

VACUUM BALANCE AND RELATED STUDIES OF COKES USED IN STEEL PRODUCTION

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ABSTRACT

The reactivities of cokes derived from coal blends used in the steel industry have been compared. Kinetics and rates of oxidation have been correlated with changes in surface area and porosity determined by gravimetric gas sorption using vacuum microbalances.

During the earlier stages of oxidation of the cokes in carbon dioxide at 1000 °C, the surface area increases considerably, reaching a maximum at about 20 % burn-off. This change in surface area is ascribed to formation of pores at the surface, including opening of initially-closed pores as the burning proceeds.

At higher percentage burn-offs, the surface area decreases to a very low value as the ash sinters with loss of porosity.

INTRODUCTION

Steel production requires metallurgical cokes of suitable physical and chemical properties. Cokes are preferred having high mechanical strength and moderate reactivity (measured by weight loss in carbon dioxide at 1000-1100 °C). Optimum properties are achieved generally by blending coals. The blends may consist entirely of coals indigenous to the United Kingdom or blends of foreign and U.K. coals.

At 1000-1100 °C, the oxidation occurs by the Boudouard reaction, viz., $C + CO_2 \rightarrow 2CO$. Kinetics and rates of oxidation will depend on the area of the coke surface and its accessibility to carbon dioxide. Thus in the present research, changes in surface area and porosity during oxidation have been studied in detail for two cokes - one derived from U.K. coals and the other from mixed foreign and indigenous coals. The constituents of the coke ash sinter appreciably at 1000 °C and tend to impede oxidation, particularly in the second half of the coke burn-off.

EXPERIMENTAL

Thermogravimetric studies of the oxidation of Scunthorpe and Redcar cokes in air or carbon dioxide were made, using a Stanton-Redcroft mass-flow balance MF-H5 (1). Larger samples of coke at various degrees of burn-off were prepared in a furnace at 1000 °C, using coke lumps of approx. 5 mm diameter. Surface

areas were determined by a gravimetric B.E.T. method (2), using nitrogen gas sorption at -196°C recorded on a C.I. Electronics Mark 2B microforce balance (3). Samples of up to about 200 mg weight could be examined, using balance ranges of 0-2.5 mg, 10 mg and 100 mg for measuring the gaseous adsorption. The adsorption isotherms also provided data on the micro- and meso-porosity of the materials. Information on the macroporosity was obtained from density measurements by gas or liquid displacement. Further information was obtained from electron-micrographs.

RESULTS AND DISCUSSION

Surface activity and kinetics during coke oxidation

Variations in surface area during oxidation of Scunthorpe and Redcar cokes in carbon dioxide at 1000°C are presented in Fig. 1 and 2.

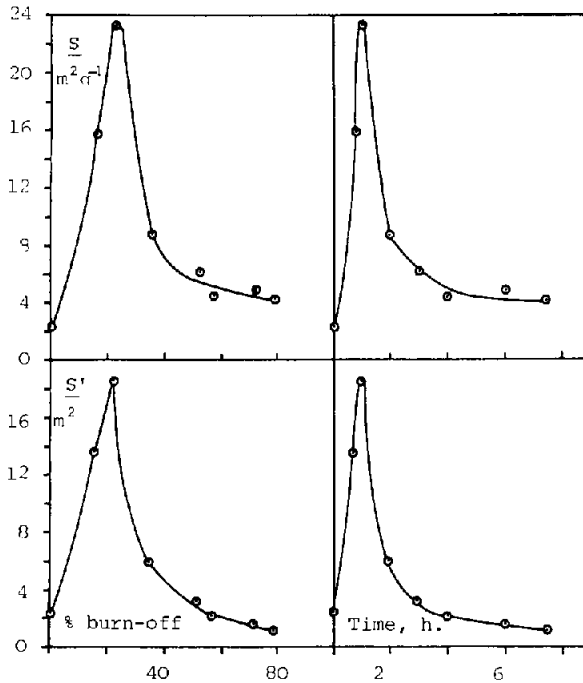


Fig. 1. Oxidation of British Steel Scunthorpe coke in carbon dioxide at 1000°C
 Indigenous:- 60% Yorkshire,
 25% Northants,
 15% S. Wales (or Kent)

