

METALLURGICAL COKES FROM OXIDIZED HIGHLY CAKING COALS

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ABSTRACT

Laboratory studies suggest that improvements of coke strength brought about by preheating caking coals before carbonization accrue from inadvertent oxidation rather than from physical changes in the coal mass due to removal of moisture. Controlled oxidation of highly caking coal, followed by carbonization, produces cokes which, in terms of strength, are equivalent to those obtained from prime metallurgical blends. Appropriately formulated blends of exhaustively oxidized and fresh caking coal similarly yield cokes whose properties are comparable to those cokes made from the same coal after oxidation under optimum conditions.

In exercising quality control over the manufacture of metallurgical cokes, it is frequently found useful to preheat the oven-charge in an inert atmosphere at some temperature between 150° and 350°C. The principal benefit of such treatment is a substantially shortened carbonization cycle (1,2) and, hence, greater oven productivity; but in some instances, it has also been observed to result in somewhat greater strength of the finished cokes, and this has been attributed to higher bulk density and better thermal conductivity of the charge after removal of moisture (2).

Bearing in mind that even very slight oxidation affects the rheological properties of caking coals (3), and that preheating tends to reduce their maximum dilatation (4), it appears, however, just as likely that greater coke strength accrues from inadvertent oxidation of the coal during preheating, and the study reported below does, in fact, indicate this to be the more correct view.

EXPERIMENTAL

For the purposes of this investigation, three Appalachian hvAb coals (see Table 1), all characterized by high (Gieseler) fluidity and very pronounced (maximum) dilatation (see Table 2), were used.

In one set of experiments, samples of these coals were preheated for varying periods of time in a sand bath at $180 \pm 3^\circ\text{C}$ while commercial "pure" nitrogen or helium (from Canadian Liquid Air Ltd. and Union Carbide Canada Ltd., respectively) was passed through them at $\sim 10 \text{ ml min}^{-1}$. In a second, the same procedure was used, but the inert gas was thoroughly purified by passing it through a fixed bed of metallic nickel on lamp black at 800°C (5) before admitting it to the coal samples.

After cooling to room temperature in the protective atmosphere, portions of the preheated samples were then tested for their dilatometric and fluidity characteristics, and others were carbonized as previously described (6) and submitted to coke strength tests. Strength was expressed in terms of the F_{5-45} Index (6) which, over a wide range of values, is directly proportional to the ASTM coke stability factor.

To avoid a basis for comparison with oxidized coal, one of the test coals (No. 3) was also exposed to oxygen (at 200°C) and to air (at 100°C and 150°C) for varying periods of time, and then examined like the preheated samples.

RESULTS AND DISCUSSION

After preheating under thoroughly purified nitrogen or helium for 24 hours, the rheological properties of all three coals were found to be entirely unchanged. But preheating under commercial "pure" nitrogen or helium caused rapid loss of fluidity and progressive decrease of the (maximum) dilatation - although at the same time very significantly raising the strength of the coke obtainable from the preheated coal. Figure 1, in which the bracketed numbers refer to coke strength, illustrate these effects for preheating in nitrogen. (Preheating in helium yielded very similar results, except that fluidities then decreased even faster, possibly due to a higher residual oxygen content of this gas.)

The enhanced coke strengths shown in Figure 1 are qualitatively paralleled by the variation of the strengths of cokes made from variously oxidized coal No. 3 (see Figure 2). As anticipated, the oxidation period to optimum oxidation depended on the severity of the treatment, and thus ranged from 15 minutes (for oxygen at 200°C) to 60 hours (for air at 100°C). But in all three cases, a limited oxidation of the coal before carbonization is seen to result in quite dramatic improvements of coke quality. The total oxygen contents of the coal samples after optimum pre-oxidation and oxidation to total loss of caking properties are shown in Table 3.

