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FINAL TECHNICAL REPORT

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“Magnetic Relaxation – Coal Swelling, Extraction, Pore Size”

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The aim of the contract was to employ electron and nuclear magnetic relaxation techniques to investigate solvent swelling of coals, solvent extraction of coals and molecular interaction with solvent coal pores. Many of these investigations have appeared in four major publications¹⁻⁴ and a conference proceedings.⁵ Another manuscript has been submitted for publication.⁶ The set of Argonne Premium Coals⁷ was chosen as extensively characterized and representative samples for this project.

The first of these studies¹ developed our application of the electron magnetic relaxation techniques to coal materials. We examined the relaxation techniques on the Whole Argonne Coal, with which it would become necessary to compare results on swollen and separated coal materials. A method was developed for separating the parts of the EPR spectrum from the inertinite macerals from the spectra of the other macerals which is based on the FID (free induction decay) and the field dependence of the spin echo intensity. The mineral matter spins do not appear in these spectra. Good inertinite spectra can be obtained by this method but obtaining non-inertinite spectra that are simultaneously free of power and uncertainty broadening and free of instantaneous diffusion artifacts is difficult to achieve. The numbers of free radicals per gram of inertinite were determined from the FID by comparison with the FID of a standard TEMPO sample, except for those cases in which the FID may be too short to appear beyond the instrument deadtime. The numbers of spins in the inertinite lines are higher and appear to be more reasonable measurements than those reported from CW EPR. The numbers of free radicals per gram in the non-inertinite macerals were determined from the field dependence of a three-pulse echo in comparison with a coal tar pitch standard sample. It is shown that, unless the inhomogeneities that are shown to exist in the instantaneous diffusion rates from one field to another in the broad, non-inertinite lines are explicitly accounted for, the numbers of spins in high spin concentration samples are likely to be overestimated. The spin-spin relaxation times T_2 of the broad line macerals were determined from plots of the two-pulse echo decay times in the limit of low pulse turning angle. The non-inertinite T_2^{-1} increase approximately linearly with the numbers of spins per gram, consistent with a dipolar spin-diffusion mechanism. The spin-spin relaxation mechanism in the inertinites appears to be due to spin exchange, which results in homogeneous line narrowing and increasing T_2^{-1} with increasing number of spins. The spin-lattice relaxation times T_1 of the broad and narrow line spectra were measured respectively by echo saturation and by FID inversion recovery methods. The spin-lattice relaxation times in all macerals were found to decrease generally with increasing carbon content and decreasing hydrogen content. Previous work suggested a mechanism in which the proton hyperfine interaction is modulated by the lattice. T_1^{-1} is proposed as an index of coal matrix flexing. Observations of broad-line coal echo spectra at various degrees of instantaneous diffusion decay reveal significantly g-shifted broad-line spectra whose shifts correlate with the oxygen and sulfur content of the coal.

The second of these publications² presents yield results from a tetrahydrofuran extraction of a range of coals (not all Argonne coals). N-methyl-2-pyrrolidinone-CS₂ (NMP-CS₂) extractions were also performed in this study. The work was performed in connection with a study of photochemical extraction that is unrelated to the present project. The importance of the present project was in developing our extraction and characterization techniques.

The third publication³ presents the electron and nuclear magnetic relaxation results on the NMP-CS₂ extracts and residues from the Argonne coals, as well as nuclear magnetic relaxation results on the whole coals.

