Performance Assessment of CO₂ Treated Fluxed Iron Oxide Pellets in Basic Oxygen Steel Making Process

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Lump lime and iron ore are generally used in BOF as flux and cooling material respectively. Owing to high melting point, poor dissolution property, fines generation and hygroscopic nature of lump lime, delay in process and operational complexities are generally encountered. On the other hand, iron ore charging creates slag foaming. In order to alleviate the above problems and to utilize waste materials, fluxed iron oxide pellets containing waste iron oxides (~70 %) and lime fines (~30 %) were prepared and subsequently strengthened with CO₂ gas treatment. This carbonated fluxed pellets exhibited very good CCS (30 kg/pellet) and DSN (150), suitable for cold handling. The performance of this pellet has been assessed in a laboratory scale bottom blowing converter for its specific use in BOF. The refining characteristic of a liquid bath, prepared with pig iron chips was studied using a laboratory scale bottom blowing converter with three flux conditions namely fluxed pellet plus additional lime, iron ore lump plus lump lime and only lump lime. It has been observed that use of these pellets improves decarburization and dephosphorization, increases the metallic yield, decreases oxygen consumption and reduces foaming. Overall, the developed pellet shows very good application potential in basic oxygen steel making.

KEY WORDS: fluxed iron oxide pellet; CO₂ treatment; refining study; oxygen bottom blowing; carbon removal; phosphorus removal; silicon removal; Mn removal; sulphur removal; metallic yield; foaming.

1. Introduction

Iron ore and lump lime are traditionally being used as coolant and flux materials in BOF.^{1,2)} Lime has hardly been challenged as a flux material and iron ore is used as an oxygen supplier in BOF. However, lump lime charging often creates problem in operation due to its high melting point, poor dissolution property, fines generation and hygroscopic nature. On the other hand, iron ore charging causes foaming. But considering its cooling effect, chemical consistency and role as an oxygen contributor,³⁾ iron ore continues to be used in oxygen steel making in view of the fact that foaming or slopping problem may be overcome by modified lance practice.⁴⁾ Other waste iron oxides fines *e.g.* blue dust, iron ore fines, LD sludge, BF dust or sludge *etc.* generated in a steel plant have potential to replace lump iron ore. However, fines or ultra fines of waste iron oxides need to be suitably agglomerated prior to use in basic oxygen steel making.

Several investigators^{3,5–9)} had prepared binder aided waste oxide briquettes (WOB) from different iron oxides wastes and subsequently, assessed its performance in basic oxygen process. They have reported replacement of scrap,^{6,7)} increase in metallic yield^{3,7–9)} and reduced oxygen consumption.^{3,7)} However, Dukelow *et al.*⁶⁾ have found high to medium slopping with WOB. To avoid foaming, continuous addition of WOB at appropriate temperature and high basicity of the bath were suggested.¹⁰⁾ It was proposed that if WOB is added at initial stages of the blow, the lance height should be kept high and the oxygen blow rate be reduced by 20–30% for 2–3 min after attainment of ignition point. It was also reported¹⁰⁾ that in FeO-enriched slags,

metal droplets decarburize fast and greatly increase at higher slag temperature. Using fluxed sinters of iron ore, Bokaro Steel, India¹¹⁾ found complete elimination of slopping, stable blow, reduced lance-jamming and thereby increased lance life. This also resulted in reduction of scrap and lime consumption. Irmiler *et al.*¹²⁾ produced fluxed sinters using iron oxide wastes and lime, limestone, or dolomite fines and used in a laboratory scale hot metal refining study. They found that use of this fluxed sinter promoted better flux dissolution, earlier slag formation, greater removal of both sulfur and phosphorous and increase in metallic yield without any slopping. Some investigators^{9,13)} used iron oxides in form of cement bonded pellets and observed lowering scrap consumption earlier slag formation and faster refining.

In general, iron oxide charging in basic oxygen converter in form of pellets, briquettes or sinter may yield the advantages of reduced scrap consumption, early slag formation, faster refining, increased metallic yield, reduced lance jamming *etc.* Lime in combination with iron oxide has lower melting point, because, a mixture of 22% CaO and 78% Fe₂O₃ exhibits an eutectic point at about 1200°C only.¹⁴⁾ If an agglomerate is made in combination of lime and iron oxide, the slag formation may be enhanced and these advantages can be increased. Choi and Kim¹⁵⁾ made lime pellets coated with iron oxides and carried out plant trial in a 100 ton converter for testing their performance. On hot metal bath a low-melting slag was formed by iron oxides and a part of burnt lime at the initial stage of blowing. This low melting slag acted as a seed for further slagging of the lime, which improved the refining efficiency and decreased the frequency of slopping compared to the conventional

process. However, the difficulties encountered in coating of lime pellets restrict its commercialization.

From the reported literature it is revealed that several attempts have been made on the use of iron oxide in BOF in the form of briquettes, pellets or sinter and very limited study has been conducted on high lime fluxed agglomerate. The existing process of sintering suffers from the limitation of non acceptance of excessive fines. Briquetting and cold pellet making requires costly binder which also has undesirable effect of silica and alumina in BOF process. Further, the fired pellet making involves with energy intensive high temperature curing process. The authors has developed a binderless, room temperature process for preparation of fluxed lime-iron oxide pellet (FLIP), containing around 30% lime which was treated with CO₂ or CO₂ containing waste gas for strength development. The Ca(OH)₂ in air dried green pellets transforms into CaCO₃ as per Reaction (1)

During this transformation, a considerable volume expansion occurs.^{16,17} The expanded volume is accommodated by the pores of the pellets, increasing the compactness and subsequently, strength of pellet increases. The details of pellet preparation and its physical as well as physico-chemical characterization has already been reported elsewhere.^{16,18} Due to very easy production process and favorable physical and physico-chemical properties, FLIP has the potential towards partial or complete replacement of scrap lime combination in basic oxygen steel making. Accordingly, this paper aims to the assessment of performance of FLIP in refining of hot metal in a laboratory scale facility, a representative of BOF.

