THE EFFECT OF VACUUM DRYING ON MOLECULAR ACCESSIBILITY IN WEATHERED APCS COAL SAMPLES: STRUCTURAL AND CHEMICAL CHANGES

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INTRODUCTION

During weathering, coals are subject to both a loss of water and oxidation, both of which have been shown to have a strong effect on coal conversion.[1,2] Lignites and subbituminous coals can contain over 30% water by weight, so drying is considered to be economically important in the conversion of low ranked coals. The transportation cost alone can be significant. However exposure to air during the weathering process is an important consideration in all coal ranks. Changes in the physical and chemical structure of fresh Argonne Premium Coal Samples (APCS) during weathering have been previously followed using an EPR spin probe technique.[3] This was possible by swelling the coal in a solvent solution of a stable free radical, known as a spin probe, containing a substituent capable of probing the chemical changes in coal. The substituents used in this study contained functional groups capable of being a hydrogen bond donor (-COOH) or a hydrogen bond acceptor (-NH_2). Removal of the solvent and washing away unreacted spin probes by a non-swelling solvent enabled the weathering process to be monitored by Electron Paramagnetic Resonance (EPR) Spectroscopy. It is the goal of this paper to investigate the changes in APCS coal upon vacuum drying, and to use these results to understand the details of weathering coal in air.

EXPERIMENTAL

Vials containing the APCS coals were opened in a moisture free, pure argon environment. The characteristics of the coal samples are given elsewhere.[4,5] The coals were vacuum dried in a vacuum desiccator for 18 hours. Weight losses for each coal are given in Table 1. After being weighed, the coals were split into several aliquots. Four of these aliquots for each coal were exposed to air with protection from dust or other contamination insured. The remaining aliquot of each coal was then swelled in a spin probe solution. The samples undergoing weathering were agitated each day to insure thorough exposure to the air. Samples were taken at 8, 14 and 35 days of weathering and swelled in a spin probe solution. The swelling solvent was removed and the spin probe retention was measured by EPR.

The three spin probes used in this study are shown in Figure 1. Spin probes 3-carboxy-2,2,5,5-tetramethylpiperidine-1-oxyl (VI), TEMPAMINE (VII) and TEMPO (VIII), were chosen so that changes in both physical structure and proton donor/acceptor characteristics could be observed. All three have similar molecular volumes, but different chemical reactivities with the coal structure. A detailed description of the experimental method for the intercalation of spin probes using swelling solvents has been previously published.[4,5]

RESULTS

Vacuum Drying

Vacuum drying fresh coals caused a weight loss that was consistent with the reported[6] moisture content of each APCS coal. The dried coal increased upon weathering. A typical example is given in Figure 2 for Beulah-Zap lignite where the data of weight loss from the previous study of coal after weathering[3] is plotted with the vacuum dried coal weight change. Both plots converge to a point which represents about 76% of the original water contained in the coal. It would appear that an equilibrium point is reached after approximately 25 days of weathering. For Fresh Beulah-Zap, the weight loss upon weathering was found to have the following dependence on time:

$$\text{Total weight lost} = 26.36x / (2.077 + x), \text{ where } x = \text{days of weathering.}$$

For vacuum dried Beulah-Zap, the weight increase with weathering is :

$$\text{Total weight lost} = 8.838e^{-0.1238x} + 24.10$$

It is clear that during weathering coal reaches a equilibrium where its moisture content is relatively constant.

Weathering

The spin probe retention for vacuum dried coals, fresh coals and fresh coals weathered in air for one week swelled in a spin probe VI solution of toluene is shown in Figure 3A. All coals except Beulah-Zap show an increase in spin probe retention over fresh coals upon vacuum drying. Illinois #6 at point (g) exhibits the largest increase in retention upon vacuum drying or weathering (over 2×10^{18} spins per gram of coal). Beulah-Zap coal, on the other hand displays a decrease in retention of spin probe VI which is nearly as intense as the increase shown for Illinois #6 coal. It can also be seen that the spin probe retention data for vacuum dried coals and fresh coals weathered for one week are very similar.

Upon vacuum drying or weathering Beulah-Zap, a large decrease in accessibility occurs for spin probe VII in toluene (*a*), as shown in Figure **3B**. Wyodak-Anderson coal likewise exhibits a decrease in retention of spin probe VII upon vacuum drying (*f*), but weathered Wyodak coal actually displays a slight increase in retention (*d*). Similar to the results shown in Figure 3A for spin probe VI in toluene, Illinois #6 shows a large increase in retention upon vacuum drying (*c*). However, fresh weathered Illinois #6 coal does not show any difference in retention over fresh coal (*e*). The other coals over 81% carbon (dmmf), Blind Canyon, Pittsburgh #8, Lewis Stockton, Upper Freeport and Poccahontas #3, show increased retention upon vacuum drying or weathering and negligible differences in retention for vacuum dried and fresh weathered coal.

