

2008

Determination of the thermal histories of coke in a blast furnace through x-ray analysis

B. J. Monaghan

University of Wollongong, monaghan@uow.edu.au

R. Nightingale

BlueScope Steel

V. Daly

University of Wollongong

E. Fitzpatrick

University of Wollongong

Publication Details

This article was originally published as Monaghan, BJ, Nightingale, R, Daly, v and Fitzpatrick, E, Determination of the thermal histories of coke in a blast furnace through x-ray analysis, *Ironmaking and Steelmaking*, 35, 2008, 38-42. Original journal article available [here](#)

Determination of the Thermal Histories of Coke in a Blast Furnace Through X-ray
Analysis

B. J. Monaghan¹⁾, R. Nightingale²⁾, V.Daly³⁾ and E. Fitzpatrick³⁾

1) Pyrometallurgical Group, Faculty of Engineering, University of Wollongong,
Wollongong, NSW 2522, Australia. E-mail, monaghan@uow.edu.au

2) Ironmaking, BlueScope Steel Limited, PO Box 1854, Wollongong, NSW 2500,
Australia. E-Mail, Robert.Nightingale@bluescopesteel.com

3) Graduate of the School of Mechanical, Materials and Mechtronics, University of
Wollongong, Wollongong, NSW 2522, Australia.

Abstract

A study has been undertaken to identify the source of coke fines sampled from the deadman area of the blast furnace. Using measurements of the coke crystallite dimension L_C , it was established that some of the fines found in the deadman area of a blast furnace were not simply the degradation products of the lump coke in this area. The L_C was measured using standard X-ray analysis techniques. The coke fines had a higher L_C than the coke lump and therefore have experienced a higher maximum temperature than the associated coke lump. This finding has been interpreted as at least some of the coke fines being blown into the deadman area (lower temperature region) from the raceway by the high velocity hot blast.

Keywords

Coke, coke fines, blast furnace, deadman, raceway, coke crystallite

1. Introduction

Though coke is a critical raw material in blast furnace ironmaking, at present our knowledge of the conditions of its passage through a blast furnace is limited. This is at least in part due to the highly complex inter-dependent thermal, physical and chemical phenomena within the blast furnace and that there is no easy access to the furnace to observe important phenomena directly.¹

Key to efficient blast furnace operation is the permeability of the packed bed in the lower zone (below the cohesive zone and above the hearth) of the furnace.² The particle size, particle size range and particle distribution of the coke in this zone is critical in determining the permeability of the packed bed.² In a blast furnace the size and distribution of the coke in the lower zone of the furnace is controlled by managing coke and ferrous burden additions to the top of the furnace.³ As the coke descends through a blast furnace it degrades and coke fines are generated.⁴⁻¹¹ The mechanisms governing degradation vary during the descent path of the coke particle and are dependent on the coke properties and the mechanical, thermal and chemical state within the furnace.

In the upper furnace, coke size reduction occurs purely by mechanical action (abrasion and volume breakage). Size reduction mechanisms in the mid and lower furnace change considerably with degradation by mechanical action enhanced by coke weakening due to coke carbon solution loss and attack by alkali metal vapours. Simultaneously, thermal stresses imposed by internal coke crystallite growth can further weaken coke. In the lower zone chemical attack by hot metal (coke dissolution) and slag, and coke carbon solution loss by reduction of coke ash

constituents, increase the tendency of coke breakage and fines generation. At tuyere level, in addition to the other fines generation processes, coke entering the raceway area can be shattered against the raceway wall by the high velocity hot blast creating fines. The coke fines generated from this process may remain in the raceway area and be consumed by combustion or due to the high velocity of the impact may have enough momentum to pass through the raceway wall and end up in the lower zone-packed bed area or deadman. A similar statement regarding fines generated higher up in the furnace and entering the raceway can also be made. Fines generated in upper regions can also move to the deadman region by gravity.

There is significant uncertainty whether fines from the raceway area can breach the raceway walls and reach the packed bed area. Given how critical the permeability of the deadman is to the efficiency and productivity of a blast furnace and the effects of particle size on permeability it is important to understand the origin of fines in this area.

It is known that above approximately 1100°C coke graphitizes with increasing temperature and that this graphitisation is irreversible.^{12-14,17} Further, it is also known that there is a significant drop in temperature from the raceway to the lower zone-deadman packed bed area.¹⁻³ Coke graphitisation can be measured using the coke crystallite dimension L_C . It is therefore possible to use measurements of L_C to identify what thermal regimes, and by inference what zones coke sampled from the blast furnace deadman has previously experienced.

The focus of this study is to identify the thermal history of coke fines sampled from an industrial blast furnace, and subsequently assess their origin.

