

Juho Haapakangas

COKE PROPERTIES IN SIMULATED BLAST FURNACE CONDITIONS

*INVESTIGATION ON HOT STRENGTH, CHEMICAL
REACTIVITY AND REACTION MECHANISM*

UNIVERSITY OF OULU GRADUATE SCHOOL;
UNIVERSITY OF OULU, FACULTY OF TECHNOLOGY



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JUHO HAAPAKANGAS

**COKE PROPERTIES IN SIMULATED
BLAST FURNACE CONDITIONS**

Investigation on hot strength, chemical reactivity and
reaction mechanism

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Abstract

The blast furnace – basic oxygen furnace route remains the most utilised process route in the production of steel worldwide. Coke is the main fuel of the blast furnace process, however, coke producers and blast furnace operators are facing significant challenges due to increased demands on coke quality and decrease of prime coking coals. The estimation of coke performance in the industrial process through accurate laboratory analyses is of increasing importance.

In this doctoral thesis, the aim was to study phenomena related to coke properties and its analysis methods in blast furnace simulating conditions. A new method was introduced to measure the hot strength of coke using a Gleeble 3800 thermomechanical simulator. The hot strengths of industrial cokes were determined at various temperatures and several coke properties, which were believed to affect hot strength, were determined. The effect of H₂ and H₂O in the blast furnace shaft gas were determined in relation to coke reactivity, threshold temperature, and the gasification mechanism.

The results obtained by this thesis show that the Gleeble device is suitable for study of coke hot strength. The coke strength was significantly decreased for all three coke grades at temperatures of 1600 °C and 1750 °C when compared to room temperature or 1000 °C. The deformation behaviour of coke was fragile up to 1000 °C, but became at least partially plastic at 1600 °C, and the plasticity further increased at 1750 °C. Notable changes were observed in the deformation behaviour between coke grades at high temperatures. The presence of H₂ and H₂O in the BF shaft gas strongly increased coke reactivity and changed the reaction mechanism of coke to be more surface centric in a specific temperature range. The reactivity of coke in the conditions 100 vol-% CO₂ did not directly correlate with reactivity in a simulated blast furnace shaft gas, which suggest that the widely utilised CRI test does not accurately estimate coke reactivity in the industrial blast furnace process.

Keywords: blast furnace, coke, deformation behaviour, fines formation, gasification, Gleeble, hot strength, reaction mechanism, reactivity, solution loss, water vapour

Haapakangas, Juho, Koksen ominaisuudet masuunin olosuhteissa. Selvitys koksen kuumalujuudesta, reaktiivisuudesta ja reaktiomekanismista

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Tiivistelmä

Masuuni – konvertteri yhdistelmä on edelleen käytetyin prosessireitti teräksen tuotantoon ympäri maailman. Koksi on masuunin tärkein polttoaine. Koksintuottajat ja masuunioperaattorit ovat suurten haasteiden edessä johtuen koksen kasvaneista laatuvaatimuksista ja parhaiden koksautuvien kivihiilten ehtymisestä. Koksen suoriutumisen arviointi masuunin olosuhteissa tarkoilla laboratorioanalyseillä on yhä merkittävämmässä roolissa.

Tässä työssä esitetyt tulokset osoittavat että Gleeble soveltuu koksen kuumalujuuden määrittämiseen. Koksen lujuus aleni merkittävästi kaikilla kolmella koksilaadulla kuumennettaessa 1600 ja 1750 °C lämpötiloihin verrattuna huoneenlämpötilaan tai 1000 °C lämpötilaan. Koksen muodonmuutos oli haurasta aina 1000 °C lämpötilassa, mutta muuttui osittain plastiseksi 1600 °C lämpötilassa ja plastisuus kasvoi kun lämpötilaa nostettiin 1750 °C:een. Eroja havaittiin eri koksilaatujen muodonmuutuskäyttäytymisessä korkeissa lämpötiloissa. H₂ ja H₂O kaasujen läsnäolo kuilun kaasuatmosfäärissä kasvatti koksen reaktiivisuutta ja muutti kaasuuntumismekanismeja pintakeskisemmäksi rajatulla lämpötila-alueella. Koksen reaktiivisuus 100% CO₂ kaasussa ei korreloinut suoraan simuloidun masuunin kuilun kaasuatmosfäärin kanssa. Tämä tulos indikoi sitä että maailmalla yleisesti käytetty CRI testi ei ennusta tarkasti koksen reaktiivisuutta masuunissa.

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Asiasanat: Gleeble, hienoaineksen muodostuminen, kaasuuntuminen, koksi, kuumalujuus, masuuni, muodonmuutuskäyttäytyminen, reaktiivisuus, reaktiomekanismi, vesihöyry

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Oulu, September 2016

Juho Haapakangas

Symbols and abbreviations

λ	Wavelength of X-ray (\AA)
B	Angular width in radians at half-maximum intensity of [002] peak
θ_B	The reflection angle of the [002] peak
L_c	Mean height [\AA] of graphite crystallites
m_0	Original mass of coke
m_t	Mass of coke at a specific time
m_{ash}	Mass of ash components in coke
X	Degree of carbon conversion
BF	Blast furnace
BFS	Blast furnace simulator
CF	Cupola furnace
CRI	Coke reactivity index
CSR	Coke strength after reaction
DI	Drum strength Index
EBF	Experimental blast furnace
LOM	Light optical microscope
PCI	Pulverised coal injection
PCR	Pulverised coal rate
TGA	Thermal gravimetric analysis
tHM	Tons of hot metal produced
VM	Volatile matter
XRD	X-ray diffraction

List of original publications

This thesis is based on the following publications, which are referred to throughout the text by their Roman numerals:

- I Haapakangas J, Mattila O & Fabritius T (2011) Effect of injection rate on coke dust formation and coke gasification in a blast furnace shaft. METEC InSteelCon Conf Proc, Düsseldorf, Germany, 27th June – 1st July.
- II Haapakangas J, Uusitalo J, Mattila O, Kokkonen T, Porter D & Fabritius T (2013) A method for evaluating coke hot strength. *Steel Res Int* 84(1): 65–71.
- III Haapakangas J, Uusitalo J, Mattila O, Kokkonen T & Fabritius T (2012) Measuring coke hot strength with a Gleeble. SCANMET IV Conf Proc, Stockholm, Sweden, 10–13 June, Vol 1: 177–184.
- IV Haapakangas J, Uusitalo J, Mattila O, Gornostayev S, Porter D & Fabritius T (2014) The hot strength of industrial cokes – Evaluation of coke properties that affect its high-temperature strength. *Steel Res Int* 85(12): 1608–1619.
- V Haapakangas J, Suopajarvi H, Iljana M, Kempainen A, Mattila O, Heikkinen E-P, Samuelsson C & Fabritius T (2016) Coke reactivity in simulated blast furnace shaft conditions. *Metall Mater Trans B* 47(4): 2357–2370.

In the Papers I and V, the responsibilities of the author of this doctoral thesis included the literature review, planning of the experiments, conducting of the experiments and a major proportion of the writing.

In the Papers II–IV, the responsibilities of the author of this doctoral thesis included the literature review, planning of the experiments, a major proportion of the writing, whereas the hot strength experiments were conducted by the device operator.

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1 Introduction

Steel is one of the most important raw materials in the world today. In 2014, crude steel production was at an all-time high with roughly 1.662 million tonnes produced worldwide, up by 1.2% compared to 2013 (World Steel Association 2015). The blast furnace (BF) remains the most utilised process route in the production of molten iron, a precursor of steel. Roughly 70% of the crude steel is produced via the blast furnace-basic oxygen furnace route. Coke, a solid fuel produced by high temperature distillation of coking coals, is the primary fuel of the blast furnace. Its properties include high porosity, high carbon content, high strength and hardness, and low amount of volatiles. Coke is also the only raw material that remains in solid state at the high temperatures of the lower BF. Coke's vital role as a structural support cannot be replaced by other raw materials and it will maintain a large role in BF based ironmaking in the foreseeable future.

Coke manufacturers and blast furnace operators worldwide are facing a significant challenge due to the depletion of prime coking coals. Blast furnace operators will have to find ways to utilise lower quality coking coals while still maintaining high coke quality, which is a requirement for efficient productivity. Coke is also the most expensive raw material charged into the BF, due to which continuous efforts have been made to partially replace coke with injected auxiliary fuels, such as coal, oil or natural gas. The chemical and physical stresses on coke in the BF have increased due to the increased sizes of modern blast furnaces and longer residence times as a result of higher injection rates. Due to lower amounts of charged coke, coke also undergoes higher mechanical load due to thicker iron ore layers and the resultant rise of the average burden weight. Another issue is the rising price of CO₂ emissions. One possibility to reduce CO₂ could be the addition of bio-material into the coking mix, which can negatively affect the strength of the coke. All of these factors increase the importance of coke quality.

The main properties of coke in the BF include high resistance against mechanical stresses and low reactivity towards oxidising gases. Coke strength is commonly measured using various drum strength indices (Micum, Irsid, ASTM, JIS), whereas reactivity and post-reaction strength are measured using the CRI (Coke Reactivity Index) and CSR (Coke Strength after Reaction) tests. Despite the historical usefulness of these tests, their ability to predict stresses in the actual BF has been questioned. The conditions and stresses induced by these tests are significantly different from the stresses caused by the actual BF. It also seems clear that the relationship between coke reactivity, post-reaction strength and BF

performance is not yet clearly understood. The current analysis methods are mainly limited to the upper part of a BF and a test for coke strength at high temperatures is lacking, yet significant degradation of coke size is only observed in the lower parts when the temperature exceeds 1400 °C (Haraguchi *et al.* 1985).

In order to answer the demands of the future, coke performance in the blast furnace must be well understood and its quality accurately estimated by laboratory analyses.

1.1 Aim and outline of the study

The aim of this study was to produce new information on coke quality and its analysis methods. The selected approach was to study coke quality in conditions which simulate the BF process as accurately as possible with laboratory equipment. The main aim was divided to two different research themes: 1) the study of coke strength at the high temperatures of the lower BF; 2) the study of coke reactivity and post-reaction strength in gas atmospheres simulating the BF shaft gas. Sub-goals were set for both research themes as follows:

Study of coke hot strength:

- Evaluate the suitability of a Gleeble 3800 thermomechanical simulator for studying the hot strength of coke.
- Develop a reproducible method to measure coke hot strength
- Compare the hot strength development and deformation behaviour of three different industrial coke grades.
- Discover the coke properties that affect its high-temperature strength.
- Estimate the statistical reliability of the hot strength results.

Study of coke reactivity and post-reaction strength:

- Study the effects of H₂/H₂O on the chemical reactivity of seven industrial coke grades in reference gases and gas atmospheres simulating the BF shaft gas.
- Determine the effect of H₂/H₂O on the threshold temperature of coke gasification.
- Estimate the validity of the CRI test: does the reactivity of different coke grades in 100 vol-% CO₂ directly correlate with reactivity in simulated BF shaft gases, which also include N₂, CO, H₂ and H₂O.

- Study the effects of H_2 and H_2O on the reaction mechanism and fines formation under mechanical stress after gasification.

An overview of the studies in this thesis is presented in Fig. 1 and the contribution of the studies to the research aim are summarised in Table 1.

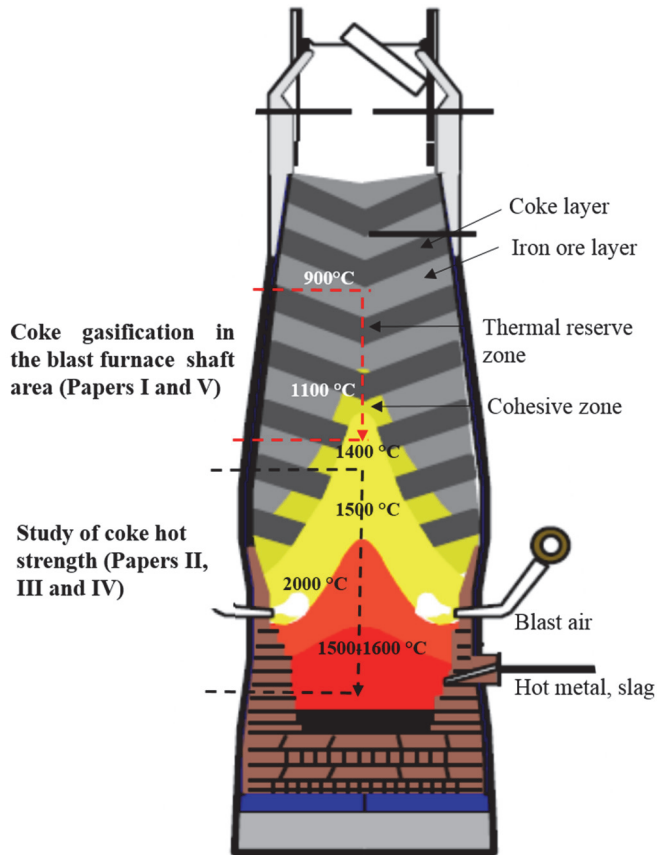


Fig. 1. Overview of the studies presented in this thesis.

Table 1. Contribution of original studies to the research aim.

Original study	Contribution to the research aim
Paper I Effect of injection rate on coke dust formation and coke gasification in a blast furnace shaft	The effect of different levels of H ₂ and H ₂ O in the gas atmosphere were studied on the coke gasification mechanism (surface vs. uniform). The post-reaction surface area and tendency to form fines under stress were measured.
Paper II A method for evaluating coke hot strength	The method to measure coke hot strength was introduced. The first coke hot strength results were obtained at 1000 °C and 1600 °C. The deformation behaviour of coke at high temperatures was discussed. The melting temperature of ash components was calculated. The suitability of the Gleeble for measuring coke hot strength was validated.
Paper III Measuring coke hot strength with a Gleeble	The steps and development of the new hot strength measurement method in Paper II were discussed in more detail. The hot strength measurements performed for Paper II were expanded to 1750 °C.
Paper IV The hot strength of industrial cokes – Evaluation of coke properties that affect its high-temperature strength.	The hot strength of two additional coke grades were tested. Several coke properties, such as porosity, graphitisation degree and weight loss under heat treatment were measured in order to explain the obtained hot strength results. High temperature deformation behaviour of different coke grades was studied.
Paper V Coke reactivity in simulated blast furnace shaft conditions	The effects of H ₂ and H ₂ O on coke reactivity were studied in gas atmospheres simulating the BF shaft gas for several coke grades and in different temperatures. The validity of the industrial CRI test was analysed by comparing reactivity in 100 vol-% CO ₂ with reactivity in simulated BF shaft gas atmospheres.

In this doctoral thesis, a new method for estimating coke hot strength is introduced using a Gleeble thermomechanical simulator. The hot strength of three industrial cokes was measured at temperatures of 1600 and 1750 °C and compared with strengths measured at room temperature and at 1000 °C. New information was produced on the deformation mechanism of coke at high temperatures. Different

coke properties were determined in an attempt to link them to the hot strength behaviour. Suggestions were made for future study of coke hot strength.

New information was obtained pertaining to the effects of H_2 and H_2O on coke reactivity in simulated BF gas atmospheres at various temperatures. The effects of the gas atmosphere on coke gasification threshold temperature were evaluated. Coke reactivity in the conditions of the CRI test was compared with reactivity in simulated BF shaft gas. Suggestions were made that detail how to improve the methods to measure reactivity and post-reaction strength of coke. Additionally, the effects of H_2 and H_2O on the coke reaction mechanism and tendency for fines formation after gasification were studied.

2 Coke in the blast furnace

2.1 Overview of the blast furnace process

In this chapter, the general outline of the BF process is summarised based on comprehensive textbooks written by Geerdes *et al.* (2009) and Babich *et al.* (2008). The blast furnace is essentially a counter current reactor. Solid raw materials are charged from the furnace top in alternating layers and molten products (slag, hot metal) are tapped from the bottom. Reducing the gases and heat required for endothermic reactions and the heating of the raw materials are produced at the raceway by the combustion of fuels with blast air blown in from the tuyeres. The gas travels upward counter current to the descending raw materials and exits through the top after imparting heat and carrying out the required chemical reactions on the raw materials. The raw materials of a blast furnace include one or more of the following: metallic materials (sinter, pellets, briquettes), fuels (coke, pulverised coal, oil, natural gas) and fluxes (limestone, dolomite, quartzite). Metallic materials, fluxes and coke are charged from the top, whereas auxiliary fuels (coal, oil, or natural gas) are injected from the tuyeres.

An overview of the different zones and temperatures in the BF are presented in Fig. 2. When considering the location of temperatures inside the furnace, it needs to be mentioned that strong variation exists in a radial direction depending on the gas flow behaviour of the ascending hot gases, which can strongly vary in different furnaces.

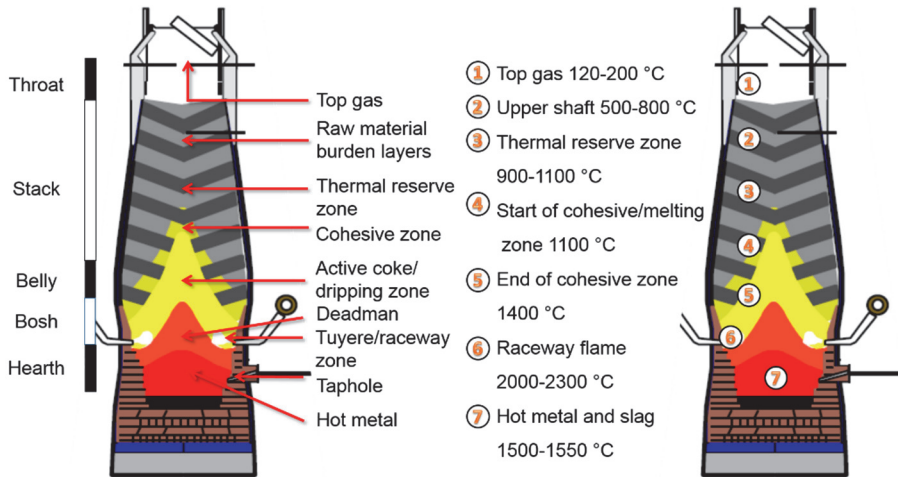


Fig. 2. Overview of different zones and temperatures in the BF. The figure is compiled based on information from Geerdes *et al.* (2009), Nakamura *et al.* (1978) and Haraguchi *et al.* (1985).

At the top of the stack area, the removal of moisture occurs before any chemical reactions, which slows the rise of temperature. Iron ore is typically charged in the form of hematite (Fe_2O_3). Reduction of hematite to magnetite (Fe_3O_4) occurs in the upper shaft at 500–600 °C, followed by reduction to FeO at 600–900 °C. FeO is generally slowly reduced to $\text{FeO}_{0.5}$ before the melting starts at temperatures of 900–1150 °C. The reduction of iron ore occurs via so-called indirect reduction or direct reduction. The direct reduction costs a lot of energy and the efficiency of the furnace is largely dependent on the ratio between the indirect/direct reductions.

