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Chemistry and Structure of Coals: Effects of Grinding Media on a Subbituminous Coal

E. L. Fuller, Jr.

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Metals and Ceramics Division

CHEMISTRY AND STRUCTURE OF COALS: EFFECTS OF
GRINDING MEDIA ON A SUBBITUMINOUS COAL

E. L. Fuller, Jr.

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CHEMISTRY AND STRUCTURE OF COALS; EFFECTS OF
GRINDING MEDIA ON A SUBBITUMINOUS COAL*

E. L. Fuller, Jr.

ABSTRACT

Coal preparation techniques used to provide feedstocks for direct utilization in combustion facilities require extensive grinding. Separation of noxious elements (mineral matter, sulfur, nitrogen, etc.) is facilitated by grinding. Current and future needs for clean air require that more complete separation be carried out. Chemical cleaning processes can be combined and carried out simultaneously by incorporation of chemicals in the grinding media. This work has shown that the argillic mineral matter hydrolyzes in aqueous grinding media and the hydrolysis is markedly enhanced in alkaline media. Direct incorporation of carbon dioxide is accomplished in the alkaline media to form ketone and acid salt groups on the surface of subbituminous coal particles. Diffuse reflectance infrared spectroscopy has been shown to be an excellent aid in defining the chemical and physical changes induced in the grinding process.

1. INTRODUCTION

There is a dire need for advanced control technology to assure that future burning of fossil fuels does not insult the environment. Coal preparation facilities are needed to remove the noxious mineral matter, sulfur, nitrogen, etc., prior to combustion. Finer grinding ostensibly will allow the liberation of at least unbound species to a greater degree. This work is part of a continuing program to study the grinding processes and the accompanying changes in the chemical and physical structure of coals of varying ranks.^{1,2} This work is performed with a sample of the Argonne National Laboratory premium coal sample suite³ and serves as a base for future comparative studies of coals of different rank, chemistry, structure, etc. A comprehensive study is warranted to permit design

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engineers to accommodate the large range of coals that are prime candidates for feedstocks in power-generating facilities. Laboratory-scale experiments are needed to economically evaluate the interaction of the various components of coals and to determine the interfacial forces that must be overcome.

2. EXPERIMENTAL

Vast reserves of subbituminous coals exist in the United States, and the sample used for this study came from the Smith-Roland seam of the Powder River Basin near Gillette, Wyoming. Chemical analyses show: C (77.7%), H (5.35%), O (18.0%), and S (0.6%), with 8.8% ash (wt %). The Premium Coal Sample Program at Argonne National Laboratory (Dr. Karl S. Vorres) supplied the material in sealed amber borosilicate glass ampoules containing 10 g of -20-mesh-size powder in a nitrogen atmosphere.

Diffuse reflectance infrared spectroscopy (DRIS) provides abundant information related to the chemistry and structure of coals.⁴ In contrast to standard KBr techniques, DRIS requires no sample preparation and is nondestructive for powders of the size range encountered in combustion facilities and preparation plants. In these studies, the DRIS data were acquired in the nitrogen purge atmosphere (99.999% purity)⁵ of the Fourier transform infrared spectrometer (FTIR). The free moisture was allowed to escape in each case. In this manner, the same thermodynamic state prevails for the DRIS data reported here. Percussive grinding was carried out in a stainless steel chamber (stainless steel pestle) driven by a "Wig-1-bug" oscillatory mill. In each case the grinding was continued (60 to 90 s) until all of the material passed a 100-mesh screen.

3. RESULTS AND DISCUSSION

3.1. SPECTRAL ANALYSES

The DRIS spectrum of the original subbituminous Wyodak coal (-20 mesh) is presented in Fig. 1. The richness of DRIS is noted in the following

