### CHAPTER 12.17

# Ironmaking

Basak Anameric, David Rohaus, and Tiago Ramos Riebeiro

Iron ore concentrate is reduced, smelted, and refined to produce steel by the processing routes shown in Figure 1 (Anameric and Kawatra 2008):

- Blast furnace (BF) and basic oxygen furnace (BOF)
- Direct reduction (DR) and electric arc furnace (EAF)
- Direct smelting (DS) and either BOF or EAF
- Direct melting of scrap in the EAF

Scrap can be the sole feed for an EAF, or it can used in conjunction with direct reduced iron (DRI) in an EAF. Scrap is a supplementary feed in the BOF, as well. BF and BOF processes are considered the traditional route. DR, DS, and scrap melting and EAF are considered alternative routes. EAF steel production is more widely used in the United States, but on a worldwide scale, BOF is more extensively used for steel production. Worldwide, approximately 65% of iron and steel is produced using traditional routes, and approximately 35% is produced using alternative routes.

The majority of the iron ore mined and beneficiated is used for pig iron production and subsequent crude steel production. On average, 2 billion t (metric tons) of iron ore, 1 billion t of metallurgical coking coal, and 520 million t of scrap are used to produce 1.6 billion t of crude steel (Worldsteel 2015).

This chapter gives a brief description of the ironmaking routes. The discussions are divided into the traditional ironmaking route (BF process) and alternative ironmaking routes (DR and DS processes).

## BLAST FURNACE IRONMAKING

The BF is a countercurrent shaft furnace, which employs carbon, mainly in the form of coke for reduction and smelting of iron oxides to produce hot metal (pig iron) and slag. The hot metal usually contains 4%–5% carbon and 0.3%–1% silicon, and is suitable for subsequent refining into steel.

The raw materials for the BF include the following:

- Solid raw materials—iron oxides, flux, and coke
- Gas raw materials—hot airblast, oxygen, and hydrocarbon hot blast injectants

The BF operation consists of periodic charging of solid raw materials from the top of the furnace, periodic tapping of the hot metal and slag produced from the bottom, continuous injection of the hot blast with hydrocarbon injectants and oxygen enrichment through the tuyeres, and continuous removal of the top gas and dust.

A BF material balance is shown in Figure 2 (Peacey and Davenport 1979; Poveromo 2010; Lankford et al. 1985b). The iron oxide raw materials used are typically hematite ($Fe_2O_3$) and occasionally magnetite ($Fe_3O_4$). They are added as pellets, sinter, or lump ore. Depending on the particular BF, the charge may contain one, two, or more of these oxide forms.

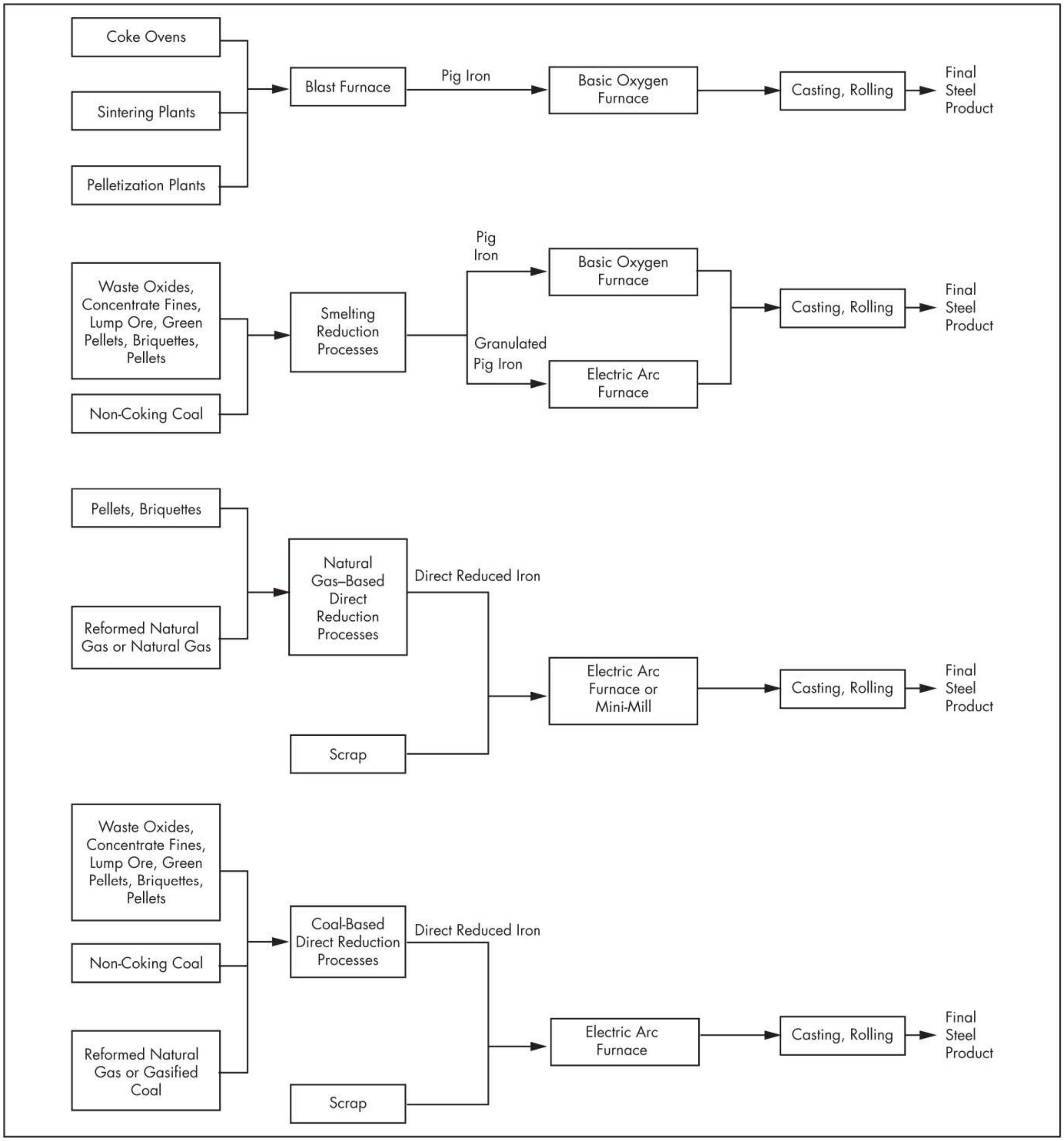
The main gangue contained in iron oxide raw materials are silicon dioxide ($SiO_2$) and aluminum oxide ($Al_2O_3$). Flux material containing calcium oxide (CaO), calcium carbonate ($CaCO_3$, limestone), magnesium oxide (MgO), or magnesium-calcium carbonate ($MgCO_3 \cdot CaCO_3$, dolomite) can be added. Pellets are produced by upgrading low-grade mineral deposits, followed by consecutive agglomeration and induration. Pellets produced without the addition of flux are referred to as *standard pellets*, and those produced with flux addition are referred to as *fluxed pellets*. In addition to the preceding list of flux materials, magnesium-iron silicates, such as olivine $(Mg,Fe)SiO_4$, are occasionally used as flux. Sinter is produced by burning fuel with various iron oxide–containing materials to produce clinker-like agglomerates. These iron oxide–containing materials may include iron ore fines, in-plant reverts (steelmaking slag, mill scale, flue dust), and fluxes (Ricketts 2017).

Flux is added to the furnace to manipulate slag composition, enabling the formation of a fusible slag and removal of the gangue minerals. Its addition rates are maintained by use of fluxed pellets and/or sinter or its individual addition. The iron oxide raw materials and fluxes are referred to as the furnace *burden*. The furnace-loading scheme is described as the burden/coke or ore/coke ratio.

Coke is added to the furnace to supply most of the reducing gas and heat needed for reduction and smelting. It is produced by heating mixtures of powdered caking coals in the

---

Basak Anameric, Chief Scientist, Basak Anameric Consulting, Grand Rapids, Minnesota, USA
David Rohaus (Retired), United States Steel Corporation, Pittsburgh, Pennsylvania, USA
Tiago Ramos Riebeiro, Researcher, Laboratory of Metallurgical Processes, IPT (Institute for Technological Research), São Paulo, Brazil



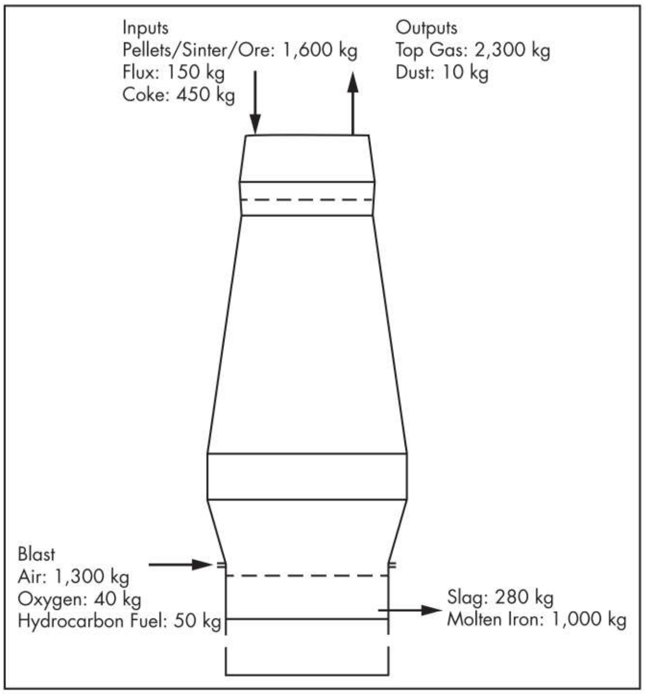
Source: Anameric and Kawatra 2008

**Figure 1 Iron and steelmaking routes**

absence of air (coking process). Coke is reactive at high temperatures and is strong enough to withstand being crushed even near the bottom of the BF. Coke is necessary to permit uniform gas flow through the burden as it softens and melts in the lower regions of the furnace. To date, no alternative materials to fully replace coke have been identified.

Hot airblast is used to burn coke in front of the tuyeres to provide heat for reduction, heating, and melting of the charge and products. It is preheated to 930°–1,330°C and in some cases enriched with oxygen. Gas, liquid, or solid hydrocarbon injections provide additional reducing gas (CO and $H_2$) for the reduction reactions. Hydrocarbon injectants include fuel oil, tar, natural gas, and pulverized coal (AIST 2018).

