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INTRODUCTION

Carboniferous and Cretaceous bituminous coals exhibit behavioural differences that are well documented (1,2). These differences, both chemical and petrographic in nature, have some bearing on how these coals behave during carbonization and are important in determining the quality of metallurgical coke. In particular, rheological properties as measured by the Ruhr dilatometer and Gieseler plastometer, are known to be dramatically different although coke qualities are comparable for these two coal types. Tectonic pressures (1) during the formation of the Rocky Mountains are thought to have been a determining factor in the metamorphosis of Cretaceous coals to ranks similar to those of Carboniferous coals which are about 200 million years older.

To gain some insight into fundamental causes for the discrepancies between coking and thermal rheological properties of Carboniferous and Cretaceous coals, four pairs of coals of approximately equal rank were selected for this study. These pairs cover a range, in reflectance terms, of $R_{o,max}$ = 0.88 to 1.66%. Thermal rheological and solvent swelling measurements were conducted on both fresh and laboratory oxidized samples of the coals. Other analytical tests including chemical, petrographic, and thermogravimetric have been used to examine selected coal samples. In addition, full-scale coking tests were carried out on the fresh coals where possible.

EXPERIMENTAL

Samples were oxidized with air from 0 to 192 h in a 0.1 L stainless steel pressure bomb at 50°C and 9.0 MPa pressure. All samples were ground under nitrogen to minus 50 mesh before oxidation and after reaction were stored in a freezer at minus 16°C prior to analysis.

Solvent swelling experiments were carried out in dimethyl sulfoxide (DMSO) using the method developed by Larsen (3). The coal samples (-50 mesh) were thoroughly dried but were not extracted with any solvent prior to solvent swelling determinations.

Rheological tests were performed on the Ruhr dilatometer (DIN 51739) and Gieseler plastometer (ASTM D-2639). Free swelling indices (FSI) were determined according to ASTM D-720.

Thermogravimetric analyses (TGA) on both original and oxidized coals were carried out on a Perkin Elmer TGA 7 under a nitrogen flow (30 mL/min) at a heating rate of 20°C/min.

Oxygen determinations were made using the Perkin Elmer 240 Elemental Analyser.

Full scale coking tests were performed on six of the eight samples using CANMET's 460 mm wide test oven. The oven charge in all cases was 330 kg and was carbonized to a final temperature of 1050°C at the centre of the coke. ASTM stability and coke strength after reaction (CSR, Nippon Steel test) were conducted on the cokes. Coke reactivity (CRI), measured during the CSR test, represents the percentage of the original 200 g of 20 mm coke that has been gasified after 2 h when reacted with CO_2 using a flowrate of 5 L/min.

RESULTS AND DISCUSSION

Table 1 presents analytical data for the eight coals. Carboniferous and Cretaceous coals are designated A and C.

ASTM coke stabilities, CSR, and CRI properties were measured for all the Cretaceous coals and two of the four Carboniferous coals. The ASTM stabilities and particularly the excellent CSR and CRI properties of the cokes made from the Cretaceous coals show their commercial significance even though their dilatation and fluidity properties are lower than target values considered necessary for many coking models used to predict coke quality.

Petrographic results were generally consistent with the literature which describes higher semifusinite, lower exinite and micrinite contents for Cretaceous coals (4). These differences are thought to contribute to differences in the dilatation and fluidity properties of these coals. Still, a few samples such as A_1 and C_1 have similar Ro, similar reactives/inert maceral ratios and similar thermal rheological properties. However, the rheological data in Table 1 show that as a group, the Cretaceous coals are clearly of lower dilatation and fluidity than Carboniferous coals. Differences observed in FSI values are probably not significant. Postulated explanations for such behaviour invoke a greater proportion of cross-links (mainly of the ether type) in Cretaceous coals (2) and also their rather high concentrations of phenolic-OH groups(1).

