

20.4 DEGASSING AND DECARBURISATION OF LIQUID STEEL

The gases, i.e. hydrogen, nitrogen and oxygen, dissolve as atomic H, N, O respectively in molten steel. However, their solubilities in solid steel are very low. Section 20.3 has already dealt with oxygen. Removal of oxygen from steel is carried out by adding deoxidisers. When liquid steel solidifies, excess nitrogen forms stable nitrides of Al, Si, Cr, etc. The dissolved nitrogen affects the toughness and ageing characteristics of steel as well as enhancing the tendency towards stress corrosion cracking. Nitrogen is, by and large, considered to be harmful for properties of steel. Its strain hardening effect does not allow extensive cold working without intermittent annealing and hence low nitrogen is essential for deep drawing steels. However, in some applications, nitrogen has a beneficial effect, such as the grain refinement by fine AlN precipitates.

While nitrogen is absorbed by molten steel during steelmaking from nitrogen in air, hydrogen is picked-up from the moisture in solid charges. Hydrides are thermodynamically unstable. Therefore, the excess hydrogen in solid steel tends to form H₂ gas in the pores and also diffuses out to the atmosphere, since H has very high diffusivity even in solid steel because of its low atomic mass. In relatively thin sections, such as those produced by rolling, diffusion is fairly rapid. Hence, excess hydrogen is less, reducing the tendency towards the development of high gas pressure and the formation of pinholes.

However, diffusion is not that efficient in forgings because of their large sizes. So H rejected by the solidifying steel accumulates in blowholes and pinholes, where high gas pressure is developed. During forging, the combination of hot working stresses and high gas pressure in the pinholes near the surface tend to cause fine cracks in the surface region. Efforts to avoid these cracks have led to the commercial development of vacuum degassing processes. Dissolved hydrogen also causes a loss of ductility of steel; hence, low H content is a necessity for superior grades of steel with high strength and impact resistance. These considerations have led to the requirement of low hydrogen in rolled products as well as in several grades of steel.

20.4.1 Thermodynamics of Degassing Reactions

The reactions are:



Table 20.3 presents the equilibrium relations for the above reactions. Degassing is effective under vacuum. Low gas pressure lowers values of *h*. At such low concentrations, *h* may be expressed as concentration in ppm (i.e. parts per million), and in weight per cent at higher concentrations.

Table 20.3 Equilibrium relations of degassing reactions

Sl. No.	Reaction	Equilibrium relation	Unit of <i>h</i>	K vs. T relation	Value at 1600°C and 1 mm Hg
1.	$[H] = \frac{1}{2}H_2(g)$	$[h_H] = K_H \cdot p_{H_2}^{1/2}$	ppm	$\log K_H = -\frac{1905}{T} + 2.409$	0.77
2.	$[N] = \frac{1}{2}N_2(g)$	$[h_N] = K_N \cdot p_{N_2}^{1/2}$	ppm	$\log K_N = -\frac{518}{T} + 2.937$	14.1
3.	$[C] + [O] = CO(g)$	$[h_C][h_O] = K_{CO} \cdot p_{CO}$	wt. %	$\log K_{CO} = -\frac{1160}{T} - 2.00$	4.7×10^{-4}
			ppm	$\log K_{CO} = -\frac{1160}{T} + 6.00$	0.47

1 matmosphere = 10^{-3} atm; for [C]–[O] reaction, $h_C = 0.05$ wt. %, i.e. 500 ppm.

As noted in Table 20.3 (Ghosh Ahindra 2001), a pressure of 1 torr (= 1 mm Hg) in a vacuum chamber is thermodynamically capable of lowering H, N and O to very low levels. This is in contrast to steels not treated under vacuum, where the H and N values can be as high as 5 ppm and 50 ppm respectively. In actual degassing operations, removal of hydrogen is fast and it often attains equilibrium, but nitrogen removal is more difficult because of kinetic reasons. The [C]–[O] reaction is utilised for removal of carbon to very low levels (ultra-low carbon steels) for special applications, such as sheets for automobile bodies. Besides the main reactions during vacuum degassing, there are some minor side reactions such as volatilisation, decomposition of inclusions and melt-refractory interactions, but these are being omitted here for the sake of brevity of this text.