An electron spin and proton magnetic relaxation study was performed on the effects of the solvent extraction of coal on the macromolecular network of the coal and on the mobile molecular species that are initially within the coal. The eight Argonne Premium coals were extracted at room temperature with a 1:1 (v/v) *N*-methylpyrrolidinone (NMP)-CS₂ solvent mixture under an inert atmosphere. As much solvent as possible was removed from extract and residue by treatment under vacuum oven conditions ($\sim 10^{-2}$ torr at 145 - 150 °C) until constant weight was achieved. The extraction, without further washing with other solvents, results in substantial uptake of NMP, apparently by H-bonding or acid-base interactions. The NMP uptake tends to be higher and the NMP tends to be more tightly bound in coal matter with higher heteroatom (N,O,S) content. The molecular material in the medium rank bituminous coals is more aromatic and heteroatom-poor than the macromolecular material and is mobilized by the extracting solvent. Likewise, the more aromatic and heteroatom-poor molecular free radicals are also extracted. However, mobilization of the molecular free radicals by solvent and the exposure of free radicals in the macromolecular matrix to solvent or species dissolved in the solvent, results in preferential reactions of the more aromatic and heteroatom-poor free radicals. Greater losses of extract free radicals, being the more aromatic, occur than residue free radicals. As a consequence, the surviving extract radicals exhibit a greater heteroatom content than the original whole coals, as determined from EPR g value changes. See Figures 1 and 2. The electron paramagnetic resonance (EPR) spin-lattice relaxation (SLR) of these coal free radicals has previously been to be from the modulation of the intramolecular electron-nuclear dipole-interactions of the CH groups in a magnetic field by motions of the radical in the coal matrix. Such a modulation depends on the flexing amplitude and frequency and to a lesser extent upon the electron spin density at the CH groups in the radical. The observed EPR, SLR rates decrease with coal rank in agreement with the smaller spin densities and the lower rocking amplitudes that are expected for increasing aromaticity with rank and increasing polycondensation at the highest ranks. The EPR, SLR rates are found to be generally faster in the extracts (than residues) where the molecular species would be expected to be smaller and more flexible than in the cross-linked, polymeric, macromolecular matrix of the residue. See Figures 1 and 2.

The work³ also clearly indicates much about the molecular interactions in the porous structure of the original whole coal and in the resulting extracts and residues. The nature of the study focuses both on the interactions and character of extractable material and on the interactions of the NMP solvent that is retained.

The extraction yields generally conform to the classic shape of extraction yield versus C content that has been observed for a wide sampling of many coals by Iino *et al.*,⁸ in which extraction yields increase to a maximum at 85 - 87% C and drop rapidly above this rank. It is at this range of C content that the intensity of the aromatic proton NMR region of the extract maximizes and begins to drop off, presumably as a result of the increasing polycondensation of aromatic rings and loss of H. Heteroatom content also tends to drop off more rapidly with rank above 87% C. As the C content of the whole coal decreases below 85% C, we observe methyl and methylene CH stretching

intensity ratios in the IR of the extracts that are indicative of increasingly longer aliphatic chain structures, which is, of course, being accompanied by an increasing heteroatom content. There is a well known propensity of coals with decreasing rank to retain increasing amounts of water or pyridine solvent, like the similar trend demonstrated here for NMP, probably through acid-base interactions or H-bonding. Given the natural, biological origin of coals, together with these facts, it seems likely that from 85% C downward, the coals become increasingly polymeric, resembling the biopolymers from which they derive in regard to H-bond cross-linkage. See Figures 1 and 2.

Thus, the amount of extractable molecular species increases with rank to 85 - 87% as the polymeric, H-bonded macromolecular network breaks up. Above 85 - 87% C the extractable, largely aromatic molecular species have been increasingly transformed with increasing rank into an increasingly polycondensed, insoluble, macromolecular matrix. This picture is also consistent with the elemental analyses of the extracts and residues from the Argonne coals. Except for the BZ lignite, the C content of the soluble, more aromatic extract is greater than the C content of the more aliphatic, insoluble, polymeric residue below 87% C. The situation reverses for the PO coal, in which the insoluble, polycondensed, aromatic residue is richer in C and the soluble, more aliphatic extract is poorer in C. Likewise, except for the BZ lignite, the heteroatom content of the soluble, more aromatic extract is less than the heteroatom content of the more aliphatic, Lewis and Brönsted acid-rich, polymeric residue below 87% C. The situation reverses for the PO coal, in which the insoluble, polycondensed, aromatic residue is poorer in heteroatoms and the soluble, more aliphatic and acid-functionality-rich extract is richer in heteroatoms. The BZ lignite is probably an exception because of the small degree of coalification of the organic matter. What very little material that can be extracted from BZ, because it is almost entirely polymeric, has a composition almost identical to the residue. See Figures 1 and 2.

