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# $^1\text{H}$ n.m.r. relaxation in bituminous coal and semicoke

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Temperature and frequency-dependent proton relaxation measurements, in conjunction with spin concentrations determined by e.s.r., have shown that for fresh and oxidized coal the relaxation mechanism involves spin-diffusion to paramagnetic centres and to rotating methyl groups on alkyl chains.  $^1\text{H}$  relaxation in semicokes is more complex; probably both direct relaxation to paramagnetic centres as well as spin-diffusion contribute.

(Keywords: coal; semicoke; n.m.r.)

Recently there has been a great increase in interest in the n.m.r. properties of coal and related materials<sup>1-5</sup>.  $^1\text{H}$  n.m.r. relaxation times of different ranks of coal have been found to range over more than an order of magnitude<sup>1,2</sup>. Although some attempts have been made to understand the relaxation mechanism, empirical relationships are frequently explored<sup>4,5</sup>.

For high rank coals ( $\approx 86$ – $95$  wt% carbon daf),  $T_1$  increases with increasing radical content<sup>1,2</sup> and it has been proposed that the relaxation mechanism involves spin-diffusion to paramagnetic centres<sup>1</sup>. However, this does not explain the trend for lower rank coals, for which  $T_1$  decreases with decreasing radical content. Also, possible contributions from other relaxation mechanisms have not been explored.

In order to elucidate  $^1\text{H}$  relaxation mechanisms in coal further, the frequency and temperature dependences of the spin-lattice relaxation time of a high volatile bituminous coal have been examined in the present work, and the unpaired spin concentration has been determined. Fresh and oxidized samples of both coal and semicoke were studied.

## EXPERIMENTAL

$T_1$  was measured at 18, 34, 60 and 180 MHz on Bruker SXP and CXP pulsed n.m.r. spectrometers by means of  $90^\circ$ – $t$ – $90^\circ$  pulse sequences. Temperature variation was accomplished in the cryostat described previously<sup>6</sup>.  $^1\text{H}$  linewidths at room temperature were measured at 180 MHz from the Fourier transformed free induction decay. The analyses of the high volatile bituminous Devco coal used in these experiments are summarized in Table 1. The samples were sealed in glass tubes under vacuum after pumping for several hours. Spin concentrations were measured at 9.5 GHz on a Varian E-3 e.s.r. spectrometer using diphenyl picryl hydrazyl (DPPH) as a calibrant.

Table 1 Analyses of coal samples

	Fresh	Oxidized	
		312 h, 100°C	192 h, 190°C
Moisture (wt% ad)	0.8	0.9	0.4
Ash (wt% ad)	2.4	2.3	2.1
Volatile matter (wt% ad)	34.3	31.7	38.2
Fixed carbon (wt% ad)	62.6	65.2	59.3
Carbon (wt% ad)	84.3	82.1	67.8
Hydrogen (wt% ad)	5.3	5.0	2.5
Nitrogen (wt% ad)	2.1	2.2	1.8
Sulphur (wt% ad)	0.7	0.6	0.6
Oxygen (wt% ad) <sup>a</sup>	4.4	6.9	24.9

<sup>a</sup> By difference

## RESULTS AND DISCUSSION

For each coal sample, the magnetization decay curves were slightly non-exponential. The time constant governing the decay at long times was taken to be the characteristic  $T_1$  value. Relaxation times at different frequencies are summarized in Table 2.

The temperature behaviour of  $T_1$  for the coal samples is shown in Figure 1. For each sample there is a shallow minimum in  $T_1$ , at 143 K for the 18 MHz measurements and at 167 K for the 60 MHz measurements.

Line shapes were approximately Gaussian and showed no evidence of two-component behaviour. The  $\approx 8\text{G}$  linewidth leads to a second moment of  $\approx 11\text{G}^2$ , indicating that extensive molecular motion does not take place.