2. Experimental

Fines of iron ore were taken as the representative of several types of waste iron oxides *viz.* sludge, grit, flue dust, blue dust, mill scale *etc.* and were used for the preparation of lime fluxed iron oxide pellets. Used iron ore fines were collected from Barbil, India. The chemical analyses of iron ore fines and commercial grade lime fines were carried out using conventional methods and are presented in **Table 1**. The details of size distribution of iron ore fine is given in **Table 2**. The details of the pellet preparation, physical and physico-chemical characterization at room temperature as well as at high temperature have already been reported in previous publications.^{16,18} However, for the sake of continuity and ease of understanding, a brief account of fluxed pellet preparation is presented below.

The pellets of 5–16 mm size range were prepared in a

Table 1. Chemical analysis of iron ore fines and lime, wt%.

Materials	Fe _{total}	SiO ₂	Al ₂ O ₃	CaO	MgO	LOI
Iron ore fines	66.46	3.05	1.34	-	-	0.5
Lime	-	0.73	1.12	95.1	0.8	2.0

Table 2. Size fraction of iron ore fines.

Size range, ASTM mesh	Wt %
-200	40
-170 +200	2.1
-150 +170	0.8
-100 +150	1.17
-72 +100	5.93
-60 +72	10.11
-52 +60	26.18
-30 +52	13.71

pelletizer. After natural drying, the green pellets were treated in a reaction chamber in presence of CO₂ for developing cold handling strength.¹⁶ The apparent best combination of making and treatment conditions have been worked out though characterization study.¹⁶ The best values in physical properties such as cold crushing strength (30 kg/pellet), drop strength (150), and abrasive resistance could be achieved for pellets prepared by mixing 25–30% lime with iron ore (1:1 mixture of (–72) and (–30+72) mesh) and treated for 15 min in CO₂ at 5 kgf/cm² gauge pressure. Accordingly, the pellet with 30% lime in base mixture and treated under the above conditions was chosen for the current investigation. On analysis after CO₂ treatment, it has been found that the pellets contained 35.9% CaCO₃, 4.7% Ca(OH)₂ and rest Fe₂O₃ along with other gangue oxides like alumina and silica. The performance of the pellet in refining of hot metal was evaluated in a laboratory set-up, designed to simulate the BOF conditions. The salient features of the experimental vessel and the procedure are described below.

The refining of hot metal was carried out in a mild steel vessel lined with sodium silicate bonded ramable magnesite (**Fig. 1**). The bottom of the vessel was fitted with a nozzle designed for the purpose. It consisted of three alumina tubes; each contains two openings of 1 mm diameter and were hot pressed in a quartz capsule. The extended portion of the capsule had provision for connecting it to the oxygen gas cylinder through rubber tube. The entire nozzle assembly was embedded in the bottom refractory of the ladle, during lining to facilitate bottom blowing.

The flow chart of the refining study in the present investigation is presented in **Fig. 2**. Approximately, 9 kg of pig iron chips (C: 3.9–4.3%, Si: 1.2–1.4%, Mn: 0.4–0.8%, P:

Fig. 1. Schematic of vessel with bottom blowing facility for refining study. a. Mild steel shell, b. Nozzle for oxygen blowing, c. Refractory lining, d. Internal chamber, e. Lever for tilting, f. Arm for holding, g. Stand, h. Oxygen inlet.

Fig. 2. Process flow chart of refining for performance study of pellet in hot metal bath.

0.2–0.25% and S: 0.05–0.08%) was first melted in a 50 kVA induction furnace and the temperature was raised to about 1650°C. The temperature of the metal bath was measured by an IR pyrometer, Model: UX 10P, Ircon Ultimax, with an accuracy of $\pm 15^\circ\text{C}$. The loss in accuracy was largely caused by the smoke formed. The hot metal was then transferred to the ladle. Certain amount of metal was lost during heating and handling and the net mass of the hot metal subjected to refining was around 8.0 kg. While the hot metal was poured into the ladle, oxygen (purity 99.7%) was streamed through the gas inlet at 10–15 lpm to preclude the possibility of solidifying of hot metal and choking of the nozzles. However, immediately on completion of charging of hot metal, oxygen flow was increased to the desired rate of 50 lpm and this was considered to be the start of refining period. Subsequently, 0.4–0.8 kg (amounting 5–10% of hot metal) of FLIP, along with predetermined quantity of lime, was charged into the bath. After 3 min of blow, 0.27 kg of burnt lime, in lump form, was added in all heats. The blow was continued for another 12–20 min, depending upon the temperature of the bath. Metal samples were collected from the bath with the help of a quartz tube at different time intervals, and were subsequently analyzed to study the progress of refining. C and S were analyzed by TCD detector (LECO, Model: CS-444), Mn by atomic absorption spectrometer (GBC-AVANTA), P by ICP (VISTA-MPX) and Si by conventional method. Slag samples were collected by dipping a cold MS rod into the slag and subsequently analyzed by conventional method. In view of detecting free CaO in slag, XRD study of selected slag samples (–100 mesh size) were done using a Siemens D500 X-ray diffractometer with Cu-K α radiation at a scanning speed of $2^\circ/\text{min}$. and peaks were identified by corresponding JCPDS files. At the end of the blow, the final liquid metal was tapped out.

In order to compare the refining performance of fluxed pellet, a few more experiments were conducted with burnt lime alone, or a combination iron ore (Fe_{total} : 66.5% SiO_2 : 2.8% and Al_2O_3 : 1.25%) and lime, as flux, for the purpose of comparison. Three different flux combinations are as follows.