The main product of the BF is hot metal (pig iron). It is tapped from the furnace at regular intervals through one or several holes near the bottom of the hearth. The composition



Adapted from Peacey and Davenport 1979; Poveromo 2010; Lankford et al. 1985b

**Figure 2 Blast furnace materials balance**

of pig iron is controlled by adjusting the slag composition and furnace temperature, particularly in the lower half of the furnace. The pig iron is transported in the molten state to an adjacent steelmaking plant, where it is refined to steel.

The by-products of the BF are slag and top gas. The slag (with an approximate composition of 30%–40% $SiO_2$, 5%–15% $Al_2O_3$, 35%–15% CaO, 5%–15% MgO, 0–1% $Na_2O$+$K_2O$, and 1%–2.5% S) contains very little iron oxide. The composition of the slag is adjusted to do the following:

- Remove $SiO_2$ and $Al_2O_3$ gangue minerals inherent to the iron oxides.
- Control the slag viscosity.
- Control the silicon content of the metal.
- Absorb potassium oxide ($K_2O$) and sodium oxide ($Na_2O$). Potassium oxide and sodium oxide enter the furnace as inherent to both coke and iron oxides. They are partially reduced to potassium and sodium vapor near the bottom of the furnace. This vapor rises to the cooler parts of the furnace, where it is re-oxidized and becomes entrapped in solid form in the descending burden. If the vapor is not absorbed by the slag, this process becomes cyclic and leads to an accumulation and buildup in the furnace. Buildup restricts the gas flow and leads to erratic descent of the charge (Peacey and Davenport 1979).
- Absorb sulfur. If the sulfur is absorbed in the slag, it does not yield in the metal. Metal with high sulfur concentrations needs to be desulfurized prior to use.

The BF top gas is collected, cleaned, and burned in auxiliary stoves to heat the hot airblast.

The main chemical events that take place in the furnace include the following steps (Lankford et al. 1985b; Peacey and Davenport 1979):

1. Burning (oxidation) of carbon by hot airblast in front of the tuyeres to generate heat and carbon dioxide ($CO_2$). This reaction takes place as shown:

$$C + O_2 \leftrightarrow CO_2$$

2. Endothermic reaction of carbon and carbon dioxide to produce reducing gas. This reaction takes place as shown:

$$C + CO_2 \rightarrow 2CO$$

$$CO + H_2O \rightarrow H_2 + CO_2$$

3. Reduction of iron oxides to metallic iron. These reactions take place as shown:

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$$

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$

$$FeO + CO \rightarrow Fe + CO_2$$

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

$$FeO + C \rightarrow Fe + CO$$

4. Formation and melting of slag. The gangue minerals inherent to the iron oxides and ash inherent to coke react with the flux materials and form a fusible slag.
5. Separation of molten iron from slag. Because the density of the slag is much lower than that of the iron, the slag floats on top of the iron.

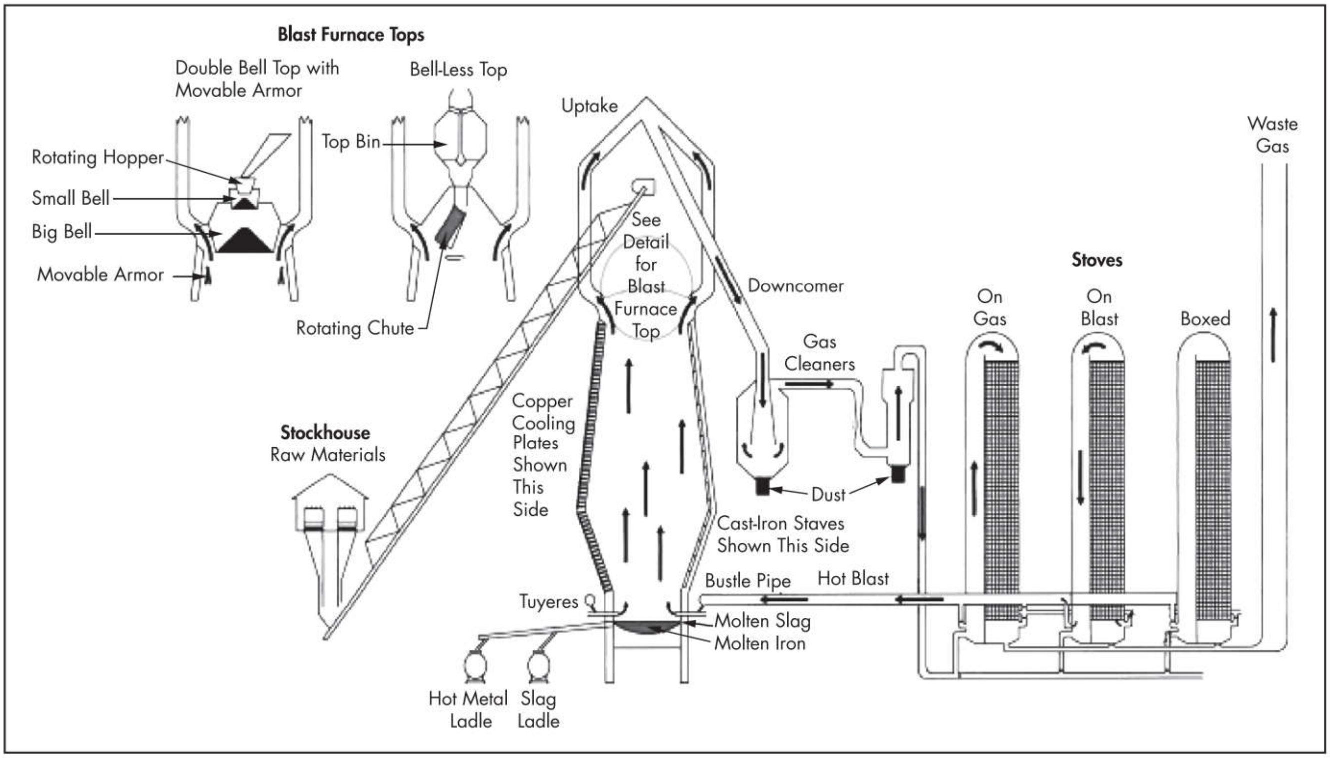
The rate at which reducing gas is generated, coke is burned, and iron oxides are reduced depends on the rate at which hot airblast is blown into the furnace. High hot airblast rates lead to rapid combustion of coke in front of the tuyeres, rapid reducing gas generation, and consequently a high rate of iron reduction.

The furnace operation is limited by the maximum allowed rate at which hot airblast can be blown into the furnace. Above this rate, the furnace gases tend to ascend through open channels in the solid charge rather than in an evenly distributed flow pattern. This causes nonuniform and/or incomplete reduction and inefficient use of carbon. Excessive ascent velocities also prevent newly melted iron and slag from descending evenly through the bosh (flooding), which may lead to an uneven descent of solid charge and erratic furnace operation (Peacey and Davenport 1979).

### Blast Furnace Plant Layout

The BF plant layout shown in Figure 3 (Peacey and Davenport 1979; Carmichael 2012) integrates various types of auxiliary plants and systems required to handle the raw materials needed to make iron and its by-products. These auxiliary plants and systems include

- Raw materials receiving and storage,
- Stockhouse,
- Charging system,
- Furnace proper,
- Casthouse,
- Slag handling,
- Hot metal handling,
- Stoves and hot blast system,
- Gas plant, and
- Utilities.



Source: Peacey and Davenport 1979

**Figure 3 Blast furnace layout**

The integrated functioning of these systems and plants evolved over centuries of ironmaking and enables the successful operation of a BF. Modifications to any one of these systems or plants may improve efficiencies at a large scale. Conversely, malfunction or upsets regarding any one of them may lead to long-term interruptions and a loss of productivity.

### *Blast Furnace Proper*

The BF proper is the main vessel for ironmaking. It is designed to support reduction and smelting reactions. BFs may be either mantle-supported or free-standing. Mantle-supported furnaces have a ring girder (mantle) located at the bottom of the lower stack of the furnace. Columns resting on the main furnace foundation support the mantle. The hearth and tuyere breast are supported by the foundation.

### *Stockhouse*

Raw materials, such as iron ore, pellets, fluxes, and coal, are delivered by bulk carriers, ship, barge, or rail car. Coke can be delivered in the same fashion or produced in the plant. Sinter can be delivered to the plant or produced in the plant using supplied ore and waste oxides (such as mill scale, pellet fines, coke breeze, sludge, etc.) generated in the plant.

Raw materials are screened, weighed, and sequenced in the stockhouse for charging (the burden) into the furnace. The raw materials are stored in individual bins and moved to the top of the furnace by skips or conveyor belts. They are charged into the furnace in separate layers. Raw materials tend to degrade and generate fines with extended outside storage and repeated handling (stockpiling, reclaiming, dumping, transfer chutes, etc.). The presence of fines decreases permeability and impairs effective gas utilization, reduces fuel efficiency, and eventually disrupts the process.

The final screening of the raw material is conducted in the stockhouse, using vibrating screens installed after the storage bins and before the weigh hoppers.

### *Charging System*

The BF is operated with a positive top pressure. When the burden is loaded into the furnace, all the materials must pass through the furnace top without loss of either top pressure or furnace gas. BF charging systems have evolved significantly to account for larger furnaces, higher production rates, and lower fuel consumption. A bell-less top and double-bell top with movable armor charging systems are shown in Figure 3.

### *Hot Blast System*

The primary components of the hot blast system are hot blast stoves, hot blast main, bustle pipe, tuyere stocks, tuyeres, back-draft stack, and auxiliary fuel-injection system. Most hot blast systems include three hot blast stoves; some plants use four (Helenbrook 2012).

Hot blast stoves are a regenerative heat exchange system used to preheat the cold blast to the BF. The top gas from the BF serves as the energy source (with a heating value approximately 0.1 that of natural gas) (Peacey and Davenport 1979; Lanyi et al. 2012). Top gas must be clean and dry to ensure stable operation and longevity of the stoves. It is burned to recover heat and to reduce carbon dioxide emissions. It is often enriched by other fuels, such as natural gas or coke oven gas, to attain the flame temperature required.

The heat exchange system includes sequential heating and cooling and regenerative mass of refractory. These steps (shown in Figure 3) include the following:

1. During the *on gas* stage, combustion of the gases and passage of the waste gas through the refractory take place. Air and gas are mixed in the combustion chamber and then burned. The combustion gases flow into and down through the checker refractory, heating them. The waste gases exit through the chimney to the exhaust stack.
2. During the *on blast* stage, cooling of the checker refractory and heating of the blast air take place. Cold blast air enters the bottom of the checker chamber and flows up through the checkers, in the process of which it is heated. If the temperature of the blast is higher than required, it is enriched and mixed with other gases (such as natural gas or coke oven gas).
3. During the intermediate stage, the gas system and blast system are in isolation where the stove is bottled or boxed. As the name suggests, all the valves are closed and the heat is retained in the stove.

