

Fe_2O_3 contents as high as 15% may be introduced in this way. A virgin alternative iron source is direct reduced iron (DRI) and with increasing availability of DRI, its usage in the appropriate size (3–15 mm) in BOF steelmaking is also increasing. When calculating the amount of the coolant required, it is important to note that DRI cools 10% more efficiently than scrap for the same weight; whereas, the *cooling factor* of iron ore is 3.0–3.5 times greater. Usage of large amounts of iron ore is often precluded by extensive slopping from the vessel mouth, since the iron ore added is not immediately ‘in equilibrium’ with the bath. Slopping can be reduced by decreasing the rate of iron ore addition and/or altering the blowing strategy so that the emulsion collapses.

16.5.3 Flux Materials

The quality of fluxes to be used for slag making is an important issue. The flux materials must have sufficient strength to withstand handling during transport to the bins above the converter. Reactivity is another factor that determines the quality of the flux. Insufficient physical strength gives rise to extensive dust generation and carry-over of the flux (as lime powder) into the exit gas, resulting in erroneous basicity of the slag as well as an increase in the p_{H} level of water in the gas-cleaning plant. This causes deposition of lime in the water treatment section, which has to be avoided to the maximum extent.

16.5.4 Oxygen

This is an important input material whose quality is often not adequately highlighted. The minimum purity of oxygen to allow the production of the full range of carbon steel products should be 99.9%. The final turndown nitrogen and hydrogen contents of steel are dependent not only on the amounts of these elements present in hot metal/fluxes, but also on oxygen.

During the early stages of the oxygen blow, when the rate of carbon monoxide evolution is high, the nitrogen content of the bath decreases, i.e. de-nitrogenisation occurs. However, when the decarburisation rate begins to fall (after 12–15 minutes) the nitrogen content can increase substantially if oxygen of adequate purity is not used.

16.6 PRE-TREATMENT OF HOT METAL PRIOR TO STEELMAKING

Owing to the stringent demands placed in recent years by steel consumers as far as the properties of steel products in terms of their strength, toughness, drawability under extreme forming conditions, etc. are concerned, it has become mandatory to reduce the impurity levels in steel drastically; in some cases, even to a few parts per million (ppm).

Silicon, carbon, sulphur and phosphorus are the elements present in hot metal that have to be removed. At the end of the oxygen blowing period, the carbon level in the bath is normally between 0.03% and 0.04%. For lower carbon levels, vacuum treatment is normally resorted to. As far as silicon is concerned, it gets removed almost completely during steelmaking since this is a thermodynamic precondition for the oxidation of carbon. However, the removal of sulphur and phosphorus are not as straightforward. These elements continue to remain in liquid steel, to various extents, at the end of the blow.

To produce internal crack-free products with acceptable surface quality, it is necessary to lower the levels of sulphur and phosphorus to less than 0.010 percent each (sometimes, even less than 0.005%). To achieve such low values, it is often desirable to charge hot metal containing low amounts of sulphur and phosphorus into the BOF. Otherwise, under the oxidising conditions prevailing during steelmaking, it becomes almost impossible to reduce both sulphur and phosphorus economically. At the same time, owing to factors like decreasing availability of low sulphur coke and the use of high phosphorus-bearing iron ores, it is not always possible to produce low sulphur, low phosphorus hot metal in blast furnaces. Hence, pre-treatment of hot metal to remove sulphur/phosphorus prior to BOF steelmaking has gained worldwide acceptance as an intermediate operation. For this purpose, an extra step (in some cases, more than one step) has to be introduced between the blast furnace and the BOF shop.

The details of the reactions involved in the removal of these elements from liquid iron have been covered in other chapters. Chapter 4 has dealt with the general physicochemical fundamentals, including slag basicity and their capacities to absorb of sulphur/phosphorus. Chapter 5 has discussed the theory of reactions of sulphur, and silicon. Chapter 15 provides an insight into the physical chemistry of steelmaking reactions for silicon, carbon, phosphorus, etc. Hence, these are not being repeated here.