2. Experimental

Tuyere probe samples, both lump (greater than 50mm in size) and in some cases fines (less than 8mm in size), were obtained from BlueScope Steel's Port Kembla No 5 Blast Furnace. These were matched with their unreacted blast furnace feed coke. The tuyere coke samples were from the raceway, and deadman areas. A schematic showing the tuyere probe sampling is given in Fig.1. The L_C for the tuyere coke (lump and fine) samples was measured. The lump coke samples position and their thermal history within the blast furnace is known with greater certainty than that of the fines, as the lump coke is not readily displaced to other parts of the furnace as a result of the high velocity hot blast of the raceway. For this reason measurements of the lump coke L_C will be used as a reference to test whether the fines sampled from raceway and deadman areas were generated in their respective areas or generated in a hotter region of the furnace and displaced by the hot blast of the raceway. Three sets of tuyere probe samples from the blast furnace have been analysed and are identified as 10/01, 12/02 and 03/05. The 10/01 sample was prior to PCI being established on the blast furnace the 12/02 and 03/05 are post PCI.

In an attempt to assess what maximum temperature the coke experienced in the blast furnace a series of experiments were carried out whereby unreacted feed coke was heat treated at a given temperature and its L_C measured. These are the feed cokes associate with the tuyere probe samples. Their identifier is distinguished from the

tuyere probe samples by the letter F. The ash content and ash composition of the unreacted feed cokes tested are given in Table 1.

The tuyere coke sampling, unreacted feed coke heat treatments, and L_C measurement are described below.

2.1 Blast furnace coke probe samples

Coke probes were extracted from the blast furnace at shutdown by driving a 200mm diameter pipe into the furnace through an opened tuyere port. Cooled probes were carefully transported to the laboratory and opened by oxy-cutting. The whole probes were then photographed. Generally, the structures described in Japanese quenched furnaces were confirmed,¹⁵ with raceway (infill) coke separated from the deadman coke by a 'bird's nest' zone where the fractions of fine coke and slag increase rapidly. These were identified, and marked before sub-division into sections of about 100-200mm in length. Typically, between 15 and 20 increments are generated per probe. Where necessary, metal and slag were manually liberated from the coke and then collected separately. On removal of each increment, the minus 8mm fraction was separated.

For selected probes, coke lumps from two raceway and two deadman locations were tested. Fines from the same deadman locations were also tested. Samples were carefully prepared to avoid inclusion of material that could contain graphite produced from surface catalysis by or precipitation from iron droplets (see Wang et al ¹⁶ study on iron catalysed graphitisation). Lumps of 19x31mm were tumbled to remove surface adhesions, then crushed with intermediate removal of minus 0.5mm fines and

ultrasonic washing until a 2x1 mm sample was obtained. This was then crushed to minus 0.5mm and then ground to a minus 74 μ m powder. Samples of deadman fines were prepared from 4x1mm materials. These were crushed to minus 1mm. After ultrasonic washing, the minus 0.5 material was removed and the remaining 1x0.5mm fraction was crushed and ground to the same minus 74 μ m size.

Fines sizes less than 1mm were excluded to limit possible coke contamination from PCI.

2.2 Heat Treatment Process

Coke samples were heated in a dried argon atmosphere to the experimental temperature in a vertical tube furnace. A schematic of the furnace setup and temperature profile used in the experiments are given in Fig.2 and 3. Experimental temperatures ranged from 1300°C to 1600°C. In this temperature range the furnace had a stable hot zone $\pm 4^\circ\text{C}$ over a length of 70mm and $\pm 10^\circ\text{C}$ over a length of 110mm. The lowest experimental temperature was selected to be greater than that the coke experiences in the coke ovens and the highest experimental temperature was fixed by the laboratory furnace capability. After heat treatment the coke sample was removed from the furnace and prepared for X-ray analysis to determine the L_C .

To prepare the coke samples for heat treatment they were cut into a square profile of approximately 18mm thick using a water cooled diamond saw. The cut samples were then oven dried overnight to remove any entrained moisture. After drying the samples they were polished using 100 grit silicon carbide paper to final dimensions of 40x40x18 mm and stored in a desiccator prior to use in the furnace.

2.3 Measurement of L_C

L_C was measured in general accordance with ISO 20203¹⁷. Key deviations from the ISO standard were that less than 100g of coke sample was used and that the Scherrer equation¹⁸ was used to calculate the L_C . The Scherrer equation, equation (1)

$$L_C = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where K is a shape factor of 0.89 radians, λ is the wavelength of the X-ray source (0.1541nm), β the line breadth of the pure diffraction peak expressed in radians and θ is the peak maximum expressed in degrees. A typical example of a coke X-ray curve is given in Fig.4. Also shown on the curve is the (002). The ISO 20203¹⁷ standard states the measurements repeatability and reproducibility will not exceed a value of $\pm 2.1\%$ and of $\pm 10\%$ respectively, in one case in twenty. In this study less than the recommended coke mass was used therefore the L_C measurements may have had an increased uncertainty resulting from the heterogeneity of the coke.¹² Three 1500°C heat treatments of the feed coke were carried out and the L_C measured. These L_C measurements for coke 02/05 had a mean L_C of 4.6nm $\pm 1.8\%$ at 1500°C. This variability is consistent with the ISO 20203¹⁷ standard. Given that the fines obtained from the tuyere probe sampling may be a mixture of coke that have experienced different thermal regimes there is the potential for a greater range of L_C values. It would therefore be inappropriate to assign the ISO 20203¹⁷ standard repeatability on L_C measurements of these coke fines.