Coke gasification generally begins at temperatures of 900–1000 °C. In the shaft area, the exothermic reduction of FeO with CO and the endothermic gasification reaction of coke with $\text{CO}_2/\text{H}_2\text{O}$, known as solution-loss, create an area called thermal reserve zone, in which both the temperature and gas composition remain fairly stable.

The softening and melting of iron ore and fluxes occurs at temperatures 1100–1400 °C, which is called the cohesive zone. The formation of melts significantly reduces the permeability of the raw material bed. Coke is the only solid raw material below this zone and it serves an important role by forming flow windows for the rising gas. The active coke/dropping zone is a packed bed of coke through which liquid iron and slag flow towards to hearth. The rest of the iron oxide is reduced by direct reduction in the cohesive and active coke zones.

The combustion of coke and injectant fuels occurs in front of tuyeres, from which pre-heated oxygen enriched blast air (temperature ~1200 °C) is blown in. Temperatures in the combustion area reach above 2000 °C. The high kinetic energy of the blast air creates a cavity in front of each tuyere known as raceway. After combustion at the raceway, the formed CO₂ and H₂O gases are reduced to CO in the active coke zone, which quickly reduces the temperature of the gas. Behind the raceway exists a tightly packed zone called the bird's nest, which contains small sized coke, unburned char and soot, and liquids.

In the centre of the furnace exists a zone called deadman, in which a pillar of coke is very slowly diluted to molten iron. Slag and iron in the hearth area are easily separated due to significant differences in viscosity. Molten iron is tapped at 1500 °C and slag at 1550 °C.

It takes roughly 5–6 hours for charged material to reach the tuyere level and 5–10 seconds for gas to reach the top from the tuyere zone, however, both are dependent on furnace size and process conditions.

2.1.1 Role of coke in the blast furnace

Coke serves multiple roles in the blast furnace. It acts as a reducing agent and source of reducing CO gas, a source of heat, a filter of dust and soot, a carburiser of hot metal and as a structural support material.

Its role as a structural support material is especially important, particularly in the lower parts of a blast furnace, since it cannot be replaced by other raw materials. A lack of permeability will restrict blowing rates and lead to poor gas distribution in the shaft area. The flow of fluids in the lower blast furnace is also strongly influenced by mean particle size and voidage of the material bed.

The most important properties of coke regarding permeability are an optimal size, good pre- and post-reaction strengths and a narrow size range. Poor coke quality leads to excessive size degradation and the formation of fines, both of which can impair the permeability of the BF. The permeability of the coke bed in the lower part determines the technological limits of the BF, including maximum driving rates, best fuel efficiency and longest campaign life (Cheng 2001b).

Poor coke quality can result in the following adverse effects in the BF: increased flue dust, changes to the shapes of the raceway and cohesive zones, increased heat losses, the channelling of flow of liquids and solids, increased pressure loss, and decreases in the drainage ability of the deadman. An overview

of different stresses in the BF and the effects of poor coke quality on BF performance are depicted in Fig. 3.

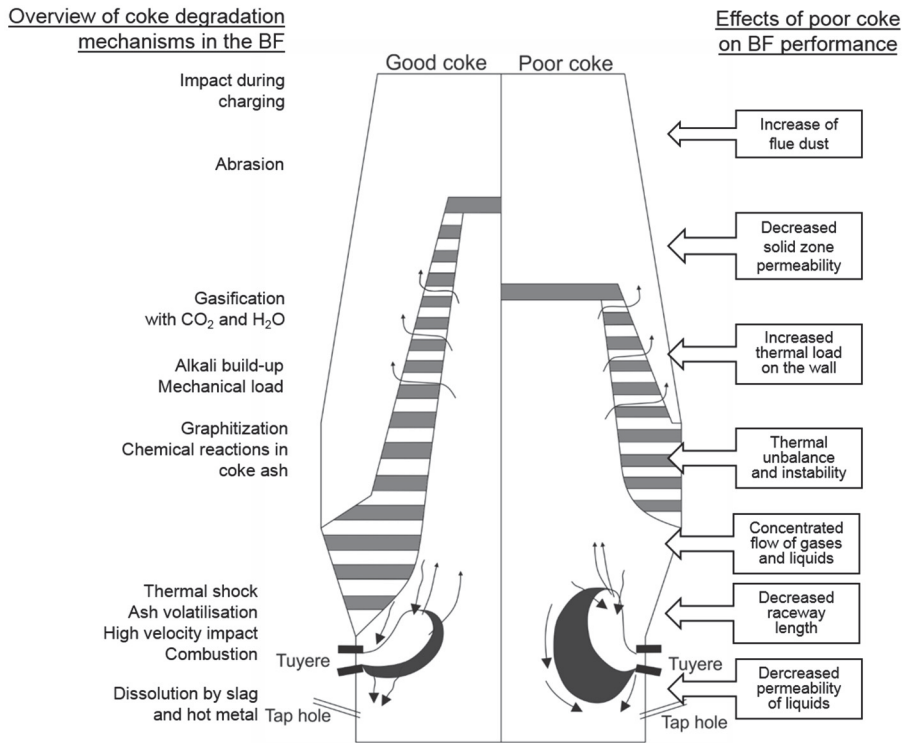


Fig. 3. Degradation mechanisms of coke and effects of coke quality on BF performance. The figure is compiled based on information from Nakamura *et al.* (1978).

The amount of coke charged depends on the amount of auxiliary fuels used and BF performance. Due to the lower price of injectant fuels compared to coke, high PCI rates of 200 kg/tHM are commonly used in modern furnaces together with roughly 300 kg/tHM of coke.

2.2 Coke gasification in the shaft area

Coke gasification in the blast furnace shaft, also known as solution-loss, is one of the main mechanisms that can degrade the strength of coke. The total amount of coke consumed by solution-loss has been reported to be largely independent of

coke reactivity (Kamijo *et al.* 1989, Nomura *et al.* 2007). In the actual blast furnace, the total amount of coke solution-loss is mainly a result of operational conditions, such as blast temperature, rate of auxiliary fuel injection, oxygen enrichment and so on. Historical estimates of solution-loss are in the range of 20–30 wt-% (Cheng 2001f), however it is strongly dependent on process conditions. Newer calculations have shown that with high PCI injection rates, the degree of coke solution-loss can be increased to 30–40 wt-% (Janhsen *et al.* 2002, Negro *et al.* 1996, Danloy *et al.* 2009). Coke gasification in the BF shaft can occur with either carbon dioxide or water vapour.

The threshold-temperature of coke gasification in conjunction with reducibility properties of the iron burden determine the temperature of the thermal reserve zone. The threshold-temperature of coke gasification has been reported to be around 900–950 °C (Van der Velden *et al.* 1999, Cheng 2001f), however, it is strongly dependent on the coke grade. Accumulation of catalysing components in the blast furnace, such as alkali, can also significantly decrease the threshold-temperature to 760–815 °C (Cheng 2001f). The rate of solution-loss intensifies when temperature or the content of oxidising gases is increased. The estimated time duration of coke in the main temperature zone of gasification, from 950 °C to the end of the cohesive zone, is 2–3 h depending on the injection rate (Janhsen *et al.* 2002).

Solution-loss reaction itself does not significantly affect coke size. It has been calculated that the removal of 20–30% of coke from an average sized lump (55 mm) would only reduce the lump size by 1–2 mm (Willmers *et al.* 1984), but solution-loss weakens the coke structure making it more susceptible to breakage under mechanical stresses. Solution-loss reactions can degrade the coke surface and subject it to fines formation under grinding stresses, or degrade the entire coke matrix and subject it to volume breakage. The strength decrease caused by solution-loss depends on the reaction mechanism, which will be explained in a following chapter.

2.3 Coke degradation in the blast furnace

Multiple studies have been conducted on size degradation and quality changes of coke in the BF. In this thesis, the general patterns of coke degradation are summarised based on reports of BF excavations and drilling studies made mainly in Europe and Japan. Coke degradation in the BF is determined by both the feed coke properties and conditions in the furnace, therefore the degree of degradation

varies based on the furnace. Coke size degrades steadily during its descent, however, the most significant size changes are limited to the lower part.

Coke degradation during its descent in the BF is a result of multiple different types of stresses, which can be classified into the following factors: mechanical stresses (impact during charging, abrasion, compressive load, high velocity impact), thermal stresses (graphitisation, thermal shock) and chemical stresses (gasification, alkali attack, combustion at raceway, erosion by slag and hot metal).

In the upper part of the BF, at temperatures up to 1000 °C, coke size decreases slightly due to abrasion, but the strength (DI) is unaffected. The strength of lump coke begins to degrade at the middle part of the shaft (1000 °C) due to selective solution-loss and continues down to the cohesive zone (1400 °C). Coke size, however, does not change. This is possibly due to weak mechanical stresses in this area, which are insufficient to peel off the reacted surface layer (Haraguchi *et al.* 1985). The size degradation in the bosh area has been found to be of only a few millimetres (Janhsen *et al.* 2002). The magnitude of strength decrease depends on whether the gasification occurs on the surface of coke or throughout the carbon matrix.

After the gasification zone, coke is subjected to alkali attack and to liquid attack below the cohesive zone. The alkali attack makes coke significantly more susceptible to size reduction by abrasion (Cheng 2001e). From the lower shaft (1400 °C) to just above the tuyeres (1600 °C), the mean size of coke decreases quickly according to Haraguchi *et al.* (1985), however, the strength (DI) in this area does not decrease because the weakened surface layer is peeled off.

At the raceway level, the degree of size degradation and the overall decrease in strength depends on the radial position. Coke near the walls descends to the raceway and is subjected to thermal shock from temperatures above 2000 °C, combustion with the blast air and high velocity impact from the blast air. The porosity of raceway coke is high, its strength low and size distribution is the lowest in the BF (Cheng 2001e). Coke near the midline descends to the deadman area and is slowly consumed by dissolution into liquid iron. The strength and porosity of deadman coke is only slightly lower than that of feed coke (Steiler *et al.* 1991). Thermal and mechanical stresses in the deadman area are low (Cheng 2001e). Coke median size decreases from furnace top (feed coke size 50–58 mm) to tuyere level at SOLLAC Fos BF varied depending on the positioning along the radius: (Janhsen *et al.* 2002)

- 24–35 mm size decrease at the raceway

- 22–35 mm size decrease at the birdnest
- 15–28 mm size decrease at the deadman

At the lower part of the BF chemical reactions in the coke ash play a major role in increasing porosity and decreasing the strength of coke. Perhaps the most important reaction is the transformation of SiO_2 . Changes in mineral matter are discussed in more detail in Chapter 3.6. Other significant reactions include vaporisation of alkali at the raceway.

The degradation of coke size is more significant in large blast furnaces due to higher abrasive forces and mechanical load (Janhsen *et al.* 2002, Haraguchi *et al.* 1985). Therefore, coke quality requirements are also higher for large blast furnaces. In small blast furnaces, the mechanical stresses are not strong enough to peel away the reacted surface layer of coke.

The increase of injection rates has drastically lengthened the residence time of coke in the blast furnace, hence it has also increased the chemical and physical stresses on coke. With PCI injection rates of 200–250 kg/tHM the residence time of coke is twice as long compared to a case without injection (Gudenau 1998). An increase of coke porosity and a decrease of strength in the lower parts has been observed when increasing PCI rates (Fukuda *et al.* 1998). Therefore, the requirements for coke quality are significantly higher in modern blast furnaces with high injection rates.

3 Review on coke properties

3.1 Cold strength

The ability of coke to maintain its size distribution during handling, charging and descent in the blast furnace is determined by its strength. Therefore, the strength of coke is considered to be one of the most important factors in efficient BF operation. Even though this thesis is mostly focused on the study of coke hot strength, it is important to understand what affects coke strength at low temperatures because many of the same properties, such as pore structure, also affect strength at high temperatures, but new factors are also introduced.

The pore structure of coke is one of the most important characteristics regarding its strength. Under compressive stress small micro cracks extend from one pore into the cell wall and to an adjacent pore. The total porosity is linearly correlated with coke strength (Grant *et al.* 1991) simply due to the reduction of solid matter. According to results of 3D modelling, the effect of the total porosity on coke strength is dominant compared to the carbon matrix bonding strength (Kim & Sasaki 2010). Asakuma *et al.* (2003) showed that both the total porosity and pore shape are important for stress concentration in coke and thereby its mechanical strength and the desired pore shape is circular.

Pore size distribution is also considered important, since it affects the distribution of stresses. It has been concluded that small pore size and a high density of pores produce higher strength compared to a small number of large pores (Grant *et al.* 1991, Andriopoulos *et al.* 2003). Thick coke cell walls should in theory be beneficial for strength, however in practice a high density of small pores tends to produce a thin cell wall. Patrick & Walker (1987) considered that large pores control the tensile strength of coke because they act as stress concentration points for crack initiation.

However, according to 3D modelling, regular pore distribution is a dominant factor regarding coke strength, whereas the number or mean size of pores is not as important (Kim & Sasaki 2010), because cracks can easily propagate through connected pores. Kubota *et al.* (2011) also identified the connectedness of pores as a key factor regarding coke strength.

Coke texture can be classified to inert maceral and reactive maceral derived components (isotropic, anisotropic, banded, etc.) based on optical properties. The elastic modulus of inert is larger than that of reactive component, therefore inert

can be treated as a reinforcing material (Ueoka *et al.* 2007). A high amount of inert texture in coke is a factor that has been linked with good strength (Andriopoulos *et al.* 2003). Inerts have also been reported to decrease the mean pore size, which may partially explain their positive effect on strength (Andriopoulos *et al.* 2003). A decrease of inert size can improve coke drum strength up to a certain limit (Kubota *et al.* 2009).

Differences exist in the hardness of reactive coke textures (Andriopoulos *et al.* 2003), however, despite some attempts to link textural distribution of coke with mechanical strength (Patrick & Walker 1985, Gupta *et al.* 2012), correlations between the two are generally not strong and it is likely that the effects of texture distribution are overshadowed by other factors.

Pre-existing fissures and cracks formed during coking and handling are also important for coke strength, however, they are not under focus in this thesis and are therefore only briefly mentioned here.

3.2 Hot strength

The strength of coke at high temperatures is arguably one of its most important characteristics. Despite this, there is little information regarding coke strength at temperatures relevant to the lower part of the blast furnace. The hot strength is not measured by the coke producers or blast furnace operators. The industrial CSR test is sometimes misleadingly called a hot strength test, but the actual strength measurement is performed at room temperature after gasification at 1100 °C.

Only a small number of scientific studies have been conducted in the past regarding coke hot strength, most likely due to difficulties in creating an experimental setup. In 1957, Holowaty and Squarcy reported that a small number of coke grades caused disturbed operation, a rise in pressure and plugging of blow pipes roughly 6–8 hours after charging. This indicated failure of coke in the lower BF despite good stability and hardness values, which began the interest towards the study of coke hot strength. The authors found coke compressive strength to increase for all coke grades at 1650 °C, however, the number of test samples was as low as three per grade.

Patrick & Wilkinson (1983) observed that coke drum strength increased at 800 °C, possibly due to the annealing of cracks, but began to decrease as temperatures rose above 800 °C all the way up to 1300 °C. They tested the room temperature strength of 12 coke grades after heat treatment at 1450 °C and found that strength decreased in the majority of the grades, although strength increased

for some grades. Tensile strength, however, was higher at 1200 °C compared to room temperature. Grant *et al.* (1991) studied the strength of seven coke grades at 1400 °C. They found increases in strength for six of the seven coke grades and a decrease for one grade. Okuyama *et al.* (1985) also found that coke strength mostly increased at 1300 °C, although some grades decreased in strength. When they increased temperature to 2000 °C, a strong decrease in strength was found for all coke grades. They also found deformation behaviour to be plastic at 2000 °C. At 2300 °C, the strength was unmeasurable due to plastic deformation.

From the previous scientific studies, it can be summarised that the reported results on coke strength development are incongruent; both increases and decreases of strength have been obtained as temperature has been increased above the coking temperature. This can be explained by the following factors; the studies in the past have been done with wide ranging methods and analysis equipment; results by some researchers, such as Patrick & Wilkinson (1983) and Grant *et al.* (1991), suggest that different coke grades behave very differently at high temperatures; it also seems that compressive strength may increase in a certain temperature range, such as up to 1300–1400 °C, but it declines when temperature is further raised. In practically all of the previous hot strength studies, the number of test samples has been low, which casts doubt on the reliability of these results. The properties of coke that define its hot strength are largely unknown.

3.3 Chemical reactivity

The reactivity of coke can be defined as rate at which coke is consumed in the presence of an oxidizing gas, such as oxygen, carbon dioxide, or water vapour. Coke reactivity is mainly determined by the ash composition, pore structure and surface area, and the rank of the parent coal.

When coke is heated it begins to approach the atomic structure of graphite. The degree of organisation of the carbon matrix of cokes is called graphitisation. A higher degree of graphitisation generally leads to lower chemical reactivity. During coking, coal particles maintain their inherent structure. Therefore, a higher coalification (rank) of the coal usually leads to a higher graphitisation degree of coke, although coking temperature also increases the degree of graphitisation. (Cheng 2001b)

Isotropic coke textures have been found to be more reactive with CO₂ gas compared to anisotropic textures. This can lead to selective solution-loss and a weakening of coke strength in the BF. Generally, lower rank coals have a greater

content of isotropic textures present in the coke. As coal rank increases, the amount of anisotropic coke texture increases and the reactivity is decreased. During gasification, isotropic and inert regions are preferentially gasified. The rate of gasification of anisotropic material is slower and decreases as the size of anisotropic regions increases, flow-type anisotropy is the most resistant to gasification (Wilkinson 1986).

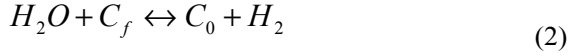
The threshold temperature of coke is determined by both the catalytic components and the structure of the carbon lattice. Accumulation of alkali in the BF can further reduce the threshold temperature. Also, the threshold temperature of coke gasification correlates well with the temperature of thermal reserve zone (Wilkinson 1986).

Concerning coke reactivity, the focal point of this doctoral thesis is to study the effects of BF gas composition on coke reactivity. As previously mentioned, the main components of the BF shaft gas includes N₂, CO, CO₂, H₂ and H₂O, of which CO₂ and H₂O can partake in solution-loss reactions, but CO and H₂ also play a role in inhibiting reactions. There is a large body of literature on coke reactivity with only CO₂ as a gasifying component (Gao *et al.* 2014, Sakurovs & Burke 2011, Pusz *et al.* 2010, Kashiwaya & Ishii 1991, Sahajwalla *et al.* 2004), but only a few studies have also researched the effects of H₂O (van der Velden *et al.* 1999, Iwanaga & Takatani 1989). This is most likely because CO₂ is more prevalent in the BF shaft gas and quite possibly because of the fact that the widely utilised CRI test is performed in 100 vol-% CO₂.

