



Energy, Mines and  
Resources Canada

Énergie, Mines et  
Ressources Canada

## CANMET

Canada Centre  
for Mineral  
and Energy  
Technology

Centre canadien  
de la technologie  
des minéraux  
et de l'énergie

$^{13}\text{C}$  n.m.r. AS A PROBE FOR THE CHARACTER OF THE LOW-  
TEMPERATURE OXIDATION OF COAL

B.N.NANDI AND J.A. MACPHEE  
COAL RESOURCE AND PROCESSING LABORATORY

JANUARY 1980

For submission to Fuel (London)

Crown Copyrights reserved

ENERGY RESEARCH PROGRAM  
ENERGY RESEARCH LABORATORIES  
REPORT ERP/ERL 80-9 (J)

<sup>13</sup>C n.m.r. AS A PROBE FOR THE CHARACTER OF THE LOW-  
TEMPERATURE OXIDATION OF COAL

by

\*\*\*J. ANTHONY MACPHEE AND BISWANATH N. NANDI\*\*\*

Energy Research Laboratories, Canada Centre for Mineral and Energy  
Technology, Department of Energy, Mines and Resources, 555 Booth Street,  
Ottawa, Ontario, Canada, K1A 0G1

Problems related to the weathering of coals have attracted a great deal of attention in recent years and already a large amount of information has been gathered concerning the low-temperature oxidation of coals of varying rank.<sup>1-4</sup> One key point in our understanding of this process involves whether or not initial attack of oxygen on coals takes place on the aromatic or aliphatic parts of the "coal molecule".<sup>2, 5, 6</sup> Indeed the existence of a dichotomy has not yet been convincingly demonstrated. So far, the consensus of opinion seems to favour attack of oxygen on the aliphatic portion of coal. The reasons why these opinions are held are manifold and may be found in the appropriate references, where they are discussed at suitable length.<sup>2, 7, 12</sup>

As part of our ongoing studies on the constitution and behaviour of coal<sup>13</sup> we decided to look at fresh and oxidized coal samples using the relatively new "cross-polarization magic angle spinning" (CP-MAS) n.m.r. technique which gives, for the first time, satisfactorily resolved<sup>13</sup> <sup>13</sup>C n.m.r. spectra on solid samples.<sup>14, 15</sup> Such spectra permit a straightforward estimation of the aromaticity of a coal sample since the aromatic and aliphatic carbons yield two distinct, resolved peaks. This technique seems ideally suited for investigating the nature of the low-temperature oxidation of coal, providing that the sensitivity of the method is sufficient to monitor the changes involved.

The coal used for this investigation is Harbour 26 Seam, Cape

Breton Development Corporation, Carboniferous, high-volatile bituminous coal. A sample of this coal (particle size 300  $\mu\text{M}$ ) was subjected to oxidation in a stream of air, flow rate 75mL/min. at 105°C. for 192 hours. The results of proximate, ultimate and petrographic analysis, and dilatometric tests, as well as, Gieseler plasticity of both fresh and oxidized coal are given in Table 1. The microscopic structure of the residue obtained from the dilatation tests of fresh coal at 550°C shows formation of coarse grain structure (CG)<sup>16</sup> and fusion of the reactive vitrinites (FM) in the micrograph shown in Figure 1. An increase of oxygen content of 3% and complete loss of dilatation and Gieseler plasticity are observed in the coal which was subjected to oxidation. Neither the formation of grain structure nor the fusion of the vitrinite are visible in the micrograph (shown in Figure 2) of the residue acquired from dilatometer tests under identical conditions to that of fresh coal.<sup>17</sup> It is evident that the reactive vitrinite is converted to inert maceral and consequently the coal suffers a complete loss of mesophase formation on carbonization due to oxidation.

The <sup>13</sup>C n.m.r. spectra obtained for these two samples are given in Figure 3. A relative increase in aliphatic content, or decrease in aromatic content, with oxidation is observed from these spectra. This, we feel, is direct evidence of the nature of transformations occurring during low-temperature oxidation of coal in relation to its coking characteristics. The relationship between oxidation level of vitrinite and its reactive nature plays an important role in coal utilization processes.

The infra-red spectra of these two samples are virtually identical, the only change being a slight thickening towards the high

frequency side of the  $1600\text{cm}^{-1}$  band indicative of the formation of carbonyl groups on oxidation. Additional work is required to explain the change in aromaticity on oxidation at the molecular level. It is also important to ascertain how other coals of widely varying rank and geological age behave on oxidation, i.e. whether the observed behaviour is general or atypical. Further experiments are in progress to this end.

