

Molten iron being poured into the furnace



Ferrous Extractive metallurgy

2

QUALITY OF COKE

The efficiency of a blast furnace is directly dependent on the permeability of the charge in the furnace which is again directly depends on the quality of the coke.

The quality of coke should be such that it gives minimum of operational difficulties and maximum of production rate at minimum of coke consumption.

The value of coke (as a BF fuel) depends on the following properties:

- (i) **Chemical composition,**
- (ii) **Reactivity,**
- (iii) **Size range,**
- (iv) **Thermal stability at high temperatures**
- (v) **Strength and abrasion resistance.**

(i) Chemical composition of the coal:

- Generally, chemical composition of coke means **fixed carbon, volatile matter, ash, sulphur, phosphorus and other impurities.**
- Fixed carbon in coke acts as a fuel as well as reducing agent in the BF.
- As the ash content increases, the available carbon of coke decreases, and subsequently, the heat supply to the furnace per unit weight of coke decreases.
- Very good quality coke should have **> 85% fixed carbon, < 10% ash, < 2% volatile matter, 0.6–1.5% S and 0.04% P.**
- **The ash** is the inorganic residue afterburning; ash contains refractory oxides, e.g., 55–60% SiO₂, 15–30% Al₂O₃, 4–10% Fe₂O₃, 2–3% CaO, 1–4% MgO, 2–8% Na₂O+K₂O and trace of TiO₂.

Due to the presence of high ash content in coke;

- (a) the coke rate in BF will be high, 1% increasing of ash, coke rate increases 1–2%;
 - (b) slag volume will be more;
 - (c) productivity of BF will be low, due high volume of slag to low utilization of useful volume of BF, 1% increasing of ash, productivity decreases 2–3%;
 - (d) phosphorus in hot metal will be increased.
- Sulphur and phosphorus, usually present in coke in form of inorganic compounds, are later transferred into hot metal.
 - Most of the sulphur and part of the phosphorus in hot metal comes from coke, and remaining phosphorus comes from the ore.
 - Increasing sulphur and phosphorus in coke means increased sulphur and phosphorus contents in hot metal and as well as more consumption of flux during steelmaking are likely to increase costs in the steelmaking.
 - If ash of coke contains excess sulphur, that coke should be avoided in BF.

The calorific value (Q) of coal is the heat generated by its complete combustion with oxygen.

- The calorific value is a complex function of the elemental composition of the coal.
- The calorific value can be determined experimentally using calorimeters.
- The following formula used for the calorific value (Q, kJ/kg) of coal, when the oxygen content is less than 10%:

$$Q \text{ (kJ/kg)} = 337C + 1442 \left\{ H - \left(\frac{O}{8} \right) \right\} + 93S$$

where C, H, O and S are the weight percent of carbon, hydrogen, oxygen and sulphur in the coal, respectively.

(ii) Reactivity of coke:

- Reactivity of coke may be defined as the rate of reaction between coke and oxygen or any other gaseous phase (e.g., CO₂, H₂O).
- The reactivity of a coke is a measure of its ability to react with CO₂ to form CO, **according to Boudouard reaction.**



i.e., for conversion of CO₂ → CO, this is also known as gasification of carbon by carbon dioxide.

- The reactivity is particularly important from the point of view of rate of its combustion at the tuyere level and its reaction with the ascending gases.

The degree of gasification of carbon (FC) is defined as:

$$F_C = \left(\frac{\text{Weight loss of carbon in the sample}}{\text{Total weight of carbon in the sample}} \right)$$

The term reactivity (RC) is commonly used to denote the rate of the gasification reaction.

$$\text{i.e. } R_C = \left(\frac{dF_C}{dt} \right)$$

The higher the reactivity of the coke, the faster is the gasification reaction.

- Reactivity has a significant influence on the reduction process; hence, coke with high reactivity values is preferred.
- The rate of coke burning of overall controls the rate of production of a BF.

The rate of coke burning is directly proportional to:

- (a) coke area exposed to the blast,
- (b) temperature and pressure of the blast and
- (c) affinity of the carbon for oxygen.