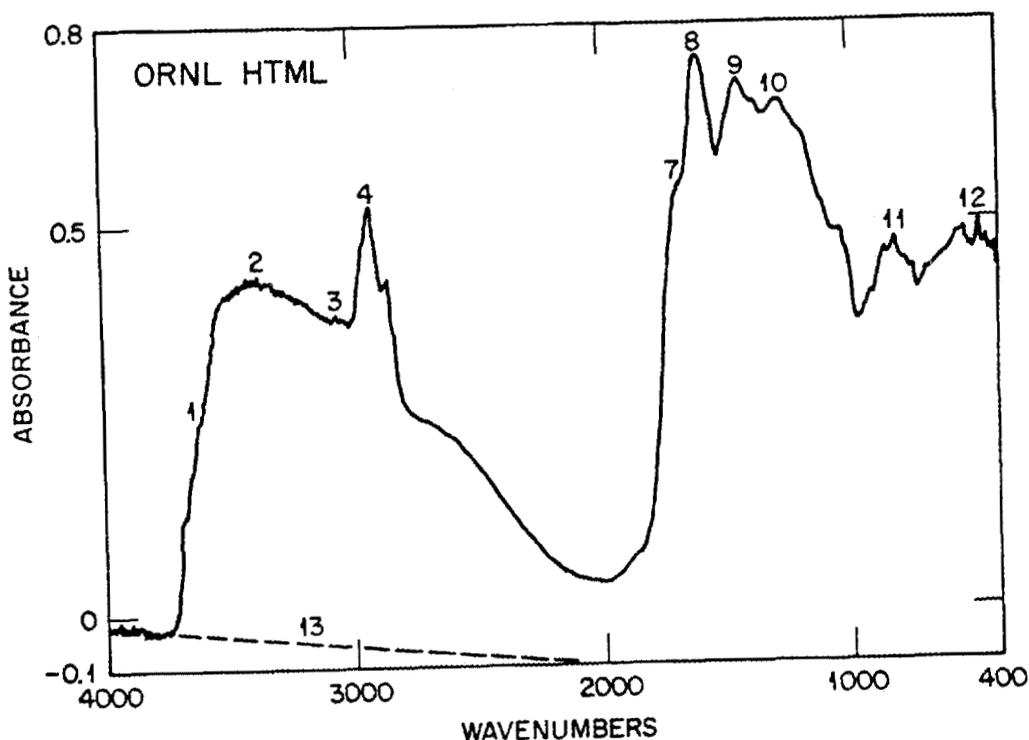


Fig. 1. Diffuse reflectance infrared spectrum of Wyodak subbituminous coal (-20 mesh) as received. The powder sample was allowed to equilibrate with the dry nitrogen purge of the spectrometer chamber. The band assignments (1-13) are discussed in the text.

band assignments, based on infrared spectral studies of coals and related singular compounds:

1. Inflection points on the side of the ascending curve at ~3600 wavenumbers are due to the presence of hydroxyl group (O-H) structural components of illitic and kaolinitic clay minerals inherent within the coal.
2. A broad composite band, arising from the O-H groups within the organic matrix of the coals (alcoholic, phenolic, acidic, etc.), spans the region from 3600 to ~2500 wavenumbers. Varying degrees of hydrogen bonding are involved with a corresponding shift to lower wavenumbers.
3. A very weak band superimposed on the O-H bands is seen at 3100 to 3000 wavenumbers and is the result of the quite low concentration of aromatic hydrocarbons (Ar-H). This stretching mode of vibration is noted

in virtually all polynuclear aromatic compounds. Olefinic ($-\text{CH}=\text{CH}-$) vibrational modes are noted to give rise to absorption in this region of the spectrum and are often noted in coals. The low level of this signal is a direct indication of the low degree of maturation of this coal.

4. The stronger group of bands at 3000 to 2850 wavenumbers is noted superimposed on the O-H bands. These bands are due to the absorption of electromagnetic radiation by the various vibrational modes of the terminal methyl (CH_3-) groups and the methylene ($-\text{CH}_2-$) and methene ($-\text{CH}-$) linking groups in the aliphatic chains appended to the coal polynuclear matrix.

5. Conspicuously absent in this low-ranked coal is the single band at ~ 2730 wavenumbers that is ubiquitous in the DRIS of other coals.^{1,5}

6. A weak inflection point at ~ 1905 wavenumbers has not been unequivocally assigned at this time. This feature appears to become more prominent in the higher ranked coals.¹

7. A prominent shoulder (inflection) is noted from ~ 1800 to ~ 1650 wavenumbers, in the realm classically noted for carbonyl species (acid groups, keto groups, aldo groups, etc.) in organic compounds. These features have been noted to be markedly enhanced by in situ DRIS analyses.⁵

8. A very strong band is noted for virtually all DRIS of coals and related polynuclear compounds.

9. The band at ~ 1450 wavenumbers is generally found as a result of the bending mode of vibration of the $-\text{CH}_2-$ within the aliphatic chains.

10. A composite band is noted as the result of other bending modes of vibration (i.e., C-C-H, C-C-O, C-O-C, C-O-H, etc.). Clay minerals also exhibit lattice modes of vibration in this region.

11. A rather weak triplet band (860, 810, and 760 wavenumbers) is the result of the small amount of organic hydrogen as it undergoes out-of-plane bending.

12. Relatively strong bands (400 to 500 wavenumbers) are found due to the lattice modes of vibration in clay minerals.

13. The entire set of species-specific bands is superimposed upon a sloping background as the incident infrared beam interacts with the powder particles by a scattering mechanism akin to that described by Mie and Rayleigh.

Although the spectral assignments outlined above are somewhat questionable, there is little doubt that the DRIS data provide a plethora of information not matched or exceeded by any other single technique. Detailed analyses of the 2300+ data points of DRIS will provide rich detail concerning the structure and chemistry of coals and the changes wrought in processing.

3.2. DRY GRINDING

After grinding the original sample in a nitrogen atmosphere, the spectrum shown in Fig. 2 was obtained. The bands associated with the O-H of the minerals (3700 to 3600 wavenumbers) are much more prominent, and the aliphatic peak (3000 to 2850 wavenumbers) is larger, both on an absolute scale and relative to the adjacent bands. These results are confirmed by examination of the difference spectrum presented in Fig. 3. This difference spectrum was obtained by direct point-by-point subtraction of the 2300 data points of Fig. 1 from those of Fig. 2 (with a proportionality constant of unity). The data are viewed on an expanded scale in this format and are relatively free of physical perturbations (i.e., scattering from the coal and mineral surfaces). Negative features (with respect to the dashed baseline) correspond to a loss of absorbing entities, and positive features correspond to an enhancement of concentration of the respective chromophores. The changes associated with the more stringent grinding are noted below.

1. The strong feature at ~3590 wavenumbers indicates a lesser concentration of rather weakly hydrogen-bonded O-H entity in the organic coal matrix. Thus, we see that the prominence of the clay mineral O-H is not entirely due to an increase in their concentration, but is due in part to the loss of organic O-H that tends to absorb infrared radiation in the same spectral regime. Some additional clay minerals are indeed exposed by the dry grinding process as witnessed by the enhanced features at 500 to 400 and 1200 to 1000 wavenumbers.