#### ACKNOWLEDGEMENTS

The authors are grateful to Dr. J.A. Ripmeester of the National Research Council of Canada for his advice and the determination of the  $^{13}\text{C}$  n.m.r. spectra. They also extend their thanks to Mr. L. A. Ciavaglia for his helpful comments on the oxidation studies, to Mr. S.E. Nixon for the petrographic analysis of the coal and direct determination of oxygen, and Mr. B.H. Moffatt for dilatometric tests and chemical and physical analysis of coal and semi-coke.

TABLE 1

## DEVCO 26, HIGH-VOLATILE BITUMINOUS COAL

<u>PROXIMATE ANALYSIS</u>	<u>FRESH COAL</u>	<u>OXIDIZED COAL</u>
	%	%
MOISTURE	0.8	0.9
VOLATILE MATTER	34.3	31.7
ASH	2.4	2.2
FIXED CARBON	62.5	65.2
	<u>100.0</u>	<u>100.0</u>
 <u>ULTIMATE ANALYSIS (db)</u>		
CARBON	84.9	82.8
HYDROGEN	5.4	5.0
SULPHUR	0.7	0.6
NITROGEN	2.2	2.2
ASH	2.4	2.2
OXYGEN (BY DIFFERENCE)	4.4	7.2
	<u>100.0</u>	<u>100.0</u>
OXYGEN (DETERMINED)	5.6	8.4
 <u>DILATOMETRIC TEST (RUHR DILATOMETER)</u>		
SOFTENING POINT, $\theta_s$ ( $^{\circ}\text{C}$ )	341	355
CONTRACTION C (%)	23	25
TEMPERATURE OF MAX CONTRACTION $\theta_c$ ( $^{\circ}\text{C}$ )	398	474
DILATATION (%)	312	NIL
TEMPERATURE OF MAX. DILATATION ( $^{\circ}\text{C}$ )	460	NIL
PLASTICITY INDEX = $c/(\theta_c - \theta_s)$	0.40	0.21
GIESELER PLASTICITY (DD/MIN)	23,850	NON-AGGLOMERATING
 <u>PETROGRAPHIC ANALYSIS</u>		
	%	
VITRINITE	73.1	
EXINITE	5.5	
MICRONITE	4.3	
SEMI-FUSINITE	7.7	
FUSINITE	5.5	
MINERAL MATTER	3.9	
	<u>100.0</u>	

MEAN MAX. REFLECTANCE IN OIL = 1.07

REFERENCES

- 1 Hazlett, R.N., Solash, J., Fielding, G.H. and Burnett, J.C. Fuel 1978,57,631
- 2 Swann, P.D. and Evans, D.G. Fuel 1979,58,276
- 3 deVries, H.A.W., Bokhoven, C. and Dormans, H.N.M. Brennst.-Chem. 1969,50,289
- 4 Marinov, V.N. Fuel 1977,56,153,158,165
- 5 Van Krevelen, D.W. Coal, Elsevier, Amsterdam, 1961, Ch.3
- 6 Huntington, J.G., Mayo, F.R. and Kirshen, N.A. Fuel 1979,58,32
- 7 Brower, K.R. Fuel 1977,56,245
- 8 Wachowska, H. and Dowlak, W. Fuel 1977,56,342
- 9 Bhowmik, J.N., Mudherjee, P.N. and Lahiri, A. Fuel 1959,38,211
- 10 Mazumdar, B.K., Chakrabartty, S.K., and Lahiri, A. J.Sci. Ind. Res. 1962,21A,84
- 11 Mazumdar, B.K., Anand, K.S., Roy, S.N. and Lahiri, A. Brennst.-Chem. 1957,38,305
- 12 Brooks, J.D. and Sternhell, S. Aust. J. Appl. Sci. 1957,8,206
- 13 Nandi, B.N., Ciavaglia, L.A. and Belinko, K., Restoration of Coking Character of Partially Oxidized Coal with Bitumen Heavy Oil, Extended Abstracts, 14<sup>th</sup> Biennial Conference on Carbon, American Chemical Society, Pennsylvania State University, June 25-29, 1979, p.371
- 14 Zilm, K.W., Pugmire, R.J., Grant, D.M., Wood, R.E. and Wiser, W.H. Fuel 1979,58,11
- 15 Maciel, G.E., Bartuska, V.J. and Miknis, F.P. Fuel 1979,58,391
- 16 Patrick, J.W., Reynolds, M.J. and Shaw, F.H. Fuel 1973,52,198
- 17 Nandi, B.N., Wachowska, H.M. and Montgomery, D.S. Fuel 1974,53,226