The presence of H₂O in the blast furnace is rarely discussed and its content in the top gas is generally not reported by BF operators because it is difficult to measure. However, previous studies on coke gasification, which included H₂O, concluded that the presence of H₂O could both increase coke reactivity and alter the reaction mechanism. In Paper I of this thesis, results from mass balance calculations combined with thermal calculation software showed that both H₂ and H₂O are always present in both the top and shaft gasses in various amounts. Their content largely depends on the type of injectant fuel and injection rate. Other sources of hydrogen in the blast furnace are coke, moisture in the injectant, and moisture in the blast air.

According to theory (Ergun 1956, Ergun 1962), the gasification reaction of coke occurs in specific atoms in the carbon lattice, called active sites. The reaction path can be summarised by Eqs. (1)–(3).





where C_f , C_0 , and n denote a free active site capable of a reaction, an occupied site possessing an oxygen atom, and the number of free active sites after reaction, respectively. Reaction sites can detach an oxygen atom from a gaseous CO_2 or H_2O molecule that collides with them producing either CO or H_2 , while an oxygen molecule is adsorbed to the solid carbon structure occupying the reaction site. In the following step, which is considered to be the slowest step of the reaction, the oxygen atom at the occupied site is released into the gas phase as CO . The number of free active sites after reaction could have a value of 0, 1, or 2 depending on the structure of the reacting carbon.

For coke, relatively few studies (van der Velden *et al.* 1999, Guo *et al.* 2015, Shin *et al.* 2015, Iwanaga & Takatani 1989) have compared the reactivity in CO_2 and H_2O , however, multiple such studies, such as Everson *et al.* (2006), Chen *et al.* (2013), Roberts & Harris (2007), Ye *et al.* (1998) and Nilsson *et al.* (2013) among others, have been conducted for coal gasification. The reactivity of carbons is strongly correlated with the number of active reaction sites. CO and H_2 have been found to inhibit reaction by decreasing the number of active sites (Huang *et al.* 2010), whereas inert gases, such as N_2 , do not affect reactivity if the partial pressure of gasifying component is maintained (Ergun 1962).

In a gas mixture with both CO_2 and H_2O , two theories have been proposed: their reactions with carbon occur on a) common active sites, or b) separate active sites. These theories have been tested for coal char gasification with incongruent results: Roberts & Harris (2007), Goyal *et al.* (1989), Mühlen *et al.* 1985) and Liu & Niksa (2004) obtained results in favour of common active sites, whereas Huang *et al.* (2010), Everson *et al.* (2006) and Blik (1984) obtained results in favour of separate reaction sites theory. Umemoto *et al.* (2013) proposed a model in which CO_2 and H_2O partially share active sites, but H_2O also has active sites in smaller pores inaccessible to CO_2 . If gasification occurs on separate sites, reactivity in a mixed CO_2 - H_2O gas can be calculated as a sum of reactivity in CO_2 and H_2O individually.

When comparing the reaction rate of carbon in the presence of H_2O and CO_2 both coke gasification studies (Iwanaga & Takatani 1989, van der Velden *et al.* 1999, Guo *et al.* 2015) and coal gasification studies (Everson *et al.* 2006, Roberts & Harris 2007, Irfan *et al.* 2011, Zhang *et al.* 2006, Ye *et al.* 1998) demonstrated

that gasification in H₂O increases reaction rate compared to CO₂. Ergun (1962) found that the relative number of reaction sites per unit weight in coke was about 60% higher in H₂O than CO₂. According to the author, this can be explained by either steam being able to react with more types of sites than carbon dioxide, or by a concentration gradient in the gas phase inside particles. Iwanaga & Takatani (1989) observed that the reactivity of coke in H₂O was higher than in CO₂ at temperatures below 1500 °C, but no difference was observed above 1500 °C.

It has been noted that H₂O is more reactive than CO₂ due to the weak hydrogen bonds in the water molecule compared to double bonds forming CO₂ molecules (Everson *et al.* 2006). Gasification with H₂O has been found to increase coal surface area during gasification and therefore also increase the number of reaction sites and reaction rate, whereas reaction with CO₂ did not have a similar effect (Roberts & Harris 2007). Besides the number of reactive sites, reactivity is also determined by the access of the reacting gas to the reaction sites. H₂O has the advantage over CO₂ in pore diffusion due to its smaller molecule size. It has been reported that coal char gasification with steam occurs primarily on microporous surfaces with a diameter larger than 6 Å (Wang & Lin 1987). Gasification of coal with CO₂, on the other hand, has been observed to occur outside the microporous network on the surfaces of larger pores (Hurt *et al.* 1991, Dutta *et al.* 1977). It was proposed that this is most likely due to active sites (graphite crystallite edges) or catalytic components being concentrated in larger pores, not due to micropore inaccessibility to CO₂ (Hurt *et al.* 1991). For anthracitic coals, the reactivity was up to ten times higher in H₂O compared to CO₂, which has been credited to the small sized microporosity of anthracite (Zhang *et al.* 2006).

Another important property of coke which affects its reactivity is the catalysing minerals in coke ash. Iron, calcium, sodium and potassium which have all been identified as having a catalysing effect on coke gasification, although only in certain forms (Grigore *et al.* 2009). For anthracite gasification Zhang *et al.* (2006) found that the catalysing effect of minerals was more impactful in CO₂ gasification compared to H₂O. To our knowledge, whether a similar effect can be found for coke has not been reported, but it is possible that such exists.

3.4 Reaction mechanism and post-reaction strength

Since the total amount of solution-loss in the BF is independent of coke reactivity, the degree to which the solution-loss weakens coke strength depends on reaction kinetics; the competition between chemical reaction and diffusion into pores. The

factor that constitutes is the limiting step can bring completely different results in terms of porosity development and post-reaction strength. If chemical reaction is the rate limiting step, gasification occurs throughout the coke matrix and the strength degradation affects the entire coke uniformly. If diffusion into pores is the limiting step, reaction occurs mostly on the surface and the strength of the inner core is unaffected. In the actual BF the situation lies between these two extremes and is strongly dependent on coke properties and operating conditions (Helleisen *et al.* 1989).

The gasification mechanism of coke can be divided into three different temperature zones by ascending temperature: Zone I (limited by chemical reaction); Zone II (limited by pore diffusion and chemical reaction); Zone III (limited by film diffusion). For 100 vol-% CO₂ gasification Hermann (2002) reported Zone I to occur up to 1100 °C, Zone II up to 1350–1450 °C and Zone III above 1500 °C. These zones have not been determined for simulated BF gases or in 100 vol-% H₂O. The temperature zone in which gasification occurs has significant implications on the post-reaction strength.

Multiple studies have been conducted on the correlation between gasification temperature and post-reaction strength in CO₂ gasification. For example, Wang *et al.* (2005) found that the higher the temperature, the more solution-loss reactions weaken the surface, but leave the inner core intact. Gasification trials at IRSID showed that coke is weaker after gasification at 970 °C compared to 1070 °C (Janhsen *et al.* 2002). Nogami *et al.* (2004) found coke gasification to occur uniformly at 1000 °C and only on the surface at 1300 °C. Shin & Jung (2015) found that CO₂ gasification gradually changes from uniform reaction at 1100 °C to surface reaction at 1500 °C, whereas gasification with H₂O occurred mostly on the surface already at 1100 °C.

In the actual BF, the decrease of coke strength is generally much lower compared to the CSR test (Ishikawa *et al.* 1983, Negro *et al.* 1996, Lundgren 2013). This is an indication of the coke solution-loss being controlled by chemical reaction in the CRI/CSR test, but mainly by diffusion in the actual BF.

3.5 Industrial analyses

Coke properties measured in the industry include strength (stability, hardness), reactivity (CRI), strength after reactivity (CSR), coke size distribution and ash composition. Cheng (2001c) summarised the coke quality requirements both in the US and countries outside the US, and estimates of coke quality requirements in the

future with low coke rate and high rates of pulverised coal (PCR), which are depicted in Table 2. High PC rates require higher strength, lower reactivity, increased mean size of coke and lower contents of harmful components.

Table 2. Current coke quality requirements and estimated requirements at low coke rates (modified from Cheng 2001c).

Current quality	Current requirement	Home	Outside	Future requirements at low coke rates (high PCR)
Strength:				
Stability	60	59	59–64	>61
Hardness	69	69	68	>70
Size:				
Mean size (cm)	5.08	5.08	5.08	>5.08
>5.08 cm (%)	46	25–75	21–75	>50
>2.54 cm (%)	94	93	93	>96
<1.27 cm (%)	2	2	3	0
Chemical properties:				
Ash (%)	8.5	8.5	7.5–10	<8.5
Sulphur (max.)	0.75	0.70	0.6–0.7	<0.75
Alkalis (max.)	0.20	0.18	0.17	<0.20
VM (max.)	0.90	0.75	0.80	<1
Moisture	5	5	5	<5
Metallurgical properties:				
CSR	61	61	60–65	>61
CRI	23	25	19–25	<22

3.5.1 Strength

In the ironmaking industry, coke strength is generally characterised by drum strength measurements performed at room temperature. Four different standards are used in different parts of the World: ASTM, JIS, Micum and IRSID. These indices describe the ability of a weighted amount of sized coke to resist degradation in a tumbler equipped with lifters for a specific amount of rotations. Much

controversy exists on whether these indices can actually simulate the stresses coke is experiencing in the actual BF (Cheng 2001d).

The drum strength indices are generally classified to measure two different properties: the ability to resist abrasion and the ability to resist volume breakage. The number of rotations and the measured size distribution are selected to highlight these strength properties. For example, indices for abrasion are: hardness by ASTM and M_{10} for Micum, and indices for volume breakage are stability by ASTM and M_{40} for Micum.

Some authors, such as Khan *et al.* (1989) have reported improvements in coke cold strength (stability) to decrease BF coke rate, improve permeability, improve furnace stability, higher allowed flame temperature and lower amount of tuyere failures. Others have found improvement of cold strength to only have an effect in larger blast furnaces where the mechanical demands are greater (Janhsen *et al.* 2002). Based on the reported requirements for coke cold strength, strength needs to be sufficiently to reduce size degradation, however, after a certain point further increases in strength will yield diminishing benefits.

3.5.2 Reactivity and post-reaction strength

Coke reactivity and post-reaction strength in the industry are commonly measured using the CRI and CSR tests, which were originally developed by Nippon Steel in the 1970s. The CRI (Coke Reactivity Index) test is the percentage of weight loss to the original coke mass after reaction in 100 vol-% CO_2 at 1100 °C for 2 h. The test is performed for 200 g of coke with a size of 19–21 mm. High reactivity of BF coke has been reported to cause increased coke size degradation, increased fines at the raceway and decreased raceway depth (Ishikawa *et al.* 1983). Generally the same correlations can be found between coke CRI and CSR and BF performance, since the results of these tests are generally linked together, as will be discussed later in this chapter.

Post-reaction strength in the industry is measured using the CSR test (Coke Strength after Reaction: percentage of coke +10 mm after 600 revolutions in an I-drum), which is performed after gasification in the CRI test. Best (2002) has summarised the reported effects of coke CSR on blast furnace performance: operators have reported multiple improvements as a result of improving the CSR of coke, such as lower coke rate, increased productivity, increased permeability, decreased coke degradation and higher PCI injection rates. Janhsen *et al.* (2002) reported that an increase of CSR leads to an increase of coke median size in the

lower parts due to lower degradation between the throat and tuyere level. In some furnaces good coke CSR has been linked with improved raceway length. Most of the improvements produced by increasing coke CSR have been derived with CSR values below 60 and further improvements generally bring diminishing benefits (Grant 1992). The reports of coke CSR and BF operation seem to also be mixed: the process improvements achieved as a result of increased CSR value in one BF are not always observed in others.

Despite the historical usefulness of the CSR test, several authors have questioned its validity (van der Velden 1999, Grant 1992) to actually simulate the post-reaction strength of coke in the blast furnace. General criticism of the tests can be summarised by the following sentences. The total amount of gasification in the CRI/CSR test is not controlled, unlike in the actual BF process where it is limited to roughly 25–35 wt-% depending on operating conditions. The unlimited amount of gasification results in a roughly linear correlation between the CRI and CSR tests (Lyaluk *et al.* 2010, Sakurovs & Burke 2011, Lindert & Timmer 1991). As a result, measuring coke strength after a varying degree of gasification does not accurately reflect the blast furnace operation. The gas atmosphere in the CRI/CSR tests can also be considered too intensive and completely different from the actual BF gas atmosphere. The conditions of the test result in a significant increase of porosity and the degradation of coke strength throughout the coke matrix (Pusz *et al.* 2010), whereas in the actual BF the inner core of cokes has been found to be mostly unreacted (Haraguchi *et al.* 1985, Lundgren *et al.* 2009, Kamijo *et al.* 1989). The drum strength of coke taken both from an industrial BF (Best 2002) and an EBF (Lundgren 2013) was much higher than coke CSR, which suggest that the CSR test is much more degrading than the BF process. Also, no correlation could be found between coke CSR and the post-reaction strength of coke excavated from the EBF (Lundgren 2013).

It should be noted that in addition to reactivity, abrasion resistance is the other factor which has been found to correlate with CSR (Best 2002). Cokes with very low or very high abrasion resistance can deviate from the linear correlation between CRI and CSR tests.

Despite the criticism, the historical benefits of the CSR test are undeniable. However, it is not entirely clear why increasing coke CSR produces improvements in BF operation. It has been suggested that the improvements may be derived more from the lower reactivity of coke instead of the actual post-reaction element of the CSR test (Grant 1992). Indeed, the effects of CSR on BF performance could probably be found also for coke CRI, since the two values are usually well correlated.

It is evident that many elements of the connection between coke reactivity, post-reaction strength and blast furnace performance are not yet fully understood.

3.6 Mineral matter

Various mineral compounds are found within coke. These are often referred to as coke ash and generally constitute around 5–10 wt-% of total mass. The major ash components of coke are SiO_2 and Al_2O_3 . Smaller amounts of CaO , Fe , MgO , S , K_2O and Ti are also typically found. Temperatures in a blast furnace are extremely high, capable of surpassing 2000 °C at the tuyere level. Mineral matter in coke undergoes changes in a blast furnace due to melting and chemical reactions.

At the lower BF, chemical reaction in the coke ash plays a major role in increasing porosity and decrease of coke strength. In terms of coke strength, the most important reaction is the transformation of SiO_2 , which is the largest constituent of coke ash. During heat treatment, the most notable changes occur between 1300 and 1500 °C. During this temperature range, quartz and cristobalite (both SiO_2) are reduced to silicon carbide (SiC). Above 1500 °C, no SiO_2 could be detected (Li *et al.* 2014, Lundgren *et al.* 2014).

Gornostayev & Härkki (2006) studied mineral matter of coke taken from the tuyere level. They found that mineral matter can migrate from inside the coke matrix and form mineral spherules inside the pores of coke. This migration may leave voids which could affect the strength of coke. This migration is expected to occur due to a rise in temperature followed by melting and the tendency of melts to form larger droplets. As temperatures rise coke gradually transforms into a two-phase system: 1) mineral matter and (2) a mineral-free carbon matrix, which is likely to cause changes in both the reactivity and physical strength of coke. Patrick & Wilkinson (1983) also stated that mineral matter in coke migrates at elevated temperatures and can in some cases cause swelling and even cracking in coke.

The composition of mineral matter in coke changes significantly in various parts of the blast furnace. In an EBF, the amount of alkali (Na_2O and K_2O) in coke increased 10-fold from the top (less than 1%) to the cohesive zone (around 4%). It was also observed that alkali is distributed evenly inside the coke matrix, not just on the periphery. Alkali build-up in coke is followed by reactions with other mineral compounds. Alkalis are high at the lower BF in the birdnest and deadman areas, but completely absent near the tuyere zone as a result of high temperature vaporisation (Hilding 2005).

3.7 Degree of graphitisation

A graphitic structure of carbon atoms can be described by regular, vertical stacking of hexagonal aromatic layers. Carbons produced by solid-state pyrolysis of organic matter can be classified into graphitising and non-graphitising. Graphitising carbons, such as coke, begin to approach the atomic structure of graphite when heated to high temperatures. The height of graphite crystallites in coke (L_c value) begins to grow as coke is heat treated at temperatures above the coking temperature, which is usually around 1100 °C. Graphitisation is made possible by the plastic phase during coking, during which carbon layers are organised in near-parallel orientations. As the temperature of solid coke is increased, it enables the continuous rearrangement of the layer-planes to take place by small stages (Franklin 1951).

The temperature history of coke can be evaluated by measuring the L_c value with an X-ray scattering device (XRD). The L_c value has been shown to be directly related to the highest temperature experienced by a coke. The L_c value is a linear function of temperature experience by the coke and has no influence from chemical reaction (Kashiwaya & Ishii 1991). This technique has been used to evaluate temperatures in a blast furnace from coke samples excavated from the BF.

The graphitisation degree also affects coke strength. In the structure of graphite, each C atom within an aromatic layer is linked through covalent bonds to three C atoms. However, bonding between aromatic layers is weak, easily broken by external forces. Non-graphitic carbon, however, contains cross-linking between the aromatic layers and a much higher force is required to dissociate them. During heat treatment, non-organised carbon is presumably attached to the edge atoms of the graphite-like layers, which enables the growth of organised layers but decreases the cross-linking between the layers. Sato *et al.* (1998) stated that coke strength becomes higher with a non-graphitic structure and this is usually associated with coke made from lower rank coals.

Coke grades have been found to have differing degrees of graphitisation after treatment in similar annealing temperatures (Gupta *et al.* 2005, Lundgren *et al.* 2014), therefore, it is important to measure the graphitisation tendency of cokes during hot strength testing.

4 Materials and methods

4.1 Materials

4.1.1 Industrial analyses of coke grades used in studies

The industrial analyses of coke grades used in different studies are presented in Tables 3 and 4. BF is an abbreviation for blast furnace cokes and CF for cupola furnace cokes. Coke 1 was used in Papers I, II and III. Cokes 1–3 were used in Paper IV. Cokes A–G were used in Paper V. Coke grades 2 and 3 are the same as BF Coke B and BF Coke C, but are labelled differently in different studies. No ash analysis was available for the CF cokes F and G used in Paper V. The CRI and CSR refer to the widely utilised tests standardised by the Nippon steel company. Micum and Irsid are coke drum strength indexes most commonly used in Europe.

Table 3. Industrial analyses of the coke grades used.

Name	Irsid > 20 mm	Irsid < 10 mm	Micum > 40 mm	Micum < 10 mm	CRI	CSR	Volatiles
Coke 1	77.2	21.1			21.5	63.6	0.2%
BF Coke A	76.7	21.0			18.4	68.3	0.2%
BF Coke B / Coke 2			85.0	5.4	31.3	57.6	0.2%
BF Coke C / Coke 3			82.7	5.8	28.2	58.5	0.2%
BF Coke D			82.2	5.1	29.2	59.9	0.2
BF Coke E			82.7	6.5	17.3	62.4	0.3
CF Coke F					41	35	0.7
CF Coke G					55	15	1

Table 4. Ash analyses of the used coke grades.

