Chapter 6

Recent Trends in Ironmaking Blast Furnace Technology to Mitigate CO_2 Emissions: Top Charging Materials

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Abstract The iron- and steelmaking is the largest energy consuming in the industrial sectors. The high energy consumption is associated with emission of CO_2 and other pollutants. The most common ironmaking process used in the world is the blast furnace which contributes around 70 % of the world's steel production. Recently, blast furnace has undergone tremendous modifications and improvements to reduce the energy consumption and CO_2 emissions. The modifications are being focused on two main approaches: (1) development of top charging materials and (2) injections of auxiliary fuels through blast furnace tuyeres. The present chapter will discuss the recent modifications and development in the top charging burden and how it could participate in minimizing the energy consumption and CO_2 emissions for more efficient and sustainable iron and steel industry. The injection of auxiliary

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fuels will be discussed in details in another chapter. The enhancement of burden material quality and its charging mode into the blast furnace has resulted in a smooth and efficient operation. Recently, the usage of nut coke in the modern blast furnace is accompanied by higher production and lower reducing agent rates. An efficient recycling of in-plant fines by its conversion into briquettes with proper mechanical strength is applied in some blast furnaces to exploit the iron- and carbon-rich residues. Nowadays, novel composite agglomerates consist of iron ores and alternative carbonaceous materials represent a new trend for low-carbon blast furnace with lower dependence on the conventional burden materials. The recent investigations demonstrated that the novel composites are able to reduce the thermal reserve zone temperature in the blast furnace and consequently enhance the carbon utilization through its higher reactivity compared to fossil fuels. The top charging of bio-reducers and hydrogen-rich materials into the blast furnace is one of interesting innovations to mitigate the CO_2 emissions. Although some of previous approaches are recently applied in the modern blast furnace, others are still under intensive discussions to enhance its implementations.

6.1 Introduction

Blast furnace (BF) is considered to be the most important ironmaking unit. During 2014–2015 BF worldwide produced about 1155 million tonnes compared to 55 million tonnes by the direct reduced iron (DRI) (www.worldsteel.org). For the foreseeable future, it will continue to occupy a primary position because of its high efficiency on both reactions and heat exchange. BF is a continuously operating shaft furnace based on the counterflow principle. Carbon-bearing materials and burden are charged from the top as distinct layers. Charge materials descend under the influence of gravity. Through tuyeres (in the lower part of the furnace), hot blast is injected. The hot blast reacts with carbon in front of tuyere, forming carbon monoxide at high temperature. The hot ascending gases including carbon monoxide help in reduction of iron oxide as well as heating and melting of the descending materials. At the bottom of the hearth, molten iron and slag are collected and tapped (Biswas 1981).

The BF can be generally divided into three thermal zones; first is the preheating zone where the temperature of the ascending gases drops from 800 to 1000 °C down to 100–250 °C, and the raw materials heated up from room temperature up to 800–950 °C. Several reactions take place in this zone like the indirect reduction of hematite to magnetite and magnetite to wustite. Other reactions which occur in the zone are release of water vapor due to drying as well as that from hydrates, decomposition of carbonates (not calcium carbonates), deposition of carbon back from the ascending gas, etc. It is worth mentioning that the coke is relatively inert in this upper zone; it is heated up and loses its moisture and most of its volatile matter. In efficient furnace, by the time the iron reaches the thermal reserve zone (second zone), reduction would have completed and the gas composition would be corresponding that of wustite-Fe

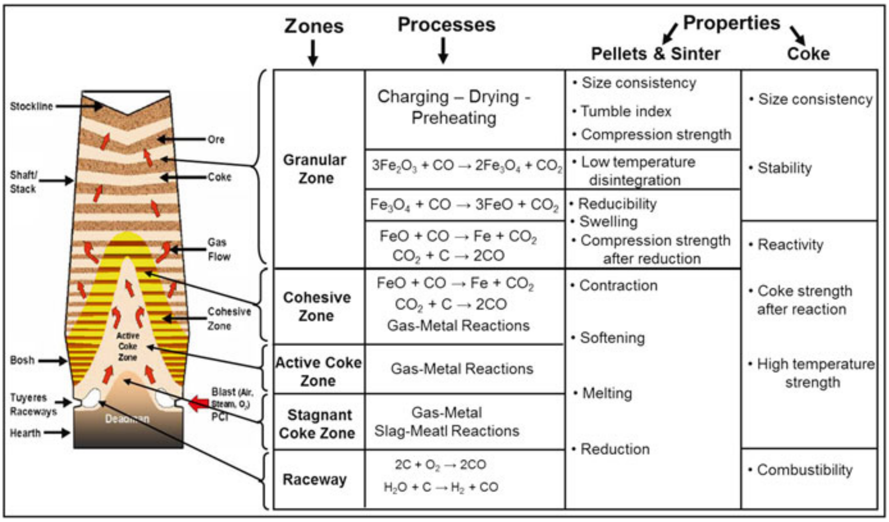

Fig. 6.1 Reaction zone and inner state of a blast furnace (Ranade and Chaubal 2004)

equilibrium. At the bottom of the thermal reserve zone, the indirect reduction of wustite to metallic iron takes place. This zone takes about 50 % of the BF height. The temperature of this zone is depended on the start of the gasification reaction, i.e., the coke reactivity. This zone is followed by the direct reduction zone where carbon gasification reaction rates are high, and the melting zone in which the molten material temperature approaches 1400–1450 °C. The ore softens in the cohesive zone, while the coke lumps act as windows for the gas to ascend through. The active coke zone starts below the cohesive zone and extends up to the raceway. The deadman zone consists of loosely packed coke through which droplets of melted material drip down to the hearth. In front of the tuyeres, the blast kinetic energy creates a semi void region with rapidly moving coke particles being combusted termed as the raceway. Dissolution of carbon into iron takes place in the melting zone when the metallic iron gets in direct contact with coke. The center area of coke zone which is known as stagnant coke zone extends through hearth and deadman zone and consists of densely packed coke. The most dominant reactions taking place in the BF and a schematic diagram showing the area where these reactions are most likely occurring are depicted in Fig. 6.1 (Mousa 2010; Peacey and Davenport 1979; Geerdes et al. 2015).

The charging system in modern BF is extremely important as it ensures good distribution of coke and burden materials inside the furnace which significantly affect the furnace performance and the productivity. The charging profile is an important tool for changing the gas distribution and to overcome the furnace irregularities such as uneven material distribution, channeling, scabs, scaffolds, hanging, etc. Bad distribution of feeding materials and ascending gases will result in poor permeability and limited access for the reducing gases through the burden materials resulting in poor reduction of descending oxides and thus consuming more carbon down there in the dripping zone through direct reduction. Direct reduction does not result only in high carbon consumption but also in weakening the coke and adversely affecting the furnace permeability. An ongoing research activity at MiMeR laboratory, Lulea University of Technology, Sweden, showed that different distribution of feeding material can also have a significant impact on holding capacity of the descending bed for the generated fines. In modern blast furnace, the top is closed as they tend to operate under high top pressure.

