to achieve a negative $\Delta G$ value for the above reaction and therefore provide reduction of MgO with Si. Applying equation (2.29) to the above reaction at 1200 °C:

$$\Delta G_{1200^\circ C} = \Delta G_{1200^\circ C}^\circ + RT \ln \left( \frac{\rho_{MgO}^{aSiO_2}}{\rho_{MgO}^{aSi}} \right)$$

$$= +244 000 + 8.3 \times 1473 \ln \left( \frac{\rho_{MgO}^{aSiO_2}}{\rho_{MgO}^{aSi}} \right) J \text{ mol}^{-1}$$

For the reduction reaction to occur at 1200 °C, $\Delta G_{1200^\circ C} < 0$ (i.e. $\Delta G$ negative). Thus

$$8.3 \times 1473 \ln \left( \frac{\rho_{MgO}^{aSiO_2}}{\rho_{MgO}^{aSi}} \right) < -244 000$$

and so

$$\ln \left( \frac{\rho_{MgO}^{aSiO_2}}{\rho_{MgO}^{aSi}} \right) < \frac{-244 000}{8.3 \times 1473}$$

This condition can be readily achieved by lowering the partial pressure of the magnesium vapour produced using vacuum techniques while the activity of SiO$_2$ is lowered by additions of lime (CaO) to the slag which collects the silica, i.e. formation of a basic slag. In practice the lime is added in the form of calcined dolomite MgO.CaO (Pidgeon process). The silicon is added as high grade ferrosilicon which is cheaper to produce than pure silicon and also improves fluidity by lowering the melting point of the slag. The reaction is conducted in an externally heated Ni–Cr retort similar to the horizontal retort used in zinc extraction.

$$2\text{MgO.CaO(s)} + \text{Fe-Si(s)} \rightarrow 2\text{Mg(g)} + \text{Ca}_2\text{FeSiO}_4$$

Again, several retorts are placed in batches. Since magnesium is the only gaseous product there is no danger of a reversion reaction to MgO during cooling.

By consultation of the $\Delta G^\circ$–$T$ relationships (Fig. 2.11) for the carbothermic reduction of MgO the minimum reduction temperature is 1850 °C:

$$\text{MgO(s)} + \text{C(g)} \rightarrow \text{Mg(g)} + \text{CO(g)}$$

If the magnesium vapour cools below 1850 °C the above reaction will reverse. Therefore, the Mg vapour must be rapidly 'shock cooled' with hydrogen or natural gas to prevent considerable reversion to MgO. The magnesium vapour condenses as a fine dust covered with oxide and which easily catches fire on exposure to air (pyrophoric). For this reason the magnesium dust is refined by vacuum sublimation which makes this process more expensive than the Pidgeon process or the electrolytic process.

### 7.2.10.5 Reduction of iron oxides

Iron occurs naturally as haematite (Fe$_2$O$_3$), magnetite (Fe$_3$O$_4$) and as the leaner limonite (Fe$_2$O$_3$.3H$_2$O) and siderite (FeCO$_3$) ores. The iron content varies from 20% to 70%.

**Blast furnace smelting**

The main method of reduction of these ores is with coke in the blast furnace. The richer ores may be added directly to the furnace in lump form while the leaner ores generally require some concentration. Agglomeration of the ores or concentrates will produce improved reaction kinetics but the agglomeration process must be substantiated by sufficiently improved production rates. Iron ore, coke and limestone as a flux are charged at the top of the furnace through a bell mechanism which helps to control
Table 7.2 TYPICAL CHARGE QUANTITIES PER TONNE OF HOT PIG IRON PRODUCED IN THE BLAST FURNACE SMELTING OF IRON ORES

<table>
<thead>
<tr>
<th>Charge material</th>
<th>Tonnes per tonne of iron produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron ore (50% Fe)</td>
<td>~2.0 depending on Fe content</td>
</tr>
<tr>
<td>Coke</td>
<td>0.35–0.6 (0.35 for agglomerated ore used with fuel injection at the tuyeres)</td>
</tr>
<tr>
<td>Limestone</td>
<td>~0.4 depending on Fe content</td>
</tr>
<tr>
<td>Preheated air through tuyeres</td>
<td>3.0 (~3.12 x 10⁴ m³)</td>
</tr>
</tbody>
</table>

the conditions at the top of the stack (Fig 7.8(c)). Table 7.2 indicates the normal charge quantities.