Verification of the conclusion that slight "accidental" oxidation of the coal during preheating increases coke strength was obtained from semi-technical-scale tests in a 500 lb movable wall oven*. In one test, fresh No. 3 coal was charged, and in a second, preheated No. 3 (96 hours at 170-190°C) was carbonized. Preheating was done in an externally gas-heated hopper through which commercial "pure" nitrogen was passed at 900 ml min⁻¹ (see Figure 3).

The data obtained from evaluation of the two coke lots made in the experimental oven are shown in Table 4 and established a 10 point improvement in the ASTM stability factor when the preheated charge was used. But perhaps even more interesting, in the control of this study, is the variability of coke strengths observed when smaller (20 lb) samples, withdrawn from different locations in the hopper, were carbonized in the laboratory. This variation is graphically presented in Figure 4 in which the bracketed numbers at the sampling points show the maximum dilatation of the preheated coal before carbonization. Comparison of Figures 3 and 4 shows that the point of nitrogen entry into the hopper charge - which is presumably also the point at which the highest concentration of contaminant oxygen would be encountered - lies in a zone from which maximum coke strengths and minimum dilatation were recorded.

Since Figure 4 shows the preheated hopper charge to have been almost as heterogeneous as a coal blend, one further series of laboratory carbonization experiments was carried out with variously formulated blends of fresh and "exhaustively" oxidized coal No. 3. ("Exhaustive" oxidation here means oxidation to total loss of caking properties.) The results of these tests are summarized in Figure 5 and show that, irrespective of the manner of oxidation, addition of oxidized coal can be an effective means for maximizing coke strength. Scanning electron micrographs (see Figure 6) underscore this conclusion by showing that the microscopic structure of cokes made from optimally composed blends of fresh and exhaustively oxidized coal No. 3 compares very favorably with that of coke made from a prime mvb caking coal alone.

*These tests were conducted in collaboration with the Energy Research Laboratories, Department of Energy, Mines and Resources, Ottawa. Fuller details of this program will be published elsewhere.

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Table 1. Composition of Test Coals

Coal	Rank	Proximate analysis, %				Fixed Carbon (d.a.f.)	Calorific Value (Gross) BTU/lb.	Ultimate analysis, % (d.a.f.)			
		(Capacity) Moisture	Ash (dry basis)	V.M. (d.a.f.)				C	H	N	S
1	hVAb	2.1	4.2	32.3	67.7	14,510	87.6	5.4	1.6	0.8	4.6
2	hVAb	1.7	6.3	34.2	65.8	14,290	87.3	5.5	1.6	1.5	4.1
3	hVAb	2.0	5.3	36.9	63.1	14,270	86.0	5.5	0.9	0.7	6.9

* by difference

Table 2. Rheological Properties of Test Coals

Coal	FSI	(Gieseler) plasticity				Ruhr-dilatation				
		Soft. temp., °C	Max. fluid. temp., °C	Solid. temp., °C	Max. fluid. temp., °C	Soft. temp., °C	Max. contr. temp., °C	Max. dilat. temp., °C	Max. dilat. %	
1	8	403	455	491	3600	365	423	519	27	182
2	8	400	443	476	13100	355	401	611	23	394
3	8	400	443	475	8200	369	412	487	29	122

Table 3. Oxygen Contents of Oxidized No. 3 Coal.
(Initial [O] = 6.2%)

Oxidation method	Oxygen contents, (% w/w)	
	after "Optimum" Oxidation	after Oxidation to Total Loss of Caking Properties
Air at 100°C	6.7 (60)*	7.4 (410)
Air at 150°C	7.1 (6)	7.8 (22)
Oxygen at 200°C	6.4 (0.25)	10.1 (0.75)

* Bracketed numbers show time of oxidation (hrs) to oxygen contents.

Table 4. Evaluation of Cokes from Tests in 500 lb Movable-Wall Oven

	ASTM Stability Factor, (%)	Factor, (%)	Breeze, (% of ½ in fraction)
1. Fresh Coal	35.2	64.5	3.9
2. Preheated Coal (Nitrogen; 170-190°C, 96 hrs)	45.8	64.5	3.6

FIGURE 1. VARIATION OF MAXIMUM DILATATION (---) AND MAXIMUM (GIESELER) FLUIDITY (---) WITH DURATION OF PREHEATING IN COMMERCIAL "P URE" NITROGEN. (BRACKETED NUMBERS SHOW THE STRENGTH INDICES OF COKES.)