(iii) Size range of coke

- Affects the distribution of materials inside the furnace and consequently the gas flow rate which control production rate directly.
- The size of coke is generally chosen to match the size of other raw materials and is much bigger than the size of the iron-bearing materials to ensure maximum bed permeability for smooth furnace operation.
- To ensure a sufficiently high permeability of the charge, the charge coke should be at least 80% of +40 mm size. If the size of iron-bearing material is 13 mm, size of coke should be 52 mm.
- Size ratio of coke: iron-bearing materials is 4 : 1, i.e., minimum size of coke should be 3–5 times more than of the iron-bearing material.
- +80 mm fraction of coke should be removed as far as possible.

(iv) Thermal stability at high temperatures:

Due to descending of coke, the BF gets gradually heated from 200 to 1600°C before it burns in front of the tuyeres.

(v) Strength and abrasion resistance:

- Coke should have sufficient strength to withstand handling and charging action before landing in the BF.
- Coke should stand high temperature and load of 23–25 m tall burden material standing above it.
- Height of the furnace is controlled by the strength of coke.
- If coke breaks down into fines under the conditions, that will affect the furnace permeability.

Preparation of Coke

Table 1: shows the typical chemical composition of coke that may be of good quality.

Table 1: Typical coke analysis.

Fixed carbon (%)	Volatile matter (%)	Ash (%)	Nitrogen (%)	Sulphur (%)
87–92	0.2–0.5	8–11	1.2–1.5	0.6–0.8

- **Coke**, which is used as fuel in blast furnaces during the ironmaking process, is made by heating coking coal at a high temperature in a series of ovens known as a coke oven battery.
- **A coke oven battery** is a group of ovens in which coals are heated to high temperature (1100°C) in the absence of air.
- The carbon is concentrated, and the volatile matter is removed from the coal to produce coke by this process.
- Metallurgical coke is produced by heating coking coal (25–30 wt% volatiles content) in the absence of air. This causes the volatiles to be distilled from the coal to give a porous coke which is (i) reactive at high temperatures and (ii) strong enough to take whole load of materials within the blast furnace.

- In general, ovens are made from silica bricks and a single battery can contain as many as 100 rows, vertical retort chambers, each separated from its neighbours by hot gases.
- Coal is heated by conduction through the walls, so that oven **width** is restricted to a maximum of about 0.5 m.
- The **height** of ovens can be as much as 7 m and their **length** 15 m. >3 mm (80–90%) particle sizes are charged to the oven by pipeline. The carbonization takes place between **12 and 20 h** to complete.
- The aim is to achieve a uniform surface temperature in the range **950–1050 °C**. The doors of the oven are removed, and the whole mass is pushed by inserting a ram from the rear side of the battery and collecting coke in a quenching car at the front side. The red-hot coke is then quickly cooled by water spraying.