- Condition-i Oxygen blow with only lump lime as flux.
- Condition-ii Oxygen blow with fluxed lime-iron ore pellets (30% lime pellet) plus additional lump lime, keeping the same amount of CaO input as in condition-i.
- Condition-iii Oxygen blow with mixtures of iron ore (coolant) and lump lime (flux), keeping the same amounts of CaO and iron oxide input as in condition-ii.

The charging sequence in different sets of experiments, presented in **Table 3** was designed in such a way that basicity remains comparable in all heats.

Table 3. Sequence of flux charge in different heats.

Batch No.	Heat Nos.	Description of heat	Total amount of flux charged	Time of charging	
				0–0.5 min of blow	3–3.5 min of blow
1	3, 8	Only lime	Lime, g 630	360	270
2	2, 4	5% pellets + lime	Pellet, g 400	400	0
			Lime, g 530	260	270
3	5, 10	8% pellet + lime	Pellet, g 640	640	0
			Lime, g 470	200	270
4	7, 1	10% pellet + lime	Pellet, g 800	800	0
			Lime, g 432	162	270
5	6, 9	Iron ore + lime	Iron ore, g 370	370	0
			Lime, g 630	360	270

3. Results and Discussion

It may be recalled that the major objective of this study was to assess the refining efficiency of the lime fluxed iron oxide pellet (FLIP) *vis-a-vis* conventional flux material like lime or lime and iron ore in combination. The reactor used and the experimental conditions employed were intended to simulate the BOF operating conditions. A scrutiny of the data presented in **Table 4** reveals that there are major differences in some of the parameters compared. However, these differences are not likely to affect the basic objective of this study.

As the time gap between taping from the induction furnace and charging hot metal in the refining vessel was short, the initial temperature at the start of refining was considered to be same as that of the tap temperature (1640°C). A typical variation of bath temperature with time during oxygen blowing in a heat with fluxed pellet plus additional lime (Heat-5) is shown in **Fig. 3**. It may be noted from Fig. 3 that during the first 1–1.5 min of oxygen blow, temperature of the bath dropped by approximately 250°C. This can possibly be attributed to the following major reasons.

- i) A much smaller size (8 kg) of the heat, compared to the 30-ton LD vessel, had a higher exposed surface area/volume ratio, resulting in higher heat loss through radiation in the present work.
- ii) The mass (30 kg) of the furnace lining was much higher compared to the mass (8 kg) of the metal. A significant amount of heat was absorbed by the lining of the furnace. Further, every refining experiment was conducted with a freshly lined vessel, pre-heated to 900°C. This preheating temperature is much lower than the LD converter temperature (1400–1500°C) at which hot metal is received by the converter during its repeated use in industry.
- iii) Charging of cold flux material.

The heat generated by bath oxidation at the initial period was not sufficient to compensate for the above heat losses, causing drop in bath temperature. In order to compensate for the high heat loss at the initial stage of blowing, the initial temperature of the hot metal was kept around 1640°C, in the present study, in contrast with the hot metal temperature of 1350–1400°C used in plants. This difference in ini-

Table 4. Comparison of the refining parameters in the present study with those from plant data.¹⁹⁾

	Mass of hot metal blown, kg	Oxygen flow rate, lpm/kg	Initial hot metal temperature, °C	Oxygen pressure, kg/cm ²	Blowing time, min	Tuyere coolant
Present study	8	6.25	1640	5	13–20	none
Plant data ¹⁹⁾	30,000	6.25	1350–1400	10	15–20	propane

Fig. 3. Variation of bath temperature against time of oxygen blow.

tial temperature is likely to affect the comparison of the two studies with regard to the thermodynamics and kinetics of removal of elements from the bath.

Within 3 min of blow, exothermic oxidation of Si, Mn, C, P and Fe resulted in an increase in the bath temperature to 1530°C. The heat of dissolution of the lime, added to maintain the slag basicity after 3 min of blow, once again caused a drop in temperature to 1450°C. Oxidation of most of the manganese and silicon took place within 6 min of oxygen blow along with some carbon and phosphorus. This resulted the bath temperature once again rise to 1640°C (Fig. 3). Subsequently, Mn and Si contents of the bath became low and heat of oxidation of C, P, Fe *etc.* was inadequate to maintain the bath temperature, resulting in gradual drop in temperature to 1540–1560°C. As a result, the slag tended to be viscous and the heat had to be tapped. The average bath temperature of identical heats measured at three different time intervals during the oxygen blow are summarized in Table 5.

3.1. Analyses of Metal and Slag in Refining

The chemical analyses of the metal samples obtained after refining under varying operating conditions are listed in Table 6. In all heats, at least 5–8 metal samples were collected at different stages of blowing and were analyzed to track the progress of refining. The removal of Si, Mn, C and P in heats under conditions-i and ii are presented in Figs. 4(a) and 4(b), respectively. It may be noted from the figure that extent of C and P removal in FLIP added heat (Heat-10) was much higher compared to heat with lime only (Heat-3) at the end of the blow (14 min). It may further be noted that under both conditions around 95% of Mn and Si got removed within first 5 min of blow. This being much lower than total blow time, removal rates of Si and Mn apparently have little impact on the total refining time. The details discussion based on thermodynamics will be presented in the subsequent sections.

It may be noted from the Table 3 that experiments under

Table 5. Average temperature of bath in different flux condition at different time of blow.

