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ROLE OF PREASPHALTENES IN COAL CONVERSION REACTIONS

First Quarterly Report, Year Two

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

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I. INTRODUCTION

Whereas the first year of the present contract was devoted primarily to the development of improved analytical techniques, the plans for the second and final year called for the application of these methods to studies aimed at elucidating the role of preasphaltenes in coal conversion reactions.

Prior experiments with fresh and weathered coals, however, had provided us with strong indications for the existence of a marked influence of weathering processes on coal structure and reactivity in general and on the production of preasphaltene-rich, short-contact-time (SCT pyrolyzate in particular).

Thus we decided to perform SCT pyrolysis experiments on coals of known weathering status (e.g., freshly mined or artificially weathered coals) with the aim of investigating possible changes in the yield and the relative abundance of preasphaltene type components.

During the past decade, coal scientists and technologists have become increasingly aware of the potentially dramatic effects of oxidation ("weathering") on the structure and reactivity of coals. Presently known effects range from autoignition in mines and piles to changes in moisture content, loss of caking properties, decreased calorific value, reduced liquefaction yields and altered char properties. A comprehensive review of the more recent literature, carried out as part of our studies, is included in this report.

Because of a lack of generally accepted and standardized analytical procedures for determining the degree of weathering (the "weathering index") of a given coal sample, most data on structure and reactivity

reported in the literature thus far have been obtained on coal samples of uncertain weathering status and should therefore be interpreted with great caution.

Until recently, this situation was compounded by the unavailability of "nonweathered" reference samples since some coal samples available from reference collections such as the Penn State/DOE coal sample bank were found to exhibit signs of weathering. Fortunately, a new collection of standard coal samples (the Premium Coal Sample Program) is now being established at Argonne National Laboratory under the most stringent collection, preparation and storage conditions.

II. WEATHERING EXPERIMENTS

An investigation of the weathering behavior of hvb Utah coals was prompted by the discovery of FSI values as high as 4.0 in coals obtained directly from fresh mine cuts in the Hiawatha and Blind Canyon seams [1]. Until then, these coals from the Wasatch Plateau field (Uinta region, Rocky Mountain province) were generally considered to be noncaking. Moreover, FSI values ≥ 2.0 might interfere with pyrolytic conversion schemes (e.g., Lurgi and Toscoal) currently under consideration by Utah Power & Light Company [2].

A bench scale coal weathering system was constructed as shown in Figure 1 and the FSI of several Wasatch Plateau coals monitored under different temperature, oxygen and moisture conditions for periods up to several months. 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 2.

Coal weathering is often accompanied by complex weight changes due to the interplay of fluctuations in moisture content and oxidative phenomena. Therefore, a series of weathering experiments was carried out while carefully monitoring changes in sample weight, as shown in Figure 3. Weight corrected weathering trends of several conventional parameters are illustrated in Figure 4. More informative about changes in reactivity and structure are the Thermogravimetry (TG) and Derivative Thermogravimetry (DTG) data in Figure 5 and, in particular, the Pyrolysis Mass Spectrometry (Py-MS) data in Figures 6, 7 and 8.

The TG/DTG results 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 accompanied by increased char yields and little or no change in the maximum rate temperature ($\sim 450^{\circ}\text{C}$).

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 naphthaleneic 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 by Figure 8. The

application of these techniques to the evaluation of pyrolysis mass spectra of coals has been described elsewhere [5,6]. The discriminant analysis results show that: (a) no detectable chemical changes occur upon "weathering" at 80°C in a nitrogen atmosphere, (b) weathering effects at 80°C and 100°C in air show strong quantitative as well as slight qualitative differences, (c) several other series of aromatic, hydroaromatic and hydroxyaromatic compounds appear to decrease beside phenols and naphthalenes, and (d) the changes in aliphatic moieties are much more complex than simply formation of carbonylic and carboxylic groups.

III. RECENT LITERATURE ON TECHNOLOGICALLY RELEVANT ASPECTS OF COAL WEATHERING

1. COAL HANDLING PROPERTIES

A. Autoignition Tendency - Weathering frequently causes autoignition of coals in coal pits [7], during shipping or pile storage [8]. Autoignition tendencies appear to be directly related to rank [7], to particle size [8] and, possibly, to coal porosity [9]. Whereas high volatile A and B bituminous coals exhibit low porosities and autoignition tendencies, subbituminous, high volatile C bituminous C and, to some extent, medium volatile bituminous coals possess higher porosities and autoignition tendencies. In laboratory experiments [10] as well as in mathematical modelling studies [11], autoignition tendency was found to be strongly dependent on the thickness of the coal layers. Finally, some experimental data suggests that oxygen absorption in coals may be accompanied [10, 12] or promoted [13] by simultaneous H_2O absorption. This may help explain why in some instances a rainfall seems to initiate a coal pile fire.