16.6.1 Objectives of Pre-treatment

Hot metal pre-treatment envisages removal of sulphur, and sometimes even silicon plus phosphorus, by the addition of suitable reagents. To increase the surface area so that the reactions occur rapidly, these reagents are normally injected into hot metal in the form of fine powder. While desulphurisation of hot metal has now become standard practice in virtually all plants, in some cases, desiliconisation also becomes necessary, particularly since it is a prerequisite for the removal of phosphorus. However, desiliconisation automatically decreases the amount of scrap that can be concurrently used in the BOF charge (the extent of heat generation becomes restricted), which is not always desirable from an economical point of view. This is particularly detrimental if the objective is to decrease the hot metal ratio from 92–95% (common in the last few years in countries like Japan owing to excess hot metal capacity) to 82–85% (at times when scrap is relatively inexpensive).

Over and above the ability to produce steel with very low levels of sulphur and phosphorus, there are some additional advantages that accrue from hot metal pre-treatment. These include:

- increased opportunity to recycle steelmaking slags (low in phosphorus) to the blast furnace for recovering iron and manganese units
- possibility of ‘slagless’ or ‘limeless’ steelmaking from hot metal low in silicon, sulphur and phosphorus. The advantage of ‘slagless’ refining is less flux consumption, decreased slopping, increased productivity, and improved hit rates at the end of the blow. The ultimate goal is to use BOFs for decarburisation alone (many Japanese plants have already been successful in achieving this goal).

16.6.2 Removal of Silicon

Silicon in hot metal can be removed by injecting an oxidising agent like mill scale (accompanied by lime to help produce a neutral slag), or by taking recourse to a separate step of oxygen

blowing in another converter to produce highly siliceous slag (in the presence of lime) before the desiliconised hot metal is transferred to a second converter, for the other reactions to proceed. This type of two-slag BOF operation gives rise to the following advantages:

- Improved dephosphorisation during steelmaking since highly basic slags can be formed early in the blow
- Reduction in the converter slag volume accompanied by an increase in the iron yield (less iron loss in the slag), longer converter campaigns (less attack on the lining from siliceous compounds in the primary slag), etc.
- Lower consumption of ferro alloys because of higher recovery arising on account of the lower levels of dissolved oxygen in liquid steel
- Easier dynamic control of the process to arrive at the desired end point.

Despite these advantages, desiliconisation is not normally practiced essentially because of problems in handling the highly siliceous slag that is produced. Such slags have high temperature and are extremely fluid, thereby causing aggressive attack on most refractories. Instead, efforts have been made to produce low silicon (0.3–0.6%) hot metal directly in blast furnaces to the maximum possible extent, as discussed in Chapter 11.

16.6.3 Desulphurisation

Desulphurisation is better at the hot metal stage rather than at the steel stage because of the reasons given in Table 16.1 (Gupta and Chatterjee, 1995). Desulphurisation of hot metal in blast furnace ladles en route to the steel melting shop has become a standard practice because:

- The productivity of blast furnaces can be improved by 6–8% when sulphur control within the blast furnace is not required, and a leaner slag chemistry as well as lower slag volume can be chosen
- The consumption of coke as well as fluxes decreases, thereby reducing the total energy consumption per tonne of hot metal
- Build-up of alkalis in the blast furnace gets restricted, and
- The production of low silicon hot metal becomes easier.

Table 16.1 Comparison of desulphurisation of hot metal vis-à-vis steel

Parameter	Hot metal desulphurisation	Steel desulphurisation
Oxygen potential	Low (slag FeO = 0.25%)	High (slag FeO = 18–20%)
Temperature	1300–1550°C	Greater than 1600°C
Activity coefficient	4.5–6	1.5
Cost of desulphurisation	Low	High
Desulphurisation efficiency	High	Low
Temperature drop	Can be manipulated	Cannot be manipulated

16.6.4 Dephosphorisation

Theoretically speaking, dephosphorisation of hot metal allows:

- Increased recycling of BOF slag to the blast furnace, thereby reducing the cost of hot metal
- Steel for continuous casting to be tapped at higher temperature without the risk of rephosphorisation
- Control on the extent of segregation of phosphorus during continuous casting
- Lower final sulphur and phosphorus contents in steel, particularly high alloy steel.

