

## CHANGES IN MOLECULAR ACCESSIBILITY IN APCS COAL OXIDIZED IN THE PRESENCE OF SUNLIGHT

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### ABSTRACT

Weathering changes the properties of coal and its utilization through oxidative and moisture loss processes. Using an EPR-spin probe method, it has been shown that the regions in Illinois # 6 coal accessible to spin probes upon O-alkylation increase if the coal is first exposed to sunlight in air rather than to air in the absence of sunlight. Analysis reveals that an increase in oxidation products and microporosity has occurred. One plausible cause for the increase is the formation and reaction of singlet oxygen. A study of Pocahontas #3, Lewiston-Stockton and Wyodak-Anderson coal in which the oxygen content varies from 2% to 17% shows that the accessibility of spin probes in toluene swelled oxidized coal depends also on the percent oxygen present and time of exposure to sunlight.

### INTRODUCTION

An EPR spin probe method developed in this lab<sup>1</sup> has been used to determine micropore size distribution and acid/base character during swelling<sup>2-4</sup>, changes in pore structure and wall chemistry upon swelling at different temperatures and with solvents of various polarities<sup>5,6</sup>, the break-up of the hydrogen bonding between the bedding planes<sup>7</sup>, and the accessible nature of the covalently cross-linked materials during swelling<sup>8</sup>. This technique has been used successfully to follow changes in the micropore structure during weathering, oxidation, dehydration, and short term oxidation<sup>9-12</sup> of APCS coal.<sup>13</sup> Upon weathering the lower ranked coals (Beulah-zap and Wydak-Anderson) were observed to undergo structural collapse which precluded retention of even the smallest probes, while medium ranked coals exhibited improved retention.<sup>9</sup>

### PREVIOUS STUDIES ON COAL OXIDATION

Eight vacuum dried APCS coals were oxidized in a pure O<sub>2</sub> environment as well as weathered in air so the effect of oxidation alone on coal structure could be determined.<sup>10,11</sup> It was shown that the removal of water was primarily responsible for the structural collapse observed in low ranked coal and for the increase in retention of polar spin probes in medium ranked coals.<sup>10</sup> Coals oxidized in a pure oxygen environment showed an increase in retention by as much as a factor of five.<sup>11</sup> Even the higher ranked coals showed significant retention of polar spin probes after four days exposure to oxygen. Short term exposure<sup>12</sup> of Illinois #6 to dry argon or oxygen showed a dramatic change in the coal structure in as little as thirty seconds. Long term weathering for as long as six months was carried out<sup>14</sup> to show that for Beulah-Zap, Illinois #6, and Upper Freeport coals little change occurs after weathering for thirty-six days. However, this is not true for Wyodak Anderson, Blind Canyon and Lewis-Stockton coals which undergo changes throughout the six months weathering period.

It has also been established that the inclusion of spin probes into the macromolecular structure of coal increases in a dramatic oscillatory manner by spiking a "poor" swelling solvent (toluene) with as little as 100 ppm of a strong swelling solvent (pyridine).<sup>15</sup> This has been explained in terms of four different processes: (1) disruption of weak hydrogen bonds which isolate the interconnected micropore system; (2) disruption of weak hydrogen bonds which protect individual micropores; (3) competition of pyridine for the active sites involved in the hydrogen bonds or the "poisoning" of sites; and (4) disruption of stronger hydrogen bonds within the macromolecules which causes an opening of the structure.

These processes were confirmed when the hydroxyl substituents were derivatized<sup>16</sup> with *n*-butyl groups in the absence of oxygen and light. The dramatic cyclic variation was eliminated due to the decrease in hydrogen bonding. It was also shown that a dramatic increase in spin probe retention occurred upon alkylation due to the existence of a more open structure (increasing microporosity) as a result of a decrease in attractive forces, and it was noted that the microporosity increased with increasing rank. In particular, upon O-alkylation, the relative value of the spin probe concentration increased by a factor of 4 for Beulah-Zap lignite (19.1% O), 2.5 for Wyodak-Anderson subbituminous (16.9% O), 5 for Illinois #6 (10.1% O), 3 for Blind Canyon (10.9% O), 1.3 for Pittsburgh #8 (6.9% O), 5.4 for Lewiston-Stockton high volatile bituminous coal (6.7% O), 10 for Upper Freeport medium volatile bituminous (4.7% O) and 6 for Pocahontas #3 low volatile bituminous (1.5% O). Previously published work by Liotta, Rose, and Hippo<sup>17</sup> indicated that an increase in microporosity occurs upon alkylation and that this increase is more pronounced in higher than lower ranked coals. Our measurements confirm these results. We also observed that the increase in microporosity depends on the structure of

