SELECTIVE REMOVAL OF PHOSPHORUS FROM HIGH CARBON FERROMANGANESE - AN IMPROVED PROCESS

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ABSTRACT

The presence of phosphorus is known to deteriorate the mechanical properties of cast steel and other metallic products. Ferromanganese, used as the last additive during steel making, is one of the main sources of phosphorus contamination. Therefore phosphorus has to be removed from the ferromanganese before it is used as a deoxidizing and alloying agent. The bulk of high carbon ferromanganese produced in India continues to have more than 0.35% phosphorus since they are produced by carbothermic reduction process. A systematic study by NML showed that it was possible to remove phosphorus from high carbon liquid ferromanganese successfully from 0.56% to 0.18% using $BaCO_3$ based fluxes at the rate of 16-wt% of the ferromanganese charged. However, the Mn loss varied in the range of 2-5%.

The objective of the present study was to optimize the flux consumption as well as minimize the Mn loss with effective dephosphorization by using BaO based calcined pellets instead of $BaCO_3$ based powders. It is easier to handle pellets under plant conditions and eliminate the loss of flux as a dust, which occurs when powder is added. These pellets can be forced towards the bottom of the melt for better efficiency. Another advantage of using pellets is that it utilizes manganese ore fines, which is a waste material in the ferromanganese industry. The results have shown that the addition of moderate amount of MnO into the pellets reduces the Mn loss while it helps dephosphorization. The results achieved indicate that it is possible to achieve more than 60% phosphorus removal using flux addition at 5% by weight of the ferromanganese charged.

1.   INTRODUCTION

The adverse effect of phosphorus on the mechanical properties of steel is well known [1,2]. The presence of phosphorus makes the steel brittle for low temperature applications. Segregation of phosphorus takes place at low temperatures due to low solubility and low diffusivity. This also affects the weldability of steel. It is well known that phosphorus induces cold shortness in steel and makes it unfit for low temperature application [3]. Therefore, phosphorus has to be removed from the ferromanganese before it is used as a deoxidizing and alloying agent.

A systematic study was taken up by NML to remove phosphorus from high carbon ferromanganese using $BaCO_3$ based fluxes [4,5,6]. The results showed that it was possible to remove phosphorus from an initial value of 0.56% to 0.18% when the flux was used at a rate of 16-wt% of the ferromanganese. However, the Mn loss varied in the range of 2-5% [6]. The main drawback of this process was temperature drop due to decomposition of $BaCO_3$, which inhibited its use for industrial application. Moreover, due to the release of CO_2 on decomposition of $BaCO_3$ the oxygen potential of bath increases resulting in higher manganese loss. In order to overcome these problems, the present study was taken up to develop a process for selective removal of phosphorus under oxidizing conditions using BaO based flux pellets instead of $BaCO_3$ powders used earlier. Another aim of this study was to optimize the flux consumption to make the process economically viable. For this purpose, flux pellets were added using a plunger, which was expected to increase the metal/flux contact time to improve the efficiency of the flux. The main advantages of using the pellets are that it can be readily used to treat liquid high carbon ferromanganese once the metal is tapped from the furnace and it is less hazardous as it does not generate dusts and fumes. It was decided to optimize the reaction conditions for removal of phosphorus using BaO based flux pellets. For this purpose, it was considered necessary to examine the thermodynamics of the process, which helped in identifying the experimental parameters.

2.   THERMODYNAMIC CONSIDERATIONS

The oxidation of phosphorus dissolved in liquid ferromanganese by a basic slag can be written as:

$$[P] + \frac{3}{2}O^{-2} + \frac{5}{4}O_2 = PO_4^{-3} \qquad (1)$$
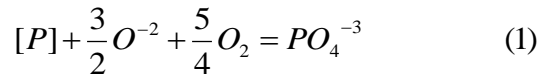
for which the equilibrium
constant (K_1) can be expressed as:

$$K_1 = \frac{(w_{PO_4^{3-}})f_{PO_4^{3-}}}{[a_P].(p_{O_2})^{5/4}.(a_O^{2-})^{3/2}} \qquad (2)$$

where $w_{PO_4^{3-}}$ is the weight pct of phosphorus as phosphate in slag, (p_{O_2}) is the partial pressure of oxygen.