	Total ash	SiO ₂	Al ₂ O ₃	CaO	Fe	MgO	S	K ₂ O	Ti	Na ₂ O ₃
Coke 1	10.60	59.90	26.70	2.45	3.91	0.72	0.76	1.28	0.88	0.38
BF Coke A	10.40	55.49	30.30	2.26	4.09	0.92	0.68	1.24	1.07	0.55
BF Coke B / Coke 2	8.69	44.88	29.92	4.37	7.02	2.30	0.53	2.42	0.81	1.61
BF Coke C / Coke 3	9.20	47.83	31.52	3.48	5.65	1.74	0.52	2.28	0.87	1.52
BF Coke D	8.31	45.73	28.88	4.57	6.86	2.29	0.51	2.29	0.84	1.56
BF Coke E	10.92	63.19	25.64	1.56	3.21	0.55	0.67	1.10	0.09	0.64

4.1.2 Sample preparation

Paper I

Spherical coke samples were used in the gasification tests in Paper I. They were prepared by cutting coke samples into cubic shapes with an edge length of 25 mm. These cubes were then mechanically formed into spherical shapes with a grinding wheel. 17–18 coke samples were used in each experiment, depending on their mass. Before the tests, the samples were held at 110 °C overnight to remove moisture.

Papers II, III and IV

Cylindrical coke samples used in the hot strength testing were prepared by drilling through coke lumps with a hollow drill and the obtained coke cylinders were cut to the desired height. The sample preparation was done in wet conditions, after which the samples were held in ethanol to remove water and finally held at 110 °C overnight to remove any volatiles. The final samples had a diameter of 16 mm and a height of 12 mm. This size and shape was found to be optimal when using the standard sample holder in the Gleeble. All of the samples used in each study were prepared beforehand and carefully mixed in order to eliminate systematic errors caused by sample location. After preparation, the samples were pre-graphitised in a chamber furnace in inert gas (nitrogen). The pre-graphitisation was made at the same temperature as the temperature that was subsequently used in the Gleeble tests. The samples were sealed in a graphite container and covered in graphite grains to avoid gasification. The graphite container containing the coke samples was placed in the furnace at 1200 °C, after which the temperature was raised up to the subsequent test temperature and held for 60 minutes to ensure a high level of graphitisation. In the literature, there are differing observations on what time frame is sufficient to ensure complete graphitisation. For example, Gupta *et al.* (2005) found no graphitisation to occur after the first 30 minutes, however, Lundgren *et al.* (2014) found that some graphitisation occurs even after 2–4 hours. Pre-graphitisation was done in order to reduce the necessary holding time in the Gleeble while simulating the thermal effects (such as graphitisation and changes in ash composition) of a blast furnace on the structure of coke. Only visibly crack-free samples were chosen for strength testing in the Gleeble.

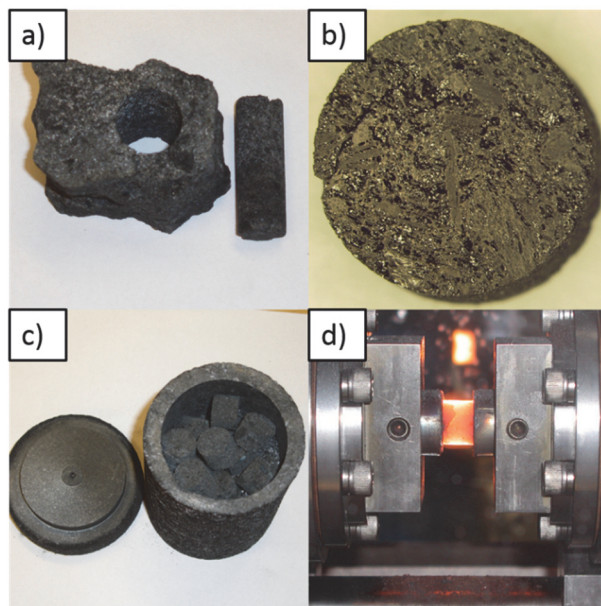


Fig. 4. a) A coke cylinder after drilling; b) a prepared coke sample; c) the graphitisation container; d) coke sample during a Gleeble test (modified from Paper II).

Paper V

Two types of samples were used in reactivity testing with TGA: coke powder of sizes under 250 μm and coke grains of sizes from 4.67–6 mm. Coke powder was used in the tests for chemical reactivity for enhanced reliability and repeatability of the results: due to the heterogeneous nature of coke, individual coke lumps can consist of a wide array of pore structures, ash components and degrees of graphitisation, therefore causing significant variance in the reactivity of individual coke lumps. The coke powder was prepared by randomly selecting at least 10 lumps for each coke grade and grinding all of the material to a sieve size below 250 μm using a ring mill. After the grinding process, the coke powder was thoroughly mixed. The ground coke powders were held at 110 $^{\circ}\text{C}$ overnight to remove moisture. Coke powder with a mass of 1.0000 ± 0.0005 g was used in each experiment.

Larger sized coke (grain size 4.67–6 mm) was used in estimating the correlation between reactivity in 100% CO_2 and the simulated blast furnace shaft gas atmospheres, since it also includes the effects of macroporosity and the reaction mechanism is closer to the actual size of BF coke. The grains were prepared by

crushing more than 10 lumps from each coke grade with a roller mill, sieving the material to the specified size range and thoroughly mixing. Coke grains with a total mass of 2.00 ± 0.02 g was used in each test, which amounted to roughly 20 grains per test.

4.1.3 Gas profiles

Paper I

Blast furnace gas atmospheres with various oil injection rates were estimated based on industrial blast furnace data. Some assumptions were made concerning the degree of reduction of iron ore and the degree of coke gasification at certain temperatures in order to estimate the mass balance in the shaft area. When mass balance in the shaft had been estimated, the gas was thermodynamically balanced with the HSC Chemistry 7.0 calculation software (Roine *et al.* 2007). The exception was the gas atmosphere of 0 kg/tHM which was chosen to be a reference gas atmosphere free of hydrogen and water vapour. The partial pressure of oxygen in the hydrogen-free gas atmosphere was selected to match the atmosphere 100 kg/tHM throughout the test. The total flow of gases was selected to be 15 l/min. An example of a gas and temperature profile with a simulated oil injection level of 120 kg/tHM is depicted in Fig. 5.

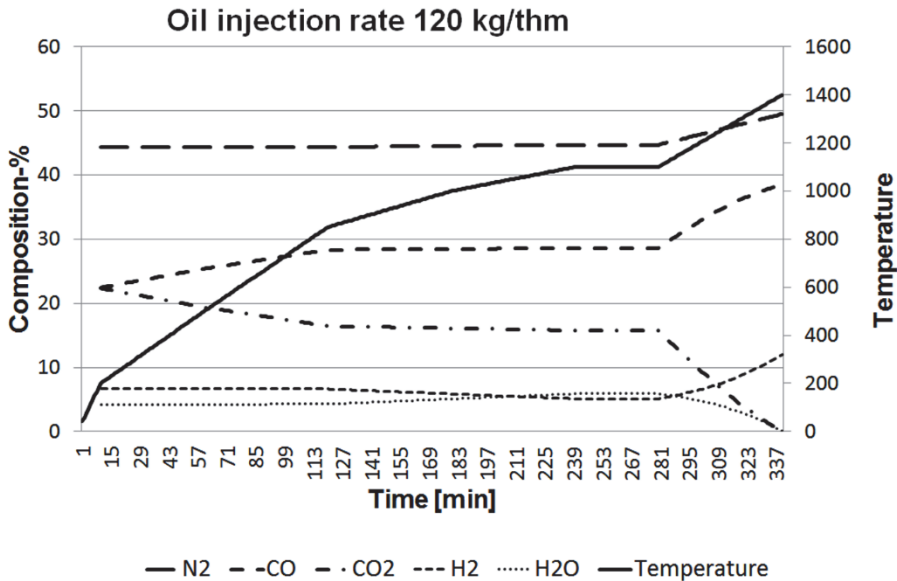


Fig. 5. The gas and temperature profile with a simulated oil injection rate of 120 kg/tHM (Paper I, reprinted with permission of the Steel Institute VDEh).

Paper V

The gas profiles used in the TGA reactivity tests of Paper V are presented in Table 5. For low-hydrogen shaft gas, the total H₂ and H₂O content was estimated based on a PCI-injection of 150 kg/tHM using a coal with a hydrogen content of 4 wt-%, whereas the high hydrogen shaft gas estimation was based on an injection rate of 250 kg/tHM using a coal with a hydrogen content of 6 wt-%. The gas atmospheres were determined by mass balance calculations and by using a thermochemical calculation software product, HSC Chemistry 7.0 (Roine *et al.* 2007), to balance the gases at 1100 °C. The thermodynamic balance of gas profiles 3 and 4 changes slightly with temperature, however, the feed gas was always kept constant independent of the test temperature.

The content of the N₂ gas was kept constant at 50 vol-% and the sum of oxidising gases (CO₂ and H₂O) constant at 20 vol-% in order to limit changing variables in the tests and to focus solely on how the ratios between CO+CO₂ and H₂+H₂O affected the reaction rate. It should be noted that in an actual blast furnace higher rates of PCI injection are usually accompanied by higher oxygen enrichment

of the blast air, which lowers the N₂ concentration of the gas. Two hydrogen-free gas atmospheres were selected as references: 1) 100% CO₂, since it is widely utilised in both scientific studies and the industrial CRI analysis; 2) a hydrogen-free shaft gas, to more closely resemble the actual shaft gas composition, but to exclude H₂ and H₂O. The gas flow rate in the TGA tests was 2 l/min.

Table 5. Gas profiles used in Paper V.

Gas profile	N ₂ [vol-%]	CO [vol-%]	CO ₂ [vol-%]	H ₂ [vol-%]	H ₂ O [vol-%]	Total CO ₂ + H ₂ O [vol-%]	Oxygen partial pressure (p _{o2})
1. 100% CO ₂			100.0			100.0	4.62 • 10 ⁻³
2. Hydrogen-free shaft gas	50.0	30.0	20.0			20.0	1.75 • 10 ⁻¹¹
3. Low hydrogen shaft gas	50.0	27.9	17.1	2.1	2.9	20.0	1.49 • 10 ⁻¹¹
4. High hydrogen shaft gas	50.0	25.5	14.5	4.5	5.5	20.0	1.27 • 10 ⁻¹¹

The total hydrogen content in the Low hydrogen shaft gas atmosphere is of a similar degree to that reported for typical blast furnace top gases in scientific literature (Lundgren *et al.* 2013, Moon *et al.* 2014). When estimating realistic upper limits for hydrogen even higher concentrations are possible. The hydrogen contents of some typical BF injectants are: pulverised coal 4–6 wt-%, coal tar 5–6 wt-%, heavy residual oil 11–12 wt-%, natural gas 25 wt-%. It has been calculated that with a potential future technology, called top gas recycling blast furnace with water-gas shift, the H₂ and H₂O contents could be as high as 30.3 vol-% and 18.9 vol-% in the top gas (Hooey *et al.* 2010), respectively. Modelling has been done on H₂ injection into the blast furnace as a potential method to achieve reductions in CO₂ emissions (Natsui *et al.* 2014).

The carbon conversion used to estimate the reaction degree was calculated by the following equation:

$$X = \frac{m_0 - m_t}{m_0 - m_{ash}} \quad (4)$$

where m₀, m_t and m_{ash} denote original mass, the mass at a given time, and the mass of the ash components, respectively.

4.2 Methods

The different analytical and experimental methods used in different studies are listed in Table 6.

Table 6. Methods used in the original research papers.

	Paper I	Paper II	Paper III	Paper IV	Paper V
BFS	x				
Gleeble 3800		x	x	x	
LOM				x	
Shaking sieve	x				
TGA					x
XRD				x	

4.2.1 Coke reactivity tests with BFS

The Blast Furnace Simulator (BFS) is a tubular oven used for simulating the temperature and gas profile of the blast furnace shaft. The maximum temperature of the furnace is 1100 °C when using a steel furnace tube, and 1400 °C when using a ceramic furnace tube. Computer is used to adjust temperature of the furnace and gas flows according to a pre-determined program. Gases available for the BFS are N₂, CO, CO₂, H₂, H₂O, K and S₂. H₂O is generated with a water bath, through which the gases are directed. Water vapour pressure is proportional to the temperature of the water bath, which is adjusted by the computer software. S₂ can be generated by reacting SO₂ with graphite. The sulphur generator also operates as a gas pre-heater. Potassium can be generated by reacting potassium carbonate with graphite. Compared to the TGA, the BFS has a larger furnace tube and bigger sized samples can be used. The layout of the BFS is presented in Fig. 6.

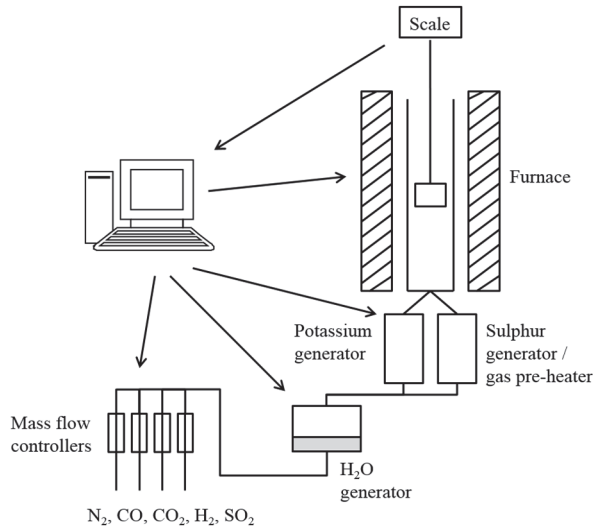


Fig. 6. Layout of the BFS (Paper I, reprinted with permission of the Steel Institute VDEh).

In the gasification experiments in Paper I, cokes were placed in the furnace before the test. Tests were performed at 1100 °C using a steel tube and at 1400 °C using a ceramic tube.

4.2.2 Shaking sieve

After gasification in Paper I, the cokes were subjected to mechanical stress using a programmable shaking sieve (model Fritsch Analysette 3). The coke pieces were subjected to 20 minutes in the shaking sieve with an amplitude of 1.0 mm. Fine coke broken off the coke pieces during shaking was collected and sieved. The pounding drum-like stresses induced by the shaking sieve differ from the grinding stresses in the lumpy zone of a BF, but they were found to be suitable for comparing gasified coke pieces in this study.

4.2.3 Coke reactivity tests with TGA

The TGA is a custom-made vertical tubular oven with an inner dimension of 28.5 mm. The temperature and gas profiles are computer-controlled. Both isothermal and dynamic conditions can be used. The furnace can hold a maximum temperature of 1500 °C. Gases N₂, CO, CO₂, H₂ and H₂O were used in the

experiments. Water was provided with a peristaltic pump directly to the gas line, which was heated to 250 °C in order to vaporise the water and avoid condensation. The layout of the TGA is depicted in Fig. 7.

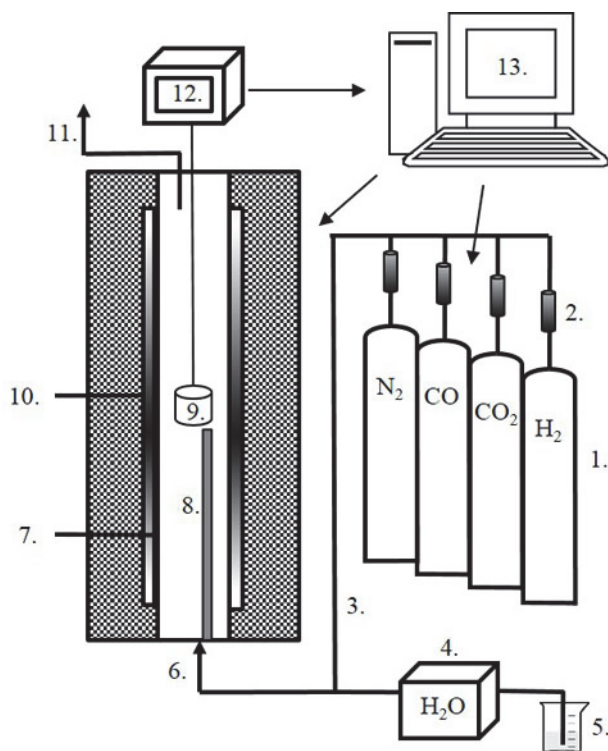


Fig. 7. Layout of the TGA furnace: 1) gas cylinders; 2) gas flow controllers; 3) heated gas lines; 4) peristaltic pump; 5) deionized water; 6) gas inlet; 7) furnace tube (Al_2O_3); 8) thermocouple; 9) sample holder; 10) heating element (SiC); 11) gas outlet; 12) analytical scale; 13) computer (Paper V, reprinted with permission of Springer).

Three types of crucibles were used in the tests: 1) a cylindrical platinum crucible (inner height 10 mm, inner diameter 10 mm) open from the top was used to hold the coke powder during reactivity tests at 1100 °C; 2) a ceramic (spinel) crucible (inner height 10 mm, inner diameter 10 mm) was used to hold coke powder in the testing the effects of various temperatures due to durability issues of platinum at high temperatures; 3) a cylindrical ceramic (spinel) crucible (inner height 28 mm, inner diameter 22 mm) was used to hold the coke grains, which was also perforated

to allow gas flow through the bottom. The samples were inserted into the TGA in a 100 vol-% N₂ gas atmosphere and pre-heated for 10 minutes at the temperature of the actual test.

In the threshold temperature tests, the sample was pre-heated before the test to 800 °C in 100 vol-% N₂ gas for 10 minutes. After pre-heating, the reactive gas was introduced into the furnace and temperature was raised 2 °C /min from 800 °C to 1100 °C.

4.2.4 Hot strength of coke (Gleeble 3800)

Gleeble devices are generally used for thermomechanical testing and physical simulation of metallic materials. The model Gleeble 3800 was used in this study. It uses a computer-controlled direct resistance heating system capable of heating rates up to 10 000 °C/s and can hold steady-state temperatures. The Gleeble can be operated in vacuum or inert gas. The Gleeble can perform both tensile and compressive strength tests. Mechanical force is applied via a hydraulic servo system capable of exerting up to 20 tons of static force in compression or 10 tons in tension. Digital stress-strain curves can be obtained and used to further analyse the deformation behaviour.

