VACUUM MICROBALANCE STUDIES ON THE COMBUSTION OF SARAJI COAL

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ABSTRACT

   Samples of Saraji coal have been oxidised in air at various temperatures and
for different times. Products have been examined by a gravimetric gas sorption
technique. Results are presented for changes in surface area and porosity with
carbon burn-off and discussed in relation to kinetics of the oxidation.
   There is considerable development of surface and porosity as the oxidation
proceeds, especially during the first half of the burn-off. However, oxidation
of the coal is only slightly accelerated, since most of the new surface is
located in micro- or meso-pores where access to atmospheric oxygen is
restricted by slow diffusion.

INTRODUCTION

   Saraji coal is an Australian prime coking coal of rank 301a. It is a

Gondwana Permian coal formed under temperate conditions showing distinct ring

structure. In contrast, European coking coals, e.g., British and Polish, have

been formed under hot, steamy tropical conditions (ref.1). Thus British Horden

coal is a high volatile, strongly caking coal of rank 501, but having an indis-

tinct ring structure.

   In earlier research (ref.2), the behaviour of Horden coal on oxidation has

been examined and in the present research it is compared with the oxidation of

Saraji coal. Gas sorption isotherms have been determined gravimetrically (ref.3)

on the solid residues of the partly-combusted coal and likewise show consider-

able development of surface and porosity for the faster burn-offs. These

changes are correlated with the oxidation kinetics.

EXPERIMENTAL

   Samples of Saraji coal at various degrees of burn-off were prepared iso-

thermally in a furnace at 300, 400 and 500°C, using lumps of approximately 5mm

diameter. Surface areas were determined by a gravimetric BET method (ref.3),

using nitrogen gas sorption at -196°C recorded on a CI Electronics Mark 2B

microforce balance. Samples of up to 200mg weight could be examined, using

balance ranges of 0-2.5mg, 10mg and 100mg for measuring the gaseous adsorption.

The adsorption isotherms also provided data on the micro- and meso-porosity of

the materials (ref.4). Information on the macroporosity was obtained from density measurements by gas or liquid displacement.

RESULTS AND DISCUSSION

Surface activity and kinetics during coal oxidation

Variations in surface area during oxidation of Saraji coal in air at 300, 400 and 500°C are presented in Fig.1 and Fig.2.
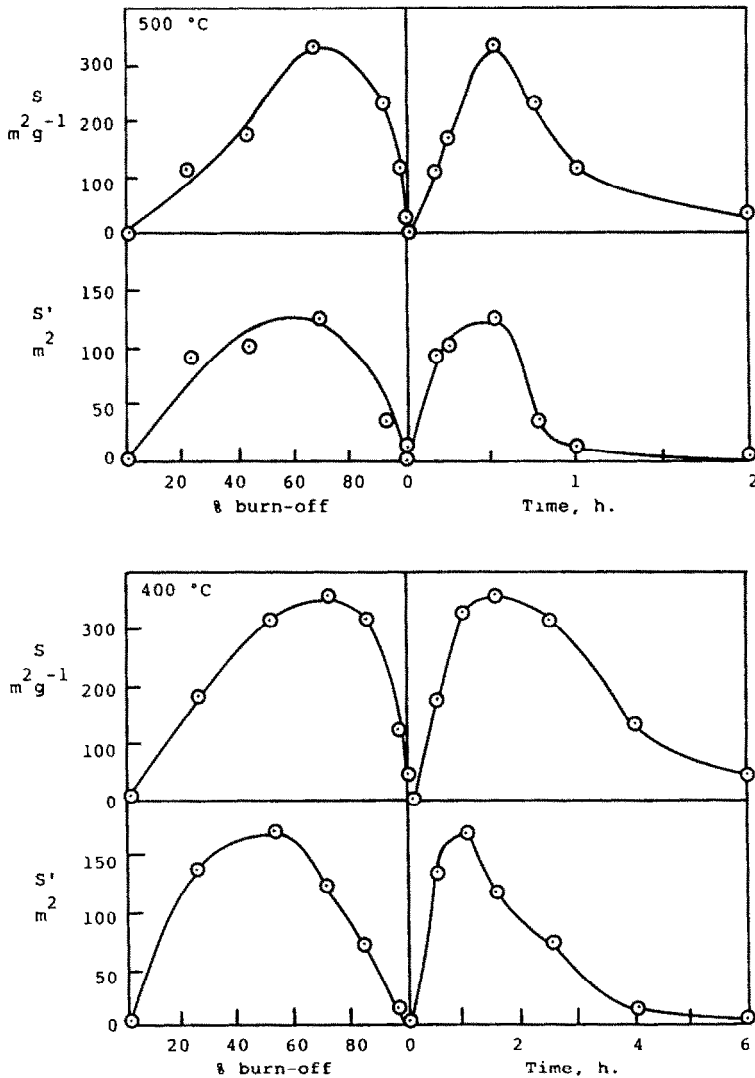