3. Results/Discussion

The L_C measurements for the tuyere probe samples and the heat treated feed cokes are given in Fig.5(a to c) and 6 respectively. In Fig.5 (a to c) it can be seen that the coke lump L_C is greater in the raceway area than in the deadman area, and that fines associated with the coke lump in the deadman area have a higher L_C value. In Fig.6 the measured L_C values of the heat treated feed cokes increase linearly as the temperature increases. Also there was no discernable difference between the measured L_C values for the two feed cokes as such they have been treated as a single data when regressed.

3.1 The Effect of Temperature on the Coke L_C Measurements

Generally, it can be stated that the temperature in a blast furnace across a horizontal plane cutting through the tuyeres decreases from the tuyere, or rather the combustion zone of the raceway to the centre of the furnace.¹⁻³ Therefore the trend in L_C with tuyere distance shown in Fig.5 (a to c) is consistent with the temperature- L_C trend that is shown in Fig.6. This temperature effect is well known and is explained by considering the effects temperature on the ordering of the carbon crystal structure in the coke. As the temperature increases the crystal structure of carbon in the coke becomes more graphite like which has a greater L_C .^{12,13}

The results of the heat treatment measurements given in Fig.6 indicate that the deadman lump coke tuyere probe samples experienced a temperature in excess of 1600°C. At first glance this may seem an anomalous result, as it is a greater temperature than what would be expected for this area in the normal operations of a blast furnace.¹⁻³ The higher than expected deadman tuyere coke L_C is most probably a result of catalysing the coke graphitisation process by other matter in the blast

furnace. In the preparation of the tuyere probe sample care was taken to prepare the coke to minimise iron graphitisation effects (see experimental section) but such preparation does not protect against a gaseous graphitisation processes. For example sulphur has been implicated in the graphitisation of coke^{19,20}. Therefore sulphur or other gaseous species active in the blast furnace can also affect the coke L_C . In our study no attempt was made to replicate the gaseous environment in the lower zone of the blast furnace in our coke heat treatment experiments.

There is also the possibility of changes in the mineral matter of the coke affecting the measured L_C value. In the excellent study by Dubrawski and Gill¹³ it was found that measured L_C was relatively insensitive to the ash content of the coke except at high (greater than 20%) ash levels. Therefore this is unlikely to be a significant factor.

It is likely that the gaseous environment and subsequent effects on graphitisation are responsible for the discrepancy between the heat treated cokes and tuyere probe cokes resulting in apparently high temperatures the tuyere probe samples have seen.

Therefore the use of the temperature L_C data in Fig.6 to predict the temperature that the coke in the blast furnace has experienced is limited.

Though we did not have access to a partner feed coke for the pre PCI tuyere samples (10/01 in Fig 5a), a similar result for L_C versus temperature, as given in Fig. 6 is expected. This is based on the similar behaviour of both feed cokes shown in Fig. 6 and that the partner coke feed for 10/01 was a similar coal blend used to produce the 12/02F feed coke. That being the case any changes in furnace environment due to PCI are not having a significant effect on the measured L_C values.

3.2 The Source of the Fines Sampled from the Blast Furnace

The question this study was attempting to address was, are the fines found in the deadman area a result of coke degradation of the lump coke found in this area or were they coke fines from raceway? The raceway was being considered as a possible source for coke fines found in the deadman since the high velocity hot blast of the raceway has the potential to carry them deeper into the furnace. These raceway fines may have been generated by coke breakage as a result lump coke being driven against the raceway walls by the high velocity gas or generated above the raceway, higher up in the furnace.

The L_C measurements for the fines from the deadman coke samples are greater than their partner lumps for all measurements reported in Fig. 5 a to c. This is indicative that some of the fines material may have experienced a hotter temperature than the lumps and is consistent with at least some of the coke fines material being blown into the deadman area from the raceway. If some of the coke fines that have been sampled from the deadman were generated in a hotter zone then the measurement of L_C for these fines represent an aggregate value for deadman and other fines. This makes assigning a maximum temperature that the coke fines sampled from the deadman area have experienced extremely difficult.

There is no obvious difference in the L_C of the fines and lump with respect to pre (Fig 5 a) and post (Fig. 5 b and c) PCI. It should be noted that it is not to say that PCI does not have an effect on the fines load of the furnace. Our experimental approach and

sample preparation were designed to exclude fines generated from the PCI process and limit the complexity of our analysis.

4. Conclusions

Measurements of coke crystallite dimension L_C , for coke samples obtained from the raceway and deadman areas of the blast furnace indicate that the coke fines have experienced a higher maximum temperature than the coke lump. This finding has been interpreted as some of the coke fines being blown into the lower temperature regions from the raceway by the high velocity hot blast.

Acknowledgements

The authors would like to thank BlueScope Steel for supplying the sample material, John Mathieson of BlueScope Steel for his support of this investigation, Harold Rogers of BHP Billiton for his expertise in L_C measurement, David Wexler of Materials Engineering at the University of Wollongong for his expertise in X-ray measurement and John Simpson for his understanding of coke and coke maceralology.

