

X-RAY CHARACTERIZATION OF SOME ACTIVATED CARBON PREPARED FROM ILLINOIS BITUMINOUS COAL 106 AT THE CAER

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INTRODUCTION

X-ray fluorescence spectroscopy (XRS) has been an established research tool for at least seventy-five years for the elemental analysis of condensed phases. Because of recent advances in materials development for the transmission and collection of soft x-rays ($\lambda > 10 \text{ \AA}$), XRS offers new advantages in the study of fossil fuels and their processed products. Wavelength dispersive x-ray fluorescence spectroscopy offers the added advantages of a very low background and excellent peak length/width ratio. Taken together, these features allow WDXRS to be used for the detection of elements in condensed phases at the parts per million abundance level, and in some cases significantly lower.¹

With WDXRS, as well as many other types of radiation experiments, attenuation of the incident and secondary radiation beams by the sample occurs. The result is that the measured intensity I_{meas} cannot be related to sample abundance.²

The absorption-corrected intensity of a WDXRS peak, $I^0(\lambda_Q)$, is directly proportional to the abundance of analyte Q at λ_Q . $I^0(\lambda_Q)$ is related to the intensity measured at λ_Q by:

$$I^0(\lambda_Q) = [\alpha \cdot \Sigma w_A \cdot \mu_A(\lambda_p) + \beta \cdot \Sigma w_A \cdot \mu_A(\lambda_Q)] \cdot I_{\text{meas}}(\lambda_Q) \cdot [1 - \exp\{-\{\alpha \cdot \Sigma w_A \cdot \mu_A(\lambda_p) + \beta \cdot \Sigma w_A \cdot \mu_A(\lambda_Q)\}\}]. \quad (1)$$

In eq. 1, w_A represents the abundance of element A in the condensed phase sample, $I_{\text{meas}}(\lambda_Q)$ is the intensity measured at wavelength λ_Q due to the presence of analyte Q in the sample. The mass absorption coefficients, $\mu_A(\lambda_p)$ and $\mu_A(\lambda_Q)$, are for the attenuation (absorption) of the primary radiation (chromium in these experiments) and for the secondary radiation emitted by the analyte Q, respectively. Constants related to the mass of the sample are represented by α and β . The terms containing the absorption coefficients are designated the "matrix absorption" due to the sample and have a pronounced effect on the relationship between the measured intensity and the absorption-corrected intensity for analyte Q.

The condition of "infinite thinness" may be achieved when the matrix absorption effect $\rightarrow 0$ and is relatively constant. When this condition is satisfied, $w_Q = I_{\text{meas}}(\lambda_Q)/K'$; and the intensity of the peak at λ_Q provides a useful measure of the abundance of analyte Q. The condition of "infinite thinness" is achieved in cleaned coal and biomass samples, where the presence of metal atoms is quite small and the structural units are predominantly either hydrocarbons and/or carbohydrates.

EXPERIMENTAL

Samples were obtained from Jagtoyen as fine powders and were examined as received using conventional x-ray diffraction and x-ray spectral methods.

RESULTS AND DISCUSSION

As seen in Figure 1, the FeS_2 , Fe_2O_3 , SiO_2 and/or CaCO_3 (which are strong absorbers of Cu K_α X rays) had been successfully removed from the IBC 106 prior to its use.

Jagtoyen and Derbyshire have discussed the processes by which bituminous coals and hardwood have been treated by their high temperature (HTT) phosphoric acid process.^{3,4}

Shown in Figure 2 are the WDXRS spectra obtained from several samples of demineralized IBC 106 coal treated by the CAER hot phosphoric acid process used over the temperature range from ambient temperature (labeled DM coal) to 650°C. At ambient temperature a

large sulfur peak ($\lambda = 5.372 \text{ \AA}$) is noted, corresponding to an organo-sulfur abundance of ca. 2.1% in the cleaned coal. Comparison of the sulfur peak intensities indicates that as the process temperature is increased, the percentage of sulfur retained in the carbon fibers reduced. When processed at 650°C, the fibers retain ca. 0.4%. Accompanying the increase in process temperature is a retention of phosphorus ($\lambda = 6.155 \text{ \AA}$).

A similar increase in phosphorus retention is found in the white oak samples treated by Jagtoyen.^{3,4}

WDXRS cannot be extended to provide detailed information about the structural role(s) of the phosphoric acid species involved in the CAER process because the technique only provides elemental (and not molecular) information.

We have previously shown⁵ that the full-width at half maximum (FWHM) for the graphene stacking peak, found at 3.5-4.0 \AA in bituminous coals, measures the regularity of the stacking of the graphene layers in coals. Shown in Figure 4 are the x-ray diffractograms (XRD's) obtained from the unprocessed IBM 106 coal and the coal processed at the several temperatures noted above. Comparison of the XRD's indicates that the FWHM of the graphene stacking are affected significantly by the process temperature, with the higher process temperatures causing improved regularity of the graphene peaks.