Little difference is detected for spin probe VIII retention in toluene for most APCS coals as shown in Figure 3C. Initial vacuum drying has a small effect except for Beulah-Zap which shows a significant decrease in accessibility of spin probe VIII. Blind Canyon coal also exhibits a higher retention for fresh weathered coal over fresh coal to a greater extent than vacuum dried coal (points *a* and *f*).

Upon vacuum drying Wyodak-Anderson, a decrease in retention occurs for spin probe VI in pyridine as shown in Figure 4A (*a*), and a significant increase in retention is observed for Beulah-Zap at point (*b*). All of the other coals show very little change in retention characteristics upon vacuum drying or weathering.

As shown in Figure 4B at point (*a*), Illinois #6, Blind Canyon, Pittsburgh #8, Lewis Stockton and Upper Freeport all exhibit unusually high retention of spin probe VII in pyridine upon vacuum drying. Beulah-Zap likewise shows improved retention upon vacuum drying as indicated at point (*e*), and, in fact, Wyodak-Anderson is the only coal for which vacuum drying produces a significant decrease in spin probe retention.

As seen in Figure 4C for coals swelled in pyridine with spin probe VIII vacuum drying causes an increase in retention for Beulah-Zap and the medium ranked coals.

DISCUSSION

The results shown in Figure 2 suggest that part of the water in coal is tightly bound since vacuum dried coals absorb water when exposed to air. The data indicates that for Beulah-Zap coal, approximately 76% of the moisture can be easily removed by drying in air and that the remaining 24% requires more intensive methods. This is consistent with other drying studies of lignites and subbituminous coals.[7-9] Recently, Miknis et al. found that after 75% of the water had been removed from Eagle Butte, Wyoming subituminous coal, greater amounts of energy were required to achieve additional water removal.[7] Likewise, Vorres determined that there were at least two different types of water present in low ranked coal and that a transition to a much slower drying mechanism occurs when 60% - 85% of the water has been removed.[8] This is supported by earlier work with DSC and FTIR results.[9]

In Figures 3A, B and C, a sharp decrease in spin probe retention is observed upon vacuum drying for Beulah-Zap. Since spin probe VIII has no functional group, the decrease in retention upon vacuum drying must be due to either an opening of the structure to such an extent that the spin probe is removed during the cyclohexane wash, or that a structural collapse has occurred upon drying[10] which will not allow any access of even small spin probes to the structure. If the structure were opened extensively, spin probes VI and VII, which exhibit hydrogen bonding, would still show significant retention. This, however, is not observed. Spin probes VI and VII likewise show a decrease of retention in Beulah-Zap upon vacuum drying, verifying that a structural collapse does indeed occur in Beulah-Zap, thus making it inaccessible in toluene.

Illinois #6 swelled in toluene exhibits a significant increase in the retention of spin probes VI and VII upon vacuum drying; for spin probe VI, as much as 2000×10^{15} spins per gram increase. This is shown in Figures 3A and 3B. It may be possible to explain this by assuming that the removal of water increases the number of available polar sites since Illinois #6 contains significant amounts of water, allowing for improved retention of the spin probes. However, Illinois #6 apparently contains enough cross-linking to avoid the structural collapse witnessed in Beulah-Zap.

In pyridine, significantly increased retention of spin probes VI and VII is observed upon vacuum drying in Beulah-Zap, in Figures 4A and 4B. The removal of water from the structure of Beulah-Zap should cause an increase in the number of sites available to these spin probes. While these sites are not accessible in toluene, because of that solvent's inability to reopen the collapsed structure, they are more readily available for interaction when pyridine is used as a swelling solvent because of its ability to disrupt polar interactions in the coal structure, and open up the structure to the spin probes. Looking at spin probe VIII retention in Figure 4C, it can be seen that Beulah-Zap undergoes a structural change upon vacuum drying which is detectable in pyridine, even though pyridine disrupts most hydrogen bonds and other polar interactions.