each coal; Pittsburgh #8 and Lewiston-Stockton have almost identical oxygen content (6.9% vs. 5.7%) yet exhibit a large difference in the change in microporosity upon O-alkylation (1.3% vs. 5.4%). A similar effect was also observed for Illinois #6 and Blind Canyon (5% vs. 3%), although the difference is smaller for these coals which contain a higher percentage oxygen.

Oxidation processes of the coal have been studied by other methods as well. The oxygen content of coal has been determined by neutron activation analysis<sup>18</sup> and by XPS analysis of the coal surface.<sup>19,20</sup> Oxidation has also been measured by noting the relative changes in the FTIR signatures,<sup>21</sup> pH,<sup>22</sup> Gieseler fluidity,<sup>23,24</sup> pyrolysis response,<sup>25,26</sup> and free swelling index.<sup>27</sup> Low temperature oxidation must be quantified even though the amount of solid oxidation products is small.<sup>28</sup> XPS measurements in conjunction with GC analysis of the gaseous products and thermal gravimetric analysis (GA) of the fuels<sup>29</sup> have been useful in determining the oxidation process. Oxidation-induced structural changes of APCS at 120 °C were observed by differential scanning calorimetry (DSC) and solvent swelling.<sup>30</sup> The changes in the free radical character of Alberta coals upon air oxidation between 20-250 °C have been studied<sup>31</sup> as a function of mineral, moisture, and exinite macerate content. Water was also found to be a suitable probe molecule for the detection and measurement of coal oxidation.<sup>32</sup> Although a number of studies have been carried out, the influence of sunlight on the weathering process has not been studied and is the subject of this paper.

### EXPERIMENTAL

The coal samples were irradiated by sunlight in the air on a clear day (30-40 °F) when the relative humidity was about 40%. A portion of the samples was swelled in toluene after exposure to sunlight, another was alkylated after exposure according to published methods<sup>17</sup> and a third portion was kept in the dark and then swelled.

A 40 mg unmodified sample of each APCS coal was added to a 10<sup>-3</sup> M solution of the nitroxide spin probe in the swelling solvent. A spin probe was selected (in this study, VII; Tempamine<sup>15</sup>) depending on the dimensions (approximately spherical) of the coal pores to be studied or the substituents (amine) on the nitroxide molecule required to interact with various functionalities present in the coal.

Each coal and spin probe mixture was stirred vigorously under a nitrogen atmosphere at room temperature. After 18 hours, the mixture was filtered by suction, and residual solvent coating the coal was removed under reduced pressure at room temperature to collapse the coal around the nitroxide spin probe. The resulting material was washed with cyclohexane to remove any spin probe attached to the surface or trapped in large open pores of the coal, and the mixture was filtered and vacuum dried to remove the residual cyclohexane. The coal sample was packed into an EPR sample tube, evacuated, and sealed. The prepared spin probe-doped coal sample was stored at 77 K to prevent the slow 2-3 week decay of the nitroxide spin probe EPR signal at 300 K. EPR powder spectra were recorded on a Varian E-12 EPR spectrometer. Because of the presence of a large central signal due to radicals always present in coal, only the Azz nitrogen hyperfine coupling was deduced. The magnetic field was calibrated using proton NMR markers, and the microwave frequency was measured with a frequency counter. The relative spin concentration per weight of undoped coal was determined by integrating the low field EPR line and comparing it to the integrated EPR spectrum of a frozen solution of the nitroxide spin probe under study. The absolute spin concentration was determined by comparison to a Cr(III) standard from the National Bureau of Standards.

### RESULTS AND DISCUSSION

#### *Changes in the Accessible Regions of Coal after Oxidation in Sunlight followed by Alkylation*

The spin probe retention as a function of swelling solvent is plotted (Figure 1) for samples of swelled Illinois #6 O-alkylated (A) under a nitrogen atmosphere, in the absence of sunlight, (B) O-alkylated in air and in the absence of sunlight, and (C) after the coal was exposed to sunlight for 1.5 hours in air and then alkylated in air. The increase (37%) in the retained spin probe concentration upon alkylation reflects the increase in accessible regions of the coal as the coal becomes oxidized and is then alkylated. The effect of sunlight is striking. The spin probe tempamine (VII) is a base approximately spherical in shape that contains an amine substituent capable of forming strong hydrogen bonds. Since upon alkylation the hydrogen-bonding OH substituents are converted to OR groups, the possibility of binding a trapping of tempamine by such hydrogen-bonding is excluded. The fact that nevertheless considerably greater amount of the spin probe are trapped (Figure 1 C) implies that micropores similar in size to spin probe VII are formed after alkylation of the coal that was oxidized in the presence of sunlight and air, and that the spin probe is not removed by the cyclohexane rinsing.

It was also noted that for toluene swelled Wyodak-Anderson (Figure 2), a decreasing spin probe retention occurred with increasing time of exposure to sunlight in the presence of air. In the case of toluene swelled Lewiston-Stockton (Figure 3), no dependence on spin probe concentration was found on time of exposure to air and sunlight; however, for toluene swelled

Pocahontas #3 (Figure 4), the spin probe concentration increased with increasing exposure to air and sunlight. It is apparent that an increase in OH groups occurs in high rank Pocahontas #3 upon air oxidation in the presence of sunlight, i.e., that addition sites for hydrogen bonding for spin probe VII are formed. However, the opposite trend occurs for coals with high oxygen content. In oxygen rich coal, cross-linking can occur by the combination of hydroperoxide radicals with existing radicals in the coal, reducing the microporosity with increasing exposure to sunlight. As the oxygen content decreases, the cross linking mechanism decreases in importance. Thus, it is expected that no dependence on sunlight will be observed for Lewiston-Stockton, a coal with 6.7% oxygen where the presence of cross-linking is balanced by the presence of hydrogen bonding as the exposure to sunlight is increased.

#### *Sunlight Oxidation Mechanism*

A clue to the reason for the increased numbers of OH (and perhaps carbonyl) groups in samples of coal exposed to sunlight in an air atmosphere was provided by the following observation. Upon irradiating a Blind Canyon coal suspension in dichloromethane, with filtered light ( $\lambda = 300 - 390$  nm) from a 200 watt Hg cw lamp, a very intense phosphorescence peak was observed at 1277 nm. This emission is known to occur in the decay of singlet oxygen to the triplet ground state. Further such a signal was not observed upon irradiating dichloromethane ( $\text{CH}_2\text{Cl}_2$  does not absorb above 240 nm) or a coal suspension in cyclohexane (a non-swelling solvent for coal). The formation of singlet oxygen is a result of energy transfer from the excited state ( $\text{D}_2$  or  $\text{D}_1$ ) of the radicals present in undoped coal, (Figure 5) to the excited singlet  $\text{S}_1$  state of oxygen which then undergoes decay to the  $\text{T}_0$  state producing the observed phosphorescence. The coal based phenoxyl and naphthalene anion radicals, for example, absorb at 390 and 340 nm, respectively. Thus, one plausible cause for the increase in oxidized products formed in coal upon exposure to sunlight is the formation and reaction of singlet oxygen. It is also possible to generate singlet oxygen by energy transfer from irradiated toluene which absorbs at 300 nm, so the choice of solvent is crucial.

#### **CONCLUSION**

Sunlight plays an important role in the weathering process. An increase in the number of OH groups in Illinois #6 occurs upon exposure to sunlight in the presence of air or oxygen. After subsequent alkylation, the micropore structure increases by 37%. One possible reason is the formation of singlet oxygen by energy transfer from excited singlet states of the radicals. The increase in microporosity decreases with time of exposure to sunlight for coals (not alkylated) with high (17%) oxygen content. For Lewiston Stockton coal not alkylated with medium (6.7%) oxygen content, there is no dependence on sunlight but for high rank coal (2%), Pocahontas #3 (not alkylated), there is an increase in microporosity with exposure to sunlight. The formation of singlet oxygen could possibly account for the increase in oxidation products in high rank coals as a function of sunlight.

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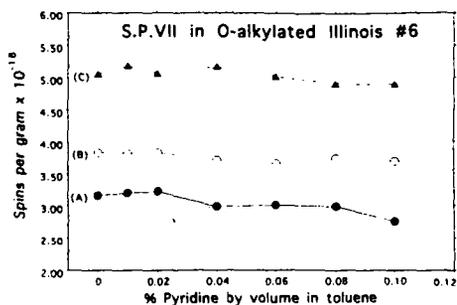


Figure 1: Spin probe VII retention concentration in O-butylated Illinois #6 versus percent pyridine by volume in toluene.

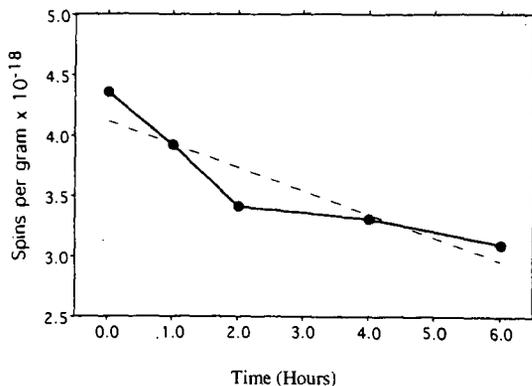


Figure 2: Toluene Swelled Wyodak-Anderson: Time of exposure to sunlight in the presence of air versus spin probe retention concentration

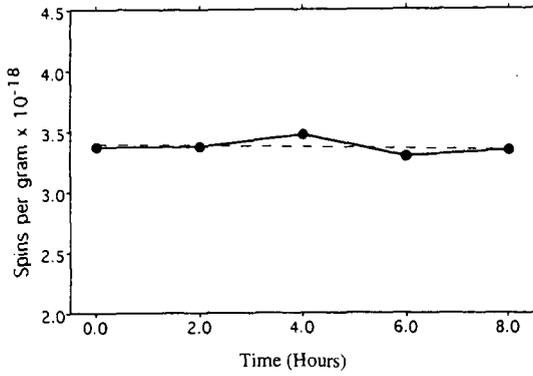


Figure 3: Toluene Swelled Lewiston-Stockton: Time of exposure to sunlight in the presence of air versus spin probe retention concentration

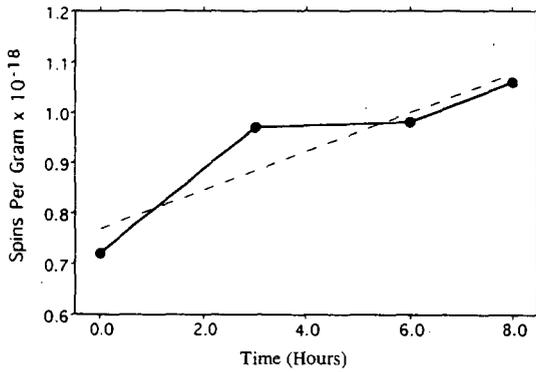


Figure 4: Toluene Swelled Pocahontas # 3: Time of exposure to sunlight in the presence of air versus spin probe retention concentration

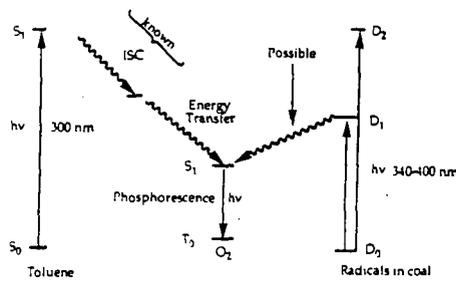


Figure 5: Energy diagram for singlet oxygen formation upon excitation of the naturally occurring radicals in coal