2. The region sensed by the DRIS beam is less populated by the broad range of O-H groups (3600 to 2500 wavenumbers). The minimum near 3200 wavenumber is markedly different from the 3550 to 3400 wavenumbers of the

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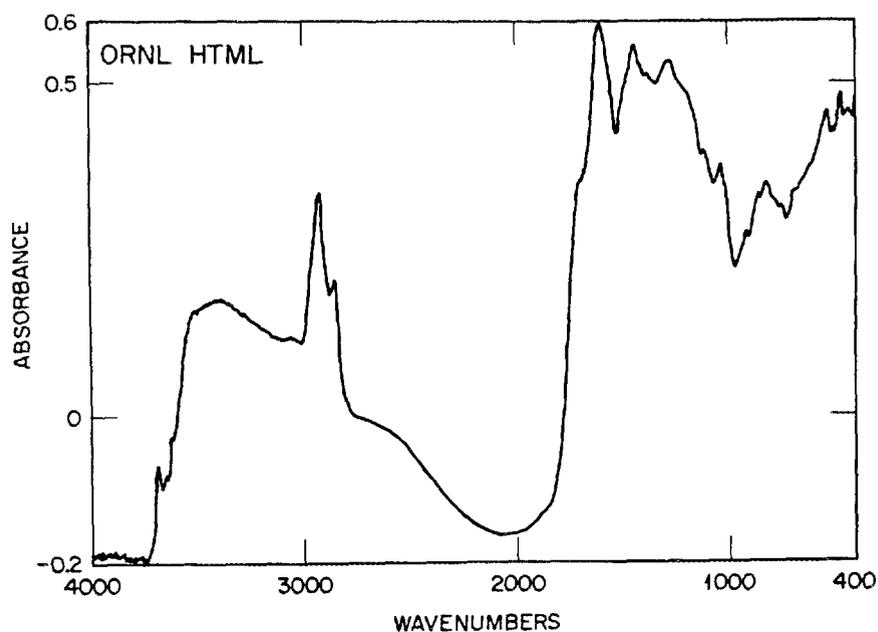


Fig. 2. Diffuse reflectance infrared spectrum of Wyodak subbituminous coal after dry grinding to -100 mesh. Additional clay mineral components noted in the hydroxyl stretch region.

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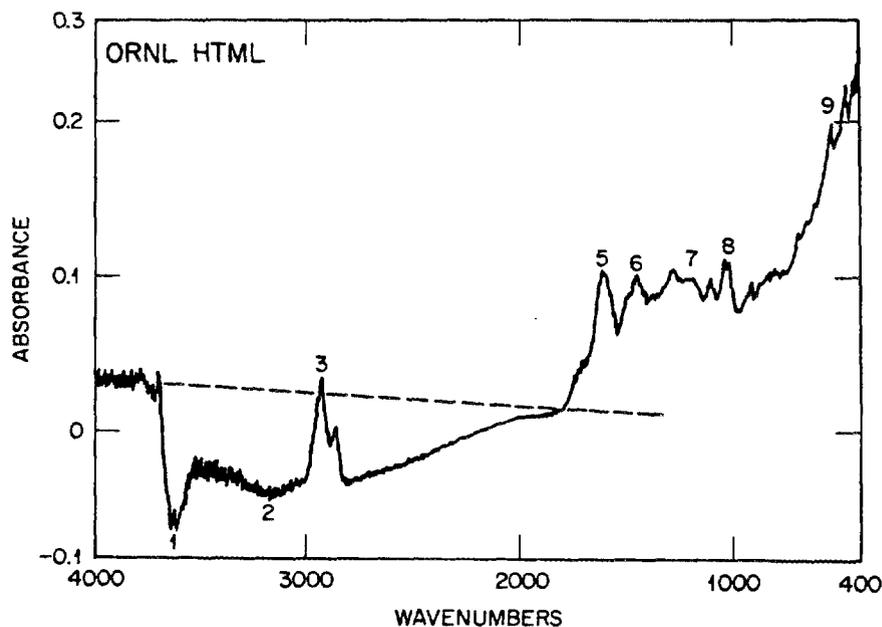


Fig. 3. Difference spectrum to evaluate the effect of the additional grinding of subbituminous Wyodak powder. Relative concentration differences are described in the text.

parent spectra. This would indicate that the distribution of hydrogen-bond energies detected is altered by the grinding process.

3. An appreciable additional amount of aliphatic hydrocarbon is sensed as noted by the enhanced band (3000 to 2850 wavenumbers).

4. The additional grinding generated a small additional component of carbonyls, either by restructuring or by exposure of the aldo/keto functionalities, which are inherent within the maturing coal. If any appreciable acidic components were generated or exposed, one would expect a corresponding positive feature in the O-H region.

5. Enhancement of the 1605 wavenumbers band is indicative of exposure and/or generation of polynuclear aromatic species. There is not appreciable enhancement of the aromatic C-H in plane band (3200 to 3000 wavenumbers) nor of the 860 to 760 wavenumbers out-of-plane vibrational feature. This may be due in part to the much lower response factor for the latter two modes of vibration.