A pyrometer was found to be the best solution to measure coke temperature due to durability issues and significant time resources required by the use of thermocouples. The coke hot strength tests were performed in vacuum. The heating rate of the samples was chosen to be 30 °C/s in order to avoid excessive thermal stresses without unduly long test times. Based on the visual glow of the samples, the heating with electrical current did not occur evenly, therefore the samples were also held 30 seconds at their respective test temperature to allow the temperature to stabilise throughout the samples. After heating, compressive force was measured while the samples were mechanically compressed up to 4 mm (33.3% of height) with a speed of 1 mm/s. The temperature of the samples during testing was measured with a pyrometer. For the pyrometer, an emissivity value of 0.95 for coke was chosen based on calibration experiments using thermocouples in conjunction with the pyrometer.

The maximum temperature when using the Gleeble was limited to 1750 °C due to device limitations and safety concerns. The total time spent on testing a single coke sample while using the pyrometer was roughly 5 minutes. Strength measurements can be done both in tensile and compressive manners. For the evaluation of coke strength, compressive force is generally considered to be more

accurate due to the heterogeneous nature of coke, hence compression was used in this study.

4.2.5 Coke graphitisation degree (XRD)

The crystallographic analysis of coke after heat treatment was performed for fine coke powder with a Siemens D5000 X-ray diffractometer with Cu anode tube K_{α} ($\lambda = 1.542 \text{ \AA}$). A graphite secondary monochromator was used in the measurements. The diffraction patterns were identified with Bruker AXS Diffrac^{Plus} Eva 12 software using ICDD PDF-2 database.

The graphitisation degree was estimated based on the graphite crystallite height (L_c). The L_c value was determined based on the 002 carbon peaks from the XRD patterns using Scherrer's equation: (Kashiwaya & Ishii, 1991)

$$L_c (\text{\AA}) = \frac{0.9\lambda}{B \cos \theta_B} \quad (5)$$

, where L_c , λ , B and θ_B denote mean height [\AA] of graphite crystallites, wavelength of X-ray (\AA), angular width in radians at half-maximum intensity of [002] peak, and the reflection angle of the [002] peak, respectively. The calculation was based on the assumption that crystallites are ideal with no strain or distortion.

4.2.6 Light optical microscopy

Light optical microscopy (LOM) was conducted with Olympus BX51 LOM equipped with a camera to examine polished coke samples. The ratios of inert maceral, reactive maceral and pores were determined by point counting at least 1000 points from five polished sections for each coke grade. The point counting was performed with a Pelcon Automatic Point Counter. Objectives with a magnification of 10 and 20X were used for point counting.

The pore size distribution and pore shape factors were determined with a MATLAB-based image analysis software (Mattila & Salmi 2008) using the same polished sections used for point counting. Five images of size 3.5 x 2.6 mm were taken from each five polished sections per grade under 4X magnification. The pore shape factor was determined by identifying pore edges from LOM images by subsequent thresholding and filtering methods. This caused the smallest pores to be excluded from the analysis as they could not be separated reliably from the darker areas of the coke matrix itself. After the pore edge detection the measured

pore surface area was used to determine round-equivalent edge length which was divided by measured real edge length on each pore. The software was programmed to ignore any pore connected to the edge of an image in the calculations.

5 Results and discussion

5.1 Hot strength of coke

Summary of the coke hot strength study in this thesis is divided to two chapters. Chapter 5.1.1 summarises the development of the new method presented in Papers II and III, in which the suitability of a Gleeble 3800 thermomechanical simulator for measuring coke hot strength was tested for the first time and the hot strength of one coke grade was determined at temperatures of 1000, 1600 and 1750 °C. Chapter 5.1.2 focuses on Paper IV, in which the hot strength of three coke grades was tested, the deformation behaviour at high temperatures was characterised and various coke properties were determined in an effort to find reasons behind the hot strength behaviour.

5.1.1 A new method to measure coke hot strength

As previously mentioned in Chapter 3.2, there are few published studies on coke hot strength, likely due to the difficulties in experimental setup. The need for a hot strength test has been stated for example in the ECSC technical report by Janhsen *et al.* (2002). In order to obtain reliable hot strength results the following conditions must be met: rapid heating to very high temperatures; an inert atmosphere or vacuum; the ability to perform a strength test at high temperatures; a sufficient sample size for reliable conclusions. The previous coke hot strength studies have been performed with purpose-built equipment. Construction of such equipment requires significant financial and time resources, and has made the study of coke hot strength out of reach for most researchers. Also, testing with many of the older experimental devices has been too slow, due to which studies have been published with low number of tests samples and the results have usually been statistically insignificant. There no previous reports in literature of using a Gleeble device for measuring the hot strength of coke.

In the early stages of developing the hot strength measurement, lots of tests were done in order to find the appropriate sample size, sample preparation method, method of measuring temperature, finding the optimal parameters for heating rate, compression rate and the amount of compression of the samples. Once the method was established, coke hot strength was measured for one coke grade at temperatures

of 1000 °C, 1600 °C and 1750 °C. 50 coke samples were tested at each temperature. The strength results from these tests are depicted in Table 7.

Table 7. Strength values of coke at different test temperatures.

Temperature [°C]	Mean ultimate strength [MPa]	Strength standard deviation [MPa]	Variance	Yield strength [MPa]
1000	15.1	7.52	56.59	15.1
1600	12.1	3.61	13.04	8.2
1750	10.7	3.34	7.26	7.3

Coke mean ultimate strength was found to decrease by 20% when heated to 1600 °C. In Paper II, the difference in the mean strengths at 1000 °C and 1600 °C was also shown to be statistically significant. When further heated to 1750 °C, the strength continued to decline being 29% lower compared to 1000 °C. The yield strength of coke, which will be defined later, decreased even further. It was 46% and 52% lower at 1600 °C and 1750 °C respectively compared to 1000 °C. The strength of coke was also found to undergo a process of homogenisation at high temperatures: both the standard deviation and variance were significantly decreased.

At 1000 °C the highest force was always measured at the very beginning of deformation. The initial linear rise of the force curve, known as Young's modulus, was followed by fragile fracture and sequential plummeting of force needed for further deformation. A typical stress-strain curve at 1000 °C is displayed in Fig. 8.

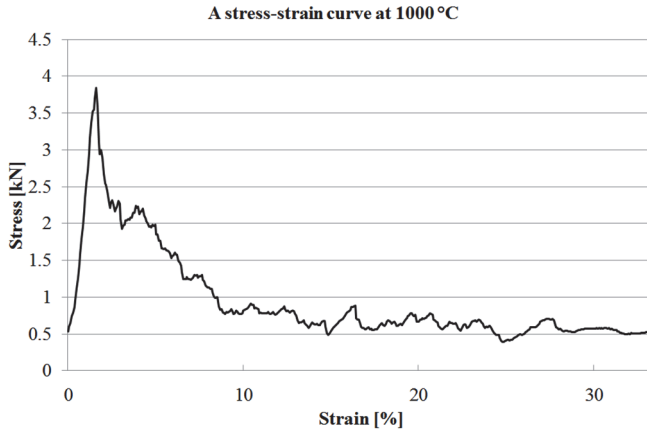


Fig. 8. A typical stress-strain curve observed at 1000 °C (Paper III, reprinted with permission of Swerea MEFOS).

At 1600 °C and 1750 °C, however, the highest force value was generally measured at the very end of the 4 mm (33.3%) compression, such as presented in Fig. 9. This was considered to be an indication of plastic deformation behaviour. For this reason, the yield strength index of coke was introduced in order to obtain an additional descriptor of coke strength at high temperatures.

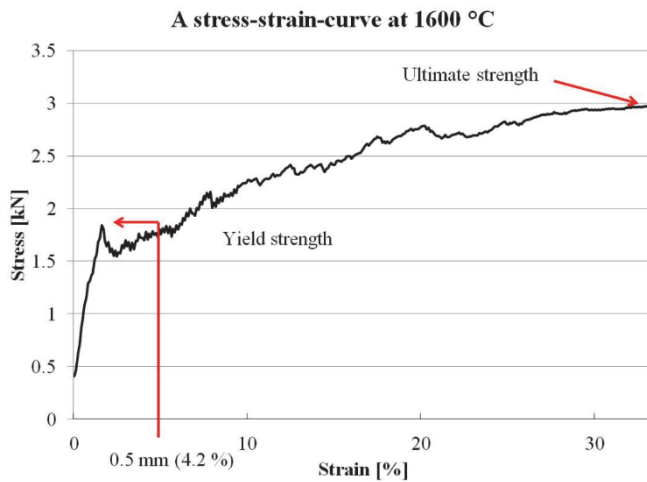


Fig. 9. Typical coke stress-strain curve obtained at 1600 °C. Obtaining yield and ultimate strength values explained (Paper III, reprinted with permission of Swerea MEFOS).

The method of obtaining ultimate strength and yield strength values at 1600 and 1750 °C is visualised in Fig. 9. There is no standard on how to determine the yield strength of coke. For many materials, for example, the yield strength is taken as the stress after a 0.2% permanent deformation. An offset yield point was chosen to be at 0.5 mm (4.2%) deformation based on earlier tests at 1000 °C; the initial – almost linear – rise of the force curve known as Young’s modulus was always over before the deformation had reached 0.5 mm. Hence, the yield strength value represents the highest force measured before the deformation has reached a value of 0.5 mm. The term “ultimate strength” refers to the highest obtained strength value during the 4 mm (33.3%) compression. In some cases this was obtained in the beginning of compression and in some at the very end.

Partial compressions were also performed to estimate the degree of plastic deformation, which at 1600 °C can be described as follows: after 1 mm compression the samples were still visibly intact; after 2 mm compression they were partially shattered; after 4 mm (33.3%) compression all coke samples were completely shattered. At 1750 °C the plasticity further increased; the centre part of coke was still intact even after 4mm compression. Plastic deformation behaviour of coke has been previously reported at 2000 °C and 2400 °C (Okuyama *et al.* 1985).

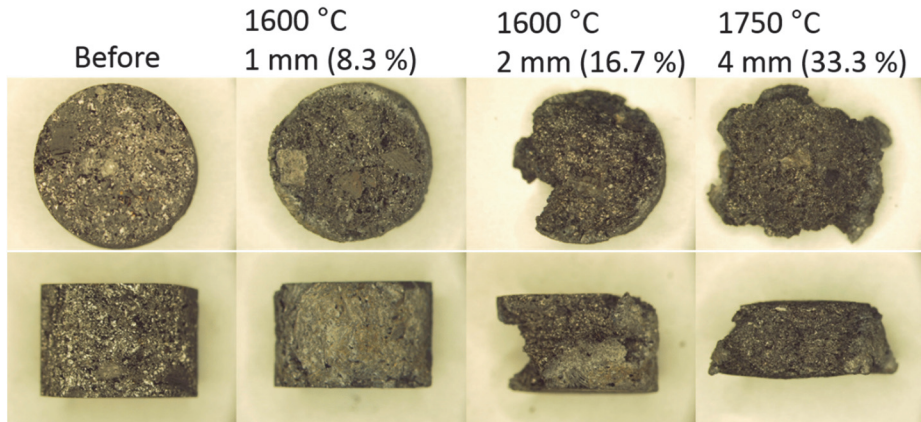


Fig. 10. Coke samples before and after plastic deformation at 1600 and 1750 °C with various degrees of compression.

The reasons behind plastic deformation behaviour are not yet clear. Possible reasons could be the melting of ash components or the softening of bonding

between carbon layers as a result of increased heat energy, which would allow re-organisation of the carbon matrix during compression.

The significant decrease of coke strength at high temperatures is in disagreement with some of the earlier studies as described in Chapter 3.2, although Okuyama *et al.* (1985) also reported a significant loss of strength at 2000 °C. The strength of coke could be improved by the healing of cracks or relief of tension and weakened by other factors such as build-up of pressure inside the coke matrix, melting and chemical reactions of ash components, or differences in the heat expansion of different textures. The significance of each factor is still unknown. Some factors may only play a role at a certain temperature range, such as melting and the reactions of ash components. Therefore, it can be expected that the hot strength results depend on many factors such as selected temperatures, the testing method, and material preparation (pre-graphitisation) used by different authors.

The Gleeble device was found to be suitable for testing coke hot strength and statistically reliable coke hot strength results were obtained for the first time. In comparison to previously proposed equipment, the Gleeble allows swift testing, visibility of the sample, accurate strength measurements, obtainment of digital stress-strain curves and no costs in construction of specific equipment.

5.1.2 Study of coke hot strength

The coke hot strength study included testing three industrially produced European coke grades at room temperature and at temperatures of 1600 °C and 1750 °C. Also, several coke properties, such as total porosity, inerts and degree of graphitisation were determined in order to study how they relate to the strength of coke both at room temperature and at elevated temperatures. The strength measurements both at room temperature and high temperatures were performed with the previously introduced method using a Gleeble 3800 thermomechanical simulator.

The obtained hot strength results are listed in Table 8. Initially 50 samples were measured at each condition, but some samples had to be discarded due to equipment malfunction.

Table 8. Obtained hot strength and room temperature strength values.

Temperature	Number of samples	Mean ultimate strength [MPa]	Strain [%]	Standard deviation [MPa]	Effect of heating on the ultimate strength [%]
Coke 1					
Room	50	16.6	2.5	7.5	
1600 °C	50	12.1		3.6	-27.0
1750 °C	50	10.7		3.3	-35.5
Coke 2					
Room	50	23.8	3.0	8.1	
1600 °C	40	15.8		5.2	-33.6
1750 °C	50	17.5		6.2	-26.5
Coke 3					
Room	49	13.3	2.5	6.7	
1600 °C	50	9.1		3.2	-31.5
1750 °C	50	9.7		3.3	-27.1

The mean strength and strain values at room temperature were similar to those reported previously by other researchers: Kim & Sasaki (2010) reported compressive strength of coke in their study to vary between 19.4 and 28.6 MPa, while strain at fracture ranged from 2.2 to 3.0%. As observed in Table 8, notable differences were found in the compressive strengths of the coke grades at room temperature; coke 2 was clearly the strongest and coke 3 the weakest.

At 1600 °C, the ultimate strength was significantly decreased for all three coke grades compared to room temperature. The magnitude of the strength decrease was of similar degree. A further increase in temperature to 1750 °C had differing effects depending on the coke grade: the strength of coke 1 suffered a further fall. The strength of cokes 2 and 3, on the other hand, seemed to recover, however, it should be noted that this result was without statistical significance. The possible recovery in strength could be explained by the increasing plasticity of the coke at 1750 °C, which could result in increased density and the surface area of coke resisting the compressive force during deformation and a higher force required for further deformation. The results indicate that the development of coke hot strength as a function of temperature may be material dependent. Coke grades 2 and 3 originated from the same geographical area, which may explain their similar strength behaviour. Despite the varying effects caused by high temperature, the relative strengths of the various coke grades remained, therefore the original room

temperature strength of coke was more significant compared to the effects produced by heating.

The statistical reliability of the hot strength results was analysed using a two-sample t-test assuming unequal variances (Welch's t-test). The analysis of statistical reliability is depicted in Table 9. A two-tailed test with p value of 0.05 was chosen as the level of significance. When the calculated value of t exceeds the critical value of t and p is below the chosen significance level of 0.05, the difference in strength is concluded to be significant.

The following hypotheses were set and evaluated:

H₀: There is no statistical difference in coke hot strength between the studied temperatures

H₁: There is a significant difference in the hot strength of coke at the studied temperatures

Table 9. Analysis of statistical reliability of the hot strength values.

Temperature	Degrees of freedom	t	Critical t	p	Statistical significance
Coke 1					
Room vs 1600 °C	70	3.790	1.994	0.000	Yes
Room vs 1750 °C	67	5.043	1.996	0.000	Yes
1600 °C vs 1750 °C	97	2.019	1.985	0.046	Yes
Coke 2					
Room vs 1600 °C	84	5.648	1.989	0.000	Yes
Room vs 1750 °C	91	4.328	1.986	0.000	Yes
1600 °C vs 1750 °C	87	1.443	1.988	0.153	No
Coke 3					
Room vs 1600 °C	68	3.955	1.995	0.000	Yes
Room vs 1750 °C	70	3.394	1.994	0.001	Yes
1600 °C vs 1750 °C	97	0.872	1.985	0.386	No

Based on the analysis presented in Table 9, the hypothesis H₀ was accepted in two cases: both for cokes 2 and 3 when comparing the hot strength between temperatures 1600 °C and 1750 °C. The differences in strength between these temperatures are statistically insignificant. In all other cases, hypothesis H₀ was rejected and the alternative hypothesis H₁ was accepted: the difference in the other studied temperatures was statistically significant.

Various types of stress-strain graphs were obtained during strength testing. These graphs can be used to analyse the deformation behaviour of different cokes in different temperatures. The types of stress-strain curves were classified into six general types. These six types are depicted in Fig. 11. They were found to present the majority of all stress-strain graphs obtained at both room and high temperatures.

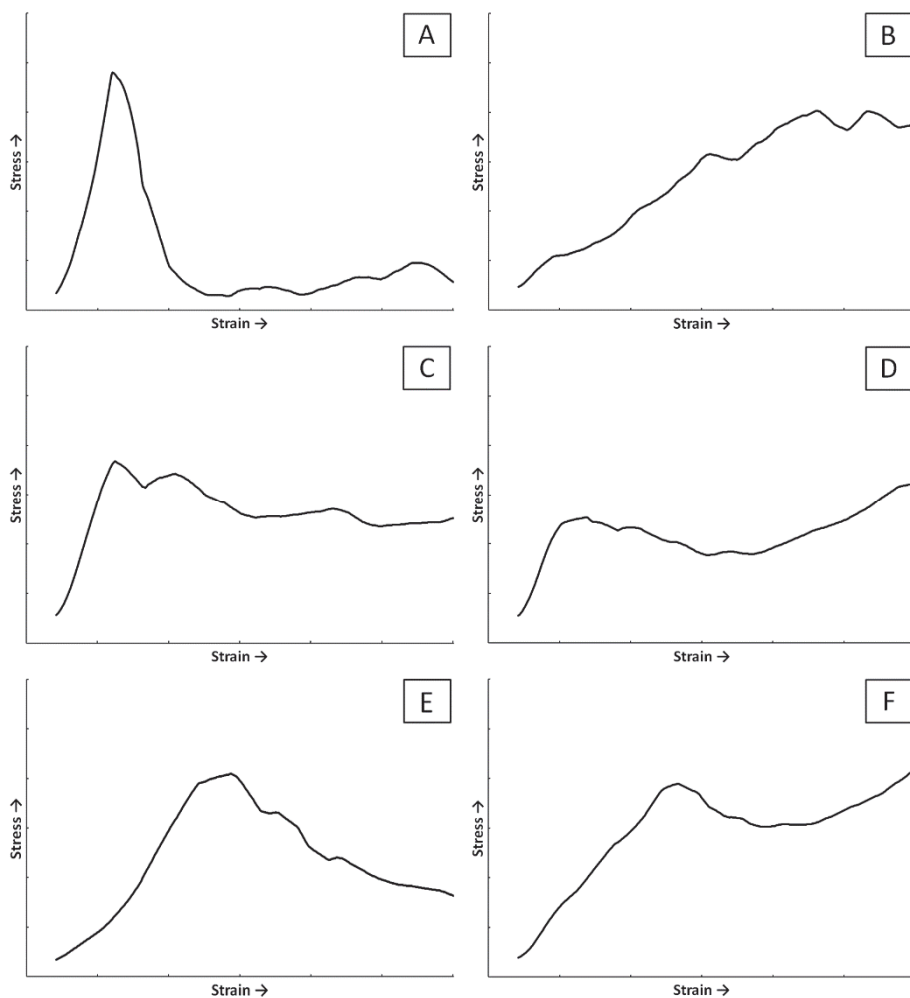


Fig. 11. Typical stress-strain curves for coke in the Gleeble tests (Paper IV, reprinted with permission of Wiley-VCH Verlag GmbH & Co. KGaA).