Combustion air, hot blast enriched with oxygen, natural gas, pulverized coal, and/or other additives supplied to the furnace through the tuyeres are referred as the *wind*. Wind composition and velocity affect the kinetics of BF ironmaking. If the wind velocity is too high, downward descent of the charge is inhibited. The wind velocity can be manipulated by the furnace top pressure: Increasing top pressure increases the pressure of incoming wind, which increases the gas density and lowers the wind velocity (Carmichael 2012; Helenbrook 2012).

### Tuyere Injection System

The most common BF injectants are coal, oil, tar, and natural gas. The main incentive for their use is to replace coke. This is caused by increasing coke prices, decreasing availability, and environmental constraints associated with coke production. In addition, some of these injectants help with cooling in the raceway and aid in introducing more hydrogen in the reducing gases. The tuyere injections are accompanied by an increase in blast temperature and oxygen enrichment, and a decrease in blast humidity. It is these changes that contribute most to increased coke savings and productivity (Helenbrook 2012).

### Cooling System

The primary technological advances in the BF in the second half of the 20th century were related to burden distribution, high top pressure, fuel injection, and increased hot blast temperature. The resulting improved process efficiency, combined with building of larger furnaces, led to increased heat flux and consequent need for cooling to ensure a stable furnace shell (Carmichael 2012). The cooling and lining systems were developed to protect the shell and increase the campaign life.

The two main types of cooling are plate cooling and stave cooling. A typical cooling plate is manufactured from cast high-conductivity copper. Single- or multiple-pass coolers may be used, depending on their position in the furnace. In the bosh, belly, and lower stock, multiple-pass coolers are installed. Staves can be applied to all walls in all areas, including the throat. Staves offer direct protection of the BF shell by providing a homogeneous cooling shield that acts as a surface on which accretions can form.

### Casthouse

The casthouse is the area where the BF is tapped and hot metal and slag are removed. BFs are typically tapped every 2–4 hours. Typical hot metal and slag tapping rates are in the range of 4–6 and 3–5 t/min. In the casthouse, hot metal and slag are directed to the appropriate handling equipment or facilities.

Various site-specific materials, equipment, and infrastructure are used for tapping and closing the furnace. These include the following:

- A tap-hole drill is used to bore a hole through the tap-hole clay into the hearth of the furnace.
- A mud gun is used to close the tap hole after casting is complete. A measured quantity of clay is pushed by the mud gun to fill the hole and to maintain an amount of clay (the *mushroom*) within the hearth. Tap-hole clays are high-temperature refractory compounds. They are very dense and require high pressure to be forced through the mud gun nozzle into the tap hole. They essentially seal of the furnace between taps.
- Trough and runner systems are used to separate iron and slag and to convey them away from the furnace. The iron trough is a refractory-lined tundish located in the casthouse floor and designed to collect iron and slag from the tap hole.

The iron flows down the trough, under a skimmer, and over a dam into an iron runner system. Trough iron level is determined by the iron dam height. Slag is lighter than iron, so it floats down the trough on top of the iron pool. The slag pools on top of the iron until there is a sufficient amount to overflow to the slag dam. It then floats down the slag runner (7% slope) into the various pieces of slag handling equipment. At the end of the cast, the slag dam is lowered so that most of the slag is drained off. The iron below the dam level remains in the trough. This reduces damage to the trough's refractory lining from oxidation and thermal shock.

The slag handling equipment includes the following:

- Pots for railway or mobile equipment are used for hauling to a dump.
- Pits are located adjacent to the furnace for air cooling and water quenching prior to excavation by mobile equipment. Pit slag is used for fill or can be crushed for use as aggregate.
- Pelletizing or granulation facilities are also located adjacent to the furnace for conversion of the slag to material suitable for backfill, aggregate, or cement replacement.

Iron is directed to hot metal transfer ladles (torpedo cars) using iron runners (3% slope) for movement to the steel shop, iron foundry, pig caster, or iron granulation unit.

## Operational Zones

Numerous heterogeneous chemical reactions take place inside a BF, each serving a particular purpose. All of these reactions contribute to the goal of producing hot metal (pig iron). Physical configuration inside the furnace, gas flow pattern, and establishing a countercurrent operation are the most critical aspects for these reactions to proceed.

The BF can be conceived as five reactors (or zones), stacked one on top of another, in a single shell. These abstract reactors are referred as *regions* or *zones*. These zones exhibit large temperature gradients and use raw materials and products in a coupled fashion. Even in the same zone, temperature gradients occur, gas flow rates differ, and chemical reactions proceed differently from center to periphery.

The five zones are as follows (Geerdes et al. 2015; Lu 2012):

1. Lumpy zone, where no liquid or partial molten material exists
2. Cohesive zone (also called *softening* and *melting* zone), where alternating layers of partially reduced iron oxides and coke exists
3. Active coke zone, where an irrigated bed of coke, with hot reducing gas moving up and liquid iron and slag moving down exists
4. Raceway, where partial combustion of coke and injected fuels takes place with preheated air to produce reducing gas that contains carbon monoxide and hydrogen
5. Deadman zone where liquid products are collected, with the coke bed being pushed down into liquid pool against the buoyant force

Heat transfer, reduction, and melting are the chemical events that take place in individual zones under countercurrent conditions. These zones are different from the separation of the furnace into two regions (upper and lower furnace) based on the coke activity isotherm, for heat and mass balance calculations. For temperatures below this isotherm (950°–1,000°C), the reaction rate of carbon gasification by carbon dioxide is insignificant, so that coke may be treated as chemically inert. This region is called the *coke-inert region*. For temperatures above the isotherm, the region is called the *coke-active region* (Lu 2012; Carmichael 2012; Poveromo 2010).

Iron oxides and coke are charged in alternate layers. They retain this layered arrangement as they move down the lumpy and cohesive zones, countercurrent to the flow of the reducing gas, which preheats and pre-reduces these materials. The cohesive zone, the second zone from the top, separates the lumpy zone for gas–solid chemical reactions and the zones for processing liquids. Softening and melting of the iron oxides start toward the bottom boundary of the cohesive zone. The physical structure of the cohesive zone is important for the whole process because it provides permeability and distribution for gas flow. The physical structure, position, and direction of the cohesive zone are influenced by the raw material quality, charging practice, overall oxide/coke ratio (coke rate), and how the other reactions proceed in the furnace (Poveromo 2010; Lu 2012; Lankford et al. 1985b; Sano et al. 1997).

The reducing gas is generated in the raceway by partial combustion of coke and injectants with oxygen from the hot blast. Reducing gas ascends in the active coke zone, cohesive zone, and lumpy zone through coke slits. The momentum of the gases from the tuyeres influences the size of the raceway. Slag levels and coke quality influence the direction of the reducing gas leaving the raceway (Poveromo 2010; Wallace et al.1999).

As the molten iron and slag are produced, they drip through the active coke zone and raceway and collect in the hearth. The hearth is filled with coke. The ease of tapping hot metal and slag depends on the coke size and quality (Poveromo 2010).

### Iron Oxide Processing

The majority of the iron oxides are introduced to the furnace in the form of hematite ($Fe_2O_3$), at ambient temperature. As they descend, they are heated and experience a series of physical and chemical changes, including reduction and metallization, crystal structure change, and softening and melting.

As iron oxides reach the lower boundary of the lumpy zone softening starts. The softening properties of the partially reduced iron oxides depend on the iron ore quality and operating conditions. The softening temperatures vary between 1,200° and 1,400°C. Softening of the iron oxides take place in the upper boundary of the cohesive zone, and melting of the iron oxides take place in the lower part of the cohesive zone (Wallace et al. 1999).

Mainly, carbon monoxide is used for reduction of iron oxides. Data from the dissection of BFs have shown that by the time iron oxides reach the cohesive zone, the degree of reduction is about 70% (Hashimoto et al. 1977). Pre-reduced iron particles stick together under the pressure of the bed above. Reducibility and size distribution of the iron oxides have a direct influence on the reduction rate and physical properties of the cohesive zone. From a point of view of reducibility, the smaller particles with large surface areas would be preferable. For gas permeability and distribution through the furnace, however, pellets and sinter with adequate size distribution are used. The iron oxide agglomerates (pellets and sinter) should provide a porous surface for reducing gases to diffuse in easily and for product gas carbon dioxide to diffuse out easily (Lu 2012; Dahlstedt et al. 2000).

The cohesive zone consists of alternating layers of partially reduced iron oxide and coke slits. The shape of the cohesive zone emulates the main path and distribution of the reducing gas. The distribution of gas flow has important consequence for efficient use of gases and protection of the lining in the lumpy zone. Because the cohesive zone separates the lumpy zone above from the liquid-processing high-temperature zone below, the size, shape, and location of the cohesive zone also play a role in the effectiveness of those zones. The location of the cohesive zone in relation to the tuyere level and the thickness of the zone depend largely on the iron oxide reducibility properties and furnace conditions (Lu 2012; Tovarovskii et al. 2009).

The gas flow in the cohesive zone can be centralized (V-shaped distribution) or wall directed (M-shaped distribution). The following factors are manipulated to obtain a centralized (V-shaped) distribution (Omori and Shimomura 1982):

- Charging pattern and difference in the angle of repose, bulk density, and size distribution for iron oxides and coke
  - The angle of repose for coke, sinter, and pellets are 35, 33, and 26 degrees, respectively.
  - The bulk density for coke, sinter, and pellets are 525 kg/m$^3$, 1,660 kg/m$^3$, and 2,150 kg/m$^3$, respectively.
- Segregation during charging

When centralized gas flow is observed, the iron oxides at the center of the furnace encounter large amounts of gas, thus they are heated and reduced faster than those charged at the periphery. This results in earlier formation of the cohesive layer at the center than the periphery, creating the conical shape of the cohesive zone.

Softening and melting of the iron oxides start in the cohesive zone. They are melted exclusively on the inner and lower surface of the cohesive layer. The softening temperature depends on the following (Omori and Shimomura 1982):

- Amount of slag components
- Fusion temperature of the slag components
- Amount of residual wüstite present (influenced by how fast the burden is heated and reduced)

The slag components include gangue minerals from the iron oxides, ash from coke, flux, and residual wüstite.