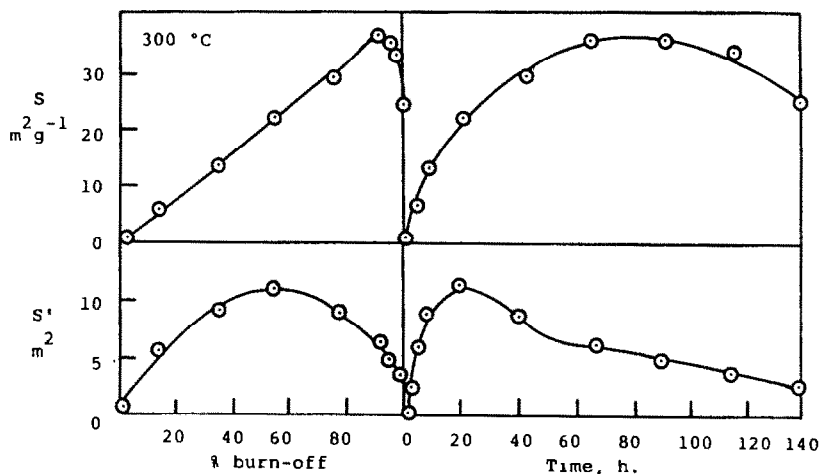Fig.1. Oxidation of Saraji coal in air at 400 and 500°C.

Fig.2. Oxidation of Saraji coal in air at 300°C.

As oxidation proceeds at each temperature, the specific surface area, S, of the partly-combusted coal progressively increases, reaching a maximum in the later stages of burn-off. Similar maxima are shown for the changes in total surface area, S', (rather than specific surface, S) of initial 1g-samples of coal at various degrees and times of burn-off. However, these maxima all occur at about 50% burn-off. The increases for the more rapid burn-offs at 400 and 500°C are considerably greater than that for the slow burn-off at 300°C, rising to $170m^2$ at 400°C and $125m^2$ at 500°C. Increases to $125m^2$ and $83m^2$ respectively were recorded for Horden coal in earlier research (ref.2). The smaller increases at 500°C compared with 400°C were ascribed to the tendency of the coal residue to form small globules, suggesting that the rate of energy transfer was insufficient to maintain an even temperature and hot spots were formed. The temperature of 500°C is well above the softening temperatures of the coals (Horden, 346°C, Saraji, 406°C) facilitating loss of volatiles and just above resolidification temperatures, 449,487°C (ref.5). Saraji coal burns more slowly than Horden coal, particularly in the later stages of oxidation, cf. Fig.3. Nevertheless, the increases in surface are correspondingly larger for Saraji than Horden coal, which is in line with the higher temperatures for Saraji coal. At 300°C, a temperature below the softening points, the increases in surface are much smaller, cf. Fig.2, but the maximum for the Saraji coal $(11.1m^2)$ is about twice that for the Horden coal $(5.6m^2)$ for practically equal oxidation rates during the first half of the burn-off. Initially the Saraji coal $(S = 0.5m^2g^{-1})$ is more compact than the Horden coal $(S = 2.0m^2g^{-1})$ and evidently is subjected to greater strain during the loss of its volatile
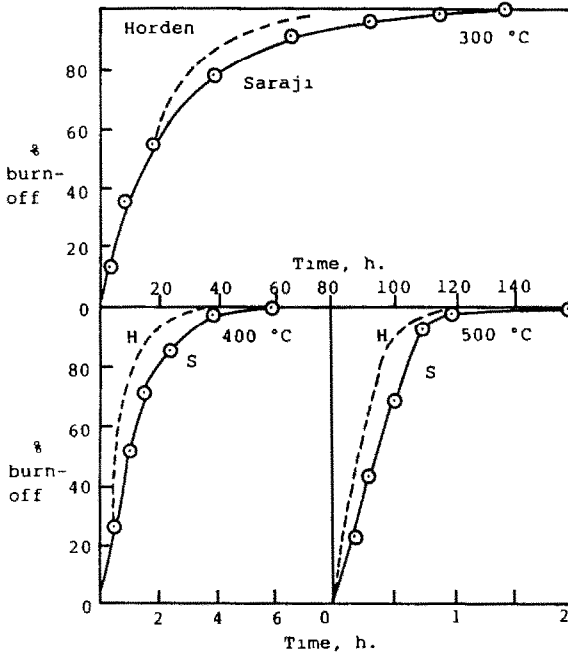
Fig.3. Combustion of Saraji coal in air at 300, 400 and 500°C.

matter (19.6-27.5 dry mineral matter free %) compared with Horden coal (32.1-
36.0 dmmf %); the Saraji coal shows a tendency to flake on combustion, thereby
forming more new surface.

