

$$L_{S,e} = \left\{ \frac{(W_S)_{\text{in slag}}}{[W_S]_{\text{in metal}}} \right\}_{\text{eq}} = K_{39} \frac{(a_{O^{2-}})}{[W_O]_{\text{eq}}} \quad (5.41)$$

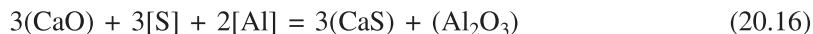
where W_S is wt. % sulphur and K_{39} is the equilibrium constant for the ionic exchange reaction:



It was also mentioned that the reaction can be written in terms of compounds, and that CaO is the most powerful desulphuriser, amongst the basic oxides present in iron and steelmaking slags. Sulphur transfer from metal to slag is better if the value of $L_{S,e}$ is higher. For this, from Eq. (5.41), it follows that the dissolved oxygen in metal, , should be as low as possible. This requires the addition of deoxidising agents into the melt.

Secondary steelmaking slags consist of CaO, Al₂O₃ and SiO₂ as the major constituents. Amongst the common deoxidisers, aluminium is the most powerful (see Section 20.3.1). Low oxygen levels can be achieved by deoxidation (referred to as *killing*, in popular terminology) using Al, and these are known as *aluminium-killed steels*.

On the basis of the above, the overall reaction may be written as:



for which the equilibrium constant is:

$$K_{16} = \frac{(a_{\text{CaS}})^3 (a_{\text{Al}_2\text{O}_3})}{(a_{\text{CaO}})^3 [h_S]^3 [h_{\text{Al}}]^2} \quad (20.17)$$

Assuming $h_S = W_S$, $h_{\text{Al}} = W_{\text{Al}}$, and (W_S) in slag proportional to (a_{CaS}) , it is possible to write:

$$L_{S,e} = \left\{ \frac{(W_S)}{[W_S]} \right\}_{\text{eq}} \propto (a_{\text{CaO}}) \frac{[W_{\text{Al}}]^{2/3}}{(a_{\text{Al}_2\text{O}_3})^{1/3}} \quad (20.18)$$

Increasing wt. % of CaO increases a_{CaO} and decreases $a_{\text{Al}_2\text{O}_3}$, thereby increasing $L_{S,e}$. Figure 20.15 demonstrates this and shows that $L_{S,e}$ increases with increase in wt. % CaO in slag and W_{Al} in molten steel for CaO–Al₂O₃ slags at 1500°C and 1650°C (Turkdogan 1983). K_{16} is a function of temperature, and is given as:

$$\log K_{16} = \frac{48580}{T} - 16.997 \quad (20.19)$$

where T is the temperature in kelvin. Hence, the lower temperature helps desulphurisation.

Suppose, the initial $[W_S]$ in steel is 0.01% and it is to be brought down to 0.002%. Let the mass of steel be 150 tonne and that of slag be 2 tonnes. It means that the amount of sulphur to be transferred to the slag would be $150 \times (0.01 - 0.002) \times 10^{-2}$ tonnes. Therefore, wt. % S in slag (W_S) would be $\frac{150 \times 0.008 \times 10^{-2}}{2} \times 10^2 = 0.6\%$. So, final $L_S = \frac{0.6}{0.002} = 300$. Since equilibrium may not be attained in the process, $L_{S,e}$ should be larger than 300. Plant trials have shown that it is possible to have effective desulphurisation, if $L_{S,e}$ is 1000 or above. Such a high value is obtained when the slag is almost saturated with CaO.