References

1. N. Sano, W.K. Lu, P.V. Riboud: *Advanced Physical Chemistry for Process Metallurgy*, Academic Press, San Diego, USA, (1997).
2. *Blast Furnace Phenomena and Modelling*, Elsevier Applied Science, London, UK, (1987), 253.
3. A. Biswas, *Principles of Blast Furnace Ironmaking*. Cootha Publishing, Brisbane, Australia, 1981.
4. M. A. Diez, R. Alvarez, C Barriocanal: *International Journal of Coal Geology*, 2002, **50**, 389.
5. T. Hilding, S. Gupta, V. Sahajwalla, B. Bjorkman and J.O. Wikstrom: *ISIJ International*, 2005, **45**, 1041.
6. M. Peters, H.W. Gudenau, M. Scheiwe, R. Sieger: 2nd European Ironmaking Congress, Maney Publishing, London, UK, (1991), 205.
7. R. Willmers and C. Bennington: 2nd International Cokemaking Congress, Institute of Materials, London, UK, (1992), 260.
8. A. Cheng: *Iron and Steelmaker*, 2001, **28**, 78.
9. M.M. Bowness, R.R. Willmers, J.E. Parratt, R.J. Davies: *Ironmaking and Steelmaking*, 1987, **14**, 157.
10. H. Haraguchi, T. Nishi, Y. Miura, M. Ushikubo, T. Noda: *Transactions ISIJ*, 1985, **25**, 190.
11. Y. Abe, K. Yamaguchi, A. Tsuda, T. Nishi, H. Haraguchi: *Transactions ISIJ*, 1985, **25**, B240.
12. E. Stach, M. Mackowsky, M Tichmüller, G.H. Taylor, D. Chandra and R. Techmüller: *Stach's Textbook of Coal Petrology*, Gebrüder Borntraeger, Berlin, Germany, (1982), 54.
13. J.V Dubrawski and W.W. Gill: *Ironmaking and Steelmaking*, 11, (1984), 7.
14. S. Gupta, V. Sahajwalla, J. Burgo, P. Chaubal and T. Youmans: *Metallurgical and Materials Transactions B*, 2005, **36**, 385.
15. N.Nakamura, Y.Togino and M. Tateoka: *Ironmaking and Steelmaking*, 1978, **5**, 1.
16. W. Wang, K.M. Thomas, R.M. Poultney and R.R. Willmers: *Carbon*, 1995, **33**, 1525.
17. International Standard ISO20203: Determination of crystallite size of calcined petroleum coke by X-ray diffraction, ISO 20203:2005(E), (2005).
18. A.L. Patterson: *Physical Review*, **56**, (1939), 978.
19. E.A. Heintz: *Proceedings of the 5th London International Carbon and Graphite Conference*, Society of Chemical Industry, London, UK, (1978), 575.
20. E. Fitzer and S. Weisseneberger: *Carbon*, 1976, **14**, 195.

Table 1. The composition of the ash in the unreacted feed cokes.

Fig. 1. Schematic showing the tuyere probe and key zones in the lower zone of the blast furnace.

Fig. 2. Schematic of the furnace setup used in the coke heat treatment experiments.

Fig. 3. Schematic of the temperature profile used in the coke heat treatment experiments.

Fig. 4. An example of a coke X-ray diffraction curve for a feed coke after heat treating to 1400°C.

Fig. 5a. L_C measurements for the tuyere probe coke samples 10/01. The open diamond symbol denotes measurements of coke fines and the solid diamond symbol measurements of coke lump.

Fig. 5b. L_C measurements for the tuyere probe coke samples 12/02. The open diamond symbol denotes measurements of coke fines and the solid diamond symbol measurements of coke lump.

Fig. 5c. L_C measurements for the tuyere probe coke samples 03/05. The open diamond symbol denotes measurements of coke fines and the solid diamond symbol measurements of coke lump.

Fig. 6. Effect of heat treatment temperature on L_C of the blast furnace feed cokes
12/02F and 03/05F.

Table 1. The % ash and mass % ash composition of the unreacted feed cokes.

Coke Identifier	%ash	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Fe	CaO
12/02F	11.3	52.7	31.3	8.7	6.1	2.7
03/05F	11.0	57.6	30.8	4.9	3.4	2.5

