1. Introduction

With the rise in the proportion of low phosphorus (P) steel grades e.g. automotive IF (Interstitial Free) and other flat product steel grades, requirements to produce low phosphorus steel is also increasing. Indian hot metal is unfavourable with regard to hot metal phosphorus and Tata Steel is no exception (Table 1 shows typical hot metal chemistry at Tata Steel). In absence of prior de-phosphorization of hot metal, achieving $P_{\text{H11349}}$ 0.015% in single BOF blowing on a consistent basis is a challenging task and calls for a close control on blowing parameters thereby achieving higher phosphorus partition during blowing (two stage blowing in some of the Japanese Plants are practiced for optimized refining of hot metal).

Hot metal chemistry at Tata Steel has been evolved to meet the overall production and quality objectives whilst keeping the cost under control. Major part of hot metal phosphorus (≈85%) comes from the indigenous coal and iron ore (Fig. 1). Relatively high hot metal silicon and sulphur with residual manganese are the result of process optimization and operational philosophy to convert hot metal into steel in a cost effective way.

Hot metal sulphur is taken care during de-sulphurization, however, removal of silicon, phosphorus along with carbon comes under the domain of BOF refining. The purpose of high hot metal silicon is to maintain adequate slag volume, enough to achieve high phosphorus partition. Blowing profile to accommodate higher levels of silicon has been perfected over the years. Manganese was lowered as it has an adverse effect on dephosphorization. Use of six-hole lance and bottom bath agitation (TBM) has been introduced to improve efficacy of BOF refining.1)

This paper summarizes other approaches to achieve high phosphorus partition during the BOF refining. Recent trials and experiences with slag chilling practice near the blow end have been discussed. Also discussed are the results of bivariate analysis on de-phosphorization using data mining methodology (through Intelligent Miner—a tool for statistical analysis). Analysis shows overriding role of turndown carbon which unfolds mysteries associated with de-phosphorization behaviour in BOF to a great extent. Underlying mechanism to explain such results during BOF refining in single blow has also been devised.

Table 1. Hot metal chemistry.

| Si, %  | S, %  | P, %  | Mn, % | C, %  |
|-------|-------|-------|-------|-------|
| 0.90  | 0.065 | 0.220 | 0.05  | 4.2   |

Fig. 1. Sources of phosphorus.
2. Experimental Procedure: Slag Chilling Near Blow End

Limestone chips (size: –15 mm) have been used to chill the slag near the blow end. Amount and timing of addition of limestone has been varied to assess its effect on dephosphorization. Limestone has been varied from 50–600 kg for different timings of addition between 80–95% of the blow (e.g. 80% of the blow means, limestone is added when 80% of blow is complete). The trial data has been categorized into four categories:

1. No addition of limestone
2. Limestone quantity <250 kg, timing of addition<95% (mode 1)
3. Limestone quantity <250 kg, timing of addition>95% (mode 2)
4. Limestone quantity >250 kg, timing of addition>95% (mode 3)

The trial was conducted at the plant level during actual blowing of a heat. Intentionally, those steel grades were chosen where target turndown temperature is high (1700°C+) because attaining low phosphorus (≤0.015%) in these grades on a consistent basis is a problem. Besides, care has been taken to segregate the performance of normal blown and rebloomed heats.

3. Data Mining Study: Bi-variate Analysis on Vessel De-phosphorization

An extensive statistical analysis has been carried out to understand correlation amongst various parameters affecting vessel dephosphorization (see Table 2 for vessel details). Bi-variate analysis through Intelligent Miner (statistical software) has been selected for the purpose of studying the relationship between the variables/parameters. Over 2500 heats made during Oct.–Dec. ’04 have been taken for analysis. Heats include both low (avg. ~0.185%) and high (avg. ~0.240%) hot metal phosphorus. Various parameters considered for bi-variate analysis are as follows:

- Hot Metal: silicon and phosphorus
- BOF Charge: amount of hot metal and scrap
- Blowing: amount of oxygen, re-blowing and blow profile*
- Turn Down Conditions: temperature, steel phosphorus and carbon, slag analysis

(* effect of blow profile has been studied separately-not through bi-variate analysis)