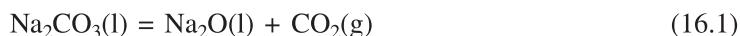
However, dephosphorisation is normally not carried out during the production of bulk steels, since from free energy considerations, it can only be done under oxidising conditions, and in the presence of a highly basic slag. This is possible only after the total removal of silicon (dictated by thermodynamics). At the same time, while phosphorus is best removed at low temperature, desiliconisation automatically increases the temperature (the reaction of oxygen with silicon is highly exothermic). The dichotomy of the situation is evident. Therefore, alternative strategies for controlling the phosphorus content of hot metal by choosing appropriate raw materials, or by adopting a modified BOF process (e.g. concurrent injection of lime and oxygen in the converter) to process high phosphorus (1–2%) hot metal, have found favour. However, some Japanese steel plants, which produce very low silicon hot metal (less than 0.3%) in their blast furnaces, have been able to practice simultaneous desulphurisation and dephosphorisation of hot metal.

16.7 REAGENTS USED FOR PRE-TREATMENT

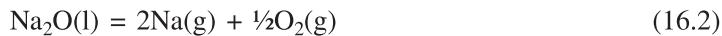
16.7.1 Soda-ash

When soda-ash (sodium carbonate) is added to hot metal, dense fumes are generated, which can create environmental problems. Disposal of soda-bearing slags gives rise to ground water contamination. This is the primary reason why the use of soda-ash has been restricted in recent times, though it is an effective reagent for both desiliconisation and desulphurisation.

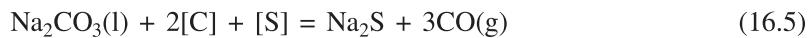
Sodium carbonate is comparatively stable up to 1200°C, above which it decomposes:



A portion of the Na₂O produced dissolves in liquid Na₂CO₃ (m.p. = 851°C) while the remainder decomposes:



In hot metal containing carbon and silicon, the following reactions take place:



Since the reactions related to the decomposition of Na_2O and Na_2CO_3 to Na (g) proceed rapidly at high temperature, lower temperatures are preferable for desulphurisation (reaction 16.5). Soda-ash is a very effective reagent for desulphurisation and dephosphorisation in the case of low silicon hot metal.

16.7.2 Mixture of Soda-ash and Sodium Sulphate

The use of sodium carbonate and sodium sulphate together for pre-treatment of hot metal has also been investigated. The incorporation of sodium sulphate helps in dephosphorisation in the following manner:



A mixture of soda ash and sodium sulphate is advantageous in pre-treating hot metal because of the low melting points of the constituents: Na_2CO_3 (m.p. = 851°C) and Na_2SO_4 (m.p. = 884°C). A mixture of the two in the weight ratio of 2 soda-ash and 1 sodium sulphate is considered to be the optimum.

16.7.3 Mill Scale, Sinter Fines, etc.

Desiliconisation can be carried out by using primary reagents like gaseous oxygen, mill scale, sinter fines, iron ore/manganese ore fines, etc. Along with the primary reagent, an auxiliary agent containing CaO , $(\text{CaO} + \text{CaF}_2)$, $(\text{CaO} + \text{CaF}_2 + \text{Na}_2\text{CO}_3)$ is also added. In several cases, BOF slag is used.

16.7.4 Calcium Carbide and Magnesium Granules

The desired level of sulphur in steel for efficient continuous casting is a maximum of around 0.020%. In the case of special steel plates, the sulphur content has to be restricted to around 0.010% normally. However, there is demand for sulphur levels as low as 10 ppm (0.001%), in the case of steel used in pipe lines (commonly referred to as line pipe steel) that have to be guaranteed against hydrogen induced cracking when sour gas is conveyed. To cater to all such requirements, the sulphur content in hot metal has to be brought down to at least 0.010–0.025%. This is normally achieved by injecting suitable powders like calcium carbide. In actual practice, calcium carbide containing limestone, lime and carbon is used as a mixture as in Table 16.2 (Dutta et al. 1996).