As discussed in Section 7.2.5 reduction of iron oxides with CO (indirect reduction) rather than with coke (direct reduction) predominates until the onset of slag formation at about 1100 °C. The series of reactions can be represented as:

\[
\begin{align*}
3\text{Fe}_2\text{O}_3 + \text{CO} & \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2 \\
\text{Fe}_3\text{O}_4 + \text{CO} & \rightarrow 3\text{FeO} + \text{CO}_2 \\
2\text{CO} & \rightarrow \text{C} + \text{CO}_2 \\
\text{FeO} + \text{CO} & \rightarrow \text{Fe} + \text{CO}_2 \\
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2 \\
\end{align*}
\]

at 400–600 °C
at 600–800 °C (FeO unstable below 570 °C. See Fig. 7.20)
at 540–650 °C (Boudouard or carbon deposition reaction)
at 800–1100 °C
at 900 °C

Onset of slag formation at about 1100 °C:

\[
\begin{align*}
\text{P}_2\text{O}_5 + 5\text{C} & \rightarrow 2\text{P}(\text{in Fe}) + 5\text{CO} \\
\text{MnO} + \text{C} & \rightarrow \text{Mn}(\text{in Fe}) + \text{CO} \\
\text{SiO}_2 + 2\text{C} & \rightarrow \text{Si}(\text{in Fe}) + \text{CO} \\
\text{S}(\text{in ore + coke}) + \text{CaO} + \text{C} & \rightarrow \text{CaS( in slag) + CO} \\
\text{C}(\text{in coke}) & \rightarrow \text{C}(\text{in Fe}) \\
\text{FeO} + \text{C} & \rightarrow \text{Fe} + \text{CO} \\
\end{align*}
\]

The above reactions should be considered together with temperature distributions within the stack (Fig 7.19). These isotherms may be levelled out to some extent by using a graded burden size or an agglomerate (sinter or pellet) charge. Fig. 7.20 shows the \( \Delta G^\circ - T \) relationships for the relevant reactions in ironmaking and steelmaking.

Using Fig. 7.20 it is possible to consider the theoretical thermodynamic relationships that occur when a pocket of preheated air enters the blast furnace via the tuyeres and reacts alternatingly with coke and iron oxides (FeO) represented in the diagram by an arrowed line. The preheated air first reacts with coke in the tuyere zone to produce \( \text{CO}_2 \) which then reacts with more coke outside the tuyere zone to produce \( \text{CO} \) by the overall reaction:

\[
2\text{C} + \text{O}_2 \rightarrow 2\text{CO}
\]

If the CO then comes into contact with a lump of iron ore, e.g. FeO, it is reduced, i.e.

\[
\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2
\]
Thus, the pocket of blast furnace gas (arrowed line) alternates between the
$2C + O_2 \rightarrow 2CO$ line and the $2Fe + O_2 \rightarrow 2FeO$ line and tries to reach equilibrium
with these reactions. Due to the conditions in the blast furnace, equilibrium is never
achieved but the blast furnace gas composition can be considered to alternate between
these two reaction lines as it ascends the stack. At the lower temperatures higher up
the stack the gas composition contains more CO than would be expected due to the
blast furnace being well away from equilibrium conditions; the rapid ascent of the blast
furnace gas flushing the CO to the top of the stack. At 545 °C to 650 °C the Boudouard
or carbon deposition reaction $2CO \rightarrow 2C + CO_2$ is at optimum. The reaction is
thought to require a catalyst—possibly an iron–refractory interface. The carbon is
deposited as a fine powder which may provide some direct reduction of the iron oxides.
This is likely to be only a small amount. Owing to the onset of slag formation just above
Figure 7.20 $\Delta G^\circ - T$ diagram for the important reactions concerned with ironmaking and steelmaking.

