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ROLE OF PREASPHALTENES IN COAL CONVERSION REACTIONS

Second Quarterly Report, Year Two

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ROLE OF PREASPHALTENES IN COAL CONVERSION REACTIONS
SECOND QUARTERLY REPORT
YEAR TWO

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I. WORK PERFORMED

The plans for the second year in the present contract called for application of analytical methods developed in the first year to the elucidation of the role of preasphaltenes in the coal conversion processes. As introduced and discussed in the last quarterly report, recent experiments have demonstrated the necessity of also studying the influence of weathering processes on coal structures and reactivity especially in regard to the production of preasphaltene-rich, short contact time (SCT) pyrolyzates. In this report we review and further develop some of the results presented in the last quarterly report as well as new information obtained in the second quarter. These results and their implications to initial coal structure and the role of preasphaltenes are discussed in respect to the following four tasks:

1. Study of the effects of laboratory weathering on the Free Swelling Index (FSI), sample weight, calorific value and ASTM proximate analysis on hvb Hiawatha coal.
2. Thermogravimetry (TG) and Derivative Thermogravimetry (DTG) of fresh and weathered hvb coal samples.
3. Pyrolysis mass spectrometry (Py-MS) analysis of fresh and weathered hvb coal samples and detailed examination of weathering effects.
4. Py-MS comparison of vacuum and pyridine extracts and SCT tubing bomb reactor products from fresh and weathered coals.

Task 1. Weathering Effects on Coal FSI, Weight, Calorific Value and Proximate Analysis

Several hundred pounds of samples were obtained from the top, middle and bottom of freshly exposed cross sections of the Hiawatha and Blind Canyon seams and immersed in water until being crushed and milled to < 60 mesh in a nitrogen atmosphere. All sample storage took place under nitrogen in hermetically closed glass bottles at -20°C in the dark. In the laboratory weathering experiments, 10-15 g aliquots of < 60 mesh coal were exposed to different temperatures and atmospheric conditions (N₂ or air; dry or H₂O saturated) for periods up to several weeks using a specially constructed bench scale weathering system as described in the first quarterly report. FSI determinations were performed according to ASTM Standard D-720-67, whereas standard ASTM proximate analysis, calorific value and total sulfur determinations were carried out by Standard Laboratories (Huntington, Utah).

The FSI was found to be a highly sensitive indicator of the weathering status of these coals with a slight, but measurable drop in FSI value occurring overnight upon exposure of fresh coals to air at room temperature. Typical FSI weathering profiles are shown in Figure 1. Since coal weathering is often accompanied by complex weight changes due to the interplay of fluctuations in moisture content and oxidative phenomena, a series of weathering experiments was carried out while carefully

monitoring changes in sample weight, as shown in Figure 2. Weight corrected weathering trends of several conventional parameters are illustrated in Figure 3a and Table I showing how misleading results are obtained if the original weight of the nonweathered sample is unknown (as is usually the case). Note that the weight corrected change in calorific value is -1.1% after 96 hours at 80°C in air and -2.1% at 100°C in air.

Task 2. TG and DTG Effects of Weathering

More informative about changes in reactivity and structure are the Thermogravimetry (TG) and Derivative Thermogravimetry (DTG) data in Figures 4 and 5. The TG/DTG analyses were performed with a Mettler I thermal analyzer under the following conditions: (initial pyrolysis run) sample weight approx. 10 mg, nitrogen flow 100 ml/min., heating rate 15°C/min, end temperature 800°C, (subsequent char combustion run; after cooling down) air flow 100 ml/min, heating rate 15°C/min, end temperature 1000°C.

The TG/DTG pyrolysis data in Figures 4a and 5a would seem to support a weathering mechanism dominated by the formation of crosslinks between coal molecules, thereby causing a widening of the temperature range of the pyrolysis process and a decrease in the maximum pyrolysis rate accompanied by increased char yields while having little or no influence on the maximum rate temperature (~450°C). The results of the char combustion runs in Figures 4b and 5b indicate a similar kinetic trend (decreased reaction rate and increased temperature range) but are less definitive due to a lower level of reproducibility than in the pyrolysis runs.