Modern blast furnaces are usually equipped with "bell-less top" charging system invented by Paul Wurth in 1972. The bell-less top system allows easier burden distribution through a rotating chute and consequently uniform distribution of voidage and particles of charged materials inside the furnace. It is worth mentioning that proper feeding material distribution ensures good permeability and hence higher productivity, higher CO utilization, and thus lower coke rate. It also enhances the burden descent and lowers the thermal loads on the walls which ensure smooth operation, less heat losses, and longer refractory lifetime (Pandey and Yadav 1999).

6.2 Conventional Top Charging Materials

In the early days, BFs were quite often relied on charcoal and lump ores. Later the charcoal has been replaced by coke. Recently, BFs have grown considerably. In the early days, the hearth diameter was 4–5 m with annual production rate of 100,000 tonnes hot metal mostly from lump ore and coke. Nowadays, the bigger blast furnaces have hearth diameter up to 14–15 m with annual production rate of 3–4 million tonnes hot metal (Geerdes et al. 2015). The burden materials have changed from lump ore to more efficient materials like sinter and pellets. The reductant materials have developed as well from 100 % coke operation to use other injectant materials through tuyeres. Attempts are being made to charge other alternative reducing agents from the top along with burden material like biomass-based materials, plastics, etc. (Ahmed et al. 2014). Modern blast furnaces favor high Fe content in ore burden. Higher grade of iron ore burden can be realized after physical beneficiation process. This consequently creates more fine materials. These fine ores are too problematic to the BF operation. As a consequent, sintering and pelletizing as agglomeration processes are favored. Sinter constitutes 70–80 % of the iron-bearing material charged into the modern blast furnaces all over the world, while other blast furnaces in Europe apply 100 % iron ore pellets. A comparison of ferrous burden composition applied in 1990 and 2008 EU-15 is given in Fig. 6.2 (Luengen et al. 2012).

The quality demands for the blast furnace burden materials include chemical composition as well as mechanical durability. The chemical composition must meet the end product properties. The mechanical durability of the burden is related to the material property in cold, hot, and during reduction to ensure the furnace permeability and consequently good performance and less operational difficulties. The reducibility of the iron ores is for large extent controlled by how easy the reducing gases can get into the iron oxide particles. The intrinsic reducibility of the burden material

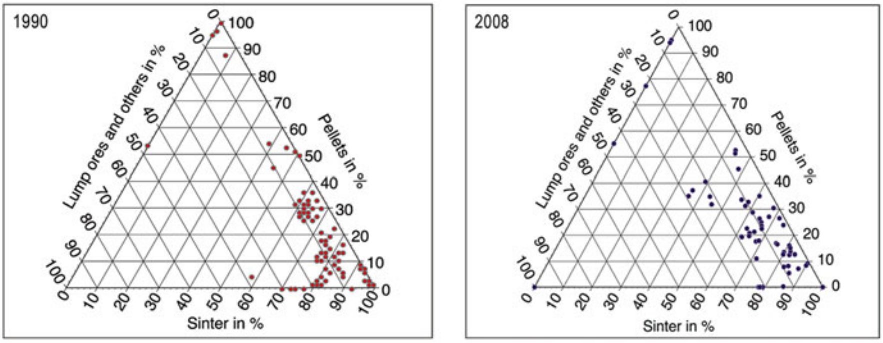

Fig. 6.2 Ferrous burden composition in 1990 and 2008 in EU 15 BFs (Luengen et al. 2012)

becomes a less important factor if no sufficient gas is transported to the reaction front and the produced gas is moved away from the reaction site. Ore burden materials are generally characterized by chemical composition, size and size distribution, cold strength, reduction, reduction disintegration, swelling, softening, and melting.

Although BF is a well-established and highly efficient process, there is a demand to enlarge its adaptability to reuse the in-plant residues and apply alternative reducing agents and novel charging composites. These modifications become essential to reduce the energy consumption and minimize the greenhouse gas emission (GHG) while keeping or even improving the furnace productivity. Therefore, the major part of this chapter will be devoted to brief the state of the art of attempts being made to meet these demands. Since these attempts are mostly based on decreasing the thermal reserve zone temperature and consequently shift the whole process toward lower CO/CO_2, it is more convenient to first discuss the fundamentals and different ways of shifting the process toward lower CO/CO_2 before discussing the developments of burden materials and alternative reducing agents.

6.3 Shifting the Process Toward Lower CO/CO_2

Enhancing the reducibility of the ore is always advantageous for blast furnace operation, especially in enhancing the productivity as well as smoother operation. If the ore can be reduced faster, then the production rate per unit volume of the furnace termed as productivity of the furnace can be enhanced. There is a possibility for further increase in the BF efficiency from the viewpoint of thermodynamics. If the rate of iron oxide reduction could be increased and the starting temperature of gasification reaction could be lowered, further increase in the efficiency of blast furnace process could be expected (Kashiwaya et al. 2001).

It is well known that an efficient blast furnace operation is characterized by a well-developed thermal reserve zone with a chemical reserve zone at the top of it.

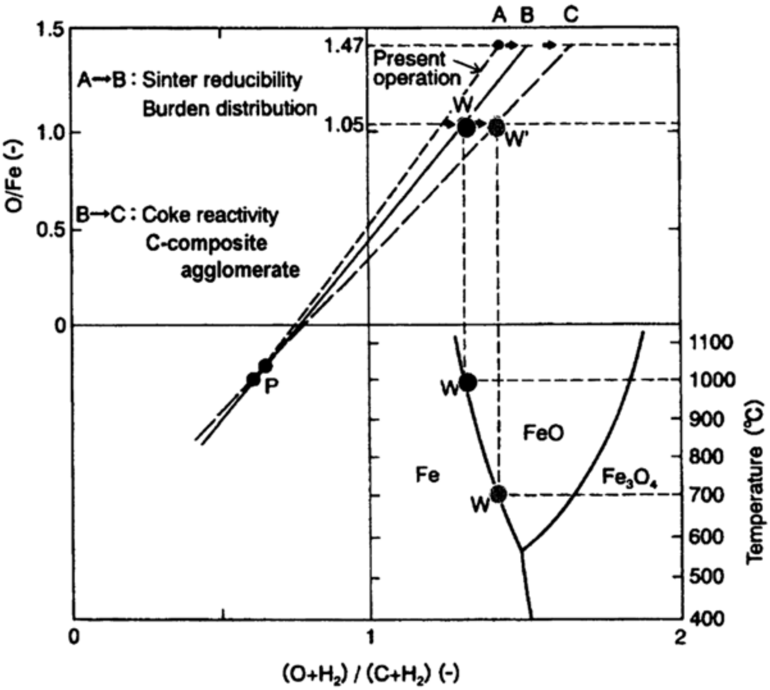

Fig. 6.3 Improvement technology of reaction efficiency on a blast furnace RIST diagram (Naito et al. 2006)