6. The enhanced infrared absorption by the aliphatic H-C-H at 1450 wavenumbers is in accord with item 3, above.

7. Appreciable enhanced concentration of various chain entities (C-C-H, C-O-C, C-O-H, etc.) gives rise to the features in the range 1400 to 1000 wavenumbers.

8. The enhanced features in the 1200 to 1000 wavenumbers region are due to the clay mineral (illites, kaolinites, etc.) enrichment of the surface regime of the coal particles.

9. The 500 to 400 wavenumbers region shows the effect of aluminosilicate clay mineral enrichment.

3.3. WET GRINDING

After grinding an aliquot of the original material in liquid water at -29°C , we obtained the DRIS data presented in Fig. 4. The subtle differences can be best visualized by allowing the computer to subtract the data of Fig. 2 and recast the data, as shown in the difference spectrum of Fig. 5. Scrutiny of this difference spectrum allows one to evaluate the modifications of the chemistry and structure due to the presence of the liquid water during the grinding processes:

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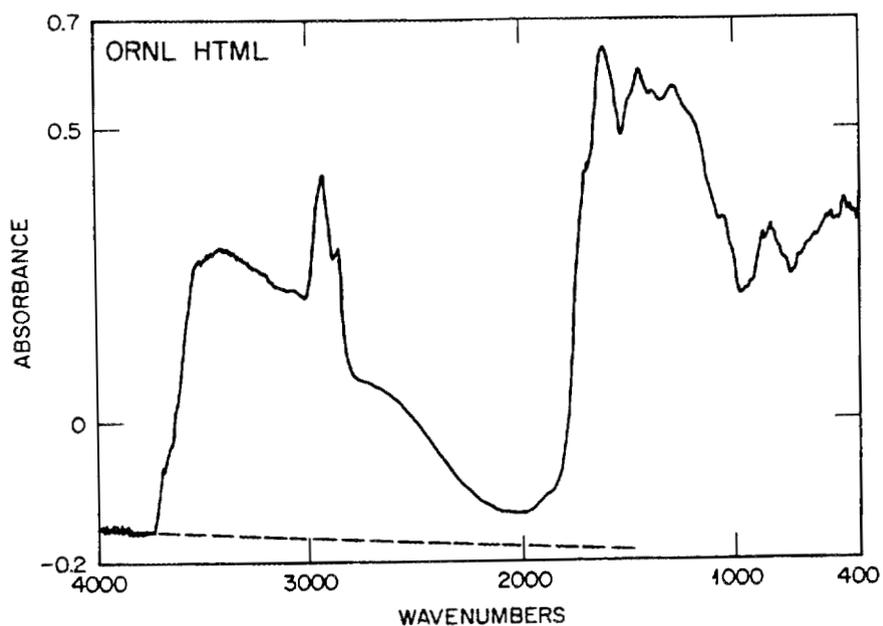


Fig. 4. Diffuse reflectance infrared spectrum of subbituminous Wyodak coal powder ground in water. Subtle differences are difficult to discern.

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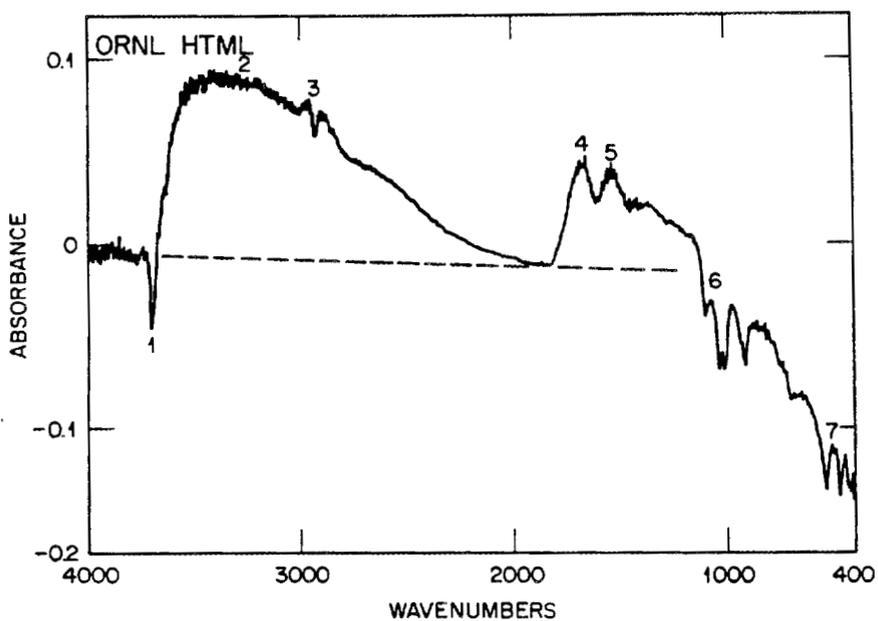


Fig. 5. Difference spectrum for subbituminous coal ground in water. Variation in mineral components, hydroxy concentration, and carbonyl content are readily discerned as noted in the text.

1. The sharp negative feature at 3600 wavenumbers may be due to a lesser amount of clay minerals in the latter case. However, a slight change in environment can lead to a small frequency shift and, consequentially, a negative feature in the difference spectrum.