The shape of the cohesive zone and the softening characteristics vary when using fluxed (pellets and sinter) and standard (pellets) iron oxides. When using fluxed iron oxides, the overall fusible slag composition is basic, and fusion temperature is higher when compared with standard iron oxides. Fluxed pellets are usually more porous, which leads to faster reduction and metallization. Thus, as these pellets start to soften, there is no wüstite left in the reduced pellets to react with the slag components. When compared with fluxed iron oxides, the overall fusible slag composition for standard iron oxides is acidic and fusion temperatures are lower. This leads to early softening and formation of cohesive layers higher in the furnace, resulting in a smaller lumpy zone for prereduction (Lu 2012; Dahlstedt et al. 2000).

If the burden consists of two kinds of iron oxides with high and low melting points of the slag components, the two kinds of iron oxides melt at a different temperature. In such cases, the cohesive layer is wider (Hashimoto et al. 1977).

If the slag formed at the lower surface of the cohesive zone has a high viscosity, the void fraction in the active coke zone becomes lower. This impairs dripping of the liquid products and the descent of the bed. Thus, the melting characteristics of the iron oxides are also very important for efficient BF operation (Hashimoto et al. 1977).

Hence, it is desirable to have a cohesive zone made of cohesive layers with high softening temperatures and permeable coke slits located low in the furnace. This promotes earlier reduction for chemical efficiency, optimum shape, and minimum height, offering higher production and protection of the lining.

### Coke Processing

The ascending reducing gas (bosh gas) at a temperature of 2,100°–2,300°C is generated in the raceway by partial combustion of carbon from coke and injectants with preheated air. It contains three gases: nitrogen, carbon monoxide, and hydrogen. Depending on the extent of hot blast oxygen enrichment, it contains about 50%–60% nitrogen by volume. The nitrogen in the bosh gas does not chemically react in the furnace, but it plays an important role as a heat carrier from the raceway to the lumpy zone (Lu 2012). The hydrogen content of the gas varies depending on the extent of the natural gas injection (Wallace et al. 1999).

This hot bosh gas moves countercurrent to the burden to the active coke zone, then to the cohesive zone, and finally to the lumpy zone. In the cohesive zone, bosh gas is capable of melting the iron and slag, as well as reducing the remaining wüstite. In the lumpy zone, it provides the reducing gas required for the reduction of iron oxides.

Carbon in coke may react with the carbon dioxide (or water vapor) from the reduction reactions at temperatures above the coke-active region isotherm of 950°–1,000°C. The following endothermic reaction is called the *solution loss reaction* (Peacey and Davenport 1979; Elliott and Gleiser 1960):

$$CO_2 + C \rightarrow 2CO$$

$$CO + H_2O \rightarrow H_2 + CO_2$$

As the solution loss reaction takes place, the mechanical strength of the coke is lowered (Poveromo 2010).

In the upper part of the lumpy zone (where the temperatures are below the coke activity isotherm), carbon in coke is chemically inert (solution loss reaction does not take place) and carbon dioxide is accumulated as a result of the ongoing reduction reactions. This weakens the reducing power of the rising gas. As the gas reaches the top of the furnace, it contains approximately equal amounts of carbon monoxide and carbon dioxide (Lu 2012).

As the iron oxides reach the coke activity isotherm, prereduction reactions are completed to an extent, and metallization starts. Along with the other reactions, the solution loss reaction proceeds. The carbon does not melt; it remains solid inside the furnace. It reacts with gases, dissolves in liquid iron, and reacts with some oxides in slag. In the deadman zone, it is consumed for liquid metal and slag refining reactions.

### Metal and Slag Refining

For the duration between tappings or longer, liquid metal and slag are retained in the deadman zone, where they are in contact with each other for a long period. During this stay, various chemical events take place. Owing to these chemical reactions, the composition of the slag and metal vary from top to bottom. These chemical events are influenced by the slag basicity, softening temperature, and rate of iron oxide reduction (Lu 2012).

These chemical events include

- Continuing reduction of iron oxides in the slag, which results in considerable variation of the slag composition from the top to bottom of the slag pool;
- Continuing carburization of the metal;
- Sinking and coalescence of the metal droplets;
- Transfer of manganese from slag to metal;
- Transfer of sulfur from metal to slag; and
- Decrease of the silicon content of the metal.

### Physical Features Required for Efficient Operation

BF operation efficiency is measured in terms of production, fuel consumption, and furnace lining life. All of these factors are limited by the countercurrent operation of the furnace and have a direct effect on the economy of the process (Hashimoto et al. 1977).

Countercurrent operation of the furnace can be achieved only by maintaining proper physical conditions and permeability in the furnace. To date, coke remains a necessary ingredient for maintaining mechanical stability and permeability and is required for good performance.

BF operations are influenced by the volume of wind and utilization rate of the reducing gases. If the wind volume is increased beyond a certain limit, the descent of the solids becomes erratic, deteriorating the countercurrent operation of the furnace. The fuel rate depends on the utilization of the gas in the furnace. The lining life depends on the thermal load to which the lining is exposed (Wallace et al. 1999; Lankford et al. 1985b; Lu 2012).

A smooth and stable BF operation and low thermal load on the lining can only be attained under stable countercurrent conditions in the furnace.

The movement of the solid bed packed with iron oxides and coke is induced by the void space created at the bottom because of melting, burning of the carbon, and tapping of the liquids. The gas flow in the opposite direction is driven by the pressure drop. The amount and rate of gas flow through the furnace dictate the rate of production. The distribution of the gas through the furnace and efficient solid–gas contact relate to efficient use of heat and reducing gases in the furnace.

Pressure drop and void fraction of the charge in high-temperature zones have the greatest effect on countercurrent condition stability. To promote this, improvements have been made to use raw materials with proper size distribution and adequate mechanical strength (Lu and Ranade 1991). The presence of fines in the bed narrows the gas path, increases the resistance to gas flow, and lowers the hot metal production rate. Raw materials lacking adequate mechanical strength generate fines in the furnace, impairing gas flow. When the conditions for adequate gas distribution in the furnace can be established, the furnace can be operated at higher wind velocities and consequently at higher top pressures. This allows for more efficient use of the reducing gas (Hashimoto et al. 1977; Peacey and Davenport 1979; Lu and Ranade 1991).

If adequate gas flow through the furnace cannot be attained and a strong localized gas flow forms in the limited cross section of the furnace, a considerable amount of gas goes to the top of the furnace without reducing the iron oxides, lowering the overall utilization of the gas. In this case, the iron oxides in other parts of the cross section have less chance to be heated and reduced by the gas. Consequently, the unreduced iron oxides proceed deeper into the furnace without being sufficiently reduced to form the cohesive layers, and the pattern of the cohesive zone changes as a result of the partial channeling of the gas in the lumpy zone.

In the cohesive layer, a dense mass of pre-reduced iron oxides impairs the gas flow. The layered charging of the iron oxides and coke allows generation of coke slits and redistribution of the gas flow in this zone. Variation in the thickness of each layer of charge over the cross section of the furnace aids in promoting the proper contact pattern for chemical reactions between solids and gas and between gas flow and the refractory lining. A sufficiently large coke slit area is necessary for stable countercurrent operation of the furnace (Hashimoto et al. 1977). A sufficiently high void fraction is necessary both for the smooth countercurrent operation in the active coke zone and for the smooth flow of iron and slag in the hearth.

## ALTERNATIVE IRON UNITS AND IRONMAKING TECHNOLOGIES

Alternative ironmaking technologies include DRI, DS hot metal, and iron oxide reduction and smelting.

### Direct Reduced Iron

DRI is a highly metalized solid, alternative iron unit. It still contains gangue minerals inherent to the raw materials used for its production. It is produced by solid-state reduction at temperatures lower than the melting temperature of iron, using hydrocarbon gases and/or carbon-bearing materials as reducing and carburizing agents.

During its production, only oxygen inherent to the iron oxide feedstocks is removed. Thus, DRI has a similar but more porous physical form than the raw materials (pellets, lump ore, fine ore) used for its production. Owing to this physical appearance, it is often referred as *sponge iron*. Depending on how the DRI will be used, its porous structure, physical degradation, and/or chemical stability features may be undesirable. In these situations DRI is often densified to hot briquetted iron or cold briquetted iron.

When hydrocarbon gases, such as hydrogen, carbon monoxide, or methane (natural gas), are used as fuel and reducing agents, the process is called *natural gas–based DR process*. When carbon-bearing materials, such as coal, gasified coal, or coke breeze are used as fuel and reducing agents, the process is called *coal-based DR process*. Some of the important features of natural gas–based and coal-based DR processes are described by Anameric and Kawatra (2007).

DRI can be used in EAF along with scrap for steel production; ferrous foundry operations as a new iron unit charge; EAF, foundry cupolas, and BOF as coolant; and BF to increase throughput (Anameric and Kawatra 2007).

DR processes and DRI utilization have reached commercial competency and are becoming increasingly important. This is because of

- Increasing worldwide production and demand for DRI in EAF steelmaking,
- Need for manufacturing routes involving smaller and more flexible equipment, and
- Developments in the natural gas industry.

#### *Direct Reduction Processes*

Shaft furnace, retort (batch) furnace, and fluidized bed reactors used for natural gas–based processes include (Zervas et al. 1996b; Markotic et al. 2002) the following:

- Shaft furnace processes
  - Midrex
  - Energiron III and ZR
  - Armco
  - Arex
  - Purofer
- Retort (batch) furnace processes—HyL I and II
- Fluidized bed reactor processes
  - Fluid iron ore reduction (FIOR)
  - Finmet
  - Circored
  - H-iron
  - High iron briquette (HIB)
  - Iron carbide

Rotary kiln, rotary hearth furnace, shaft furnace, multiple hearth furnace, and fluidized bed reactors used for coal-based processes include (Zervas et al. 1996b; Markotic et al. 2002) the following:

- Rotary kiln reactor processes
  - Stelco-Lurgi/Republic Steel National (SL/RN)
  - Krupp-CODIR (coal-ore-direct-iron-reduction) and Krupp-Renn
  - Direct Reduction Corporation (DRC)
  - ACCAR/OSIL (Allis-Chalmers controlled atmospheric reduction/Orissa Sponge Iron and Steel Limited)
  - Tata Iron and Steel Company (TISCO) direct reduction (TDR)
- Fluidized bed reactor process—Cirofer
- Shaft furnace processes—Kinglor-Metor and Höganäs
- Multiple-hearth furnace process—Primus

- Rotary-hearth furnace processes
  - International Metals Reclamation Company (Inmetco)
  - FastMet
  - SidComet and Comet
  - Iron Dynamics Inc. (IDI)
  - Iron Technology Mark 3 (ITmk3)
  - DRyIron

**Shaft furnace.** A shaft furnace is a moving bed reactor where iron oxide pellets, lump ore, or briquettes descend under gravity in a countercurrent flow to the reduction gas. The temperature and composition of the reducing gas in the furnace are controlled to maintain optimum bed temperature, degree of metallization and carburization, as well as efficient utilization of the reducing gas. Its operation efficiency depends on even distribution of the gas flow across the cross section of the shaft. This is best achieved by use of a charge of uniformly sized particles free from fines. Pellet metallurgical properties, such as low-temperature disintegration index and sticking properties, are important for shaft furnace operation. Fines generation and bridging in the furnace alter the bed permeability and impair the reduction efficiency and productivity (Zervas et al. 1996a, 1996b).