This is illustrated using the RIST diagram in Fig. 6.3 (Peacey and Davenport 1979). The point “W” corresponding to the chemical reserve zone is marked both in the RIST diagram and in the Fe-O equilibrium diagram. When the thermal reserve zone is equal to the W point (wustite-iron reduction equilibrium point) of the RIST diagram, the shaft efficiency of a blast furnace becomes 100 %, theoretically. In order to achieve that efficiency of furnace inner reactions, it would be necessary to shift the operation curve (the dotted line AP in Fig. 6.3) toward the W point, maintaining the present temperature condition of the thermal reserve zone unchanged (A → B), or to lower the thermal reserve zone temperature, shift the W point toward the high η_{CO} side ($\eta_{CO} = CO_2/(CO + CO_2)$).

Decreasing coke consumption in the blast furnace by means of shifting the equilibrium point of FeO-Fe reduction affecting decrease of thermal reserve zone temperature is being discussed intensively (Ariyama et al. 2005; Schmöle and Lüngen 2005; Nomura et al. 2005). Thermal reserve zone temperature is determined by the heat balance between the endothermic gasification reaction of coke and the heat supply from the gas flow. Thus, improving the gasification reaction, which is basically determined by the carbonaceous material reactivity, will reduce the thermal reserve zone temperature (Ueda et al. 2009a).

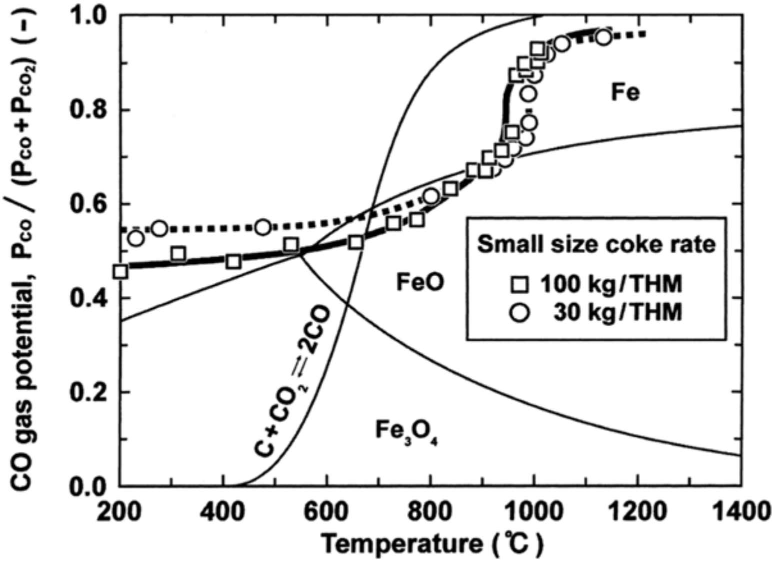

Fig. 6.4 Relationship between temperature and CO potential (Rist and Bonnivard 1963)

Using two facing sheets of hematite and graphite, the coupling between reduction and gasification was confirmed (Kashiwaya et al. 2001). Since mass transfer is a decisive variable in the reduction reaction inside the furnace, the degree of contact between the carbonaceous material and iron oxide would significantly affect the overall reaction rate. If the degree of contact between carbonaceous material and iron ore could be increased up to an ideal level, the starting temperature of the solution loss (gasification) reaction could be lowered (Kasai and Matsui 2004). Then, the equilibrium concentration at FeO-Fe reduction reaction will be shifted to higher CO gas utilization efficiency, resulting in the improved CO gas utilization efficiency at the furnace top and decreasing the reducing agents rate. This phenomenon is further explained by means of the Fe-C-O equilibrium diagram (Fig. 6.4) and the RIST diagram (Fig. 6.3). It was demonstrated experimentally that this phenomenon could be reached by using high reactive coke or carbon composite iron ore agglomerate (Kasai and Matsui 2004). Consequently, the gasification reaction could be improved, and the permeability and heat balance could also be improved, resulting in better performance under low reducing agent rate (Sawayama et al. 2009b).

It is worth mentioning that it would be a mistake to think that carbon consumption can be directly decreased and the process can be shifted toward the ideal blast furnace operation by just lowering the starting temperature of FeO-Fe reaction. However, decreasing the thermal reserve zone temperature using high reactive coke may intensify heat exchange and direct reduction in the lower zone. Carbon saving at lower reserve zone temperature can be realized only under certain conditions, for example, complete reduction of Fe_2O_3 to Fe_3O_4 at lower temperature such that no

Table 6.1 Effect of thermal reserve zone temperature on carbon and blast requirements

	Thermal reserve zone temperature, °C		
Parameter	823	923	1023
$(O/C)^{gwrz}$	1.34	1.30	1.28
$n_O{}^B$	94	0.99	1.05
$n_C{}^A$	49	1.58	1.65
Total carbon, moles of C/mol Fe	1.74	1.83	1.90

Note: $(O/C)^{gwrz}$ is the oxygen carbon molar ratio in the gas phase existing the wustite reduction zone, $n_O{}^B$s number of moles of oxygen in blast per mole of produced Fe, $n_C{}^A$s number of active carbon (carbon that goes to the gas phase) per mole of produce Fe

hematite or magnetite reaches the wustite reduction zone (Babich et al. 2009). Peacey and Davenport (1979) have presented predictions of carbon and blast requirements based on different reserve zone temperatures (Table 6.1). Their predictions are based on minimum heat demand (production of Fe, 5 % C from wustite, no flux, gangue nor heat losses) and blast temperature 1123 °C assumptions.