Task 3. Py-MS Study of Laboratory Weathering Effects

Curie-point pyrolysis mass spectrometry (Py-MS) gives the most informative data on the effects of weathering as shown in Figures 6, 7, 8 and 9. The analyses were performed with an Extranuclear 5000-1 instrument under the following conditions: sample weight 20 µg (deposited from a fine suspension in MeOH), heating rate approx. 100°C/s, end temperature 610°C, total heating time 10 s, electron energy 12 eV, mass range scanned m/z 20-260, total number of spectra summed 150, total scanning time 30 s. Computerized data analysis involved normalization of signal intensities by means of the NORMA program [1] followed by factor analysis, discriminant analysis and canonical variate analysis using the SPSS program package [2].

Inspection of the pyrolysis mass spectra in Figure 6 shows the structural effects of weathering to be dominated by a decreased yield of phenolic and naphthalenic moieties and a relative increase in the yield of aliphatic carboxylic and carbonylic moieties, as further illustrated by the scatter plots of selected peak intensities in Figure 7. These findings are in excellent agreement with current views on chemical effects of coal weathering, according to which the process is characterized by the formation of ether bridges between aromatic nuclei with concurrent

reduction in free phenolic hydroxyl groups [3], and by the oxidation of aliphatic moieties to carbonylic and carboxylic functional groups [4]. A more detailed picture of the complex changes in the pyrolysis mass spectra can be obtained by means of multivariate analysis techniques such as discriminant analysis, as illustrated in Figure 8. The application of these techniques to the evaluation of pyrolysis mass spectra of coal has been described elsewhere [1,5,6]. The discriminant analysis results in Figure 8 show that: (a) the first discriminant function exhibits no detectable changes in the coal spectra upon "weathering" at 80°C in a nitrogen atmosphere, (b) weathering effects at 80°C and 100°C in air show strong quantitative differences, (c) several other series of aromatic, hydroaromatic and hydroxyaromatic compounds appear to decrease besides phenols and naphthalenes, and (d) the changes in aliphatic moieties are much more complex than the simple formation of carbonylic and carboxylic groups. Examination of the second discriminant function (not shown) confirmed the absence of detectable changes at 80°C in N₂ but revealed the presence of slight but significantly qualitative differences between the 80°C and 100°C weathering trends, apparently reflecting transient chemical phenomena (peroxide formation?) during the weathering process.

Although, at first sight, the "classical" coal weathering concept of crosslinking through ether bridge formation between macromolecular chains appears to fit our observations quite well, modern view of vitrinite as a binary system consisting of a "mobile" phase and a macromolecular "network" phase necessitate a rethinking of the crosslinking concept. The binary phase model, recently summarized by Given [7], assumes that up to 50% or so of the bulk of the coal sample consists of relatively small, mobile molecules trapped in cages formed by a macromolecular network which makes up the remainder of the bulk. Direct evidence for the presence of a trapped mobile phase can be obtained by Time-resolved Py-MS, as shown in Figure 9. Approximately 50% of the C₂-alkylnaphthalene signal in Figure 9 is recorded well below typical pyrolysis temperatures for covalent bonds but far above the expected vacuum binary phase system as presented in Figure 10, demonstrating that, in principle, three possibilities for intermolecular bond formation exist in such a system: (1) "crosslinking" between network chains, (2) "condensation" between mobile phase constituents, and (3) "grafting" of mobile phase constituents onto the network chains.

Task 4. Py-MS Analysis of Vacuum and Pyridine Extracts and SCT Reactor Products from Fresh and Weathered Coals.

To obtain a better insight into the behavior of the two phases, fresh and artificially weathered (212 hours at 100°C in air) hiawatha coal samples were submitted to vacuum distillation (30 hours at 180°C and 10⁻³ Torr), pyridine extraction (24 hours in Soxhlet extractor), short contact time (SCT) pyrolysis in a tubing bomb reactor (2.5 g coal in 5.0 g benzene, heating rate 20°C/s, end temperature 420°C, total heating time 40 s, H₂ pressure 1,000 psi initial to 1,700 psi final) and direct Curie-point Py-MS (1.5 X 10⁻⁵ g coal in vacuo, heating rate 100°C/s, end temperature 610°C, total heating time 10 s). Subsequently, the distillates, extracts or pyrolyzates, as well as the residues were analyzed by Py-MS. Preliminary results are shown in Table II and illustrate the dramatic effect of weathering on vacuum distillation yields, pyridine extraction yields and SCT tubing bomb reactor (TBR) pyrolysis yields. The yield of

the small vacuum distillate fraction (4%, dominated by alkylnaphthalenes; see Figure 11a), shows a fourfold decrease upon weathering. The much larger pyridine-extractable fraction 22%, also dominated by alkylnaphthalenes but containing significant contributions from other aromatic moieties; see Figure 11b) decreases by a factor of five to six after weathering.

