Slag Composition Variations Causing Variations in Steel Dephosphorisation and Desulphurisation in Oxygen Steelmaking

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Study of plant analytical data for BOS and OBM processes revealed that the iron oxide content of slag has a decisive effect on the extent of steel dephosphorisation and desulphurisation. The slag/metal distribution ratios $(\%P)/[\%P]$ and $(\%S)/[\%S]$ from the plant data are scattered about the calculated equilibrium values for the slag–metal reactions involving the iron oxide content of the slag. The data also revealed consistent interrelations between the concentrations of FeO, CaO and SiO₂ in the slag at the end of oxygen blowing. However, there are variations in the slag composition in the interrelations between the oxide contents: 5 to 6 % FeO and 4 to 5 % CaO or SiO₂ between the low and high values. These unpredictable variations in slag composition from one heat to the next bring about variations in the extent of steel dephosphorisation and desulphurisation. Consequently, the observed distribution ratios $(\%P)/[\%P]$ and $(\%S)/[\%S]$ are scattered within a slag composition range, bordered by the equilibrium curves for the low and high iron oxide contents with the corresponding CaO and SiO₂ contents of the slag.

KEY WORDS: oxygen steelmaking processes; slag compositions; slag–metal–gas equilibrium; decarburisation; dephosphorisation; desulphurisation.

Introduction

It is indeed an honour to have been invited by The Iron and Steel Institute of Japan to deliver the Yukawa Memorial Lecture, which is a tribute to the late Mr. Masao Yukawa for his great leadership and contribution to the growth of the steel industry in Japan.

For many years, various studies have been made of plant analytical data in an attempt to assess the state of steelmaking reactions at the end of oxygen blowing. Invariably, there were variations in the results of these independent studies and conclusions drawn therefrom.

In this Lecture, I shall present my recent observations from a study of plant data, on unpredictable variations in the slag composition which bring about variations in the extent of steel dephosphorisation and desulphurisation, from one heat to the next.

Plant Data

The plant data used in this study are those which the author acquired about ten years ago from the BOP and Q-BOP shops of the Gary Works of USX Corporation. The analytical data were for slag and steel samples taken from the vessel at turndown for tap. For a better assessment of the state of steelmaking reactions over a wide range of carbon contents, the plant data chosen are for the earlier “catch-carbon practice.” The slag and steel compositions and melt temperatures were within the ranges shown in **Table 1**. A more detailed information on these plant data

are given in the author’s recent publication.¹⁾

To be consistent with more widely used terminology, BOS will be used instead of BOF or BOP for the oxygen top blowing process and OBM instead of Q-BOP for the U.S. Steel oxygen bottom blowing process.

Interrelations between FeO, CaO and SiO₂ Contents

The sum of the three major oxides CaO+FeO+SiO₂ is in the range 82 to 90 % with slag basicities of $V = \%CaO/\%SiO_2 = 2$ to 4. The total iron oxides in the slag is represented as FeO.

As would be expected from the shape of the liquidus isotherm in the composition diagram of the system CaO–FeO–SiO₂ saturated with di-calcium silicate, the iron oxide content of the slag varies in a systematic manner with the lime and silica contents of the slag as shown in **Figs. 1** and **2**. Most of the data points are scattered within the

Table 1. Summary of analytical data from BOP and Q-BOP shops of Gary Works for the earlier “catch-carbon practice”.

Temperature:	1610 ± 20 °C
Slag, mass%:	40–60 CaO, 3–10 MgO, 4–30 FeO (total), 3–8 MnO, 12–26 SiO ₂ , <3 P ₂ O ₅ <0.3 S, CaO/SiO ₂ ratio 2–4.
Steel, mass%:	0.01–0.8 C, 0.1–0.4 Mn, 0.002–0.03 P, 0.015–0.030 S.

Fig. 1. Relation between total iron oxide (as %FeO) and lime contents of slags at vessel turnaround.

Fig. 2. Relation between total iron oxide (as %FeO) and silica contents of slags at vessel turnaround.

hatched area.