Cross-linking is particularly important in determining the solvent swelling behaviour of coals (4). Another parameter which is of great importance is hydrogen bonding (5). Figure 1 shows the solvent swelling parameters in DMSO (Q_{DMSO}) for the eight coals along with various oxidized samples of these coals. Immediately obvious is that both Carboniferous and Cretaceous coals lie on the same relatively smooth curve, instead of two curves. A small but definite increase in swelling with oxidation is observed for the lower rank coals (i.e. A_1, A_2, C_1, and C_2); for the higher rank coals there is no observable change in swelling after oxidation for 192 h at 50°C. Although the changes in swelling in the lower rank coals with oxidation are small (<10%) they would appear to be reproducible. There is no observable decrease in swelling of an oxidized coal relative to the corresponding fresh coal in contrast to a recent report (5). Formation of

cross-links during oxidation is expected to reduce the extent of solvent swelling. Our observation that solvent swelling increases after oxidation in certain cases, indicates that cross-linking may not be an important oxidation pathway for bituminous coals. The results in this paper refer to laboratory oxidized coals. However, it has been our experience that naturally weathered Cretaceous coals also exhibit an increase in solvent swelling.

The rheological properties (dilatation and plasticity) of the coals as a function of oxidation have been measured where possible. For coals A1 and C1 the dilatations of the original coals are similar making it possible to use this parameter to compare the relative rates of oxidation. This is shown in Fig. 2 where the sensitivity of both coals to oxidation is approximately the same for the reaction conditions used in this work, i.e. 50°C and 9.0 MPa pressure. Figure 3 shows a linear relationship between dilatation as a function of oxygen content for coal A_3. This behaviour is typical for these coals (7). It is probable that parallel reactions incorporating oxygen functionalities occur during the oxidation of the coal. Which functional group or groups are responsible for the loss of rheological properties on oxidation is a subject of controversy. A linear relationship exists also between log (fluidity) and oxygen content which implies a linear relationship between log (fluidity) and dilatation which was substantiated for the single coal (r=0.996). If we consider a more general correlation of this kind involving the eight whole coals in Table 1, the results exhibit more scatter with a correlation coefficient of 0.88.

TGA experiments (in nitrogen) were conducted on the whole and oxidized coals for 192 h. As expected (8) the maximum rate of weight loss (dw%/dt) is lower for the oxidized coals relative to the fresh samples. The maximum rate of weight loss for the whole coals is a function of rank. A simple correlation of dwt%/dt(max) with $R_{o,max}$ has a correlation coefficient of 0.82, and with log (fluidity) a correlation coefficient of 0.90. A double correlation of dwt%/dt(max) with both log(fluidity) and $R_{o,max}$ yields an excellent result with a multiple correlation coefficient of 0.96. This is shown in Fig. 4 where experimental and calculated values of dwt%/dt(max) are compared. The TGA results show no fundamental difference between the behaviour of the Carboniferous and Cretaceous coals. The data for both sets of coals fall on the same line.

CONCLUSIONS

Carboniferous and Cretaceous coking coals while exhibiting wide differences in rheological properties have been shown to behave in a similar fashion in a number of processes as follows:

a) Solvent swelling in DMSO for both fresh and oxidized coal
b) Rate of loss of dilatation as a function of oxidation.
c) Rate of weight loss in a thermogravimetric experiment

This indicates that structural differences between the two coal types do not necessarily result in differences in behaviour. In addition solvent swelling measurements on oxidized bituminous coals indicate that cross-linking may not be important in the reaction mechanism.