The tuyeres any further reduction of iron oxide below this position in the stack is mainly by direct reduction with carbon. The pick up of Si, S, Mn, can be controlled to some extent by slag basicity and temperature on examination of the thermodynamic relationships involved.

Control of silicon in pig iron

The $\Delta G^\circ - T$ relationship* for the reduction of SiO$_2$ with carbon is given as

$$\text{SiO}_2 + 2\text{C} \rightarrow \text{Si(\text{in Fe})} + 2\text{CO}$$

$$\Delta G^\circ = +59750 - 3967 T \text{ J mol}^{-1}$$ (7.XI)

Thus, increasing hearth temperature will make $\Delta G^\circ$ more negative favouring the forward reaction and increasing silicon pick up in the pig iron. At the same time SiO$_2$ is

*The $\Delta G^\circ - T$ relationship is normally given in the form $\Delta G^\circ = A + BT$ where $A$ is $\Delta H^\circ$ and $B$ is $\Delta S^\circ$, both of which can be positive or negative (Section 2.2.2.1).
an acidic oxide. Therefore, using a basic (CaO) slag the activity of \( \text{SiO}_2 (a_{\text{SiO}_2}) \) is reduced due to the reaction:

\[
\text{SiO}_2 + 3\text{CaO} \rightarrow \text{Ca}_2\text{SiO}_4 + \text{excess CaO}
\]

If the van't Hoff isotherm for non-equilibrium conditions (equation (2.29)) is applied to reaction (7.XI):

\[
\Delta G = \Delta G^\circ + R T \ln \left( \frac{a_{\text{Si}(\text{in Fe})}P^2_{\text{CO}}}{a_{\text{SiO}_2}a_{\text{C}}} \right)
\]

using a basic slag reduces \( a_{\text{SiO}_2} \) which makes the term positive, thereby making \( \Delta G \) more positive and favouring the reverse reaction,

\[
\text{Si}(\text{in Fe}) + 2\text{CO} \rightarrow \text{SiO}_2 + 2\text{C}
\]

Therefore, silicon pick-up in the iron is lowered using a basic slag and increased using an acidic slag. In the same way the distribution of other elements between the slag and the pig iron can be deduced.

The corresponding relationship for MnO (basic oxide) reduction with carbon is\(^{13}\):

\[
\text{MnO} + C = \text{Mn(Fe)} + \text{CO} \quad \Delta G^\circ = +290 \, 300 - 173 \, 700 \, \text{J mol}^{-1}
\]

Thus, Mn pick up is favoured by a high hearth temperature and a basic slag. The removal of sulphur to the slag relies on the formation of a more stable sulphide, e.g. CaS, than FeS which will separate into and react with the slag. This is best achieved by employing a basic (CaO) slag. Therefore, sulphur removal depends on the reaction,

\[
\text{FeS}(\text{in Fe}) + \text{CaO} \rightarrow \text{CaS}(\text{in slag}) + \text{FeO}
\]

which is more usually written as the ionic equation\(^{14}\):

\[
\text{S}(\text{Fe}) + \text{O}^{2-}(\text{in slag}) \rightarrow \text{S}^{2-}(\text{in slag}) + \text{O}(\text{in Fe}) \quad \Delta G^\circ = +72 \, 000 - 387 \, 700 \, \text{J mol}^{-1} \quad (7.XII)
\]

Thus, increasing hearth temperature will make \( \Delta G^\circ \) more negative favouring the removal of sulphur from the iron to the slag. Since each reaction tries to reach equilibrium, examination of the equilibrium constant will indicate the conditions which will favour sulphur removal to the slag.