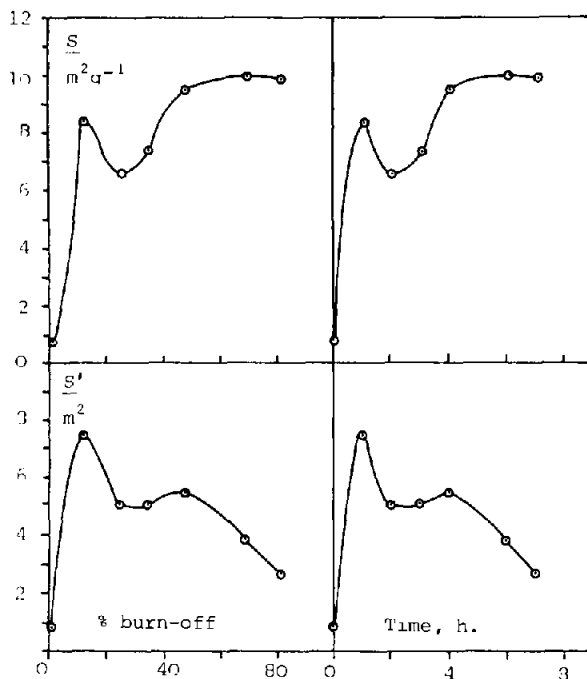


Fig. 2. Oxidation of British Steel Redcar coke in carbon dioxide at 1000°C
50% British (Durham), 30% Polish,
20% Australian.

At lower percentage burn-offs, the surface areas increase considerably, reaching maxima during the first 25 % burn-off. There is evidently formation of pores at the coke surface, including opening of initially-closed pores as the oxidation proceeds. Thus although the original coke samples have only macroporosity, yet they develop full ranges of mesoporosity (pore sizes of 2-50 nm diameter) in the earlier stages of burn-off in carbon dioxide or in air, cf. Fig. 3 and 4, where there is adsorption hysteresis in the relative pressure range 0.37-0.96. Similar maxima are shown for the actual changes in surface, S' , (rather than the specific surfaces, S) of 1 g-samples of initial coke blend at various degrees and times of burn-off. The Redcar coke shows a second maximum at about 40-50 % burn-off, which is ascribed to the behaviour of the Polish component. Experiments on cokes prepared from indigenous coals, e.g., Scunthorpe coke and separately on South Wales cokes (Nantgarw and Cwm) show development of maximum surface at 10-25 % burn-off, whereas the Polish coke produces maximum surface at as much as 40-50 % burn-off, (4). The Polish component helps the Redcar coke to retain its reactivity in the later stages of burn-off, where the

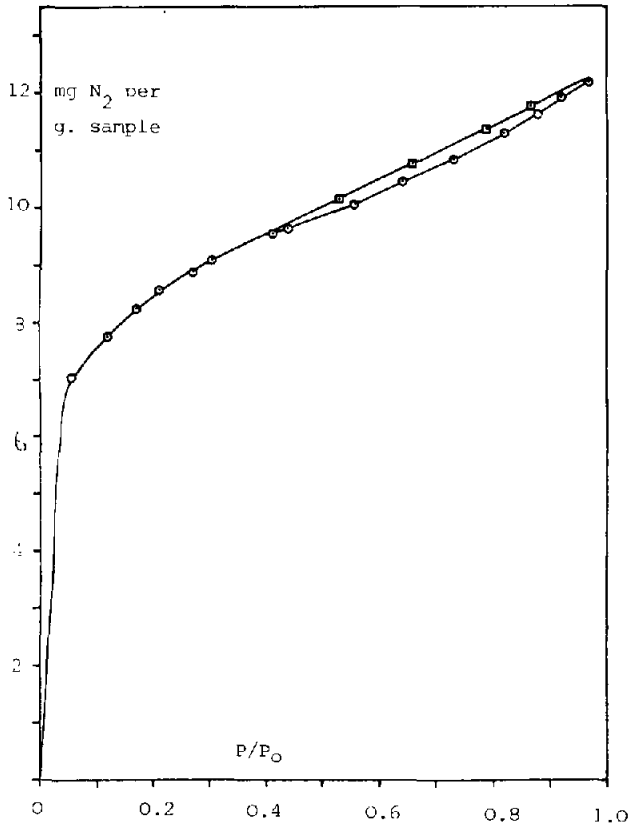


Fig. 3. Adsorption of N₂ on Scunthorpe coke oxidised 22.6% in CO₂ at 1000°C.