Shown in Figure 5 is evidence that the reduction in FWHM is not due to thermal effects.

Jagtoyen⁶ has measured the BET surface area of the activated carbon produced from the IBC 106 as a function of process temperature. In addition, the CAER team reports a significant reduction in the hydrogen component of the activated carbon produced by their HTT process.³ The increase in surface area and the reduction in hydrogen content parallel, at least crudely, with phosphorus uptake (measured by WDXRS) and the re-alignment of the graphene layers in the activated carbon (measured by XRD).

CONCLUSIONS

The two x-ray characterization methods, wavelength dispersive x-ray spectroscopy and x-ray diffraction, each provide limited information about carbon fibers prepared by Jagtoyen and Derbyshire. Unfortunately, neither method provides definitive information about the structural and/or bonding roles of the phosphorus moieties in the activated carbon.

REFERENCES

* Support via a DOE-EPSCoR Graduate Fellowship is gratefully acknowledged.

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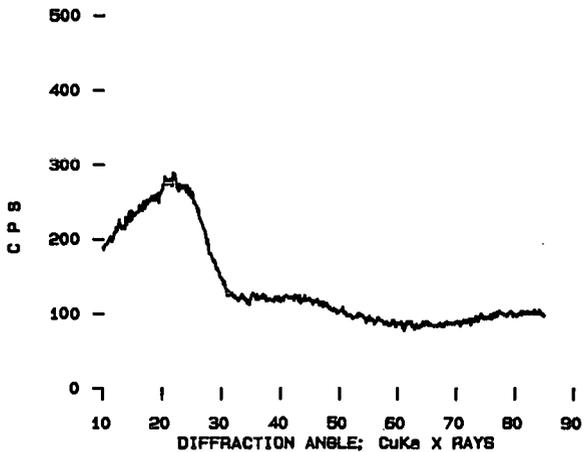


FIGURE 1. XRD OF THE CLEANED IBC 106.

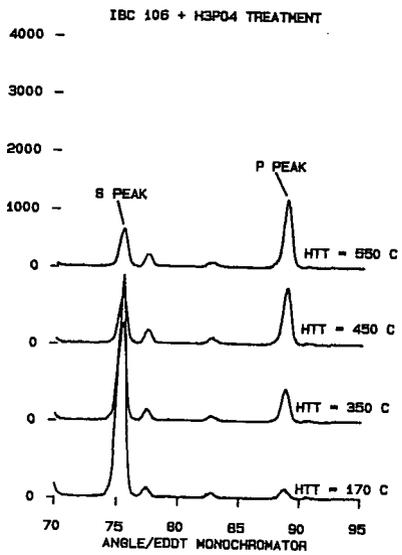


FIGURE 2. WAVELENGTH DISPERSIVE X-RAY SPECTRA OF THE IBC SAMPLES TREATED WITH THE KCAER HTT TREATMENT OVER THE RANGE FROM AMBIENT TO 550°C. SULFUR AND PHOSPHORUS PEAKS ARE LABELED.

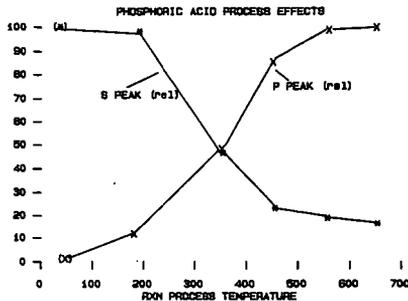


FIGURE 3. HTT EFFECTS ON ORGANO-SULFUR AND PHOSPHORUS UPTAKE.

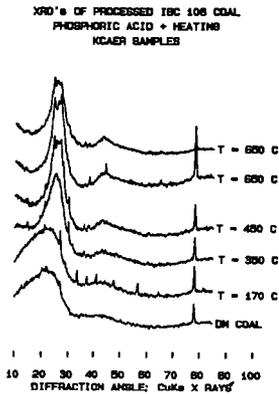


FIGURE 4. HTT EFFECTS ON THE XRD'S OF THE ACTIVATED CARBONS.

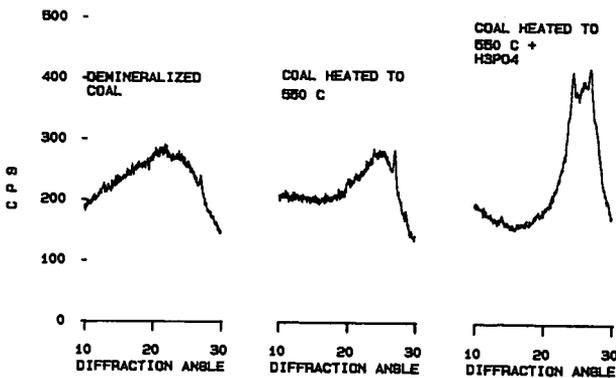


FIGURE 5. CORRELATION OF PHOSPHORUS RETENTION WITH BET SURFACE AREA⁶ MEASURED FOR THE ACTIVATED CARBONS.