Ways of Shifting the Process Toward Lower CO/CO₂ The use of highly reactive or activated carbonaceous materials is suggested as one of the ways to reach this goal. Small-sized (Babich et al. 2009) or highly reactive coke usage significantly improves the gasification reaction (Naito et al. 2006). Coke reactivity can be enhanced significantly by means of catalytic effect (Babich et al. 2009). The activation energy could be lowered and the gasification rate increased on applying alkali vapor. When CRI (carbon reactivity index) is low, the catalytic effect appears strongly and almost disappears on using high reactive coke as well as on rising temperature. Fe and Ca are promising as catalysts to improve the coke reactivity at the condition of the thermal reserve zone in BF (Iguchi and Takada 2004). There are two basic ways to apply the catalyst to the coke (Nomura et al. 2005; Nomura et al. 2007): the post addition and the pre-addition of catalyst to the coke and coal blend, respectively. The selection of a suitable catalyst addition method could shift the reaction mode to a more homogeneous one at a lower reaction temperature, leading to an increase in the postreaction strength (Reddy et al. 1991). Additives such as Li_2O, $NaCO_3$, etc. can significantly affect the reduction rate by enhancing the rate of carbon gasification (Iguchi and Takada 2004; Reddy et al. 1991; Rao and Han 1984).

6.4 Recently Developed Top Charging Materials

6.4.1 Active Coke

Coke which is the reducing agent in blast furnace ironmaking is known to provide the structure through which the gas can ascend and distribute through the whole descending burden. Coke is a solid and permeable material up to very high temperature. Down there in the blast furnace below the melting zone, coke is the only solid material. So the total weight of the blast furnace content is supported by the coke. Therefore, blast furnace requires special coke size as well as relatively low reactive coke to maintain the furnace permeability in lower part of the shaft (Lacroix et al. 2001). In addition, the size distribution should be narrow to maintain a stable operation and low coke rate (Podkorytov et al. 2009). The required size is in the range of 40–60 mm which can be achieved by screening the produced coke, the screening results in generation of undersieve coke which known as nut coke. Due to difficulties and GHG emissions to produce coke, there are several attempts that have been carried out to utilize this undersieve coke or nut coke in the blast furnace which of course will affect the furnace permeability and operation smoothness as well as productivity.

Several studies have been conducted to address the effect of charging nut coke with the burden material on the process efficiency and hence the productivity (Mousa et al. 2010b, 2011; Mousa 2010; Mousa et al. 2010a; Babich et al. 2008; Babich et al. 2009). The attempts started by charging this undersieve coke with different ratios (5–30 %) within the coke layer. It resulted in reducing the productivity by 0.9–6.5 %. It also led to nonuniform distribution of ascending gases (Nikitin et al. 1999). Other researchers (Loginov et al. 1976, 1977) have suggested charging the nut coke along with the burden material. The idea was successfully tested and followed by a good improvement in the blast furnace productivity and lowered coke rate. Figure 6.5 depicts how the size as well as its distribution affects the furnace permeability and liquid drainage.

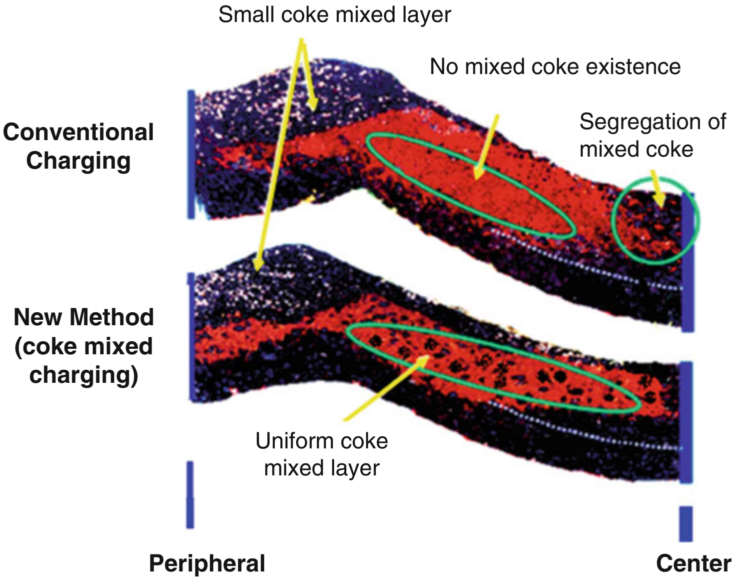

Fig. 6.5 Comparison between conventional charging method and coke-mixed charging method (Watakabe et al. 2006)

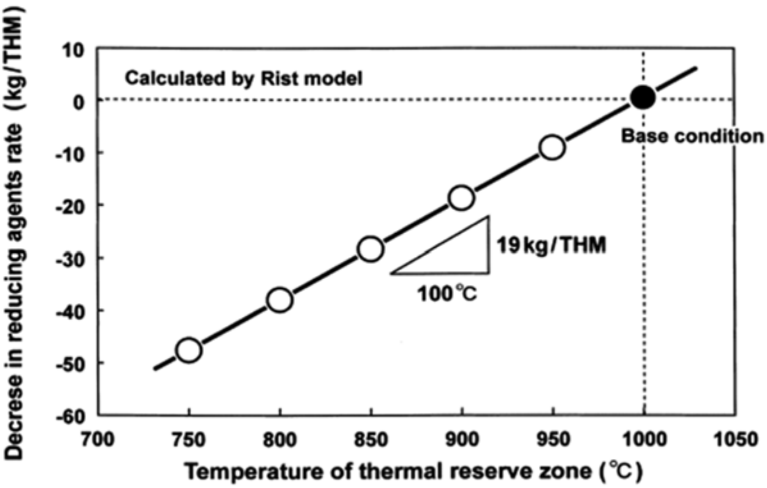

Fig. 6.6 Reducing agents rate and thermal reserve zone temperature (Kasai and Matsui 2004)

This success has inspired researchers to conduct an intensive research to study the effect of nut coke on different process parameters like permeability, reducibility, total coke consumption, etc. (Babich et al. 2009; Mousa et al. 2010a, b, 2011; Babich et al. 2008; Yaroshevskii et al. 2000; Watakabe et al. 2006). One of the important issues that should be taken care of is the uniform mixing of nut coke in the ore layer to maintain proper gas distribution and maintain the required permeability especially in the cohesive zone (Nikitin et al. 1999). Mixing of nut coke within the ore bed was very effective to increase the rate of carbon solution loss (Kasai and Matsui 2004). This further decreases the gasification reaction temperature which consequently decreased the lower limit of the thermal reserve zone temperature, thus decreasing the total coke consumption (Kasai and Matsui 2004). Figure 6.6 shows the relation between the thermal reserve zone temperature and coke rate consumption. Mixing of nut coke in the ore layer is not only expected to improve the solution loss reaction but also expected to protect the lump coke from gasification and consequently abrasion (Sawayama et al. 2009a).

The reactivity of small-sized coke was further increased by means of surface coating with compounds that contains hematite and Ca. It was found that activated nut coke shows even higher rates of gasification compared to original ones. The activation was more pronounced for coke with low coke reactivity index (CRI) values and further reduces the coke rate consumption (Ökvist et al. 1999).