surface activity gets reduced by sintering of the increasing proportion of ash present, cf. Fig. 5, 6 and 7. Hence the kinetics of the later stages of burn-off of the Scunthorpe coke resemble a two-thirds order reaction impeded by solid products (Fig. 8), where the two-thirds order plot deviates from linearity, becoming concave upwards.

Development of porosity during coke oxidation

Electron-micrographs of sections of initial coke particles in Fig. 9 indicate mainly macroporosity internally and externally. Apparent density measurements from gas or liquid displacement enable the closed pore volumes to be estimated. In Table 1, the apparent densities have been determined by nitrogen gas displacement on the vacuum microbalance. The pore volumes have been estimated

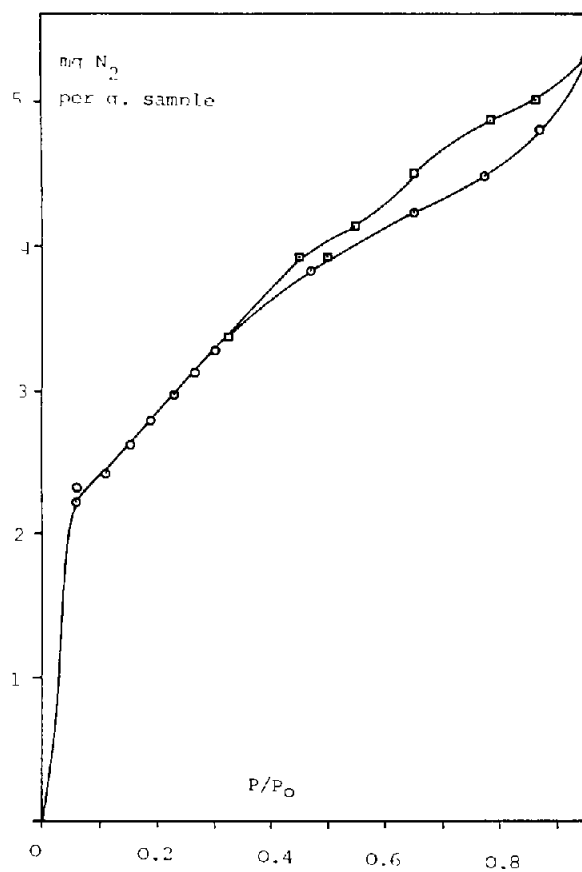


Fig. 4. Redcar coke burnt at 1000°C in air (½h) 16.8% burn-off Adsorption of N₂ at -196°C.

TABLE 1

Apparent densities and pore volumes of cokes

Coke	Apparent density	Pore volume, cm ³ g ⁻¹	
		A	B
Scunthorpe	1.27	0.346	0.261
Redcar	1.34	0.305	0.220
Polish, Cwm	1.40	0.273	0.188
Nantgarw	1.48	0.232	0.150