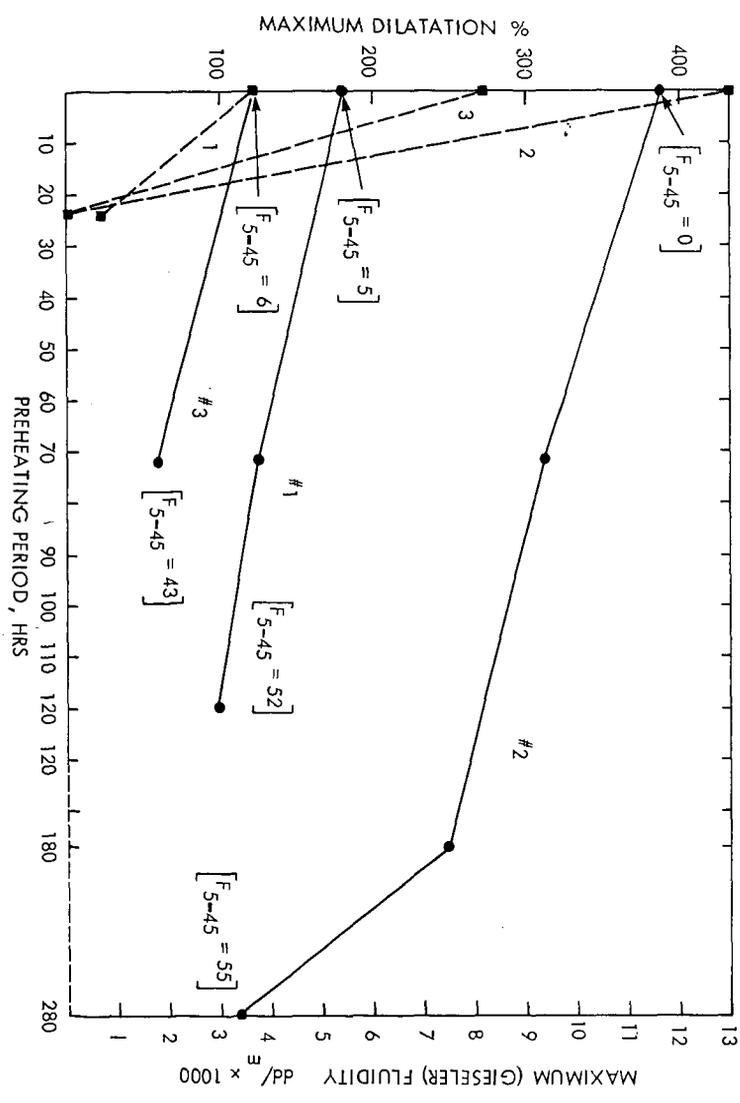


FIGURE 2. EFFECT OF OXIDATION ON STRENGTH OF COKES FROM COAL NO. 3

- A. OXYGEN AT 200°C