In slags not saturated with lime as di-calcium silicate, the iron oxide contents will be higher, which may partly account for the scatter in the distribution of the data points. The scatter is also due to uncertainties in the analytical data on steelmaking slags for the following reasons.

- (i) Contamination of slag samples by dust on the melt shop floor and rust on the steel rod used for slag sampling.
- (ii) Incomplete separation of minute steel droplets dispersed in the slag sample.
- (iii) Samples taken from silicate-saturated slags may contain dispersed particles of lime and magnesia, coated with di-(Ca,Mg) silicate.

Slag Basicity

In most steelmaking slags containing $\text{MgO} < 8\%$ and $\text{P}_2\text{O}_5 < 3\%$, the slag basicity is adequately defined by the mass ratio $V = \% \text{CaO} / \% \text{SiO}_2$. The lime and silica contents for the same iron oxide concentrations in Figs. 1 and 2 give the relationships shown in Fig. 3 between the slag basicity and lime or silica contents of the slag. As shown in Fig. 4, there is a corollary relation between the slag basicity and iron oxide content of the slag.

Fig. 3. Interrelations between slag basicity and lime and silica contents of slags at vessel turnaround.

Fig. 4. Interrelation between basicity and total iron oxide content of slags in oxygen-steelmaking processes.

Carbon–Oxygen Relation

The plant data plotted in Fig. 5 show the relation between the concentrations of oxygen and carbon in steel at vessel turnaround for tap. The dotted line, corresponding to the product $[\text{ppm O}][\% \text{C}] = 20$, is the equilibrium relation for 1 atm pressure of CO. The oxygen contents of steel at all carbon levels in the BOS and for $\text{C} > 0.2\%$ in the OBM steelmaking, are scattered about the equilibrium values for a pressure of 1.5 atm CO, which is assumed to be an average gas-bubble pressure in the steel bath. For the case considered, the carbon–oxygen equilibrium relation in the steel bath is represented by $[\text{ppm O}][\% \text{C}] = 30 \pm 2$.

At low carbon levels in the melt near the end of the blow, much of the oxygen is consumed by the oxidation of iron, manganese and phosphorus, resulting in a lower volume of CO generation. Because of the presence of hydrogen in the gas bubbles in OBM steelmaking, the partial pressure of CO in the gas bubbles will be lowered when the rate of CO

Fig. 5. Relations between concentrations of oxygen and carbon in steel at vessel turn-down.

generation decreases at low carbon contents. Hence the oxygen contents are lower than those in the BOS. In OBM steelmaking at $C < 0.15\%$, the carbon–oxygen relation may be approximated by the product $[\text{ppm O}]\sqrt{\%C} = 80 \pm 10$.

Carbon–Iron Oxide Relation

With respect to the complete slag–metal–gas (CO) equilibrium, the carbon–iron oxide equilibrium relation is represented by

$$K_{CF} = \frac{p_{CO}(\text{atm})}{[\%C]a_{FeO}} \quad \text{.....(1)}$$

where a_{FeO} is the activity of total iron oxide with respect to pure molten FeO. From the thermochemical data compiled in the author's recent book,²⁾ the temperature dependence of the equilibrium constant K_{CF} is given by the equation below.

$$\log K_{CF} = -\frac{5730}{T} + 5.096 \quad \text{.....(2)}$$

Noting that the total number of mols of oxides in 100 g of steelmaking slags is 1.65 ± 0.05 , the iron oxide activity is represented by the following equation in terms of the mass concentration of FeO and its activity coefficient γ_{FeO} .

$$a_{FeO} = \frac{\%FeO}{72 \times 1.65} \gamma_{FeO} = 0.0084(\%FeO)\gamma_{FeO} \quad \text{.....(3)}$$

According to the author's recent re-assessment of the numerous slag–metal equilibrium data, γ_{FeO} is primarily only a function of slag basicity in both simple and complex slags. The assessed values of γ_{FeO} are given in Table 2.