20.4.2 Kinetics of Desorption and Absorption of Nitrogen by Liquid Steel

As mentioned above, the removal of nitrogen during vacuum treatment poses problems on account of slow kinetics. The extent of nitrogen removal is approximately in the range of 20 to 40%. Therefore, the salient features of desorption and absorption of nitrogen by molten steel are being presented here. Owing to its importance as well as its complex nature, it has been investigated by many investigators from as early as 1960s in the laboratory along with several theoretical analyses. The findings can be summarised as follows.

1. The rate is controlled by all the kinetic steps, viz. mass transfer in the melt, slow surface chemical reaction, as well as mass transfer in the gas phase.
2. The surface chemical reaction was originally treated as a first order reversible process. The rate of desorption from the melt (r_N) was given by the equation:

$$r_N = Ak_N([W_N] - [W_N]_e) \quad (20.15)$$

where, A is the gas–metal interfacial area, k_N is the *first-order rate constant*, $[W_N]$ and $[W_N]_e$ are wt. % N in the melt and that at equilibrium with N_2 in the gas phase. However, of late, the surface chemical reaction has been proposed to be a *second-order* reaction.

3. k_N was found to decrease with increasing wt. % of oxygen dissolved in the melt as shown in Figure 20.9 (Pehlke and Elliot, 1963). It was subsequently found that sulphur has a similar effect. It is well-established that O and S are *surface active solutes* in molten iron, copper, etc. Thus they tend to block the surface sites and thus retard the rate.

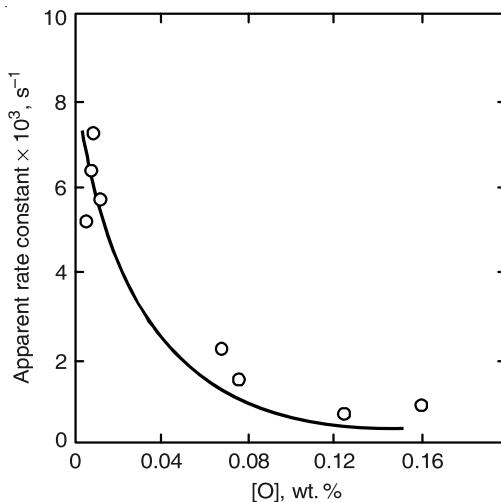


Figure 20.9 Influence of oxygen content on the absorption rate of nitrogen by liquid iron at 1823 K.

Figure 20.10 taken from a comprehensive kinetic study by Harada and Janke (1989), shows the variation of the second-order chemical rate constant (k_c) with oxygen and sulphur contents of the iron melt. Curve 1 and data points correspond to experiments under vacuum. These do not agree with experiments under normal pressure (curves 3, 4, 5). The authors did not provide any satisfactory explanation for the same. The retarding influence of O and S dissolved in molten steel is very well-established for vacuum degassing in steel plants as well. Therefore, the melt should be well-deoxidised and well-desulphurised first for efficient removal of nitrogen from steel.

20.4.3 Vacuum Degassing Processes

For more comprehensive information, besides (Ghosh Ahindra 2001), readers may consult other sources such as (Fruehan 1990). Vacuum degassing processes have been traditionally classified into the following categories:

- Ladle degassing processes (VD, VOD, VAD)
- Stream degassing processes
- Circulation degassing processes (DH and RH).

Currently, stream degassing no longer exists. Ladle degassing processes are widely used. Amongst the circulation degassing processes, DH is virtually non-existent, while the RH (Ruhrstahl Heraus) process and its variants are the most popular.

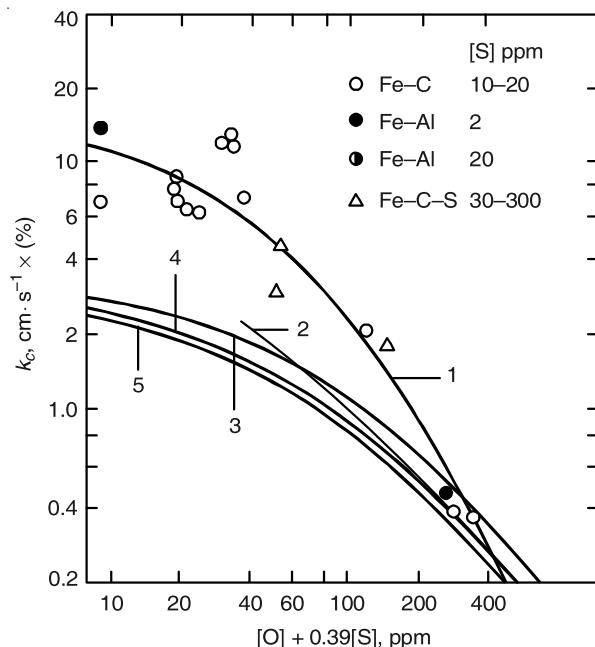


Figure 20.10 Variation of the second order rate constant for nitrogen desorption with dissolved oxygen and sulphur content of molten steel at 1873 K.

