Production of low phosphorus steels from high phosphorus Indian hot metal: Experience at Tata Steel

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Abstract. The position in India on the phosphorus front vis-a-vis iron and steel operations elsewhere in the world is, and will remain, most unfavourable since Indian iron ores contain high phosphorus and coal (and therefore, also the coke), has high ash and phosphorus in the Indian subcontinent. While dephosphorization of hot metal is theoretically ruled out in the Indian context, dephosphorization of liquid steel can also not be considered because of its adverse effect on ladle refractories and steel cleanliness.

For a large proportion of the steels made through the LD-slab caster–hot strip mill route at Tata Steel, the phosphorus content required in the product is 0.020% max and in some grades, it is restricted to 0.015% max. Various control strategies evolved to make low phosphorus steel at Tata Steel are discussed in the paper. The major steps which have significantly reduced the phosphorus levels are described.

Keywords. Low phosphorus; bath agitation; three hole lance; six hole lance; ladle-furnace; Thyssen's blowing metallurgy.

1. Introduction

The product mix at Tata Steel, after the introduction of slab casting and the hot strip mill, has necessitated a major change in the approach to steelmaking since extra deep drawing, TMBP, API and other grades of strips for special applications are being produced. For a large proportion of these steels, the phosphorus content in the product is 0.020% max and in some grades, the phosphorus has to be restricted to 0.015% max. For hot charging continuously cast slabs, ultimately it would be necessary to restrict the phosphorus content to 0.0020% max even in other grades—thus phosphorus control to very low levels has become the order of the day at Tata Steel.

Control of phosphorus requires a system approach, since most aspects of steel-making have an impact on the level of phosphorus in the end product. Various approaches are possible for reducing the phosphorus content to 0.020%, which include: limiting the input phosphorus through careful selection of all raw materials including scrap, hot metal dephosphorization, removal of phosphorus during steelmaking and post treatment of liquid steel. At Tata Steel, about 60–65% of the phosphorus input into blast furnaces comes through the iron-bearing raw materials and rest through coke. Given the requirement that the bulk of the iron-bearing materials at Tata Steel have to come from Noamundi–Joda and coal primarily from Jamadoba–West Bokaro, the hot metal phosphorus will always vary from 0.25% to 0.28%. Practical problems of temperature drop, slag removal, silicon content, etc associated with dephosphorizing hot metal, by any of the known methods, will not permit its adoption at Tata Steel. It is, therefore, essential to concentrate on ways and means of dephosphorization within the LD vessels.

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2. Strategy at Tata Steel

A strategy to make low phosphorus steel has been developed at Tata Steel. It is now possible to meet the market/process demand of 0.020% max phosphorus by adopting the following:

- Use of 0.6–0.7% silicon hot metal to obtain the optimum slag volume and slag basicity/fluidity in the oxygen converters.
- Early slag formation in the converters and stability of this slag with respect to its phosphorus holding capacity throughout the blow.
- Optimum FeO content in the converter slag, better slag-metal interaction arising out of bath agitation, use of a six-hole lance, choice of proper blowing conditions and adoption of post-blow stirring.
- Low manganese content in the bath at tap.
- Low tapping temperature and concurrent usage of a ladle furnace.
- Use of special low phosphorus ferro alloys.

Tata Steel is at present actually preparing for the period beyond the immediate future and for a sea change in India's industrial scenario. The projected growth in conventional, mostly commercial grade products, is 6 to 8% per annum but more importantly, the Indian steel industry will be expected to meet higher product and quality specifications, provide better service levels and more new products to a growing set of customers in the last few years of the twentieth-century. Many of these customers will be exporters who will have duty-free access to steel from the international market at very competitive prices. This is the challenge facing the Indian steel industry and to meet this challenge, Tata Steel has been pursuing a continuing programme of expansion and modernization.

Modernization phase III, now almost complete, has launched Tata Steel into its boldest step since its inception in 1907. Entering modern wide flat products for the first time, the Company has installed a 1700 mm wide hot strip mill, which has an initial capacity of one million tonnes per annum in coils of up to 28 tonnes weight with thickness down to 1.6 mm. The steelmaking capacity has been augmented by adding

Table 1. Impact of Tata Steel's modernization programmes since early eighties.