For an average turn-down temperature of 1610°C , slag basicity of $V=2.75$, for which $\gamma_{FeO}=1.2$, and $p_{CO}=1.5$ atm, the carbon–iron oxide equilibrium relation is reduced to

$$(\%FeO)[\%C] = 1.38 \quad \text{.....(4)}$$

The iron oxide and carbon contents of the melts at vessel turn-down are compared in Fig. 6 with the above average equilibrium value. The oxygen contents of the steel, in accord with the data in Fig. 5, are indicated on the top abscissae of the diagrams. It is seen that there are departures from the slag–metal–gas (CO) equilibrium: the product

Table 2. Activity coefficients of iron oxide, with respect to pure molten FeO, as related to the slag basicity: $B=(\%CaO+1.4\times\%MgO)/(\%SiO_2+0.84\times\%P_2O_5)$ and $V=\%CaO/\%SiO_2$. For $MgO < 8\%$ and $P_2O_5 < 3\%$, $B \approx 1.17 \times V$.

B	V	γ_{FeO}
2.34	2.0	2.00
2.93	2.5	1.33
3.51	3.0	1.11
4.10	3.5	0.98
4.68	4.0	0.87

Fig. 6. Iron oxide and carbon contents at vessel turn-down are compared with the equilibrium values for average slag basicity $V=2.75$.

$(\%FeO)[\%C]$ is below the equilibrium value at low carbon contents and above the equilibrium value at high carbon contents. On the other hand, as noted from the data in Fig. 5, the carbon–oxygen relation is in general accord with the metal–gas (CO) equilibrium over a wide range of carbon contents.

(%P)/[%P] Ratio in Relation to O & C Contents of Steel

Using data obtained from many independent laboratory experimental work with simple and complex slags, the author³⁾ derived the following relation for the slag–metal phosphorus reaction, over a wide range of slag composition and melt temperature.

Fig. 7. Phosphorus distribution ratios and carbon contents at vessel turn-down are compared with the equilibrium values for $1610 \pm 20^\circ\text{C}$ and $50 \pm 5\%$ CaO.

$$K_{\text{PO}} = \frac{(\%P)}{[\%P]} [\%O]^{-2.5} \quad \text{.....(5)}$$

$$\log K_{\text{PO}} = \frac{21740}{T} - 9.87 + 0.071 \times \text{BO} \quad \text{.....(6)}$$

where $\text{BO} = \% \text{CaO} + 0.3 \times \% \text{MgO}$. For an average 6% MgO content of steelmaking slags, Eq. (6) is simplified to

$$\log K_{\text{PO}} = \frac{21740}{T} - 9.727 + 0.071 \times \% \text{CaO} \quad \text{.....(7)}$$

The slag/metal phosphorus distribution ratios are plotted in Fig. 7 against the carbon contents of melts at vessel turn-down. The oxygen contents of the steel, in accord with the data in Fig. 5, are indicated on the top abscissae of the diagrams. At low carbon contents, the $(\%P)/[\%P]$ ratio in the BOS melts are below the slag-metal equilibrium values. In the OBM process at low carbon contents, e.g. $<0.05\%$ C, the phosphorus distribution ratios are scattered about the equilibrium values. In contrast, there are considerable departures from equilibrium at high carbon contents. That is, in the BOS melts with $C > 0.1\%$ and in the OBM melts with $C > 0.05\%$, the steel is dephosphorised to a much greater extent than the equilibrium state for the correspond-

ing low oxygen contents of the steel. This behaviour is similar to the oxidation of iron above the equilibrium state at high carbon contents. In fact, a similar behaviour was noted in a previous study³⁾ for the oxidation of manganese in the steel bath.