Since, an additional temperature drop of 20–40°C occurs during secondary steelmaking and temperature control of the steel melt is important for proper casting, provisions for heating and temperature adjustment have been made in RH, as well as in ladle degassing [*vacuum arc degassing (VAD)*]. *Vacuum-oxygen decarburisation (VOD)* where oxygen lancing is done under vacuum was originally developed for stainless steel refining, but is now used for the production of *ultra-low carbon steels (ULC)* as well. Similarly, RH–OB, where oxygen is blown into the RH chamber, is used for the production of ULC steels.

Besides degassing and decarburisation, modern vacuum degassers are used to carry out various other functions such as desulphurisation, heating, alloying and melt homogenisation. Injection of argon below the melt is a must for good homogenisation, fast processing and inclusion removal. The carry over slag from steelmaking converters has to be modified by the addition of deoxidisers and CaO.

Figure 20.11 shows the RH process schematically. Molten steel is contained in the ladle. The two legs of the vacuum chamber (known as *Snorkels*) are immersed into the melt. Argon is injected into the upleg. Rising and expanding argon bubbles provide pumping action and lift the liquid into the vacuum chamber, where it disintegrates into fine droplets, gets degassed and comes down through the downleg snorkel, causing melt circulation. The entire vacuum chamber is refractory lined. There is provision for argon injection from the bottom, heating, alloy additions, sampling and sighting as well as video display of the interior of the vacuum chamber.

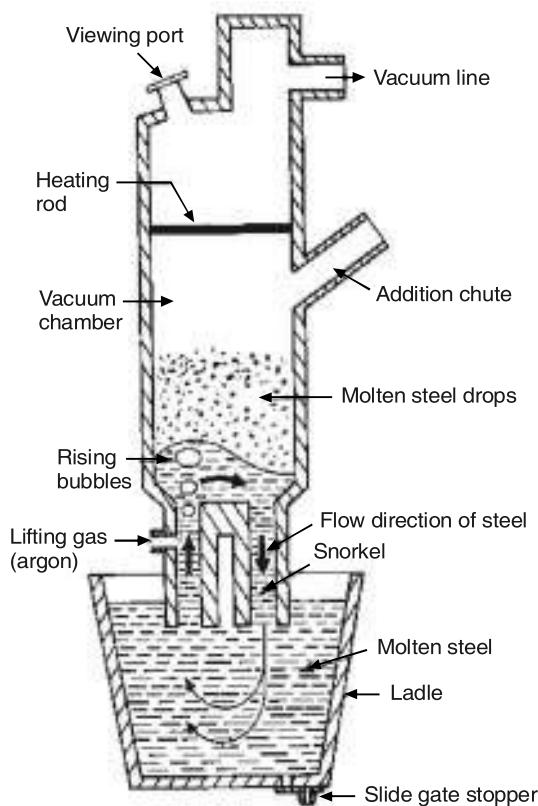


Figure 20.11 Sketch of a RH degasser (Courtesy: Messo Metallurgie).

Figure 20.12 shows the VAD process schematically. Heating is done by the arc with graphite electrodes, as in a ladle furnace. Heating, degassing, slag treatment and alloy adjustment are carried out without interrupting the vacuum.

As far as the vacuum generating system is concerned, mechanical vacuum pumps remove the bulk of air and gas from the chamber. However, they are not capable of lowering the vacuum chamber pressure to very low values of about 1 torr, which is required by the process. This is achieved by the use of steam ejector pumps in conjunction with mechanical pumps. A jet of steam issues through a nozzle at high velocity and drags the surrounding gases along with it (i.e. jet entrainment). Steam also helps in condensing the dust and volatiles coming out from the vacuum chamber. For a modern 200 t VD unit, a pumping capacity higher than 500 kg of air per hour with 1 torr chamber pressure is required.