6.4.2 *In-Plant Fines*

One more promising reducing agent is iron- and steelmaking residues. Large quantities of residues are annually generated during iron and steel production, a significant amount having potential of being valuable resources of carbon. Efforts have been made during the past decades to return generated by-products as substitutes to raw materials in the steelmaking process. Part of the residues are therefore today recycled, mainly to the sinter strand but also to the blast furnace in the form of a cold-bonded briquette. Injection of dry BF dust into the BF is practiced at SSAB in Sweden. However, there are still substantial amounts of carbon-containing residues deposited. Examples of the latter include sludge from the blast furnace and sludge from the basic oxygen furnace (BOF), for which the recycling is limited due to impurity elements (zinc, lead, alkalis) or physical properties (particle size, wet material).

Most of the residues from the integrated steel industry are today recycled in the process either via the sinter plant or in cold-bonded agglomerates. Residues are also recycled through other applications outside the process, e.g., in road construction and in the cement industry or in external processes as the rotary hearth furnace (RHF) processes. When considering residues rich in carbon produced at the integrated steel plant, the blast furnace is the production unit responsible for the production of these. There are two such residues, namely, the blast furnace dust (BF dust) and the blast furnace sludge (BF sludge). As the dust is dry, it is more convenient to recycle. Typical carbon content for the dust from a production site in Sweden is 43.6 % making the residue eligible for utilization as reduction agent in the blast furnace. When operating the blast furnace on iron ore pellets, all the dry dust may be recycled through injection in the tuyeres and by cold-bonded agglomeration (Grip 2005).

The carbon content of a few different blast furnace sludges is reported to be in the range of 18.5–33.0 % (Itoh and Fieser 1982; Heijwegen and Kat 1984; Steer and Griffiths 2013; Vereš et al. 2012), making this residue eligible for utilization as reducing agent as well. However, problems arise when attempting to recycle both the dust and sludge from the gas cleaning system back to the blast furnace. The main issue is the accumulation of zinc in the furnace which may lead to high zinc loads which in turn disturb the smooth running of the process (Biswas 1981). An additional problem is the cost related to drying of the sludge prior to recycling.

Typically, the dominating output of zinc from the furnace is through the gas phase, in which the extent is determined by, e.g., the top pressure operated at the furnace. Therefore, in order to recycle both residues leaving the gas cleaning equipment of the blast furnace, a proper way of zinc removal has to be introduced. This can be achieved by upgrading the sludge using, e.g., physical separation, hydrometallurgical, or pyrometallurgical routes.

Upgrading of blast furnace sludge using a hydrocyclone has been demonstrated in previous studies (Butterworth et al. 1996; Heijwegen and Kat 1984; Itoh and Fieser 1982). Butterworth et al. (1996) have reported the results of laboratory and pilot plant trials using a one-stage hydrocyclone to remove zinc from the sludge. In average the pilot plant trials suggested that 66 % of the sludge can be recovered and recycled back to the process while removing 89 % of the zinc. Itoh and Fieser (1982) report that the hydrocyclone can be used in full-scale operation to remove zinc from the blast furnace sludge. The presented results suggest that the underflow, low in zinc, is enriched in both carbon and iron. Although some losses of carbon are realized through the zinc removal, a fraction with higher carbon content than the original sludge may be recycled and utilized for its iron content and reducing properties.

Another way to reduce the zinc content of the blast furnace sludge is by leaching. This has been realized in different leaching reagents such as sulfuric acid (Vereš et al. 2012), hydrochloric acid (Van Herck et al. 2000), and carboxylic acids (Steer and Griffiths 2013). The leaching of blast furnace sludge in 0.5 M sulfuric acid showed that almost 88 % of zinc can be recovered with an iron loss of about 9 % (Vereš et al. 2012). A pilot plant leaching experiment was conducted by Van Herck et al. (2000). The leaching was performed with hydrochloric acid under oxidizing conditions. The plant successfully removed an average of over 95 % of the zinc in the different sludges tested in the study.

On the other hand, effective utilization of carbon-rich integrated steelmaking residues based on pyrometallurgical treatments has been also investigated (Robinson 2005; Su et al. 2004). Producing agglomerates with self-reducing properties which is used further to produce DRI (direct reduced iron) has previously been suggested as a promising recycling method for the dust and sludge instead of landfills. Production of DRI by heat treatment also contributes to significant reduction of Zn, which enables introduction of carbon-rich by-products with high Zn contents to the blast furnace.

6.5 Novel Top Charging Materials (Iron Ore-Carbon Composite)

Composite pellets (Dutta and Ghosh 1994), carbon composite agglomerates (CCAs), briquettes (CCB), and self-reducing agglomerates, all refer to carbon-bearing materials mixed with iron-bearing materials into agglomerates. It can be mixtures of fine iron ore (hematite, magnetite, dust and pre-reduced iron-bearing ore fine, etc.) and fine carbonaceous materials (fine coke, fine coal, charcoal, char, etc.) adding some binding agents in most cases (Chu et al. 2004). Possibly, using these agglomerates in blast furnace as well as in other ironmaking processes, one can derive the following benefits simultaneously, i.e., (1) usage of alternate carbonaceous materials having significant hydrogen which can replace expensive coke like plastics and biomass and (2) shifting the BF operation toward lower CO/CO_2 ratio by shifting the thermal reserve zone to lower temperatures as explained earlier.

Therefore, in the context of process optimization, energy saving, waste recycling, and environmental concerns, CCAs have been attracting much attention as future raw materials for ironmaking. For blast furnace operation with CCAs or CCBs, the following advantages are being envisaged (Chu et al. 2004):

- Decrease the energy consumption and environmental loads through the less dependency on sinter and coke.
- The effective use of noncoking coal, and iron-bearing dust and sludge in steel industry, extends the variety of raw materials and promotes resource recycling.
- The short distance between close-packed fine iron ore and carbonaceous materials in the agglomerates ensures fast reduction reaction of iron oxide.

– Furthermore, carbon gasification reaction and iron ore reductions are mutually accelerated and occur at lower temperature due to the coupling effect (Dutta and Ghosh 1994; Kasai and Matsui 2004).

In light of the above, in the following sections, the current status and gaps in understanding of such composites as well as challenges and research needed for realizing them as an effective raw material for ironmaking have been presented.

6.5.1 Producing of Iron Ore-Carbon Composites

Carbon composites are made in the form of pellets (cold bonded with and/or without binder) or briquettes (which can be either hot or cold pressed). Specific studies on the production aspects of these pellets require further improvement, especially as usage in blast furnace calls for higher qualities in terms of strength. Currently, usage of cold-bonded ordinary pellets (not containing carbon) itself pose difficulties in terms of accommodating them in significant proportion for blast furnace process owing to their poor strength.

