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SURFACE AREA DEVELOPMENT OF THREE COKES IN RELATION TO THE ZINC-LEAD BLAST FURNACE

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ABSTRACT

The development of surface area on burn-off for three metallurgical cokes has been studied and correlated with rates of oxidation in carbon dioxide. The role of boric oxide, B_2O_3, as inhibitor of oxidation is discussed. The effect of ash build-up in the later stages of coke burn-off is evaluated in relation to surface area changes.

INTRODUCTION

The successful production of zinc and lead by a blast-furnace process relies on the Imperial Smelting Furnace. Zinc is collected as a vapour and a lowering of furnace temperature allows its reoxidation. As with the reduction of other metal oxides, the reducing agent is carbon monoxide via the reaction, $ZnO + CO \rightarrow Zn + CO_2$; the carbon monoxide is generated from the coke by the endothermic Boudouard reaction, $C + CO_2 \rightarrow 2CO$. If coke is of a high reactivity (measured by rate of reaction with carbon dioxide at 1000 °C) there is consequent wastage of carbon and lowering of furnace temperature. It is known that certain inorganic compounds such as borates and phosphates, present in or on the carbon, will inhibit the Boudouard reaction (ref.1). Preliminary investigation by Imperial Smelting Processes had shown (ref.2) that treatment with boric oxide, B_2O_3, would lower the reactivity of formed and metallurgical coke. Low reactivity South Wales cokes are used for zinc/lead production as described by Cross (ref.3).

EXPERIMENTAL

Three metallurgical cokes (Nantgarw, Cwm and Polish) were studied. Rate of oxidation in carbon dioxide (dried by passage through magnesium perchlorate) at 1000 °C was determined for approximately 30 mg samples in the form of 500-710 μm granules on a Stanton-Redcroft 781 thermal balance. Air and carbon dioxide oxidations of Nantgarw coke lumps (approx. 100 mg samples) were also run on the above instrument, heating the furnace to the programmed temperature at a fast rate with the sample held under nitrogen.

Lump samples were prepared to various degrees of burn-off in carbon dioxide at 1000 °C and their surface areas determined by gravimetric nitrogen sorption at 77 K using CI Electronics Microforce Balance, Mark 2B (ref.4).

The cokes were treated with boric acid solution, and heated to give B_2O_3-doped cokes which were examined as above.

The mineral matter of the coke, which remained as ash after the carbon was burnt away, was examined by X-ray powder diffraction.

RESULTS AND DISCUSSION

The "proximate analysis" of the three cokes, as used industrially, is given in Table 1.

TABLE 1

Proximate analysis of the Metallurgical Cokes.

	Nantgarw	Cwm	Polish
Moisture	<1%		
ash (dry basis)	9.36%	7.94%	11.32%
volatiles (dry basis)	0.90%	1.01%	1.33%
sulphur	0.90%	0.77%	1.11%
reactivity to CO_2 at 1000 °C			
(Nantgarw ratio	1.0	1.55	3.06
(ECE test	0.11	0.19	0.43

Reactivity is determined by the ECE test (ref.5) and by comparison with a low-reactivity coke (Nantgarw). Both tests involve reaction with carbon dioxide at 1000 °C; in the former the rate of CO_2 to CO conversion is measured by sampling the effluent gas, while in the latter the rate of coke weight loss is measured. Polish coke is seen as the most reactive, followed by Cwm coke. This is shown also in Fig. 1 by TG for the oxidation at 1000 °C, the ratios of the slopes of the initial portions of the weight loss curves corresponding to the industrial "Nantgarw ratios".

Previous research (ref.6) has shown that the development of surface on burn-off (in air or carbon dioxide) for Nantgarw coke is dependent on the absence of diffusional control of rate. Where diffusional effects are minimal there is a maximum development of surface on gasification as "internal burning" takes place.

The specific surface area of Nantgarw coke lumps burnt off in carbon dioxide at 1000 °C (Fig. 2) passes through a maximum at about 15% carbon burn-off, possibly by opening of initially closed pores and formation of new pores. In contrast, the surface area and porosity of the B_2O_3-doped coke do not increase considerably on burn-off. At 1000 °C boric oxide is effective at preventing formation of pores and new surface and consequently the rate of coke reaction to oxidising gases is lowered.