Table 16.2 Typical calcium carbide mixtures used for desulphurisation

Grade	Reagent composition, %			
	CaC_2	CaCO_3	CaO	C
CAD 60	48	31	17	4
CAD 70	56	22	19	3
CAD 80	64	14	20	2
CAD 85	68	9	22	1

Lime contributes towards enhancement of the basicity of the micro-slags that are formed, while dissociation of limestone provides carbon dioxide that is beneficial for agitation. On the other hand, carbon in the mixture helps in maintaining the necessary atmosphere at the reaction sites. These mixtures are injected using nitrogen (in some special cases argon) as the carrier gas. Co-injection of carbide and magnesium metal granules (in the ratio of 2.5–7.0 : 1) at injection rates of typically 20–25 kg/min. and 10–12 kg/min. is also resorted to when extremely low levels of sulphur in hot metal (circa 0.010%) are required. The use of magnesium granules helps to reduce the injection time as well as the slag volume. Addition of lime/soda ash during injection is also practised, when it is necessary to bring down the slag raking time or to reduce the metal loss in the slag. External desulphurisation with such mixtures produces very dry slags, in which substantial amount of metal as granules (below 3 mm) tend to get entrapped.

16.7.5 Injection of Desulphurising Agents

A schematic representation of the entire equipment system employed for the injection of powders into melts is given in Figure 16.4 while Figure 16.5 provides a pictorial view of the same. The powder injector (Figure 16.6) is the most important component of the system.

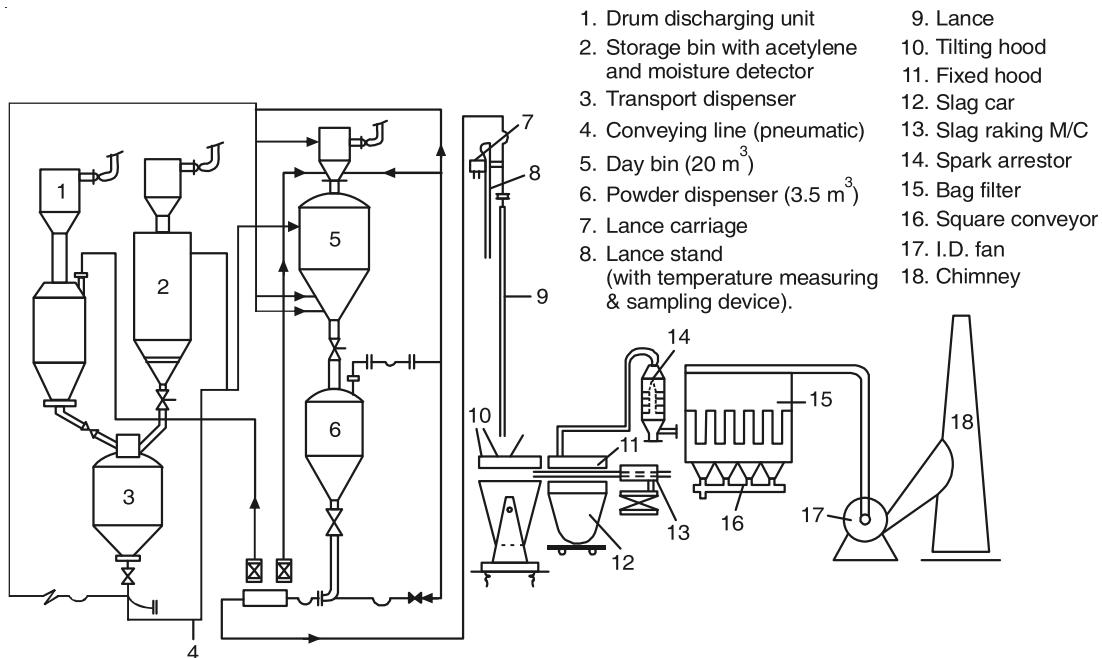


Figure 16.4 Schematic representation of the entire powder injection system.