Possibly, improving the binding system could significantly reduce the accompanying operational difficulties that can arise from low strength composites. Experience on ordinary pellet production over the past decades has led to the identification of a number of criteria that a binder must satisfy (Qiu et al. 2003). They include good mechanical properties, while they are green, dry, and fired pellets, e.g., deformation under load, resistance to fracture by impact and by compression, and resistance to abrasion.

Bentonite is the most commonly used binder in iron ore pelletization and significantly improves physical properties of the pellets. However, there are some drawbacks with the use of bentonite. The most remarkable is the contamination of the product with gangue (silica). For example, addition of 1 % bentonite to an iron ore concentrate results in a lowering of acid pellet iron content by 0.6 % (Souza et al. 1984). In the case of direct reduction pellets, every percent of acid gangue addition is associated with an increased energy consumption of 30 kWh (Heerema et al. 1989).

Cold-bonded pellets (CBPs) containing metallurgical by-products and cement as binder have been investigated (Robinson 2008). The effect of particle size distribution and hydration extent on the cold strength of CBPs was carefully studied. They have concluded that an optimal blend of fine and coarse BOF sludge in CBPs significantly improves the particle size distribution as well as bonding during hydration therefore significantly improves the cold strength. On the other hand, several experiments were conducted with an aim to study the strength development with a focus on swelling (swelling has two consequences: loss of strength and degradation or disintegration during reduction) of briquettes of steel industry by-products during curing and reduction (Singh 2002). The briquette swelling was found to be significant only when the average particle size increases as well as in the presence of cement. However, swelling is significantly hindered when reduction of briquettes is carried out under load. Researchers (Adolfsson et al. 2008) have tried even to utilize steelmaking by-product (Ladle slag) in CBP as a supplement and/or partial substitute for ordinary cement.

Mantovani and Takano (2000) studied the behavior of self-reducing pellets at room temperature and upon heating. They have produced pellets of EAF dust with total iron between 30 and 50 %, coal fines (70.5 % fixed carbon, 15.4 % ash, and 17 % volatile matter), and additives (commercial Portland cement and $CaCO_3$) then left in open air for 28 days for gaining strength to handle. They could get cold strength up to 60 N/pellet for 5 % cements containing pellet, which is still not enough for charging in shaft furnaces. They found that pellets with Portland cement and low moisture content present low decrepitation. At 600 °C the formed hydrated component started to decompose, and consequently it loses its strength. In addition, at 1000–1100 °C the strength is critical due to swelling.

In addition, during reduction of CCA, large voidage is created by the consumption of carbonaceous materials and can lead to low strength values in the pellets during reduction. Therefore, special attention was devoted to understand the strength development in CCAs during reduction. Talano and Mourao (2001) studied the strength development of self-reducing pellets at high temperatures. The pellets face sharp decrease in their compression strength from room temperature to 900–950 °C due to the decomposition of the hydrates, which are the main components of the cold strengthening mechanism of curing when cement is used. As the temperature increases, iron starts sintering and therefore the strength increases (Adolfsson et al. 2008). Higher strength at room temperature correlates generally well with higher strengths at elevated temperatures.

Unlike inorganic binders, organic binders have no side effect on iron ore grade. It also improves the wettability as well as the chemical bonding and results in strong and heat-resistant organic chain skeleton. Qiu et al. (2003) investigated the functions and the molecular structure of organic binders for iron ore pelletization (no available data for CCA in literature) based on the basic principles of molecular design, interface chemistry, polymer science, and failure model of binding system. The authors suggest “Funa” as one of the best organic binders which is prepared from lignite or weathered coal and with humates as major constitutes. Min et al. (2009) proved the possibility of applying an organic synthetic binder referred SHN to iron ore pellets instead of inorganic binders (bentonite). Table 6.2 shows comparison between different binders and the effect of the pellet compression strength.

Another way of improving the agglomerate strength is by producing iron ore coal briquettes by hot pressing. The fluidity phenomenon of coal at temperature 350–600 °C can be utilized in gaining high density and high strength without the addition of any binding materials (Matsui et al. 2003). Utilization of thermal plasticity of coal is being under development as agglomerate without binder. Compared with other carbon-containing agglomerates, this briquette showed better reducing performance, lower cost, and higher strength due to thermal plasticity of coal (Chu et al. 2004). Hayashi (2009) has presented the behavior of coal composite iron ore briquettes at high temperatures. Also, this kind of binderless agglomerates offers less slag ratio and enables a high heat transfer thus higher reaction rate. On studying the reaction behavior and softening and melting of such briquettes (hot-pressed briquettes) under N_2 at 1400 °C, both density and cold crushing strength were increasing by increasing coal content in the briquettes. The thermal plasticity of coal could provide a strength more than required for practical blast furnace.

Table 6.2 Effect of binder types on the quality of iron ore pellets

Binder type	Dosage, %	Wet drop strength	Wet compressive strength	Shock temperature, °C	Dry compressive strength, N/P	Fired compressive strength, N/P
Ca-bentonite	4.00	3.6[a]	9.75	530	705	2813
Na-bentonite	2.00	4.1[a]	12.63	475	569	2768
SHN	0.06	4.0[a]	11.63	>600	488	2534
Funa	1.50	13.7[b]	27.8	780	287	NA[c]

[a] Times per 0.5 m
[b] Times per 1.0 m
[c] Not available

Briquettes with high amount of coal tend to melt at higher temperatures, while those having less amount of coal tend to melt earlier due to the melting of slag containing unreduced iron oxide. Higher coal content briquettes will be preferred in blast furnace to avoid forming low melting slag then maintaining the furnace gas permeability.

Thus, current understanding in making CCAs suitable for blast furnace process is very limited. Systematic and comprehensive studies on making of CCA suitable for blast furnace usage with new binders, carbonaceous, and iron ore sources followed by characterization in terms of strength and other metallurgical properties such as reducibility, swelling, pressure drop during reduction, etc. need to be conducted. While exploring new binders, care needs to be taken to not bring environmentally and metallurgically harmful elements such as P, S, As, etc., into the product. It should also not adversely affect iron grade and increase impurities such as silica.