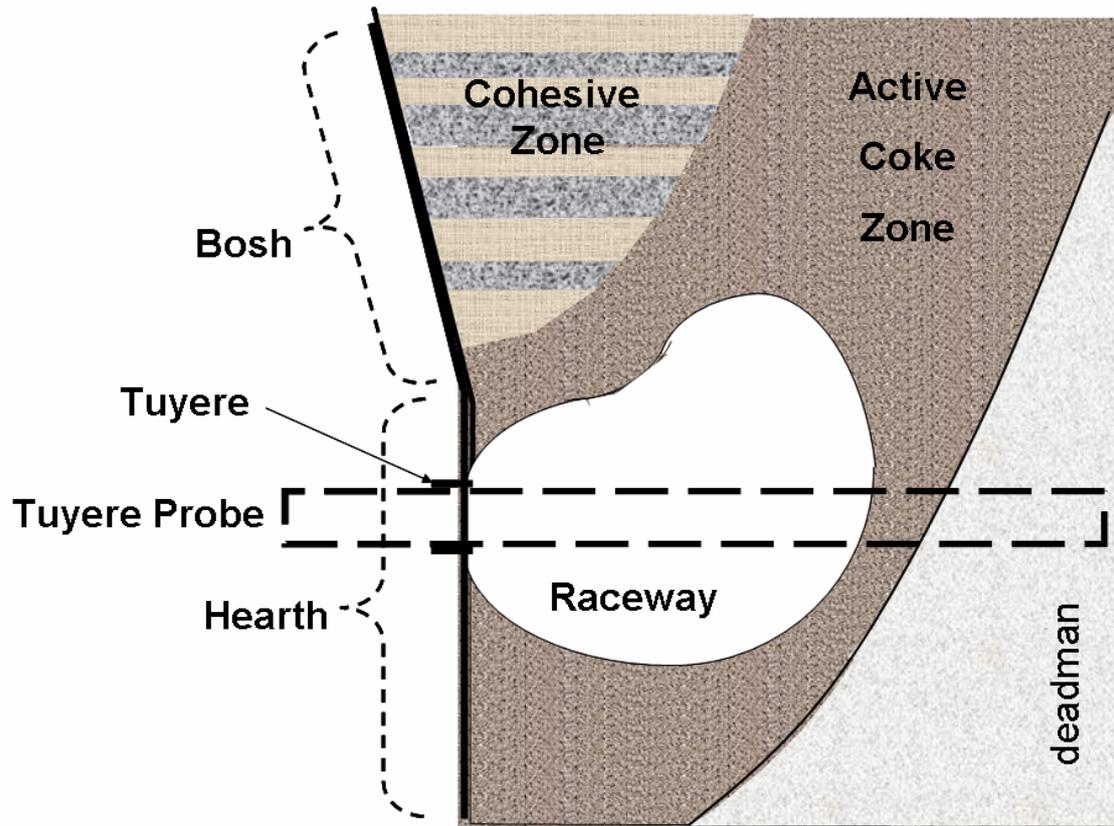


Fig. 1. Schematic showing the tuyere probe and key zones in the lower zone of the blast furnace.

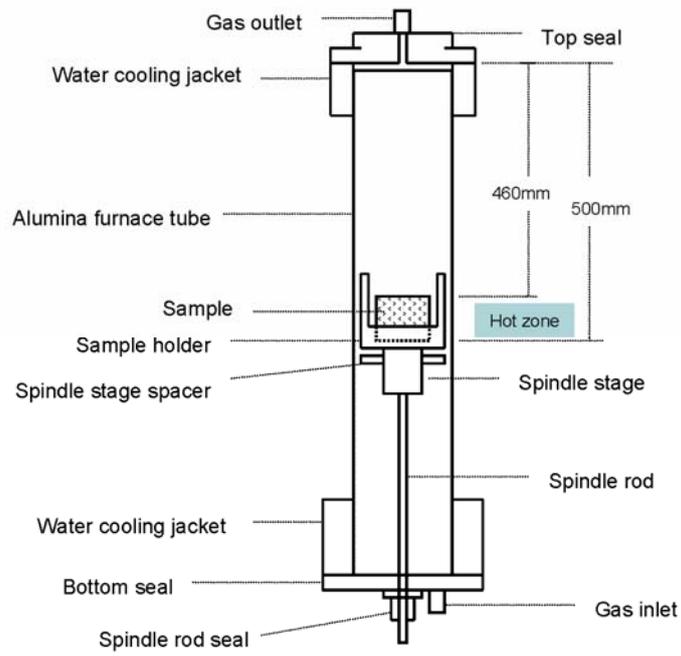
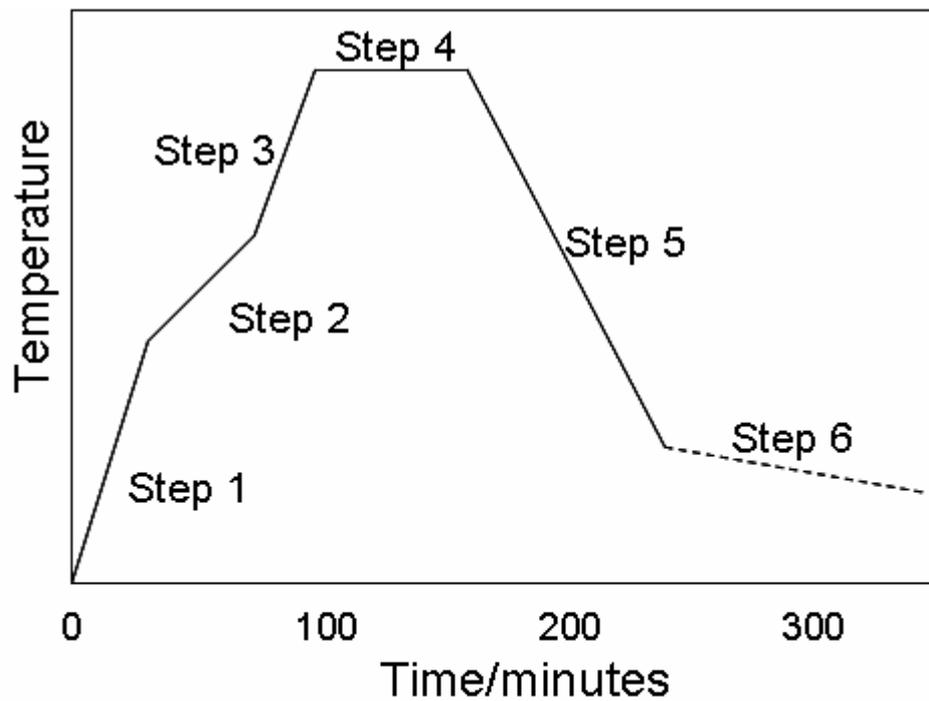