The result generated by the Intelligent Miner (a statistical tool) shows two overlapping distributions in the form of a histogram (see the Fig. 2, one of the figures taken from Annexure-II for interpretation sake). Figure 2 shows the effect of turndown or end blow temperature (EB_TEMP_ACT, °C, X-axis) on steel phosphorus (%P, Y-axis). The distribution with grey fill and black border shows overall distribution (i.e. distribution of all the heats with respect to proportion of heats on Y-axis for given turndown temperature range on X-axis) whereas other overlapping distribution (with red border) shows proportion of low phosphorus heats (P≤0.015%) for the same turndown temperature range. It is clear from Fig. 2 that the proportion heats with low phosphorus (P≤0.015%) is higher for turndown temperature (<1680°C) than lumps for quick heat absorption and to avoid boulder formation due to localised chilling in slag. Addition of 0.5 t limestone in 20 t of slag would cool it down by 25°C. Therefore, if one can bring down the temperature of slag/slag–metal interface selectively, say by 25°C, a better dephosphorization is expected. One of the possible ways to cool down the slag selectively is to add limestone/dolomite chips during the last few seconds of the blow (The concept has been discussed by Brahmadeo et al.4). Calcination of limestone (CaCO3→CaO+CO2) is highly an endothermic reaction and provides instant chilling.

A rough heat balance calculation shows that 0.5 t of limestone chips added to 20 t of slag would cool it down by 25°C. It may be noted that it is better to use chips rather than lumps for quick heat absorption and to avoid boulder formation due to localised chilling in slag. Addition of 0.5 t limestone in 20 t of slag is not going to influence the chemistry and other behaviour of slag perceptibly.

Iron ore has got a higher cooling capacity particularly if conditions exist for its reduction, but addition of iron ore...
towards the end of blow is not advised because it tends to raise the dissolved oxygen level in metal, make the slag more corrosive to refractories. Because of its higher density its cooling effect is felt in the metal also.

Plant trial of limestone addition (size: −15 mm) near the blow end shows interesting results. Trials are conducted purposefully for steel grades where tap (turndown) temperature is higher −1700°C. Over 100 heats have been observed with different levels of limestone addition at different point in time near the blow end (put as modes in Figs. 3 and 4). It is quite clear that limestone addition helps controlling steel phosphorus (measured as LSA P i.e. Ladle Sample Analysis Phosphorus) as compared to heats with no limestone addition. Limestone addition, not only provides chilling effect but also nascent lime which helps in containing phosphorus in the slag. It has also been observed that phosphorus reversion is lower with limestone added heats (phosphorus reversion: difference of LSA and turn down phosphorus). This is reflected in lower standard deviation with regard to steel phosphorus.

One additional advantage of this practice is to have lesser nitrogen (measured as LSA N, i.e. Ladle Sample Analysis Nitrogen) pick up by the steel in the end blow period owing to evolution of CO2. De-carborization reaction is almost complete near the blow end, as a result there is very less or no CO2 evolution and vessel becomes susceptible to air ingress. Limestone addition provides huge amount of CO2 which prevents air ingress by maintaining a positive pressure and a foamy slag inside the vessel during blow end.

Mode 3 gives best result in terms of steel phosphorus and nitrogen. Mode 3 entails addition of 300–400 kg of limestone just before the end of the blow (i.e. when 95–98% of the blow is complete).

4.2. Datamining Study on De-Phosphorization

Steel phosphorus at turn-down greater than 0.015% has been considered as high and analysis is made with respect to identify process conditions leading to higher turn-down phosphorus with a purpose to avoid such conditions and to produce low steel phosphorus at turn-down (≤0.015%) on a consistent basis. To assess the effect of hot metal phosphorus, overall data has been divided into two categories e.g. low hot metal P (average ~0.180%) and high hot metal phosphorus (average ~0.230%) with proportion of each being 20.5% and 79.5% respectively. All the known operating parameters which affects turn-down phosphorus has been considered for the data mining analysis e.g. hot metal silicon and phosphorus, turn-down temperature and turn-down carbon, slag CaO, SiO2, Total Fe and V-ratio (i.e. slag basicity), lime and limestone addition, total blowing oxygen, iron ore, rebloows etc.

Data mining results clearly reveal that turn-down temperature and turn-down carbon have significant effects (effects of turn-down carbon being more than that of turn down temperature, see Fig. 5). This is true across the board i.e. irrespective of vessel or blow profile or other operating parameters. Slag CaO is the next important variable and its effect is visible with high hot metal phosphorus i.e. P ~0.230% (see Appendix II and III, Appendix II and Appendix III are data mining results for low (~0.180%) and high (~0.230%) hot metal phosphorus respectively. Each appendix has 3 figures column wise which indicate effect of concerned parameters for achieving turn-down steel P>0.015% (High) and P≤0.015% (Low) respectively).

