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THE EFFECTS OF SAMPLE PREPARATION AND STORAGE ON THE THERMAL RHEOLOGICAL PROPERTIES OF COKING COALS

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by

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ABSTRACT

The thermal rheological properties of coals of Canadian and foreign origin were studied under various conditions of preparation and storage. Coals were stored in air at ambient temperatures for periods of up to 25 weeks. Each individual coal showed approximately a constant decrease in fluidity, dilatation and Free Swelling Index as a function of storage time, for three particle sizes investigated. The effects of storage on the rheological properties varied appreciably for the different coals tested.

Various coals were stored in argon, nitrogen, carbon dioxide and water for prolonged periods of time. Samples which were stored in water showed slightly enhanced stability relative to those stored in the other three media. In addition, some samples were stored in refrigerated air (4 - 5°C) and these were found to exhibit by far the greatest resistance to oxidation.

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INTRODUCTION

The reactivity of coals towards oxygen has been primarily regarded as an academic problem. Many workers have studied the mechanism by which oxygen alters the chemical structure of the coal skeleton and the kinetics of this process (1 - 4). Oxidation of coals is also of great practical importance when dealing with their storage. Storing coals in the presence of oxygen can result in significant changes in their rheological properties, thereby altering their carbonization characteristics.

A study is currently in progress at the Energy Research Laboratories of the Department of Energy, Mines and Resources to investigate the effects of oxidation on the thermal rheological properties of selected coking coals. Several methods of sample preparation and storage are being examined to ascertain the optimum conditions under which the properties of the coal are not appreciably altered over extended periods of storage.

The purpose of this report is to examine how certain specific properties of the coal, e.g., fluidity, dilatation and Free Swelling Index, are affected by particle size and by storage under various conditions. The relative sensitivity of these three parameters as a measure of oxidation will also be discussed.

EXPERIMENTAL PROCEDURE

Selection of Coals

The coals used in these studies were as follows:

No. 1 - Western Canadian (Elco 2; low volatile)
No. 2 - Western Canadian (Elco 18; high volatile)
No. 3 - Western Canadian (Comp C; coal blend)
No. 4 - German (Ruhr; coal blend)
No. 5 - American (low volatile)
No. 6 - American (high volatile)

All six coals were used to investigate the effects of particle size on the rheological properties during storage in air. Coals No. 1, 2, 5 and 6 were selected for studies on the effect of storage in different media.

Some physical and chemical properties, including petrographic analyses, for these various coals are given in Table 1.

Sample Preparation

Samples were crushed mechanically to the desired particle sizes using a grinding mill. Three sizes were used in these studies:

(a) Coal as received (< 4 mm)
(b) Minus 12 mesh US Standard (< 1.7 mm)
(c) Minus 50 mesh US Standard (< 0.3 mm)

Storage studies using various media were carried out with coals crushed to minus 50 mesh US Standard.

Oxidation Studies

The coals used for storage studies in air were spread out on cardboard sheets, 25 cm x 40 cm, to a thickness of approximately 6 mm. These samples were exposed to air at ambient temperatures, 21 - 23°C. Representative samples of 10 - 12 gm for each coal were collected after various time intervals ranging from one week to twenty-five weeks. Dilatations and Free Swelling Index (FSI) measurements were done on all the samples collected. Fluidity measurements were only carried out on samples collected after 19 and 25 weeks of exposure.

Storage of coals in distilled water were carried out in stoppered 500 cc Erlenmeyer flasks. Samples for dilatation were collected after 4, 9, 14, 19 and 26 weeks. Fluidity measurements were only done on samples collected after 19 and 26 weeks.

Coals which were stored in argon, nitrogen and carbon dioxide were placed in individual plastic bags. The bags were initially evacuated and the filled with the appropriate gas. Twist-ties were used to seal the bags. This same procedure was repeated after each sample was collected at the specified elapsed time.