In industrial vacuum degassing, the treatment time should be short enough to match logically with converter steelmaking on the one hand and continuous casting on the other. To achieve this, in addition to proper choice and design of the process, the principal variables are as follows:

- Pumping rate of the vacuum equipment (also known as *exhausting rate*)
- Rate of injection of argon below the melt.

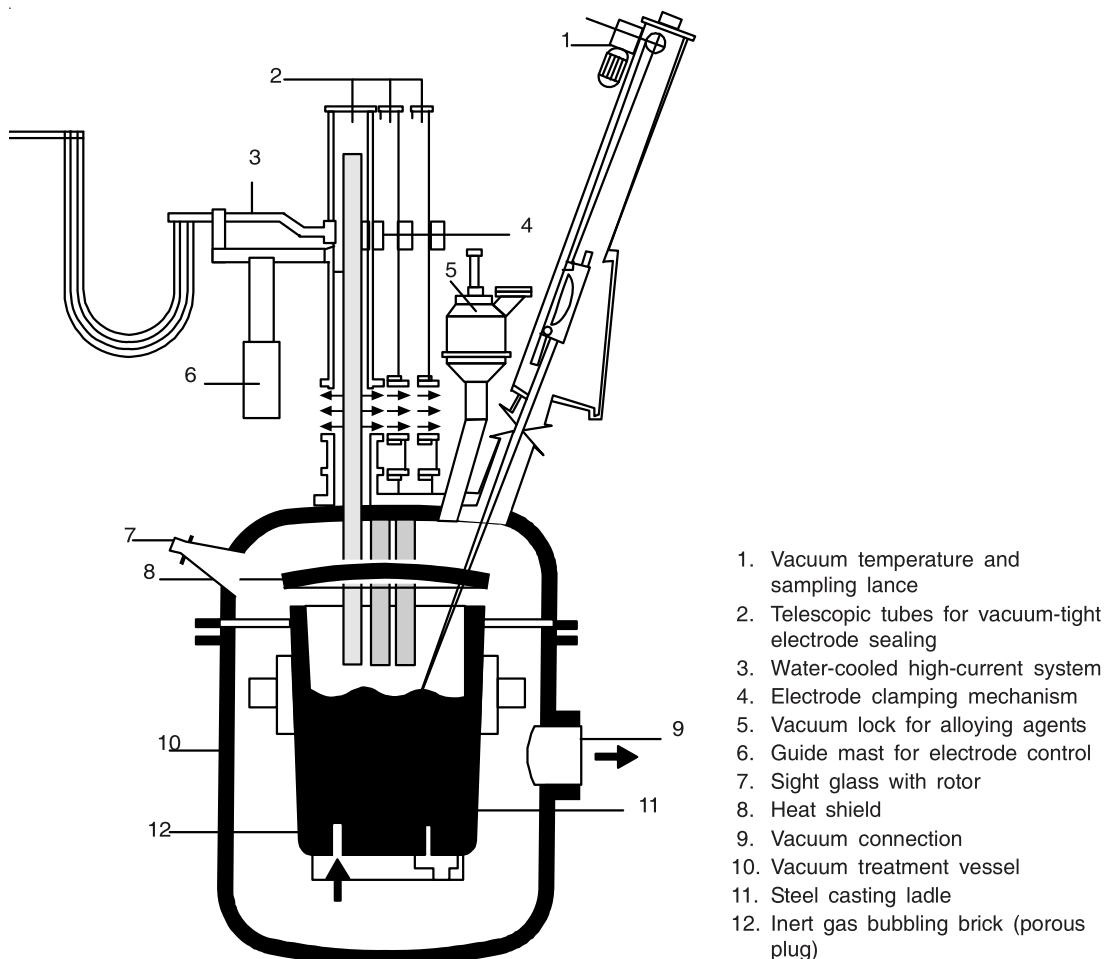


Figure 20.12 Sketch of a VAD unit (Courtesy: Messo Metallurgie).

Increasing the argon flow rate increases the rate of degassing and gas evolution. This tends to raise the chamber pressure and requires a higher exhausting rate. Hence, optimisation of the two is required. Figure 20.13 presents some theoretically calculated curves with different values of reaction rate constants (k) for a RH degasser (Soejima et al. 1987). It shows that there is no advantage in increasing the pumping rate if the argon flow rate is not adequate. Also, there is no advantage of having large argon flow rates until there is a certain minimum exhausting rate.