The increases in total coal weight and the increases in elemental N upon extraction indicate that solvent is being retained in spite of the rigorous vacuum heating to constant weight under strictly oxygen-free conditions. The extract IR spectra, the extract solution proton NMR spectra, the proton NMR spectra of the acetone- d_6 washings and the proton NMR spectra of the solid extract and residue all show retention of NMP. The absence of any detectable CS₂ in the extract or in the acetone wash ¹³C NMR spectra and the well-behaved elemental S content, together with the rigor of the "vacuum oven" conditions of solvent removal relative to the high CS₂ vapor pressure and low boiling point, all indicate that it is only NMP that is being retained.

The total amount by weight of NMP that is retained in the extraction appears to rise generally with heteroatom content in the whole coal, perhaps with LS and BC coals dropping below the trend. (We have chosen to associate heteroatom content with the combined O and S content because, while the *actual* coal N content is generally small and not highly variable, the *measured* elemental N contents of the extracts and residues are severely complicated by NMP retention.) The amount of NMP that cannot be washed from the residues increases roughly with heteroatom content of the residue, suggesting that not only does NMP retention *increase* with heteroatom content but that it is *more tightly bound*. The fact that the amount of NMP retained in the extract so very closely follows the amount that can be washed from the residue (except for the PO fractions), suggests that the entities to which NMP binds tightly are largely absent in the extract. More specific evidence about the tightness of NMP binding comes from the solid proton NMR

studies in which it was found that only a fraction of the total NMP retained had rotational correlation times short enough (1.35×10^{-6} s) to observe the NMR peak of NMP. This fraction drops precipitously with heteroatom content or, in other words, the fraction of highly immobilized NMP increases dramatically with heteroatom content. These results appear to be consistent with the H-bonding or acid-base immobilization mechanism that has been proposed⁹ for pyridine-coal interactions. The unusually large amount of solid NMR-observable NMP in the Pocahontas coal residue may have to do with a substantial depletion of the heteroatom-containing sites to which NMP could tightly bind and which would result in the disappearance of NMP from the NMR line. Even the Pocahontas coal extract, which has almost twice the combined O and S content, found in the Pocahontas coal residue, has enough tight binding sites to suppress the observable NMP NMR considerably.

Work on the porous nature of coals turned to probing molecular siting and motion in the pores. The paramagnetic nitroxide spin probes had been used recently to probe the shape and chemical environment of the pores.¹⁰ Therefore we began preparations to use the nitroxide, TEMPO, and the odd-alternate hydrocarbon, phenalenyl, to probe the pores in the coals and coal residues. It was necessary to calibrate initially the use of phenalenyl, as a probe of molecular motion in systems of uniform pore size, for which we used series of alkali cation-exchanged faujasite zeolites.⁴ Some development of the theoretical basis for these analyses was also developed.⁵