Fig. 2. Schematic of the furnace setup used in the coke heat treatment experiments.



- Step 1** Ramp to 800°C at 25°C/min
- Step 2** Ramp from 800°C to 1200°C at 10°C/min
- Step 3** Ramp from 1200°C to target furnace set-point at 30°C/min
- Step 4** Dwell at experimental temperature for 60 minutes
- Step 5** Ramp from target furnace set-point to 550°C at 10°C/min
- Step 6** Furnace cooled to 300°C and then switched off

Fig. 3. Schematic of the temperature profile used in the coke heat treatment experiments.

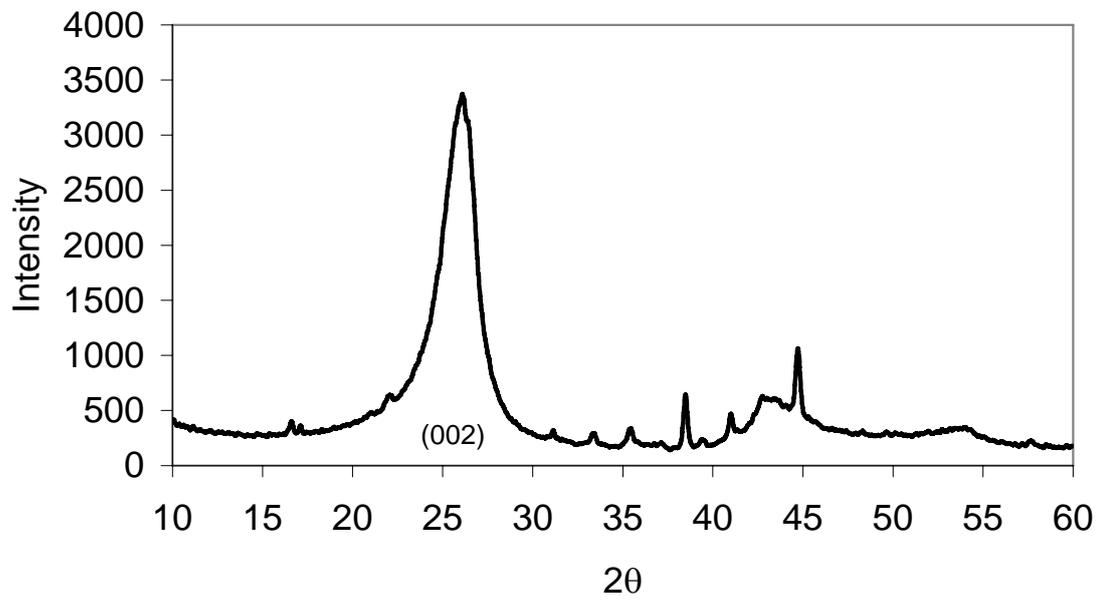


Fig. 4. An example of a coke X-ray diffraction curve for a feed coke after heat treating to 1400°C.