- B. AIR AT 150°C
- C. AIR AT 100°C

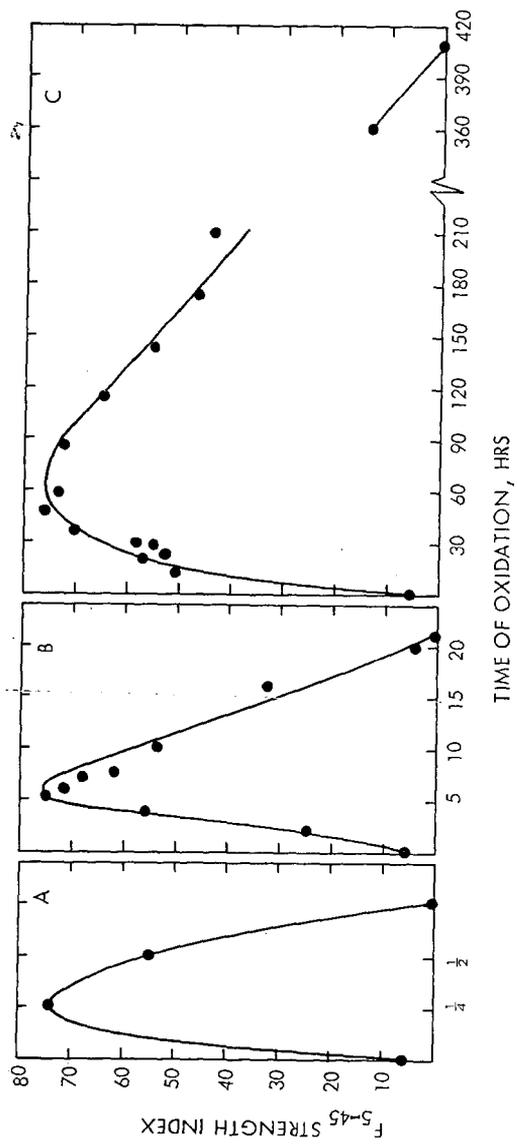


FIGURE 3. PREHEAT HOPPER FOR 500-LB