Coals which were refrigerated at 4 - 5°C were placed in plastic bags under an atmosphere of air. The bags were tightly sealed with twist-ties.

RESULTS AND DISCUSSION

The effects of particle size on the dilatation and fluidity of the coals which were stored in air are summarized in Tables 2 and 3, respectively. A decrease in both these parameters was observed for all the coals tested, as a function of storage time. Each individual coal showed approximately a constant decrease in fluidity and dilatation, during storage, for the three particle sizes investigated. Based on the dilatation data, Table 2, the German coal blend (No. 4) was appreciably more sensitive to oxidation than the remaining five coals. The American low volatile (No. 5) coal exhibited the greatest decrease in fluidity during storage in air, Table 3.

The F.S.I. results for the six coals stored in air are given in Table 4. A slight decrease in the F.S.I. was observed for all six coals tested as a function of storage time. In general, particle size had little effect on the F.S.I. measurements. The F.S.I. of the American low volatile (No. 5) coal appeared to be the least to vary as a function of storage time.

Dilatation data for the four coals stored in argon, nitrogen, carbon dioxide and water are presented in Table 5. Although a decrease in dilatation was observed for each coal stored in the various media as a function of storage time, the rate of decrease was significantly less than that observed during storage in air (c.f. Table 1). Water was found to be a relatively more desirable storage medium for the coals than the three gases investigated. The equilibrium concentration of oxygen in water is ca. 2.2×10^{-3} moles/litre (5), which would explain why the coals experienced a certain degree of oxidation during storage in this medium.

Fluidity measurements of the coals stored in the various media appeared to be much more sensitive to oxidation than dilatation measurements, Table 5. For each of the four coals tested, appreciable changes in fluidity were observed as a function of storage time. As in the case of the dilatation data, fluidity measurements revealed that storage in water was slightly more desirable than in any of the three gases investigated.

F.S.I. data for coals stored in the various media are given in Table 7. This parameter was not found to be sufficiently sensitive to degrees of oxidation, and can therefore not be reliably used in the detection of coal degradation during storage.

Coals which were stored at low temperatures (4 - 5^{o}C), in air, were far the most resistant to oxidation, Table 8. Both dilatation and fluidity measurments revealed an enhanced stability for coals stored under refrigeration. This method of storing coals may therefore be the most reliable in preserving the coking characteristics of coals.

CONCLUSIONS

For the range of particle size used in these studies, this parameter was not found to significantly influence the thermal rheological properties of the coals, during storage in air. In general, the rate of decrease in dilatation, fluidity and F.S.I. as a function of storage was approximately the same for all three particle sizes investigated.

The medium in which the coals were stored appeared to have a very noticeable affect on the rheological properties of the coals. Water was found to be a slightly more inert environment for coal storage than argon, nitrogen or carbon dioxide. Storage of coals at low temperatures, 4 - 5^{o}C, even in the presence of air was found to be the most efficient of all the methods tested in terms of preserving the characteristics of the coals.

Dilatation and fluidity measurements were found to be relatively sensitive parameters for the detection of coal oxidation. F.S.I. measurements, on the other hand, were found to be too insensitive in detecting coal degradation due to oxidation.

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TABLE 1

Properties of the Coals Used in These Studies

Coal No.	1	2	3	4	5	6
Ash (%)	9.4	7.5	9.3	8.1	5.9	4.9
Volatile Matter (%)	20.6	31.2	20.6	24.5	18.6	32.9
Fixed Carbon (%)	70.1	61.3	70.1	67.4	75.5	62.2
F.S.I.	9.0	9.0	7.5	7.5	9.0	8.5
Dilation (%)	48	179	-1	45	48	139
Gieseler Fluidity (dd/m)	73	2050	4	39	237	5350
Maceral Analysis						
Vitrinite	56.3	75.7	48.3	74.0	80.1	73.7
Exinite	0.0	4.0	0.1	4.8	-	6.4
Micrinite	1.9	1.8	1.5	3.3	2.6	4.7
Semi-Fusinite	29.9	9.1	35.1	8.9	8.9	6.4
Fusinite	6.2	5.1	9.7	4.3	5.0	5.8
Ro (Max)	1.43	0.98	1.31	1.28	1.55	1.03