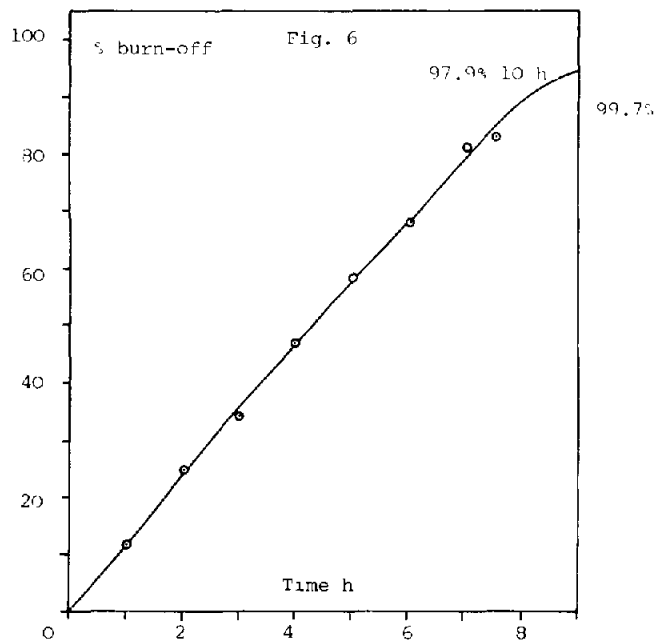
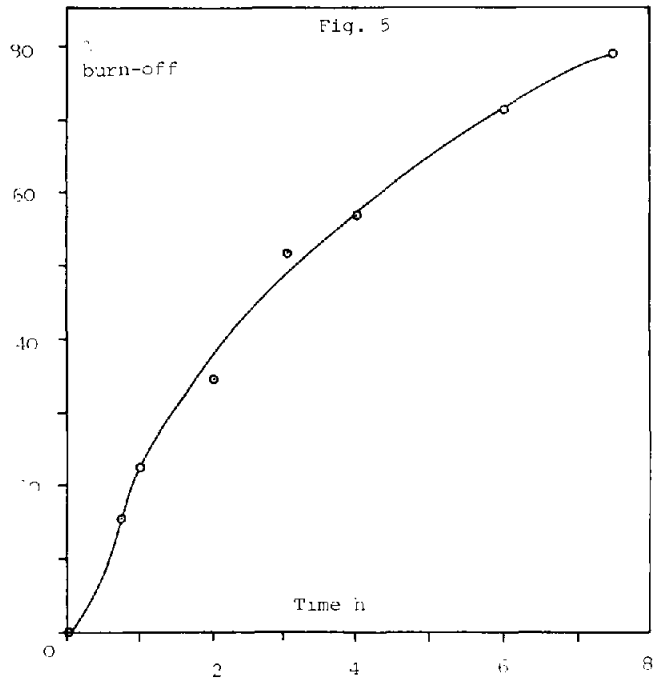


Fig. 5 and 6. Scunthorpe and Redcar cokes oxidised in CO_2 at 1000°C

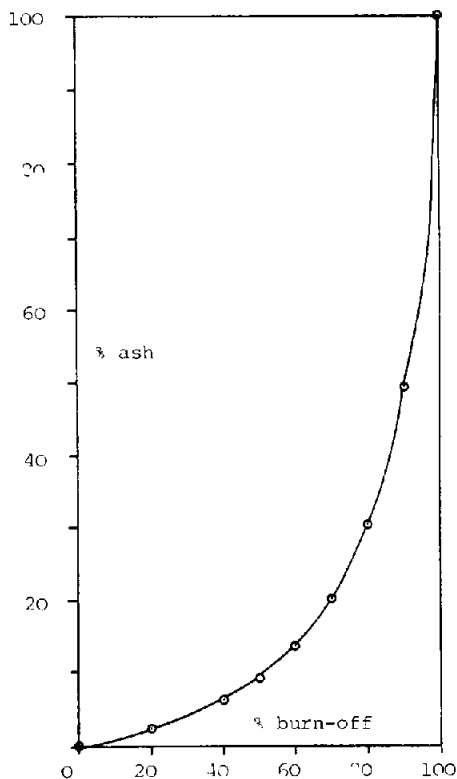


Fig. 7. Proportion of ash in burnt-off Redcar coke.

using true densities and volumes of (A) 2.27 and $0.441 \text{ cm}^3 \text{ g}^{-1}$ and (B) 1.90 and $0.526 \text{ cm}^3 \text{ g}^{-1}$ corresponding to values adopted for the X-ray density of graphite and the true density of cokes carbonised at 1000-1100 °C.