Hydroxyaromatics (e.g, phenols, dihydroxybenzenes), which are among the most abundant homologous ion series in pyrolysis mass spectra of fresh whole coals (see Figure 11d) are nearly absent in the vacuum distillate (Figure 11a) and relatively low in the pyridine extract (Figure 11b) but make a more prominent appearance among the SCT-TBR products shown in Figure 11c. Probably these hydroxyaromatics are partially produced through pyrolytic bond scissions and thus may represent the network phase. Additional support for this contention is provided by the much smaller reduction factor (2X) for the SCT-TBR yields from weathered coal.

A speculative interpretation of these finds might envisage a mobile phase representing 20-30% of the bulk of the fresh Hiawatha coal and undergoing a 4-6 fold reduction under the above weathering conditions. Presumably, this reduction is due to the formation of strong (diarylether?) bonds with hydroxyaromatic moieties in the network phase ("grafting"; see Figure 10). On this view, SCT pyrolysis results in partial degradation of the network into hydroxyaromatic compounds and other small, mobile molecules. However, the pyrolysis conditions used appear to leave most of the new bonds formed in the weathering process intact, thus resulting in a marked decrease in overall pyrolysis yields from weathered coals.

Visual comparison of the four MS patterns in Figure 11 reveals an obvious trend towards increasing complexity from the vacuum distillate (Figure 11a) to the Curie-point pyrolyzate (Figure 11d). For the first three fractions this trend corresponds directly with increasing yields (from 4% for the vacuum distillate to 30% for the TDR pyrolyzate) and, if extrapolated, would indicate a yield of between 40-50% for the Curie-point pyrolyzate, which is in good agreement with previous estimates for hvb Utah coals [5].

At the same time, these observation highlight the fact that under SCT pyrolysis conditions some 50% of the (m.a.f.) coal forms a char. This char, which is difficult to analyze by most techniques currently available, might incorporate as much as 2/3 of the network phase. This leads to the question whether the pyrolysis products obtained from the network phase are representative for the overall chemical structure of the network. In his comprehensive discussion of the binary phase nature of coal, Given [7] concludes that in spite of all available data from sophisticated analytical methods, including FTIR and ^{13}C NMR, the chemical nature of the network phase remains pretty much a mystery.

If the binary phase concept is valid indeed, much effort will have to be devoted to the elucidation of key structural features of the macromolecular network if a more comprehensive picture of the effects of weathering on the structure and reactivity of coals is to be obtained within the foreseeable future.

II. HIGHLIGHTS OF THE SECOND QUARTER

1. Mild oxidation of a freshly mined, anaerobically sampled, hvb Hiawatha coal under controlled environmental conditions was found to cause a drastic reduction in the FSI as well as significant changes in the calorific value and proximate analysis of hvb coals.

2. TG and DTG analysis of weathered samples showed a widened pyrolysis temperature range and decreased maximum pyrolysis rate.

3. The mild oxidative weathering of the hvb Hiawatha coal caused a drastic reduction in the overall vacuum and pyridine extraction yields as well as SCT pyrolysis yields in general and in the yields of polar preasphaltene-type products in particular.

4. Computerized pyrolysis MS analysis of the weathered coal, coal extracts and SCT reactor products revealed clear structural changes such as a marked decrease in (hydroxy)aromatic and (hydroxy)hydroaromatic moieties accompanied by a relative increase in the abundance of polar, aliphatic products.

5. Because of the dramatic influence of weathering, literature data on coals of unknown weathering status should be interpreted with great caution. Therefore it is imperative to study the influence of weathering on the reactivity and structure of fresh, anaerobically handled coal samples.

6. On the basis of the above findings and in light of new structural concepts of coals as a binary mobile phase/network phase system, a novel subdivision of ether bridge forming weathering processes into "cross-linking", "condensation" and "grafting" mechanisms was proposed.

7. "Grafting" was found to be the mechanism most likely responsible for the observed weathering phenomena in hvb Hiawatha coal.