Dephosphorisation Related to Lime and Iron Oxide Contents of Slag

Because both the iron and phosphorus are oxidised far above the slag-metal equilibrium states over a wide range of carbon contents, it would appear that the extent of steel dephosphorisation may well be controlled by the iron oxide content of the slag, as represented by the equations below.

$$K_{\text{PF}} = \frac{(\%P)}{[\%P]} (a_{\text{FeO}})^{-2.5} \quad \text{.....(9)}$$

The solubility of oxygen in iron in equilibrium with iron oxide in the slag is represented by the following equilibrium constant.²⁾

$$\log \frac{[\%O]}{a_{\text{FeO}}} = -\frac{5730}{T} + 2.397 \quad \text{.....(10)}$$

Combining Eqs. (3), (7) and (10) gives for the equilibrium constant K_{PF} in terms of mass %FeO

$$\begin{aligned} \log K_{\text{PF}} &= \frac{(\%P)}{[\%P]} (\% \text{FeO})^{-2.5} \\ &= \frac{7415}{T} - 8.924 + 0.071 \times \% \text{CaO} + 2.5 \log \gamma_{\text{FeO}} \quad \text{.....(11)} \end{aligned}$$

The equilibrium values of $(\%P)/[\%P]$, calculated using Eq. (11) for the FeO and CaO contents of slags, are compared in Fig. 8 with the plant analytical data for the phosphorus distribution ratio over a wide range of carbon contents: 0.03–0.8% C in BOS and 0.01–0.8% C in OBM steelmaking. The calculated and plant data points are scattered within the hatched area on both sides of the 45° line. The scatter in the calculated and plant data points is due primarily to

- (i) uncertainties in the values of the equilibrium constants K_{PO} and K_{PF} , derived from the results of numerous laboratory experimental work on slag-metal reactions, cited in Ref. 3),
- (ii) errors in taking samples from the converter at vessel turn-down,
- (iii) uncertainties in the plant analytical data.

Relative Effects of FeO and CaO on Steel Dephosphorisation

The relative effects of FeO and CaO contents of the slag on steel dephosphorisation are

- (i) direct effect of FeO appearing as $(\% \text{FeO})^{-2.5}$ in the equilibrium constant K_{PF} ,
- (ii) indirect effect of FeO on the value of γ_{FeO} which decreases with an increasing slag basicity as the iron oxide content of the slag increases,
- (iii) an increase in the CaO content is accompanied by a

Fig. 8. Slag/metal phosphorus distribution ratio derived from plant analytical data are scattered about the slag-metal equilibrium values.

decrease in the FeO content of the slag, partially nullifying the positive effect of lime.

Variations in lime and iron oxide contents of the slag, as depicted by the plant data in Fig. 1, inevitably will cause variations in the extent of steel dephosphorisation. To demonstrate this effect, the equilibrium phosphorus distribution ratios are calculated, using Eq. (11), for slags containing 8, 12, 16, 24 and 32 % FeO and the corresponding high and low %CaO as given in Fig. 1. The results for an average turndown temperature of 1610°C are plotted in Fig. 9. The plant analytical data are scattered within the hatched area, bordered by the calculated equilibrium curves for low and high lime contents for the indicated iron oxide contents. As noted from the shape of the top curve, the slags most favourable for steel dephosphorisation contain about 14 to 24 % FeO and 54 to 48 % CaO, respectively.

(%S)/[%S] in Relation to O Content of Steel and FeO Content of Slag

Many independent experimental studies have been made in the past of the slag-metal sulphur reaction, pertinent to iron and steelmaking processes. The equilibrium relations are described both in terms of the oxygen content of iron and the iron oxide content of the slag, as given below.

$$K_{SO} = \frac{(\%S)}{[\%S]} [\%O] \dots\dots\dots(12)$$

$$K_{SF} = \frac{(\%S)}{[\%S]} [\%FeO] \dots\dots\dots(13)$$

Fig. 9. Variations in the equilibrium (%P)/[%P] ratio with variations in FeO and CaO contents of the slag in accordance with the interrelation shown in Fig. 1.

Fig. 10. Relations K_{SO} and K_{SF} derived from plant data are compared with the slag-metal equilibrium values.

The values of K_{SO} and K_{SF} increase with an increasing slag basicity and a corresponding decrease in the SiO_2 and P_2O_5 contents of the slag. The experimental data used in assessing these equilibrium relations are cited in Ref. 3).