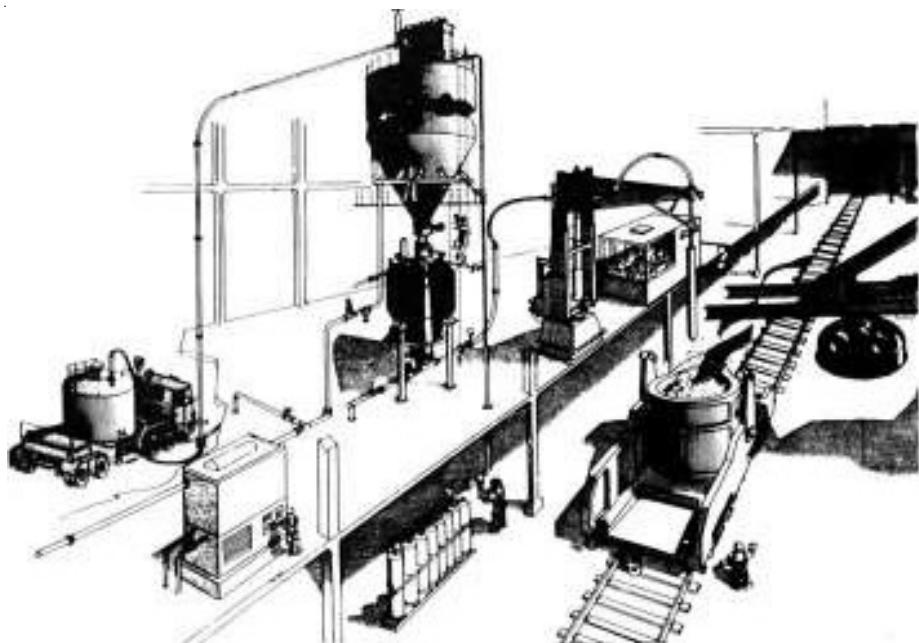


Figure 16.5 Pictorial view of powder injection into a ladle.

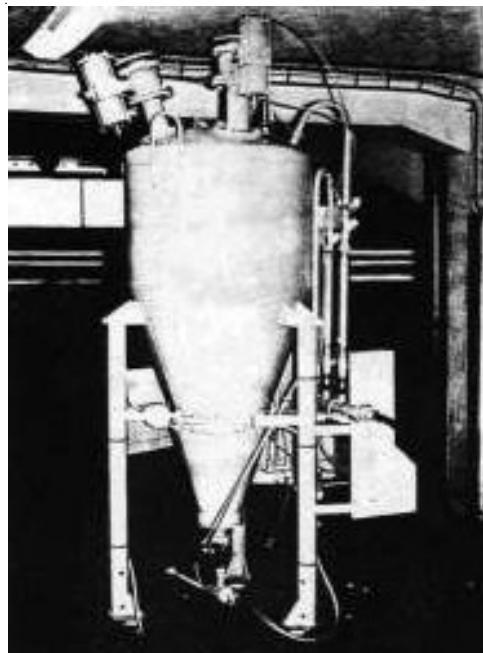


Figure 16.6 Close-up of a typical powder dispenser.

When a powder like calcium carbide is injected, using a carrier gas (nitrogen/argon), the gas and calcium particles penetrate into the liquid hot metal as a gas particle jet until their momentum is dissipated, which has been confirmed by water model studies. At the bottom of the jet, a *plume* (photograph taken in room temperature model studies shown in Figure 16.7) is created, where the gas forms spherical-cap bubbles, 20 to 100 mm in diameter. The physical and chemical phenomena in the plume are shown schematically in Figure 16.8.



Figure 16.7 Photograph of the plume (air-water room temperature model).