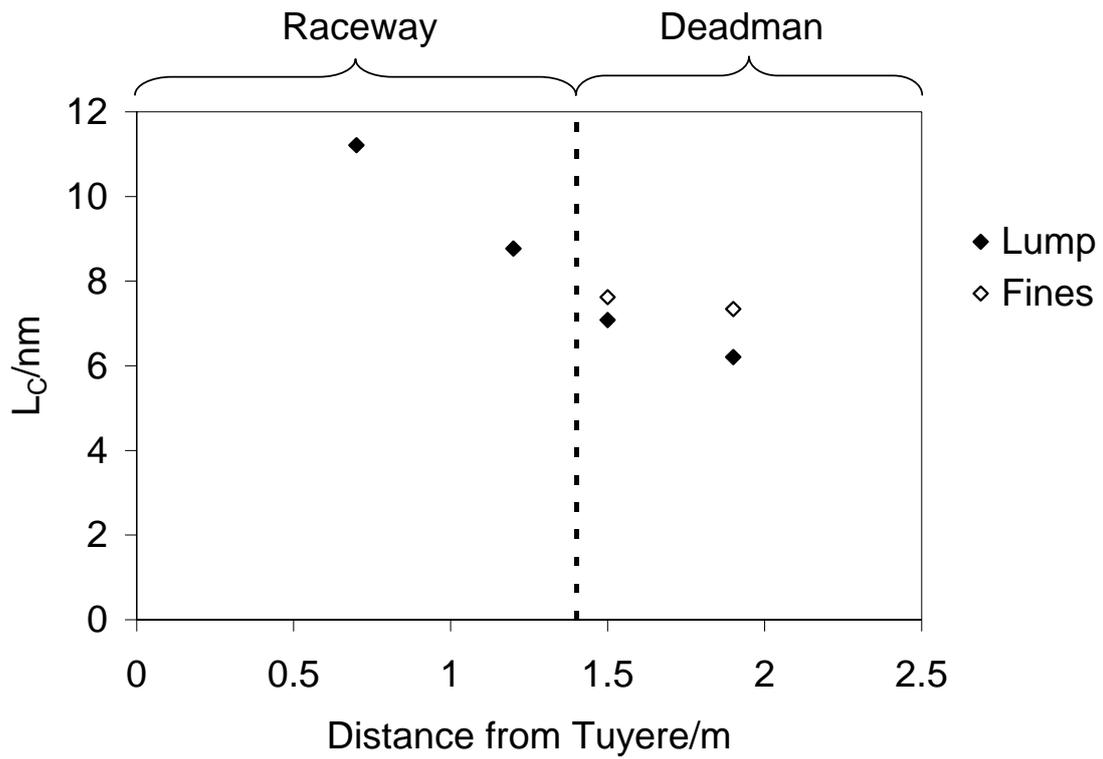


Fig. 5a. L_c measurements for the tuyere probe coke samples 10/01. The open diamond symbol denotes measurements of coke fines and the solid diamond symbol measurements of coke lump.

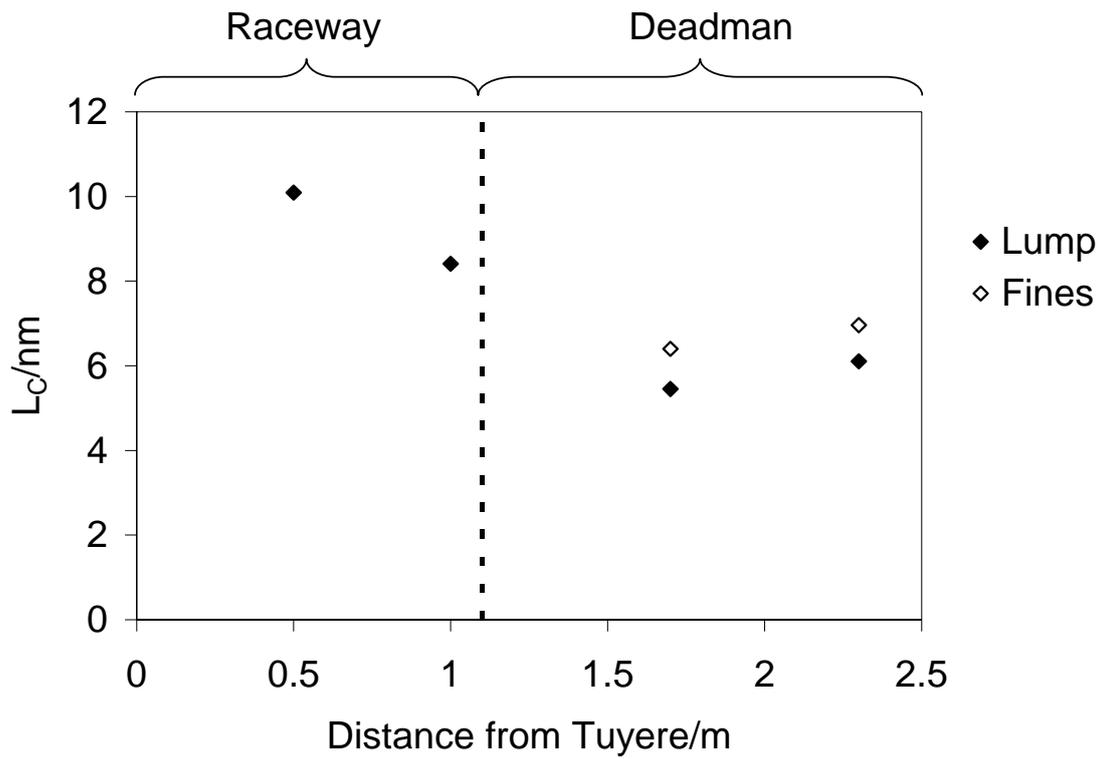


Fig. 5b. L_C measurements for the tuyere probe coke samples 12/02. The open diamond symbol denotes measurements of coke fines and the solid diamond symbol measurements of coke lump.