The major constituents of Nantgarw coke ash, as revealed by X-ray diffraction

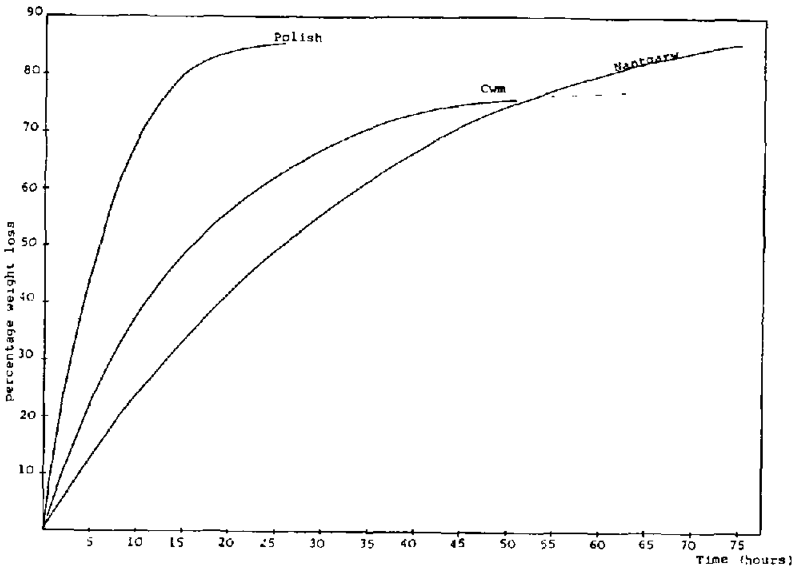

Fig. 1. Oxidation of three metallurgical cokes at 1000 °C in carbon dioxide (flow rate 17.6 cm^3 min^{-1})

are given in Table 2.

TABLE 2

Principal constituents of Nantgarw coke ash.

500 °C ashing	1000 °C ashing
sillimanite $Al_2O_3SiO_2$	sillimanite $Al_2O_3SiO_2$
anhydrite $CaSO_4$	anorthite $CaO.Al_2O_3.2SiO_2$
iron III oxide γFe_2O_3	iron III oxide αFe_2O_3
iron II III oxide Fe_3O_4	

Since 1000 °C is above the Tammann temperature of the ash minerals, sintering of the ash as it progressively accumulates on the coke will tend to lower the specific surface area in the carbon dioxide burn-offs, especially in the later stages. Changes in specific surface of the three cokes on carbon dioxide burn-off at 1000 °C are compared in Fig. 2. Values pass through a maximum and then fall as ash accumulates on the coke surface. Metallurgical coke is a heterogeneous material and a greater spread of results was found for