2. The very strong positive feature spanning the 3600 to 2500 wavenumbers regime results from the incorporation of considerable amounts of O-H into the organic coal matrix. The hydrogen-bond distribution is approximately the same as that of the parent material as witnessed by the range of stretching mode frequencies of the O-H+O bands. This is undoubtedly chemically bound within or onto the polynuclear organic phase. Apparently, there is some hydrolysis to form phenolic (Ar-O-H), alcoholic (Al-O-H), or acidic (-COOH) groups. In addition, certain acidic salts are known to form hydrates (-COONa·H₂O) strong enough to persist in the ultradry environment of our FTIR purge.

3. The small perturbation on the O-H band at 3200 to 2850 wavenumbers is probably due to a restructuring of the C-H entities and not to an appreciably different concentration of either aromatic or aliphatic entities in the wet-ground and dry-ground materials.

4. The difference band at -1650 wavenumbers is due to the enhanced carbonyl (-C=O) entity of aldehyde/ketone groups $\begin{matrix} \text{-C=O} \\ | \\ \text{H} \end{matrix}$, $\begin{matrix} \text{-C=O} \\ | \\ \text{C} \end{matrix}$ in the wet-ground material.

5. A companion peak at -1550 wavenumbers is attributable to the linear carbonyl vibration in an ionized organic acid salt (-COOM, where M denotes a metal). These low-ranked western coals contain appreciable salts of alkali metals (sodium, potassium, etc.). Most of the clays also have an appreciable content of exchangeable cations that could ion exchange during the hydrous processing. This aspect of the study shows the importance for a complete understanding of the ion-exchange properties of both the organic and inorganic phases of the coal. Much of the change noted here appears to be synergetic interactions between the two components.

6. The three or four negative bands here are due to the loss of clay minerals either by dissolution or by restructuring during hydrolysis.

7. These negative bands (500 to 400 wavenumbers) are the result of the hydrolytic loss of clay minerals.

The complexity of the grinding in aqueous media is great and points out that one must be cognizant of the acid/base interactions as well as the ion exchange that occurs between the composite phases that coexist in coals. These and other transport processes within the coal substrate are of prime importance.⁶

3.4. EFFECTS OF GRINDING IN ALKALINE SOLUTION

The DRIS spectrum of Wyodak coal after grinding in alkaline medium is shown in Fig. 6. This spectrum was obtained after about 1 h in the FTIR nitrogen purge (this amount of exposure time was shown to be adequate to achieve steady state, as proven by additional exposure for 96 h). Further DRIS changes were noted for additional exposure of the base-treated material, as shown in Fig. 7 (17-h total exposure to dry purge gas). The DRIS continued to change for ~40 h to a sensible steady state equal to that depicted in Fig. 8. Direct observation allows one to discern that the major portion of the slow equilibration involves loss of O-H groups involved in rather weak hydrogen bonding (3600 to 2600 wavenumbers).

Analyses of the difference spectra provide much more information as shown in Fig. 9 (Fig. 6 data minus Fig. 2 data) for the initial drying from the basic medium. The changes wrought on grinding in the NaOH solution are noted below.

1. A strong increase in the O-H concentration for very weakly hydrogen-bonded species is noted at ~3600 wavenumbers.
2. In addition, there is considerable increase in the amount of O-H hydrogen bonded to a degree associated with ~3200 wavenumbers and a distribution down to ~2200 wavenumbers.
3. A weak negative feature at ~3000 wavenumbers indicates the loss of C-H entities via a base hydrolysis process. This may be a carbonation to an organic acid by a Kolbe/Schmidt reaction. Direct hydrolyses to an alcoholic/phenolic functionality may also occur at the sites activated by percussive impact in the basic medium.
4. The broad band at ~2150 wavenumbers may be due to an ultrahigh energy, hydrogen-bonded O-H. Alternatively, this band is probably due to a

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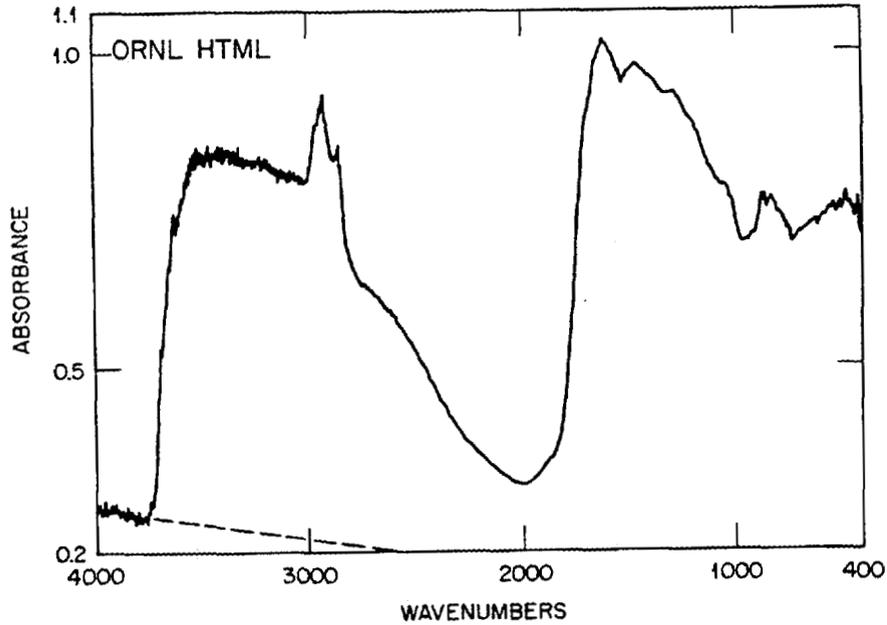


Fig. 6. Diffuse reflectance infrared spectrum of Wyodak subbituminous coal after grinding in aqueous alkali medium. A relatively high concentration of hydroxyl groups is obvious, compared to the previous spectra.