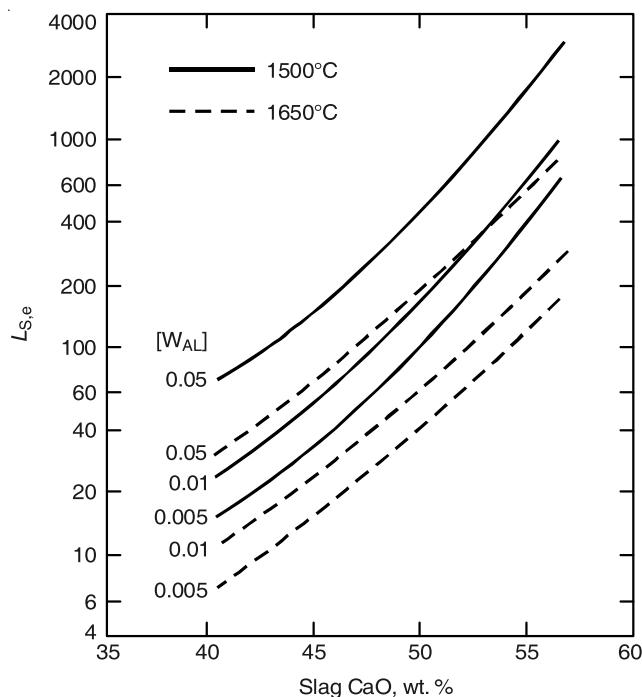


Figure 20.15 Equilibrium sulphur partition ratio between liquid iron with dissolved Al and CaO–Al₂O₃ slags.

20.5.2 Kinetic Aspects

Nowadays it is a standard practice to carry out some desulphurisation of hot metal in the transfer ladle after tapping from the blast furnace and before charging it into the primary steelmaking furnace. This is known as *external desulphurisation* and is a part of *hot metal ladle pretreatment*. It has been discussed in Chapter 16, and, in this connection, the kinetic aspects of desulphurisation in ladles have been reviewed. Hence, the following brief write-up is concerned only with special kinetic features of desulphurisation in ladles during secondary steelmaking.

The major difference between the two is that normally the hot metal ladles do not have bottom stirring through porous plugs, while in secondary steelmaking, ladles are fitted with bottom porous plugs for argon purging. Therefore, in hot metal desulphurisation, a lance has to be immersed into the melt from the top for gas stirring and injection of desulphurising agents. This comes under the broad area of *Injection Metallurgy (IM)*.

As stated in the introductory remarks (Section 20.5), IM is practiced in secondary steelmaking only for deep desulphurisation for the production of ultra-low sulphur (ULS) steels. Otherwise, desulphurisation by treatment with synthetic slag on top of molten steel in the ladle, ladle furnace or during vacuum treatment is sufficient. The principal additions are CaO and Al, though some CaF₂, SiO₂ and Al₂O₃ are also required for slag formation.

The desulphurisation reaction has been found to behave approximately as a first-order reversible process

$$-\frac{d[W_S]}{dt} = k_{S,\text{emp}} \left\{ [W_S] - \frac{(W_S)}{L_{S,e}} \right\} \quad (20.20)$$

where $k_{S,\text{emp}}$ is an empirical rate constant, and has the dimension of s^{-1} . Again, $k_{S,\text{emp}} = k a$, where k is specific rate constant per unit slag–metal interface area, and a is specific interfacial

area, i.e. $a = \frac{\text{interfacial area}}{\text{volume of liquid metal}}$

Neglecting the reverse reaction and integrating Eq. (20.20) from $t = 0$ to $t = t$, the following can be obtained

$$\ln \left\{ \frac{[W_S]_0}{[W_S]} \right\} = k_{S,\text{emp}} \cdot t = k a t \quad (20.21)$$

where $[W_S]_0$ is initial wt.% S in steel at $t = 0$ (i.e. at the start of desulphurisation).

The $k a$ parameter is a function of the bottom argon flow rate Q . Figure 20.16 presents a log-log plot of some $k a$ vs. Q data for desulphurisation in a gas-stirred ladle of pilot plant size (Asai et al. 1983). The data could be fitted properly with two inter-connected straight lines with different slopes. In general, literature data indicate that the $k a$ parameter lies between $(0.5$ and $3) \times 10^{-3} \text{ s}^{-1}$ for low gas flow rates, and $(3$ and $15) \times 10^{-3} \text{ s}^{-1}$ for high gas flow rates.