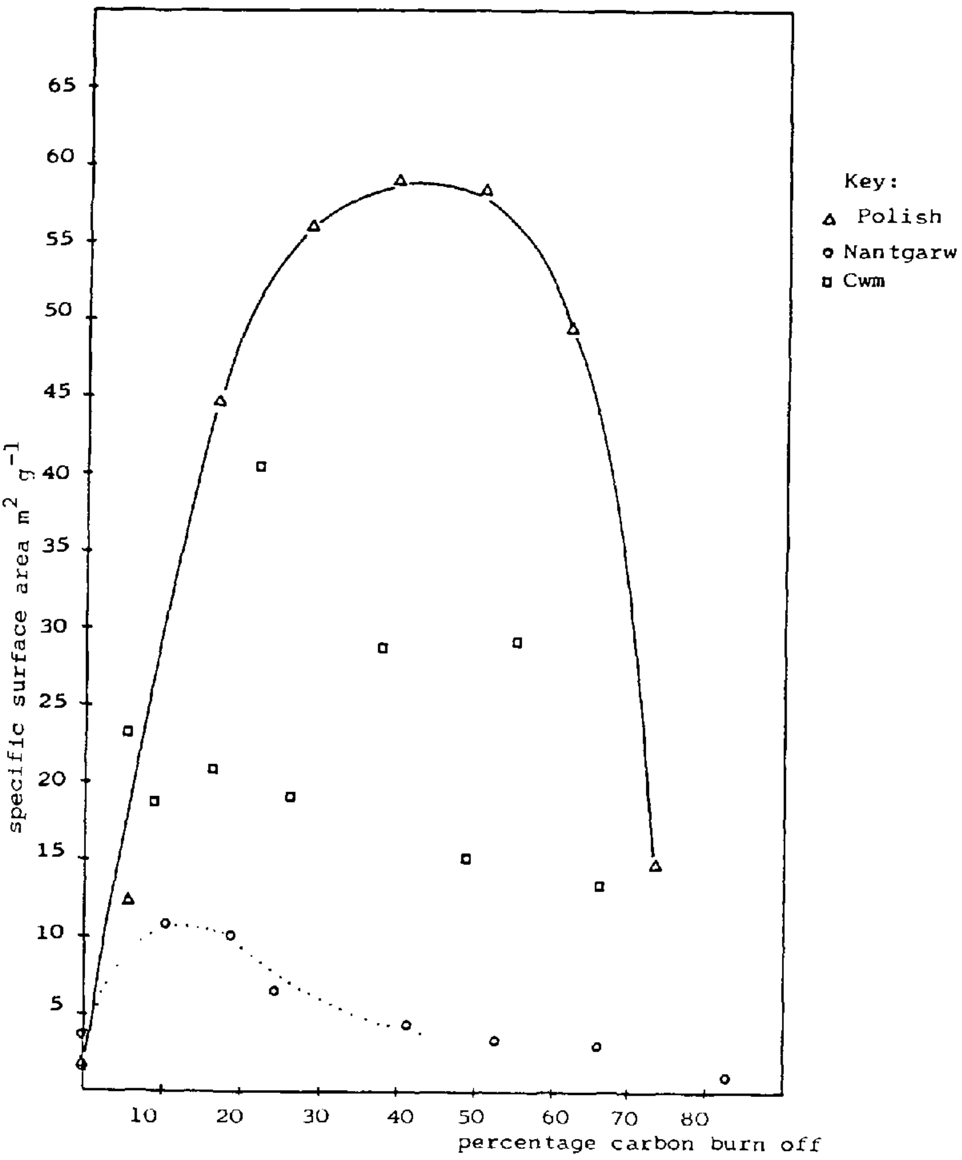

Fig. 2. Variation in specific surface area with burn-off in carbon dioxide for Nantgarw, Cwm and Polish cokes.

Cwm coke. Both Cwm and Nantgarw cokes are prepared from coal blends, with Cwm incorporating coke breeze. The initial surface area values can be seen to bear no relationship to the "reactivities" of the cokes. However, the development of specific surface area is greatest for the most reactive coke. Surface area and porosity initially increase for each of the cokes as carbon is removed from the surface on gasification. Of the surface that develops, not all is available for gaseous attack. The specific surface area maximum values are in the approximate ratio 1:3:6 for Nantgarw:Cwm:Polish cokes, taking a mean value for Cwm coke. The reaction rates of the cokes to carbon dioxide at 1000 °C are in the approximate ratio 1:2:4, as given in Table 3.

TABLE 3

Coke	Reactivity by Nantgarw ratio test.	Rate of reaction in CO_2 at 955 °C $\times 10^6$ g s^{-1} g^{-1}	Maximum specific surface area m^2 g^{-1}
Nantgarw	1	6.96	10
Cwm	1.55	13.89	28
Polish	3.06	30.88	59

Adsorption isotherms for some of the burnt-off Polish coke samples are shown in Fig. 3 The desorption points (closed circles) show hysteresis due to the porosity developed. The closure of the desorption and adsorption branches only at low relative pressures indicates development of a range of pore sizes from micropores (below 2 nm diameter) and mesopores (2-50 nm diameter) to macropores (above 50 nm diameter), although not all of this porosity contributes to the effective surface area for oxidation. If the volume of carbon lost on burn-off to maximum specific surface area is equal to the pore volume developed, the mean maximum pore radius (for cylindrical pores) may be calculated and is given in Table 4.

TABLE 4

Coke	Mean maximum pore radius (nm)
Nantgarw	33.4
Cwm	15.8
Polish	15.3

These pore diameters are very high, since they occupy the higher part of the mesopore range corresponding to relative pressures of 0.94-0.96. Hence it is probable that only a small proportion of the carbon burnt off leads to new micro- and meso-pore formation. This is confirmed from the magnitude of the nitrogen adsorption (Figs 3-5). Even if all of the nitrogen adsorbed on the new surface filled the micro- and meso-pores, the total pore volume is less than 15% of the volume of carbon burnt off, even for the most reactive Polish coke. After allowing for small changes in external surface and additional surface caused by opening of initially-closed macropores on burning, most of the increase in surface (over 83%) is due to formation of new micro- and meso-pores. In

