

CARBON RADICAL RELAXATION PROPERTIES IN ARGONNE PREMIUM COALS

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ABSTRACT

We have applied Electron Spin Echo (ESE) spectroscopy to the analysis of demineralized samples of Argonne Premium Coals. The goal of the present work has been to examine the detailed form of the magnetization recovery in spin lattice relaxation (T_{1e}) and phase memory decay measurements and to trace the temperature dependence of the T_{1e} processes to get a clearer understanding of the mechanisms responsible for carbon radical relaxation. The demineralized coal samples have been chosen for this study because the presence of paramagnetic transition metal ions tends to obscure the effects in the starting coal samples. We find a significant degree of non-exponentiality in the recovery of the carbon radical magnetization, to the best of our knowledge the first of such observations in coals. Such a result could have three sources: spectral spin diffusion among the radical species, a distribution of T_{1e} values due to inequivalent structures for the radicals, or non-uniform spatial distributions of the radicals. A comparison of the T_m and the temperature dependence of these properties suggests that this non-exponentiality is intrinsic to the radicals.

INTRODUCTION

There has been considerable recent interest in the application of transient Electron Paramagnetic Resonance (EPR) techniques to the studies of a variety of materials [1]. These techniques are widely varied, including Electron Spin Echo (ESE) determinations of the relaxation properties of the paramagnetic species as well as more elaborate Electron Nuclear Double Resonance (ENDOR) techniques. Recent studies in coal samples indicate a significant potential for important results in these areas [2, 3]. The present report will focus on the former of these advanced transient EPR techniques: a study of the functional dependence of the magnetization dynamics for carbon radicals in coal using ESE techniques.

The early work in this laboratory on the ESE properties of carbon radicals in coal was performed on a series of coal macerals (vitrinites, exinites, and inertinites) isolated from the starting coal by gravity density centrifugation techniques [4]. In this previous survey [5], the magnetization recovery of the samples was found to be closely approximated by an exponential. For the vitrinite members of this series, the phase memory decay rate, T_m^{-1} , the analog of the spin-spin relaxation time in nuclear magnetic resonance, was found to be proportional to the density of the carbon radicals in the sample, suggesting that the T_m relaxation arose from dipolar coupling. The spin-lattice relaxation rate for the radicals, T_{1e}^{-1} , was found to increase dramatically for higher rank coals, the increase initiating in the vicinity of ~ 82% carbon. It was suggested that this increase in T_{1e}^{-1} resulted from the onset of short range local order with increasing rank for the aromatic molecules which serve as the hosts for the radicals.

While these results were encouraging, there was some concern about whether they reflected the intrinsic properties in the native coal. These materials were prepared from samples of coal from the Penn State (PSOC) coal bank. The history and storage conditions of these samples were not carefully documented. Furthermore, these materials were exposed to air during the grinding and centrifugation processes. At the time, conventional EPR techniques were used

to trace variations in g -value, linewidth, and lineshape of the radicals at each stage of the process [6]. While no major changes were noted, there were still concerns about the chemical nature of the as-received PSOC samples and the chemical forms of the carbon radicals. Finally, the scale of the centrifugation process, as practiced at that time, produced very small amounts of material (~ 10 mg) which severely affected the signal to noise in the ESE experiments.

The availability of the Argonne Premium Coal samples [7] has provided the opportunity to address these concerns about the nature of the radical chemistry. Prior to receipt in this laboratory, the samples have been handled to avoid air exposure. However, a previous survey [3] indicated that the g -values, linewidths, radical densities, and relaxation properties for these samples—as received—were not consistent with the chemical variations expected during the maturation process. An EPR survey of the samples indicated high levels of transition metal ions, especially Fe^{3+} , in the as-received samples, with the effect being particularly pronounced in the highly functionalized lower rank coals. Subsequent removal of the transition metal impurities, by acid wash (e.g. with citric acid) or by HCl/HF demineralization, removed these transition metal ions and produced a much more consistent carbon radical behavior [8]. Now that these mineral effects are understood, we are returning to a detailed study of the organic matter in coal. There have been concomitant advances in the ESE systems in which the experiments are performed. In particular, the introduction of loop gap resonators provides higher microwave power levels and approximately a hundred fold increase in sensitivity for the ESE signals, greatly improving the precision of a study of the functional dependence of the magnetization dynamics.

