Coke Oven Carbon Deposits Growth and Their Burning Off

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Burning off is the main method of carbon deposit removal from coke oven chambers. Optimisation of this operation is of a great interest both from the point of view of current production loss reduction and of coke oven plant lifetime extension. In this study the deposits originating from different parts of chambers have been characterised by chemical analysis, optical microscopy, XRD, Raman spectroscopy and mercury porosimetry. This investigation has shown that deposits contain two carbonaceous phases: the char from pyrolysed carry over coal particles and the pyrolytic carbon from raw gas cracking.

Furthermore, the monitoring method for carbon deposits growth in coke oven chamber is presented. The statistical analysis of the visual inspection data has been a useful tool in the evaluation of the rate of deposit growth in individual coke oven chambers.

The combustion kinetics of carbon deposits were studied by thermogravimetry under non-isothermal conditions with natural air draft and under isothermal conditions at controlled air flow rate. It was found that the reactivity of carbon deposits is in-between metallurgical coke and electrographite reactivity. At the temperatures below 700°C, under laboratory conditions, the combustion rate (on the basis of external surface) is controlled by surface reaction at higher temperature and activation energy is around is 170 kJ/mol. At temperature higher than 700°C combustion is controlled by gas film diffusion.

Modelling of combustion in thermobalance experiments and in industrial coke oven chamber was carried out on the basis of measurement of kinetics using commercial CFD software.

KEY WORDS: coke oven; carbon deposition; combustion kinetics; thermogravimetry; CFD.

1. Introduction

Carbon deposition on the walls of coke oven is a frequently mentioned problem that affects stable operation and shortens lifetime of coke oven batteries. At different plants the intensity of carbon deposition varies but the causes are similar. In fact, carbon deposition depends on a number of parameters: temperature of the chamber wall and in the gas phase, residence time of volatiles in the hot zone, composition and content of volatile matter and the nature of the surface on which the deposition takes place. In Japan, pioneering studies on the carbon formation mechanism and the carbon deposit characterization were done by Yoshida et al.¹¹ and Nagata et al.²¹ Nakagawa et al.³,¹² studied the influence of coal moisture and fine coal particles (carry over) on carbon deposition. By laboratory measurements and by inserting test pieces into the coke oven chambers, they clarified the carbon deposition mechanism and measured its rate at different locations in the chamber. Carbon deposition in a coke oven at high coking rate of new coke making process SCOPE21 was also investigated by Uebo et al.⁵,⁶ The influence of temperature, fine coal and water presence on carbon deposition was also studied in laboratory tests and in the pilot plant oven using test brick pieces. In France, Krebs et al.³,⁴ studied in detail the influence of coal moisture content on carbon deposition yield and microstructure. Dumay et al.⁵,¹³ studied the cracking conditions in the coke oven free space to better asses the parameters for carbon deposits control. They used a special device enabling in situ measurement of carbon deposit growth. In Russia, the mechanism and kinetics of carbon deposition was also studied in order to establish more efficient procedures and methods for carbon deposition prevention and deposits elimination.⁹,¹⁰ Presently used methods for carbon growth control are: manual or mechanical removal by spear, burning-off by natural air flow from open door or charging hole, burning-off by air blowing through the pushing ram or lance from charging hole,¹¹ air blowing into ascension-pipe and decomposition by blowing exhaust gas into top space. Two different methods are also proposed to prevent carbon deposition: water spray into the top space and wall coating by glassy products and blowing carbon away.¹³,¹⁴

Because carbon deposit removal from coke oven chamber by burning-off is still the main method of its elimination, there is a need to optimise this operation for at least two reasons: firstly, to minimise its time in order to reduce production losses and secondly, to avoid wall damage by overheating which contributes to shortening of battery lifetime. From the previous studies it is known that carbon deposit is a low ash content mixture of pyrolytic carbon and char.¹–⁸ Its burning in air could therefore be considered as a specific case of solid carbon combustion which has been extensively studied for many years, especially in the case of char. There are excellent reviews of the earlier work on car-
bon combustion and gasification.\textsuperscript{15,16} In general, char particle combustion is considered as a heterogeneous reaction whose overall rate depends on heat and mass transfer across the boundary layer surrounding the solid particle, diffusion through the porous structure of the particle and reaction of oxidant gases with solid surfaces within the particle.