When 1 g of Redcar coke burns off 16.8 % carbon in air at 1000 °C (wt. loss 15.1 %), its surface area increases from 0.8 to 6.9 m^2 . If it had burnt as particles which were non-porous contracting spheres without forming new pores, its surface would have decreased from 0.8 m^2 to 0.72 m^2 , i.e., $0.8 \times (\text{fractional wt. left})^{2/3}$. Thus 6.2 m^2 of surface was developed in burning off $0.151/1.90 \text{ cm}^3$ of carbon = 0.0795 cm^3 , compared with pore volume opened of $0.151 \times 0.220 = 0.0332 \text{ cm}^3$. Since the pores opened are mainly macropores $>$ about $0.1 \mu\text{m}$ diameter, the surface of the opened pores is estimated from the formula radius of cross-section, $r/2 = \text{Volume}/\text{Surface}$, whence $r/2 > 25 \text{ nm} = 0.22 \times 10^{24}/8 \times 10^{20}$ making $s < 8.8 \text{ m}^2$ per g coke, i.e., $< 1.3 \text{ m}^2$ for 0.151 g coke. Thus most of the increase in surface is due to formation of new pores.

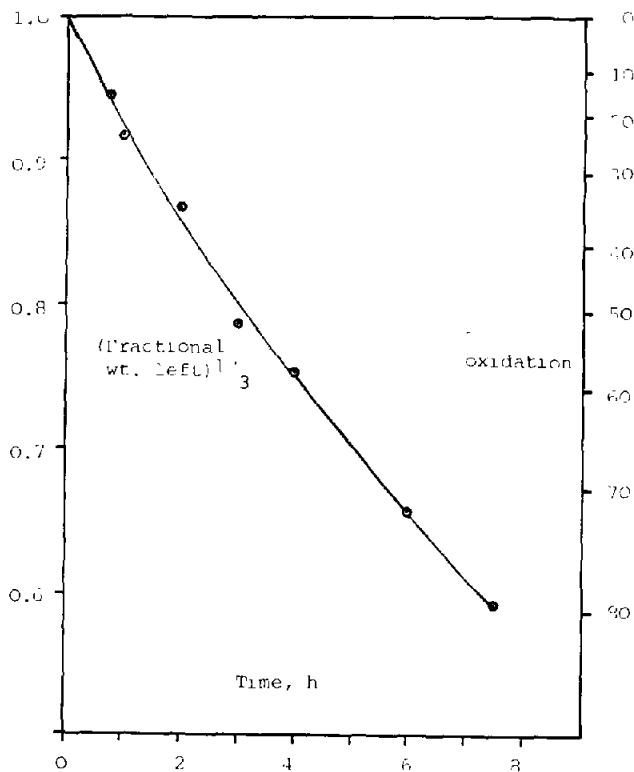
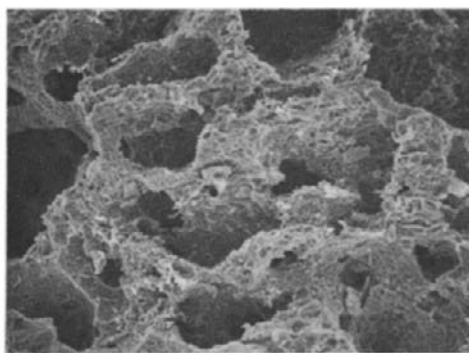
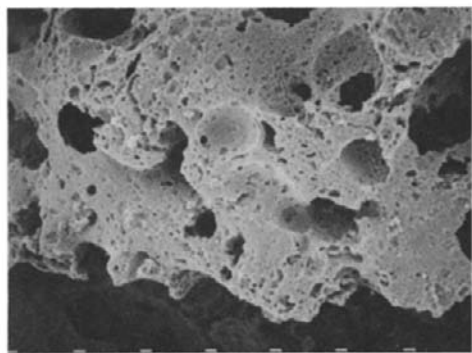


Fig. 8. Two-thirds order kinetics plot for oxidation of Scunthorpe coke in CO_2 at 1000°C .

These should have an average size of about 65 nm or less, depending on how much of the oxidation forms new pores. There will be direct burn-off from the external surface, but some oxidation can form new pores or open and enlarge macropores. Accordingly, the hysteresis loop of the nitrogen adsorption isotherm (Fig. 4) indicates pore sizes across the whole of the mesopore range of 2-50 nm, the commonest size (at the widest part of the loop) being about 7 nm.

Similar calculations for the Scunthorpe coke give a development of surface of 16.5 m^2 for 22.6 % burn-off of a 1 g-sample, compared with $< 2.2 \text{ m}^2$ for opened macropores. This leads to an estimate of 31 nm or less for the size average of the newly-formed pores. Again the nitrogen adsorption hysteresis loop indicates pore sizes over the whole of the mesopore range of 2-50 nm, the commonest size being about 5 nm.