From the equation (2) it is obvious that to promote dephosphorization the favorable conditions are:

i)   a high activity coefficient of phosphorus (f $_{[P]}$) and a high oxygen partial pressure (p_{O_2}),

ii)   a high oxygen activity (a_O^{2-}) in slag which is a function of basicity of slag and a low activity coefficient of the phosphate ion ($f_{PO_4^{3-}}$) in the slag phase. A low temperature is also beneficial since the reaction involved is exothermic.

Phosphate Capacity: The phosphate capacity ($C_{PO_4^{3-}}$) is a measure of the ability of slag to absorb phosphorus in the form of phosphate [2]. The definition is defined on the following reaction:

$$1/2P_2 + 3/2(O^{2-}) + 5/4O_2 = (PO_4^{3-}) \qquad (3)$$
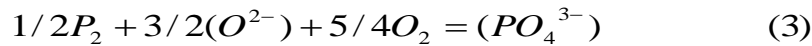
$$C_{PO4^{3-}} = \frac{(w_{PO_4^{3-}})}{p_{P_2}^{1/2}.p_{O_2}^{5/4}} = K_1\frac{(a_{O^{2-}})^{3/2}}{f_{PO_4^{3-}}} \qquad (4)$$

where $w_{PO_4^{3-}}$ is the weight pct of phosphorus as phosphate in slag, P_{P_2} is the partial pressure of phosphorus.
From the above definition, the phosphate capacity is a function of the composition of slag, basicity and the temperature.

Phosphorous Partition Coefficient: This is an important parameter to measure the extent of dephosphorization and is defined as:

$$L_P = \frac{(\%P)}{[\%P]} \qquad (5)$$

where (%P) & [%P] are the weights of phosphorus in slag and metal.

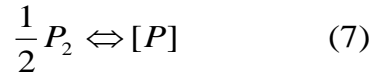Since, moles of phosphorus in slag   = moles of phosphate in slag

(One mole of phosphorus is oxidized to provide one mole of phosphate)

$$\frac{(\%P)}{M_P} = \frac{(w_{PO_4^{3-}})}{M_{PO_43-}}$$

Substituting the value of (%P) in equation (5),

$$L_P = \frac{M_P}{M_{PO_4^{3-}}} \cdot \frac{w_{PO_4^{3-}}}{[\%P]} \qquad (6)$$

A relation between gaseous phosphorous and the dissolved phosphorous can be obtained by considering the following equation:

$$\frac{1}{2} P_2 \Leftrightarrow [P] \qquad (7)$$

The equilibrium constant for this equation can be written as:

$$K_7 = \frac{f_P[\%P]}{p_{P_2}^{1/2}} \qquad (8)$$

An effective correlation between phosphate capacity and partition ratio can be obtained by combining Eq. (4), Eq. (6) and Eq. (8) as:

$$\log L_P = \log C_{PO_4^{3-}} + 5/4 \log P_{O_2} + \log f_P - K_7 - \log(\frac{M_P}{M_{PO_4^{3-}}}) \qquad (9)$$

The equation 9 explains the parameters on which dephosphorization practice depends. The affecting factors are discussed below:

Effect of oxygen partial pressure: The phosphorus removal is favored with increase in oxygen partial pressure of the bath. However, it also increases the Mn loss. Therefore, dephosphorization is required to be carried out at relatively low oxygen potentials ($<10^{-17}$) [10]. To select the appropriate oxygen partial pressure, the predominance diagrams for the Ba-P-O ternary system were constructed earlier and renewed under standard as well as non-standard conditions at different temperatures from 1573 to 1873 K to find the effect of variation of temperature on the phosphorus removal [11]. The Mn-MnO equilibrium was superimposed in these diagrams in order to find out the desirable test conditions for dephosphorization without loss of manganese. For effective dephosphorization at 1573K, the oxygen partial pressure PO_2 is to be maintained below 3.0×10^{-17} atm [11].