6.5.2 *Reduction Behavior of Composite Pellets*

Understanding the reactions occur within a composite pellet is very essential for its usage in blast furnace as well as in other ironmaking processes. Both experimental and theoretical investigations have been carried out along this direction. A possible behavior of CCB in a blast furnace is described by Chu et al. (2004) assuming that the CCB consists of hematite, carbon, and gangue (SiO_2, CaO, MgO, and Al_2O_3), and it fits the BF requirements mechanically and chemically. After charging CCB into blast furnace, it gets heated up through heat exchange with the ascending gases. When CCB temperature reaches to a particular level, reduction of hematite and magnetite starts to happen by ascending reducing gas from the thermal reserve zone. Reduction of wustite to metallic iron starts at the thermal reserve zone. As the CCB descends further and enters high-temperature zone, softening and melting of reduced iron, iron oxide (if still exists), and gangue in CCB occur. They have theoretically evaluated the effect of charging carbon composite agglomerates on blast furnace operation based on multifluid blast furnace model (Austin et al. 1997, 1998; Castro et al. 2000) under constant inflow conditions of blast and pulverized coal and hot metal temperature. On charging CCB, the predicted blast furnace productivity was improved, coke rate showed notable decrease, and total reducing agent rate tended to lower. For charging 30 % CCB, the productivity is increased by about 6.7 %; coke rate and reducing agent rate are reduced by 26.8 and 3.4 %, respectively, compared with base case without CCB charging. Kasai and Matsui (2004) have proposed a decrease in the thermal reserve zone temperature to 727 °C by charging of 20 % mass CCB which leads to a decrease in the reducing agent rate by 51 kg/tHM.

Several fundamental studies have been carried out on the reduction kinetics and mechanism of CCAs (Dutta and Ghosh 1994; Srinivasan and Lahiri 1977; Rao 1971; Sharma 1997; Fruehan 1977; Huang and Lu 1993). The main difference between iron ore agglomerates and CCAs is the rate-controlling step of the reduction of iron oxides. In case of iron ore agglomerates, the reduction takes place at gas-solid interfaces. Reducing gases move from the gas stream to the agglomerate surface then to the interior surface of the pores. In CCAs, carbon is present inside and so the chemical reaction can proceed very fast because of the large surface area available. Furthermore, mass transfer to and from reaction sites by gaseous diffusion could be also very fast because of the short traveling distance (Sun and Lu 1999a, b).

Reaction Sequence Reduction of hematite goes via three stages of reduction, hematite to magnetite then to wustite and finally to metallic iron. The reduction to wustite is relatively faster than to iron because the equilibrium CO_2-CO gas mixture consists almost of CO_2, while in the later the ratio becomes 0.4 (Fruehan 1977). The overall reaction and mechanism are represented by Eqs. (6.1), (6.2), and (6.3) and Fig. 6.7. Solid-solid reaction (reduction of iron oxide by solid carbon in the solid state) can be visualized as the early beginning as a result of the contact points between iron oxide and carbon particles which can be there only when gaseous products (CO and CO_2) are removed from the reaction system as fast as they are generated (Rao 1971). At thermodynamically reasonable temperatures, generation of carbon monoxide by carbon gasification (Eq. 6.3) and reduction of iron oxide by carbon monoxide (Eq. 6.1) start.

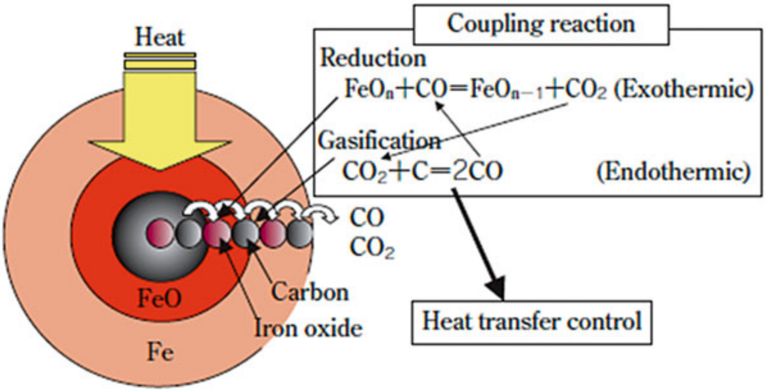

Fig. 6.7 Reduction mechanism of CCA (Michishita and Tanaka 2010)

$$Fe_xO_y\left(s\right)+CO\left(g\right)=Fe_xO_{y-1}\left(s\right)+CO_2\left(g\right) \tag{6.1}$$

$$\text{Coal} = \text{C} + \text{volatile matter} \tag{6.2}$$

$$C+CO_2\left(H_2O\right)=CO+CO\left(H_2\right) \tag{6.3}$$

Factors Affecting the Reaction Rate and the Rate-Controlling Step The complexity of studying the reaction mechanism and kinetics of self-reducing pellets or CCAs arises from the simultaneous reactions such as direct reduction of iron oxide, indirect reduction by CO, carbon gasification, etc. The reaction mechanism would vary significantly with the change of degree of oxidation and type of iron ore, carbon type, density, diameter, particle size, size distribution, state and area of contact, and state of crystal. These conditions will affect the chemical reaction, heat transfer, and gas diffusion (Khaki et al. 2002). Also, coal fluidity seems to affect the composite reactivity; the higher the coal fluidity, the higher the composite reactivity. Increasing the fluidity improves the contact state between the iron ore and coal (Nishioka et al. 2009).

Srinivasan and Lahiri (1977) studied the reduction of a single hematite/carbon-containing pellet isothermally. Moisture and small amount of bentonite (1.5 %) were added as binder. They found that the CO_2/CO ratio tend to approach wustite equilibrium for low C/Fe_2O_3 ratio and Boudouard equilibrium for high values of this ratio. A decrease in C/Fe_2O_3 ratio leads to higher values of CO_2/CO ratio and lower rate of carbon gasification decreasing the partial pressure of CO inside the sample. The results indicated a changeover in the reaction mechanism; Boudouard reaction seems to be initially rate limiting and the final stages being probably controlled by the reduction of wustite by CO. Fruehan (1977) and Rao (1971) have observed that the gasification reaction is dominating at low temperatures, while it turns to be controlled by wustite reduction at higher temperatures. In their studies, higher reaction rates were observed on using catalysts such as lithium and slower rates in the presence of inhibitors such as sulfur reinforcing the argument of control by carbon gasification.

In fact, some investigators believed that the reaction of carbon composites is controlled by the gasification reaction at the initial stages, marked by large activation energy, while the heat transfer is dominating at the later stages of the reduction marked by significant reduction in apparent activation energy (Ueda et al. 2009a; Michishita and Tanaka 2010). In contradictory, some others (Sun and Lu 1999a, b) have reported that the rate-controlling step is the heat transfer from surrounding to the outer surface then to the interior partially reacted system. They have referred their thinking to that there is no heat generation within the agglomerates; the rate of the overall reaction is determined by the endothermic reaction (Eq. 6.3) which cools down the whole system. However, the approach of testing the possible rate-determining step by comparing the apparent activation energy values reported in the literature for the gasification, reduction reaction, or heat transfer may not be relevant under non-isothermal conditions (Seaton et al. 1983).