To achieve turn-down phosphorus ≤0.015% on a consistent basis, data mining results delineate the cut off point for turn-down temperature and turn-down carbon as <1680°C and >0.03% respectively. Slag CaO cut-off limit is 51% (min.) for achieving low turn down P (especially for high hot metal phosphorus, see Appendix II and III).

| Temperature, °C | 1700 | 1675 | 1650 |
|----------------|------|------|------|
| Equilibrium Phos – Partition, (% P in slag)/ (%P in metal) | 148 | 205 | 286 |

Table 3. Equilibrium phosphorus partition at different temperatures.
Unsuitability of getting low turndown phosphorus (≤0.015%) at high turndown temperature is a well-known fact and needs no discussion. However, effect of turndown carbon is rather an interesting finding and in fact contrary to steel makers’ belief that lower carbon means higher bath oxygen and hence lower phosphorus (but analysis shows exactly opposite). The effect of turndown carbon on BOF dephosphorization needs to be understood.

Actual data shows that lower turndown carbon is associated with higher slag Total Fe. Higher slag Fe leads to higher temperature. A rough theoretical calculation shows that 0.5% rise in slag Fe results in 5°C rise in the slag temperature (using Healy’s equation, see Eq. (1)). Rise in the slag temperature is bad for achieving low turndown phosphorus (≤0.015%) as it causes phosphorus reversion (i.e., phosphorus from slag goes back to the metal/steel). Lime-stone addition near the blow end checks phosphorus reversion by cooling/chilling the slag and this helps in containing turndown phosphorus (≤0.015%).

Healy’s Equation:

\[ \log(\%P)/\log(\%P) = 22.350/T + 0.08(\%CaO) + 2.5 \log(\%T.Fe) - 16.0 \text{………(1)} \]

(where,  \( T \) = temperature in Kelvin)

Actual data shows that with turndown temperature <1680°C and turndown carbon >0.03%, turndown phosphorus is consistently at the level of 0.010% irrespective of other operating conditions (this is result of 200 odd heats, see Table 4). This explains two things as far as de-phosphorization in BOF is concerned:

1. Combined effect of turndown temperature and turndown carbon is very strong to get low turndown phosphorus (≤0.010%)
2. Hot metal phosphorus has little effect (for the range mentioned above)

Low turndown phosphorus at lower turndown carbon is expected by general considerations as lower turndown carbon implies higher level of slag oxidation. The reverse trend as carbon falls below 0.03% poses an interesting question for BOF refining of hot metal containing relatively higher silicon (≈0.9%). The explanation of this phenomenon is as follows:

Slag volume being adequate for hot metal containing higher hot metal silicon. Hot metal phosphorus is continuously removed and it joins slag during BOF blowing and this happens till turndown carbon is lowered to 0.03–0.05%. As hot metal carbon is lowered further (<0.03%), reverse phenomenon happens i.e., phosphorus from slag joins back to metal/steel. Why this happens?

Lower turndown carbon (<0.03%) means prolonged blow, which requires more oxygen to remove residual carbon (the equilibrium carbon–oxygen in liquid steel follows an exponential relationship). Even small drop in carbon content in the lower carbon range (0.03%, say) needs disproportionately high amount of blowing oxygen. As a result, slag–metal suffers oxidation leading to higher slag and metal temperature near the slag–metal interface. During blow end, bath is rather quiet (carbon being low, no bath boiling) and hence the increase in the temperature at slag–metal interface is not equalized quickly enough over the steel mass. Bottom blowing affects temperature equalization and therefore restricts phosphorus reversion, but intensity of bottom blowing matters (problem gets compounded when bottom blowing is not operational). It has also been observed in actual practice that 1 min bottom blowing after main/top blow helps in achieving lower turndown phosphorus.

The effect of slag–metal interface temperature on vessel dephosphorization is strong as evident from the reverse effect of cooling of slag metal interface by adding limestone chips (turndown phosphorus is lower with limestone addition at the blow end). Moreover, it is the slag–metal interface temperature and not the steel temperature which affects dephosphorization (data shows spells of low turndown phosphorus at higher steel temperature).

Based on above hypothesis, mechanism of high turndown steel phosphorus (P>0.015%) in case of low turndown carbon (<0.03%) can be devised (see Table 5). Table 5 also shows schematic figures on of equilibrium C–O relationship and phosphorus reversion phenomenon.

Relationship with other operating parameters e.g. lime (tons), slag V ratio, SiO2, T.Fe, oxygen, iron ore, reblow, vessel life etc. has not found to be so strong or definite (these parameters may be operating in an optimum range). Hot metal silicon usually varies between 0.8–1.1% and analysis shows that performance with respect to achieving low turndown phosphorus (≤0.015%) in this range being better than other two ranges (i.e. silicon ≤0.8% or silicon >1.1% with latter being the worst). The effect aggravates with turndown temperature (see Fig. 6).