In Figure 4B, it can be seen that the medium and high ranked coals (Illinois #6, Blind Canyon, Pittsburgh #8, Lewis Stockton and Upper Freeport) swelled in pyridine, all exhibit unusually high retention of spin probe VII upon vacuum drying. This is not observed for spin probe VI shown in Figure 4A. This suggests that active sites are made available upon the removal of water, even in higher ranked coals, and that the sites must be more acidic (hydrogen bond donating) in nature since selective retention was observed for spin probe VII over VI.

In Figure 3B it is shown that for Illinois #6 swelled in toluene with spin probe VII, a much higher retention for vacuum dried coal than fresh weathered coal is observed. This would suggest that during the weathering process, the coal under goes some changes in chemical structure due to oxidation which is not sensitive to the inclusion of spin probe VI, but causes a decrease in the intercalation of spin probe VII. This indicates a reduction of accessible acid (hydrogen bond donor) sites upon oxidation.

CONCLUSION

It is shown that the removal of water and volatile components from coal during the weathering process is primarily responsible for the changes which occur in swelling character. It is also verified that the collapse of lower ranked coals during weathering is due to the removal of water. Medium ranked coals appear to have enough crosslinking to resist structural collapse upon water removal, but not enough crosslinking to prevent an opening of the structure upon swelling in mild solvents. Changes in the retention of polar spin probes in Illinois #6 coal swelled in toluene indicate that vacuum drying increases the total number of active sites available for polar interactions, but that oxidation during weathering reduces the number of available hydrogen bond donor sites. It is also shown that the removal of water can increase the retention of polar spin probes in high ranked coals swelled in pyridine.

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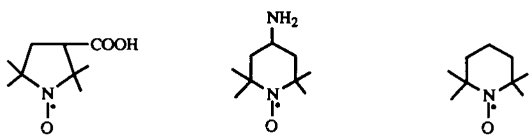
Table 1. Weight loss (%± 0.4%) of APCS coals after vacuum drying.

Coal	Carbon Content	Moisture Context	% Weight Loss
Beulah-Zap	74.05%	32.24%	32.6%
Wyodak-Anderson	76.04%	28.09%	28.0%
Illinois #6	80.73%	7.97%	----
Blind Canyon	81.32%	4.63%	4.7%
Pittsburgh #8	84.95%	1.65%	1.7%
Lewiston-Stockton	85.47%	2.43%	2.2%
Upper Freeport	88.08%	1.13%	1.0%
Pocahontas	91.81%	0.65%	0.8%



VI VII VIII

Figure 1. Spin probes VI, VII, and VIII.

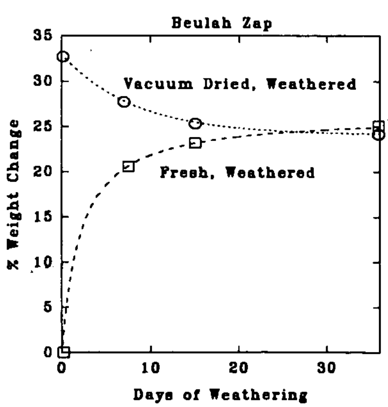


Figure 2. Percent weight change (loss) for (0) vacuum dried and (□) fresh Buelah zap coal weathered in air for 0 to 35 days.