The distribution of all stress-strain curves to the six general types is depicted in Table 10. It was found that different coke grades produced different types of stress-strain graphs at high temperatures.

Table 10. Distribution of stress-strain curves to the general types.

	Type A [%]	Type B [%]	Type C [%]	Type D [%]	Type E [%]	Type F [%]
Room Temp						
Coke 1	76.0		24.0			
Coke 2	88.0		12.0			
Coke 3	72.0		28.0			
1600 °C						
Coke 1	2.0	40.0	22.0	22.0	14.0	
Coke 2		15			67.5	17.5
Coke 3	18.0		46.0	16.0	16.0	4.0
1750 °C						
Coke 1		42.0	18.0	4.0	30.0	6.0
Coke 2		4.0	10.0	4.0	62.0	20.0
Coke 3	4.0		56.0	12.0	22.0	6.0

At room temperature, the ultimate strength values were obtained at the very beginning of deformation for all three grades. On a stress – strain curve, this is reflected by an initial almost linear rise in compressive force until fragile fracture occurred at 0–4% strain (mean value 2.5–3.0%) and in most cases followed by a significant decrease in force required for further deformation. At high temperatures, the ultimate strength value was often at the very end of the 4 mm (33.3%) compression, which was considered an indication of plastic deformation in which the density and surface area are increased during the compression.

From the distribution of strength results depicted in Fig. 12, it can be seen that the strength of coke at high temperatures undergoes a process of homogenisation. This can also be observed from the decreased standard deviations in Table 8.

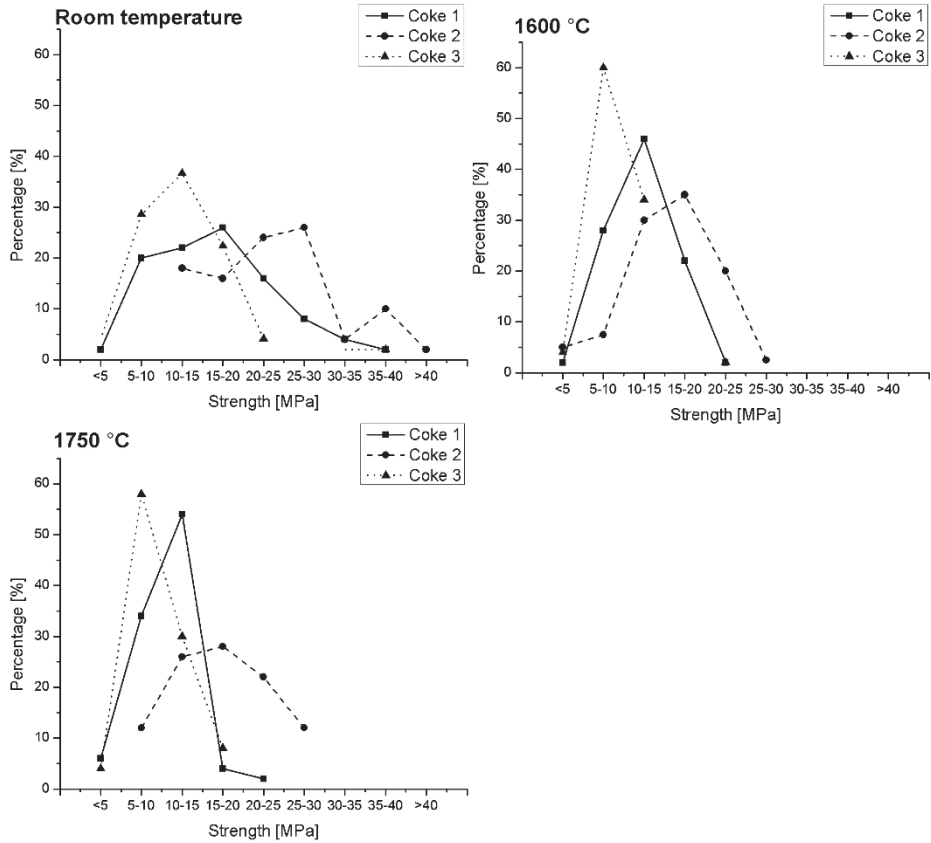


Fig. 12. Distribution of coke strengths at different temperatures (Paper IV, reprinted with permission of Wiley-VCH Verlag GmbH & Co. KGaA).

As previously mentioned, the coke samples were pre-graphitised in inert gas at the test temperature before the Gleeble test. Heat treatment above the temperature of the coking furnace affects coke strength in different ways: 1) it promotes further graphitisation, which changes the atomic carbon network into a more highly ordered one; 2) it causes significant weight loss as displayed in Table 11 due to melting and chemical reactions of the ash components; 3) it could have healing effects on cracks and fissures; 4) it could induce crack formation, which was regularly observed after graphitisation, possibly as a result of rising gas pressure or differences in the heat expansion of different textures.

Table 11. The weight loss of cokes during pre-graphitisation.

Coke grade	1600 °C	1750 °C
Coke 1	-7.2%	-10.1%
Coke 2	-4.9%	-7.6%
Coke 3	-6.2%	-8.7%

As was shown in Table 4, coke grade 1 contained the highest amount of SiO₂, therefore its ash had the highest potential to react with the carbon matrix (forming SiC and CO) and to induce weight loss. The weight loss is a result of chemical reactions, vaporisation and re-organisation of mineral matter in the coke.

In order to answer the question, is the decrease of strength at high temperatures caused by the pre-graphitisation or the high temperature itself, a strength test was made to study how much merely the preceding heat treatment affects the room temperature strength. This study was done for coke 2 by testing the strength at room temperature of 50 non-graphitised samples and 50 samples pre-graphitised at 1750 °C. The obtained strength values are displayed in Table 12. Young's modulus was determined from the angular coefficient of linear elastic part of the stress – strain curves.

Table 12. Compressive strength values of coke 2 before and after heat treatment at 1750 °C.

	Mean strength [MPa]	Standard deviation [MPa]	Strain [%]	Young's modulus [MPa]	Change in strength [%]
Non-graphitised	23.75	8.09	3.0	1337.1	
Pre-graphitised (1750 °C)	15.32	5.42	3.1	724.3	-35.5

The pre-graphitisation weakened the coke strength significantly. Also, as can be seen from the standard deviation, the strength undergoes a process of homogenisation during heat treatment. The results presented in Fig. 13 on the distribution of strengths show that there is an absence of high strength samples post-graphitisation.

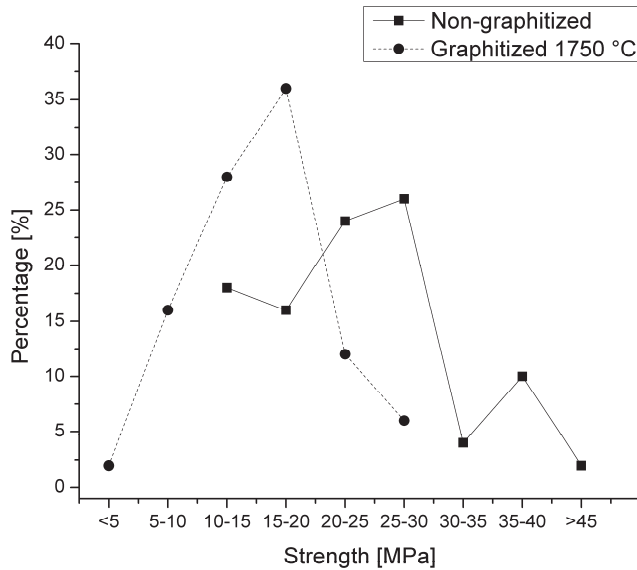


Fig. 13. Distribution of strength of coke 2 samples before and after heat treatment at 1750 °C.

The decreased strength is likely a result of factors, including increase of porosity as a result of changes in the ash components and changes in the crystalline structure of coke. It has been stated that as the crystalline structure of coke approaches that of graphitic carbon, the cross-linking between carbon layers is decreased and the coke matrix weakened (Sato *et al.* 1998). Heat treatment at 1750 °C did not have any noticeable effect on the shape of stress – strain curves, except for the angular coefficient of the elastic phase (Young’s modulus). Therefore, the plasticity of coke observed at high temperatures is purely a result of the temperature during the compression, not the preceding heat treatment.

In addition to weight loss during graphitisation, the graphitisation degree (graphite crystallite height, L_c) and pore structure of coke were determined as possible explaining factors of coke strength. The L_c value was calculated from X-ray diffraction profiles using Scherrer’s equation (Eq. 5 in Chapter 4.2.5) (Kashiwaya & Ishii 1991, Sahajawalla *et al.* 2004). Despite earlier reports that the graphitisation could be dependent on the coke grade (Gupta *et al.* 2005), all three coke grades in this study had very similar graphitisation behaviour as evidenced by

L_c values in Table 8 of Paper IV. The graphitisation tendency of a coke grade may play a role in hot strength, but it could not be determined in this study.

Also, in order to explain the differences in strength between coke grades total porosity and the contents of inert and reactive texture were determined. The distribution of these structural parameters was done by a standard point counting method by counting 1000 points from five polished sections for each coke grade. Structural data obtained by these analyses is displayed in Table 9 of Paper IV. The differences in the content of inert material between the coke grades proved to be small. The high strength of coke 2 reported in Table 8 could at least partially be explained by its slightly lower total porosity. However, all of the studied cokes were fairly close in measured structural characteristics and due to the heterogeneous nature of coke substantial amounts of polished sections would have to be analysed in order to draw more accurate conclusions.

5.2 Effects of H₂ and H₂O on coke gasification in the BF shaft

5.2.1 Chemical reactivity

Coke reactivity at 1100 °C

In order to study the influence of H₂ and H₂O on the reactivity of coke, the reactivity of seven different coke grades was measured with a TGA using the previously described method. The final carbon conversions of the coke grades in four different gas atmospheres are presented in Table 13 together with the CRI values reported by coke manufacturers. Carbon conversion graphs from the reactivity tests are presented in Fig. 14.

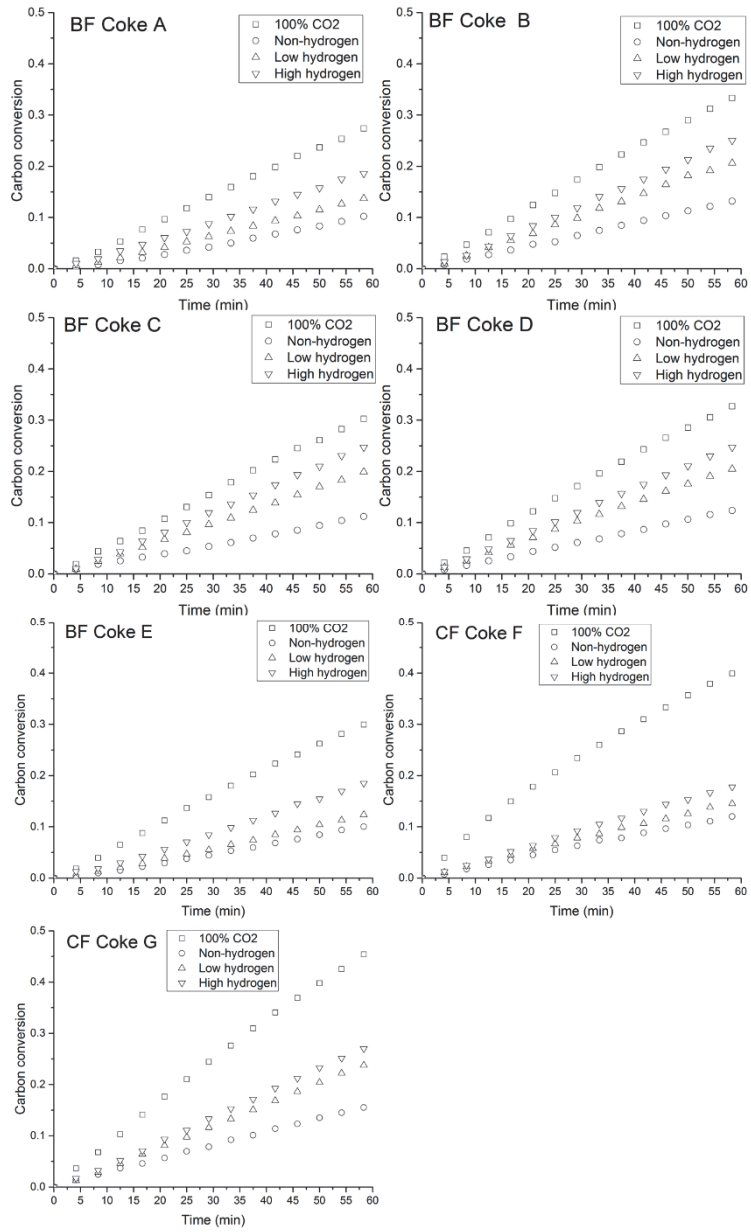


Fig. 14. Carbon conversions at 1100 °C for different coke grades.

Table 13. CRI values provided by the manufacturers and the final carbon conversion values of fine coke (< 250 μm) at 1100 $^{\circ}\text{C}$.

	CRI (industrial value)	100% CO ₂	Hydrogen-free shaft gas	Low hydrogen shaft gas	High hydrogen shaft gas
BF coke A	18.4	0.282	0.104	0.143	0.192
BF coke B	31.3	0.340	0.136	0.213	0.260
BF coke C	28.2	0.312	0.116	0.205	0.254
BF coke D	29.2	0.339	0.128	0.211	0.255
BF coke E	17.3	0.307	0.105	0.127	0.188
CF coke F	41.0	0.408	0.124	0.150	0.183
CF coke G	55.0	0.466	0.160	0.246	0.281

Based on the results depicted in Table 13, it is clear that the partial replacement of CO/CO₂ with H₂/H₂O significantly increased the chemical reactivity of cokes. This occurred despite the sum of the gasifying components (CO₂ + H₂O) remaining constant in each of the three shaft gas atmospheres and oxygen partial pressure of gas also relatively close. The final conversion degree in the High hydrogen shaft gas was 1.5–2.2 times higher compared to the Hydrogen-free shaft gas depending on the coke grade. Also, large differences in the reaction degree between the coke grades were observed when the total amount of H₂ and H₂O was increased from 0 to 5 vol-% (low hydrogen). The increase in reactivity varied from 2.4% up to 8.0% depending on the coke grade. However, when the H₂ + H₂O concentration was further raised from 5 to 10 vol-% (high hydrogen) the increases in reaction degree was more predictable: 6 of the 7 coke grades had an increase by between 3.7–4.5%. Only CF coke F remained outside the mentioned range with only a 2.4% increase in reactivity. The large differences in these cokes can be attributed to changes occurring in the reaction mechanism.

A surprising result was the low reactivity of CF coke F in the shaft gas atmospheres, however, too much importance should not be placed on comparison between the coke grades after significant changes in physical structure have occurred as a result of the grinding process. The lack of direct correlation as evidenced in Table 13 between the industrial CRI value and the measured TGA reactivity in 100% CO₂ can be explained by the fact that the TGA tests were done for coke powder with a grain size below 250 μm , therefore the effects of the larger sized macroporosity on reactivity remain beyond consideration in this experiment.

In the past, coke reactivities have been measured in laboratory conditions in N₂-CO-CO₂ gas atmospheres aiming to simulate their actual ratios in the blast furnace shaft (Sakurovs & Burke 2011). The reactivity of coke in these tests is in

general much lower coke reactivities compared to those that have been calculated or observed from excavated blast furnaces. The lower reactivity in laboratory studies has been explained by the accumulation of catalysing components on the surface of the coke in actual blast furnaces, which has been shown to increase coke reactivity (Sahajwalla *et al.* 2004). Based on the results in this study, the presence of H₂ and H₂O in the blast furnace shaft gas may also play a large role in explaining higher coke reactivities in the industrial process. The results also suggest that the injection rate and the composition of the auxiliary fuel may significantly affect coke gasification behaviour in the blast furnace shaft, since the injectant is the largest source of hydrogen in the blast furnace.

Threshold temperature of gasification

The threshold temperature of gasification is the initial temperature when noticeable weight loss of coke begins to occur in the presence of an oxidising gas component. Information of the threshold temperature is valuable because together with the reduction properties of iron ore it determines the temperature of the thermal reserve zone, which impacts the energy efficiency of the BF. The threshold temperature of coke may also have significant implications on the post-reaction strength of coke, since the gasification temperature has a large influence on the reaction mechanism. The threshold temperature is an individual property for each coke grade and is affected by the catalysing components in coke ash and the atomic lattice of the carbon itself.

The effects of gas atmosphere on the threshold temperature were studied using the TGA. These tests were conducted by measuring the reactivity of BF Coke A in the four gas profiles previously used and presented in Table 5 in dynamic temperature conditions from 800 °C up to 1100 °C. A reference test was also done in 90% H₂O, in which 10% N₂ was required as a carrier gas. The tests were originally made using a spinel crucible, but later repeated using a platinum crucible due to the fact that spinel was found to have a catalytic effect on gasification. The obtained carbon conversion curves as a function of temperature are shown in Fig. 15.

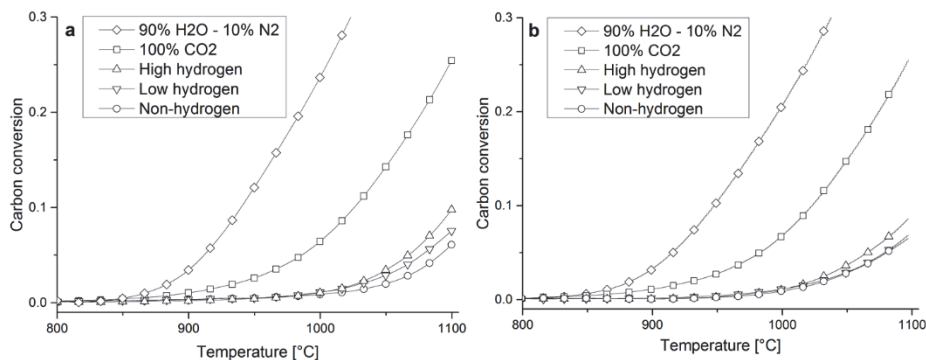


Fig. 15. Threshold temperature of gasification for BF coke A in four different gas profiles using; a) spinel crucible, b) platinum crucible (Paper V, reprinted with permission of Springer).