Two models of coal char combustion are mainly used: one-film model and two-film model.\textsuperscript{17,18} The first model assumes that the only reaction in the system is a heterogeneous reaction of oxygen with solid carbon on its non-porous surface: \( \text{C} + \text{O}_2 = \text{CO}_2 \). Its rate depends on relative contribution of surface reaction kinetics (intrinsic reaction) and external (gas film) diffusion steps. The second model assumes that solid carbon is first oxidized, mainly by \( \text{CO}_2 \) and eventually by oxygen, to carbon monoxide: \( \text{C} + \text{CO}_2 = 2\text{CO} \) and \( 2\text{C} + \text{O}_2 = 2\text{CO} \). Carbon monoxide produced in these reactions diffuses outward through a first film and is consumed at more or less sharp flame sheet, where it meets an inward-diffusing flow of oxygen: \( 2\text{CO} + \text{O}_2 = 2\text{CO}_2 \). The equations of the second model are more complex and require more kinetics constants, but even so, they are not always sufficient to describe combustion of real solid fuels with varying structure and properties.\textsuperscript{19}

The objective of the present paper is, firstly to characterise the carbon deposits from different locations in a coke oven chamber, secondly to measure their reactivity and thirdly to model their combustion under laboratory conditions and in an industrial coke oven chamber.

2. Experimental

2.1. Carbon Deposits Characterisation

The proximate analysis, namely ash and volatile matter content in the deposit samples, was performed using standard methods for coke characterisation. The real and apparent densities were measured by the pycnometric and Archimedes methods. The open porosity and the pore size distribution were measured by mercury porosimeter (Micromeritics Poresizer 9320). The deposits polished sections were examined by Reicherdt-Junge optical microscope with polarized light. The crystal structure was analysed by XRD (Siemens D5000) on powdered samples of deposits and by Raman spectroscopy (Dilor JYH Labram spectrometer equipped with an Olympus optical microscope) on the polished sections of the deposits. The last method enables to separately examine the structure of distinct carbonaceous phases of deposits.

2.2. Thermogravimetry

The kinetics of deposit combustion was studied using TG technique in two distinctive series:

- first, under non-isothermal conditions and natural air draft,
- second, under isothermal conditions and controlled air flow.

In both series, the samples for combustion were cut from the massive deposit samples using a diamond saw. They had a shape of a thin slab measuring \( 10 \times 15 \times 2.5 \text{ mm} \) and weighing approximately 500 mg. They were placed on the alumina sample holder which is shown in Fig. 1(c).

The objective of the first series was a quick reactivity assessment of the carbon deposits from different locations as compared with two well known carbonaceous materials: metallurgical coke and electrographite. A very simple procedure was used in this TGA experiment. A sample placed on a sample holder was directly introduced into Linzeis L81 thermobalance furnace without a protective alumina tube ensuring the ambient air flow in the vertical furnace due to natural convection (air draft) (Fig. 1(a)). Each sample was first quickly heated up to 600°C at a heating rate of 30 K/min and then up to 900°C at 5 K/min.

The purpose of the second series was to measure the combustion rate under isothermal and controlled air flow conditions in the temperature range of 500 to 900°C. The same Linzeis L81 thermobalance was used (Fig. 1(b)), but the sample was placed in the alumina protective tube (I.D. 30 mm). It was heated in nitrogen up to the suitable temperature at 20 K/min and then, after the temperature stabilisation (5 min), nitrogen was replaced by air (Alphagaz grade 2). The air flow rate was controlled by mass flow controllers (Brooks Instrument). For each dwell temperature, the influence of air flow rate in the range of 50 to 1000 mL/min was tested.
3. Results and Discussion
3.1. Carbon Deposit Composition and Microstructure

The carbon deposit samples under study came from Arcelor-Mittal Dunkirk coke oven plant but were collected during the cleaning operation at different locations in the oven chambers: charging hole, roof, wall, door, ascension pipe and gooseneck. This coke plant operates the battery B6 (55 ovens) and the battery B7 (63 ovens) to produce 1.4 million tonnes of coke per year. The batteries are pushed at 19.5 h coking time (143 ovens/d). The mean flues temperature is around 1240°C. The dimensions of the chambers are (6.53 m × 0.46 m × 15.65 m). There are four charging holes and the nominal level of the charge is 6.20 m. The volume of one chamber is 44.45 m³ and the weight of coal around 36.5 metric tonne. The volatile matters of the blend are around 24% (dry basis). The moisture content varies between 7 and 9.5%. The coal size distribution is: 18.5% less than 160 μm and 69–70% less than 2 mm. The coal blend contains roughly 55% of Low Volatile; 30% of Medium Volatile, 150% of High Volatile coals.