20.4.4 Manufacture of Ultra-Low Carbon (ULC) Steel by RH-OB Process

It has already been mentioned that the use of oxygen blowing under vacuum (VOD process) was started for refining stainless steel. Prior to VOD, the *argon–oxygen decarburisation* (AOD)

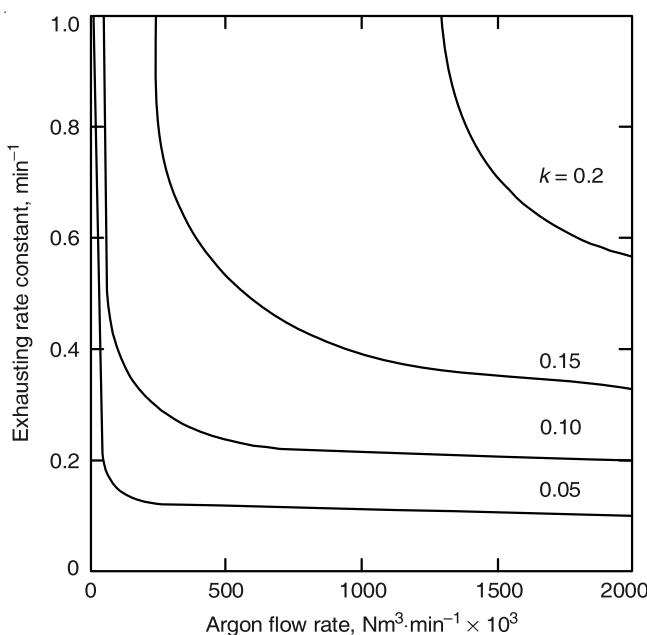


Figure 20.13 Influence of pumping rate and argon flow on decarburisation rate constant in a RH degasser.

process was invented. The thermodynamic basis for these processes had already been known for some time. However, AOD was not commercially viable till the price of argon became reasonably low. These will be taken up further in Chapter 21 dealing with stainless steel manufacture.

To meet the increasing demand for cold-rolled sheets with improved mechanical properties and to cope with the changeover from batch to continuous annealing, the demand for ULC ($C < 20 \text{ ppm}$) is increasing. As stated in Section 20.4.3 that, in this connection, the RH process was modified by oxygen blowing under vacuum. It is known as RH-OB and was first developed by Nippon Steel Corp. in Japan for producing stainless steel in 1972 and subsequently, employed for the production of ULC steels. The present thrust is to bring down the carbon content of the melt from 300 ppm to 10–20 ppm in 10 minutes. RH-OB was subsequently made more versatile by incorporating provisions for chemical heating by aluminium addition. Oxidation of aluminium generates heat rapidly and counters temperature drop during degassing. Powder injection for desulphurisation, alloy additions, etc. were later incorporated. This versatile and flexible process is known as the *RH-injection process*, and is shown in Figure 20.14.

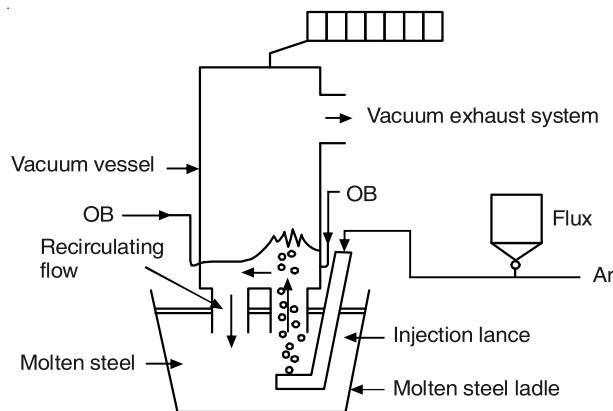


Figure 20.14 The RH-injection process.

EXAMPLE 20.3

- (a) Consider argon purging of liquid steel in a ladle at 1600°C through bottom tuyeres. The gas bubbles coming out contain 10% CO, 5% N₂, 5% H₂, and rest Ar. Assuming the gas to be at equilibrium with molten steel at the exit, calculate the hydrogen content of steel. The steel contains 1% C, 2% Mn and 0.5% Si.

Given: $e_H^C = 0.06$, $e_H^{Mn} = -0.002$, $e_H^{Si} = 0.027$, $e_H^H = 0$

- (b) Calculate the rate of circulation of molten steel (R) through the vacuum chamber in RH degassing to lower the hydrogen content of steel from 5 to 2 ppm in 15 minutes. Assume that molten steel attains equilibrium with respect to hydrogen gas inside the vacuum chamber.