The tests in 100 vol-% CO₂ and 90 vol-% H₂O gas had a significantly lower threshold temperature compared to the simulated BF shaft gas atmospheres, which may be explained by the higher ratio of oxidising components, which is also indicated by the partial oxygen pressure of the gas in Table 5. The threshold temperature between 100 vol-% CO₂ and 90 vol-% H₂O seemed to be of a similar degree initially, but as temperature increased reaction proceeded to be much faster in 90 vol-% H₂O. However, very few differences in reactivity can be observed in the three simulated shaft gas atmospheres for BF Coke A below 1000 °C, furthermore the differences could be explained by variance. It can be concluded that the presence of H₂ and H₂O did not have a noticeable effect on the gasification threshold temperature of the tested coke grade in the simulated blast furnace gases. Their reactivity increasing effect began to have an effect at temperatures above 1000 °C. Based on these results, H₂ and H₂O contents in the BF shaft gas are unlikely to have a significant effect on the threshold temperature of coke gasification in the industrial process.

Effects of H₂ and H₂O on coke reactivity in a temperature range of 1000–1300 °C

It is well established that increasing reaction temperature strongly increases the reaction rate of carbon in an oxidising gas. Previously in chapter 5.2.1 it was shown that reactivity was strongly increased at 1100 °C for the studied coke grades when CO/CO₂ was partially replaced with H₂/H₂O. In the following phase, the reactivity

was measured in the gas profiles previously utilised at a wider range of temperatures (1000–1300 °C). These tests were performed using BF Coke A and the same testing protocol as in the previous TGA tests. The difference in these tests was the fact that the sample crucible was made of a different material (ceramic) due to durability issues with platinum at higher temperatures. The final carbon conversion values are shown in Table 14 and the carbon conversion graphs are depicted in Fig. 16.

Table 14. The final carbon conversion at various temperatures for BF Coke A.

	100% CO ₂	Hydrogen-free shaft gas	Low hydrogen shaft gas	High hydrogen shaft gas
1000 °C	0.123	0.023	0.027	0.028
1100 °C	0.367	0.153	0.216	0.339
1200 °C	0.757	0.392	0.406	0.519
1300 °C	0.987	0.601	0.639	0.682

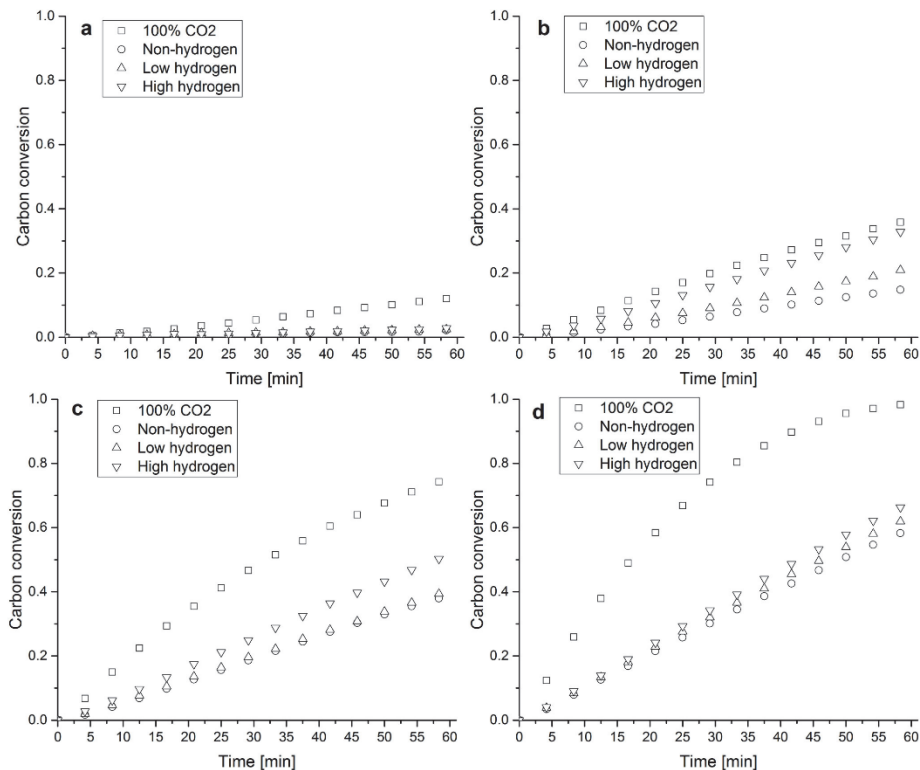


Fig. 16. The final carbon conversion values of coke at different temperatures for BF Coke A at: a) 1000 °C, b) 1100 °C, c) 1200 °C, d) 1300 °C (Paper V, reprinted with permission of Springer).

Little increase in reactivity can be observed with the addition of H₂ and H₂O at 1000 °C. The result is in accordance with the previous observation that the threshold temperature of coke remains largely unaltered by the addition of H₂/H₂O. The reactivity increasing effect of H₂/H₂O is clearly the highest at 1100 °C. The partial replacement of CO/CO₂ with H₂/H₂O did also increase reactivity at temperatures of 1200 °C and 1300 °C, but to a lesser degree. It is clear that the difference in reaction rate between CO₂ and H₂O diminishes as temperature is further increased. The result can be explained by reactivity with H₂O becoming limited by mass transfer instead of chemical reactivity at lower temperatures compared to the CO₂ case, which is further explained below.

The gasification reaction rate of carbon is limited by the slowest step of the reaction: either by the rate of the actual chemical reaction, or by mass transfer

through diffusion. The mass transfer can be limited by diffusion into pores or by gas film diffusion. At lower temperatures chemical reaction is the slowest step of reaction and the reaction rate increases linearly with temperature. When temperature increases, the rate of chemical reaction eventually exceeds the rate of diffusion and reaction rate becomes mass transfer controlled. Because the rate of chemical reaction with H₂O increases much faster compared to CO₂, it becomes limited by mass transfer at lower temperatures, and the increase of reaction rate with temperature begins to slow down considerably. When both reactions (gasification with CO₂ and H₂O) are under mass transfer control, their reaction rates become very similar.

The reactivity increasing effect of H₂ and H₂O is dependent on the reaction temperature, and in this study it was at its highest at 1100 °C, which is close to the temperature of the blast furnace shaft. In this test set the reactivities at 1100 °C were higher than in the previous TGA tests, despite the fact that same coke, gas profile and temperature were used. There could be some diffusional differences between the crucibles due to differing outer radius, however, the difference in reactivity was likely resulted from a reaction catalysing effect from the spinel crucible. This theory was supported by additional tests performed in conditions under chemical reaction control (100% CO₂ gas, 1000 °C, size below 90 µm, 100 mg sample) which resulted in roughly 35% higher carbon conversion when using the spinel crucible.

Reaction kinetics

Reaction kinetics were determined in order to compare the reactivity results to those obtained by other researchers. The kinetics study was performed using BF Coke A in a temperature range of 950–1025 °C in gas atmospheres of 90% CO₂-10% N₂ and 90% H₂O-10% N₂. 10% N₂ was required as a carrier gas with high amounts of H₂O.

For reliable activation energy calculations it is important to verify that reactivity is limited by chemical reaction. In the selected temperature range changing the gas flow rate had no effect on gasification, therefore film diffusion control was ruled out. Also, intra-particle diffusion may be disregarded when material is ground to sufficiently small size, because of the short intra-particle diffusion trajectories (Ollero *et al.* 2002). Coke with a mass of 50 mg was used in each test with a size below 90 µm, a particle size which has been considered safe for coal gasification to rule out intra-particle diffusion (Gomez & Mahinpey 2015).

Inter-particle diffusion control was ruled out by performing tests at 1050 °C with 50, 100 and 150 mg of material with both H₂O and CO₂, in which no difference in conversion rate was observed.

By using kinetics models the reaction process can be predicted by using simple equations. Several kinetic models have been used to study coal char gasification of which the homogenous model (Wen 1968) and the shrinking core model (Levenspiel 1999) were applied to model the gasification of coke. The kinetics study, along with equations of the models, carbon conversion graphs and Arrhenius plots, are presented in more detail in Paper V. Using these models, the kinetic parameters depicted in Table 15 were obtained.

Table 15. Predicted kinetic parameters obtained by using the homogenous and shrinking core models.

	CO ₂		H ₂ O	
	Homogenous model	Shrinking core model	Homogenous model	Shrinking core model
Activation energy, E _a [kJ/mol]	204.1	198.6	143	130.8
Pre-exponential factor, k ₀ [1/min]	2.099 x 10 ⁶	3.944 x 10 ⁵	9770.3	1052.2

The activation energies calculated by the homogenous model were 204.1 kJ/mol for CO₂ gasification and 143 kJ/mol for H₂O gasification, and 198.6 kJ/mol for CO₂ gasification and 130.8 kJ/mol for H₂O using the shrinking core model. The higher activation energy with CO₂ indicates its lower reactivity compared to H₂O. Zhao *et al.* (2012) have previously obtained similar activation energy values for coke gasification: 214.77 kJ/mol for CO₂ and 154.47 kJ/mol for H₂O gasification. The reactivity estimated by the models was compared against measured reactivity values in Fig. 17.

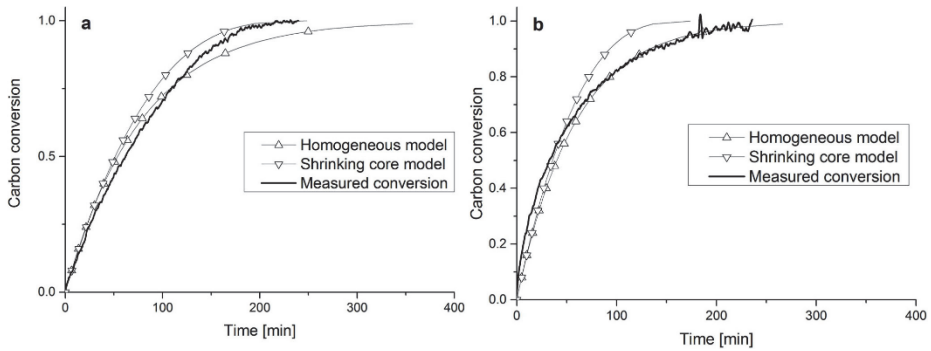


Fig. 17. Measured carbon conversion compared to conversion predicted by the models at 1298 K (1025 °C) in a) 90% CO₂–10% N₂, b) 90% H₂O–10% N₂ (Paper V, reprinted with permission of Springer).

Estimation of the validity of the industrial CRI test

The reactivity of coke is commonly measured using the CRI test in 100 vol-% CO₂ gas, which is strongly different from the actual BF shaft gas. In Paper V (Fig. 2) the correlation between reactivity of fine coke (< 250 μm) in different gas atmospheres was estimated. It was found that a decent correlation was found between gas atmospheres 100% CO₂ and N₂-CO-CO₂, but when H₂ and H₂O was added, the correlation became weaker. However, it was considered that additional tests for larger sized coke were required in order to include the effects of macroporosity on coke reactivity.

The reactivity of seven coke grades of grain size of 4.67–6 mm was measured with TGA and the results are presented in Table 16. These reactivity tests were performed in the four gas profiles previously shown in Table 5. The grain size was selected in order to include the effects of macroporosity on gasification, hence obtaining a reaction mechanism closer to lump sized coke, while still having a sufficient number of samples to counteract the heterogeneous nature of coke.

Table 16. Industrial CRI values and final carbon conversions of coke grains (4.67–6 mm) at 1100 °C.

	CRI (industrial value)	100% CO ₂	Hydrogen-free shaft gas	Low hydrogen shaft gas	High hydrogen shaft gas
BF Coke A	18.4	0.161	0.029	0.033	0.053
BF Coke B	31.3	0.238	0.080	0.088	0.122
BF Coke C	28.2	0.241	0.075	0.080	0.096
BF Coke D	29.2	0.270	0.086	0.085	0.105
BF Coke E	17.3	0.176	0.038	0.065	0.082
CF Coke F	41.0	0.281	0.096	0.145	0.177
CF Coke G	55.0	0.421	0.140	0.174	0.220

Correlations between the reactivities in different gas profiles are presented in Fig. 18. Linear regression lines were used to highlight possible correlations. The correlation factors (Adjusted R-Square) indicate the correlation between the values on the X and Y-axis (1.00 indicating linear correlation).

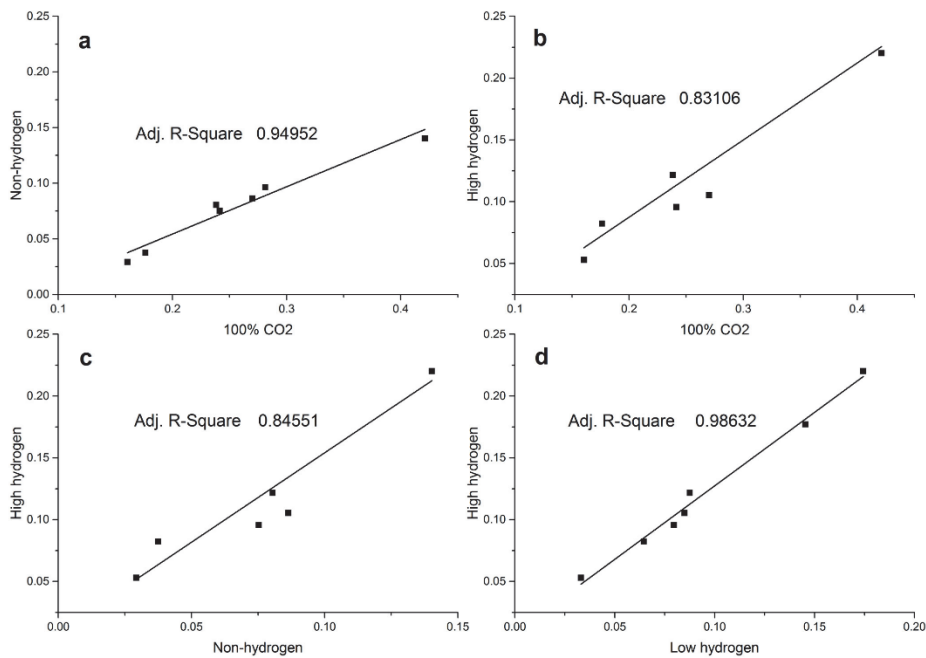


Fig. 18. Correlation between reactivity of coke grains (4.67–6 mm) at 1100 °C between gas atmospheres: a) non-hydrogen vs. 100% CO₂; b) high-hydrogen vs. 100% CO₂;

c) high-hydrogen vs. non-hydrogen; d) high hydrogen vs. low hydrogen (Paper V, reprinted with permission of Springer).

When using grain sized coke a better correlation was found between the reactivity in 100% CO₂ and the simulated blast furnace shaft gas atmospheres compared to the tests made with coke powder, but the final result was the same. There was a good correlation between reactivities in 100% CO₂ and a gas atmosphere of N₂-CO-CO₂ (Fig. 18a), but when H₂ and H₂O were introduced to the gas atmosphere the correlation was weakened (Fig. 18b and Fig. 18c). This result indicates that the gasification mechanism altered by the addition of H₂ and H₂O. There was a very strong correlation between Low hydrogen shaft gas and High hydrogen gas atmospheres (Fig. 18d), therefore it may be sufficient to study coke reactivity in only one blast furnace gas atmosphere independent of the blast furnace and injectant fuel properties.

For both technical and economic reasons, it is important to get an accurate estimation of coke reactivity in the industrial process. However, based on the results of this study the CRI test cannot be considered entirely accurate in predicting coke reactivity in the actual blast furnace. Multiple factors may contribute to the lack of correlation: 1) the number of active reaction sites in different cokes may vary depending on the gasifying component; 2) water vapour has better access to smallest micropores compared to carbon dioxide (Zhang *et al.* 2006), therefore the small sized micropore structure could affect coke reactivity in a simulated BF shaft gas, but not in 100% CO₂; 3) results from an anthracite gasification study suggest that catalysing mineral components can have differing effects depending on whether the gasifying component is CO₂ or H₂O (Zhang *et al.* 2006). Additional research is required in order to determine the significance of each factor.

5.2.2 Fines formation under mechanical stress

In 2011 oil injection was still the only injectant fuel used in Finnish blast furnaces. An increase of carbon-rich dust was observed in the top gas during periods of high oil injection rates. The use of heavy residual oil has a significant effect on the gas composition of a blast furnace due to increase of H₂ and H₂O. The goal of this study was to estimate the effect of oil injection rate on coke gasification and fines formation in simulated blast furnace shaft conditions. The research was carried out studied by gasification in Blast Furnace Simulator (BFS) in dynamic temperature and gas conditions up to temperatures of 1100 and 1400 °C. After the gasification

runs, the coke pieces were subjected to mechanical stress using a shaking sieve. The goal was to evaluate how the gasifying atmosphere affected coke pieces' tendency to produce fine coke dust in a blast furnace under mechanical stress. Increasing the simulated oil injection rate, hence increasing H₂ and H₂O contents in the gas atmosphere, significantly increased the solution-loss rate of coke, which is in accordance with previous results on the effects of H₂ and H₂O on coke gasification rate (van der Velden *et al.* 1999).

The amount of coke gasified in the BFS tests and fines formed under mechanical stress are depicted in Fig. 19. Unreacted coke was tested as a reference sample. The tests 100 kg/tHM and 120 kg/tHM simulated the BF shaft gas atmosphere with different ratios of N₂-CO-CO₂-H₂-H₂O. The test 0 kg/tHM was added as a reference gas which was chosen to only contain N₂-CO-CO₂ with similar oxygen partial pressure as the other tests. The test 0 kg/tHM was also repeated in order to assess the reproducibility of the tests. Another reference test labelled 0 kg/long was added aiming for the same weight loss as the test 120 kg/tHM, but in a gas atmosphere without H₂ and H₂O.

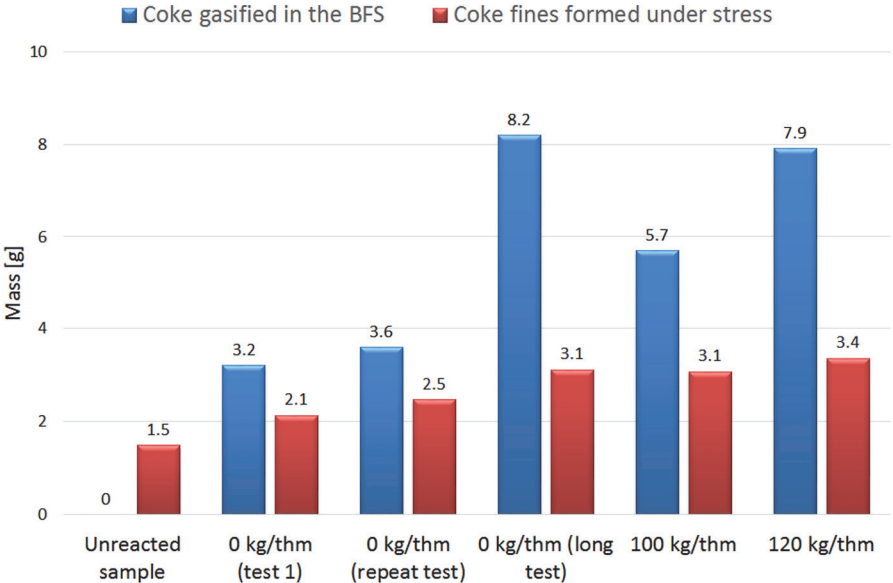


Fig. 19. The amount of coke gasified in the BFS tests in dynamic temperature conditions up to 1100 °C and the amount of fines formation under mechanical stress after gasification.

