Note

Change in Phosphorus Partition during Blowing in a Commercial BOF

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1. Introduction

Basic oxygen steelmaking involves oxidation of solutes from hot metal and formation of liquid steel with low residuals (>99% Fe). The continuous change in the chemical composition and temperature of the BOF slag is commonly termed as “slag path”. The physico-chemical characteristics and the thermodynamic driving force for any refining reaction depend on the chemical composition and temperature of the slag and metal phases, at any instant of time. Knowledge of the slag path is therefore essential for predicting the refining capacity of the BOF slag.^{1–4)} Improper slag path can, in addition to insufficient refining, also lead to operational problems like slopping or lance skull formation.⁵⁾

Removal of phosphorus is a reaction of utmost importance in basic oxygen steel making since the BOF offers the conditions conducive to oxidation of phosphorus—oxidizing atmosphere and high basicity. Different researchers have published widely differing values of the phosphorus partition ratio, achievable in the BOF.^{6–15)} Unfortunately, very little published data is available on the evolution of phosphorus partition along the blow and its deviation from the equilibrium value. Also, most of the earlier investigations were based on BOF slag containing MgO, as well as MnO and/or Al₂O₃. However, BOF slag largely free of MgO, MnO and Al₂O₃, is encountered in several steel plants, including in Tata Steel. Also, the hot metal in Tata Steel typically contains 0.7–1.0 mass% Si, 0.18–0.24 mass% P and less than 0.1 mass% Mn. Such high-Si low-Mn high-P hot metal is different from that experienced in most steel plants. Therefore, determining the BOF slag path under Tata Steel’s input conditions, and evolution of phosphorus partition ratio along the blow, has been attempted in the present work.

2. Phosphorus Partition

Samples of liquid steel and slag were collected and bath temperature was measured after 5 min, 10 min, 12 min and

15 min from the start of blow in a commercially operating BOF to determine the nature of variation in slag and steel composition. The blow was interrupted at the desired time for sample collection. A clean steel rod was rapidly lowered into the converter and withdrawn, leaving a layer of slag frozen on its surface. The slag sample thus collected contained some particles of entrapped steel, which were removed by magnetic separation. At the same time, steel sample was collected by inserting a “lollypop” sampler in to the metal bath. On certain occasions, collection of sample was delayed due to slopping inside the converter and/or evolution of flames from vigorous oxidation of carbon. Sampling at the end of the blow (17–18 min) was carried out as per the usual operating routine. The collected steel and slag were subjected to detailed chemical analysis.

The phosphorus partition ratio was expressed as $L_P = (\%P)/[\%P]$ where (%P) and [%P] stand for the mass percent of phosphorus in slag and steel respectively. The equilibrium phosphorus partition ratio, corresponding to the changing chemical composition along the blow, was calculated using the Regular Solution model proposed by Ban-ya.¹⁶⁾ The measured and calculated values have been shown, using the discrete points and the continuous line respectively, in Fig. 1. The rate of change of equilibrium partition ratio is not uniform but varies with time, primarily due to the variations in slag composition along the blow.

3. Slag Path

Figures 2 and 3 illustrate the variation of slag and steel composition along the blow. The continuous lines have been calculated using mass balance based on the input conditions and continuously measured off-gas analysis. The

Fig. 1. Variation of phosphorus partition ratio along the blow.

Fig. 2. Calculated and measured variation of slag composition during the blow.

Fig. 3. Calculated and measured variation of steel composition during the blow.

Fig. 4. The “slag path” shown on a CaO–FeO–SiO₂ quasi-ternary diagram. The italicized figures denote the time (in min) after start of blow.

discrete points indicate the intermediate measurements. CaO, SiO₂ and FeO_x, together with MgO, typically constitute more than 95–96% of the total mass, in the type of BOF slags investigated. Therefore, the “slag path” can also be represented as the composition locus on the CaO–FeO_x–SiO₂, or (CaO+MgO)–FeO_x–SiO₂, quasi-ternary diagram, showing the variation in chemical composition with progress of blow. This has been presented in **Fig. 4**, showing the relative changes in the slag composition on a CaO–FeO–SiO₂, quasi-ternary, during the progress of the blow.

4. Discussions

The equilibrium phosphorus partition ratio represents the maximum value of the partition that might be possible under ideal situation. In reality, kinetic constraints would limit the partition ratio achievable in commercial steelmaking furnaces. The ratio between the actual phosphorus partition ratio and the equilibrium value is designated ‘approach to equilibrium’, and typically takes a value between 0 and 1, the upper limit corresponding to an ideal situation. In practice, this parameter represents the deviation of measured phosphorus partition from theoretically calculated equilibrium value.

It can be seen in **Fig. 5** that the phosphorus partition ratio remains closer to equilibrium during the early part of the blow but gradually decreases with time. It decreases from a mean value of around 60% at 5 min to approximately 40% after 15 min of blow and the extent of decrease is particularly significant beyond 12–13 min of blow.

Figure 2 clearly illustrates that the overall basicity of the

Fig. 5. Deviation of phosphorus partition ratio along from equilibrium along the blow.

slag continuously increases during the blow and exceeds 2.5 within the 13th minute of blow. Calculations using thermodynamic software ThermoCalc have shown that BOF slag of such high basicity typically consists of two (liquid+solid) phases and the presence of the second phase tends to increase the overall viscosity of the slag.¹⁷⁾ This might result in a kinetic limitation for efficient dephosphorization.

In addition, the concentration of FeO on the slag drops to around 10 mass% or less during 10th–12th minute of the blow. This situation is commonly termed as “dry slag” in steel plant jargon and is characterized by a slag of very low fluidity. Such slags inevitably retard the transfer of phosphorus from the liquid metal to the slag phase and lead to poor phosphorus partition ratio. The iron oxide concentration in the slag does begin to increase after that and exceeds beyond 15 mass% within the 14th minute. Such change in FeO concentration might have had some positive effect on the fluidity of the slag but it appears from Figs. 2 and 5 that the increase in FeO concentration towards the end of the blow is not sufficient to fully compensate the increase in viscosity arising from the presence of a 2-phase slag, and formation of dry slag. Thus, the approach to equilibrium experiences a marked decrease beyond 12–13 min of blow.

Further, it can be seen from Fig. 3 that the concentration of carbon in the liquid metal decreases to less than 25% of its initial value after 13 min of blow, leading to a decrease in the rate of decarburization. In fact, the increase in FeO concentration after 12–13 min of blow coincides with the reduction in the carbon content in the bath. This reduces the extent of stirring inside the BOF and is likely to further deteriorate the kinetics of dephosphorization, which might explain the increasing deviation of phosphorus partition ratio from equilibrium as the blow progresses.

5. Conclusions

- (1) Phosphorus partition ratio during steelmaking in commercial BOF typically remains in the range 40–60% of the equilibrium value.
- (2) The approach to equilibrium reduced with progress of the blow. This phenomenon may be the result of changing FeO concentration and increasing basicity, leading to reduction in slag fluidity.

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