6.6 Alternative Reducing Agents

One of the most important benefits that could be realized upon charging carbon composites into BF is the possibility and flexibility of top charging hydrogen-rich and bio-carbon carbonaceous materials. The fact that cost reduction as well as GHG emission is greatly affected by coke led to increase effort to reduce the coke consumption rate in the BF. Production of 1 tonne of hot metal generates 1.5 tonne of CO_2 (Ng et al. 2012). The total worldwide CO_2 emission associated with blast furnace ironmaking in 2014–2015 is about 1733 million tonnes which mainly comes from the use of fossil fuel (www.worldsteel.org).

6.6.1 Plastic Materials

One alternative reducing agent is plastic-containing materials. The demand for plastics has grown significantly over the past decades and will continue. As carbon is a major constituent of waste plastics, clearly they have the potential to be a cheap and readily available auxiliary source of carbon. It has been reported that plastics have higher combustion and gasification efficiencies compared with pulverized coal (Hata et al. 2009). As plastics generally have high hydrogen content, these could also help reduce overall CO_2 gas emissions. Injection of waste plastic, excluding polyvinyl chloride (PVC), has been proposed to be a substitute reducing agent (Matsui et al. 2009), and injection of pure waste plastic and its behavior in a BF has been practiced (Grip 2005). Combustion and gasification behavior of waste plastic in a commercial BF is much different from that of pulverized coal. Plastic particles will be gasified completely in the raceway, which is claimed to improve process efficiency and sustain the gas permeability along the BF cohesive zone.

Plastics Xhave been used as reductants in blast furnaces to some extent, although the amount of plastic waste used for this purpose is quite low in comparison to the worldwide generation of plastic waste. For use in blast furnaces and in steelmaking in general, it is required to have pure plastic materials, free from other metal content than iron. Elaborated upgrading processes exist today, where such pure plastic material fractions can be generated. However, the price for these pure plastic fractions is comparably high in comparison to fossil carbon sources.

Upon heating plastics in absences of oxygen, it undergoes what is known as pyrolysis wherein the materials decompose into gases, oils, and chars. In pyrolysis of plastic polymers, macromolecular structures of polymeric materials are broken down into smaller molecules, and a wide range of hydrocarbons are formed. The quality of pyrolysis product and product distribution depends on temperature, residence time, and some other factors. Temperature is the most important operating variable. High temperature (>600 °C) favors the production of simple small gaseous molecules which is likely to be the case in the lower part of the BF shaft; low temperature (<400 °C), which is likely to be the case in the upper part of the furnace, leads to more viscous liquid products. The residual solid after pyrolysis is known as char in which solid carbon is the major constituent. Quite often the residual solid carbon has higher reactivity compared to carbon from coke which makes it easy to gasify at relatively lower temperature.

6.6.2 Biomass

Biomass originating from forest residues, waste wood, etc. is today to large extent used or intended for use in a number of different applications in addition for use in production of pulp and paper. Some examples include district heating and production of biofuel. A tough competition for the raw material can therefore be foreseen which might result in a price which is not competitive with coal. The price for charcoal is today in Sweden not on a level which is competitive. Therefore, a lot of development is on the way to produce a partly carbonized or torrefied material. Again, as for the use of plastics as reductant, the possible interference of the volatiles with the process and to what extent the volatiles can be utilized for reduction will be crucial for the possibility to use a torrefied material.

The use of charcoal as a reductant in smaller blast furnaces is widely practiced in, e.g., Brazil (Assis et al. 2015). Utilization of biomass in metallurgical processes has been studied by many researchers, e.g., revealing high reactivity and high combustion degree for biomass (Janiana et al. 2009; Matsumura et al. 2008). Carbonization of biomass to attain selective removal of oxygen and improve the crushability, combustibility, and reactivity is required. The carbonized biomass char (400–1000 °C) would have the following features: (1) remaining duct structure of the wood, (2) larger specific surface area, and (3) noncrystalline structure. The above features make it highly reactive. The gasification of biomass char is reported to be faster than that of coke in couple of dozen times (Ueda et al. 2009b). The use of biomass as reducing agent for low-grade ores has been evaluated by Hata et al. (2009) and Matsui et al. (2009), and its high efficiency has been proved. The low crushing strength of biomass-derived reductant does not allow a complete substitution of coke on large BFs. Possibly a smaller part of the coke added from the top can be exchanged with biomass. A more promising route to introduce biomass in a BF is as replacement for coal injected through the tuyeres. An additional limitation refers to the high alkali content.

The use of biomass as a reductant in ironmaking has been investigated in the last few decades. Vladimir investigated the iron ore reduction with biomass “saw dust” (Strezov 2006). Urvashi et al. (Srivastava et al. 2013) and Yasuaki et al. (Ueki et al. 2013) studied the behavior of self-reducing iron oxide wood biomass composite pellets in an electrically heated furnace. Results showed that high-quality pig iron nuggets not only can be produced at various temperatures; they can also be produced at very short residence times.

6.7 Summary

The present article has thoroughly discussed the recent modifications and development which have been recently conducted in the blast furnace top charging materials to reduce energy consumption and CO_2 emissions. The conventional top-charged burden into the blast furnace including sinter, pellets, and metallurgical coke has reached a high level of quality that makes further improvement extremely hard. Although the blast furnace is nowadays working very close to the ideal conditions, there is still a demand to enlarge its adaptability to reuse the in-plant residues and maximize the overall efficiency. Successful trails have been done and implemented in the full-scale blast furnace on charging active/nut coke in the iron ore burden layers. The gas permeability, gas utilization, and iron ore reduction rate were improved which are accompanied by lower coke consumption and higher productivity of hot metal. The recycling of in-plant by-products and residues, which are rich with carbon and iron, into the blast furnace by its agglomeration in the form of sinter or cold-bonded agglomerates was succeeded in the mitigation of waste landfill and saving the virgin ores. Intensive work are being done on the partial replacement of conventional agglomerates with novel top charging materials including self-reducing pellets, carbon composite agglomerates, and carbon composite briquettes. The concept behind the novel composites is not only the efficient usage of the waste fines from carbonaceous materials and iron ores but also to reduce the coke consumption by using alternative sources of carbon. The recent investigations demonstrated that such novel composites are able to shift the wustite-iron equilibrium to a higher CO gas utilization at relatively lower temperature compared to that of conventional agglomerates. On the other hand, the mechanical strength of the novel composites is low for top charging into the blast furnace and required further investigations. The top charging of alternative reducing agents including waste plastics and biomass represent one of the promising ways to reduce the fossil fuel utilization in the blast furnace; however, the comparative prices and the required pretreatment of these materials represent the main challenges for its implementation.

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