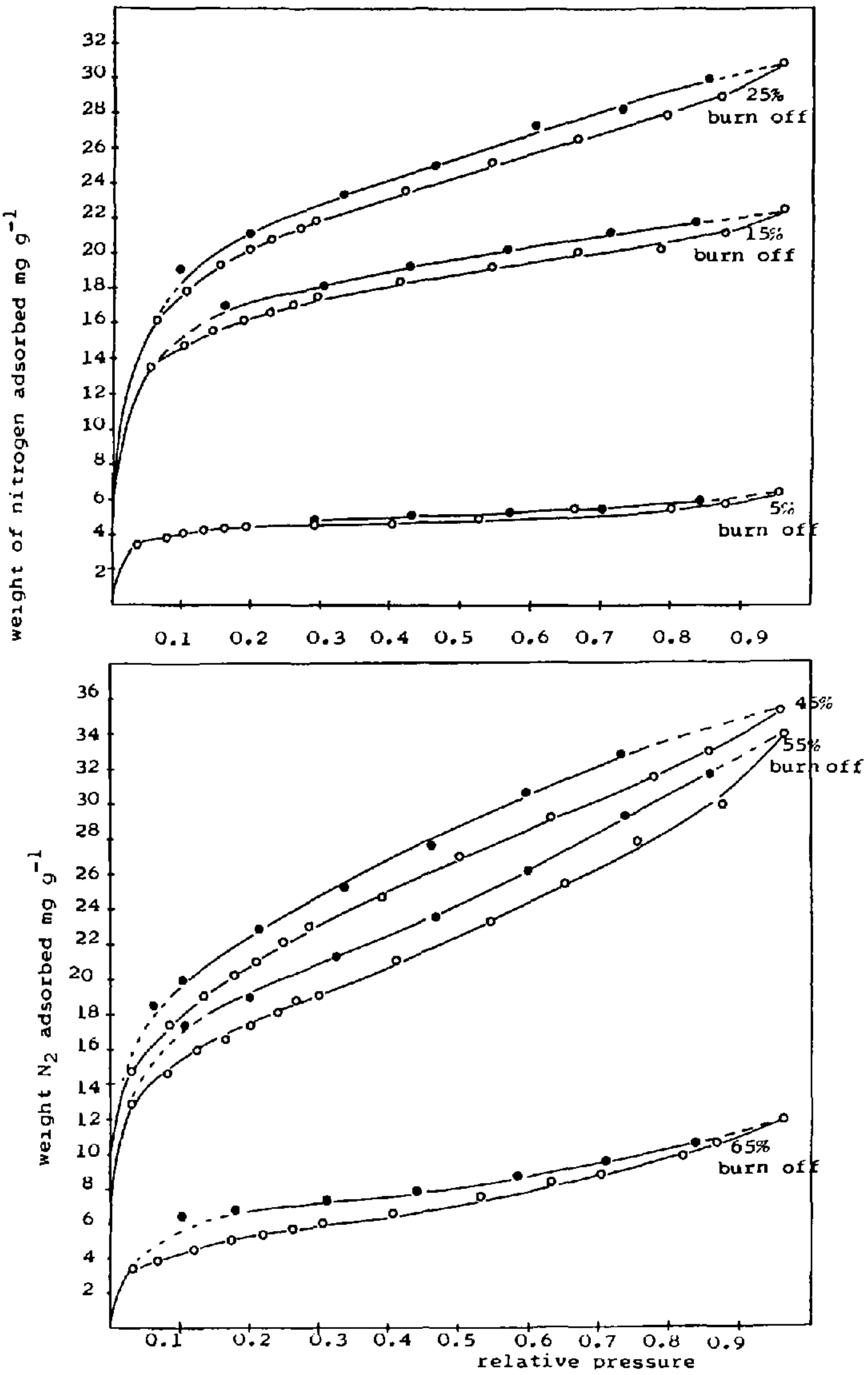

Fig. 3. Nitrogen adsorption isotherms at 77 K for Polish coke burnt off ir carbon dioxide at 1000 °C.