Batch No.	Heat Nos.	Flux conditions of heats	Temperatures of bath, °C		
			4 min of blow	6 min of blow	8 min of blow
1	3, 8	Only lime	1640	1670	-
2	2, 4	5% pellets + lime	1485	1630	1640
3	5, 10	8% pellet + lime	1450	1600	1635
4	7, 1	10% pellet + lime	1395	1535	1575
5	6, 9	Iron ore + lime	1490	1630	1650

all five combinations were repeated to confirm the reproducibility of the results. For example, Figs. 5 and 6 present the carbon removal and phosphorus removal data, respectively, as a function of time for the two identical Heat-5 and 10 (8% fluxed pellets). A best fit line in each figure is drawn using data from both heats. It is apparent from the figures that the data points from both the heats closely follow the best fit curve. Hence, the experimental results tend to exhibit excellent reproducibility. The curve drawn utilizing the data of both heats typically represents the progress of carbon and phosphorus removal from hot metal in presence of lime-fluxed iron ore pellets in an oxygen bottom

Fig. 4. Lowering in concentration of impurity elements against time of oxygen blow (a) in bath with lime only and (b) in bath with fluxed pellet plus additional lime.

Table 6. Chemical analyses of metal before and after refining.

Heat No	Blow time, min	Chemical analysis of metal, wt%											
		Before refining						After refining					
		C	Si	Mn	P	S	Fe (and others)	C	Si	Mn	P	S	Fe (and others)
1	15	3.89	1.17	0.30	0.23	0.071	Rest	0.50	0.03	0.01	0.03	0.059	Rest
2	17	3.61	1.19	0.55	0.20	0.064	Rest	0.50	0.03	0.04	0.03	0.058	Rest
3	14	3.96	1.19	0.46	0.19	0.097	Rest	1.99	0.05	0.08	0.052	0.055	Rest
4	18	4.83	1.10	0.42	0.21	0.038	Rest	0.82	0.04	0.06	0.01	0.030	Rest
5	13	3.99	1.12	0.44	0.26	0.046	Rest	0.34	0.02	0.03	0.02	0.041	Rest
6	12	4.10	1.17	0.36	0.29	0.062	Rest	1.92	0.03	0.03	0.04	0.046	Rest
7	15	3.83	1.20	0.30	0.25	0.069	Rest	0.56	0.03	0.01	0.02	0.055	Rest
8	15	3.91	1.16	0.62	0.22	0.060	Rest	1.55	0.03	0.06	0.07	0.038	Rest
9	13	4.01	1.20	0.61	0.25	0.063	Rest	1.91	0.03	0.02	0.013	0.055	Rest
10	14	3.88	1.18	0.27	0.26	0.066	Rest	0.19	0.03	0.01	0.012	0.055	Rest

Fig. 5. Reproducibility of C removal for 8% pellet added heats under identical conditions.

Fig. 6. Reproducibility of P removal for 8% pellet added heats under identical conditions.

Table 7. Slag compositions and basicities at different stages of blowing.

Heats	Particulars	At different time of blow			
		3 min	8 min	11 min	13 min
Condition-i (Only lime, Heats 3 and 8)	Fe _{total} (wt%)	8.02	13.40	17.12	18.81
	CaO (wt%)	61.07	55.41	50.98	49.46
	SiO ₂ (wt%)	20.19	16.5	16.35	15.85
	Basicity, B	-	3.36	3.12	3.12
Condition-ii (8% pellet + lime, Heats 5 and 10)	Fe _{total} (wt%)	19.40	19.51	22.01	27.02
	CaO (wt%)	49.32	51.01	47.52	42.65
	SiO ₂ (wt%)	17.64	14.83	14.86	13.37
	Basicity, B	-	3.44	3.19	3.18
Condition-iii (Iron ore + lime Heats 6 and 9)	Fe _{total} (wt%)	20.11	20.98	24.10	28.02
	CaO (wt%)	46.72	48.03	44.10	41.33
	SiO ₂ (wt%)	17.31	14.44	14.76	14.05
	Basicity, B	-	3.32	2.98	2.89

blown process.

In order to maintain similar slag basicity in all experiments, the total mass of CaO added, either singly or in combination, was kept fixed at about 600 g, which is about 7.5% of the hot metal charged. Similarly, to facilitate the comparison of the refining trends in heats fluxed with iron ore plus lime (Heat-6 and 9) and heats fluxed with fluxed pellets plus additional lime (Heat-5 and 10), an equal concentration of iron oxide was maintained in either case. The concentration of the major chemical constituents in slag (average of reproducible heats) and slags basicities at different blowing stages for experiments under condition-i-iii are listed in Table 7. XRD analysis of slag samples after 8 min of blow for heats under the three conditions were car-

Fig. 7. XRD pattern of slag sample after 8 min of blow (a) for heat with only lime, (b) for 8% pellet added heat and (c) for iron ore added heat.

ried out and are presented in Figs. 7(a)–7(c). It may be noted that the figures do not exhibit presence of any peak for CaO or Ca(OH)₂. Hence, all lime is considered to be present in combined form with other oxides after 8 min of blow. The basicities at any given stage of blowing in these three cases are nearly the same. The concentrations of Fe_{total} in the two cases of condition-ii and iii (iron ore addition) are higher than that in the remaining case in which lime alone was used as the flux. The reason may be due to the addition of FLIP or iron ore in bath, FeO and Fe₂O₃ content of slag increased.

3.2. Comparison of Refining

3.2.1. Refining under Varying Proportion of Pellet Addition

The ratio of instantaneous carbon to initial carbon is

plotted against the blowing time in **Fig. 8**, for varying proportions of pellet addition (relative to the mass of the hot metal). It is clear that heats with a pellet addition exhibit improved decarburization than those without. The extent of decarburization of metal after 13 min of blow for all the four levels of pellet addition, 0%, 5%, 8%, and 10%, relative to the mass of the hot metal charged, is shown in **Fig. 9**. The extent of decarburization increases nonlinearly with increasing proportion of the pellet in the charge, up to 8%.