TABLE 1- Analytical Results on Whole Coals

	A1	A2	A3	A4	C1	C2	C3	C4
Coal Sample								
Analyses								
Proximate (wt%,db)								
Ash	6.0	6.2	6.8	5.9	6.8	7.0	9.2	7.0
Volatile Matter	36.5	33.4	26.2	19.4	32.2	26.4	21.6	16.7
Fixed Carbon	57.5	60.4	67.0	74.7	61.0	66.6	69.2	76.3
Ultimate								
carbon	79.7	81.8	83.1	85.0	80.5	81.6	81.3	84.7
Hydrogen	5.2	5.1	4.7	4.4	5.0	4.7	4.4	4.2
Oxygen (by diff.)	6.6	4.3	3.0	2.4	5.6	4.8	3.4	2.4
Nitrogen	1.6	1.8	1.7	1.7	1.7	1.5	1.3	1.3
Sulphur	0.9	0.8	.07	0.6	0.4	0.4	0.4	0.4
Thermal Rheology								
FSI	6	8	7.5	8	8.5	7.5	7.5	8.5
Dilatation (%)	45	190	224	34	43	15	-13	nil
Contraction(%)	26	27	27	24	28	26	27	25
Fluidity(dd/m)	1580	20400	7900	32	365	24	18.4	1.4
$R_{o,max}$	0.88	0.95	1.22	1.65	0.90	1.01	1.27	1.62
Q_{DMSO}	1.41	1.11	1.11	1.11	1.41	1.20	1.10	1.07
ASTM stability	33.9	39.8	-	-	45.1	55.7	58.1	55.4
CSR	30.1	47.4	-	-	62.1	64.3	73.9	68.7
CRI	37.5	34.4	-	-	24.0	28.5	19.5	22.6

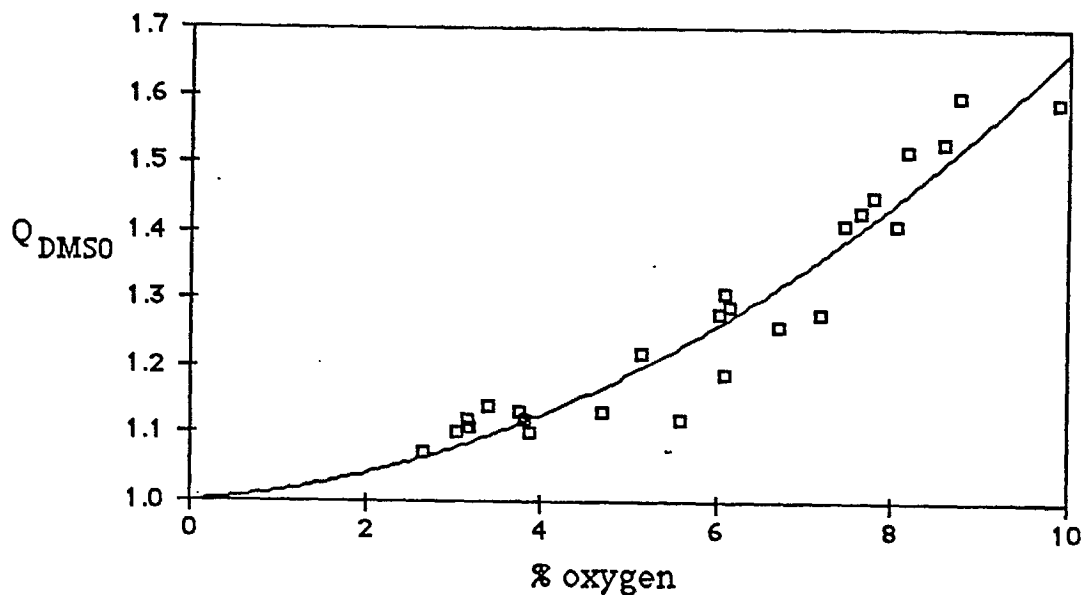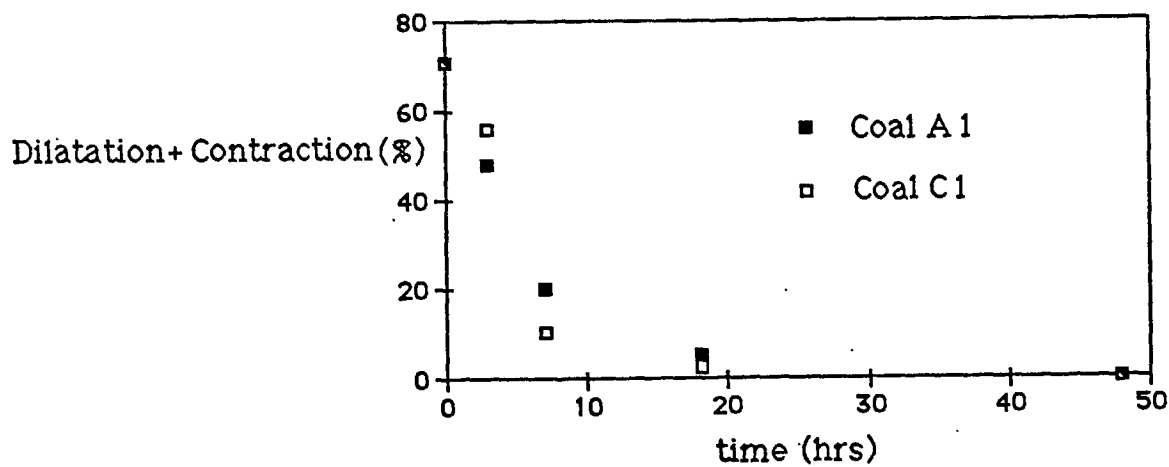Fig. 1 Solvent swelling of fresh and oxidized coals.