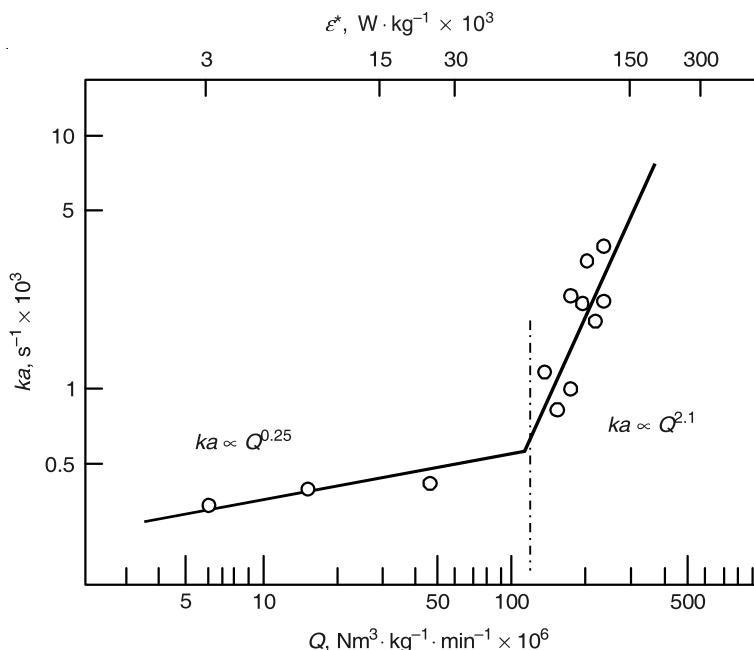


Figure 20.16 Effect of gas flow rate on ka parameter for desulphurisation reaction.

Therefore, effective desulphurisation in gas-stirred ladles is possible only above a critical minimum gas flow rate. Porous plugs are not suitable, since only slit plugs are capable of delivering such high flow rates. From experiments in water models, it has been found that at high gas flow rates there is extensive slag–metal emulsion formation, resulting in a large slag–metal interfacial area, which speeds-up sulphur transfer from the metal to slag.

EXAMPLE 20.4

For ladle desulphurisation of liquid steel, calculate the following.

- Wt. % sulphur in steel after desulphurisation, assuming slag–metal equilibrium
- Initial desulphurisation rate, assuming initial S in slag as 0.1% and $k_{S,\text{emp}}$ as $2 \times 10^{-3} \text{ s}^{-1}$
- Per cent desulphurisation after 2.5 minutes of slag treatment.

Given: Temperature = 1650°C, Slag is CaO–Al₂O₃ having 55 wt. % CaO, Wt. % Al in metal = 0.05%, Steel weight = 150 tonnes, Slag weight = 2 tonnes, Initial wt. % S in steel = 0.01%.

Solution:

- From Figure 20.15, for the conditions mentioned, the equilibrium slag–metal sulphur partition ratio ($L_{S,e}$) is approximately 500. If detailed slag composition is used, a more exact value could be calculated (see Example 4.9, Chapter 4).

Initial amount of sulphur in metal = amount of sulphur in slag + metal at equilibrium (in kg)

$$\text{i.e. } 150 \times 0.01 \times 10^{-2} \times 10^3 = 10^{-2} \times 10^3 \{150[W_S]_f + 2(W_S)_f\}, \text{ in kg}$$

where $[W_S]_f$ and $(W_S)_f$ are final wt. % S in metal and slag respectively.

$$\text{i.e. } 15 = 10 [W_S]_f (150 + 2 \times 500) \text{ kg}$$

Calculations give $[W_S]_f = 0.0013\%$

- From Eq. (20.20), the rate of desulphurisation = $-\frac{d[W_S]}{dt} = k_{S,\text{emp}} \left[[W_S] - \frac{(W_S)}{L_{S,e}} \right]$

Noting that $k_{S,\text{emp}} = 2 \times 10^{-3}$, and other data given above,

$$\text{Rate of desulphurisation initially} = 2 \times 10^{-3} [0.01 - 0.1/500] = 1.96 \times 10^{-5} \text{ wt. \% S/s.}$$