With a purpose to attain higher turndown carbon, the aim carbon in the static blowing module (supervisory control system) has been changed to 0.03 to 0.04% since Aug-05. This has favourable impact in terms of achieving higher proportion of heats seeing high turndown carbon. However, blowing profiles are being modified to further raise the proportion of heats finishing higher turndown carbon (0.03—0.05%).

Concurrently, to check the consistency of the effect of turndown carbon, over 5000 heats are analyzed during Sep’05–Jan’06. The average turndown phosphorus is plotted against various carbon ranges clearly shows that influ-

### Table 4. Combined effect of temperature and carbon.

| Parameters | Si ≤ 0.8% | 0.8%< Si ≤ 1.1% | Si> 1.1% |
|------------|-----------|----------------|----------|
| Low P Hot metal (-0.185%) | Low | Medium | High |
| Total Heats | 7 | 56 | 34 |
| Heats with turn down steel P≤0.015% | 0 | 0 | 0 |
| Avg. TDP*, % | 0.0095 | 0.009 | 0.009 |
| High P Hot metal (-0.240%) | Low | Medium | High |
| Total Heats | 15 | 69 | 27 |
| Heats with turn down steel P≤0.015% | 1 | 1 | 0 |
| Avg. TDP*, % | 0.0116 | 0.0098 | 0.0092 |

*TDP: Turn Down Phosphorus
ence of turn down carbon is consistent and repeatable (Fig. 7). Irrespective of other blowing conditions, the turn down phosphorus shows lowest value for turn down carbon in the range of 0.04–0.05%.

5. Conclusion

In absence of any pre-treatment process, consistent production of low phosphorus steel (≤0.015%) form high hot metal phosphorus in a single BOF blow is a great challenge. The approaches mentioned in paper show the way out. Results of slag chilling near the blow end are found encouraging enough to implement this practice for heats which are by design turned down at high temperature (~1 700°C).

Data mining results on dephosphorization have been found to be another area worth serious attention. Overriding effect of turndown carbon over other variables on BOF dephosphorization is a new finding. Turndown carbon represents the oxidation state of the blown heat (e.g. underblown or overblown heat) and maintaining turndown carbon in a range of 0.03–0.05% holds a promise for enhancing dephosphorization potential in BOF vessel for hot metal having relatively high silicon and phosphorus.

### REFERENCES

1. T. Mukherjee and A. Chatterjee: Bull. Mater. Sci., 19 (1996), No. 6, 893.
2. Internal Report, “How to Improve De-phosphorization in Steelmaking—Some New Thoughts”, Flat Products Technology Group, Tata Steel, (2003).
3. E. T. Turkdogan: Fundamentals of Steelmaking, Institute of Materials, Minerals and Mining, London, (199), 186.
4. B. Deo et al.: Asia Steel Conference—2003, Jamshedpur, India, Vol. 2, 2.6.5.1.
5. Internal Report, “Data Mining Project Report on De-phosphorization Performance of LD Vessel”, Flat Products Technology Group, Tata Steel, (2005).

### Appendix I. Calculation of Phosphorus Partition at Different Temperatures

#### Source Equations:

1. \( \log(K_{P\text{O}}) = 21.740/T - 9.87 + 0.071 \times \% \text{BO} \)
2. \( K_{P\text{O}} = \% \text{P} \times \% \text{O}^{2.5} / \% \text{P} \)
3. \( \text{BO} = \% \text{CaO} + \% \text{CaF}2 + 0.3 \times \% \text{MgO} \)

(Typical operational practice, \( \% \text{BO} = 53\% \) & \( \% \text{O} = 0.08 \))

#### Calculations:

| Temperature | 1700°C | 1675°C | 1650°C |
|-------------|--------|--------|--------|
| \( K_{P\text{O}} \) | 81470.42 | 112979.59 | 157761.13 |
| Phosphorus Partition | \( \% \text{P} / \% \text{P} = K_{P\text{O}} / \% \text{O}^{2.5} \) | 147.46 | 204.49 | 285.54 |
Appendix II.

Appendix III.

(Legends - EB_TEMP_ACT: Tap (turn-down) Temp°C; EB_C: Tap carbon, %; SLAG_CAO: Tap slag CaO, %)

(Legends - EBT: Tap (turn-down) Temp°C; EBC: Tap carbon, %; CAO_SL: Tap slag CaO, %)