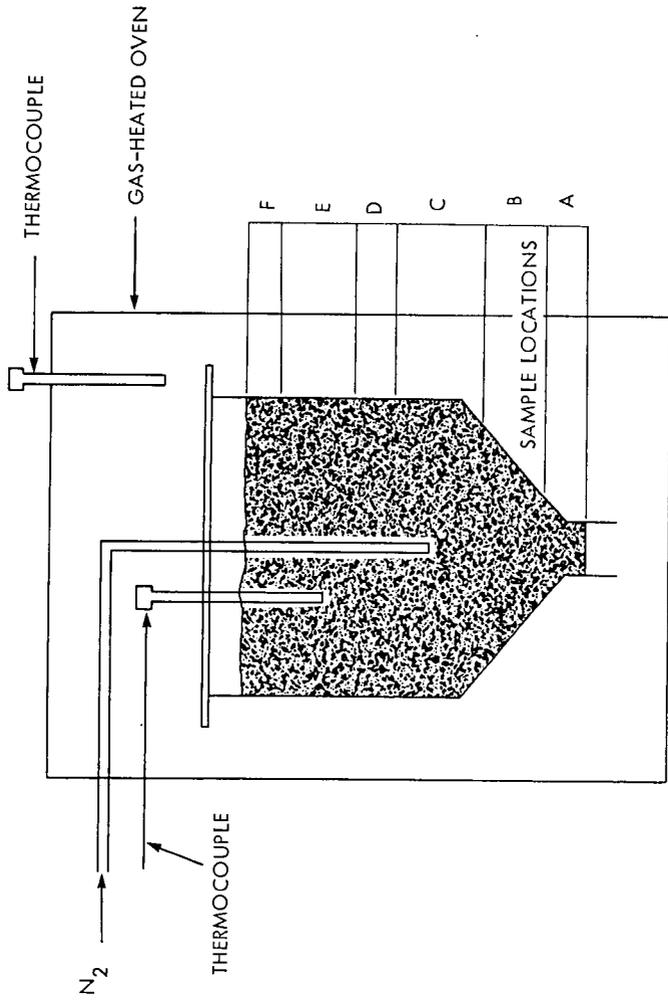
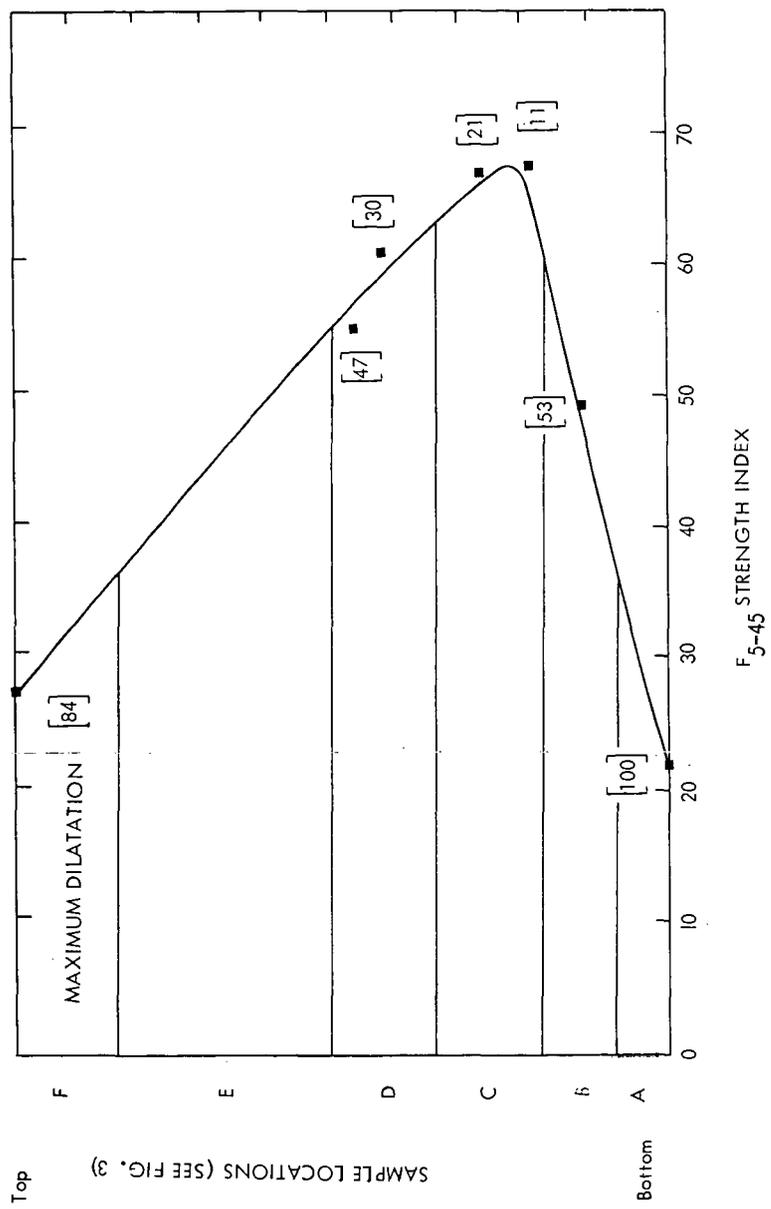
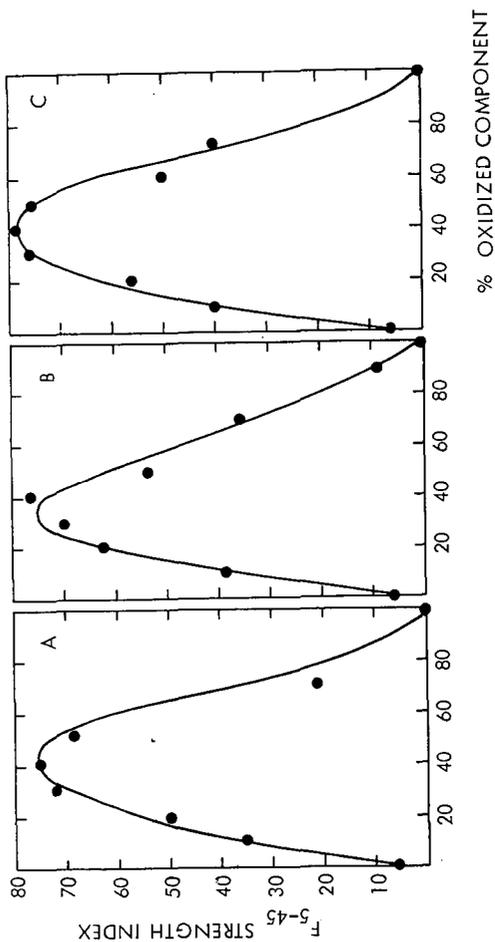