The equilibrium constant \( (K) \) for reaction (7.XII) is:

\[
K = \frac{a_{\text{S}^{2-}(\text{in slag})}a_{\text{O}(\text{in Fe})}}{a_{\text{S}(\text{in Fe})}a_{\text{O}^{2-}(\text{in slag})}}
\]

from which the ratio of sulphur in the slag to sulphur in the iron is seen to be:

\[
\frac{a_{\text{S}^{2-}(\text{in slag})}}{a_{\text{S}(\text{in Fe})}} = K \frac{a_{\text{O}^{2-}(\text{in slag})}}{a_{\text{O}(\text{in Fe})}} \quad (7.3)
\]

To achieve maximum sulphur removal to the slag this ratio needs to be as large as possible which, from equation (7.3), requires the ratio \( a_{\text{O}^{2-}(\text{in slag})}/a_{\text{O}(\text{in Fe})} \) to be as large as possible in order to maintain \( K \) at its constant value. It is clear then that the oxygen ion activity of the slag must be high and the oxygen potential of the pig iron must be low to provide a high removal of sulphur to the slag. The oxygen ion activity of the slag is increased by using a lime addition to the charge, i.e. basic slag formation:

\[
\text{CaO} \rightarrow \text{Ca}^{2+} + \text{O}^{2-}
\]
while control of the oxygen potential of the pig iron is more difficult. Adjustment of the $a_{O_{2}}(\text{in } \text{Fe})$ value is used to a much greater extent in removal of sulphur during steelmaking which will be discussed later.

Thus, sulphur removal is favoured by a high temperature and basic slag, although it may be noted that oxygen solubility in Fe increases as the melt temperature increases. This latter point becomes important in steelmaking processes where highly oxidising conditions prevail.

Use of blast preheat, oxygen enrichment of the blast, injection of hydrocarbons and steam into the blast furnace and increasing the pressure of the blast furnace gas at the top of the stack (high top pressure) have resulted in considerable improvements in productivity rate and furnace efficiency. The main aim of the blast furnace manager is to achieve a rapid but regular charge descent.

Blast preheat and oxygen enrichment

Preheating the air blast means that less coke need be burnt to supply the heat. The blast furnace reduction of iron oxide requires extremely expensive high quality coke and any savings in the use of this material will lead to considerable cost improvements. The air is preheated by passing through a heated refractory network in hot blast (Cowper) stoves. Enriching the preheated air with oxygen will also reduce the coke rate (amount of coke consumed per tonne of iron produced) in the same way as preheated air. However, replacing some of the air with oxygen produces a reduction in blast furnace gas volume which can be passed up the stack. Hence, the amount of heat transferred from the ascending gas to the charge is decreased which reduces the amount of indirect reduction that can take place and therefore necessitates an equivalent increase in the amount of direct reduction in the hearth. As discussed earlier in the chapter, direct reduction is endothermic while indirect reduction is exothermic. Thus, oxygen enrichment is kept well below 9%.

It is cheaper to use an increased air preheat than oxygen enrichment but the preheat temperature is limited to the refractory properties in the hot blast stoves. Typical preheat temperatures vary in the range 900–1200 °C.

Hydrocarbon and steam injection

Injection of hydrocarbons into the stack of the blast furnace results in their combustion to provide two reducing gases, carbon monoxide and hydrogen, although some carbon dioxide and steam will also be produced. For example,

$$2\text{CH}_4 + \text{O}_2 \rightarrow 4\text{H}_2 + 2\text{CO} \quad \Delta H_{298}^{\circ} = -71.4 \text{ kJ}$$

As discussed earlier (Section 7.2.5), hydrogen is a better reducing agent for metal oxides than carbon monoxide below 800 °C while CO is a better reducing agent than $\text{H}_2$ above 800 °C. The combination of these two reducing gases provides an increase in the efficiency of the indirect reduction reactions. However, the exothermic value of the combustion of the hydrocarbon is less than that for coke,

$$2\text{C} + \text{O}_2 \rightarrow 2\text{CO} \quad \Delta H_{298}^{\circ} = -222 \text{ kJ}$$

(see reaction 7.111), and an increase in blast preheat is required to maintain hearth temperature. The hydrocarbons most commonly used are: (i) natural gas; (ii) atomised oil; and (iii) pulversed coal. All of these are injected into the furnace via the tuyeres, although a CO + H$_2$ mixture has also been injected just above the tuyeres. In most cases an increase in the amount of indirect reduction and reduction in coke rate has been produced. The injection of steam through the tuyeres also results in H$_2$ and CO formation but with an endothermic reaction with coke:

$$\text{H}_2\text{O} + \text{C} \rightarrow \text{H}_2 + \text{CO} \quad \Delta H_{298}^{\circ} = +132 \text{ kJ}$$

(7.XIV)
Therefore, steam injection will quickly lower the hearth temperature and is used in conjunction with a high blast preheat and/or oxygen enrichment to rapidly and efficiently control the hearth temperature. Typical values for steam injection vary between 1 to 4% enrichment of the blast, again resulting in an increased amount of indirect reduction, reduced coke rate and increased production.