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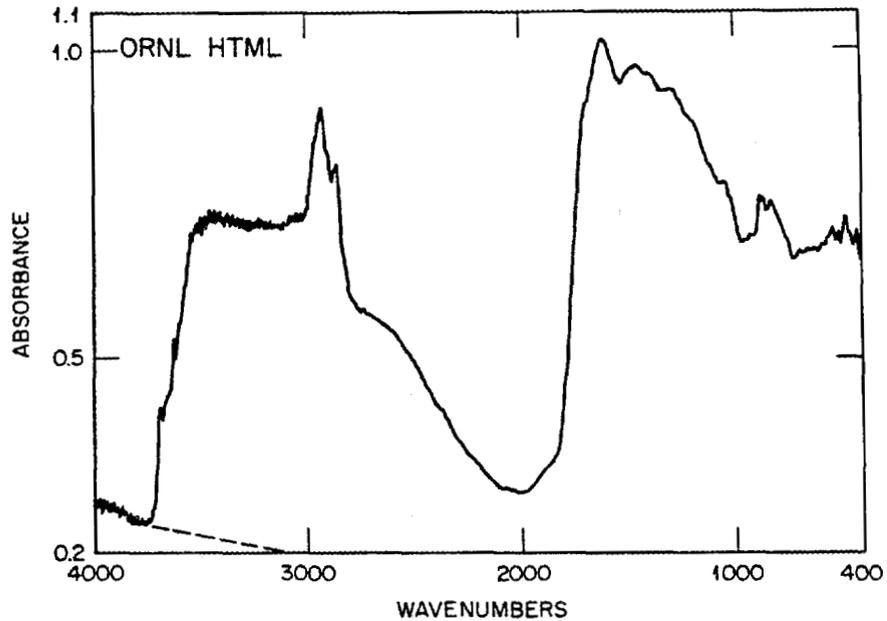


Fig. 7. Diffuse reflectance infrared spectrum of base ground Wyodak coal after 12-h exposure to dry nitrogen purge gas. Lesser amounts of hydroxyl are noted due to slow dehydration.

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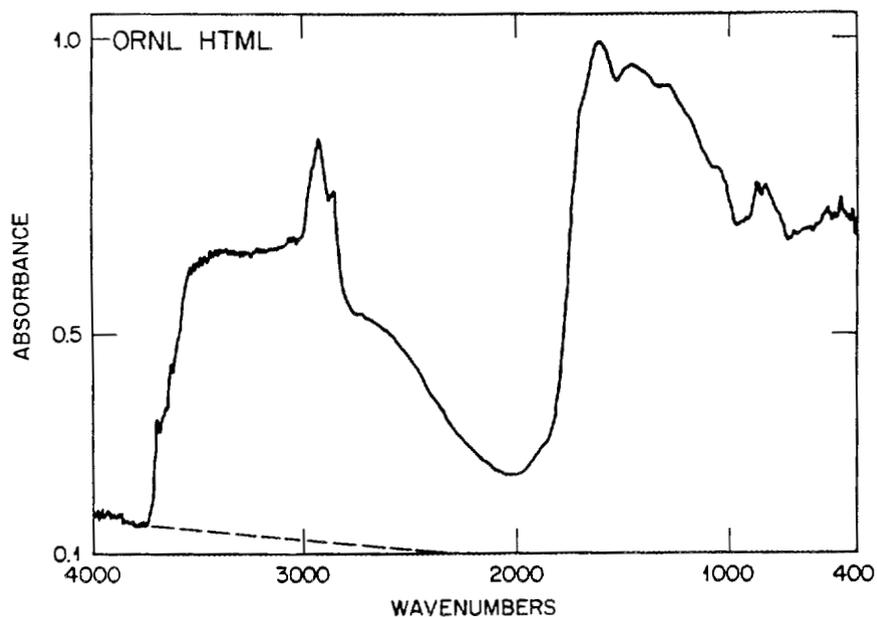


Fig. 8. Diffuse reflectance infrared spectrum of base ground Wyodak coal after prolonged exposure to dry nitrogen purge gas. Steady state conditions are noted to prevail (no further changes in DRIS).

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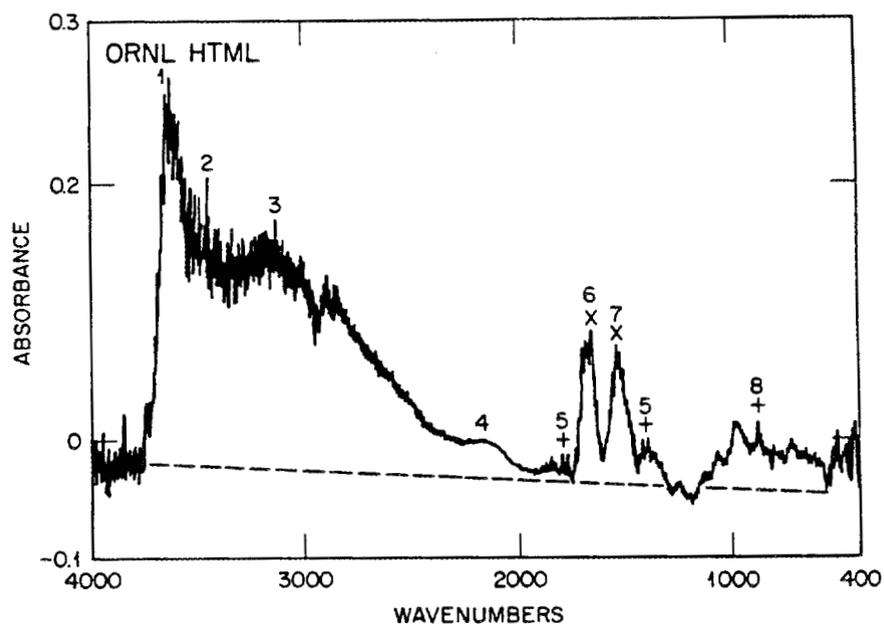