The values of K_{SO} and K_{SF} derived from plant data, which decrease with an increasing silica content of the slag, are compared in Fig. 10 with the slag-metal equilibrium values. It is self evident that in both the BOS and OBM processes, the steel desulphurisation is in a non-equilibrium state with respect to the oxygen content of steel at vessel turndown. It is the iron oxide content of the slag which has a decisive effect on the state of desulphurisation.

Because of variations in silica and iron oxide contents of the slag, as depicted in Fig. 2, there will be corresponding variations in the extent of steel desulphurisation. The equi-

Fig. 11. Variations in the equilibrium ratio (%S)/[%S] with FeO and SiO₂ contents of the slag in accordance with the interrelation shown in Fig. 2.

librium sulphur distribution ratios, calculated for 6, 8, 16, 24 and 32 % FeO and the corresponding high and low SiO₂ contents are plotted in Fig. 11. The plant data are scattered within the hatched area, boarded by the equilibrium curves for the low and high SiO₂ contents, or for the low and high FeO contents for a given SiO₂ content of the slag.

As shown in the Appendix, in the lime-saturated CaO–FeO melts, the equilibrium sulphur distribution ratio is 5.9 at 1622°C, derived from the experimental data of Turkdogan and Darken⁴⁾ on sulphur reaction in calcium ferrite melts. It is significant to note that when the top and bottom curves in Fig. 11 are extended to zero percent SiO₂, which corresponds to the lime-saturated CaO–FeO melt, they merge at a point that is close to the equilibrium value of (%S)/[%S]=5.9.

Concluding Remarks

The theoretical analysis of the BOS and OBM plant data presented in this Lecture substantiates the view that for a given slag basicity, steel dephosphorisation and desulphurisation are governed primarily by the iron oxide content of the slag, but not by dissolved oxygen in the steel, over a wide range of carbon contents of the steel.

For any given concentration of iron oxide in the slag (governed by carbon content of the steel), lime and silica contents of slag in the plant data vary by 4 to 5 % between the low and high values. For this reason, the equilibrium slag/metal phosphorus and sulphur distribution ratios are scattered within a composition region bordered by the equilibrium curves for low and high FeO, CaO and SiO₂ contents of the slag. Consequently, there will be unpredictable variations, from one heat to the next, in the extent of steel dephosphorisation or desulphurisation from those pre-

scribed by the computer aided charge control models and monitoring of the oxygen blowing operation.

If it were possible to measure the iron oxide content of the slag in the converter near the end of the oxygen blowing, using a suitable emf sensor attached to the sub-lance, some corrective steps could be taken by appropriate flux additions, which would further enhance steel dephosphorisation or desulphurisation.

With extensive hot metal refining that is 90 to 95 % of the metallic furnace charge, as practiced in most of the Japanese steel industry, there may well be lesser variations in slag composition, hence less unpredictable variations in steel dephosphorisation and desulphurisation from one heat to the next. With this point in mind, I would be most interested in studying a set of BOS plant analytical data for the Japanese steelmaking practice where the metallic furnace charge is almost entirely pre-refined hot metal.

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Appendix

From their experimental data on the sulphur equilibria between gases and calcium ferrite melts, Turkdogan and Darken⁴⁾ obtained for the sulphide capacity of the lime-saturated CaO–FeO melt

$$C_S = (\%S) \left(\frac{p_{O_2}}{p_{S_2}} \right)^{1/2} = 0.098 \quad \text{at } 1622^\circ\text{C} \dots\dots(A1)$$

In terms of the slag–metal equilibrium, as shown elsewhere,²⁾

$$7.5 \times C_S = k_s = \frac{(\%S)}{[\%S]} [\%O] \dots\dots\dots(A2)$$

which gives for the lime-saturated CaO–FeO melt

$$\frac{(\%S)}{[\%S]} [\%O] = 0.735 \quad \text{at } 1622^\circ\text{C} \dots\dots\dots(A3)$$

At lime saturation, the thermodynamic activity of FeO is about 0.5 for which the equilibrium oxygen content of liquid iron is 0.125 % at 1622°C. The foregoing data give for the equilibrium sulphur distribution ratio (%S)/[%S]=5.88 in the lime-saturated CaO–FeO melt.