Measure	Pre-modernization	Phase-I	Phase-II	Phase-III
Year	Before 1980	1983	1988	1994
Crude steel, tonnes (000 per annum)	1957	2,250	2,470	3,050
Yield-crude to saleable (%)	82.9	84.8	85.0	88.5
Product mix (%)				
— Semis	43	60	39	20
— Non-flats	35	25	40	31
— Flat products	22	19	21	49
LD steel (%)	Nil	39	44	62
Continuous cast (%)	Nil	14	34	64
Energy (Gcal/t) crude steel	10.5	9.3	9.3	8.7

Figure 1. Production and product mix at Tata Steel: Pre- and post-modernization phase III.

a second LD Shop consisting of bath agitation facilities (TBM) and slag retention devices. The steelmaking capacity of the new Shop (LD 2), commissioned in 1994, is 1.1 million tonnes per year for which the only outlet is slab casting. The product mix for the new LD Shop contains a wide range of qualities, some with fairly stringent analysis specifications. The extent of change in the product mix of Tata Steel under the modernization programmes, started in the early eighties, can be gauged from table 1. Figure 1 summarizes the effect of the Modernization Phase III on the product mix distribution (Irani and Deverel 1991). These changes have had a broad impact right across Tata Steel but the greatest impact, of course, has been in the market place. Tata Steel's market has become more competitive with existing and new customers, demanding better quality and service. This is the sea change facing Tata Steel as the 1990s flow into the 21st century and the strategy adopted by Tata Steel has been geared to cater to these requirements.

3. Product mix at Tata Steel and its quality requirements

Tin mill black plates, long and cross members for trucks, etc demand low residuals with the internal specification for these grades varying from 0.015 to 0.020% max each of sulphur and phosphorus (table 2). Difficulties are to be expected in achieving the requirement of 0.015% phosphorus in API and TMBP grades; also achieving 0.020% phosphorus in special light plates and extra deep drawing qualities. Therefore, for the present, the approach which is based on an understanding of the product requirement in the first few years of operation of the hot strip mill, is to restrict the phosphorus levels in the product to 0.020% max in all coils.

The following facilities have been incorporated to achieve these specifications:

- Modified blast furnace burdening and operation to achieve consistently hot metal with lower manganese and silicon contents (Mn 0.15–0.20%; Si 0.6–0.8%).
- Hot metal desiliconization in the blast furnace runner as and when the need arises.
- Selective desulphurization of hot metal in the LD Shop (s).
- Transfer ladle skimming facility.

Table 2. Product mix for Tata Steel's LD 2 (modernization Phase-III) and phosphorus requirements.

Steel grade	Phosphorus (% max) (specification)	Tonnages
Long and cross members	0.015	59,000
Light plates	0.020	1,18,000
High tensile plates	0.020	24,000
EDD strips	0.020	1,27,000
TMBP strips	0.015	2,70,000
HR strips for cold rolling	0.020	1,07,000
Medium and high carbon strips	0.020	54,000
Strips for commercial steels	0.020	1,00,000
LPG strips	0.020	82,000
Corten plates	0.07–0.15	24,000
Strips for precision tubes	0.020	97,000
API	0.015	43,000

- Modified LD fluxing and blowing practices by bath agitation and the use of a six-hole instead of a three-hole lance to achieve low phosphorus at turn-down.
- Secondary steelmaking facilities including gas stirring, ladle furnace and powder injection.

4. Deleterious effects of phosphorus and its control

Phosphorus causes steels to become embrittled, thus reducing the toughness and increasing the possibility of breakage during processing, fabrication and service (Bloom *et al* 1990). Phosphorus also causes intergranular segregation during continuous casting and deteriorates the ductility and toughness of products such as high strength plates and pipes, cryogenic steels, pressure vessel plates, etc (Marique and Nilles 1984).

According to Obinata (1981), future needs for heavy wall pipes will necessitate 0.020% max phosphorus. For the transmission of corrosive gases, less than 0.010% phosphorus is desirable. Less than 0.010% phosphorus will thus become indispensable in some cases in the not too distant future. It is to be appreciated that from a product consistency standpoint, tight control of phosphorus is perhaps more important than reducing the phosphorus level below about 0.020% max in some cases.

The control of phosphorus in steel should be reviewed as a 'holistic system', since each link in the metallurgical chain can influence the amount of phosphorus that reports to the final steel. Specific process environments greatly influence whether the phosphorus levels can be adjusted during a given processing step in the steel production system. For example, the conditions in the blast furnace are not conducive for phosphorus removal and virtually all the phosphorus input reports to the hot metal. In contrast, the steel refining process can be very effective for eliminating phosphorus. The most fundamental way to control phosphorus is to not let too much get into the

Table 3. Phosphorus balance in blast furnaces at Tata Steel.