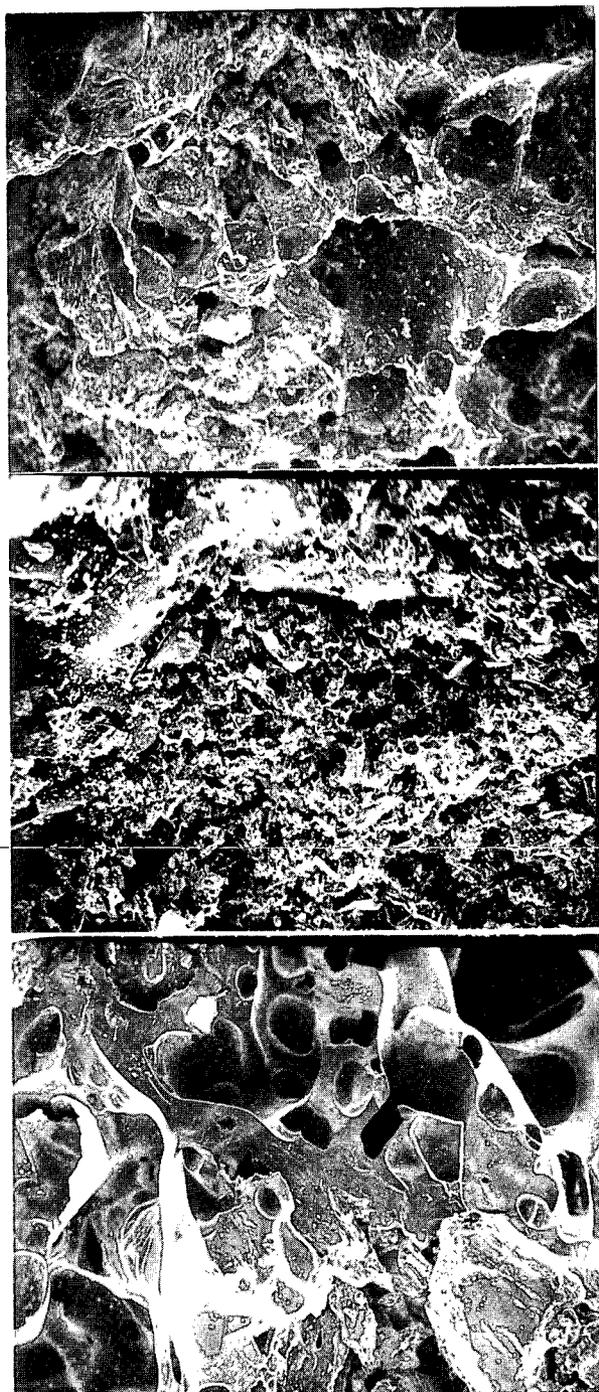
FIGURE 4. MAXIMUM DILATION OF PREHEATED NO. 3 COAL SAMPLES AND STRENGTH OF COKES AS FUNCTIONS OF LOCATION IN PREHEAT HOPPER.



SAMPLE LOCATIONS (SEE FIG. 3)

FIGURE 5. STRENGTH OF COKES FROM BLENDS OF FRESH AND "EXHAUSTIVELY"
 OXIDIZED COAL NO. 3.
 (OXIDIZED COMPONENT PREP. BY TREATMENT WITH)
 A. OXYGEN AT 200°C, 2.5 HRS
 B. AIR AT 150°C, 22 HRS
 C. AIR AT 100°C, 407 HRS





A.

B.

C.

Figure 7. Scanning Electron Micrographs ($\times 100$) of cokes

A. - coke from a blend containing fresh (60 parts) and "totally" oxidized (40 parts) No. 3 coal

B. - the same as A but in the 80:20 ratio

C. - coke from mvb prime coking coal from Cardinal River