B. Caking Properties - Changes in caking properties, especially those regarding fluidity and swelling, have been studied more extensively than any other effects of coal oxidation. It is known that coal weathering in outcrop [1] and in coal storage [1, 14] significantly reduces caking properties, as measured by FSI [1,14,15] and plasticity tests [1, 15]. Because fluidized bed and high temperature cyclone reactors require nonagglomerating coal with an FSI of 1.5 or less [14, 16], decaking procedures have been carried out under mild (e.g., 80-100°C) [17] as well as more severe (e.g., 200-250°C [9, 18] or even 360-450°C [19]) temperature conditions. At the higher temperatures, BTU losses of more than 10% (especially for low rank coals) may occur although this fact is largely ignored by most authors. There is general agreement that the underlying mechanisms controlling decaking involve formation of ether crosslinks by condensation reactions (elimination of H₂O) [18, 20, 21] resulting in coal molecules with higher average molecular weight and reduced mobility. To some extent, the decaking effects of coal oxidation can be reversed by procedures capable of breaking the ether bonds, e.g., by reaction with alkali tetrahydrofuran mixtures in the presence of naphthalene [17,20,22]. Moreover, it has been reported that phenol and naphthol additives improve caking properties of fresh (or lightly weathered) coals [20]. Finally, antioxidants [16] and surfactants [21] have been found to prevent or delay coal oxidation to a certain degree.

C. Electrostatic Charge - A marked change in the electrostatic properties of weathered coals has been described by Gray *et al.* [14]. Whereas fresh coal showed a positive electrostatic charge (up to +12 V under the test conditions described), weathered coal exhibited a negative (up to -8 V) charge. The possible role of changes in electrostatic

properties on coal handling (e.g., dry cleaning) operations does not seem to have been investigated thus far.

D. Coal Suspension pH and Flotability - Aqueous coal suspensions can show marked pH changes during weathering, e.g., from pH 8 for fresh coal to pH 5 for severely weathered coal [14]. Because pH changes may be expected to have a strong influence on the stability of aqueous coal suspensions, further investigation of this phenomenon may prove to be important for the future development of coal slurry technology. The observed marked changes in coal flotation behavior during weathering [14] are highly important for coal beneficiation procedures. Because of the loss of hydrophobicity and associated flotability during weathering, major quantities of oxidized coal may be lost during beneficiation procedures. This not only results in BTU losses but also increases the volume of refuse which has to be disposed of.

2. COAL CONVERSION PROPERTIES

A. BTU Losses - Under natural weathering conditions, BTU losses of high volatile bituminous coals appear to be limited to a few percent per year [14] (probably even less in well-packed coal piles). Although no direct estimates are found in the literature, the overall susceptibility of some low rank (e.g., subbituminous or high volatile C bituminous) coals to oxidation [9] indicates that substantially higher BTU losses may be expected for these coals under typical weathering conditions.

As discussed before, decaking procedures between 200-250°C may well result in BTU losses between 10-20% for low rank, 5-10% for medium rank and 2-5% for high rank coals [9]. As shown by our own studies [1], however, decaking a high volatile bituminous Hiawatha coal to an FSI ≤ 1.5 at 100°C for a minimum of 13 hours (based on kinetic calculations) should result in a BTU loss of only 1%.

B. Yield and Composition of Coal Derived Liquids - Tar yields (as well as volatile matter content) of oxidized coals are generally reduced by several percent [22, 23]. The oxidized coals and the tars derived from them appear to contain less phenolic hydroxyl [12, 23, 24, 25] and more carbonyl and carboxyl groups [8, 12, 24, 25, 26].

C. Yield, Strength and Reactivity of Char - Char yields (as well as Fixed Carbon content) of oxidized coals are generally increased by several percent [19, 23]. Moreover, chars of oxidized coals show increased reactivity [15] and reduced strength [14, 15, 16]. In steel-making operations this may result in overheating of the tuyeres [14] and mechanical problems with the combustion beds.

IV. LITERATURE REFERENCES

1. Hill, G.R., Meuzelaar, H.L.C., "Free Swelling Index of Utah High Volatile Bituminous Coals", Report to the Utah Power and Light Company, Contract R&D 1003-83, Sept. 1982 - Aug. 1983.
2. Thurgood, J.R., "Feasibility of Commercial Coal Pyrolysis to Produce Char and Oil", presented Synfuels 3rd Worldwide Symp., Washington, D.C., November 3, 1983.
3. Neavel, R.C., Coal Plasticity Mechanism: Liquefaction Studies, in "Coal Science", eds. M.L. Gorbaty, J.W. Larsen and I. Wender, Academic Press, 1982.
4. Painter, P.C., Synder, R.W., Pearson, D.R. and Kwong, J., Fuel, 59, 282 (1980).
5. Meuzelaar, H.L.C. Harper, A.M. and Hill, G.R., Characterization and Classification of Rocky Mountain Coals by Curie-point Mass Spectrometry, Fuel, in press.
6. Harper, A.M., Meuzelaar, H.L.C., Correlations Between Pyrolysis Mass Spectra and Conventional Coal Parameters, Fuel, in press.
7. Saranchuk, V.I., Khimiya Tverdogo, Topliva, Solid Fuel Chemistry, 11, 63 (1977).
8. Bouwman, R. and Freriks, I.L.C., Fuel, 59, 315 (1980).