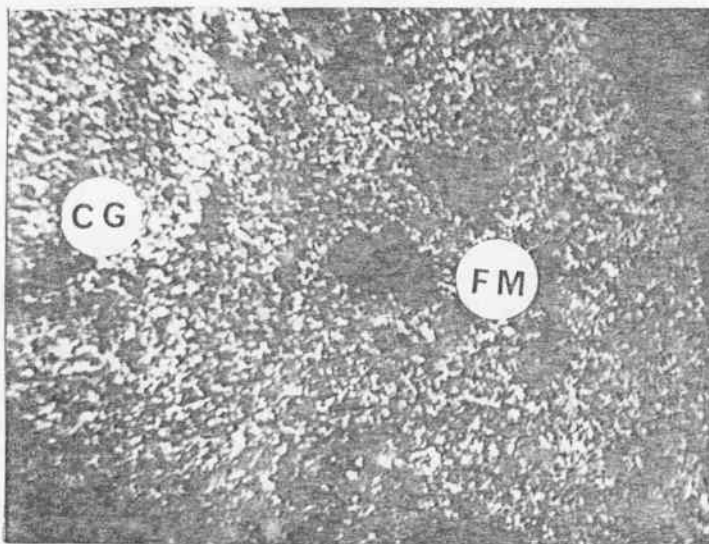


Figure 1. Micrograph of dilatation residue from fresh coal showing coarse grain (CG) formation in the semi-coke and fusion of reactive vitrinite (FM)

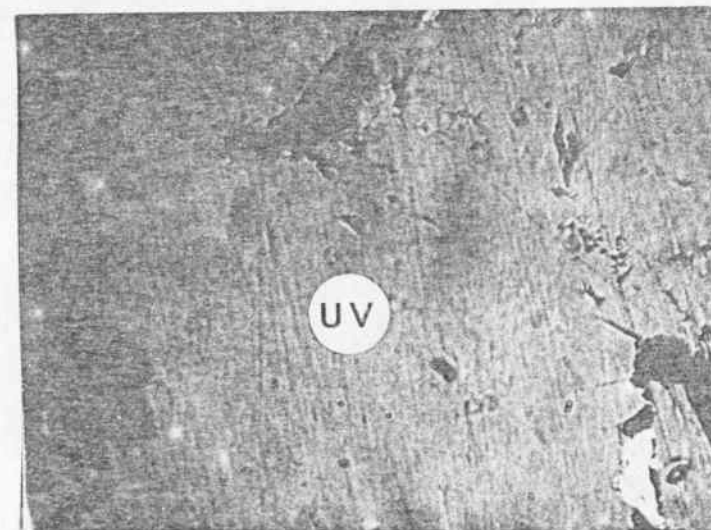


Figure 2. Micrograph of dilatation residue from coal oxidized at 105° for 192 hours showing unaltered vitrinite (converted to inert maceral) in char(UV).

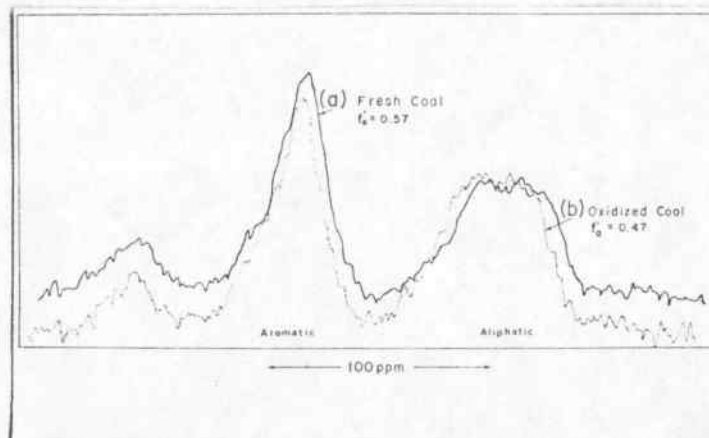


Figure 3. <sup>13</sup>C n.m.r. spectra of fresh and oxidized coal (Bruker CXP-180 spectrometer),  $f'_a$  apparent aromaticity<sup>15</sup>.