TABLE 2

Dilatation Results for Coals of Different Particle Sizes Stored in Air

Particle Size	Coal No.	Per Cent Dilatation				
		0 weeks	3 weeks	8 weeks	13 weeks	25 weeks
- 4 mm	1	48	48	55	32	31
	2	179	166	147	137	130
	3	-1	-5	-7	-5	-13
	4	45	47	27	28	10
	5	48	48	50	42	42
	6	139	134	113	106	80
- 1.7 mm	1	48	43	39	36	29
	2	179	170	150	148	130
	3	-1	-7	-12	-14	Nil
	4	45	34	22	22	7
	5	48	47	47	39	33
	6	139	128	114	103	84
- 0.3 mm	1	48	46	42	35	32
	2	179	175	157	149	129
	3	-1	-2	-6	-13	Nil
	4	45	35	25	13	7
	5	48	46	43	37	31
	6	139	130	112	99	82

TABLE 3

Gieseler Fluidity Measurements for Coals of Different Particle Sizes Stored in Air

Particle Size	Coal No.	Max Fluidity (dd/m)		
		0 weeks	19 weeks	25 weeks
	1	73	24	17
	2	2050	390	265
- 4 mm	3	4	4	1
	4	39	10	5
	5	237	16	8
	6	5350	2900	1180
	1	73	35	23
	2	2050	625	415
- 1.7 mm	3	4	2	1
	4	39	11	5
	5	237	16	7
	6	5350	2320	1300
	1	73	36	20
	2	2050	650	370
	3	4	2	1
	4	39	7	5
- 0.3 mm	5	237	10	5
	6	5350	1900	940

TABLE 4

Free Swelling Indeces for Coals of Different Particle Sizes Stored in Air

Particle Size	Coal No.	Free Swelling Index				
		0 weeks	3 weeks	8 weeks	13 weeks	25 weeks
- 4 mm	1	9.0	8.5	9.0	8.5	8.0
	2	9.0	8.5	8.0	8.0	8.5
	3	7.5	6.0	6.0	6.5	6.0
	4	7.5	7.0	6.5	7.5	6.5
	5	9.0	8.5	9.0	9.0	9.0
	6	8.5	7.5	7.5	8.0	7.0
- 1.7 mm	1	9.0	7.5	8.0	8.0	8.0
	2	9.0	8.5	8.5	7.5	8.0
	3	7.5	5.0	5.0	5.5	5.0
	4	7.5	7.5	6.0	6.5	5.0
	5	9.0	9.0	9.0	9.0	8.5
	6	8.5	7.0	7.5	7.5	7.0
- 0.3 mm	1	9.0	9.0	8.0	8.5	8.0
	2	9.0	7.5	8.0	8.0	8.0
	3	7.5	5.5	5.0	5.5	5.0
	4	7.5	7.5	5.5	6.0	6.0
	5	9.0	9.0	9.0	8.5	8.5
	6	8.5	7.0	7.5	7.5	7.5

TABLE 5

Dilatation Results for Coals Stored under Various Conditions

Storage Media	Coal No.	Percent Dilatation					
		0 wks	4 wks	9 wks	14 wks	19 wks	26 wks
Argon	1	48	46	42	40	39	37
	2	179	177	170	158	150	143
	5	48	47	44	40	38	37
	6	139	132	122	107	100	93
Nitrogen	1	48	46	43	39	38	38
	2	179	164	158	151	140	133
	5	48	47	44	40	40	37
	6	139	127	116	106	88	88
Carbon Dioxide	1	48	48	41	40	37	36
	2	179	155	143	147	129	124
	5	48	47	45	38	37	35
	6	139	131	116	108	95	86
Water	1	48	50	46	40	42	41
	2	179	160	157	154	159	142
	5	48	49	43	41	42	40
	6	139	131	127	120	121	108