The samples were taken on the battery B6 which is very sensitive to carbon deposition. In effect, at this battery, due to a design fault of the reversing point of the flues, the free space is very narrow (0.33 m) and too hot (900°C) so the carbon deposition is very difficult to prevent.

As an example, the photo of a deposit coming from lower part of a charging hole is presented in Fig. 2. It was 7 cm in thickness and covered a surface of 2–3 m². At the side, by which it was stuck to the silica wall (Fig. 2(a)), its surface was smooth with an apparent trace of the brick joints. The face, which was turned toward the chamber and was in contact with coke and gas is not uniform and has a rough texture. A fractured cross-section of the same piece, presented in Fig. 2(b), shows that the deposit is stratified with dense layers unevenly separated by cavities and fissures oriented more or less parallel to the wall surface. The deposits found on the vertical heating wall are not so thick, but very often they are denser, harder and less porous. Their thickness is limited by abrasion during the coke pushing-out from the chamber.

Some characteristics of the deposits from different locations in the chamber are listed in Table 1. The ash content varies from 1 to 5%. Because the only source of ashes in deposits is coal char (the pyrolytic carbon is basically ash free), its mass fraction could be simply calculated from ash balance by the following formula:

\[
\%\text{Char} = \frac{\text{Ash(in deposit)}}{\text{Ash(in char)}} \times 100
\]

The average ash content in the coke (char in deposit could be considered as a coke) during the period of the deposits formation under study was approximately 8% so the char fraction in the deposits was evaluated to be about 20–30% of the total mass of deposit. This char is formed from fine coal particles that are being carried over during the charging operation and then stick and pyrolyse at the wall. The other part of deposit is the pyrolytic carbon produced by the raw gas cracking on the char.

The volatile matter content (less than 0.5%) in all deposit samples is lower then in the regular coke sample where, basically, it is around 1%. Such low volatiles result from a long residence time of carbon deposits in coke oven chamber (from some weeks to several months). The only exception is the deposit from gooseneck which contains up to 10% of volatiles and 4.5% of ashes. This composition, density and porosity show that it is a mixture of non carbonised coal particles aggregated by condensed heavy hydrocarbons (tar) only partially devolatilized. The real density as measured by pycnometer is 1.9 g/cm³ and 1.98 g/cm³, respectively for deposits from the charging hole and from the wall. The bulk density measured by the Archimedes method for the same samples is 1.3 and 1.54 g/cm³, respectively resulting in the porosity of 31% for the charging hole deposit and 22% for the chamber wall deposit.

![Fig. 2. Deposit from lower part of charging hole: a) side by which it was stuck to the wall with clear trace of brick joints, b) cross-section showing stratified structure.](image)

<table>
<thead>
<tr>
<th>Deposit location</th>
<th>Ash % d.b.</th>
<th>VM % d.b.</th>
<th>Density, g/cm³</th>
<th>Porosity %</th>
<th>Char content %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charging hole</td>
<td>1.8</td>
<td>0.5</td>
<td>1.90</td>
<td>1.30</td>
<td>31</td>
</tr>
<tr>
<td>Roof</td>
<td>1.5</td>
<td>0.3</td>
<td>2.06</td>
<td>1.50</td>
<td>27</td>
</tr>
<tr>
<td>Wall</td>
<td>1.7</td>
<td>0.5</td>
<td>1.98</td>
<td>1.54</td>
<td>22</td>
</tr>
<tr>
<td>Door</td>
<td>2.0</td>
<td>0.4</td>
<td>2.10</td>
<td>1.55</td>
<td>26</td>
</tr>
<tr>
<td>Gooseneck</td>
<td>4.5</td>
<td>10</td>
<td>1.50</td>
<td>1.40</td>
<td>7</td>
</tr>
</tbody>
</table>