Raw material	Consumption (kg/thm)	Phosphorus (%)	Amount of phosphorus (kg)	Contribution (%)
Noamundi ore	464	0.075	0.348	12.51
Joda ore	275	0.076	0.209	7.52
Sinter	801	0.150	1.201	43.19
Coke	670	0.150	1.005	36.14
Mn ore	10	0.090	0.009	0.32
Dolomite	10	0.090	0.009	0.32

Assumptions: Sinter in burden: 52%, Coke rate: 670 kg/thm

Table 4. Hot metal phosphorus in various plants.

Plant	Hot metal phosphorus (%)
Sidmar, Belgium	0.090
Appleby Frodingham, BSC	0.130
Lackenby, BSC	0.110
Thyssen, Germany	0.100
Republic Steel, USA	0.050
Inland Steel, USA	0.083
Solmer, France	0.120
Indian Plants	0.25–0.280

steelmaking system right from the start. Raw materials such as coke, sinter, iron ore and fluxes at the blast furnace and hot metal, calcined fluxes, scrap and ferroalloys at the steelmaking stage must have very low phosphorus contents.

5. Effect of Indian raw materials on phosphorus

At present, the contribution to the total phosphorus input to Tata Steel's blast furnaces from coke, iron ore, sinter and fluxes are 36%, 21%, 43% and 0.64% respectively as shown in table 3. Almost two-thirds of the total phosphorus input comes through the iron bearing materials, while the rest comes primarily from coke.

Table 4 shows the Indian hot metal phosphorus vis-a-vis phosphorus in hot metal in plants elsewhere. The position in India on the phosphorus front vis-a-vis iron and steel operations elsewhere in the world is, and will remain, most unfavourable. Nowhere else is experience available to produce low phosphorus steel from such inputs. Even in combined blowing with inert gas post-blow stirring at the end of refining, there is no international experience which shows that hot metal with phosphorus above 0.25%

can be consistently dephosphorized in the steelmaking converters alone (Tifac Report 1990).

Reduction in phosphorus in Indian hot metal by pretreatment from 0.25/0.28% to 0.14% or lower, will only be possible by first desiliconizing the hot metal to below 0.2% silicon. However, under Indian conditions, when the lowest projected silicon in hot metal is 0.5/0.7%, the expected silicon level in hot metal even after runner desiliconization can at best be around 0.4%. Even if pretreatment becomes theoretically feasible, it would not be practically possible to dephosphorize such a metal because of a large temperature drop during treatment (from 1350°C in the ladle to less than 1200°C). Therefore, the possibility of dephosphorizing hot metal, which appears to be *prima facie* attractive, is ruled out in the Indian context.

Desiliconization of hot metal prior to its use in oxygen steelmaking, is possible. This would help in the formation of high basicity in-blow slags required for phosphorus removal. However, very low silicon levels in hot metal will again not be conducive for phosphorus removal since at low converter slag volumes, the phosphorus partition coefficients have to become very high to take care of the high phosphorus load arising from Indian hot metal. Silica will have to be used to increase the amount of slag and the cost of additional silica to be added to the converter, plus the cost of desiliconizing at the blast furnace are such that the option to desiliconize in the blast furnace runner to below 0.5% silicon is not always economical.

Dephosphorization in steel ladles should not be considered because of its adverse effect on ladle refractories and steel cleanliness, and, in any case, in contrast to the blast furnace process, steelmaking itself is a very efficient means of eliminating phosphorus from the system. The actual chemical reactions taking place involving phosphorus during steelmaking have been summarized in many ways. The following equation is a good illustration (Chatterjee *et al* 1991)

The reaction is exothermic and generates significant amounts of heat. The reaction will proceed to the right if the amount of active lime and oxygen content in the slag are high and the activity of P_2O_5 in the slag phase is low. High slag volume will generally help to keep this value low. The phosphorus partition coefficient $[(\% \text{P})/(\% \text{P})]$ is determined by the thermodynamics of the steel/slag system and by the kinetics of the dephosphorization reaction. Both the thermodynamic equilibrium and the reaction kinetics can be expected to be influenced by the blowing practice. In the case of standard top blown vessels, the transport of phosphorus from the steel bulk to the reaction interface between steel and slag is poor, whereas in combined blown converters, this transport is activated and controlled (Chatterjee *et al* 1991).