The molecular motion of the phenalenyl (PNL) spin probe in the supercages of cation-exchanged X- and Y-zeolites (faujasites) has been physically characterized by pulsed and continuous wave (CW) electron paramagnetic resonance (EPR).⁴ Both X- and Y-zeolites, whose cation sites were exchanged with the alkali metal ions, Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺ were examined. There is a good correspondence between the temperature dependences of the PNL electron spin phase memory time and the CW EPR spectra. Both display evidence of a thermal activation from a stationary, non-rotating molecular state to a low-temperature state of in-plane rotation. The rate of in-plane rotation is an activated process, with $E^*_{\parallel}/R = 1,289 \pm 35\text{K}$ and $1,462 \pm 47\text{K}$ in NaX- and KX zeolites, respectively. The rotation appears to be about an axis along which the half-filled, non-bonding π orbital interacts with the exchanged cation in the supercage. Both CW and pulsed EPR also show a higher temperature activation from the in-plane rotating state to an effectively isotropic state of rotation of PNL in which the PNL-cation bond is thought to be broken, with $E^*_{\perp}/R = 2,050 \pm 110\text{K}$, $1,956 \pm 46\text{K}$, $1,335 \pm 97\text{K}$ in LiX, NaX and KX zeolites, respectively. The strength of the PNL-cation bonding decreases with increasing cation atomic number as indicated by $E^*_{\perp}$ and the peripheral repulsion (crowding) of PNL increases with cation size as indicated by $E^*_{\parallel}$. There are qualitative indications that the binding of PNL to the cations in the Y-zeolite is stronger than in the X-zeolite.

The theoretical development⁵ necessary for analysis of the PNL data from the zeolites involved overcoming an inappropriate assumption for PNL at low reorientation rates. Measurement of electron spin coherence decay has been applied recently to determinations of the rate and anisotropy of the molecular reorientation of spin probes.^{4,11} The application from our laboratory employed the approximation of Van't Hof and Schmidt.¹² The approximation was not strictly applicable to the conditions of our experiments at low reorientation rates. However, the algebraic form of the approximate solution asymptotically approaches the correct, lifetime-induced rate at

low reorientation frequency. Exact solutions to the coupled differential equations governing the magnetization have been found. The exact solutions are compared with the approximate solutions and with experimental data from the reorientation of phenalenyl radical in zeolite supercages. The predicted temperature dependence of the coherence decay rates gives a narrower peak near the temperature of maximum dephasing than does the approximation and is in better agreement with experiment. The coherence decay rate constants are the magnitudes of real parts of the eigenvalues of the characteristic matrix of the set of coupled differential equations. The corresponding imaginary parts of the eigenvalues correspond to the reorientation-induced shifts in resonance frequency of the spin systems.

Our doping of PNL into the coal and charcoal samples generated different EPR spectra than were originally present in the samples. The spectra were not simply the sums of the coal/charcoal EPR lines but rather a new line with a linewidth different than the original coal/charcoal EPR line. The shape and width of the line was unchanged to <10 K. The evidence was not consistent with PNL undergoing progressively increased molecular reorientation in the coal/charcoal pore, as it does in the zeolite, with little exchange-narrowing of the EPR line. Rather the evidence points either to (1) chemical reaction of the PNL with the coal/charcoal pore surface or (2) extremely fast exchange processes in the coal/charcoal pore that completely narrow the broad PNL hyperfine components into a single narrow EPR line. While the latter process may be facilitated by intimate access of the planar π system of PNL to the graphitic layers exposed to the surface of the pore, the results with TEMPO in these systems suggests that PNL reacts chemically instead. The TEMPO results will be discussed next.

The EPR spectrum of the TEMPO-doped pores exhibits the powder pattern typical of stationary TEMPO molecules from 10 K up to ca. 160 K. Above ca 160 K the spectrum slowly approaches an exchange-narrowed form rather than the three-line pattern of a rapidly tumbling TEMPO molecule. This seems to imply a non-negligible inhibition of TEMPO reorientation by the structure or chemical character of the pore, while permitting some spin-exchange processes to occur. This suggests that TEMPO molecules slide around the surfaces of the pores enough to encounter other TEMPO molecules, while remaining sufficiently bound to inhibit reorientation.