The carbon removal in the basic oxygen process is primarily attributed to the following gas-metal reaction

In addition, the iron oxide (FeO) formed in the tuyere zone of an oxygen bottom blowing process partly oxidizes carbon to CO which traverse the metal bath as bubble, according to the following slag-metal reaction

$$\Delta G^\circ = 121\,700 - 99.07T \text{ J}$$

Further, in the present study when fluxed pellets are added to the hot metal bath, an oxidizing slag, composed of $\text{FeO}_x\text{-CaO}$ is formed at the surface of the bath, owing to the dissolution of added pellet and thus promotes Reaction (3). Figure 8 indicates that there is no significant difference in decarburization on use of different quantity of FLIP in first 2 min of blow. It appears that at the initial stage of blow, decarburization predominantly takes place *via* Reaction (2). However, at a later stage; a fluid oxidizing slag produced in case of heats with FLIP, promotes carbon removal through Reaction (3) and facilitates faster decarburization. As per Molleseau and Freuhan,¹⁰⁾ with increase in FeO content, critical temperature, T_c (temperature above which the decar-

burization rate increases significantly) decreases *i.e.* speed of slag-metal Reaction (3) increases. However, the advantageous effect of FLIP addition in case of Heat-2 and 7 is not observed from the figure between 2–6 min and 2–9 min, respectively. The possible reason may be explained as follows. In 5% FLIP added heat, (Heat-2) the critical temperature is expected to be higher than that in 8% FLIP added heat (Heat-5). Hence the advantageous effect of FLIP addition in Heat-2 was observable only after increasing the bath temperature (Table 5). For Heat-7, the temperature of the bath was dropped severely up to about 1395°C due to higher amount of pellet addition; therefore, decarburization rate was increased when temperature of bath became sufficiently high after 8 min of blow (Table 5). This needs further exploration for better understanding.

Figure 9 also shows that pellet addition beyond 8%, there is a decline in the decarburization. This possibly due to a drop in bath temperature caused by the increasing proportion of cold pellets in the charge. It may be noted that Reaction (3) is endothermic and, hence, unfavorable at low temperatures. Nevertheless, in the industrial practice where specific heat loss is lower than the present laboratory scale experiment, addition of pellet beyond 8% is not likely to have so much adverse effect on bath temperature and may improve decarburization further.

Figure 10 presents the fraction of phosphorus removal plotted against blowing time with varied proportion of pellet addition. It is clear that with increasing proportion of FLIP addition (up to 8%), there was an increase in the extent of dephosphorization. These may be explained as follows.

The phosphorus reaction between metal and slag may be represented by the Reaction (4)

For which the modified equilibrium constant may be defined as^{20,21)}

$$k_p = (\% \text{P}_2\text{O}_5) / [\% \text{P}]^2 (\% \Sigma \text{FeO})^5 \dots\dots\dots (5)$$

where, k_p is the product of the following four terms: (i) the equilibrium constant, $K_{(4)}$, of Reaction (4), (ii) the activity coefficient ratio, $(\gamma_{\text{FeO}}^5 \cdot f_{\text{P}_2\text{O}_5} / \gamma_{\text{P}_2\text{O}_5})$, (iii) the conversion factor (m_1) between the mole fraction ratio ($x_{\text{P}_2\text{O}_5} / x_{\text{FeO}}^5$) and the wt% ratio ($\text{wt\% P}_2\text{O}_5 / (\text{wt\% FeO})^5$), and (iv) the conversion factor (m_2) between wt% FeO and wt% ΣFeO (the total iron as oxides in the slag), which is obtained from the equilibrium relation between wt% FeO and wt% Fe_2O_3 in the slag. It is to be noted that the terms (ii), (iii) and (iv) are dependent on the slag and metal compositions.

Therefore,

Fig. 8. Variation in C removal with time of oxygen blow for different proportion of pellet addition.

Fig. 9. Extent of decarburization *versus* quantity of pellet addition for 13 min of oxygen blow.

Fig. 10. Variation in P removal with time of oxygen blow for different proportion of pellet addition.

$$k_p = K_{(4)} \cdot \frac{\gamma_{\text{FeO}}^5 \cdot f_P^2}{\gamma_{\text{P}_2\text{O}_5}} \cdot m_1 \cdot m_2 \dots\dots\dots (6)$$

The importance of Eq. (5) is that it relates k_p with readily measurable quantities. Further, the constant k_p is again closely related to the phosphorous partition ratio, D_p (wt% P in slag)/(wt% P in metal) through the term, $\% \Sigma \text{FeO}$ such that when $\% \Sigma \text{FeO}$ increases, D_p increases. Hence with increase in $\% \Sigma \text{FeO}$ in slag, the extent of the removal of phosphorous from the metal phase increases at a given temperature and given basicity of the slag for which the value of k_p is essentially constant. Balajiva *et al.*^{22,23)} made a detailed investigation of Reaction (4) and found that k_p increases with decreasing temperature (which increases $K_{(4)}$) and increasing concentration of calcium oxide in the slag (which decreases $\gamma_{\text{P}_2\text{O}_5}$). Therefore, thermodynamically the phosphorous content of the metal, $[\%P]$, decreases with decreasing temperature, increasing concentration of calcium oxide in the slag and increasing total iron (as oxides, $\% \Sigma \text{FeO}$) in the slag.

The dissolution behavior of FLIP in hot metal bath had been separately studied²⁴⁾ using a resistance heated pot furnace. It had been found that a single pellet of 10 mm diameter took around 40 s for complete dissolution at 1450°C in hot metal bath. It is well known that lump lime does not melt/dissolve at this temperature unless some iron oxide is produced by oxidation of liquid iron. Lime and iron oxide being inherently present in the FLIP added heats (Heat-5, for example) CaO–FeO_x type slag is produced at the early stage of blow, which apparently resulted in a greater extent of dephosphorization than that achieved in heats with lime alone (Heat-8, for example), as shown in Fig. 10.