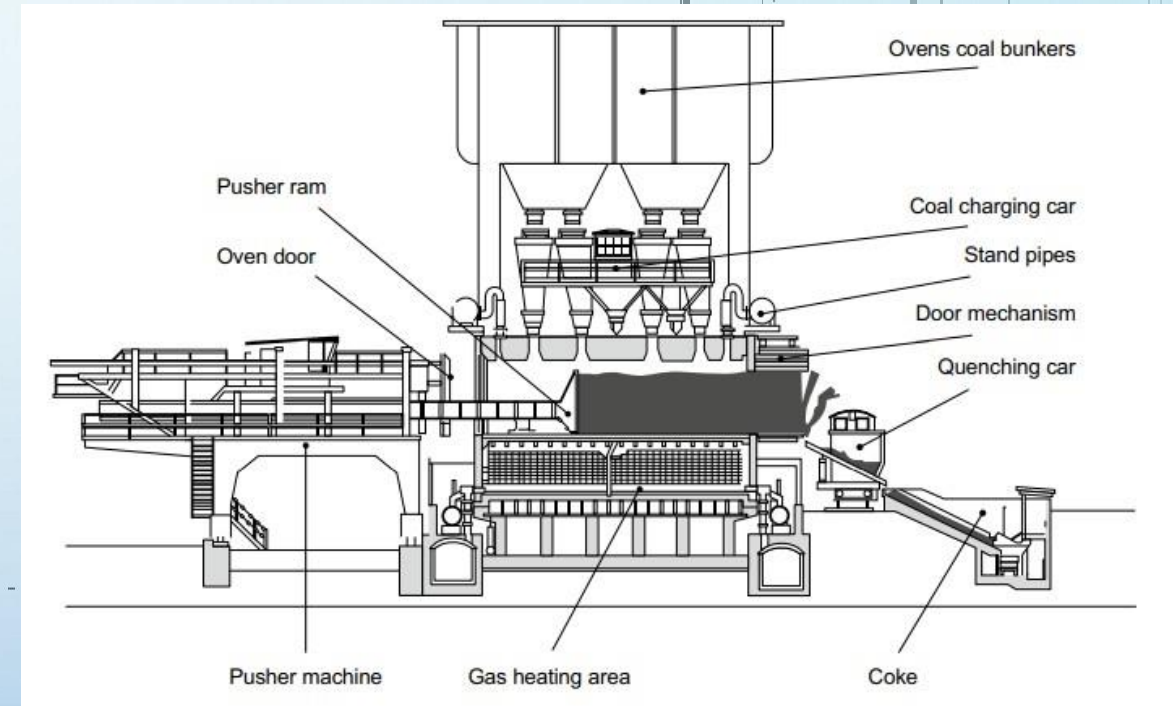


Fig. 1. General layout of a typical coke oven battery.

The conversion of coal to coke takes place by the process of **carbonization**, which consists of heating the coal in a closed chamber in absence of air. As the temperature rises, the coal blend becomes plastic (i.e., semi-fused) and distillation of the volatiles occurs.

This can be divided into three stages as follows:

- (i) Pre-plastic stage !** evolution of moisture and a little of volatile matter at temperature up to 300 °C,
- (ii) Plastic stage !** extensive molecular disruption and evolution of large amounts of volatiles. Volume changes occur due to temperature raised from 300 to 700 °C,
- (iii) Post-plastic stage !** coal solidifies as a hard porous residue known as coke. Temperatures increased from 900 to 1200 °C, and high-temperature carbonization produces the strong coke.

Cokes, carbonized at lower temperature, are faster rate of reaction with oxygen. Since strength is generally considered to be more important than reactivity, high-temperature coke is preferred by most BF operators.

Dry Cooling of Coke

Modern battery uses coke dry cooling system to produce coke of moisture free. The coke dry cooling system is based on the coke dry quenching media, i.e., cooling of hot coke with inert gas circulating in close loop between the chamber of hot coke and the waste heat.

Fluxes

- A flux is a substance which is added during smelting to help lower down the softening point of the gangue materials of ore, as well as ash of coke; to reduce the viscosity to the slag and to decrease the activity of some of its components for making stable in the slag phase.
- Slag is formed by the combination of gangue and flux, which is product (i.e., molten oxides) of smelting operation.
- Limestone and dolomite act as fluxing material in blast furnace. It should contain less than 5% insoluble (i.e., ΣSiO_2 , Al_2O_3 , Fe_2O_3). The value of a flux is expressed in terms of available base.

$$\text{available base} = [\%(\text{CaO} + \text{MgO}) - (\%\text{SiO}_2) \cdot B]$$

Where B is the basicity of slag.

- Limestone CaCO_3 decomposes at 900–950 °C; dolomite $\text{CaMg}(\text{CO}_3)_2$; it provides the MgO for blast furnace slag formation. Dolomite decomposes at (700 - 950 °C).
- Calcined limestone (CaCO_3) and dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) fluxed the gangue materials (i.e., silica and alumina impurities) of ore and ash of coke to produce a low melting point (1300 °C) fluid slag.

Air Supply

One of the most important raw materials in BF practice is the air supply. Steam and gas are operated by turbo-blower. The blast pressure normally ranges from 1 - 4 kg/cm² at the tuyeres, so that the turbo-blowers are designed to withstand pressure of 6 – 7 kg/cm².

Agglomeration Processes

The blast furnace is a counter-current gas–solid reactor in which the solid charge materials are moving downwards, while the hot reducing gases are flowing upwards.

The best possible contact between the solids and the reducing gas is obtained with permeable burden which permits not only a high rate of gas flow but also a uniform gas flow rate with a minimum of channelling of the gas. 25–50 mm fraction of solid materials is considered most favourable sizes.

Agglomeration: is the process for aggregate (i.e., bonding) of the small or fine particles to a useful size. The primary purpose of agglomeration is to improve burden permeability and gas–solid contact, thereby reducing blast furnace coke rates and increasing the rate of reduction, i.e., productivity.

The most important specification in the agglomerate:

- 1- Should be contained 60% or more of iron, a minimum of undesirable constituents, and size range of material 5–12.5 mm.
- 2- Should be strong enough to withstand degradation during stock-piling, handling and transportation; to arrive at the furnace skip with a minimum of approximate 85–90% of plus 5 mm materials.
- 3- Must be able to withstand the high temperature and the degradation forces within the furnace without slumping or decrepitating.
- 4- Should also be reasonable reducible, so that it can reduce at a satisfactorily high rate in the blast furnace.