**Retort (batch) furnaces.** Retort (batch) furnaces operate on a similar principle to shaft furnaces. Iron oxides are charged in fixed beds in series, and the reducing gas is transported from one bed to another. Prior to injection of the reducing gas into each reactor, it is preheated and conditioned with steam. Fresh reducing gas is injected into the last retort furnace, which is the cooling furnace. Final reduction and carburization of the DRI takes place in the cooling furnace. When the reducing gas first comes in contact with the iron oxides, reduction takes place very rapidly. As the reducing gas descends in the furnace, the reaction speed slows, and reduction potential is considerably lower. This leads to uneven reduction of the charge (Zervas et al. 1996b; Anameric and Kawatra 2007).

**Fluidized bed reactors.** Fluidized bed reactors often consist of series of superimposed hearths in which fluidized solids flow from one to the next below in the opposite direction to the gas flow. This allows for intimate mixing of the solids with the gases. Their efficiency depends on the effective mixing of the charge, complete fluidization of the bed, mass flow, and reducing gas velocity. Fine ore, without preagglomeration and induration, is used as the iron oxide source. Fine ore size distribution is closely controlled to ensure complete fluidization and minimal carryover to the waste stream. Because the surface area of the fine ore is higher than that of the pellets, lump ore, or briquettes, the rate of reduction is faster. Fluidized bed reactors are operated at elevated pressures to ensure optimum gas velocity, that is, optimum fluidization. The sticking tendency of the highly metallized materials may cause operational problems because larger particles formed by sticking of the finer particles may interfere with fluidization of the bed (Anameric and Kawatra 2007; Chatterjee 1994; Zervas et al. 1996b).

**Rotary kiln.** A rotary kiln is composed of a slightly inclined rotating cylindrical kiln with an internal refractory lining. The residence time in the kiln can be adjusted with the inclination and rotation speed of the kiln. Coal and iron oxide feedstocks in the form of pellets, lump ore, or greenballs are charged together. Generation of the reducing gas and reduction of iron oxides take place simultaneously in the kiln. Controlled combustion of the coal is achieved by injecting air both at the discharge end of the kiln and through the blowers mounted along the kiln length. The burner located at the discharge end of the kiln provides the energy required for the reduction reactions. The kiln is operated with a slightly positive pressure to prevent the intrusion of unregulated air. The coal feed is adjusted to slightly excess, so that unreacted carbon can be present in the product. This prevents the product from reoxidation (Venkateswaran and Brimacombe 1977). The kiln product is cooled in a rotary cooler. Air flow in the kiln is controlled to minimize temperature fluctuations. Localized temperature increases can result in the formation of accretions on the kiln lining and ball-shaped clusters within the bed (Anameric and Kawatra 2007).

**Rotary hearth furnace.** Rotary hearth furnaces can be operated in multiple zones: initial reduction zone, final reduction zone, and cooling zone. Temperature, gas flow, and gas composition are controlled to provide the required conditions in each zone. The opposite rotation of the furnace hearth and gases enables countercurrent interaction of the solids and gases. The energy required for the reactions is supplied by burners located at the furnace walls. These burners are fired at the stoichiometric deficiency of air to maintain a reducing atmosphere in the furnace. The layering thickness of the solids on the hearth dictates the reduction efficiency. At low thicknesses, higher degrees of reduction can be attained and the product has more uniform properties. The production capacity of the process is directly proportional to the furnace hearth area; to achieve high capacities, proportionally large (when compared with other furnaces with the same production capacity) furnaces are needed (Zervas et al. 1996b; Anameric and Kawatra 2007).

## Direct Smelting Hot Metal (Pig Iron)

DS processes aim to produce hot metal that has similar properties as the BF pig iron. They differ from DR processes in that the iron oxides are reduced and smelted. The gangue minerals inherent to the raw materials are separated from the metal via formation of a fusible slag.

DS hot metal can be used in BOF and EAF for steel production and ferrous foundry operations as a new iron unit charge.

### *Direct Smelting Processes*

DS processes were developed as an alternative to the BF process to overcome built-in disadvantages of that process. The incentives behind development of DS processes can be summarized as follows (Anameric and Kawatra 2008):

- Beneficiation and use of widely available non-coking coals as reducing and carburizing agents, instead of coke
- Beneficiation and use of low-grade iron oxide reserves or waste oxides, which cannot be beneficiated in the BF
- Lessening environmental emissions; elimination of coke ovens, sinter plants, and induration kilns
- Lower capital and operational costs because of minimal ancillary plant and material handling requirements
- Direct use of iron ore fines or concentrate (instead of pellets, sinters, and lump ore)
- Economic operation at modest throughput rates
- Compatibility and ability to complement the existing iron- and steelworks.
- Flexible operation that can be shut down and easily restarted

- Lower energy losses and utilization of secondary energies associated with the process
- Overall lower energy consumption
- Advantages associated with the use of upgraded charge (known chemical composition, slag-free structure) for steel production

The DS process can be subdivided into two distinct procedures, based on the methods used for generation of reducing gases (Zervas et al. 1996a; Meijer et al. 2013):

1. Processes where the reducing gases are generated in the same reactor along with reduction and smelting. These processes can be subdivided as follows:
    - Complete reduction and smelting in a single-stage reactor, such as a rotary hearth furnace or linear hearth furnace, for example, ITmk3 and nodular reduced iron (NRI)
    - Complete reduction and smelting in a molten metal bath, such as direct iron ore smelting (DIOS) and high-intensity smelting (HIsmelt)
    - Complete reduction and smelting in a molten slag bath, such as Romelt and Ausiron
2. Processes where reducing gases are generated externally in two-step processing, for example, Corex, Finex, FastMet/FastMelt, RedSmelt, IDI, Inmetco, Elred, Plasmasmelt, and Inred (Smith and Corbett 1987). Corex and Finex processes are currently operating commercially.

**Melter-gasifier furnace.** In the melter-gasifier furnace, coal is charged from the top, where it is dried and devolatilized using the gases produced from smelting (occurs at the bottom of the furnace) and transformed into char. This char creates a bed and supports the pre-reduced iron oxides as they are smelted. The furnace operates in a countercurrent manner. The temperature at the top of the furnace is about 1,000°–1,200°C, and the temperature at the bottom of the furnace is about 1,500°C. The engineering and operational principles of this furnace resemble a BF bosh area. The commercial examples of processing schemes that use this furnace include Corex and Finex.

**Electric melter-gasifier furnace.** In the electric melter-gasifier furnace, reducing gas generation and final reduction and smelting of the iron oxides take place. These furnaces were designed drawing on EAF design. An early example of this process is the strategic-Udy process, in which prereduction was carried out in a rotary kiln followed by smelting in an electric furnace (Udy and Udy 1958; Udy 1959). For these furnaces, the off-gases from reduction and the electric furnace are combined and used for electricity generation. In most cases, the energy generated using the off-gases is sufficient for the process needs. The examples of processing schemes that use this furnace include Inred and Elred.

**Metal bath or slag bath melter-gasifier furnace.** Bath melter-gasifier furnaces include an extended bath, similar to that used in open-hearth steelmaking. This bath can be metal based or slag based. Fine ores and coal are injected into the bath where reduction, smelting, and coal gasification take place. The examples of processing schemes that use metal slag melter-gasifier furnaces include Romelt and Ausiron. The examples of processing schemes that use metal bath melter-gasifier furnaces include DIOS and HIsmelt.

## Iron Oxide Reduction and Smelting Fundamentals

Ore reducibility depends on mineral properties, reaction mechanisms, and rate-controlling steps.

### *Iron Oxide Reduction*

The kinetic aspects of iron oxide reduction include consideration of rates at which chemical reactions involved in the production of iron from its ores will take place. The reducibility of an ore, defined as the ease with which the ore can be reduced, embodies the principles of reduction kinetics. Reducibility of an ore depends on other properties such as density, porosity, particle size distribution, surface area, grain size and structure, and type and dispersion of gangue minerals. The success of the DR process depends on the reducibility of the ore and satisfying the kinetic aspects of reduction. Further discussion regarding the reduction fundamentals and kinetics is provided by Lu and Ross (Lu 1999; Ross 1972; Ross 1973).

Iron oxide reduction kinetics are important for DR processes, as they control the rate at which metallic iron is produced. This influences the production rate, product quality, economic feasibility, and competitiveness of one process with another. The rate of chemical reactions increases as the temperature increases. The reduction rate is less important in the BF process than in the DR process, because the BF operates at much higher temperatures. Rather than reaction kinetics, the BF process is limited by the availability of heat and reducing agents (i.e., concurrent gas flow and pressure drop). For DR processes, reduction takes place in the solid state, thus the maximum temperatures that can be achieved and the corresponding reduction rate are limited (Lu 1999; Ross et al. 1980; Ross 1972). Porosity and pore size distribution are the most important factors in controlling reducibility (Joseph 1936). The soft earthy hydrated ores have the best reducibility, followed by the soft hematites, the hard hematites, and finally the hard dense magnetites (Lu 1999; Joseph 1936). If a particle of a hard dense partially reduced ore is sectioned, a topochemical type of reduction can be observed. It would include a core of hematite surrounded by three concentric layers: an inner layer of magnetite, a layer of wüstite, and an outer layer of metallic iron. For porous ores, homogeneous-diffusion types of reduction with no district interfaces but a gradual transformation from iron on the outside to hematite at the center can be observed. However, at very high magnifications, the microstructure of the grains making up the porous particle will also indicate a topochemical type of reduction (Ross 1973; Bitsianes and Joseph 1955).