Another observation in Fig. 10 is that phosphorous removal in 8% and 10% pellet added heats (Heat-5 and 7) are high even at the initial stages (2 min of blow) of blow but for heat with 5% pellet addition (Heat-2) and only lime (Heat-8) significant removal observed after 5 and 9 min of blow, respectively. This may be explained considering the phosphate capacity of slag, $C_{\text{PO}_4^{3-}}$, which measures the dephosphorizing power of the slag for a given p_{P_2} and p_{O_2} and may be defined as follows²⁵⁾

$$C_{\text{PO}_4^{3-}} = \frac{(\text{wt}\% \text{PO}_4^{3-})}{p_{\text{P}_2}^{1/2} \cdot p_{\text{O}_2}^{5/4}} \dots\dots\dots (7)$$

As per reported literature,^{21,25–27)} phosphate capacity of slag increases with the increasing basicity of the slag (*i.e.*, with the increasing ionic nature of the slag, releasing more O^{2-} ions) and with the decreasing temperature of the slag. In pellet added heats as CaO–FeO_x type slag was produced earlier and dissolution of lump lime (charged separately with the pellets) was enhanced by FeO in slag. This resulted in an early increase in the concentration of O^{2-} ions and hence phosphate capacity of slags of Heat-5 and 7 increases. While the initial bath temperatures of all heats were practically the same (1640°C), the bath temperature later decreased in the FLIP-added heats owing to the dissolution of the pellets. It may be noted from Table 5 that the bath temperature measured after 4 min of blow was lower with higher proportion of pellet addition. This is possibly due to higher amount of CaO–FeO_x type slag formation with increased FLIP. The presence of relatively higher FeO, lower bath temperature and greater concentration of O^{2-} ions at the initial stage of blow caused a greater extent of dephosphorization in Heat-5 and 7.

Figure 10, however, shows that there is no noticeable increase in the rate and extent of dephosphorization with the FLIP addition beyond 8%. Presumably, the decrease in the

Fig. 11. Comparison of C removal among pellet added heat, iron ore added heat and only lime added heat.

bath temperature (Table 5) with the greater proportion of the cold charge beyond 8% slowed down the kinetics of dephosphorization (Reaction (4)) just enough to offset the favorable thermodynamic effects of the greater $\% \Sigma \text{FeO}$ and lower temperature.

3.2.2. Refining with Different Flux Materials

From the above it is clear that maximum decarburization and dephosphorization could be obtained with 8% pellet addition under condition-ii. Therefore, the results of heats with 8% FLIP were used for the following comparisons.

• C Removal

Figure 11 compares the carbon removal as a function of the blow time for heats fluxed with 8% pellet (condition-ii) against those under condition-i and iii. It is evident from the figure that since very early stage of blow, the extent of decarburization is higher in condition-ii than in condition-i. It may further be noted that same quantity of iron oxide equivalent to 8% FLIP in form of iron ore was used for experiments under condition-iii. A major difference in bath characteristics could be observed during refining under condition-ii and iii. Bath with iron ore (condition-iii) exhibited excessive foaming. On the contrary, no noticeable foaming could be detected for bath with fluxed pellets (FLIP). This is possibly due to the fact that while melting, iron oxide in composite pellet got arrested by lime, available in the immediate vicinity, preventing foam formation. Excessive foaming under condition-iii resulted limited slag–metal contact. This caused Reaction (3) to be relatively ineffective, leading to less decarburization compared to condition-ii even with same amount of iron oxide addition.

• P Removal

Figure 12 presents the dephosphorization behavior of the bath refined under the three flux condition. It is apparent that the bath under condition-ii (8% FLIP) exhibit much improved dephosphorization compared to the bath under condition-i (only lime). Choi and Kim¹⁵⁾ have also reported improvement in dephosphorization when iron oxide coated lime pellet was charged as flux material. The reason for the same has already been discussed in the previous section. It is interesting to note that bath under condition-iii, having equal iron oxide and lime contents, and performed at about the same temperature, however, no detrimental effect of foaming could be observed in dephosphorization. This observation needs further exploration.

Fig. 12. Comparison of P removal between pellet added heat, iron ore added heat and only lime added heat.

Fig. 13. Comparison of Si removal among pellet added heat, iron ore added heat and only lime added heat.

• Si Removal

The removal of Si is found to be more or less same under all the three conditions as presented in Fig. 13. Being highly oxidizing element, Si in metal directly react with oxygen bubbles during blow and the reaction may be represented as:

Under the same input p_{O_2} and temperature, and for the same hot metal composition and basicity of the slag, the removal rate of silicon from the hot metal is likely to be thermodynamically same under the three types of heats fluxed with lime alone, pellets (8% of hot metal) plus lime, and ore plus lime, having the same CaO content. However, on close examination it is found that the rate of silicon removal is slightly greater with the FLIP added heat (Heat-5) and Iron ore added heat (Heat-9) than with only lime (Heat-8). This small difference may be explained by considering the additional silicon oxidation by the FeO in the slag²⁸⁾ for Heat-5 and 9:

The formation of CaO-FeO_x type slag with the FLIP plus lime addition or iron ore plus lime addition provides the required basic and oxidizing condition favorable for silicon oxidation according to Reaction (9) to a greater extent than with the lime alone (less oxidizing).

Fig. 14. Comparison of Mn removal among pellet added heat, iron ore added heat and only lime added heat.