Based on Fig. 19. the differences in the fines formation behaviour after gasification in different gas atmospheres were not major, but tentative conclusions can be drawn. The total amount of gasification is a significant factor concerning fines formation, but the gas atmosphere also plays a role. The test 120 kg/tHM produced slightly more fines compared to 0 kg/tHM (long) despite lower total gasification. Also compared to the test 0 kg/tHM, the test 100 kg/tHM produced a similar amount of fines after a significantly lower total gasification.

BET-surface area analyses were conducted in order to estimate the mechanism of gasification: the extent of solution-loss reactions taking place inside the coke pieces versus on the surface. After the mechanical stress tests, the intact coke spheres were broken into smaller (3–4 mm size range) pieces for the analysis. These were used to present the porosity of the inner core of coke. The porosity of fine coke broken off during the mechanical stress, on the other hand, presents the outer surface. The results of the BET-analyses are depicted in Fig. 20.

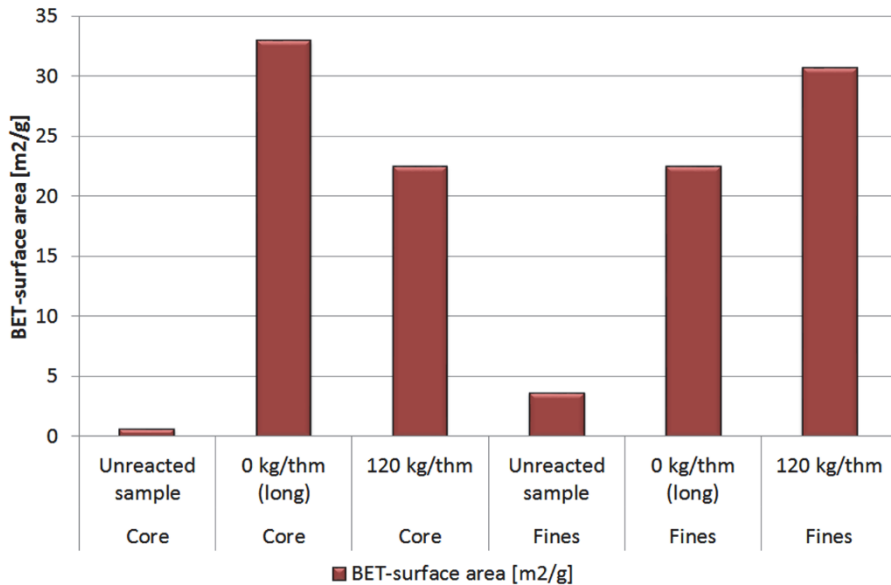


Fig. 20. BET-surface area analyses of cokes gasified in dynamic temperature conditions up to 1100 °C.

Based on the BET-results the porosity the inner core increases more in the N₂-CO-CO₂ gas atmosphere 0 kg/tHM (long), whereas the fines were more porous after the test 120 kg/tHM, which also contained H₂ and H₂O. The BET-surface area

analyses support the earlier results of fines formation; increase of H₂ and H₂O in the gas atmosphere changes the reaction at temperatures up to 1100 °C to more surface centric.

The fines formation behaviour and BET-surface area were also studied after gasification in dynamic temperature conditions up to 1400 °C and the results are depicted in Fig. 6 of Paper I. Only small differences (less than 6%) were found between gas atmospheres 100 kg/tHM and 135 kg/tHM. It is postulated that effect of the gas atmosphere on the gasification mechanism at higher temperatures is much less pronounced. This result is in accordance with observations by Iwanaga & Takatani (1989) who found that gasification with both CO₂ and H₂O occurs solely on the surface at 1500 °C.

The results of this study indicate that the presence of H₂/H₂O in a simulated BF shaft gas atmosphere changes the reaction mechanism to become more surface centric compared to gas atmospheres only containing N₂-CO-CO₂. This result is in agreement with an earlier study by van der Velden *et al.* (1999) and a recent study by Shin & Jung (2015). H₂O could have a protective effect on the post-reaction strength of coke in the BF, however, there are still many research areas in this field that require more clarification. The results suggest that increase of H₂O as a result of higher oil injection rates could have some impact on coke fines formation, however, the fines formed after gasification of coke in the shaft are not the only factor producing carbonaceous flue dust. The flue dust could also be originated from unburned injectant oil at the raceway (soot).

5.3 Further discussion on the results and their industrial relevance

5.3.1 Research of coke hot strength

As a result of the hot strength tests, it was found that the strength of coke strongly decreased for all three coke grades studied at high temperatures. This results should be verified in the future by testing multiple new coke grades, preferable prepared from coals from different geographical areas. Two of the cokes used in this study originated from the same geographical area, which explains their similar behaviour. Testing of cokes from different parts of the world would show whether the origins of the apparent coals play a role in coke hot strength.

It was to be expected that no dramatic strength decrease was observed with the coke grades studied in this thesis, since all three coke grades have been in industrial

use and proven to be functional. There are some reports in the past, such as by Janhsen *et al.* and Holowaty & Squarcy 1957, which have stated that despite good analysis values in the standard tests, some coke grades, such as beehive cokes, have not performed well in the actual BF process. Performing hot strength tests for such coke grades with the Gleeble would be of great interest.

Despite the usefulness of CRI and CSR tests, they are limited to the upper parts of the BF. Since no single analysis method is capable of simulating blast furnace conditions, multiple different tests are required to obtain a thorough description of coke quality. The hot strength measurement with a Gleeble device could prove to be of value in studying coke performance in the lower areas of the BF, which is currently left in the dark. My preliminary investigation shows that a significant decrease in coke strength can already be found at 1400 °C, whereas almost no change can be seen at 1200 °C. In the actual BF the temperature reaches 1400 °C just below the cohesive zone and remains above 1400 °C all the way down to the deadman area, reaching above 2000 °C near the raceway. Therefore, it can be stated that the temperatures in which a significant decrease of coke strength was observed are very relevant to the industrial BF process.

The most authentic strength test could be to test pre-gasified coke in a thermomechanical simulator, such as the Gleeble instrument. The pre-gasification could be performed in a furnace such as the BFS. The tested coke could be also originated from a dissected blast furnace or an experimental blast furnace, in which case it would also include the presence of circulating elements.

In the future, it is also important to define the role of ash components in the development of hot strength, and whether they affect the deformation behaviour at high temperatures. Based on the results presented in Paper IV, it is possible that certain ash components, such as SiO₂ have a large influence in the development of hot strength due to their chemical reactions with the carbon matrix at high temperatures, which strongly increases coke porosity. It is possible that it is the heat treatment (pre-graphitisation) at high temperatures which permanently lowers coke strength, and the actual high temperatures may even increase the strength due to plastic deformation behaviour.

5.3.2 Improved tests for reactivity and post-reaction strength

It was found (Paper V) that H₂ and H₂O strongly impact the reactivity of coke even in fairly small amounts relevant to the actual BF shaft gas. Also, the reactivity in 100 vol-% CO₂ did not correlate well with the simulated BF shaft gases containing

H₂ and H₂O. A new measurement for coke reactivity should be developed in order to obtain a more accurate estimation of reactivity in the BF process. Such a test could include the effects of all relevant gas components in the BF shaft gas, N₂, CO, H₂ and H₂O in addition to CO₂, in thermodynamically balanced ratios resembling the actual shaft gas atmosphere.

For determination of coke reactivity it may be sufficient to measure the reactivity in only a mixture of CO₂/H₂O or by measuring reactivity in 100 vol-% CO₂ and H₂O separately. Further clarification on this is still required. However, in order to obtain a realistic post-reaction strength measurement after gasification, a mixture of all main gas components is likely required. Constructing such test equipment is not considered to be overly laborious compared to the standard CRI test.

The fact that coke reactivity is currently measured in 100 vol-% CO₂ leads to coke quality at the coking plant is also being controlled to be low in 100 vol-% CO₂, not in the actual BF shaft gas. This could result in suboptimal control of coke properties and quality. As an example, the coals which are high in minerals catalysing CO₂ gasification can only be used in very small quantities, whereas in the actual BF process it can be expected that a large part of the gasification occurs with H₂O and the minerals catalysing reaction may not be as significant for H₂O gasification.

There are many different equations and models to predict coke reactivity in 100 vol-% CO₂ based on ash composition and rank of the parent coals, but none for coke reactivity in a simulated BF shaft gas. Below are listed some of the potential benefits which could be acquired when parameters affecting coke reactivity in the actual BF shaft gas are fully understood and utilised:

- A more accurate assessment of coke reactivity in the BF
- An improved view of coke post-reaction strength, which requires the development of a new test method
- Cheaper coke grades could possibly be utilised
- Cheaper coals, such as coals with higher ash components could possibly be used in the coking coal mix
- The reactivity of coke at the coking plant can be controlled to be low in the conditions of the actual BF process, not in 100 vol-% CO₂.

Despite the historical usefulness of the CSR test, there are multiple issues about the test, which make it controversial whether the test has an accurate relevance for blast furnace operation. The CSR-value, despite its label “coke strength after reaction”,

can be considered to be mostly a result of chemical reactivity, not strength per se, although abrasion resistance does affect coke CSR to some degree. A new test method should be developed in order to get a more realistic estimation of post-reaction strength in the actual BF process. The gasification mechanism in this improved post-reaction strength test should resemble that of the mechanism inside the actual BF.

This could be achieved by the following way:

1. The total amount of solution-loss should be fixed, for example to 25–35 wt-%, such as in the industrial process. Currently, the unlimited amount of gasification causes the CSR value to be largely a result of coke reactivity. This can cause, for example, the post-reaction strength of highly reactive cokes may be somewhat underestimated.
2. The temperature in the test should not be a fixed value, but it should be based on the threshold temperature of the individual coke grade, which is the case in the industrial BF process. The gasification temperature affects the rates of chemical reaction and diffusion, which decide the reaction mechanism (uniform/gradient/surface). If the total amount of solution-loss is fixed, but the threshold temperature not taken into account, it could cause for example the post-reaction strength of highly reactive cokes, which generally have lower threshold temperatures, to be overestimated.
3. Another alternative would be to calculate the temperature of the thermal reserve zone with a mathematical model that takes into account both the reactivity properties of coke and the reducibility properties of the iron ore. Due to the strong connection between the gasification temperature and the gasification mechanism, the high threshold temperature of low reactive cokes could be the true reason why they perform better in the industrial BF process. This is another important subject for future studies.
4. The gas atmosphere should resemble that of the actual BF shaft gas and include all the main gas components N_2 -CO-CO₂-H₂-H₂O in realistic and balanced ratios. The gasification condition in 100 vol-% CO₂ is too intensive and does not take into account the effects of all major gas components.

It will never be possible to perfectly simulate the actual BF with any single laboratory test due to the complexity of the industrial process, however, with these improvements the testing protocol of coke quality could be greatly improved compared to the currently utilised tests.

6 Conclusions

The development of a new coke hot strength measurement method was reported in Papers II and III. In these studies, the suitability of a Gleeble 3800 thermomechanical simulator for testing of coke hot strength was evaluated, a method of testing hot strength developed and the hot strength of one coke grade measured. Statistical reliability of the hot strength testing was also evaluated. From Papers II and III the following conclusions are drawn:

- The Gleeble was found suitable for determining coke hot strength and it was found to offer swift testing, visibility of the sample, inert conditions to avoid gasification, accurate strength measurements, obtainment of visual stress-strain curves and no need for capital and time costs for constructing specialised equipment.
- Statistically reliable hot strength results were obtained for the first time at temperatures of 1000, 1600 and 1750 °C. The ultimate strength of coke was decreased by 19.9% at 1600 °C and 29.1% at 1750 °C compared to tests at 1000 °C.
- The yield strength of coke was 45.7% and 51.7% lower at 1600 and 1750 °C respectively compared to 1000 °C.
- The deformation of coke was fragile at room temperature and 1000 °C, but became at least partially plastic at 1600 °C and the plasticity further increased at 1750 °C.

The coke hot strength study was expanded to include three coke grades in Paper IV at room temperature and at temperatures of 1600 and 1750 °C. The hot stage deformation behaviour was evaluated in more detail. The different properties of coke, such as porosity, content of inerts and reactive macerals, as well as graphitisation degree were measured in an effort to explain the observed hot strength results. The following conclusions from Paper IV are drawn:

- A large statistically significant decrease (roughly 30%) in compressive strength was observed for all three coke grades tested in this study at 1600 °C. Coke 1 suffered a further statistically significant fall in strength at 1750 °C, whereas the strength of cokes 2 and 3 seemed to recover. This could indicate individual differences in hot strength of different coke grades.

- The strength of coke at high temperatures undergoes a process of homogenisation; the standard deviation values at 1600 °C were reduced by 36–50% compared to room temperature, depending on the coke grade.
- Preceding heat treatment of coke at 1750 °C caused a 35.5% decrease in the mean strength of coke at room temperature. This may be explained by chemical reactions in coke ash, and by the increased graphitisation degree of coke during heat treatment.
- The stress-strain curves were similar in shape at room temperature for all three coke grades; early linear elastic phase followed by fragile fracture. In some cases significant force had to be applied all the way up to the 33% deformation, which may be an indication of layered crushing.
- At temperatures of 1600 and 1750 °C, all three coke grades showed unique distributions of stress-strain curves. Despite the complexity of these curves, certain general types were found for each grade.

The study on the effects of H₂ and H₂O on coke reactivity in simulated BF shaft gases is reported in Paper V. The effects of H₂ and H₂O on the reactivity of seven different coke grades were measured for both coke fines and grain sized coke in four different gas atmospheres, included two reference gases and two simulated BF shaft gases. The effects of gas atmosphere on the threshold temperature of coke gasification were determined. The effect of H₂ and H₂O coke reactivity was also determined in a wider temperature range of 1000–1300 °C for one coke grade. The following conclusions are drawn:

- The reactivity of all seven coke grades was increased by 2.4–8.0% after the replacement of 5 vol-% of CO/CO₂ with H₂/H₂O despite the sum of gasifying components (CO₂ + H₂O) remaining constant. The increase of total H₂ + H₂O from 5 to 10 vol-% further increased reactivity by 2.4–4.5%, depending on the coke grade.
- The partial replacement of CO/CO₂ with H₂/H₂O did not have an observable effect on the threshold temperature of coke gasification in the simulated blast furnace shaft gas atmospheres. Gasification in 100% CO₂ or in 90% H₂O, on the other hand, had a significantly lower threshold temperature of gasification due to higher ratio of oxidising components in the gas atmosphere.
- The coke reactivity increasing effect of H₂/H₂O was negligible at 1000 °C and clearly at its highest value at 1100 °C. The addition of H₂/H₂O also increased the reactivity's at 1200 °C and 1300 °C, but the effect diminished as the temperature was increased. This can be explained by reactivity with H₂O

becoming limited by mass transfer, instead of chemical reactivity, at lower temperatures compared to CO₂.

- Reaction kinetics were calculated using the homogenous and shrinking core models. The calculated activation energies of gasification were 204.1 kJ/mol for CO₂ and 143.0 kJ/mol for H₂O using the homogenous model, and 198.6 kJ/mol for CO₂ and 130.8 kJ/mol for H₂O using the shrinking core model.
- A good correlation was found between the reactivities in 100 vol-% CO₂ and in an atmosphere of N₂-CO-CO₂. However, when H₂ and H₂O were introduced to the gas atmosphere the correlation with CO₂ was weakened, which indicates that the gasification mechanism was altered by the addition of H₂ and H₂O. This result implies that the industrial CRI test does not accurately predict coke reactivity in the actual BF process.

The effect of H₂ and H₂O on coke gasification and fines formation under mechanical stress was evaluated in Paper I. Reactivity tests were performed for spherical coke samples in simulated BF shaft gases with different oil injection rates and in reference gases. The porosity of coke after reaction was measured with BET-surface analysis. The following conclusions are drawn:

- In a simulated BF shaft gas atmosphere and in dynamic temperature conditions up to 1100 °C the presence of H₂ and H₂O in the gas atmosphere changes the location of reaction; they occur more heavily on the surface of coke. This was indicated by BET-surface area analysis and the increase of fines formation under mechanical stress when H₂ and H₂O were present in the gas atmosphere.
- A gasification test was also performed up to a temperature of 1400 °C, but similar effects from H₂ and H₂O addition were not observed. It is considered that the differences in the reaction mechanism between CO₂ and H₂O are limited to lower temperatures. This result is in accordance with observations by other researchers.
- The increase of H₂ and H₂O in the gas atmosphere could increase fines formation in the shaft, but it could protect the inner core of coke from solution-loss reactions and reduce coke size degradation in the lower parts of the BF.

6.1 Suggestions for future research

Further studies are required to clarify several aspects related to coke hot strength. The reason for plastic deformation behaviour at high temperatures is yet to be discovered. The significance of different factors affecting hot strength should be quantitatively studied; what is the significance of the heat treatment (graphitisation, changes in coke ash and increase of coke porosity) on strength compared to the material itself being in a hot state during the experiments. There are some published studies on the role of different minerals in coke ash on the high temperature strength, however, more research should still be done to clarify this issue. Also, the hot strength behaviour of more coke grades produced from different coal types and geographical areas needs to be studied.

More research is needed on the reactivity of coke in simulated BF shaft gas atmospheres. The reason behind differences between coke grades with respect to reactivity between CO_2 and H_2O should be clarified. A study on the differences of catalysing minerals on coke reactivity H_2O and CO_2 could help to explain these differences.

The relevance of the CSR test should be carefully studied. It is possible that the connection between coke CSR values and BF performance is more related to the reactivity or threshold temperature of coke rather than the actual post-reaction strength properties of the coke. More research is needed on the post-reaction strength of coke in simulated BF gases, including H_2 and H_2O . Water vapour could have a protective effect on the strength of coke from solution-loss reactions, but more evidence of this is needed. The importance of the coke threshold temperature on the gasification mechanism (surface vs. throughout) should be further clarified. The development of a new test to determine the post-reaction strength is recommended to get a more accurate estimation of actual post-reaction strength of coke in the industrial process.

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