There is evidently formation of pores at the coal surface, including opening
of initially closed pores as the oxidation proceeds. Thus although the
original coal samples have mainly macroporosity and some mesoporosity, they
develop full ranges of mesoporosity (pore sizes 2-50nm diameter) and some
microporosity during the burn-offs. This is shown by the nitrogen isotherms
developing adsorption hysteresis in the relative pressure range 0.37-0.96
corresponding to mesopores and then at relative pressures below 0.37 (micropore
range), cf. Fig.4 and ref.4, which shows examples of Saraji coal approximately
half-burnt at 400°C and at 500°C. Thus there is considerable development of
surface and porosity as the oxidation proceeds, especially during the first
half of the burn-offs. However, most of the new surface is located in the
micro- or meso-pores where access to oxygen (from air) is restricted by slow
diffusion. There are not the large increases in oxidation rate which are
suggested by the plots of S' against time in Figs.1 and 2 (where S' should be
proportional to rate of oxidation and the oxidation-time curves should be
acceleratory and sigmoidal). In practice, the oxidation of the coal is only
slightly accelerated, so that the diminution in oxidation rate according to the
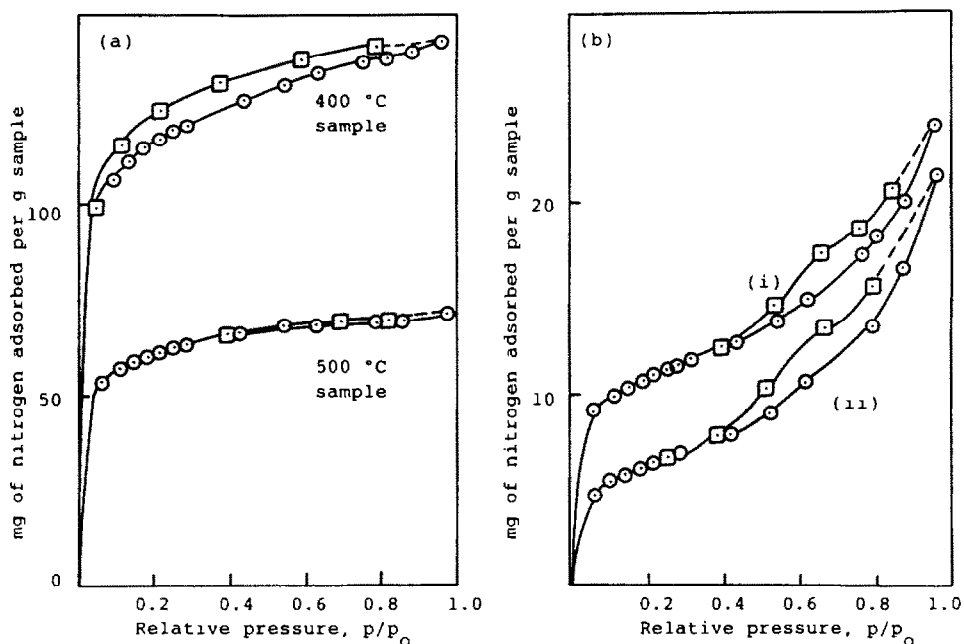
Fig.4. Nitrogen adsorption isotherms on (a) partly-burnt Saraji coal,
(b) Saraji coal ash.

ideal two-thirds order law (for the contracting sphere model) is just
compensated enough to make the earlier stages of oxidation approximately linear
with time, cf. Fig.3. This is found also for oxidation of the coal in air,
oxygen or carbon dioxide (Boudouard reaction) under dynamic (gas flow)
conditions.

Formation and sintering of the coal ash

Although the surface area changes and combustion rates were considerably
different at 300, 400 and 500°C, yet the surface areas of the ashes were
approximately the same. In Fig.4(b) nitrogen adsorption isotherms are shown
(i) for the ash formed when the coal combustion at 500°C was just complete (in
2h), and (ii) when the ash had been sintered at 500°C for a further 8h. The
isotherms for the ash are of type II (BET classification, ref.6) in contrast
with those of the partly-burnt coal which are of type I, cf. Fig.4(a). The
surface area of the newly-formed ash (i) was $30m^2g^{-1}$ which decreased to
$18.5m^2g^{-1}$ on 2h heating at 500°C and remained practically constant during a
further 6h heating (ii), $S = 18.1m^2g^{-1}$. The main components of the ash were
silica, alumina or alumino-silicates and iron oxides, Fe_2O_3 and Fe_3O_4. Since
the Tammann temperatures (half m.p. in K) correspond to 890°C for alumina,
730°C for silica and 650°C for ferric oxide (ref.7), there is no possibility of

ash sintering proceeding by crystal lattice diffusion at the lower temperatures of 300-500°C. Therefore sintering is possible only by surface diffusion, which becomes appreciable above about one-third of m.p. in K, i.e. 500°C for alumina, 400°C for silica and 340°C for ferric oxide. Since only the lower-temperature mechanism is available, sintering is restricted, i.e. some initial loss of surface is followed by comparatively slow sintering, as was found earlier for Horden coal ash (ref.2). The nitrogen adsorption isotherms on the ash in Fig.4(b) indicate a small amount of mesoporosity and no microporosity and the surface areas indicate average crystallite sizes of approximately 0.1-0.2μm. The surface areas are somewhat higher than those found for the ashes of metallurgical cokes oxidised in air at 500°C (ref.8), where there will have been some sintering produced by the higher temperatures used in the initial coking of the coals.

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