VM: volatile matter
In order to better characterise the deposits microstructure and morphology, their samples were examined by optical microscopy and by mercury porosimetry. The microscopic observations show clearly (Fig. 3) two distinct carbonaceous phases. The first is the pyrolytic carbon with characteristic ribbon like morphology that recovers and sticks together the porous char grains different in size and shape which constitute the second phase. Big inter-granular pores are also seen on these micrographs, uneven in shape, sometimes larger than 100 μm as well as the spherical and small (<10 μm) pores mainly located inside the char phase. Total porosity and the pore size distribution were also measured by mercury porosimetry. The cumulative and differential volumes of mercury intrusion for two samples coming respectively from a charging hole and from a wall are presented in Fig. 4. The first has 31% of the open porosity and the second only 22% but both exhibit two distinct pore size populations: the large pores—with a diameter from 10 to 500 μm and small pores—with a diameter below 0.1 μm. It is clear from the figure that the difference in the total open porosity is mainly due to the big pores volume contribution. The nature of carbonaceous phases in deposits, especially their crystal structure was also studied by XRD and Raman spectroscopy. X-ray diffraction patterns presented in Fig. 5 show that (0002) peaks observed for three deposit samples are very broad and slightly shifted toward the lower diffraction angle as compared with the peak given by a well crystallized electrogaphite used as a reference carbonaceous material. It means that the deposits are composed of very weakly crystallised turbostratic carbon. The Raman spectra presented in Fig. 6 exhibit two characteristic bands: G and D. The first (G) corresponds to well crystallized graphite phase and the second (D) is distinctive for a disordered carbon phase. It is evident from the Fig. 6 that the char as well as the pyrolytic carbon which constitute the deposit are weakly crystallized forms of carbon. This conclusion is in accordance with earlier works1–9) on carbon deposits from coke oven chamber. It should be emphasized that it is wrong to call the carbon deposits in a coke oven chamber “the graphite” as currently cokemakers do.
3.2. Statistical Study of the Carbon Deposits Growth

As explained before, the operation of the battery B6 commissioned in 1987 is still difficult because of the intensive carbon deposition. Some countermeasures were taken in the last decade to limit carbon deposition and its impact on the coke plant operation. The time period between successive cleaning of the coking chamber has been increased from 3 to 6 months. This actions aim at:

- decreasing of the fines of coals in the coal blend by applying a variable speed drives on the crushers;
- decreasing of the flames length in the flues by introducing constant flow rate and constant air factor;
- getting the best level of the charge due to high bulk density (750 kg/m³ on dry basis) and fast moving leveller bar and eleven strokes.

In order to evaluate the efficiency of all these countermeasures and to manage the cleaning operation of coking chambers, a monitoring system was introduced at the coke oven plant a few years ago. It is based on monthly visual evaluation of the carbon deposition degree in each chamber and, especially, in the charging holes where the deposition is most intensive. Figure 7 shows the photos of two charging holes: one freshly cleaned and the second partially obstructed. The schematic representation of the visual evaluation of carbon deposition degree in charging hole is also presented in this figure.

An arbitrary scale, varying from 0 to 80%, is used for monitoring the progressive growth of deposit in the holes. Knowing the area of deposition surfaces in the chamber and the apparent density of the deposits at different locations, the corresponding amount of carbon deposit is estimated. The chambers are cleaned every 6 month on the average. Extensive data sets have been collected during recent years from which the relationships between the degree of carbon deposition and time elapsing from the last cleaning were plotted by linear regression. Figure 8 shows the data related to charging hole number 3 where the carbon deposition is the most intensive when compared to the holes number 2 and 4. The deposition rate in charging hole number 1 (situated at the coke side of the battery) is very low and has not been not monitored. The deposition rate obtained by linear regression in %/d, in kg/d and in kg/m²/d as well as the determination coefficient $R^2$ and the number of points in the corresponding data sets are shown in Table 2.

Figure 9 shows separately the data for the two chambers (611 and 606) collected during three successive campaigns. It can be seen that the rate of deposition varies between the chambers. In chamber 611 the growth is quicker during the first weeks and the deposition degree rises to about 30% after 6 months. In chamber 606 after 6 months it attains only 20%. It is interesting to note that the individual character of the deposition in each chamber shows repetitive patterns during the three successive campaigns.

These facts suggest that there are two types of factors influencing carbon deposition. Firsts, like the coal blend characteristics (volatile matter, moisture content and size) and the operational conditions (working rate, coking time, charge amount) are common for all battery. Second, that gives distinct and repetitive patterns for each chamber, is the wall overheating which extent change from oven to oven.
oven and can persist for long period.