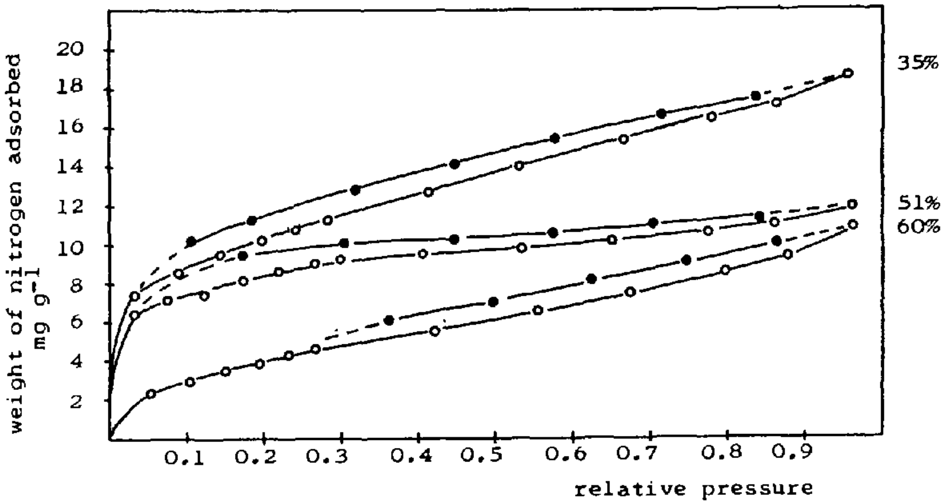

Figure 4. Nitrogen adsorption Isotherms at 77 K for Cwm coke burnt off in CO_2

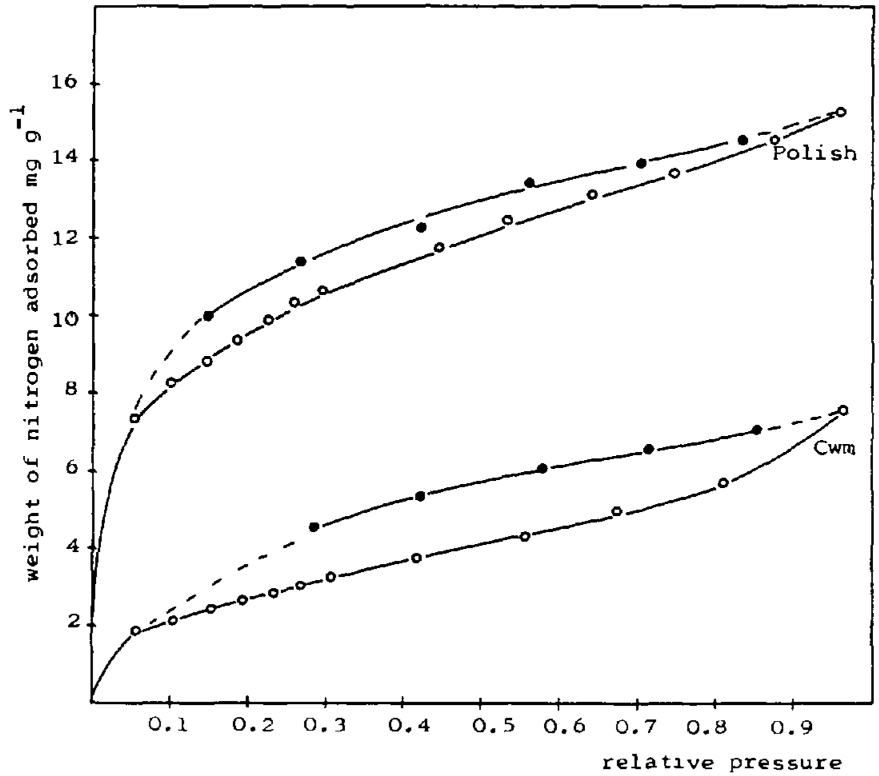

Fig. 5. Nitrogen adsorption isotherms at 77 K for B_2O_3 doped Cwm and Polish cokes burnt off 15% in CO_2.

relation to the volume of adsorbed nitrogen, the mean pore diameter of the combined micro- and meso-pores is about 3 nm, in keeping with the wide range of pore sizes covering the lower and upper relative pressure ranges (0-0.38 and 0.38-0.96) associated with micro- and meso-pores. Similar calculations for the partly-burnt Cwm and Nantgarw cokes of highest surface area also show that most of the increase in surface, 68% and 79% respectively, is due to the formation of new micro- and meso-pores. Likewise, only a small percentage of the carbon burn-off creates new micro- and meso-pores, viz., less than 8% and 3% respectively, the latter figure being in good agreement with other research in these laboratories on steel-making cokes derived from coal blends (ref.7).

The effect of boric oxide additive in reducing the surface area and reactivity of Nantgarw coke has been reported earlier (ref.6). The Cwm and Polish cokes had smaller initial surface areas (1.2 and 1.6 $m^2 g^{-1}$) than Nantgarw coke (3.6 $m^2 g^{-1}$) and thus retained less B_2O_3 on doping. They gave smaller percentage reductions in surface area on burn-off. cf. Fig. 3-5 and Table 5.

TABLE 5

Coke	% B_2O_3 retained	% reduction in specific surface area at 15% burn off in CO_2	% reduction in rate of CO_2 oxidation at 955 °C
Nantgarw	1.1 to 1.5	86	58.9
Cwm	0.8	57	variable (80% to 30%)
Polish	0.2	39	53.9

However, since much of the surface of the partly-burnt coke is located in micro- and meso-pores, this is comparatively inaccessible to carbon dioxide. Thus the effectiveness of B_2O_3 as an inhibitor of the Boudouard reaction on coke is due mainly to its ability to block larger pores where much of the gasification takes place.

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