- This will require integration of Eq. (20.20) from $t = 0$ to $t = t$. It is given in Eq. (20.21) ignoring the backward reaction. If the backward reaction is also considered, the sulphur balance in (a) above is to be modified as follows.

$$150 \times \{0.01 - [W_S]\} = 2(W_S); \text{ i.e. } (W_S) = 0.75 - 75[W_S]$$

$$\text{Hence, } [W_S] - (W_S)/L_{S,e} = 0.85 [W_S] - 15 \times 10^{-4}$$

$$\text{Integration of Eq. (20.20), therefore, gives: } \ln \left[\frac{0.85 [W_S]_0 - 1.5 \times 10^{-4}}{0.85 [W_S] - 1.5 \times 10^{-4}} \right] = k_{S,\text{emp}} \cdot t$$

Noting that $t = 2.5 \text{ minutes} = 150 \text{ s}$, and solving, $[W_S] = 0.0063 \text{ wt. \%}$

20.5.3 Injection Metallurgy (IM)

IM is practised in secondary steelmaking not only for the removal of sulphur from metal, but also for inclusion modification. In Chapter 16, the description of IM processes has already been presented and hence, will not be repeated. The processes may be broadly classified into the following two categories:

1. Continuous injection of solid powdered reagents into molten steel along with a stream of argon, through a lance immersed from the top.
2. Continuous injection (i.e. feeding) of powdered regents, encased in a steel tube immersed inside molten steel. This is known as *Cored Wire Feeding*. Important desulphurising agents for powder injection in secondary steelmaking are indicated in Table 20.4.

Table 20.4 Important desulphurising agents for powder injection in secondary steelmaking

Agent	Composition, wt. %	Injected amount, kg/t steel
Ca–Si alloy	Ca–30, Si–62, Al–8	2–4
CaO–CaF ₂	CaO–90, CaF ₂ –10	3–6
CaO–Al ₂ O ₃ –CaF ₂	CaO–70, Al ₂ O ₃ –20, CaF ₂ –10	2–5

The addition of calcium metal into the melt in the form of Ca–Si alloy causes deep deoxidation, deep desulphurisation and modification of inclusions to yield desirable properties. The initiative came after extensive deposits of natural gas were discovered in cold Arctic regions, like Alaska in North America. The line-pipe steel for transporting gas over long distances has to withstand high pressure, corrosion from H₂S in gas, and sub-zero temperatures without any tendency towards brittle fracture. The steel for this purpose required treatment by calcium.

Calcium is a gas at steelmaking temperatures. The vapour pressure vs. temperature relationship for pure calcium is:

$$\log p_{\text{Ca}}^0 \text{ (in atm)} = -\frac{8920}{T} - 1.39 \log T + 9.569 \quad (20.22)$$

At 1600°C (1873 K), $p_{\text{Ca}}^0 = 1.81$ atm. This is quite high and is likely to lead to instantaneous violent vapour formation resulting in a very little Ca reacting with the melt.

In Ca–Si alloy,

$$p_{\text{Ca}} = p_{\text{Ca}}^0 \times [a_{\text{Ca}}] \quad (20.23)$$

In the composition of Ca–Si alloy employed, a_{Ca} is approximately 0.1, thus making $p_{\text{Ca}} < 1$ atm and eliminating the possibility of vapour formation. Even then, there is considerable loss of Ca as vapour, since the solubility of Ca in steel is very low (0.025 wt. % at 1600°C).

In powder injection processes, therefore, the powders should be injected as deep as possible into the melt. In wire feeding, Ca–Si powder is encased in a hollow steel tube and swaged before the tube plus powder is continuously fed into the melt by a machine. Powder injection gives better desulphurisation owing to the increased surface area. However, wire feeding is particularly suitable for inclusion modification. It is worth mentioning here that wire feeding is practised for

other purposes—such as Al wire feeding for deoxidation and alloy powder feeding for precision alloying. Many steel plants, therefore, have provision for both powder injection and cored wire feeding.