It is also worth to note that the rates of carbon deposition obtained by linear regression (5–10 g/m² h) are close to some published data obtained in special industrial measurements but are noticeably lower than the deposition rate measured in laboratory tests (Table 3).

3.3. Combustion Kinetics

3.3.1. Combustion Under Non-isothermal and Air Draft Conditions

A typical combustion results for a wall deposit sample obtained under non-isothermal conditions are shown in Fig. 10. During the first stage, the rapid heating up to 600°C, there is no visible mass loss of the sample. In fact, the oxidation starts at a measurable rate only in the second stage when the temperature reaches about 650°C and it continues until the sample is completely burnt off at about 900°C. The combustion rate on a mass basis \( r_c \) was calculated from the mass loss curve:

\[
r_c = \frac{1}{m} \frac{dm}{dt} \quad \text{(1/s)}
\]

Figure 11 shows that at the beginning the combustion rate increases very quickly (exponentially) and later on almost linearly with temperature. It is also interesting to note that at the beginning of combustion (ignition) the temperature of the sample holder rises 50°C above its programmed temperature (a dotted line) due to the combustion heat and this difference persists until the complete combustion of the sample.

Figure 12 shows the rate of combustion of different deposits and two reference carbonaceous materials: electrographite and metallurgical coke, measured under non-isothermal conditions which are presented together on the Arrhenius diagram. It can be seen that the deposits reactivity appears just between that of the coke (with a highest reactivity) and that of the electrographite (with a lower reactivity). It is evident that the reactivity of deposits from diverse locations in the coke chamber is also different. Those coming from the charging hole are more reactive then those coming from the roof and the oven walls, which are less porous and contain more pyrolytic carbon. It can also be seen in Fig. 12 that almost all curves exhibit a slope change at the combustion rate around 0.0005 1/s. This occurs at different temperature for different carbonaceous material studied and the more reactive the carbon the lower this temperature.

To better illustrate the control regime identification in the thermobalance combustion experiments, the rate of wall deposit sample combustion is plotted alone as an example in the Arrhenius diagram of Fig. 13. At low temperatures (600–700°C) the apparent activation energy \( E_a \) is found to be 205 kJ/mol. At higher temperatures it is only about 60 kJ/mol. This means that when the temperature increases the mass transfer phenomena, namely the internal diffusion (in the carbon pores and in the ash shell) and the external

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Table 3. Comparison between statistically determined rate of carbon deposition and the published data.

<table>
<thead>
<tr>
<th>Author</th>
<th>Ref.</th>
<th>Year</th>
<th>kg/m² cycle</th>
<th>kg/m² h</th>
<th>μm/min</th>
<th>g/m² h</th>
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<tr>
<td>Jonoto</td>
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<td>1969</td>
<td>0.03 – 0.1</td>
<td>30–100</td>
<td>0.30 – 1</td>
<td>30–100</td>
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<tr>
<td>Krebs</td>
<td>7</td>
<td>1994</td>
<td>Lab</td>
<td></td>
<td></td>
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<tr>
<td>Nakagawa</td>
<td>4</td>
<td>1998</td>
<td>Lab</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Uebo</td>
<td>5</td>
<td>2002</td>
<td>Lab</td>
<td>0.15 – 1</td>
<td>20–100</td>
<td></td>
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<tr>
<td>Fursawa</td>
<td>3</td>
<td>1998</td>
<td>Plant</td>
<td>0.2 – 0.8</td>
<td>10 – 40</td>
<td></td>
</tr>
<tr>
<td>Stepanow</td>
<td>9</td>
<td>2001</td>
<td>Plant</td>
<td>0.004–0.04</td>
<td>4–40</td>
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<td>ECP</td>
<td>2005</td>
<td></td>
<td>Plant</td>
<td>0.04–0.08</td>
<td>2–4</td>
<td></td>
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<tr>
<td>ECP</td>
<td>2006</td>
<td></td>
<td>Stat</td>
<td></td>
<td>5–10</td>
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</table>

Lab– laboratory experiments, Plant– coke oven experiments, Stat - statistical study

Fig. 10. Typical TG measurements results for a wall deposit sample under non-isothermal conditions.

Fig. 11. Combustion rate measured by TG for a wall deposit sample.