The relaxation behaviour of the fresh coal and lightly oxidized coal is much the same,  $T_1$  values for the oxidized sample being slightly shorter at all temperatures (Figure 1). For bituminous coals containing  $\approx 86$  wt% carbon it has been suggested that relaxation is due to spin-diffusion to paramagnetic centres. Spin concentrations, as

Table 2 Summary of relaxation times and linewidths at room temperature

Sample	Linewidth (gauss)	$T_1$ (s)				No. of spins $10^{19} \text{ g}^{-1}$
		18 MHz	34 MHz	60 MHz	180 MHz	
Coal						
Fresh	8.0	0.167	0.236	0.337	0.573	0.88
Oxidized 312 h, 100°C	8.1	0.134	0.187	0.219	0.486	1.5
Oxidized 192 h, 190°C	6.1	0.27	—	0.46	0.873	0.50
Semicoke						
Fresh	8.1	0.022	0.018	0.017	0.046	4.0
Oxidized	7.8	0.033	0.031	0.031	0.078	4.5

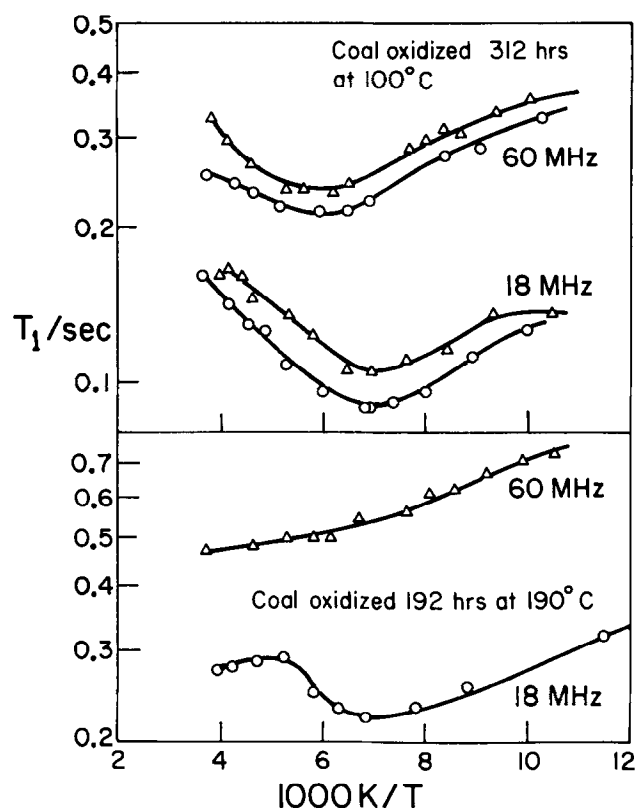


Figure 1 Log  $T_1$  plotted against reciprocal temperature for fresh and oxidized coal samples at different frequencies.  $\Delta$ , Fresh coal;  $\circ$ , oxidized coal

determined by e.s.r. (Table 2), show that the unpaired-spin content increased on mild oxidation but decreased in the case of severe oxidation. The <sup>1</sup>H spin-lattice relaxation times at different frequencies decreased on mild oxidation and increased on severe oxidation, as shown in Table 2 and also in the log-log plot of  $T_1^4$  against  $\omega^2$  (Figure 2). The fact that this plot gives reasonably straight lines for the three samples confirms that the main relaxation mechanism involves spin-diffusion to paramagnetic centres. Hence the proton  $T_1$  values should vary inversely with unpaired spin content, as is indeed the case. Such a relaxation mechanism also explains the non-exponential initial magnetization decay<sup>8</sup>.

On the other hand, the minimum observed in the plot of log  $T_1$  against  $1/T$  and the frequency dependence of the  $T_1$  minimum is reminiscent of a classical BPP  $T_1$  minimum due to molecular motion<sup>9</sup>. At the relatively low temperatures of the  $T_1$  measurements, the only motion rapid enough to give a  $T_1$  minimum in a complex material such as coal is methyl group rotation. The usual criteria for  $T_1$  minima due to motions cannot be expected to apply, as methyl rotation is not the exclusive relaxation