Fig. 2 Changes in dilatation of coals A1 and C1
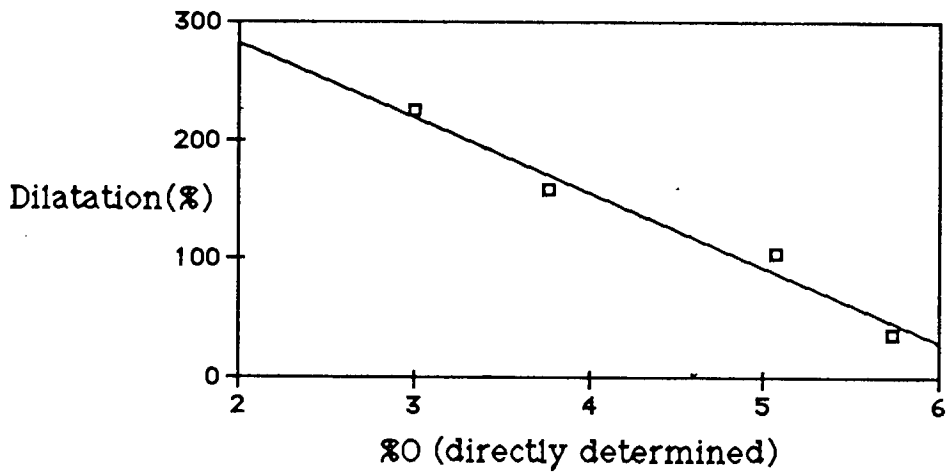as a function of oxidation.
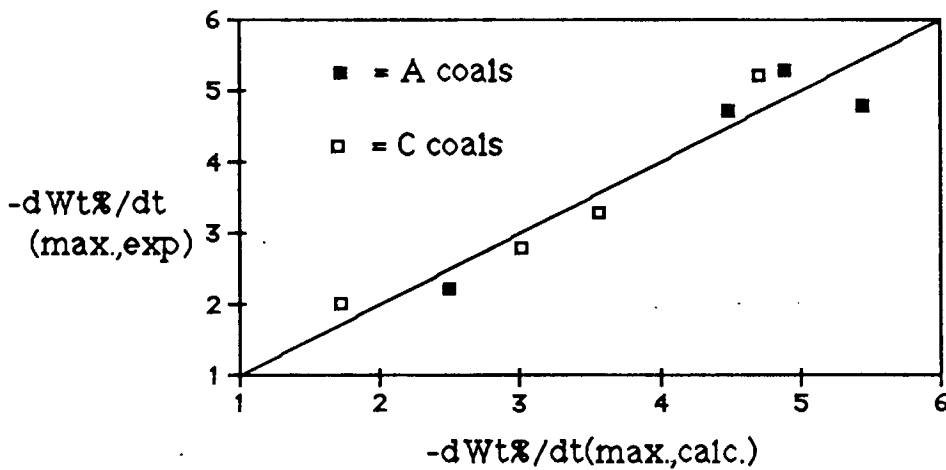
Fig. 3 Oxidation of coal A3 at 50°C, $r = 0.99$.

Fig. 4 Experimental maximum rate of weight loss versus calculated as a function of $R_{o,max}$ and log(fluidity), $r = 0.96$.

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