The TEMPO pulsed EPR spin dephasing rate, $1/T_M$, in these samples is relatively constant up to about 40 K, where it begins a very gradual increase up to 200 K. Above 200 K the signal is too small and/or the dephasing rate is too fast for further measurement. The results, in which any peak in $1/T_M$ that may be present must lie above 200 K, suggest that neither the TEMPO molecular reorientation rate in the coal/charcoal pores nor the spin-exchange rate exceeds the frequency differences in the spectrum that must be averaged to collapse the spectrum into narrow line(s). Quantitatively one can say that the TEMPO reorientation rate and the TEMPO bimolecular collision frequency in the coal pores are less than the order of 100 MHz at 200 K. These pulsed EPR conclusions are in essential agreement with the CW EPR conclusions above.

We have examined the spin coherence memory times in the pyridine-swelled Argonne whole coals and reswelled residues. The spin coherence memory times T_M of the swelled whole coals and the swelled residues versus coal rank are shown in Figures 3 and 4. (The echo decay times T_2 were measured at various power levels and the T_M were extracted from the plots $1/T_2$ versus $\sin^2 \theta/2$,

where θ is the magnetization turning angle of the microwave pulse.) There appear to be generally increasing trends in T_M with coal rank, with somewhat longer T_M in the swelled residues than in the swelled whole coals. While the latter trend could be rationalized on the basis of the lower density of spins left in the swelled residue after extraction, the former trend runs counter to the increasing density of spins with rank. The exceptional behavior of the swelled whole coals at higher and lower ranks is noteworthy. The low rank behavior may be due to the fact that the sample is actually a lignite, not a coal. The very short T_M in the high rank whole coal may have to do with spin exchanged processes.

We also measured the T_1 in the swelled whole coal and swelled residue, broad, vitrinite EPR line and measured the T_1 and T_2 times of the FID of the narrow, inertinite EPR lines in these samples. See Table 1. Surprisingly there are few, if any, obvious, systematic differences between these quantities in the swelled whole coals and in the swelled residues. Comparisons with the unswelled whole coals and residues^{1,3} reveals markedly shorter, narrow line T_1 values in the swelled samples that appear to be similar to the T_2 values. This seems to imply a dominant spin exchange relaxation mechanism that is faster in the swelled samples. Although the inertinite certainly retains its rigidity, heat exchange from the spin system to the lattice must be facilitated by the presence of solvent. The broad line T_1 are also markedly shorter than in the unswelled samples, but do not approach the limit of dominant spin exchange ($T_1 \approx T_2$).

We have measured the proton NMR spectra and T_1 times of the pyridine- d_5 swelled whole coals and residues. There are a number of features common to most of the sets of spectra and T_1 times. First, the linewidths of the swelled samples are greatly (of the order of 10x) reduced from those of the corresponding unswelled whole coals and residues. Thus the pyridine is loosening the structure of both whole coal and residue to such an extent that the dipolar interactions between the protons are, to a large extent, averaged out. The simple dimensional changes that occur in swelling cannot account for the line narrowing. The reason is that the swelling influences only intermolecular or inter-polymer distances and does not change distances between protons in the same or covalently adjacent functional groups in the coal structure. These results are consistent with the gel structure of swollen coals proposed by Larsen and co-workers^{13,14} and do not require an understanding of the pores in the structure. Second, the spectra of the swollen whole coals often exhibit discernible aromatic and aliphatic regions. The swollen residues exhibit only an attenuated, or even absent, aromatic region. This is consistent with our earlier findings in the extraction study,³ in which extraction removes aromatic-rich molecular material and leaves behind a more aliphatic, heteronuclear, macromolecular matrix in coals with $\approx 90\%$ C. See Figures 1 and 2. In the swollen whole coals and the residues, the aliphatic and aromatic regions all exhibit similar T_1 times. The T_1 in the swollen coal residues are a factor of ten longer in the unswelled residue, while swelling of the whole coal leads to little change. The results seem to show that it is the macromolecular molecular matrix that is affected by swelling, as opposed to the molecular species.^{13,14} Evidently the molecular motions in the macromolecular matrix of the flexible gel structure^{13,14} are increased in frequency and moved further above the 300 MHz resonance frequency. (A decrease in amplitude of the motion upon swelling seems an unlikely alternative explanation.)