• Mn Removal

It is apparent from the Fig. 14 that Mn removal is faster in condition-ii and iii than in condition-i.

The manganese exchange between metal and slag may be represented by,

The modified equilibrium constant, k_{Mn} may be defined as²¹⁾

$$k_{\text{Mn}} = (\% \text{MnO}) / (\% \text{Mn})(\% \Sigma \text{FeO}) \dots\dots\dots (11)$$

The constant k_{Mn} is the product of the following three terms: (i) the equilibrium constant, $K_{(10)}$, of Reaction (10), (ii) the activity coefficient ratio, $(\gamma_{\text{FeO}} \cdot f_{\text{Mn}} / \gamma_{\text{MnO}})$, and (iii) the conversion factor (m_2) between wt% FeO and wt% ΣFeO (the total iron as oxides in the slag). It is to be noted that the mole fraction ratio $x_{\text{MnO}}/x_{\text{FeO}} \approx (\text{wt\% MnO})/(\text{wt\% FeO})$, and the terms (ii) and (iii) are dependent on the slag and metal compositions.

Therefore,

$$k_{\text{Mn}} = K_{(10)} \cdot \frac{\gamma_{\text{FeO}} \cdot f_{\text{Mn}}}{\gamma_{\text{MnO}}} \cdot m_2 \dots\dots\dots (12)$$

Since the ratio of the activity coefficients $\gamma_{\text{FeO}}/\gamma_{\text{MnO}}$ decreases with increasing basicity of the slag, the value of k_{Mn} decreases with increasing basicity of the slag. For example, Turkdogan²⁰⁾ found the following relation between k_{Mn} and the basicity, B for steelmaking temperatures:

$$k_{\text{Mn}} = 6/B \dots\dots\dots (13)$$

Thus, the extent of manganese removal at equilibrium is favored at low basicity and high $\% \Sigma \text{FeO}$. Considering that the basicity of the three types of heats are comparable, the higher value of $\% \Sigma \text{FeO}$ in heats fluxed with FLIP (8% of hot metal) plus lime or with ore plus lime lead to faster Mn removal from the hot metal than in heats with lime alone, as shown in Fig. 14. Notably, unlike in the OBM steelmaking, there is no reversion of manganese to the metal (the so-called Mn-hump) in the present study, presumably due to the absence of a marked increase in temperature or of a decrease in the FeO content of the slag during the course of the refining.

• Sulphur Removal

The sulfur-oxygen exchange may be represented by the metal-slag reaction,

where, equilibrium constant,

$$K_{(14)} = \frac{h_{\text{O}} \cdot a_{\text{S}^{2-}}}{a_{\text{O}^{2-}} \cdot h_{\text{S}}} \dots\dots\dots (15)$$

or, alternatively, by the gas–slag reaction,

The equilibrium constant of Reaction (16), $K_{(16)}$, for a given temperature is represented by the equation

$$K_{(16)} = \left(\frac{\gamma_{\text{S}^{2-}}}{a_{\text{O}^{2-}}} \right) \left(\frac{p_{\text{O}_2}}{p_{\text{S}_2}} \right)^{1/2} (x_{\text{S}^{2-}}) \dots\dots\dots (17)$$

In order to avoid difficulties in evaluating the activity of the oxygen ($a_{\text{O}^{2-}}$) and the activity coefficient of the sulfur ($\gamma_{\text{S}^{2-}}$), Turkdogan²⁰ defined an equilibrium relation, called the sulfide capacity C_{S} in terms of measurable quantities:

$$K_{(16)} \left(\frac{a_{\text{O}^{2-}}}{\gamma_{\text{S}^{2-}}} \right) \equiv C_{\text{S}} = (\text{wt\%S}) \left(\frac{p_{\text{O}_2}}{p_{\text{S}_2}} \right)^{1/2} \dots\dots\dots (18)$$

According to Eq. (18), the sulfide capacity of a slag increases with temperature (due to an increase in $K_{(16)}$) and with the basicity of the slag (due to an increase in $a_{\text{O}^{2-}}$).

Now, considering the metal–slag equilibrium, Reaction (14), for which the modified equilibrium constant may be written as^{21,25}

$$k_{\text{S}} = \{(\% \text{S}) / [\% \text{S}]\} (\% \Sigma \text{FeO}) \dots\dots\dots (19)$$

Under the employed experimental condition, it is assumed that the following reaction will attain equilibrium.

Hence, utilizing $K_{(14)}$ and $K_{(20)}$ and adopting similar procedure as described for calculation of k_{p} and k_{Mn} , k_{S} may be written as

$$k_{\text{S}} = \frac{K_{(14)} \cdot K_{(20)} \cdot a_{\text{O}^{2-}} \cdot f_{\text{S}} \cdot m}{\gamma_{\text{FeO}} \cdot \gamma_{\text{S}^{2-}}} \dots\dots\dots (21)$$

in which $K_{(20)}$ is the equilibrium constant of Reaction (20) and m is, the conversion factor between mole fraction FeO and wt% ΣFeO . In Eq. (19), ($\% \text{S}$) refers to the slag and $[\% \text{S}]$ refers to the metal. It is easy to see the closeness of the two equilibrium relations k_{S} and C_{S} by comparing Eqs. (18) and (19) and noting the relation between p_{O_2} and $\% \Sigma \text{FeO}$ and that between p_{S_2} and $[\text{wt\% S}]$.