9. Avison, N.L., Winters, R.M. and Perlmutter, D.D., AICHE, 25, 773 (1979).
10. Marinov, V.N., Fuel, 56, 158 (1977).
11. Nordon, P., Fuel, 58, 456 (1979).
12. Marinov, V.N., Fuel, 56, 153 (1977).
13. Bhallacharyya, K.K., Fuel, 50, 367 (1971).
14. Gray, R.J., Rhoades, A.H. and King, D.T., Society of Mining Engineers, AIME, Transactions, 260, 334 (1976).
15. Crelling, J.C., Schrader, R.H., and Benedict, L.G., Fuel, 58, 542 (1979).
16. Habermehl, D., Orywal, F. and Byer, H.-D., "Chemistry of Coal Utilization", 2nd Supplementary Volume, M.A. Elliot, Ed., Wiley-Interscience, New York, Chichester, Brisbane, Toronto, 1981.
17. Wachowska, H.M., Nandi, B.N. and Montgomery, D.S., Fuel, 53, 212 (1974).
18. Kam, A.Y., Hixson, A.N. and Perlmutter, D.D., Industrial and Engineering Chemistry, Process Design and Development, 15, 416 (1976).
19. Gromicko, F.N., Sarott, L., Gasior, S. and Strakey, J., American Chemical Society, Division of Fuel Chemistry Preprints, 23, 121 (1978).
20. Rus'yanova, N.D., Khimiya Tverdogo Topliva, Solid Fuel Chemistry, 12, 1 (1978).
21. Otsuka, K., Miyakoshi, H., Sato, H., Sato, I., Kato, H. Oda, N. and Kondo, Y., Journal of the Mining and Metallurgical Institute of Japan, 98, 946 (1982).
22. Wachowska, H. Pawlak, W., Fuel, 56, 422 (1977).
23. Furmisky, E., MacPhee, J.A., Vancia, L., Ciavaglia, L.A. and Nandi, B.N., Fuel, 62, 395 (1983).
24. Markova, K.I. and Rushev, D.D., Khimiya Tverdogo Topliva, Solid Fuel Chemistry, 13, 33 (1979).
25. Marinov, V.N., Fuel, 56, 158 (1977).
26. Kucher, R.V., Butuzova, L.F., Kompanets, V.A., Luk'yanenko, L.V. and Deytyar, N.M., Khimiya Tverdogo Topliva, Solid Fuel Chemistry, 12, 17 (1978).

A: Steam generating flask	B: Moisture saturator	D: Quartz dispersion head
F: Final stream saturator	K: Wet test meter	H: Heater
R: Inline regulator.	S: Reactor	M: Metering valve
V: On-off valve	W: Water make-up	T: Thermometer

Figure 1. Schematic overview of coal weathering apparatus.

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

Figure 3. Effect of weathering on weight of Hiawatha seam coal. Note usefulness of control samples in N₂ for distinguishing effect of moisture loss (~4.4%) from effect of oxidative weight gain. Error bars represent range of values for 3 independently weathered aliquots.

Figure 4. Effect of weathering on proximate analysis of Hiawatha coal. Note that without correction to 100% of non-weathered sample weight, effects on Volatile Matter content would tend to be diminished; effects on Fixed Carbon content exaggerated; and spurious effects on Ash content introduced.

Figure 5. Effects of weathering on TG/DTG profiles of Hiawatha coal. Note broadening of pyrolysis reaction temperature range, reduced maximum reaction rate and increased char yield.

— fresh coal; --- weathered at 80°C in air (96 hours); ... weathered at 100°C in air (96 hours)

Figure 6. Curie-point pyrolysis 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 32); altered distribution of aliphatic hydrocarbon series. The phthalate fragment ion peak at m/z 149 may be due to contamination. Experimental conditions: 20 µg sample, 610°C, 10 s (TRT 5 s), 14 eV electron energy.

△ HIAWATHA #1
○ BLIND CANYON
□ HIAWATHA #2

WEATHERING TIME /AIR AT 80°C; 80cm³ min⁻¹

1. 0 hr (fresh coal)
2. 26 hrs
3. 49 hrs
4. 77 hrs
5. 287 hrs

Figure 7. Bivariate plots of selected relative peak intensities in Curie-point pyrolysis mass spectra of fresh and weathered coal samples from 3 Wasatch Plateau mines. Points represent average values from 3 replicate spectra. Note marked decrease of phenolic signals (Figure 7A) and increase of carboxylic acid signals (Figure 7B) upon continued weathering.

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 and each aliquot 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 four "discriminant spectra" correspond to the positive and negative components of both discriminant functions. Note that DI shows the progressive effect of weathering whereas DII appears to reveal a "transitory" effect in the 80°C air weathered samples.

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