TABLE 6

Gieseler Fluidity Measurements for Coals
Stored under Various Conditions

Storage Media	Coal No.	Max Fluidity (dd/m)		
		0 weeks	19 weeks	26 weeks
Argon	1	73	44	31
	2	2050	784	400
	5	237	16	9
	6	5350	2550	1200
Nitrogen	1	73	40	29
	2	2050	650	430
	5	237	13	9
	6	5350	2230	928
Carbon Dioxide	1	73	40	26
	2	2050	540	340
	5	237	14	8
	6	5350	2225	1410
Water	1	73	53	36
	2	2050	860	429
	5	237	18	13
	6	5350	3250	1589

TABLE 7

Free Swelling Indeces for Coals
Stored under Various Conditions

Storage Media	Coal No.	Free Swelling Index					
		0 wks	4 wks	9 wks	14 wks	19 wks	26 wks
Argon	1	9.0	9.0	8.5	8.0	9.0	8.5
	2	9.0	8.0	8.0	7.5	7.5	7.0
	5	9.0	9.0	9.0	8.0	8.5	8.5
	6	8.5	8.5	8.5	8.0	7.0	7.5
Nitrogen	1	9.0	8.5	8.0	8.0	8.5	8.5
	2	9.0	8.5	8.0	8.5	8.5	8.0
	5	9.0	9.0	9.0	9.0	8.5	8.5
	6	8.5	8.0	7.5	7.0	7.5	8.0
Carbon Dioxide	1	9.0	9.0	8.5	8.5	8.5	9.0
	2	9.0	8.5	8.5	8.0	8.5	8.0
	5	9.0	9.0	9.0	8.5	9.0	8.5
	6	8.5	8.5	7.0	7.5	7.5	8.0
Water	1	9.0	8.5	9.0	8.5	9.0	9.0
	2	9.0	9.0	8.5	7.5	8.0	8.0
	5	9.0	9.0	9.0	8.5	9.0	8.5
	6	8.5	8.5	8.0	8.5	8.0	7.5

TABLE 8

Thermal Rheological Properties of Coals
Stored in Refrigerated Air

Coal No.	Percent Dilatation					
	0 weeks	4 weeks	7 weeks	14 weeks	19 weeks	26 weeks
1	48	48	48	47	42	47
2	179	175	162	172	167	167
5	48	47	48	45	46	44
6	139	140	138	130	126	124

Coal No.	Max Fluidity (dd/m)		
	0 weeks	19 weeks	26 weeks
1	73	69	66
2	2050	1380	860
5	237	26	18
6	5350	5330	2840

Coal No.	Free Swelling Index					
	0 weeks	4 weeks	9 weeks	14 weeks	19 weeks	26 weeks
1	9.0	9.0	8.5	8.5	8.5	8.5
2	9.0	8.5	8.5	8.0	8.0	7.5
5	9.0	9.0	9.0	9.0	8.5	9.0
6	8.5	7.5	7.5	8.0	6.5	7.5

REFERENCES

1. Kam, A.Y., Hixson, A.N. and Perlmutter, D.D. "The oxidation of bituminous coal." Chem. Engn. Sci.; v 31, no. 9, p 821; 1976.

2. Iskra, J. and Laskowski, J. "New possibilities of investigating air-oxidation of coal surfaces at low temperatures." Fuel, London; v 46, p 5; 1967.

3. Mazumdar, B.K., Chakrabarty, S.K. and Lahiri, A. "Determination of the aromaticity of coal by oxidation." J. Sci. and Ind. Res.; v 21, p 84; 1962.

4. Wachowska, H.M., Nandi, B.N. and Montgomery, D.S. "Oxidation studies on coking coal related to weathering." Fuel; v 53, p 212; July 1974.

5. "International critical tables of numerical data: physics, chemistry and technology." v III, p 272; 1928.