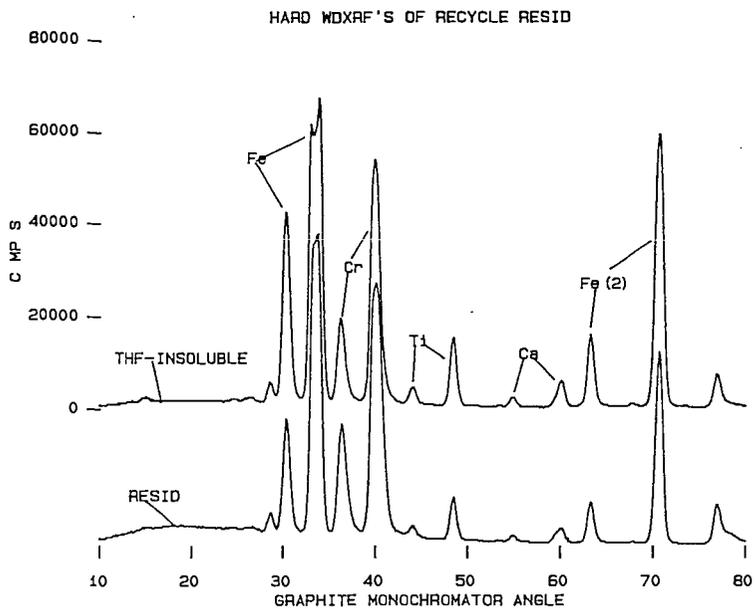


FIGURE ONE. Hard x-ray spectra of the recycle resid and its THF-insoluble fraction.

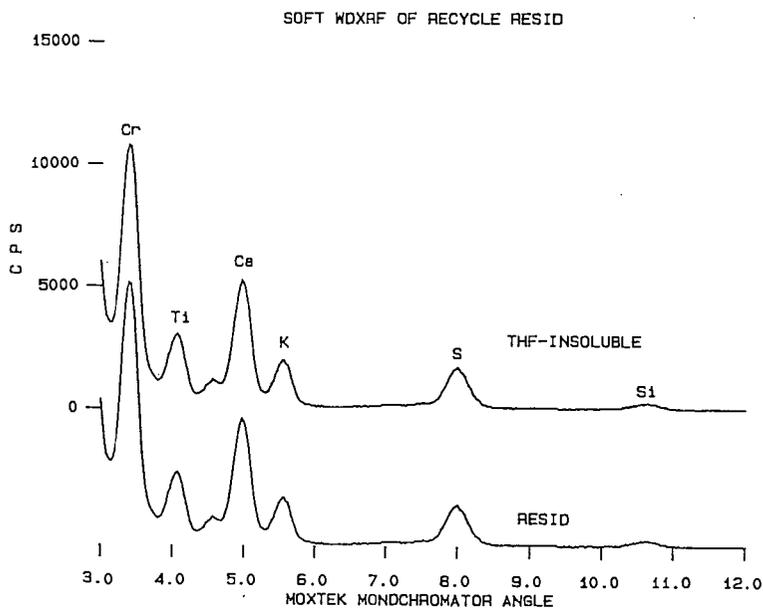


FIGURE TWO. Soft x-ray spectra of the recycle resid and its THF-insoluble fraction.

DIFFRACTION FROM Al (311) PEAK

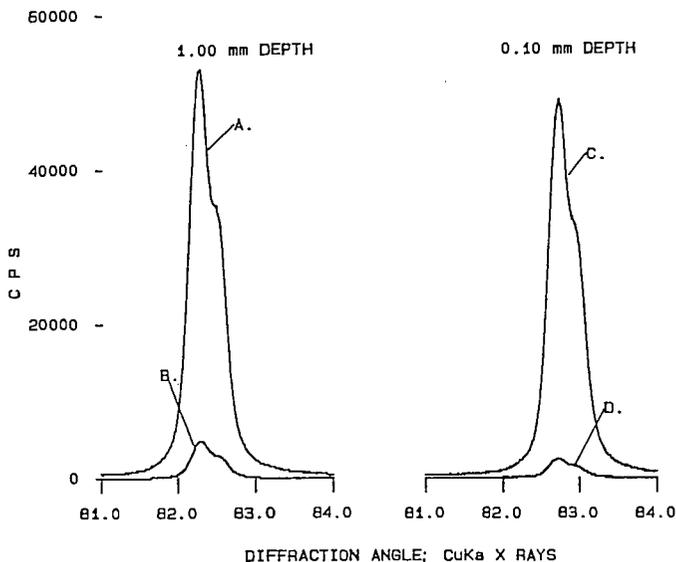


FIGURE THREE. Diffraction from the (311) of the aluminum sample holders. (A) Diffraction intensity from the sample holder with 1.00 mm depth, and (B) intensity from the sample holder with 0.3351 g of the recycle resid deposited onto it. (C) Diffraction intensity from the (311) peak of the aluminum sample holder with 0.10 mm depth, and (D) intensity from the sample holder with 0.1036 g deposited onto it.