Fig. 9. Difference spectrum for base ground Wyodak coal for short exposure to dry nitrogen purge gas. The additional hydroxyl concentration is noted and carbonyl bands are prominent.

weakly bonded (i.e., adsorbed, absorbed, or coordinated) carbonato species much akin to the carbon monoxide and carbon dioxide found sorbed to metals and catalysts.⁵

5. Two relatively weak bands are seen at 1480 and 1700 wavenumbers that reveal the fact that the residual sodium hydroxide reacted with the carbon dioxide of the air in the drying process to form solid sodium carbonate on the surface of the coal particles.

6. The 1650 wavenumber band due to the carbonyl vibration in free aldehyde/ketone functionality is quite prominent.

7. Drying from the basic medium leaves the organic acids in the form of their sodium salts ($-\text{COONa}$ and $-\text{COONa}\cdot\text{H}_2\text{O}$) as noted in the characteristic band at 1550 wavenumbers.

8. The very sharp band at ~ 860 wavenumbers is due to the existence of solid sodium carbonate in the processed sample.

Prolonged exposure to the anhydrous atmosphere of the FTIR slowly decreases the excess hydrating water content, as depicted in the series of spectra in Figs. 9 through 12. The vast majority of the hydrating water is quite weakly hydrogen bonded and probably in conjunction with the acid and carbonato salts ($-\text{COONa}\cdot\text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$). Virtually all of the other DRIS features remain fixed during this dehydration process when one considers varying intensity scales. The 2150 wavenumber feature is lost in the process, indicating that it may be associated with the hydrating water molecules. The slow restructuring indicates that the hydrating water is involved in a diffusional transport from the inner reaches of the organic coal substrate and probably involves an appreciable volume change and alteration of subsequential reactivity (combustion, gasification, etc.). At this writing, we cannot delineate the process since "the distinction between 'micropores' and 'gaps between molecules' in a bulk solid is not always clear."⁷

4. CONCLUSIONS

Additional grinding does reduce the particle size of subbituminous coal. In addition, there seems to be a release of an appreciably greater amount of mineral matter due to the fracture along the mineral/organic

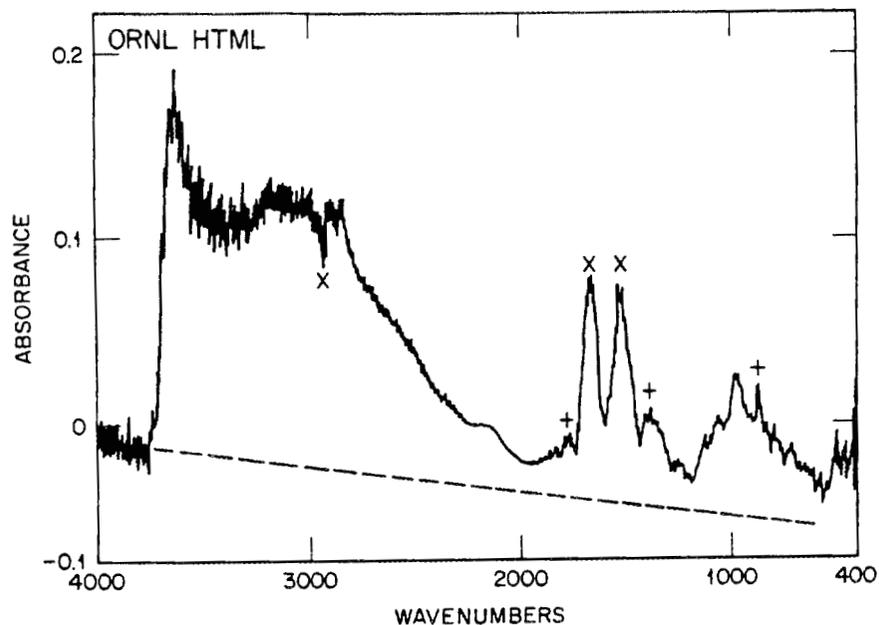


Fig. 10. Difference spectrum for base ground Wyodak coal after 12-h exposure to dry nitrogen purge gas. Hydroxyl loss is noted to dominate the drying process.