Agglomeration can be classified into four types as follows:

1. Sintering,
2. Pelletizing,
3. Briquetting,
4. Nodulizing.

1. Sintering

- Sintering is a process of heating fine materials (+3 mm sizes) to an elevated temperature without complete fusion such that the small solid particles are in contact with one another adhere and agglomerate into larger, more useful sizes.
- Sinter is an agglomerate made from small particles of iron ore or iron-bearing materials that are semi-fused or fritted together at a high temperature that is produced by combustion of coal.
- Flux of small size is also added to the sinter mixture to flux partially of the gangue materials of iron ore to form slag before it is smelted in the blast furnace.

Small particles (+3 mm) of iron ore are mixed with **5–10% coal (fuel)**, **5–10% limestone** (flux, will be more for self-fluxed and super-fluxed sinters) and **6–8% moisture**.

- The sinter process is initiated by igniting the fuel in the top layer of the sinter mixture and is maintained by sucking air (down-draft) through the charge.
 - The small ore particles in the bed are bonded together to a fused aggregate by the action of high temperature; combustion zone is moving in the direction of air flow.
- The incoming air is pre-heated by hot sinter before reaching the flame front and the waste gases pre-heat the green charge.
- Combustion air and charge meet each other in a pre-heated state in the combustion zone and produce a heat accumulation leading to incipient fusion.

Figure 1.11 shows a cross-sectional profile of sinter bed.

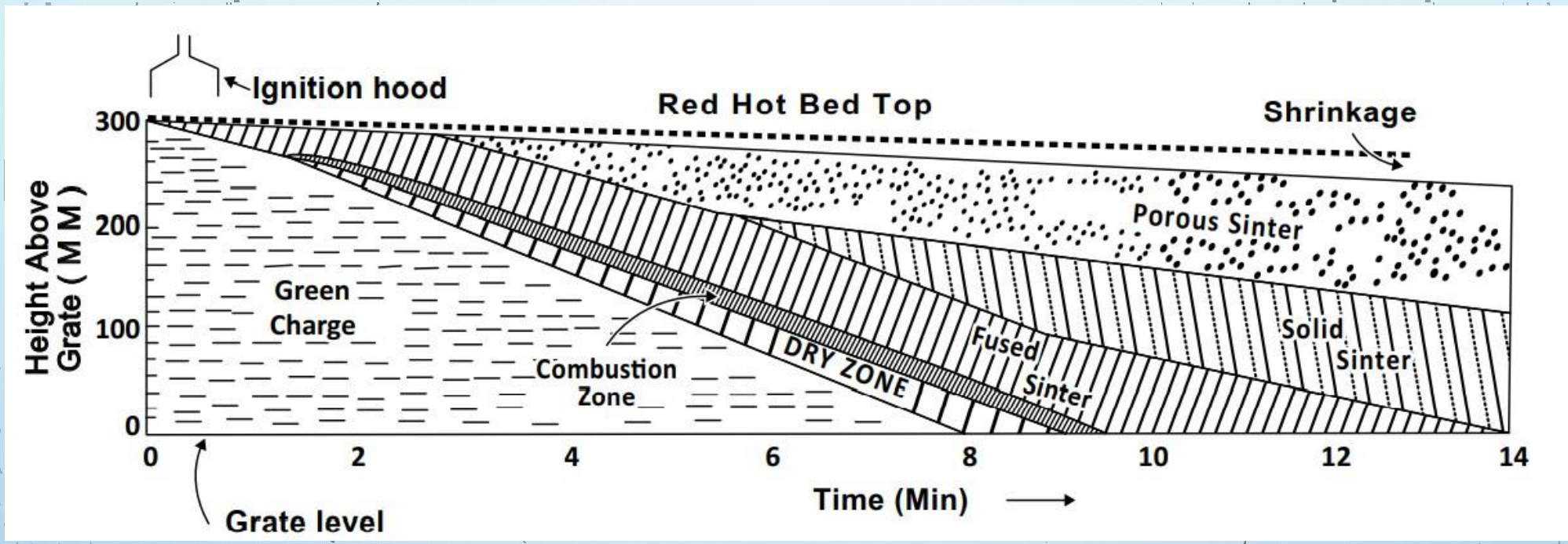


Fig. 2: A cross-sectional profile of sinter bed

The whole sintering process based on the heating stages can be split into five steps:

Step 1 Haematite (Fe_2O_3) reacts with CaO to generate the first calcium ferrites at around $1100\text{ }^\circ\text{C}$ (solid–solid reaction). Around $1200\text{ }^\circ\text{C}$, these calcium ferrites start to convert into the liquid phase. The liquid is rich in CaO and Fe_2O_3 and begins to combine with ultra-fine iron oxides, SiO_2 , Al_2O_3 , and MgO.