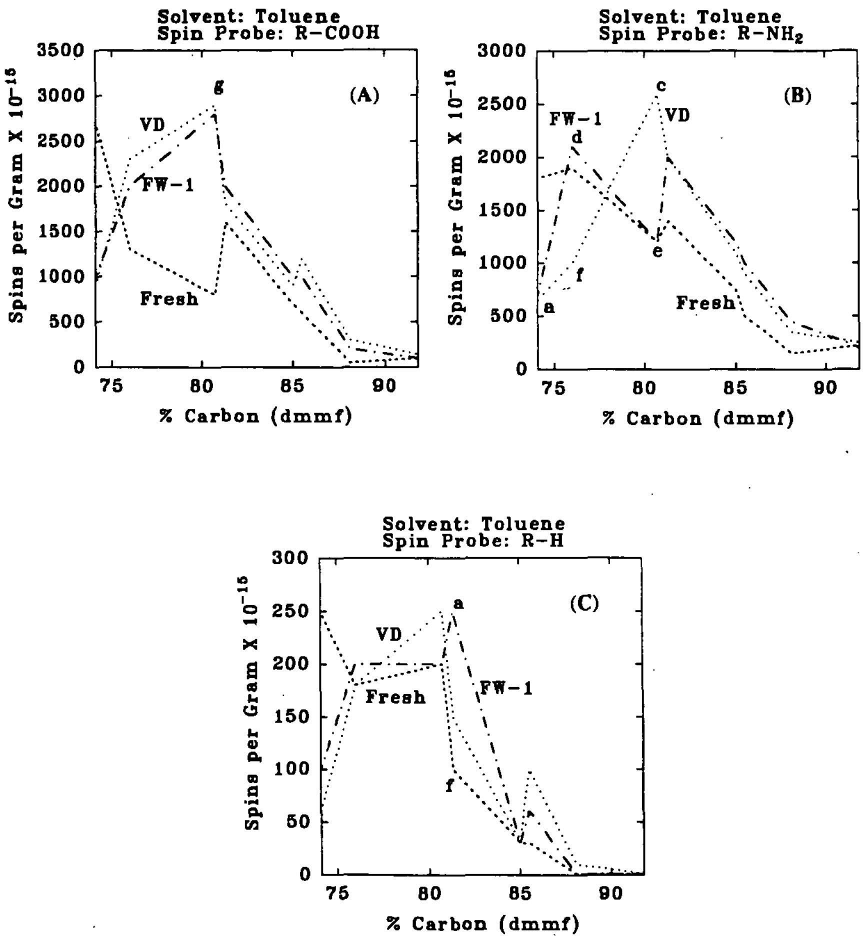


Figure 3. Nitroxide radical concentration in EPR spins per gram of coal vs. percent carbon (dmmf) with toluene as the swelling solvent. For ... vacuum dried coals (VD), --- fresh coals (fresh) and -·-- fresh coal weathered for one week (FW-1), (A) using spin probe VI, (B) using spin probe VII and (C) using spin probe VIII.

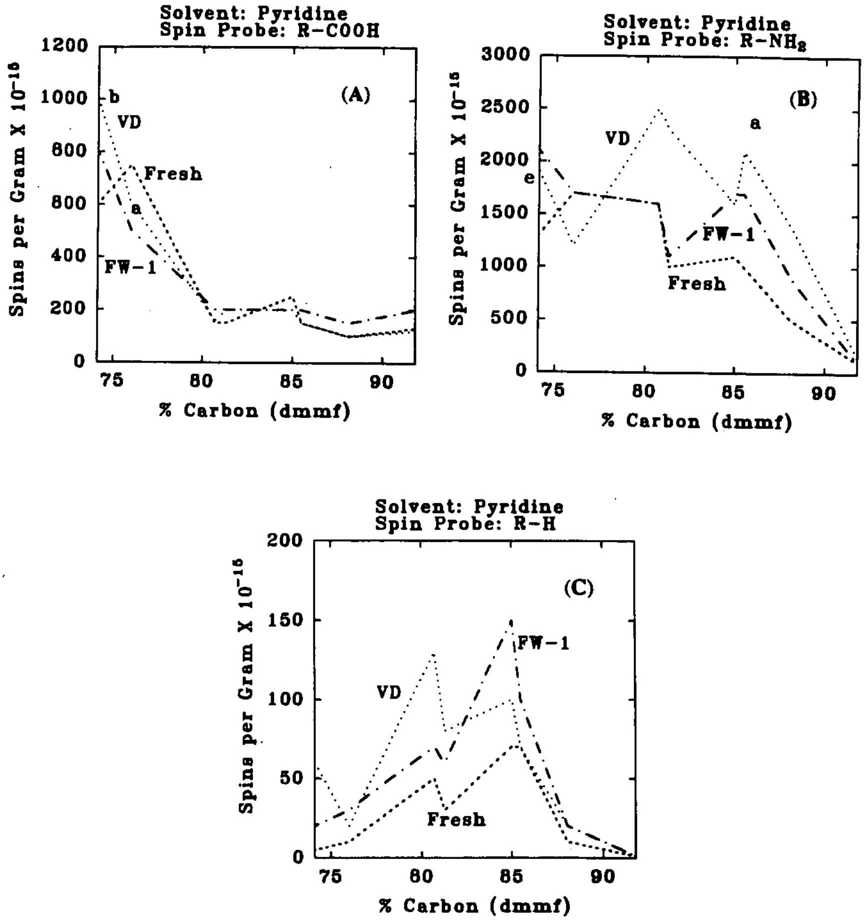


Figure 4. Nitroxide radical concentration in EPR spins per gram of vs. percent carbon (dmmf) with pyridine as the swelling solvent for ... vacuum dried coals (VD), --- fresh coals (fresh and —·—·— fresh coals weathered for one week (FW-1), (A) using spin probe VI, (B) using spin probe VII and (C) using spin probe VIII.