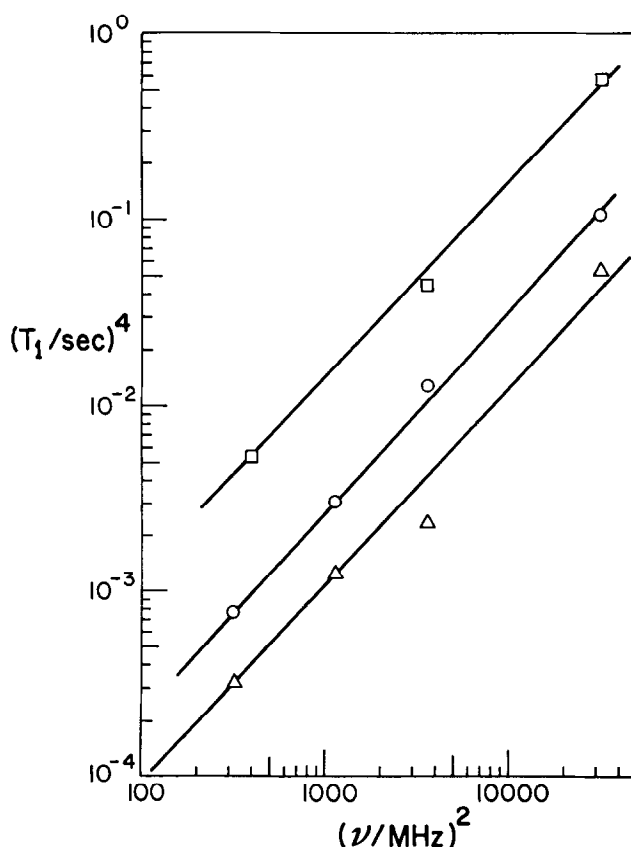


Figure 2 Log-log plot of the fourth power of relaxation time against frequency squared for fresh and oxidized coal samples.  $\circ$ , Fresh coal;  $\Delta$ , coal oxidized 312 h at 100°C;  $\square$ , coal oxidized 192 h at 190°C

mechanism. Also, because of the non-crystalline nature of coal, there must be a distribution of motional parameters<sup>10</sup>, and the usual dependence of  $T_1$  on the square of the frequency at low temperatures and the frequency independence of  $T_1$  above the  $T_1$  minimum can no longer hold<sup>10</sup>. However, at the  $T_1$  minimum the relation  $\omega\tau_c \approx 0.62$  is valid and the frequency dependence of the  $T_1$  minimum can be used to estimate an activation energy for the motion from

$$E_a = \frac{R \ln(\omega_a/\omega_b)}{1/T_b - 1/T_a} \quad (1)$$

where  $\omega_a$ ,  $\omega_b$  = the radio frequencies; and  $T_a$  and  $T_b$  = the temperatures of the corresponding relaxation minima. The above equation applied to the data in Figure 1 yields an activation energy of 11.3 kJ mol<sup>-1</sup>, a reasonable value for methyl groups terminating alkyl chains<sup>11</sup>. Methyl groups directly attached to aromatic rings have much lower activation energies<sup>12,13</sup>.

A rough estimate can be made of the number of methyl groups required to give a minimum of the observed depth. In the presence of spin-diffusion to methyl groups,  $T_1$  is given by

$$T_1^{-1} = f_{Me} T_{1Me}^{-1} + (1 - f_{Me}) T_{1N}^{-1} \quad (2)$$

where  $f_{Me}$  = the fraction of protons in methyl groups;  $T_{1Me}$  is the relaxation time for an isolated methyl group; and  $T_{1N}$  is the relaxation time of the other protons. If we estimate  $T_{1N}$  to be 400 ms (*Figure 1*) and calculate the minimum  $T_{1Me}$  to be 33 ms from the modified BPP equation<sup>14</sup>,  $f_{Me}$  is found to be 0.063. Because a distribution in motional parameters makes relaxation at the minimum less effective<sup>10</sup>, this value of  $f_{Me}$  represents a lower limit. For the heavily oxidized coal, the same  $T_1$  minimum due to methyl group rotation is still evident, although at higher temperatures a new relaxation process sets in. This is in agreement with the fact that the coal structure is altered considerably during the oxidation process. The smaller proton linewidth as compared with the linewidth for the other two coal samples, as well as the appearance of a new relaxation mechanism, suggest increased molecular mobility, perhaps due to depolymerization.

Whereas the details of the variation in relaxation time with temperature apparently reflect molecular motion, the gross  $T_1$  values reflect changes in radical content. Mild oxidation increases the radical content, but more severe oxidation causes a subsequent decrease. This is in agreement with a recent n.m.r. and e.s.r. study<sup>15</sup> of the radical content as a function of oxidation for several coking coals.

As is evident in *Table 2*, the  $^1H$  relaxation time in the semicokes is an order of magnitude shorter than in the coals. An attempt to measure  $T_1$  at lower temperatures showed that the magnetization decay curves became

extremely non-exponential. Since a lower proton density is to be expected as a consequence of the absence of volatiles, it is perhaps surprising that the proton linewidth is unaltered from that of fresh coal.

The frequency dependence of  $T_1$  at room temperature for the semicokes does not show a simple trend and evidently does not fit a plot of  $T_1^4$  against  $\omega^2$ . If extensive aromatization has taken place during the coking process, considerable delocalization of any unpaired spins present in the sample may be expected. Perhaps in addition to spin-diffusion to radical centres, many protons are relaxed directly by interactions with unpaired spins.

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