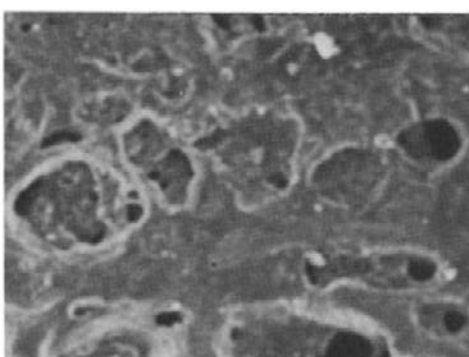
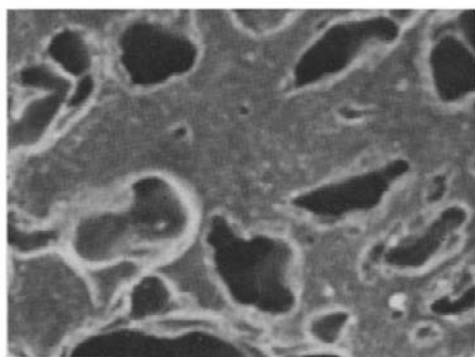
An estimate of how much of the oxidation forms new pores can be made by measuring the uptake of nitrogen during the filling and emptying of the



(a) Scunthorpe coke before burn-off

(b) Redcar coke before burn-off

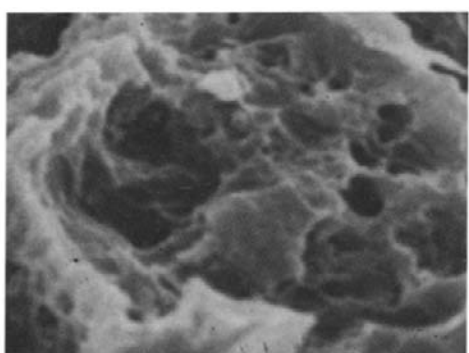
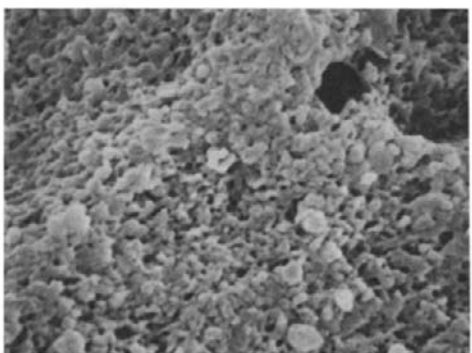
100 μm



(c) Scunthorpe coke after 63 % wt. loss

(d) Redcar coke after 52 % wt. loss

100 μm

(e) Scunthorpe coke after 63 % wt. loss
at greater magnification(f) Redcar coke after 52 % wt. loss
at greater magnification

10 μm

Fig. 9 Scanning electron-micrographs of Scunthorpe and Redcar cokes.

mesopores from the adsorption isotherms (Fig. 3 and 4). This is approximately the difference between the highest and lowest weight readings of the hysteresis loop, using a value of 34.67 cm^3 for the volume of a mole of liquid nitrogen at -196°C . These calculations indicate that only about 2.6 % of the oxidation of the Redcar coke in air and 2.5 % of the Scunthorpe coke in carbon dioxide forms mesopores, so that the appreciable increases in surface are associated with only a small proportion of the oxidation and the new surface is located in mesopores, giving it poor access to air or carbon dioxide. Hence, any increase in oxidation rate due to new surface being formed will be comparatively small, but could tend to make a two-thirds order rate become approximately linear during the earlier stages of oxidation, as is often encountered in coke reactivity tests.

REFERENCES

- 1 Stanton-Redcroft, p.l.c., Copper Mill Lane, London
- 2 D.R. Glasson, J. chem. Soc., 1956, pp. 1506-1510.
- 3 C.I. Electronics, p.l.c., Salisbury, England.
- 4 M.A. Carter, D.R. Glasson and S.A.A. Jayaweera, *Thermochemica Acta*, 1984, this volume.