It had been proposed to do maceral separation by the density flotation method on the Argonne Coal with the richest non-inertinite maceral distribution, namely the Lewiston-Stockton coal. The experiments were proposed in order to ensure that no non-inertinite maceral-dependent phenomena were complicating the results, as judged by CW EPR spectra. No surprises were found and the question was pursued no further. Details follow.

Density flotation in an oxygen-free $N_2(g)$ atmosphere of a pulverized sample of the Argonne Lewiston-Stockton Coal was done on a CCl_4 -hexane binary liquid at appropriate densities. Eighteen densities between 1.24 g/cm^3 and 1.56 g/cm^3 were separated and combined into the seven density ranges and single density indicated in Table 2. Floating sample was removed from the top of a 2 liter graduated cylinder with a pipette, filtered and dried. The density of the filtered liquid was measured with a density balance. The sample was not demineralized, in order to avoid subjecting the sample to another procedure that could affect the number of spins.

The radicals with the narrow EPR line appear only in the samples with densities above 1.48 g/cm^3 . This appears to be consistent with the fact that the inertinite group of macerals is known to have the highest densities. The EPR linewidths of the narrow lines decrease with increasing density, presumably due to increased exchange narrowing with the more highly polycondensed ring systems. Free radicals with broad EPR lines from the other macerals appear at all sample densities. These broad line EPR linewidths also decrease with sample density due to increased proton hyperfine interaction. The excinite maceral group is known to have the lowest density and the vitrinite is intermediate between excinite and inertinite. The density separations results are ordinary except for a large density of free radicals in the lowest (excinite) fraction. Thus further experiments were not pursued.

Demineralization processes were omitted in this study in order to eliminate the difficulty of doing them in as strict absence of oxygen as the other procedures. We were also concerned about the possibility uncontrolled chemical effects of demineralization on reactive, coal free radicals and physical effects on coal porosity in the extraction process. Possible complications in the measurement of EPR parameters in the presence of mineral matter are discussed next.

It was noted by Silbernagel, et al.¹⁵ that CW EPR measurements of the numbers of spins per gram of organic matter in whole coals are, with few exceptions, increased by as much as a factor of three by demineralization of the whole coal. No similar systematic study of pulsed EPR measurements of numbers of spins in coal has been done.¹ If, as suggested by Silbernagel, et al.,¹⁵ different relaxation times in the presence of mineral matter are a problem, the ability of pulsed EPR to measure these relaxation times should be employed. In order to check that present results are not being complicated by the presence of mineral matter, we have examined the effects of the HF/HCl demineralization procedure of Silbernagel, et al.,¹⁵ on several relevant samples. We examined whole, dried Pittsburgh No. 8 and Pocahontas No. 3 Argonne coals, which Silbernagel, et al.¹⁵ found to have the greatest increase in numbers of spins, and dried Ashland pitch and charcoal samples, which contain no mineral matter. The samples exhibited decreases of 5-14% in the T_1 of the narrow line, the largest of which was observed in the mineral matter-free charcoal. The samples showed T_2 increases for the narrow line of 4-44%, the largest of which was observed in the mineral matter-free charcoal narrow line. Decreases of 27-53% were observed in the T_1 of

the broad line, the largest of which were in the coals. While we observed a 10% increase in the spin coherence decay time, T_M , for the broad pitch line, 34-59% decreases were observed in the coals.