20.6 CLEAN STEEL TECHNOLOGY

20.6.1 Introduction

In general, non-metallic inclusions in steel have been found to be harmful for desirable mechanical properties and corrosion resistance of steel. The inclusion particles are mostly oxides and to some extent, sulphides. This is more so in the case of high-strength steels for critical applications. As a result, there is a move to produce what is known as *Clean Steel*, i.e. steel free from inclusions. However, no steel can be made totally free from inclusions and therefore, cleanliness is a relative term. Which steel is clean and which is dirty can be decided only when it is known what the intended application is and what are the consequent property requirements.

The sources of inclusions may be classified into the following.

1. Precipitation due to reaction with molten steel or during freezing because of reaction between dissolved oxygen and the deoxidisers, with consequent formation of oxides (also reaction with dissolved sulphur as well). These are known as *endogenous inclusions*.
2. Mechanical and chemical erosion of the refractory lining
3. Entrapment of slag particles in steel
4. Oxygen pick up from the atmosphere, especially during teeming, and consequent oxide formation.

Inclusions originating from contact with external sources as listed in items 2 to 4 above, are called *exogenous inclusions*. These are formed during the entire process of secondary steelmaking; therefore, it is necessary to make a summary as shown in Figure 20.17. Technological measures for inclusion control are briefly outlined below.

20.6.2 Cleanliness Control during Deoxidation

Section 20.3 has already discussed this subject; however, the important measures for clean steel production are summarised below once again.

1. Carryover slag from the furnace into the ladle should be minimised, since it contains high percentage of FeO + MnO and makes efficient deoxidation fairly difficult.
2. Deoxidation products should be chemically stable. Otherwise, they would tend to decompose and transfer oxygen back into liquid steel. SiO_2 and Al_2O_3 are preferred to MnO. Moreover the products should preferably be liquid for faster growth by coalescence agglomeration and hence faster removal by floatation. Complex deoxidation gives this advantage.

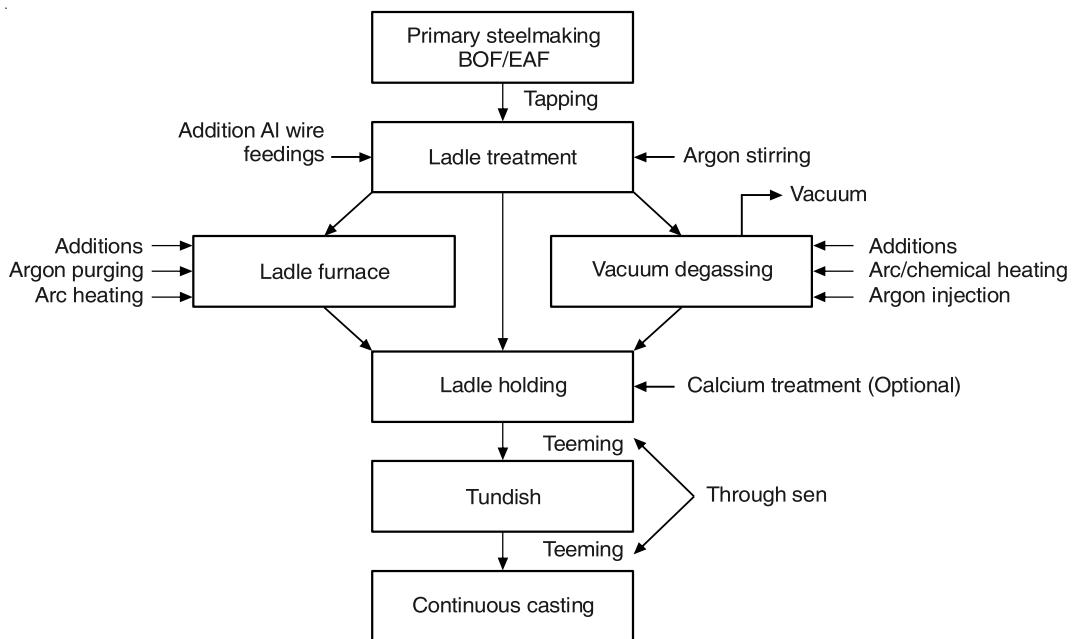


Figure 20.17 Secondary steelmaking route from tapping to continuous casting.