Fig. 12. Arrhenius diagram for the combustion rate under non-isothermal and natural air draft conditions.
diffusion (gas film) of the oxidant gas to the reaction surface progressively become the rate controlling steps. So we can conclude that at low temperatures (500–700°C) the combustion of deposits in air is under kinetics control, in the narrow temperature range (700–800°C) under a mixed kinetic-diffusion control and at higher temperatures (800–900°C) under external gas film diffusion control. When overall kinetics is under external diffusion control the reaction rate depends on the gas flow rate and this dependence has been studied in the second series of combustion experiments.

3.3.2. Combustion under Isothermal and Air Controlled flow Conditions

In order to study the influence of air flow rate on the combustion kinetics a second series of TG measurements under isothermal conditions in the temperature range from 500°C to 900°C and with the air flow rate changing from 50 to 1 000 mL/min has been carried out. Figure 14 shows the typical results obtained under isothermal conditions. After a rapid heating at 30 K/min up to the programmed dwell temperature (850°C), the nitrogen is replaced by air and the combustion starts. In this run the sample had the initial mass \( m_i \) of 980 mg and its initial external surface area \( S_o \) was 5.5 cm\(^2\). The combustion rate on an initial surface basis \( r_s \) is calculated from the initial slope of a burn-off curve:

\[
 r_s = \frac{1}{S_o} \frac{dm}{dt} \quad (g/cm^2 s) \quad \ldots \ldots (2)
\]

It can be seen in Fig. 14 that the combustion rate up to 30–40% of burn-off does not depend significantly on it. Consequently, the initial combustion rate could be used as a good measure for the carbon deposit reactivity.

Figure 15 shows that, as could be expected from the non-isothermal combustion series, the combustion rate under isothermal conditions depends on the air flow rate. At low temperatures (500–600°C) this influence is very weak, but at higher temperatures (700–900°C) the combustion rate rises notably when the air flow increases.

In Fig. 16 the rates of combustion measured in the isothermal TG experiments at different temperatures and air low rates are put together in the Arrehnius diagram. Data fitting below 700°C, where combustion rate does not depend on air flow rate, give the following formula:

\[
 r_s = 15 \cdot 10^4 \exp \left( \frac{-170 000}{RT} \right) \quad (g/cm^2 s) \quad \ldots \ldots (3)
\]

This combustion rate expression could be compared with well established Field equation for the rate per unit area of external carbon surface as a function of temperature and oxygen partial pressure \( p_{O_2} \) (cited by Amundson\(^{15}\)):

\[
 r_s = 8 \cdot 712 \cdot \exp \left( \frac{-149 440}{RT} \right) \cdot p_{O_2} \quad (g/cm^2 s) \quad \ldots \ldots (4)
\]

This relationship, plotted in Fig. 16 for \( p_{O_2} = 0.21 \), shows quite good agreement between our result and Field correlation, especially when looking at the activation energies which are 170 and 149 kJ/mol, respectively. Of course both rate equations do not fit the experimental data above 700°C where combustion rate is under external diffusion control.
The data concerning the deposits combustion obtained by Uebo et al.\textsuperscript{5} are also shown in Fig. 16 where they show good agreement with our experimental points. The net influence of the rate of carbon combustion and gas flow rate, as well as relatively low apparent activation energy (70 kJ/mol) indicate that in Uebo experiments, like in ours, the combustion was also under external diffusion control.

4. Combustion Modelling by CFD

A CFD software (Fluent) was used to model carbon deposit combustion in the thermobalance tube as well as in the coke oven chamber. In both cases a Wall Surface Reaction Model was applied. In this approach, the calculation of the species concentration at reacting surfaces is based on a balance of the convection and diffusion of each species to/from the surface and the rate at which it is consumed/produced at the surface. The surface kinetics was described by the combustion rate on the external surface basis (Eq. (3)). Otherwise, the governing equations used were mass conservation, momentum conservation, energy conservation and species conservation in gas phase (O\textsubscript{2}, CO\textsubscript{2}, N\textsubscript{2}).
4.1. Combustion in the Thermobalance Tube

When modelling combustion in the thermobalance tube we neglected surface reaction heat considering the isothermal conditions in the gas phase and in the carbon small deposit sample. Inlet gas velocity and outlet gas pressure were given as boundary conditions for the reaction tube. The calculation was done for the steady state conditions, which prevail at least for 40% of burn-off, as we demonstrated earlier. Figure 17 shows the mass fraction of CO2 around the reacting sample for three different conditions of temperature and air flow rate. Note that CO2 mass fraction near the sample surface is much higher then in the bulk flow, especially for higher temperature, indicating the external mass transfer control.