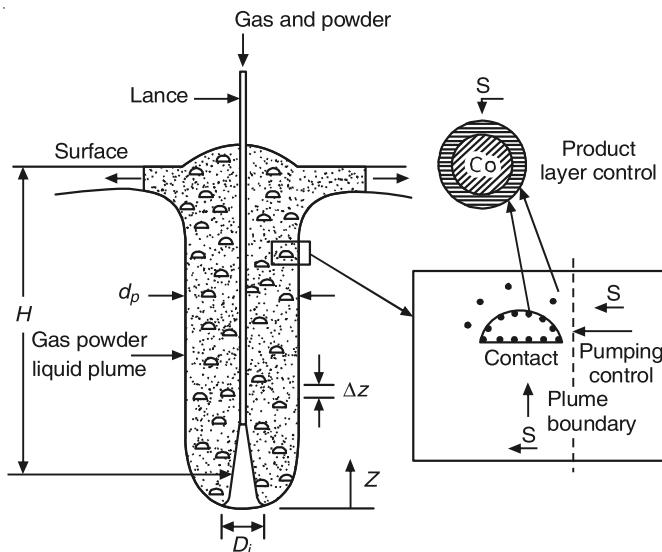


Figure 16.8 Physical representation of bubble formation and powder dispersion following injection.

Owing to buoyancy the gas rapidly accelerates and the drag force between the gas and the liquid causes the liquid to be accelerated as well. The carbide particles which are also buoyant then start to rise—a fraction of the particles rise on the bubble interfaces, while the remainder rises, dispersed in the melt. The particles and gas are heated as they rise, and the particles react, resulting in the removal of sulphur. The rate of mass transfer is governed by the rate at which sulphur-rich liquid is pumped into the plume by entrainment (normally termed *pumping control*) as well as the rate at which sulphur diffuses through the boundary layers to the particles (normally called *contact control*). The rate of desulphurisation with respect to time follows first order reaction kinetics, and the rate of desulphurisation in the plume is determined by the reduction of the sulphur content and the flow rate of liquid at the top of the plume.

Some typical results obtained in an operating unit are presented in Figure 16.9 (Pandey et al. 1996). It is clear that following calcium carbide injection, the kinetics of desulphurisation can be described as first order, with respect to the sulphur content in the hot metal. The first order rate constant is approximately proportional to the square root of the gas flow rate, and the cube of the slag weight. Therefore, removal of slag to the maximum possible extent prior to external desulphurisation, is extremely important.

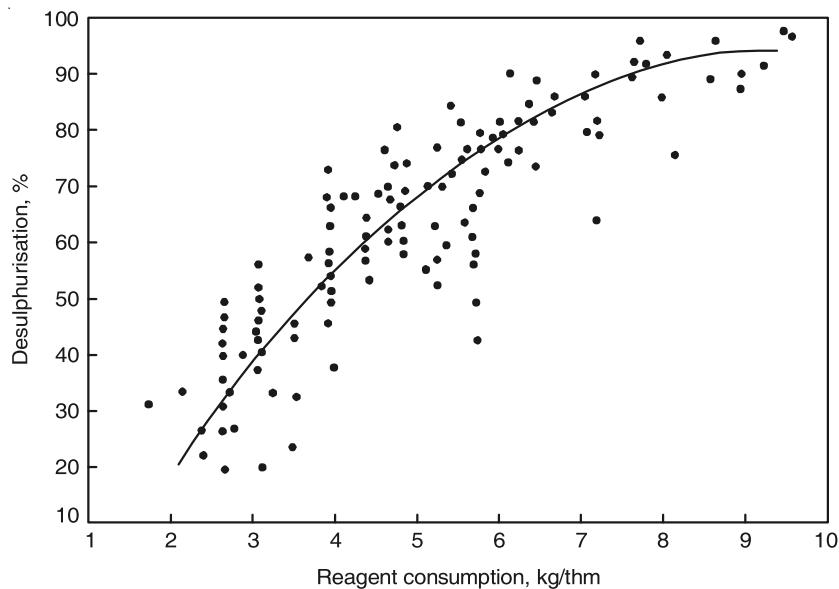


Figure 16.9 Degree of desulphurisation as a function of reagent consumption (CAD 80).

Reaction mechanism

When calcium carbide is injected into hot metal, it first decomposes to form calcium vapour and a layer of graphite. The calcium vapour reacts with the sulphur in hot metal to form a layer of calcium sulphide over the graphite layer. The effective diffusivity of calcium vapour through the product layers is approximately $7 \times 10^{-7} \text{ m}^2/\text{s}$, which results in calcium fluxes much greater than