According to Eq. (21), the value of k_{S} decreases with decreasing basicity of the slag (*i.e.*, with decreasing $a_{\text{O}^{2-}}$) and increases with increasing temperature (due to an increase of $K_{(14)}$). For a given value of k_{S} (fixed chiefly by fixing the temperature and the basicity of the slag), the sulfur partition ratio, (wt% S)/[wt% S], is inversely proportional to the $\% \Sigma \text{FeO}$ in slag, as can be found from Eq. (19). Therefore, the sulfur removal thermodynamically increases with increasing basicity, decreasing $\% \Sigma \text{FeO}$ in slag and increasing temperature of the bath. This has also been established from Kor's²⁹ results. The experimental result of desulphurization in terms of amount and percentage of sulphur removal in three conditions (condition-i–iii) is presented in

Fig. 15. Comparison of S removal among pellet added heat, iron ore added heat and only lime added heat.

Fig. 16. Comparison of blow time between heats with pellet and without pellet for identical end point carbon.

The figure clearly indicates that 37% sulphur removal was achieved in heat fluxed with lime alone (condition-i), while only 12.5% and 11% removal were achieved in heats where iron oxide was added to the bath along with lime in the form of FLIP (condition-ii) and iron ore (condition-iii), respectively. Although, the basicities in all the three conditions were comparable, the $\% \Sigma \text{FeO}$ in condition-ii and iii were higher than that in condition-i. Further, Table 5 shows that bath temperature in conditions-ii and iii is much lower than condition-i. Therefore, the percentage desulphurization was lower in condition-ii and iii. Thus, the experimental result is in clear agreement with the thermodynamic principle, particularly with respect to the $\% \Sigma \text{FeO}$ content of the slag and temperature of bath.

• Oxygen Consumption

Oxygen consumption in the basic oxygen process depends mainly upon the duration of blowing and reblowing. In the present study, the extent of decarburization and dephosphorization being more in condition-ii than those under condition-i and condition-iii (Figs. 11 and 12), the oxygen consumption is expected to be less in heats fluxed with composite pellet (condition-ii). Generally, the blow time depends upon the initial carbon content of the metal and the targeted end-point carbon. In the present study, after 13 min of blow, the carbon content of the metal in the pellet-fluxed heats was 0.34% and after 15 min of blow, the corresponding figure in the heats fluxed with lime alone, was 1.55% while, initial carbon was nearly same for both the cases. For the purpose of comparison, the decarburization plot under condition-i was extrapolated down to 0.34% C and the projected blowing time was found to be about 17 min, as shown in Fig. 16. The data presented in Fig. 11 were utilized for this purpose. This indicates oxygen saving

Table 8. Metallic yield slag volume in different experiments.

Batch of Experiment	Description	Average metallic yield, %	Average weight of slag, kg	Recovery of Fe from added flux / iron ore, %
1	Only lime	86.3	1.205	-
2	5% pellet+ lime	87.5	1.310	60
3	8% pellet + lime	87.86	1.384	51
4	10% pellet + lime	87.92	1.435	41
5	Iron ore + lime	87.21	1.431	32

of around 24% in the first case. However, in actual practice, the oxygen consumption also depends upon other parameters like reblowing, endpoint control and tap temperature. So, the projected saving of oxygen for pellet-fluxed heats may be considered as an approximate one and it is likely to differ in industrial practice.

• Metallic Yield

The average metallic yields (wt of steel/wt of metallic charge) for heats under different conditions, shown in **Table 8**, are found to vary in the range of 86.3–87.9%. An iron loss of 1–2% in the slag was caused by the high viscosity of the slag at the end of blow, when the bath temperature considerably decreased. Yield improvements by 1.56% in pellet-fluxed heats (8%), and by 0.91% in iron ore-fluxed heats, over the heats fluxed with lime alone were observed. Mukherjee *et al.*⁴⁾ had reported 0.8% metallic yield improvement when iron ore was charged in refining bath. Observed metallic yield in iron ore fluxed heat is in agreement to the reported data. From Table 8, it is also found that recovery of Fe from charged flux is around 51% in case of 8% pellet added heat. It decreases if pellet percentage is increased further.

• Foaming

Heats fluxed with iron ore plus lime, were found to generate excessive foam from the very beginning of blowing. In contrast, moderate foaming was observed in the latter stage of the blow (2.5–3 min) in heats with fluxed pellets.

Generally speaking, slags with low surface tensions and high viscosities tend to foam in processes involving extensive gas evolution. In the present study, with both pellet-fluxed heats and iron ore-fluxed heats, the CO evolution rate was high because of the fast decarburization [Reaction (3)], facilitated by large concentration of FeO in the early slag formed. However, in the former case, the slag formed was sufficiently fluid due to the ready availability of lime and the formation of a low-melting compound of FeO and CaO. This reduced the chance of foaming. On the other hand, in the latter case, the initial lime added along with the iron ore took a longer time (3 min, approximately) for dissolution. Therefore, the initial slag produced was viscous, leading to the foaming and slopping. (It may be noted in passing that the foaming/slopping could be controlled by the repeated addition of fluorspar, which increased the fluidity of the slag.) Heats fluxed with lime alone were accompanied by a less concentration of FeO in the slag, and, as a result, no significant foaming was observed during the blow.

4. Conclusions

(1) Addition of fluxed lime iron oxide pellet (FLIP) appears to enhance removal of C, P and Mn from hot metal in comparison to iron ore along with lime or lime alone.

(2) Addition of FLIP amounting 8% of hot metal showed better results than that of higher or lower amount of FLIP addition.

(3) Heats fluxed with FLIP plus additional lime and iron ore plus lime show lower extent of sulfur removal than

heat fluxed with lime alone.

(4) Use of FLIP in refining of steel shows improved metallic yield.

(5) Oxygen consumption is likely to reduce by use of FLIP because of a shorter blowing time.

(6) Fluxed lime iron ore pellets, developed in a binder-less room temperature process utilizing waste materials and green house gas has favorable melting and refining characteristics, to warrant their application as a partial/complete substitute of the traditional scrap-lime combination in basic oxygen steel making.

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