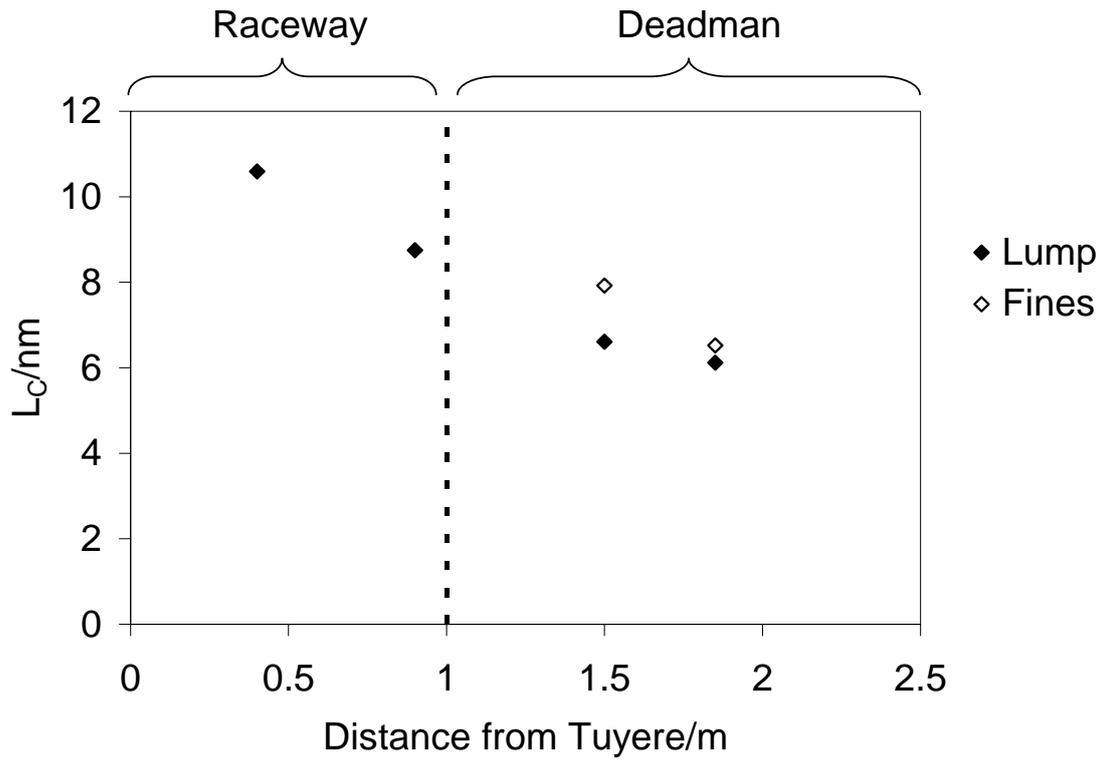


Fig. 5c. L_C measurements for the tuyere probe coke samples 03/05. The open diamond symbol denotes measurements of coke fines and the solid diamond symbol measurements of coke lump.

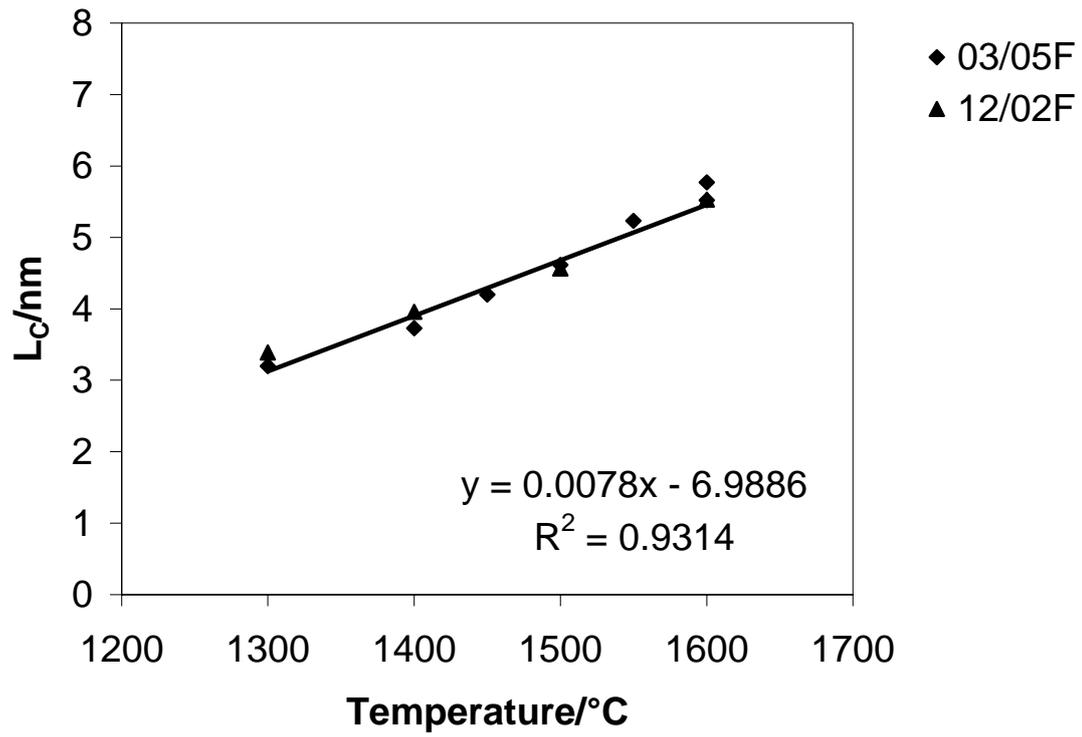


Fig. 6. Effect of heat treatment temperature on L_C of the blast furnace feed cokes 12/02F and 03/05F.