For the reduction reactions to take place, the reducing agents must contact the surface of the iron oxide phases. This requires the reacting gas to diffuse inward and the product gas to diffuse outward at least through the outer iron layer to react with the wüstite layer. Several different mechanisms to facilitate this have been proposed. The most widely accepted mechanisms include the following:

- For dense ore particles where the reducing gas is unable to contact the magnetite layer or hematite core, it is predicted that solid-state diffusion of ferrous ions as proposed by Edstrom takes place (Edstrom 1953; Edstrom and Bitsianes 1955). The solid-state diffusion of ferrous ions through the wüstite crystal lattice is facilitated by the presence of lattice vacancies. Some of the ferrous ions

and electrons migrate to nucleation sites where they precipitate as metallic iron; other ferrous ions and electrons diffuse across the wüstite and magnetite layers where they react with magnetite and hematite to produce wüstite and magnetite. The solid-state diffusion rate of ferrous ions through wüstite is much greater than the gaseous diffusion rate of either hydrogen or carbon monoxide through the pores of the ore particles at the temperatures used for DR processes. Thus, solid-state diffusion is not usually a rate-determining step (Lu 1999; Ross 1972).
- For very porous ores, reducing gases can penetrate faster than they can react at any one interface.

#### *Reaction Mechanisms*

For reduction of hematite by a reducing gas, reduction mechanisms include (Lu 1999; Lien et al. 1971) the following:

- Diffusion of the reducing agent from the moving gas stream to the surface of the ore particle and then to the interior of the particle
- Reaction of the reducing agent with one oxygen atom from iron oxide to form carbon dioxide or water at one of the solid–solid interfaces (hematite–magnetite, magnetite–wüstite, wüstite–iron)
- Diffusion of the reduction product gases (carbon dioxide and water) to the exterior of the particle and through the main gas stream to be carried away

These steps are sequential, and the slowest step will be the rate-controlling step for complete reduction of the iron oxide.

Hydrogen reduction is endothermic; adequate heat must be supplied to the reaction site for completion of these reactions. Thus, heat transfer to the reaction site, rather than diffusion, may be the overall rate-controlling step.

The rate of endothermic reactions increases faster with an increase in temperature rather than effective gas diffusivity. Wüstite reduction by hydrogen tends to be controlled by interfacial reaction at a lower temperature, shorter reaction time, and smaller particles. At higher temperatures, longer reaction time, and larger particles, however, gas diffusion is a rate-controlling step.

Heterogeneous reactions take place only in the interfacial reaction zone. This region is located at the phase boundary with a finite thickness including the absorbed gas molecules on the solid surface in a gas–solid system. Effective diffusion through the interfacial reaction zone depends on the pore structure, which changes with time because of phase changes and sintering at high temperatures.

The changes in the pore structure can be explained by changes in crystal structure that take place during stepwise reduction of hematite through magnetite and wüstite to metallic iron (Weiss et al. 2011). In hematite, the oxygen atoms are arranged in the hexagonal close-packed structure. As the hematite reduces to magnetite and wüstite, oxygen atoms undergo a severe readjustment, to form a face-centered cubic structure. This results in approximately a 25% increase in volume (Edstrom 1953; Edstrom and Bitsianes 1955). This tends to open up the structure and facilitate further reduction reactions. In the transformation of magnetite to wüstite, the oxygen lattice remains unchanged while iron atoms diffuse in to fill the vacant sites in the iron lattice. Wüstite has a variable composition: There is a small increase in volume as its composition changes from that in equilibrium with magnetite to that in equilibrium with metallic iron (approximately 7%–13% volume increase). The nucleation and growth of iron crystals result in shrinkage, leading to an increase in porosity and greatly enhancing diffusion and reduction (Edstrom 1953; Elliott and Gleiser 1960).

For completion of iron oxide reduction reactions, kinetically the most important reaction is the reduction of wüstite to metallic iron. At the beginning of wüstite reduction, the gas–solid interface recedes as oxygen atoms are removed by the reducing gas and iron ions and electrons diffuse into the interior. Wüstite composition gradually changes across its stability field from the boundary value with magnetite toward equilibrium value with metallic iron. This interplay between interfacial reaction and solid-state diffusion in wüstite determines the mechanism of nucleation and growth of metallic iron. The mechanisms of nucleation and growth of metallic iron include the following (Lu 1999):

- When the rate of creation of excess iron atoms is much faster than solid-state diffusion to the interior of the wüstite grain, the Fe/O ratio increases rapidly, and the nucleation zones become supersaturated with iron and wüstite. This leads to iron nucleation at numerous sites and the growth of iron nuclei to overlap and cover the whole surface of the grain.
- When the accumulation of excess iron atoms near reaction sites is minimal, the Fe/O ratio is uniform and increases as the interfacial reaction proceeds. As the reaction proceeds, wüstite grain becomes supersaturated, and the nucleus of iron appears on the surface of wüstite. Then the excess iron atoms move to the nucleus, leading to its growth.

The mechanism of growth of the iron nucleus with fresh iron involves pushing up the previously nucleated iron. In the case of an area where the base is constant, the shape of iron growing out may look like whiskers (Lu 1999; Bahgat et al. 2009). In the case of an area where the base is enlarged laterally, the shape of iron growing out may look like pyramids.

#### *Rate-Controlling Steps*

Among researchers, there is a considerable diversity of opinion about the mechanism of iron oxide reduction and rate-controlling steps. Numerous viewpoints have emerged from the studies conducted, including the following (Seth and Ross 1965):

- Rate is controlled by the diffusion of gas through the boundary layer of stagnant gas. This theory is true mainly for packed beds where the flow of gas through the bed is crucial. For a single particle, the boundary layer may be prevented from being the rate-controlling step if the flow rate of the reducing gas is above the critical flow rate (Chatterjee 1994).
- Rate is proportional to the area of metal–oxide (Fe–FeO) interface. Several researchers have reported a linear advance of the Fe–FeO interface, which support the theory for reduction being controlled by surface area (porosity) (Turkdogan and Vinters 1972). However, several other researchers have reported that this theory is not always applicable and when it is applicable, it does not

hold in the final stages of reduction when the Fe–FeO interface is supersaturated.

- Rate is controlled by the transportation of reducing gas from the main stream to the metal–oxide interface and the product gas out from the metal–oxide interface to the main stream. In addition to the researchers who supported this theory, others have indirectly proved that sintering and recrystallization of iron cause a decrease in reduction rate by inhibiting the transportation of gas through the sintered layer (Udy and Lorig 1942). Several researchers have rejected this theory on the basis that they could not obtain a relationship between the particle diameter and time required to reach a certain degree of reduction.
- Rate is controlled by multiple steps with their relative contributions varying during the course of reduction.
- Several researchers have reported that in the beginning of the process, the rate-controlling step was the surface reaction, but after a layer of iron was formed, the diffusion of gas became the rate-controlling step. Toward the end, rate was controlled by porosity (Seth and Ross 1965; Turkdogan and Vinters 1971, 1972; Turkdogan et al. 1971). This is the most widely accepted theory for determination of the rate-controlling step and process control.

## Reducing Gas Generation and Gas Reforming

Reducing gas generation is achieved by the gasification of a carbonaceous solid fuel or the reforming of natural gas. Natural gas is approximately 80% methane ($CH_4$) and composed of a mixture of hydrocarbons and in some cases contains low amounts of nitrogen. The use of natural gas directly in ironmaking faces the issue of gas decomposition and consequent carbon deposition on the iron oxide. The deposited carbon may act as a barrier to contact between the reducing gas and iron oxide, hindering the reduction reaction. Therefore, natural gas needs to be reformed.

Carbonaceous solid fuels need to meet specific requirement for use in BFs and in DR processes such as SL/RN. Coking coal with low amounts of ash and sulfur is needed for use in cokemaking and further in BFs. Reactive coals with high volatile matter content and high ash-softening temperature are the ones used in DR. If those requirements are not met, the gasification of a low-quality coal may be an alternative for ironmaking.

In both reforming and gasification, the reducing gas will be mainly composed of a mixture of CO and $H_2$ in different amounts. This gas is injected into a shaft furnace where reduction of iron ore is performed to produce DRI.

### *Reforming of Natural Gas*

Following are the main reactions related to reforming of natural gas:

Dry reforming: $CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO$

Steam reforming: $CH_4 + H_2O \leftrightarrow 3H_2 + CO$

Water–gas shift reaction: $H_2O + CO \leftrightarrow CO_2 + H_2$

Methane conversions for dry reforming are higher than for steam reforming, demonstrating a higher thermodynamic efficiency for the use of $CO_2$ as the reforming agent. Some dry reforming happens in the steam reforming reactor and vice versa. This is because of the water–gas shift reaction that causes the interchange between $CO_2$ and $H_2O$. Moreover, the final proportion between CO and $H_2$ in the product gas is also dependent on the water–gas shift reaction.

Parallel reactions include carbon deposition, which takes place according to the following reactions:

$$2CO \leftrightarrow C + CO_2$$

$$CH_4 \leftrightarrow 2H_2 + C$$

$$H_2 + CO \leftrightarrow C + H_2O$$

Inside the reduction reactor, carbon deposition and formation of iron carbide are desirable. However, in the reforming reactor, carbon deposited on the surface of the catalyst will reduce its activity, causing a drop in efficiency. In extreme cases, a blockage of the reactor may occur. Additionally, the metallic material used in the reactor walls can fail because of pit corrosion, termed *metal dusting*. This failure is caused by the carburization of the metal with initial formation of carbides that then decompose into fine particles of metal and solid carbon. This type of corrosion causes holes in the reformer tubes.

Therefore, reforming reactors are operated in conditions in which carbon deposition is avoided. In practice, steam reforming reactors operate with steam-to-carbon ratios ($H_2O/C$ or $H_2O/CH_4$) greater than 1, as pressures are usually higher than 10 atm. Dry reforming is operated at temperatures as high as 1,000°C and a $CO_2/CH_4$ ratio of 1.

Industrial application of reforming of natural gas for DR of iron is mainly applied in the Energiron III, Energiron ZR, and Midrex processes. The only industrial application of dry reforming of natural gas is in the Midrex process. The reformer is a reactor composed of several tubes containing a bed of a catalyst of nickel supported on alumina. The Midrex reformer is a stoichiometric reformer, and hence, the amount of natural gas is controlled to react with all the $CO_2$ and some of the residual $H_2O$ present in the reforming gas. In the Midrex process, the reformed gas does not need to be cooled prior to injection into the shaft furnace, which saves some energy.