Given: (i) Composition and temperature of steel same as in (a) above, (ii) pressure in the vacuum chamber is 1 milli-atmosphere, (iii) weight of steel in the ladle (W) is 150 tonnes.

Solution:

- (a) The reaction is: $[H] = \frac{1}{2} H_2(g)$ (20.12)

From Table 20.3, $[h_H] = K_H \cdot p_{H_2}^{1/2}$; $\log K_H = -\frac{1905}{T} + 2.409$, where the unit of h is ppm. $T = 1873$ K, $p_{H_2} = 0.05$ atm at the bubble exit at the top of the melt. Solving with the above values, $h_H = 5.5$ ppm = 5.5×10^{-4} in wt. % scale.

$$\log h_H = \log f_H + \log W_H = e_H^C \cdot W_C + e_H^{Mn} \cdot W_{Mn} + e_H^{Si} \cdot W_{Si} + e_H^H \cdot W_H + \log W_H$$

Putting in values, and solving, the following can be obtained: $W_H = 4.69 \times 10^{-4}$ wt. % = 4.69 ppm

(b) Hydrogen Balance

m_1^* = Rate of removal of H from steel (g/min)

m_2^* = Rate at which H is transferred to vacuum (g/min) (Ex. 20.4)

$$m_1^* = -W \times 10^6 \times \frac{d[\text{ppm}] \times 10^{-6}}{dt} = -W \times \frac{d[\text{ppm}]}{dt} \quad (\text{Ex. 20.5})$$

$$m_2^* = R \times 10^6 \times \{[\text{ppm H}] - [\text{ppm H}]_{\text{eq}}\} \times 10^{-6} = R \{[\text{ppm H}] - [\text{ppm H}]_{\text{eq}}\} \quad (\text{Ex. 20.6})$$

Equating Eqs. (Ex. 20.5) and (Ex. 20.6),

$$\frac{d[\text{ppm H}]}{[\text{ppm H}] - [\text{ppm H}]_{\text{eq}}} = \frac{R}{W} dt \quad (\text{Ex. 20.7})$$

Integrating Eq. (Ex. 20.7) between the limits: $t = 0$, ppm H = 5, and $t = 15$ min, ppm H = 2,

$$R = \frac{150}{15} \ln \frac{5 - [\text{ppm H}]_{\text{eq}}}{2 - [\text{ppm H}]_{\text{eq}}}$$

On the basis of part (a), and assuming that the gas in the vacuum chamber is only H_2 , calculations give $[\text{ppm H}]_{\text{eq}} = 0.66$ ppm, thus giving $R = 11.75$ tonnes/min.

20.5 DESULPHURISATION IN SECONDARY STEELMAKING

Except in free-cutting steels, sulphur is considered to be a harmful impurity, since it causes hot shortness. Therefore, it is necessary to limit it to 0.02% for general carbon steels. In special steel plates, the normal specification for sulphur is at present 0.005%, but there is demand for *ultra-low sulphur* (ULS) steels with as low as 10 ppm (0.001%) S in grades such as line-pipe steel, HIC resistant steels and alloyed steel forgings.

Sulphur comes into iron principally through coke ash, and is effectively removed first during ironmaking (see Chapter 5, Section 5.4.3) and further during hot metal pre-treatment in ladles (see Chapter 16). However, levels below 0.01% have to be achieved by further desulphurisation during secondary steelmaking. There are now processes such as the MPE process of Mannesmann and the EXOSLAG process of U.S. Steel, where desulphurisation is done, to some extent, by adding a synthetic slag. Desulphurisation by use of synthetic slags is also carried in IGP, ladle furnace and vacuum degasser; but deep desulphurisation can only be achieved by the injection of powders like calcium silicide into the melt.

20.5.1 Thermodynamic Aspects

Chapter 4, Section 4.4.3, has introduced the concept of *Sulphide Capacity* (C_s) as the potential capacity of a slag melt, at a temperature, to hold sulphur as sulphide. Equations (4.50) to (4.52) have given the definition and mathematical expressions related to C_s . Chapter 5, Section 5.4.3 has discussed thermodynamics of sulphur reactions in the blast furnace hearth between slag and metal. The *equilibrium partition coefficient for sulphur* ($L_{S,e}$) is defined as: