Thermodynamics of refining in electric furnace steelmaking

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Introduction

In general, the input impurity levels in the electric and induction furnace charge is low, so refining does not pose any special problems. But the use of poor quality or unsorted scrap or high phosphorus sponge in the charge can lead to significant increase in the input impurity level. Besides, quite often the desired final impurity level is very low. Composition control in these cases pose a problem particularly because a large refining time leads to a higher power consumption and low productivity. To overcome this difficulty, ladle refining as secondary steelmaking practices are widely used along with the electric steel making. In this lecture refining principles both in electric furnace and ladle furnace will be discussed.

Even at steelmaking temperatures, the reactions do not attain equilibrium unless the slag and metal phases are well stirred for a reasonable length of time. In this sense, equilibrium thermodynamics cannot give quantitative idea about the extent of actual refining that can be attained in electric and induction furnace.

Dephosphorisation

The dephosphorisation reaction can be written as

$$2\,\underline{P} + 5(FeO) \longrightarrow P_2O_5 + 5Fe$$

This slag metal equilibrium is quite often represented as follows :

$$K_p = \frac{(\%P_2O_5)}{\%\,\underline{P}^2(\%FeO_t)^5} \qquad (1)$$

where $\%\,FeO_t = \%\,FeO + 1.35\%\,Fe_2O_3$ in the slag. K_p is related to slag composition by

$$log(K_p) = 10.78\,log\,(\%CaO) - 0.00894T - 6.245 \qquad (2)$$

where tempeature is in °C

Eqs. 1 and 2 clearly show the strong influence of *% CaO* and *%FeO* in slag in phosphorus removal. Fig.1 shows the affect of basicity and *% FeO* on phosphorus partitioning. The optimum *% FeO* is around 14-16%. At higher percentage, the dephosphorising power falls off due to excessive replacement of CaO by FeO in the slag.

Eqn.2 further shows that low temperature is favourable for phosphorus partitioning. Hundred degree increase temperature will reduce the phosphorus partitioning between slag and metal by a factor of about 7.

Addition of Fluorspar between 1.5% in the slag, increases phosphorus partitioning, K_p by a factor of three.

When Na_2O slag is used for dephosphorisation, at 1600°C.

$$log(K_p) = 8.67\ log\ (\%Na_2O) - 14.55 \qquad (3)$$

The value of log (K_p) for Na_2O based slag is higher than those for *CaO* based slag by 1.5 - 2.5. This means that when *CaO* is replaced by Na_2O, the distribution ratio of phosphorus between slag and metal is expected to be 30-300 times higher. The temperature dependence of log (K_p) is similar to that for *CaO* based slag.

Soda ash or Na_2CO_3 is an effective dephosphorising agent. At steelmaking temperatures Na_2CO_3 decomposes to Na_2O and CO_2.

overall reaction in this case appears to be

$$Na_2CO_3(l) + \frac{4}{5}\underline{P} \longrightarrow (Na_2O) + \frac{2}{5}(P_2O_5) + \underline{C}$$

Data of equilibrium partitioning of phosphorus between slag and metal is not available. But it is found that soda ash is a better dephosphorising agent than a mixture of Na_2O and Fe_2O_3. Laboratory studies show that reaction with *CaO* based slag reaches equilibrium in about 40-60 min. in an induction furnace. On the other hand the reaction attain equilibrium in about 30 min. time for the sodium oxide, iron oxide system.

Desulphurisation

The transfer of sulphur from metal to slag can be represented by the following reaction.

$$\underline{S} + O^{2-} \longrightarrow S^{2-} + \underline{O}$$

Since the oxygen in metal, $\underline{O}$ is in equilibrium with *FeO* in the slag the above equilibrium is sometimes represented by

$$K_s + \frac{(\%S)}{\%\,\underline{S}} \text{ x } (\%FeOt) \qquad (4)$$

where K_3, is the function of temperature and composition. Fig.2 shows the variation of K_3 with slag composition. In the temperature range of 1530-1730°C. K_3 appears to be independent of temperature. The definition of K_3 and Fig.2 clearly show that for good desulphurisation a reducing condition, low % *FeO* in slag, and high basicity are essential.

Addition of CaF_2 does not increase the equilibrium partitioning of sulphur between the slag and metal but possibly enhances the rate of reaction by improving the fluidity of slag. The time required to attain equilibrium is almost same as that for dephosphorisation.

Calcium aluminate based slags are widely used in ladle refining for the production of high quality clean steel. Molten calcium aluminate enhances the extent of deoxidation of steel and has a high sulphide capacity. The overall desulphurisation reaction can be written as follows :

$$(CaO) + \frac{2}{5} Al + S \longrightarrow (CaS) + \frac{1}{3} (Al_2O_3)$$

Fig.3 shows[3] the equilibrium partitioning of sulphur between lime saturated calcium aluminate melts and low alloy steels as a function of aluminium content of steel. Fig.3 indicates that at 1600°C, the equilibrium sulphur level of metal containing 0.04% Al will be less than 0.002%. In the melt at lime saturation, the CaO content is 55% C and 65% at 1700°C and the solubility of CaS in this slag corresponds to about 2% S.

Na_2O, Na_2CO_3 and CaC_2 are other commonly used desulphurising agents. Capacity of desulphrization of Na_20 is about 10^3 times more than that of *CaO* on weight % basis. Soda ash desulphurises according to the overall reaction.

$$Na_2CO_3 + S + 2C \longrightarrow (Na_2S) + 3CO$$

Besides, it decomposes as Na_2O which acts as a desulphurising agent. Eqn. 7 clearly suggests that for low carbon steel its effectiveness is comparatively less. The overall reaction for CaC_2 is as follows :

$$CaC_2 + S \longrightarrow (CaS) + 2C$$

It is one of the strongest desulphurising agent. At equilibrium, sulphur of the metal will be insignificant but it leads to carbon pick up. For each 0.01% removal of sulphur from the metal, there will be 0.0075% carbon pick up by the metal. However, the actual carbon pick up could be much more because of the reaction:

$$(FeO) + CaC_2 \longrightarrow (CaO) + Fe + 2\underline{C}$$

Estimation of slag composition

Both the eqs. 1 and 4 show that the extent of dephosphorisation and desulphurisation are strongly dependent on $\% FeO$ in slag. The former is favoured by high $\% FeO_t$, in the slag whereas the later requires low value. Normally, the slag is not routinely analysed, so actual $\% FeO_t$ is not known. However for CaO saturated slags $\% FeO_t$ can be roughly estimated as :

$$\% \underline{C}.\% \mathrm{FeO} \approx 0.33 \qquad (5)$$

at 1600°C. Even when slag is not saturated with base, the above equation can be used for rough estimation.

Phosphorus in the slag comes only from the oxidation of the element. Oxidation of 0.01%P gives rise to 0.23 kg. of P_2O_5 in the slag per ton of steel.

SiO_2 in the slag comes from the flux and ore added and the oxidation of silicon in the metal. Oxidation of 0.1% Si gives rise to 2.1 kg of SiO_2 in the slag per ton of metal.

Deoxidation

The deoxidation reaction can be represented as follows :

$$x\underline{M} + y\underline{O} \longrightarrow M_xO_y$$

Fig.4 shows the deoxidation equilibrium for the common deoxidant. It shows that among usual deoxidant, aluminium is the strongest deoxidiser. When the residual level of Al in the steel is 0.01% the residual oxygen level is only 0.002%.

Complex deoxidiser like Si-Mn, Ca-Si, Ca-Si-Al etc. are strong deoxidisers, particularly the last two. Fig.5 shows[2] the equilibrium oxygen level of deoxidation with Si-Mn. It shows that for 0.1% residual Si in metal dissolved oxygen decreases from 0.015% to 0.012% when % Mn is increased from 0% to 0.08%.

For the appropriate addition of deoxident, a correct estimate of %0 in the bath is essential. Assuming the C-0 reaction attains equillibrium, the % 0 in the bath can be estimated.

$$\% \, 0 = \frac{(0.002)}{\% \, C}$$

The actual % 0, in general, will be higher than the value obtained from the above equation.

References

[1] I.K. Baljiva, A.G. Quarrell and P. Vajragupga; J. Iron & Steel Inst. 1946. Vol. 153. 115.

[2] E.T. Tarkdogan : Physico-chemical properties of molten slag and glass : The Metals Society, 1983.

[3] E. T. Tarkdogan : Ironmaking & Steelmaking, 1985, Vol. 12, 64.

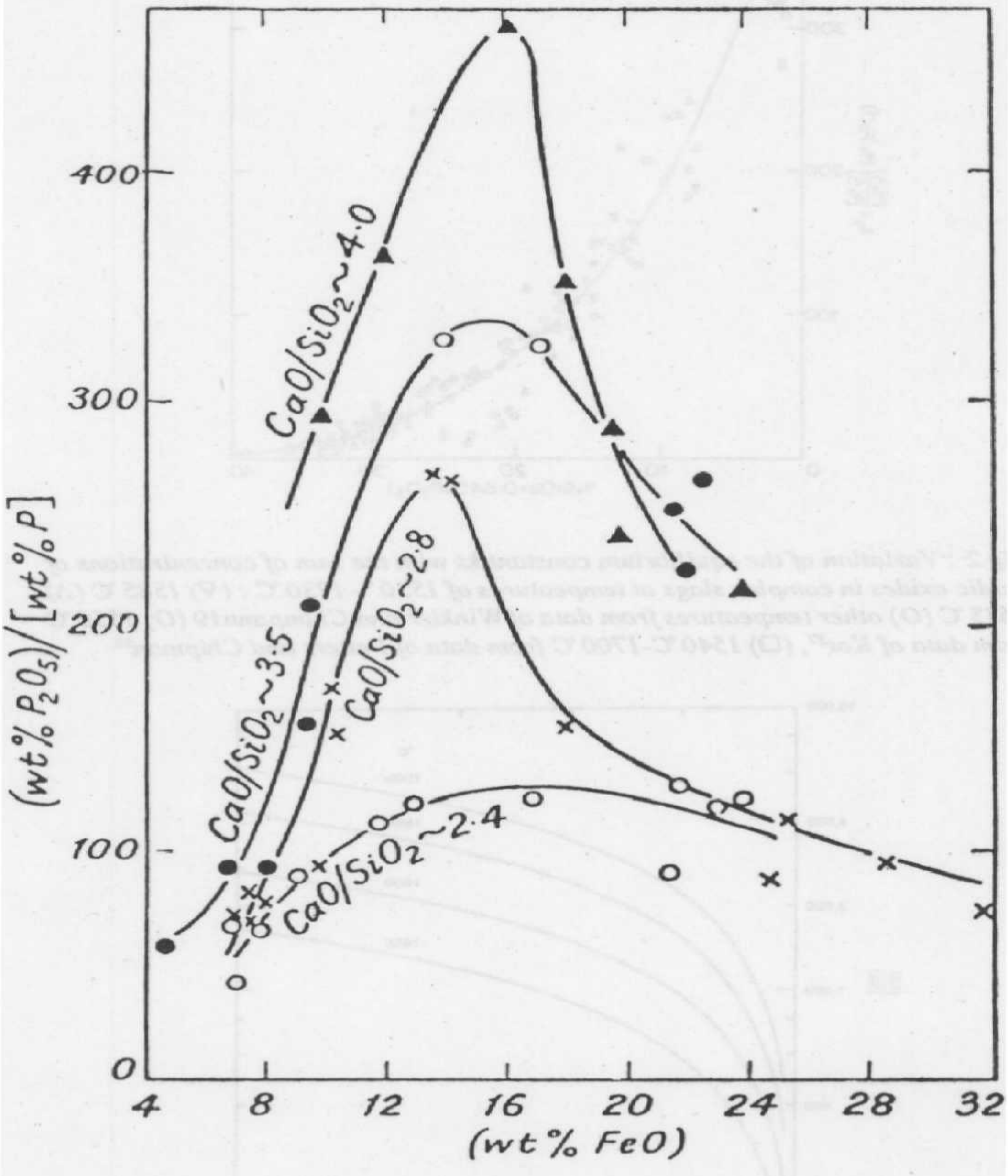

Fig.1 : Dependence of the distribution ratio (wt.% P_2O_5)/(wt.% P), on the iron oxide content of slags with constant (wt% CaO) (wt % SiO_2) ratios in laboratory experiments at a corrected temperature of 1685 °C (from Balajiva, Quarrell and Vajragupta[1]

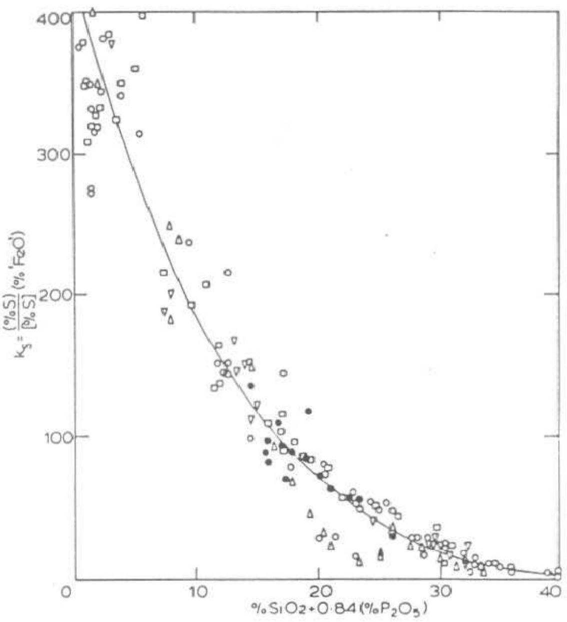

Fig.2 : Variation of the equilibrium constant ks with the sum of concentrations of acidic oxides in complex slags at tempeatures of 1530°- 1730℃ : (∇) 1585℃ (Δ) 1635℃ (O) other tempeatures from data of Winkler and Chimpann19 (O) 1550℃ from data of Kor[27], (☐) 1540℃-1700℃ from data of Fetters and Chipman[30]

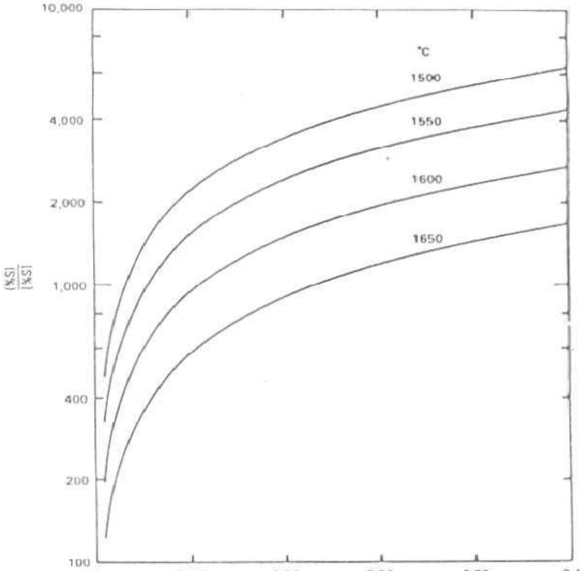

Fig.3: Equillibrium sulphur distribution between lime saturated calcium aluminate melts and low-alloy liquid steel as function of aluminium content of steel for indicated tempeatures

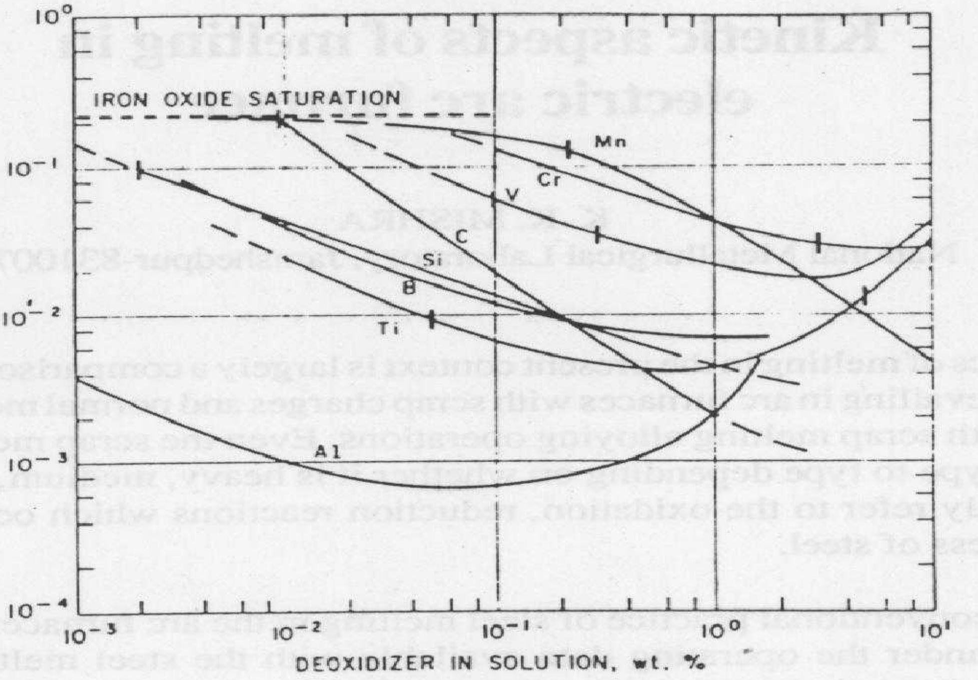

Fig.4 : Deoxidation equilibria in liquid iron alloys at 1600 °C

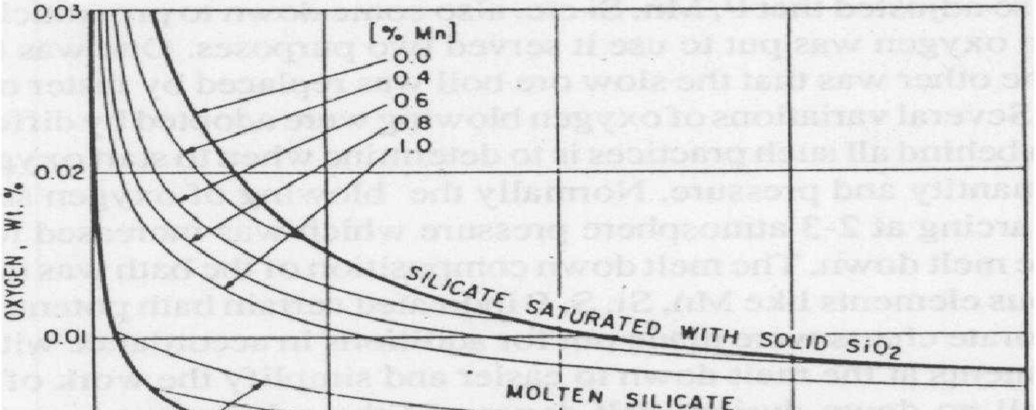

Fig.5 : Equilibrium data on simultaneous deoxidation of steel by silicon and manganese at 1600 °C