Several conclusions may be drawn from these studies of the effects of the demineralization process. One is that the process used for demineralization does not have a negligible effect on the EPR relaxation times of free radicals in carbonaceous materials in the absence of mineral matter. The second is that the conclusion of Silbernagel, et al.¹⁵ that the demineralization process causes changes in the spin relaxation rates is confirmed by these results, especially for the broad EPR line. However, the broadline coal T_M are determined in large measure by instantaneous diffusion¹ while the low spin concentration pitch T_M are not.¹⁶ Instantaneous diffusion depends on the spin concentration of the resonant spins. Clearly more work needs to be done on this subject and one should refrain from drawing conclusions about EPR T_1 , probably T_2 and spin concentration differences of less than a factor of 2-3.

Table 1. EPR spin-lattice relaxation times T_1 in the inertinite and non-inertinite macerals of the pyridine- d_5 -swollen whole Argonne coals and their swollen residues.^(a) Uncertainties are given in parentheses.

	<u>Inertinite</u> <u>(nsec)</u>	<u>T_1</u> <u>Non-Inertinite</u> <u>(μsec)</u>
Pocahontas No. 3		
Whole	----	59.634(0.051)
Residue	240(84)	82.86(0.47)
Upper Freeport		
Whole	97(21)	19.83(0.18)
Residue	142.2(4.7)	----(b)
Lewiston-Stockton		
Whole	----	11.627(0.068)
Residue	----	27.58(0.38)
Pittsburgh No. 8		
Whole	----	59.634(0.051)
Residue	150(78)	82.86(0.47)
Blind Canyon		
Whole	----	34.33(0.75)
Residue	----	29.0(3.3)
Illinois No. 6		
Whole	----	11.3(1.2)
Residue	63.6(5.5)	23.955(0.065)
Wyodak-Anderson		
Whole	----	35.2(1.1)
Residue	----	20.63(0.11)
Beulah-Zap		
Whole	----	30.58(0.20)
Residue	----	27.58(0.38)

(a) Missing values of inertinite T_1 are for samples whose inertinite content was too low for T_1 measurement.

(b) Intensity of inertinite FID was too large and interfered with echo detection of the non-inertinite T_1 .

Table 2. Density ranges and density flotation yields for an undemineralized Lewiston-Stockton coal sample on CCl₄-hexane binary solvent. Only the combined samples examined by EPR are given.

Density or Density Range <u>(g/cm³)</u>	Sample Weight <u>(g)</u>
1.34 – 1.37	0.0485
1.39 – 1.41	0.0941
1.42 – 1.44	0.0467
1.46	0.0651
1.48 – 1.52	0.0125
1.56 – 1.57	0.0829
>1.57	0.0677

Figure Captions

1. Schematic representation of the variation of the whole coal chemical characteristics that are consistent with the study of extraction. The long saw-tooth lines represent covalently or H-bonded cross-linked polymer. The short saw-tooth lines represent aliphatic hydrocarbons.
2. Schematic representation of the chemical characteristics of the coal fractions and the free radicals in them that are obtained from the extraction of medium rank (bituminous) coals.
3. The electron spin phase memory times T_M of the non-inertinite macerals of the pyridine-swelled Whole Argonne Premium Coals as a function of coal rank.
4. The electron spin phase memory times T_M of the non-inertinite macerals of the pyridine-swelled extraction residues from the Argonne Premium Coals as a function of coal rank.

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Whole Coal Structures

Aliphatic

Heteroatom-Rich

Highly Polymeric - Cross-linked
(Mainly Macromolecular)

Few Molecular Species

H-Bond Cross-linked

Low Polycondensation

Mixed Aliphatic-Aromatic

Intermediate Heteroatom Content

Least Polymeric, Polycondensed
(Least Macromolecular)

Rich in Molecular Species

H-Bonding between Molecular Species

Intermediate Polycondensation
and Aliphatic Chain Length

Aromatic

Heteroatom-Poor

Highly Polycondensed
(Mainly Macromolecular)

Few Molecular Species

Polycondensed, Covalently Cross-linked

Shorter Aliphatic Chains

Figure 1

Figure 2

Molecular Extraction
75 - 87 % C

Swelled Whole

Figure 3

Swelled Residue

Figure 4