The raw combustion rate data are presented once more in Fig. 18 where a comparison is made with the results obtained by CFD simulation (solid lines). It is clear from this comparison that surface reaction approach with the Arrhenius expression obtained from pure kinetic control region is good enough to simulate the influence of air flow rate on the overall combustion rate of the deposits over the whole temperature range. Therefore we used this model and CFD software to simulate the deposit burn-off in a coke oven chamber.

4.2. Carbon Deposit Burning Off from Coke Oven Chamber

For 3D steady state simulation of carbon deposit burning off from coke oven chamber presented here, it has been assumed that carbon deposits were present only at the charging holes and roof surfaces as shown in the schematic picture in Fig. 19. The charging holes are numbered from 1 to 4 and the gas outlet hole has a number 5. The numbers from 6 to 11 are assigned to the roof segments. It has also been assumed that the wall, the roof and the charging holes temperatures are constant during the operation. These temperatures are in the range of 600 to 1200°C, which corresponds to the temperatures of the coke oven chambers. The heat transfer from such isothermal walls to the blowing air as well as the combustion rate on the surfaces covered by carbon and the total carbon combustion rate in the chamber were calculated.

The examples of the calculated contours of gas temperature and velocity as well as of the CO2 mass fraction in a coke oven chamber for two blowing operations: the first (a), with one lance placed in the hole 1 and the second (b), with two lances placed in the holes 2 and 3 are presented in Fig. 20. As one would expect, dissimilar fields of air flow and temperature are obtained. These differences induce different local carbon combustion rates. For the case (a) the combustion rate is of 0.31 g/m²/s in the charging hole 1, where a blowing lance is placed and only 0.16, 0.13 and 0.2 g/m²/s, respectively in the holes 2, 3 and 4 where the velocity of circulating air is low and consequently the combustion rate is limited by external diffusion. When comparing the local combustion rates for case (a) and (b) one finds that for the same air flow rate per lance, the carbon combustion in the charging holes with blowing lance is similar for both cases. However, the total carbon flow found in the outlet hole is 1.6 g/s for case (a) and only of 1.1 g/s for case (b). The difference is due to relatively higher roof carbon combustion rate for the case (a). This higher roof carbon combustion rate results from better air flow distribution near the roof segments 7 to 11 in the case (a) and relatively worse air flow near the segments 6 and 7 in the case (b).

These two examples show clearly that air flow distribution in the chamber is more important than the total quantity of air blown and they illustrate well the possibilities offered by CFD for the optimisation of burning off operation by choosing the best blowing scheme, i.e. the number and location of the lances, the air flow rate per lance, the lance design, etc.

5. Conclusions

The deposits taken from different parts of the industrial coke oven chambers contain two distinct carbonaceous phases: about 70 to 80% of the pyrolytic carbon which is a bonding phase for about 20 to 30% of char resulting from carry-over coal particles which stick to wall and are pyrolysed. Both phases are weakly ordered carbon, as XRD and Raman spectroscopy show. The deposits are more or less porous and their reactivity in air is lower then that of the metallurgical coke but higher then that of the electrode graphite.

The data sets obtained by a monitoring system of carbon deposition were statistically analysed and the average rates of deposit growth were estimated by linear regression. It was found that each coking chamber has its own, individual and relatively repetitive pattern of deposits growth.
The deposits combustion in air measured by TG at lower temperature (<700°C) is under surface reaction control and does not depend on air flow rate. The Arrhenius expression obtained for the combustion rate on the basis of initial external surface of the carbon deposit samples gives the activation energy around 170 kJ/mol. At temperatures higher than 700°C under laboratory conditions the combustion is controlled by the gas film diffusion, and consequently, the combustion rate depends on the air flow rate.

The CFD software with its standard Wall Surface Reaction Model was used to simulate laboratory rate combustion experiments. Comparison of measured and calculated combustion rates shows that the Surface Reaction Model fits quite well the laboratory data. It was consequently used in 3D modelling of the deposits combustion in the coke oven chambers. This modelling technique is a valuable tool for the optimisation of the burning-off operation still remaining the main way of carbon deposits elimination from coke oven chambers.

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