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Molecular Accessibility in Oxidized and Dried Coals

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INTRODUCTION

The objective of this research project is to determine the molecular and structural changes that occur in swelled coal as a result of oxidation and moisture loss both in the presence and absence of light using our EPR spin probe method. The proposed study will make it possible to deduce the molecular accessibility distribution in swelled, oxidized APCS coal as a function of sunlight for each rank as a function of (1) size (up to 6 nm) and shape, (2) the relative acidic/basic reactive site distributions, and (3) the role of hydrogen bonding as a function of swelling solvents. The advantage of the EPR method is that it permits molecules of selected shape, size and chemical reactivity to be used as probes of molecular accessible regions of swelled coal. From such data an optimum catalyst can be designed to convert oxidized coal into a more convenient form and methods can be devised to lessen the detrimental weathering processes.

PREVIOUS WORK

Long-Term Weathering of APCS coal

A detailed study of long term weathering of 8 APCS coals using spin probe VII in toluene has been reported. The intercalation of potential catalysts in APCS coal Illinois #6 during the swelling process in binary solvent mixtures was studied using spin probes with various functionalities as model guest compounds. An invited paper on the current status of spectroscopic techniques used to study the porous structure of coal has been presented. Results of long term weathering for periods up to six months of exposure to air have been analyzed for spin probes VI (3-carboxyl-2,2,5,5-tetramethylpiperidine-1-oxyl) and VIII (TEMPO).

Binary Swelling Results

Binary swelling data has been collected for all Argonne Premium Coal Samples (APCS). As the rank of the coal increased, the presence of interconnected
weak hydrogen bonds decreased and the strong oscillatory up-take of spin probes as a function of percent pyridine in toluene swelling-solvent observed at low rank$^4$ with increasing pyridine concentration, decreases markedly. The results to date for Upper Freeport and Lewiston-Stockton coals were presented$^5$ in light of the previous study of Wyodak-Anderson and Beulah-Zap coal.

Analysis of the binary swelling data for the APCS coals studied to date can be explained in terms of four different processes: one, disruption of weak hydrogen bonds which protect or isolate the interconnected micropore system; two, disruption of weak hydrogen bonds which protect individual micropores; three, the competition of pyridine for the active sites capable of establishing hydrogen bonds or the "poisoning" of active sites; four, disruption of stronger hydrogen bonds within the macromolecular structure which cause an opening of the structure. The contributions of each of these factors to the spin probe retention with increasing concentrations of pyridine vary up to 5% pyridine. At concentrations above 5% pyridine, the first factor becomes less significant, and variations in the others require greater changes in pyridine concentration.

**O-alkylation**

To further examine the swelling behavior in the presence or absence of internal hydrogen bonding using the EPR spin probe technique, known O-alkylation procedures$^6$ have been used to remove internal hydrogen bonding in APCS coal samples by derivatizing the hydroxyls. Removing the internal hydrogen bonding prevents the polar spin probe retention. On the other hand, an increase in coal swelling by nonpolar solvents such as toluene has been observed. By swelling O-alkylated APCS coals in nonpolar as well as polar solvents using spin probes VII
and VII yield the spin probe retention as a function of rank when internal hydrogen bonding due to hydroxyls is removed.

Papers have been published on the Influence of Binary Swelling Solvents\textsuperscript{7} and on the Swelling Behavior of O-Alkylated APCS Coal\textsuperscript{8,9}. It was found that upon O-alkylation, the hydrogen bonding is removed and the microporous structure increases in size. The strong oscillatory variation in spin concentration as a function of percent pyridine in a toluene swelling solvent was eliminated. A paper was presented in the coal Liquefaction/Coprocessing Symposium of the National ACS meeting held in Orlando, FL, Aug. 25-29 entitled "Changes in Molecular Accessibility in APCS Coal Oxidized in the Presence of Sunlight." This study was carried out for Pocahontas #3, Lewiston-Stockton and Wyodak-Anderson coal in which the oxygen content varied from 2\% to 17\%. A paper subsequently published\textsuperscript{10} (reprint attached) on the topic examined the reason that sunlight played an important role in the weathering process. One possible reason is the formation of singlet oxygen by energy transfer from the excited singlet states of the naturally occurring naphthalene and phenoxy anion radical in the coal to the singlet excited state of oxygen.

**SUMMARY OF CURRENT ACTIVITIES**

The effect of sunlight on the weathering of APCS coal has been carried out for Beulah-Zap (~20\% oxygen content), Illinois #6 (~14\% oxygen content) and Upper Freeport coal (~8\% oxygen content). Plots of spin probe uptake for coal swelled in toluene versus time (0 to 10 hours) of exposure to air and sunlight has been recorded. A decrease in spin probe uptake by a factor of two over that found for exposure to air in the absence of light was observed to occur for Beulah-Zap (Fig. 1). No dependence on sunlight was detected for Illinois #6 and an approximate 50\%
increase in spin probe uptake occurred for Upper Freeport (Fig 2) upon exposure to sunlight over a 10 hour period. It appears that the trend as a function of oxygen content in the coal follows the same dependence as found earlier for Pocahontas #3, Lewiston-Stockton and Wyodak-Anderson. Upon alkylation, it was previously deduced that cross-linking by the combination of hydroperoxide radicals with radicals existing in the coal occurred for oxygen rich Wyodak-Anderson and also presumably - Beulah-Zap. As the time of exposure to sunlight increased a decrease in molecular accessibility (decrease in spin probe VII uptake) occurred due to an increase in cross-linking character. However for high rank coal (Pocahontas #3 and also presumably Upper Freeport), this effect was not present to any significant degree and the increase presence of functional groups and subsequent hydrogen bonding caused an increase in the uptake of polar spin Probe VII. These two mechanism essentially counter-balanced each other for Lewiston-Stockton or in the present case of Illinois #6. Further study of this effect will require alkylation of the coal after exposure to sunlight. So far it has been determined that the microporosity depends on the structure of the coal; coals with similar percent oxygen content do not show the same percent increase in microporosity. In oxygen rich coal, evidence exists for crosslinking as a function of exposure to air and sunlight.

STUDIES PLANNED FOR NEXT QUARTER

The uptake of spin probe VII will be measured for Upper Freeport after the sample has been exposed to air and sunlight and then alkylated. This will give some measure of the hydrogen bonding that contributes to the molecular accessibility in high rank coal.
REFERENCES


Figure 1. Uptake of spin probe VII in Beulah-Zap coal swelled in toluene after exposure to air as a function of sunlight. The dashed line is a straight-line average. Over this same period of time, the uptake in the absence of light decreases by 10%.

![Graph showing uptake of spin probe VII in Beulah-Zap coal.](image)

Figure 2. Uptake of spin probe VII in Upper Freeport swelled in toluene after exposure to air as a function of sunlight. The dashed line is a straight-low average. Over this same period of time, the uptake in the absence of light decrease by 10%.

![Graph showing uptake of spin probe VII in Upper Freeport.](image)