The Energiron III process uses a steam reformer operated at temperatures above 700°C and pressures above 5 atm. Therefore, an excess of steam is necessary to obtain high conversions of methane. The steam-to-carbon ratio used in the reforming process is 2 or higher. Consequently, the reformed gas needs to be cooled to condense this excess steam. The cooled reformed gas is then mixed with the top gas coming from the shaft furnace. Finally, the reformed gas mixed with the top gas is directed to the gas heater to reach the necessary temperature for reduction and then directed to the shaft furnace.

The Energiron ZR process brings a different concept without a reformer. In this case, reforming reactions occur inside the shaft furnace and the DRI serves as the catalyst. The top gas from the shaft furnace is treated in the same way as in the Energiron III for removal of water and $CO_2$. This gas is then mixed with natural gas and humidified with controlled amounts of water. The humidified gas passes through the gas heater and is then directed to the shaft furnace.

The amount of CO in the reducing gas is higher for the Midrex process because it is produced by dry reforming. Reducing gas for the Energiron process is richer in $H_2$, and for the ZR concept, the amount of $CH_4$ is particularly high.

In addition to reforming, oxygen and natural gas may be mixed with the reformed gas before injection into the shaft furnace. Oxygen is used to partly combust the reducing gases (CO, $H_2$, and $CH_4$) for temperature increase. This will enhance the rate of reduction inside the shaft furnace. Natural gas is injected either to burn or to carburize the reduced iron.

Both the Midrex and Energiron processes have adapted versions to work with coke oven gas. Reforming is also necessary because of the high amounts of hydrocarbons in this gas. Midrex has patented a technology—the Thermal Reactor System—in which a partial oxidation of the coke oven gas is performed to generate the reducing gas rich in $H_2$ and CO.

## ENVIRONMENTAL CONSIDERATIONS

Ironmaking processes produce solid, gaseous, and liquid emissions, which are of environmental concern.

### Blast Furnace Technology

The BF ironmaking process produces solid and gaseous emissions. There may also be liquid emissions, depending on how the cooling system is designed and how the gaseous and solid by-products are treated.

The BF generates a large quantity of off-gas, approximately 1,600 $m^3$/t of hot metal (Lankford et al. 1985b). On a dry basis, the gas is composed of roughly 23% $CO_2$, 21% CO, 3% $H_2$, and the balance $N_2$. There may also be small amounts of sulfur and volatile organic compounds, depending on the charge materials. The actual BF gas volume and composition depend on the thermodynamic equilibrium in the furnace and a function of the top-charged materials as well as the fuels and oxygen that may be injected into the lower portion of the furnace through the tuyeres. The gas has a heating value of approximately 3.54 KJ/$m^3$, which is a function of the gas composition (Lankford et al. 1985b).

During BF operation, lighter-weight, smaller solids are entrained in the off-gas. A dry separator that forces the gases to make an abrupt direction change causes the heavier solids to fall out of the gas by centrifugal force. The solids collected by this process are dry. A wet venturi scrubber may be used to remove the smaller particulate. Venturi scrubbers use water droplets and the energy from a high pressure to force water droplets to combine with the particulate and other water droplets to form slurry drops large enough to fall out of the gas stream. The particulate concentration in the BF gas exiting the venturi scrubbers is significantly reduced, and the gas is ready to be used as an energy source or flared. The slurry collected by the venturi scrubber may be treated by a filter press or other means to separate the particulates from the water. The water may be treated and recycled to the scrubber. The removed solids are in sludge form and may contain enough carbon to be used as a solid fuel. However, its use may be limited by the presence of iron oxide or other elements originating from steel scrap or other materials charged into the furnace. The sludge may be landfilled if all regulations that apply for the sludge composition are met. Recycling the sludge in an iron ore agglomeration process or separating the carbon and iron from undesirable elements, such as zinc, has been considered, but usually the processing costs outweigh the benefits of recovering the fuel or raw materials.

Roughly up to 65% of the BF gas is used to heat the stoves. The remainder is used elsewhere in the integrated plant or flared. The solids removed from the BF gas are either dry particles or a sludge-type material. The solids may be recycled within the integrated process, in either ore agglomeration or coke making, or landfilled, depending on the composition and regulations.

The major solid by-product of the BF ironmaking process is slag. It can be used as an ingredient to make cement. It is an attractive substitute for limestone as it contains a significant amount of calcium that does not need to be calcined. Initially, slag may contain a significant amount of iron or iron oxide. The iron-bearing portion is magnetically removed after the solidified slag is crushed into manageable portions.

It should be noted that sulfur is typically part of the BF ironmaking process. A majority of the sulfur originates from the coke but some may also be introduced via the iron oxide feed materials. Nearly all of the sulfur exits the BF as part of the liquid iron or slag. In some cases, the slag chemistry may be altered to maximize sulfur pickup and minimize the amount of sulfur in the iron. The iron desulfurization capability downstream of the BF is a factor in determining the slag chemistry.

Regardless, the BF slag will likely contain sulfur in some form. Consideration should be given to the possible emission of gases containing sulfur as the slag is cooled in the slag pits. In the case of slag granulation, the water may pick up sulfur compounds and need to be appropriately treated.

The liquid iron or hot metal produced may be desulfurized before the steelmaking process. The sulfur is typically removed by injecting an alkali reagent into the liquid metal. This process generates a slag type of material that is skimmed from the liquid metal. The iron-bearing materials in the slag may be removed from the slag and recycled into the process. The sulfur content in both the iron-bearing and non-iron-bearing materials influences how those materials may be recycled, landfilled, or used outside of the process. These are additional solids emitted from the process.

BF operation requires significant cooling, which is done with water. The water-cooling system can be an open- or closed-loop system. Open systems are noncontact systems in which the cooling water is not part of the process and is confined to being discharged, usually into the original body of water. Monitoring of the amount of water consumed and the discharge temperature may be required by regulations. In the case of closed cooling systems, any blowdown discharge required to meet optimal water chemistry may also be regulated.

Any water discharged may be regulated. The dewatering process discharge may contain suspended and dissolved solids that need to be removed before being recycled into the process or discharged to maintain proper water chemistry.

### Alternative Technologies

In general, the solid, gaseous, and liquid emissions from the alternative ironmaking processes are similar to the BF process. The DRI exhaust gases emerge from the top of the reactor at a temperature in the range of 250°–350°C and usually at a higher pressure, up to 6.8 atm, than BF gas (Lankford et al. 1985a; J.O.L. Morales, personal communication). The gas consists of carbon dioxide, water vapor, nitrogen, carbon monoxide, and hydrogen as a result of the iron reduction thermodynamic equilibrium. Similar to the BF process, the DRI exhaust gas has chemical energy, but it is not used as a fuel; rather, it is treated so that the reducing gases may be recycled through the process.

The gases from the top of the reactor contain dust particles that are dragged out of the reactor because of the direct contact between the gas and the solid. The exhaust gas is cleaned and quenched. Typically, most of the carbon dioxide is removed from the exhaust gas to recycle the reducing gases, hydrogen, and carbon monoxide into the process. The removed carbon dioxide may be released to the atmosphere or liquefied and sold as appropriate.

In the solid-based DRI process, the gases exiting the reactor, usually a rotary hearth furnace, are fully oxidized, hot, and near atmospheric pressure. The thermal energy may be recovered via heat exchanger. The exhaust gases will likely contain particulates, nitrogen oxides (NOx), and sulfur dioxide ($SO_2$). The fuel and reductant in the solid-based DRI process is usually coal that contains some sulfur. Depending on the volume and concentrations, the exhaust gas will likely be passed through a system to remove the particulates and may be treated to remove some of the $SO_2$ and NOx.

In both the gas- and solid-based DRI processes, it is necessary to supply thermal energy to support the chemical reactions. Depending on how the system is designed, the thermal energy may be provided by indirectly preheating the process gases before they enter the reactor. The fuel for the indirect heating is typically natural gas, and the exhaust gases from the indirect heating process will essentially be free of particulates and $SO_2$. However, it may be necessary to treat the exhaust gases for NOx.

Similar to the BF process, the solids removed from the exhaust gas of either the gas- or solid-based DRI processes are either dry particles or a sludge-type material. They may be recycled into the iron ore pellet process, sold, or landfilled, depending on the composition and regulations.

Fines are generated during the handling of both the iron ore pellets fed to the reactor and the DRI produced. Material handling systems equipped with highly efficient dust collecting units are employed to capture the airborne fines. These solids may be briquetted and fed into the reactor with the iron ore pellets.

Both the gas- and solid-based DRI processes require a significant amount of cooling, which is done with water. The water-cooling systems are similar to those used for the BF process, and the environmental considerations are similar.

### Greenhouse Gas Emissions

Currently, there is some concern about the emission of carbon dioxide ($CO_2$) and other gases that may contribute to climate change. Although $CO_2$ emissions are not regulated by the U.S. federal government, several U.S. states and several countries around the world have established cap-and-trade or other systems in an attempt to reduce $CO_2$ emissions.

As with nearly all energy-intensive processes, such as the manufacture of electricity, cement, glass, paper, and chemicals, the ironmaking process emits a relatively large amount of $CO_2$. On an intensity basis, the BF process to make iron emits roughly 1.3 t of $CO_2$ per ton of liquid, carbon-saturated iron (IEA 2000). Alternatively, roughly 0.8 t of $CO_2$ is emitted in making a ton of liquid iron (containing some carbon) from melting DRI in an EAF. The amount of energy required to reduce and melt the iron from iron ore is the same in both processes. The lower $CO_2$ emissions from the DRI-EAF process can be primarily attributed to the use of natural gas as both a fuel and reductant. Although a significant amount of natural gas may be used in the BF process, the process requires some minimum amount of coke (from coal) to maintain bed porosity within the furnace.

Note that the calculation of $CO_2$ emissions can be complex and should be well thought out, particularly if the calculated emission intensity is used to compare processes. To understand the meaning of the value, it is important to note the basis of the $CO_2$ emission calculation; whether it is scope 1, scope 2, scope 3 (EPA 2018), or some other type of calculation. Briefly, the scope 1 emission only accounts for carbon that crosses the boundary in liquid or solid form. The scope 2 calculation adds the emissions associated with energy, typically electricity, which crosses the boundary either into or out of the process. Scope 3 calculations account for emissions associated with preparing the materials that cross the boundary. For example, the DRI iron ore pellets usually have a higher iron content than BF pellets, and thus, more $CO_2$ may have been emitted to prepare the higher-quality pellets. It may be somewhat obvious that a thorough scope 3 or other type of in-depth calculation may require at least a few assumptions and the development of standard $CO_2$ emission factors for various materials.