6. LD operation at Tata Steel

Since limiting the input of phosphorus through raw materials is difficult and hot metal dephosphorization is impossible, the approach adopted at Tata Steel has been to optimize the LD operation (Chatterjee *et al* 1991). Extensive work has been carried out at Tata Steel to establish the relationship between manganese and phosphorus content in steel at turndown, and the effect of manganese in hot metal on manganese at turndown. As shown in figures 2 and 3, the lower the manganese at turndown, the lower

Figure 2. Manganese and phosphorus content in steel at turndown.

Figure 3. Effect of manganese in hot metal on manganese at turndown.

is the phosphorus at turndown and to get lower manganese at turndown, the hot metal manganese has to be low. On the basis of this work, it was decided to lower the hot metal manganese to a level of 0.15–0.20% for which, addition of manganese ore in the blast furnaces and in the converters was stopped and the practice of using low manganese hot metal in the converters was started thereafter. Soviet research has also shown that dephosphorization in oxygen converters improves with lower manganese content in hot metal. Higher amount of MnO in the slag retards dephosphorization owing to simultaneous reduction of manganese and phosphorus from the slag. With increasing manganese concentration in the metal, the surface activity of phosphorus is also reduced, thereby inhibiting its oxidation and transfer to the slag.

High silicon in hot metal gives rise to numerous disadvantages in LD steelmaking such as very high slag volume, higher lime consumption, high loss of iron in the slag as FeO, lower lining life, delayed formation of slag, higher incidence of slopping, higher frequency of lance jamming (especially when the hot metal manganese is low), difficulties in operating with slag basicities above 3.0, etc. As the bath phosphorus depends upon the P_2O_5 content of the slag (as shown in figure 4) and the larger the slag volume, the greater is its total phosphorus holding capacity, an optimum volume of slag is needed, which corresponds to an optimum hot metal silicon level. On the basis of theoretical calculations and practical observations, the optimum hot metal silicon for Tata Steel was found to be 0.6–0.7% to operate the converters at a slag basicity of 3.5–4.0 with a slag volume of around 165 kg/t of liquid steel to arrive at phosphorus partition coefficients greater than 100 and tap phosphorus levels less than 0.015%.

Figure 4. Effect of P_2O_5 in slag on bath phosphorus levels.

Figure 5. Effect of total iron content in slag on bath phosphorus levels.

Role of bath agitation: In straight top blown converters, the phosphorus content decreases in the first 30–40% of the blowing period followed by rephosphorization of the metal. The phosphorus reversion is a consequence of ‘drying up’ of the slag. With combined blowing, if proper care is taken to maintain a reasonable FeO content of the slag so that the slag is always fluid even at high basicities, phosphorus would not revert. For proper phosphorus removal, it is very necessary to remove the phosphorus from the bath and keep it tied-up as a stable phosphorus compound in the slag. This is how bath agitation helps in reduction of phosphorus at turn down. The effect of iron content of the slag on the turndown phosphorus for converter operations with bath agitation at Tata Steel, is shown in figure 5. With bath agitation, the ideal FeO content of the slag was found to be 18% and the turndown phosphorus improved from 0.029 to 0.023%.

Figure 6. Comparison between actual and calculated phosphorus partition coefficients.

Table 5. Details of bath agitation process (BAP) adopted at Tata Steel's LD shop 1.

Commissioning of BAP	Jan 91–Feb 91
No. of holes at vessel bottom	Four in bottom plate for locating four canned elements
Position of holes	Equidistant from the centre
Stirring gases	Nitrogen, density, 1.1822 kg/m ³ at 15°C, 1 bar absolute. Argon, density 1.6867 kg/m ³
Maximum flow rate	1200 Nm ³ /h nitrogen or argon

The details of the bath agitation system installed in Tata Steel is given in table 5 and the improvement in the phosphorus partition coefficient is clear from figure 6.

A study was thereafter conducted to find out the effect of post-blow stirring for about 2–3 min on the reduction of turndown phosphorus. It was observed that a further reduction of phosphorus by 2–3 points was easily achieved by post-blow stirring. The more intense mixing of the metal and a higher iron-bearing slag as a result of stirring at the end of the blow, permit closer approach to equilibrium. Lower phosphorus in the bath then becomes feasible without having to increase the amount of lime or slag basicity, particularly since a large volume of slag of the required chemistry is available at this stage to remove phosphorus.