Step 2 Liquid phase starts to generate while temperature keeps on rising, and the superficial disintegration of haematite starts.

Step 3 The liquid melt assimilates with CaO and Al_2O_3 , and the evolution of the reaction between liquid and haematite forms acicular calcium ferrites in the solid state (needle form), which are rich in Al_2O_3 and SiO_2 .

Step 4 If the process temperature does not reach above $1300\text{ }^\circ\text{C}$ or the residence time above $1300\text{ }^\circ\text{C}$ is very short, the microstructure after cooling will be rich in acicular calcium ferrites in a bulk of crystalline silicates and granular haematite. That is the heterogeneous sinter.

Step 5 If the process temperature exceeds $1300\text{ }^\circ\text{C}$ and the residence time above $1300\text{ }^\circ\text{C}$ is long, columnar calcium ferrites and coarser recrystallized particles precipitate from melt. During the cooling step, skeletal rhombohedral haematite precipitates from the liquid phase, and calcium ferrites crystallize as long columnar form flakes, i.e. the homogeneous sinter.

Many efforts have been made to develop new technologies aiming at decreasing the fossil fuels utilization due to the environmental restrictions and decrease the process carbon intensity.

Actual sintering machine is developed to improve the flexibility of the process and allow simultaneously operation with gas recycling, fuel gas utilization, operation with partial operation of mill scale and biomass together with fossil fuels as coke breeze or anthracite.