## ACKNOWLEDGMENTS

The authors express their appreciation to Jane M. Grochowski for her time and efforts in reviewing this chapter and her valuable edits. Appreciation is also extended to Jack E. Grochowski for his contributions in preparing some of the schematic drawings, his time and efforts in reviewing the chapter sections, and his commendable edits.

Special thanks go to Joseph J. Poveromo, John A. Ricketts, Baojun Zhao, Jianling Zhang, Yuexin Han, Chu Mansheng, Joel Morales, Naryan Govidaswami, Ronnie Dabideen, and Mahdi Farahani for their technical input and guidance.

## REFERENCES

AIST (Association for Iron and Steel Technology). 2018. *AIST Industry Roundups: North American Blast Furnace Roundup*. Warrendale, PA: AIST.

Anameric, B., and Kawatra, S.K. 2007. Properties and features of direct reduced iron. *Miner. Process. Extr. Metall. Rev.* 28(1):59–116.

Anameric, B., and Kawatra, S.K. 2008. Direct iron smelting reduction processes. *Miner. Process. Extr. Metall. Rev.* 30(1):1–51.

Bahgat, M., Abdel Halim, K.S., El-Kelesh, H.A., and Nasr, M.I. 2009. Metallic iron whisker formation and growth during iron oxide reduction: $K_2O$ effect. *Ironmaking Steelmaking* 5(36):379–387.

Bitsianes, G., and Joseph, T.L. 1955. Topochemical aspects of iron oxide reduction. *Trans. AIME* 7(5):639–645.

Carmichael, I.F. 2012. Blast furnace design I (Lecture no. 6). Presented by D. Berdusco at the 22nd McMaster University Blast Furnace Ironmaking Course, Hamilton, ON, May 13–18.

Chatterjee, A. 1994. *Beyond the Blast Furnace*. Boca Raton, FL: CRC Press.

Dahlstedt, A., Halin, M., and Wikstrom, J-O. 2000. Effect of raw material on blast furnace performance. In *The Use of an Experimental Blast Furnace: 4th European Coke and Ironmaking Congress Proceedings*. Vol. 1. pp. 138–145.

Edstrom, J.O. 1953. The mechanism of reduction of iron oxides. *J. Iron Steel Inst.* 175(11):289.

Edstrom, J.O., and Bitsianes, G. 1955. Solid state diffusion in the reduction of magnetite. *J. Met.* 7(6):760–765.

Elliott, J.F., and Gleiser, M. 1960. *Thermochemistry for Steelmaking*. Boston: Addison-Wesley.

EPA (U.S. Environmental Protection Agency). 2018. Greenhouse gases at EPA. www.epa.gov/greeningepa/greenhouse-gases-epa. Accessed July 2018.

Geerdes, M., Kurunov, I., Lingiardi, O., and Ricketts, J. 2015. *Modern Blast Furnace Ironmaking: An Introduction*, 3rd ed. Amsterdam, Netherlands: IOS Delft University Press.

Hashimoto, S., Suzuki, A., Yoshimoto, H. 1977. Burden and gas distribution in the blast furnace. In *Ironmaking Proceedings*, vol. 36. New York: AIME.

Helenbrook, R.G. 2012. Blast furnace design II. Presented at the 22nd McMaster University Blast Furnace Ironmaking Course, Hamilton, ON, May 13–18.

IEA (International Energy Agency). 2000. *Greenhouse Gas Emissions from Major Industrial Sources. III: Iron and Steel Production*. Report No. PH3/30. Paris, France: IEA. www.ieaghg.org/docs/General_Docs/Reports/PH3-30%20iron-steel.pdf.

Joseph, T.L. 1936. Porosity, reducibility, and size preparation of iron ores. *Trans. AIME* 120:72–98.

Lankford, W.T., Samways, N.L., Craven, R.F., and McGannon, H.E. 1985a. Direct reduction and smelting processes. In *The Making, Shaping and Treating of Steel*, 10th ed. Edited by W.T. Lankford, N.L. Samways, R.F. Craven, and H.E. McGannon. Pittsburgh, PA: Association of Iron and Steel Engineers.

Lankford, W.T., Samways, N.L., Craven, R.F. and McGannon, H.E. 1985b. The manufacture of pig iron in the blast furnace. In *The Making, Shaping and Treating of Steel*, 10th ed. Edited by W.T. Lankford, N.L. Samways, R.F. Craven, and H.E. McGannon. Pittsburgh, PA: Association of Iron and Steel Engineers.

Lanyi, M.D., Cao, J., and Terrible, J.A. 2012. A sensible route to energy efficiency improvement and $CO_2$ management in the steel industry. Presented at the 2012 Iron and Steel Technology Conference and Exposition (AISTech).

Lien, H.O., El-Mehairy, A.E., and Ross, H.U. 1971. A two-zone theory of iron-oxide reduction. *J. Iron Steel Inst.* 209:541–545.

Lu, W-K. 1999. Kinetics and mechanism in direct reduced iron. In *Direct Reduced Iron: Technology and Economics of Production and Use*. Edited by J. Feinman and D.R. MacRae. Warrendale, PA: Iron and Steel Society.

Lu, W.K. 2012. Blast furnace reactions (Lecture no. 2). Presented at the 22nd McMaster University Blast Furnace Ironmaking Course, Hamilton, ON, May 13–18.

Lu, W.K., and Ranade, M.G. 1991. Recent advances in blast furnace ironmaking in North America. *ISIJ Int*. 31(5):395–402.

Markotic, A., Dolic, N., and Trujic, V. 2002. State of the direct reduction and reduction smelting processes. *J. Min. Metall. Sect. B* 38(3-4).

Meijer, K., Zeilstra, C., Teerhuis, C., Ouwehand, M., and van der Stel, J. 2013. Developments in alternative ironmaking. *Trans. Indian Inst. Met.* 66(5-6):475–481.

Omori, Y., and Shimomura, Y. 1982. Flow of gas, liquid and solid. In *Blast Furnace Phenomena and Modelling*. Edited by Committee on Reaction within Blast Furnace Joint Society of Iron and Steel Basic Research, The Iron and Steel Institute of Japan. London: Elsevier Applied Science.

Peacey, J.G., and Davenport, W.G. 1979. *The Iron Blast Furnace, Theory and Practice*. Oxford: Pergamon Press.

Poveromo, J.J. 2010. Coke in the blast furnace (Lecture no. 2). Cokemaking Course. McMaster University, Hamilton, ON.

Ricketts, J.A. 2017. How a blast furnace works. http://foundrygate.com/upload/artigos/How%20a%20Blast%20Furnace%20Works.pdf. Accessed July 2018.

Ross, H.U. 1972. The kinetics of iron ore reduction. www.aimehq.org/doclibrary-assets/books/Ironmaking%20Proceedings%201972/Ironmaking%20Proceedings%201972%20-%20044.pdf. Accessed July 2018.

Ross, H.U. 1973. The fundamental aspects of iron ore reduction. In *Symposium on Science and Technology of Sponge Iron and Its Conversion to Steel*. Jamshedpur, India: National Metallurgical Laboratory.

Ross, H.U., McAdams, D., and Marshall, T. 1980. Kinetics and mechanisms in direct reduced iron. In *Direct Reduced Iron: Technology and Economics of Production and Use*. Edited by J. Feinmen and D.R. MacRae. Warrendale, PA: Iron and Steel Society.

Sano, N., Lu, W.K., and Riboud, P.V. 1997. *Advanced Physical Chemistry for Process Metallurgy*. New York: Academic Press.

Seth, B.B.L., and Ross, H.U. 1965. The mechanism of iron oxide reduction. *Trans. AIME* 233:180.

Smith, R., and Corbett, M. 1987. Coal-based ironmaking. *Ironmaking Steelmaking* 14:49–75.

Tovarovskii, I.G., Bol'shakov, V.I., Togobitskaya, D.N., and Khamkhot'ko, A.F. 2009. Influence of the softening and melting zone on blast-furnace smelting. *Steel Transl.* 39(1):34–44.

Turkdogan, E.T., and Vinters, J.V. 1971. Gaseous reduction of iron oxides: Part I. Reduction of hematite in hydrogen. *Metall. Trans. B* 2(11):3175–3188.

Turkdogan, E.T., and Vinters, J.V. 1972. Gaseous reduction of iron oxides: Part III. Reduction-oxidation of porous and dense iron oxides and iron. *Metall. Trans. B* 3(6):1561–1574.

Turkdogan, E.T., Olsoon, R.G., and Vinters, J.V. 1971. Gaseous reduction of iron oxides: Part II. Pore characteristics of iron reduced from hematite in hydrogen. *Metall. Trans. B* 2(11):3189–3196.

Udy, M.C. 1959. Recent developments in strategic-Udy smelting process. In *Electric Furnace Conference Proceedings*. New York: AIME.

Udy, M.C., and Lorig, C.H. 1942. Low temperature gaseous reduction of a magnetite. Presented at the Metals Technology Meeting, AIME, Cleveland, OH.

Udy, M.C., and Udy, M.J. 1958. Production of iron and steel by the strategic-Udy process. In *Electric Furnace Proceedings*. Warrendale, PA: Association for Iron and Steel Technology.

Venkateswaran, V., and Brimacombe, J.K. 1977. Mathematical model of the SL/RN direct reduction process. *Metall. Trans. B* 8(2):387–398.

Wallace, J.P., Dzermejko, A.J., Hyle, F.W., Goodman, N.J., Lee, H.M., and Zeigler, R.W. 1999. The blast furnace facility and equipment. In *The Making, Shaping and Treating of Steel*, 11th ed. Ironmaking Volume. Edited by D.H. Wakelin. Warrendale, PA: Association for Iron and Steel Technology.

Weiss, B., Sturn, J., Voglsam, S., Strobl, S., Mali, H., and Schenk, J. 2011. Structural and morphological changes during reduction of hematite to magnetite and wüstite in hydrogen rich reduction gases under fluidized bed conditions. *Ironmaking Steelmaking* 38(1):65–73.

World Steel Association. 2015. Fact sheet: Steel and raw materials. www.worldsteel.org. Accessed July 2018.

Zervas, T., McMullan, J.T., and Williams, B.C. 1996a. Direct smelting and alternative processes for the production of iron and steel. *Int. J. Energy Res.* 20(12):1103–1125.

Zervas, T., McMullan, J.T., and Williams, B.C. 1996b. Gas-based direct reduction processes for iron and steel production. *Int. J. Energy Res.* 20(2):157–185.