Use of a six-hole lance: The adoption of multi-hole nozzles is one of the prominent outcomes of the continued efforts towards increased efficiency and improved quality of LD steelmaking. Converters of up to 350–400 tonnes equipped with seven or eight hole nozzles have come into vogue (Chatterjee 1973). A comparative analysis of the lance tips used in Europe (Cottage and Echols 1992) indicates that 46% of the tips used are six-hole, 32% are five-hole and 20% are four-hole tips. The main advantage of increasing the number of outlets on a lance is to allow the total oxygen throughput to be increased without effectively increasing the pressure exerted by the jets impinging on the bath surface. By increasing the number of nozzle openings, it is therefore possible to increase the rate of oxygen supply without simultaneously decreasing the metal yield or increasing the risk of burning the converter bottom because of too deep penetration. These advantages are a direct consequence of the total energy of the jet being distributed over a larger surface area of the bath. Because of effectively 'harder' blowing

Table 6. Details of three-hole and six-hole lances used at Tata Steel.

	Three hole lance	Six hole lance
Throat dia, mm	46.0	25.7
Exit dia, mm	60.0	37.3
Area ratio, A exit/A throat	1.701	2.106
Inclination of holes from central axis, degrees	12.0	17.3
Mach No.	2.01	2.255

Table 7. Comparative evaluation of LD operating parameters with three-hole vis-a-vis six-hole lance.

Parameters	three hole lance	six hole lance
Average slag basicity, CaO/SiO ₂	3.2	3.6
Average turn down phosphorus (%)	0.023	0.017
Average phosphorus partition coefficient	65	100
Turndown carbon (%)	0.05	0.03
Heats tapped without reblow (%)	15	35
Slopping	Frequent	Rare occurrence
Average vessel lining life, Number of heats	350–400	600–700

with a three-hole lance, a result of the jets impinging on a more limited surface area of the bath, the slag formed is 'drier' than in the case of a six-hole lance for example.

On the basis of extensive cold model studies at Tata Steel, it was concluded that the shallower depth of penetration and the larger area of contact with the bath in the case of increased number of holes in the lance would improve the efficiency of phosphorus removal. It was conclusively proven that a lance with a larger number of holes with optimized gas injection from the converter bottom gave the best results as far as bath mixing and mass transfer were concerned (Ajmani *et al* 1994). A six-hole lance, details of which are shown in table 6, was put into operation at LD 1 from October 1993. A comparative evaluation of the LD operating parameters with the three-hole lance used earlier vis-a-vis the six-hole lance (table 7) shows overall improvements, the most significant being in dephosphorization.

Lower tapping temperature: Temperature has marked effect on phosphorus removal and the use of a ladle furnace recently installed at Tata Steel to lower the tapping temperature, has had a significant effect. For a reduction of 10°C in tap temperature, phosphorus is reduced by about 0.002% and this has also contributed towards achieving the phosphorus levels required.

Arresting slag carryover: The potential for phosphorus reversion in the ladle depends upon the P_2O_5 content of the slag and the amount of slag carried over into the ladle. High hot metal phosphorus levels tend to give rise to high slag P_2O_5 and the slag stopper system recently installed at Tata Steel has helped in minimizing the slag carryover to a great extent.

7. Conclusions

There are various ways of controlling the final phosphorus content in steel, but the best way is to limit the phosphorus input by careful raw material selection. The other alternatives are pretreatment of hot metal, optimization of steelmaking practice and post-treatment of steel. The choice amongst these later approaches would depend upon the metallurgical and process efficiency targets for the steelmaking system employed at any given steel plant, since the ultimate methodology used would be plant specific. At Tata Steel, the methodologies adopted to achieve product phosphorus levels of 0.015–0.020% include the following:

- Use of 0.6–0.7% silicon hot metal.
- Use of low manganese hot metal (manganese 0.15–0.20%) and elimination of manganese ore usage in the LD converters.
- Bottom agitation with inert gas and proper blowing conditions including post-blow stirring.
- Use of a six-hole lance instead of a three-hole lance.
- Lower tapping temperatures using a ladle furnace.
- Incorporation of a slag stopper system to arrest the high phosphorus bearing final slag within the converter and proper slag skimming thereafter.
- Use of low phosphorus ferroalloys to adjust the composition of steel tapped.

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