3. Stirring of the melt in the ladle by argon flowing through bottom tuyeres is a must for mixing and homogenisation, faster growth, and floatation of the deoxidation products. However, very high gas flow rates are not desirable from the cleanliness point of view, since it has the following adverse effects:
 - Re-entrainment of slag particles into molten steel.
 - Increased erosion of refractories and consequent generation of exogenous inclusions.
 - More ejection of metal droplets into the atmosphere with consequent oxide formation.

20.6.3 Cleanliness Control during Teeming

Subsequent to processing in LF/CAS-OB/Vacuum degasser and/or injection treatment, the liquid steel is held in the ladle for 20 to 40 minutes before and during teeming. Larger non-metallic particles get plenty of time to float up. The presence of a well-deoxidised top slag does not allow much atmospheric re-oxidation. Refractory erosion is also low, since there is no gas stirring. However, during teeming, if no precautions are taken, the melt will become dirty because of:

1. Oxygen absorption by the teeming stream
2. Slag entrainment consequent to funnel formation
3. Erosion of the nozzle refractory.

The falling stream of liquid steel absorbs oxygen from the surrounding air by the *jet entrainment effect*. The oxygen content of steel has been found to increase by as much as 40 to

400 ppm, depending on the nature of the stream. This leads to the formation of large inclusions, rich in FeO and MnO. Moreover, it increases the dissolved oxygen content and causes further generation of inclusions by reaction during solidification in the mould. Atmospheric oxidation has been eliminated by the use of *Submerged Entry Nozzles* (SEN) in the continuous casting route, where the nozzle tip is submerged into the melt. Additional protection can also be provided by shrouding the stream further with a gentle flow of argon.

Section 20.3.5 has outlined the problem of slag carryover from primary steelmaking furnaces into the ladle during tapping. Formation of a *funnel-shaped cavity* towards the end of tapping causes the slag to flow out along with the metal. This phenomenon also leads to entrainment of slag by metal during teeming from the ladle and tundish. This can be minimised by:

- Not emptying the ladle completely.
- Employing a refractory float on the funnel vortex.
- Using an electromagnetic sensor around the nozzle that gives a signal when entrained slag begins to flow out through the nozzle along with the metal.

For producing clean steels, the refractory used in the teeming nozzles is of considerable importance, since there is a high probability that inclusions and impurities introduced at the stage of teeming will not be eliminated. Here, both erosion and corrosion are severe owing to the high flow velocity of liquid steel through the nozzle. Adequate thermal shock resistance of the lining is also required to prevent its spalling. Nowadays, zirconia (ZrO_2)-based linings are the most preferred—such as ZrO_2 -graphite, ZrO_2 -CaO-C. Since ZrO_2 is expensive, Al_2O_3 -based material (e.g. Al_2O_3 -C-SiC) is employed as the back-up layer. One alternative to zirconia is Al_2O_3 -based linings.

20.6.4 Tundish Metallurgy for Clean Steel

The tundish is a shallow, refractory-lined vessel that is located in between the ladle and the continuous casting mould. Liquid steel flows from the ladle into the tundish and from the tundish into the mould. A tundish is a must in continuous casting for proper regulation of the rate of flow into the mould.

A detailed description of the tundish and its metallurgical aspects will be taken up in Chapter 23. At this juncture, it will suffice to state that proper design and operational control of the tundish is extremely important for the final cleanliness of steel. It is worth mentioning here that proper metallurgical control is required even in the casting mould (both for continuous as well as for ingot casting) to ensure meticulous fine control of steel cleanliness.

20.7 MISCELLANEOUS TOPICS

20.7.1 Inclusion Modification

Despite all attempts, it is very difficult to make steel with as low an inclusion content as is desired. This gives rise to the second option of inclusion modification, which consists of adding some reagents into molten steel with the specific objective of altering the nature of the inclusions