EXPERIMENTAL

Samples of the demineralized Argonne Premium Coal samples have been examined at room temperature by the ESE techniques. For the radical spin-lattice relaxation measurements, a distinctly non-exponential magnetization recovery is observed. We will characterize this recovery in the following form:

$$(1) \quad (M_z(t) - M_0)/M_0 = \exp\{-(t/T_1')^\beta\},$$

where T_1' is a relaxation time (not a T_{1e}) and β is the exponent of the magnetization recovery. An example of this magnetization recovery is shown in Figure 1. In examinations of Beulah-zap, Illinois #6, and Pittsburgh #3 samples from the Argonne Premium Coal series, values of β ranging from ~ 0.5 to ~ 0.8 have been observed.

To test for possible instrumental effects, we have examined the effect of sample size and position in the resonator. The results suggest that we are not observing an instrumental effect.

DISCUSSION

In addition to these effects, there are several other sources for non-exponential magnetization recovery during spin-lattice relaxation measurements. Spectral spin diffusion among the radicals during the magnetization recovery process can lead to the effect. Alternatively, a distribution in T_{1e} values among the radicals in the sample could also lead to non-exponentiality, since in that case:

$$(M_z(t) - M_0)/M_0 = \int \rho(\alpha) \exp\{-\alpha t\} d\alpha \quad (2)$$

where α represents the T_{1e} value for a given class of radicals and $\rho(\alpha)$ represents the

probability distribution for radicals with that T_{1e} value in the coal sample. This distribution in radical types might not be so prominent in weathered coal samples like the isolated coal macerals observed previously. A third alternative might be that the *spatial distribution* of the radicals in the coal might be causing a distribution in recovery properties, which has been examined in some detail for other systems (e.g. γ -irradiated frozen solutions) [9]. The spatial inhomogeneity will influence both T_{1e} and T_m , and is currently under investigation.

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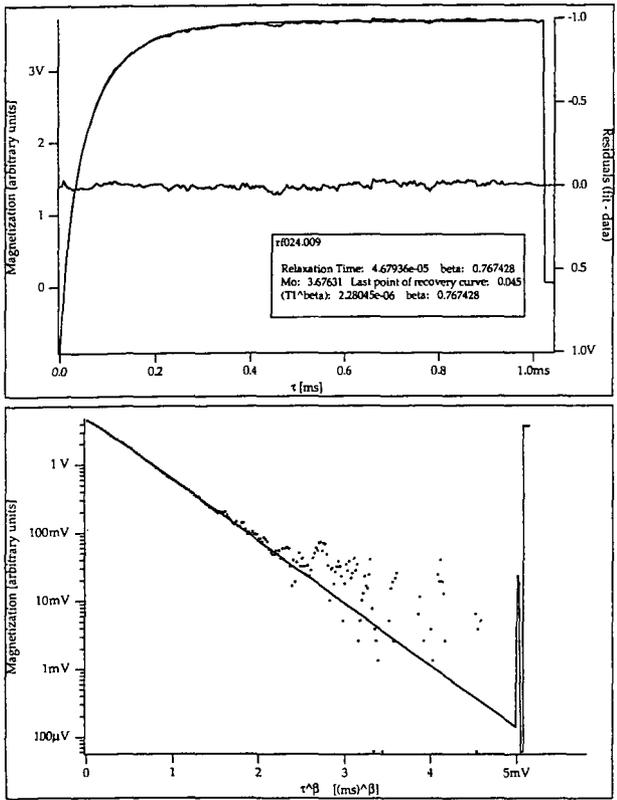


Fig 1 Non-exponential magnetization recovery for a sample of Pittsburgh #3 coal. An exponent of $\beta = 0.767$ is observed in this case. The residuals shown in the upper portion of the figure provide some measure for the goodness of fit for the data.