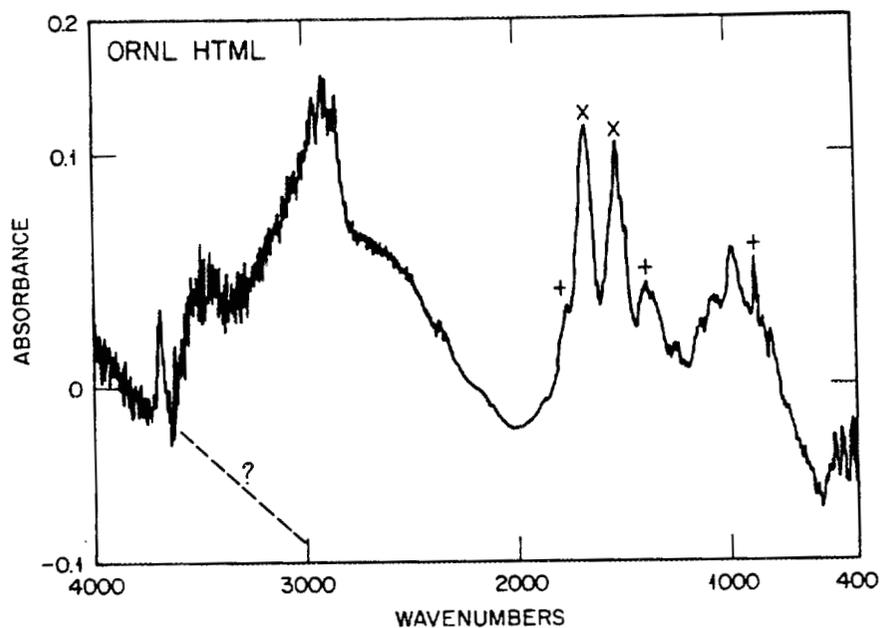


Fig. 11. Difference spectrum for base ground Wyodak coal after 48-h exposure to dry nitrogen purge gas. More water is lost and the aldo carboxyl and acid salt carboxyl bands are of nearly equal intensity.

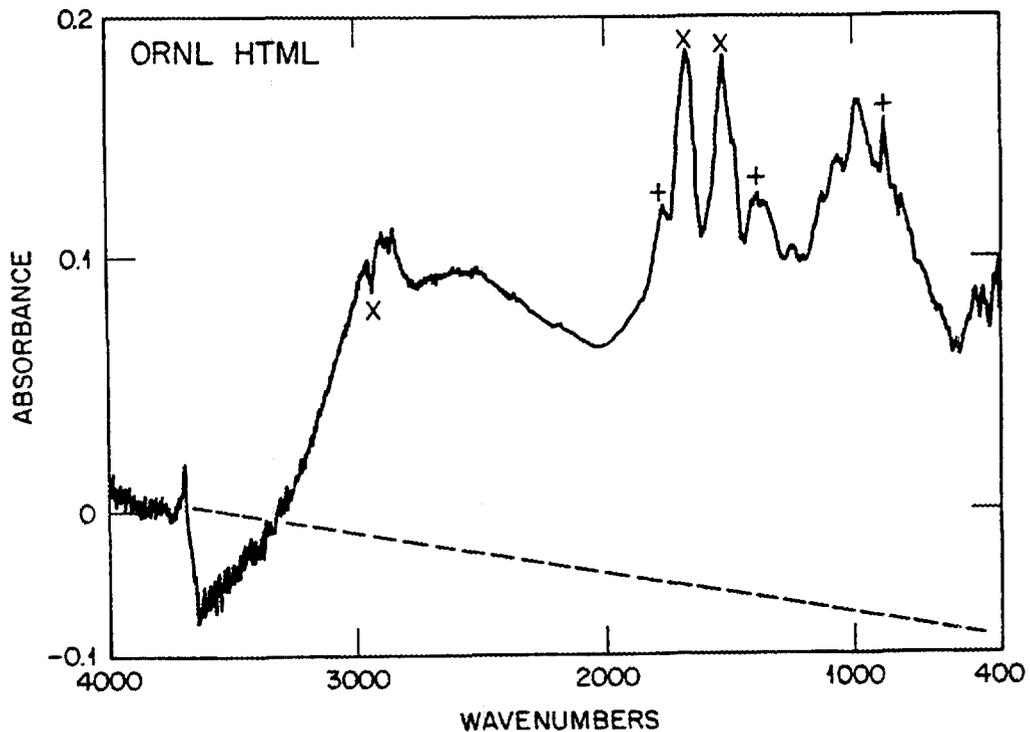


Fig. 12. Difference spectrum for base ground Wyodak coal after prolonged exposure to dry nitrogen purge gas. Steady state data show a rearrangement of the hydroxyls with respect to those found in the original material.

interface boundary. When the grinding is carried out in an aqueous medium, additional reactions occur involving hydrolysis of both the organic and inorganic phases. The hydrolysis processes are much more extensive when the grinding process is performed in basic media.

The merits of the DRIS technique to study these processes are quite evident:

1. the technique is nondestructive;
2. no sample preparation is required for powdered samples;
3. no hindering matrix (i.e., KBr) is used as an encapsulant;
4. environment can be varied (dry, wet, vacuum, etc.); and
5. hydroxyl studies need not be corrected for matrix water.

Monitoring of the changes associated with hydroxyl loss noted here would have been extremely difficult by any other technique.

This work is for a single coal from the Argonne National Laboratory premium coal sample suite and will require analyses as part of the overall scheme with respect to other coals (both within and outside the suite).¹ Even then, one must be cautious to assure documentation of the processing history of each sample, especially with respect to moisture content.⁸

5. ACKNOWLEDGMENTS

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