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TABLE I
EFFECT OF WEATHERING ON CALORIFIC VALUE

Calorific Value (BTU)	Fresh	80°C in N ₂ 120 hours	Δ* (%)	80°C in air 96 hours	Δ* (%)	100°C in air 96 hours	Δ* (%)
- as received	12028	12556	+4.4	12299	+2.3	12063	+0.3
- dry	12457	12575	+0.9	12318	-1.1	12078	-3.0
- weight corrected	12028	12003	-0.2	11893	-1.1	11773	-2.1

* difference with corresponding "fresh" value.

TABLE II
WEATHERING EFFECTS ON HIAWATHA COAL PROCESS YIELDS

Process	% Yield	
	Fresh Coal	Weathered Coal
Vacuum Distillation	4	1*
Pyridine Extraction	22	4
SCT-TBR Pyrolysis	38	17

* Value from a single experiment; all other values averaged from two or more experiments.

Figure 1. Effect of weathering at 50°C in air on FSI of coal samples from 1 Blind Canyon and 2 Hiawatha seams mines.

Figure 2. Effect of weathering on weight of Hiawatha seam coal. Note usefulness of control samples in N₂ for distinguishing effects of moisture loss (~4.4%) from effects of oxidative weight gain. Error bars represent range of values for three independently weathered aliquots.

Figure 3. Effect of weathering on proximate analysis of Hiawatha coal.

Figure 4a and b. Effects of weathering on TG/DTG profiles of Hiawatha coal. Each curve averaged from three replicate runs. W_0 =original sample weight. — fresh coal; weathered at 80°C in air (96 hours); weathered at 100°C in air (96 hours).

Figure 5a and b. Effects of weathering on selected TG/DTG parameters. The "Reaction Temperature Range" is defined as the temperature range over which the (pyrolysis or combustion) reaction rate is $>3\%$ of the maximum rate (compare with Figure 4). Data points on replicate weathering experiments connected by solid lines.

Figure 6. Curie-point mass spectra of fresh and weathered Hiawatha coal samples. Note high degree of similarity between spectra a) (fresh coal) and b) (80°C in N₂) and obvious changes in spectra c) (80°C in air) and d) (100°C in air). Overall weathering effects appear to be: decreased aromatic series; increased carbonylic (C_nH_{2n}O) and carboxylic (C_nH_{2n}O₂) series; decreased H₂S peak (m/z 34); increased CO₂ (m/z 44) and SO₂ (m/z 64) peaks; increased MeOH solvent retention (m/z 23); altered distribution of aliphatic hydrocarbon series. The phthalate fragment ion peak at m/z may be due to contamination.

Figure 7a and b. Scatter plots of selected ion intensities from the pyrolysis MS data set (compare with Figure 6) showing the effects of weathering on alkylphenol signals (strong decrease; see Figure 7a) and on short chain carboxylic acid signals (marked increase, see Figure 7b).

Figure 8. Discriminant score plot and associated "discriminant spectra" obtained on pyrolysis mass spectra of fresh and weathered Hiawatha coal samples (see Figure 6). Air and N₂ exposures were carried out with three different aliquots analyzed in triplicate, resulting in 27 spectra representing 3 categories (80°C in N₂, 80°C in air, 100°C in air). The triplicate spectra of the fresh coal sample were treated as "unknowns" in the discriminant analysis procedure. The two spectra correspond to the positive (DI⁺) and negative (DI⁻) components of the discriminant function.

Figure 9. Time-resolved recording of the mass peaks at m/z 156 (mainly C_2 -alkylnaphthalenes), m/z 158 (e.g., methylnaphthol and/or C_2 -alkyl dihydronaphthalenes) and m/z 160 (e.g., C_2 -alkyl tetralins) during Curie-point pyrolysis of a 20 μ g sample from a hvb Wasatch Plateau coal. Note bimodal character of the signal at m/z 156.

Figure 10. Highly schematized representation of all three possible types of weathering-induced bridge formations is a binary phase (mobile phase/network phase) coal model.

Figure 11. Curie-point desorption/pyrolysis mass spectra of tar fractions from a nonweathered ("fresh") Hiawatha coal obtained by different techniques. Compare with Table I. Note increasing complexity from a to d (exaggerated in d by the presence of gaseous, low molecular weight products, e.g., alkenes, lost during collection of a-c). Peaks labeled "P" represent pyridine residues and/or background signals.

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