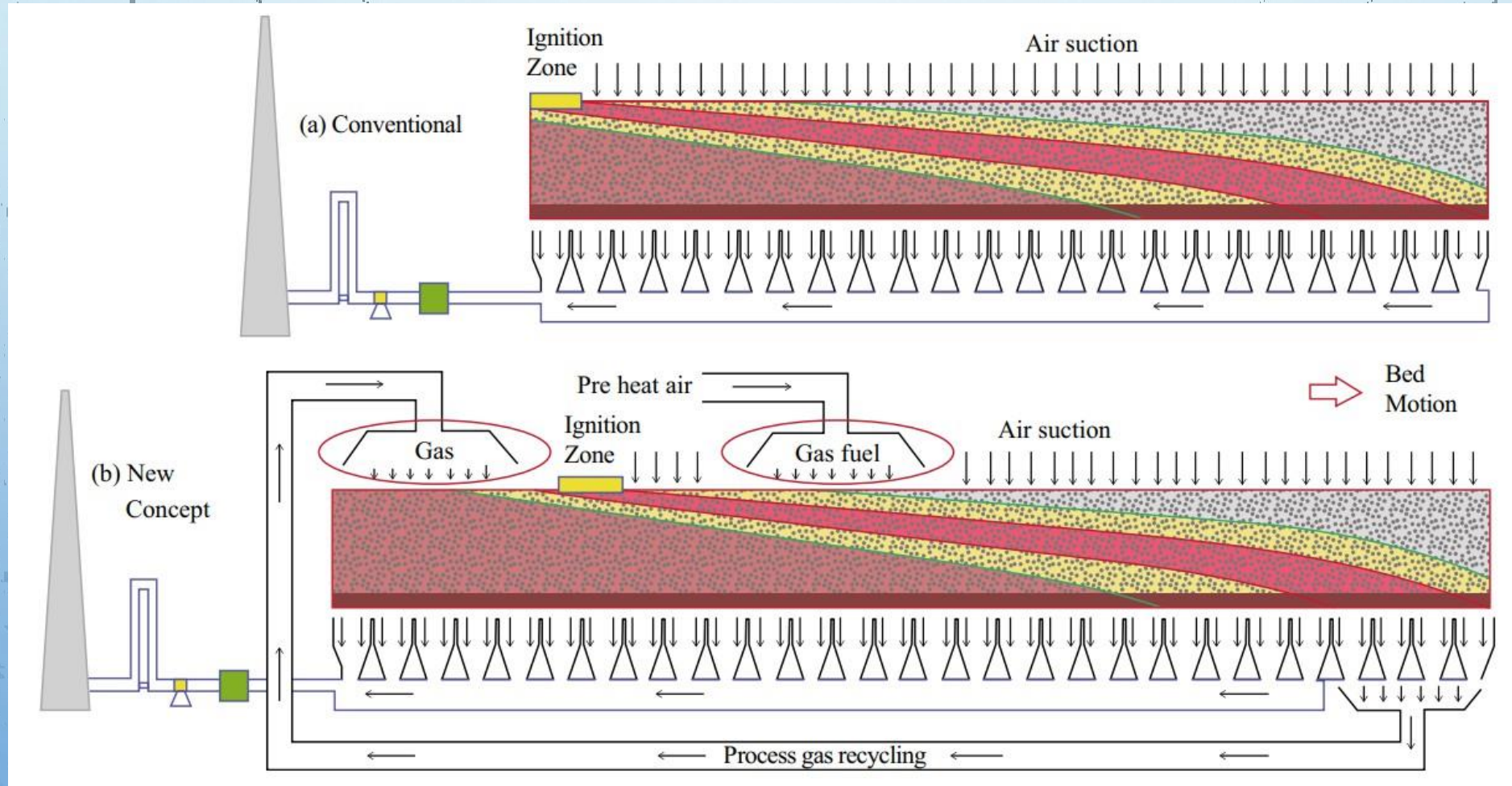


Fig. 3: New technology for sintering using recycling gas and gaseous fuels [6].

Factors affecting sinter quality:

- (i) **Particle size:** Particle size of the charge is one of the most important factors affecting permeability of sinter bed. On the other hand, if the proportion of coarse grains are considerable, the heat content of waste gas cannot be sufficiently absorbed by the solid. In general, the mix consists of 8–10 mm, coke breeze of 4–5 mm, and fluxes of minimum grain size and return fines of 7–10 mm.
- (ii) **Moisture:** The most important factor affecting bed permeability is the water content. Proper control of water should give maximum porosity and permeability. Water level is also important as a regulator of the speed of combustion front. Too little water increases speed and causes separation of combustion and heat fronts. Too much water requires high amounts of fuel and affects permeability.
- (iii) **Fuel:** Generally, large amounts of fuel in the sinter mix increases sintering rates by giving higher flame front speed, if the air flow can be increased. But the maximum temperature increases with more fuel, this influences the nature and extent of slagging, and the sinter quality is adversely affected. Sinter contains 5–20% metallic iron due to present of solid fuel.
- (iv) **Flux:** Production rates have been found to increase in the addition of limestone.

Additionally, limestone is added to the sinter mix to produce self-fluxing sinter with respect to the ordinary sinter. This is attributed to the correct slag formation resulting in higher bed permeability in the high-temperature zone. Additions of lime to the charge will increase the permeability of green bed.



Fig. 4: Agglomerate of the sintered iron ore.

Types of sinters are as follows:

- (a) Acid sinter: when the basicity ratio (CaO/SiO_2) is less than 1.0, i.e., sinter without flux,
- (b) Self-fluxed sinter: when the basicity ratio is more than 1.0,
- (c) Super-fluxed sinter: when the basicity ratio is more than 2.0.

Advantages of using sinter in blast furnace:

1. Any free or combined moisture in the ore is removed and the carbonates are decomposed,
2. A part of the sulphur present in the charge is removed during the sintering process,
3. The gangue constituents of the ore are pre-slagged in fluxed sinter,
4. Some amount of heat in the blast furnace is saved as dissociation of carbonates takes place during sintering,
5. Using super-fluxed sinter, the amount of limestone charged in the BF is reduced, and thus, the solution loss reaction (i.e., $C(s) + \{CO_2\} = 2\{CO\}$) in BF is decreased,
6. The evolution of CO_2 gas in BF, due to dissociation of carbonates, is much reduced, therefore favouring the indirect reduction of iron ore,
7. The productivity increases as the volume of material charged per tonne of hot metal is reduced by use of super-fluxed sinter,
8. The irregular surface of sinter helps to maintain an adequate permeability and permits high blowing rate,
9. It is generally possible to use higher top pressure and carry high blast temperature.