High top pressure

Increasing the pressure of the blast furnace gas at the top of the stack will provide a smaller increase of the gas at the tuyere level. In this way the pressure difference between the gas at the top of the stack and that at the tuyeres will be reduced. Reducing the pressure difference in the stack will slow down the rate of ascent of the gases, increasing their residence time in the stack and increasing their contact with the iron oxides. This produces an increase in the efficiency of coke combustion and pig iron production rate and is represented diagrammatically in Fig. 7.21. Typical top pressures vary from 50.6 to 289.6 kN m$^{-2}$ (0.5 to 2.8 atm) although pressures up to 361.8 kN m$^{-2}$ (3.57 atm) have been tried.

![Graph showing variation of pressure difference of blast furnace gas at tuyeres to that at the top of the stack using different high top pressures.](image)

Figure 7.21 Variation of pressure difference of blast furnace gas at tuyeres to that at the top of the stack using different high top pressures. (Based on data presented in Blast Furnace Theory and Practice edited by J.H. Strassburger, published by Gordon and Breach Science Publishers for American Institute of Mining, Metallurgical and Petroleum Engineers Inc.)

Blast furnace practice using the above techniques has resulted in production rates in excess of 10 000 tonnes per day producing an impure pig iron with 3.5–4% C, 1–2% Si, about 1% Mn, 0.2–2.5% P and 0.04–0.2% S. However, blast furnace production has certain disadvantages:

(i) Control over pig iron composition is generally poor with composition varying from tap to tap.
(ii) The large production rates may not be required, especially for developing countries whose steel outlets are limited.
(iii) High capital and operating costs are incurred.

Alternatives to blast furnace production of iron include:

(i) Smelting in an electric arc furnace where cheap electricity is available.
(ii) Low shaft furnace smelting similar to the bottom third of the blast furnace and using 9% oxygen enrichment. The smaller stack allows the weaker, cheaper carbon forms such as coals and lignites to be used as the reducing agent.

Both these processes rely mainly on direct reduction reactions with only a small amount of indirect reduction.

Direct reduction (DR) and direct smelting (DS) processes

The most important alternatives to the blast furnace are the direct reduction (DR) and direct smelting (DS) processes. In the DR processes carbon in the form of coal dust, coke breeze, char or anthracite or, alternatively, carbon monoxide and hydrogen are added to the reduction unit resulting in direct conversion of oxide to steel in one step. Therefore, even though CO and H₂ may be used as the reducing agents they are being used directly without any intermediate reactions; carbon monoxide and hydrogen being formed by combustion of hydrocarbons with air or steam prior to their use as reducing agents.

The processes are almost totally direct reduction processes with very little, if any, indirect reduction reactions taking place. Solid reducing agents (coal dust, coke breeze, char or anthracite) are used in rotary kiln reduction of pelletised iron ore; CO and H₂ are used in static bed reactors, low shaft furnaces (similar to the bottom third of the blast furnace) or fluidised bed furnaces in the reduction of pelletised iron ore. Diagrammatic representations of these processes are given in Fig. 7.22. The operating temperatures are in the range 1000–1200 °C except for the fluidised bed process using hydrogen as the main reducing agent. In this case a lower temperature, 750 °C, can be used.

![Diagram of direct reduction processes for iron ore](image-url)

**Figure 7.22** Diagrammatic representation of direct reduction processes for iron ore: (a) gaseous reduction in a shaft furnace; (b) gaseous reduction in static bed retorts; (c) gaseous reduction in fluidised beds; (d) solid reduction in a rotary kiln