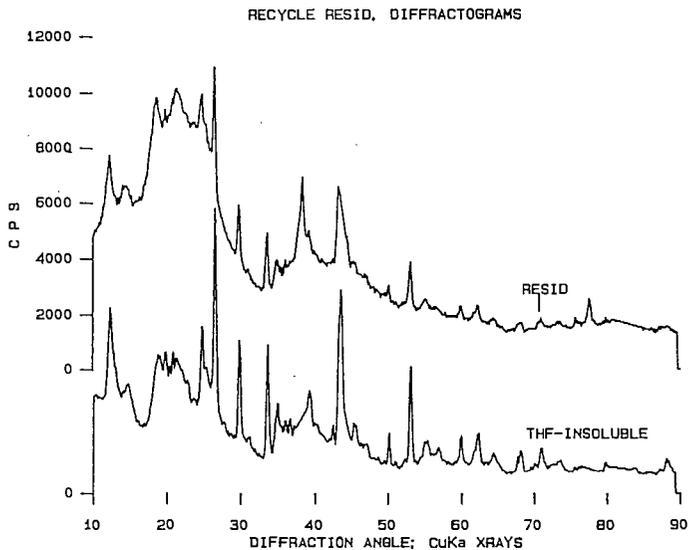


FIGURE FOUR. Absorption corrected diffractograms of the recycle resid and its THF-insoluble fraction.

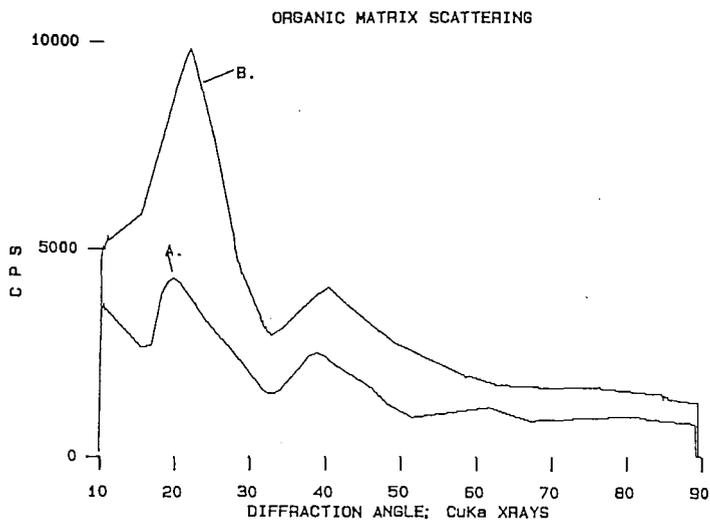


FIGURE FIVE. The diffuse scattering from the recycle resid (B) and its THF-insoluble fraction (A).

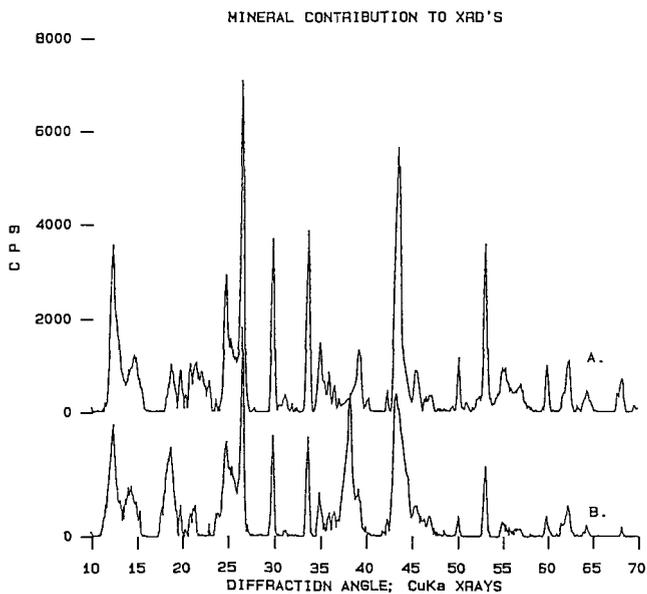


FIGURE SIX. Conventional diffraction from the crystalline materials in its THF-insoluble fraction (A) and the recycle resid.