The role of each component of the BaO-BaF$_2$-MnO flux pellets used in laboratory scale tests is discussed below:

Effect of BaO: Amongst the various flux materials available, a BaO based flux was selected in view of its known effectiveness in increasing the basicity of the slags [7]. It was possible to achieve the basicity in the range of 3 to 5. Higher basicity helped us to carry out dephosphorization within a narrow range of oxygen potential due to the high phosphate capacity of BaO-based fluxes ($>10^{26}$), which helped minimize Mn loss [7].

Effect of BaF$_2$:.The addition of barium fluoride (BaF$_2$) facilitates melting of BaO-based flux pellets at moderate temperatures. The presence of BaF$_2$ also increases the fluidity of slag, which is desired for good metal/slag reaction. The activity coefficient of MnO is reported to increase with the addition of BaF$_2$, which helps in the selective removal of phosphorus [8].

Effect of MnO: The addition of MnO acts as the source of oxygen in the bath for oxidation of phosphorus to P$_2$O$_5$, which is required when BaO is used as the primary flux. The addition of MnO also increases the activity of MnO in slag, which is desired for improving the extent of phosphorus removal [9].

Thus, thermodynamic analysis helped us in selecting favorable conditions for selective dephosphorization of ferromanganese. Experiments were carried out accordingly in order to confirm the predictions of the thermodynamic analysis.

3. EXPPRIMENTAL DETAILS

On the basis of results obtained in a previous study [6] and thermodynamic analysis, different proportions of $BaCO_3$, BaF_2 and MnO_2 were selected for the preparation of green pellets. These flux pellets were first calcined at 1050-1100^{0}C for 1 hr for the formation of BaO from $BaCO_3$ and MnO from MnO_2 before their use for the treatment of liquid ferromanganese. A master alloy of homogeneous composition (C-3.50%, Mn-67.60%, P-0.49%, Si-0.36%) was prepared for use in each test. The dephosphorization tests were carried out in a medium frequency induction furnace at moderate temperatures (1300-1500^{0}C) under oxidizing conditions using calcined flux pellets. The following parameters were varied to study their effect on the degree of dephosphorization: (i) type of flux, (ii) quantity of flux, (iii) effect of temperature, (iv) time and (v) the mode of addition. Several tests were carried out to study the effect of identified parameters on dephosphorization. The results of tests (Test Nos T1 to T4) helped us in choosing the most suitable composition amongst the fluxes tried. This composition was used for all subsequent tests. Test Nos 5 to 9 were taken up to study the variation of flux weight on the phosphorus removal. The objective of these tests was to optimize the flux consumption in order to make the process economically viable. For this purpose a plunger system was used to improve the efficacy of the flux added. Tests (T5 to T9) were carried to study the effect of change in temperature and time on phosphorus removal as well as minimizing the Mn loss. As the flux is ultimately required to work under simulated conditions in ferromanganese manufacturing plant, it is important to improve the kinetics of the process so that the desired phosphorus level is achieved before the slag is solidified. Metal and slag samples were taken by silica tubes at 5, 10, 15 & 20 minute's interval after the addition of flux pellets. The temperature of the liquid alloy was measured using Digilance II (immersion type thermocouple). The final sample was collected in graphite mold before pouring the liquid ferromanganese in ingot mold.

4. RESULTS AND DISCUSSION

The effect of following parameters on phosphorus removal were examined and are discussed below:

a). **Type of flux**: The effect of change in composition on the extent of dephosphorization is shown in Table 1.

Table1: Effect of change in flux composition on degree of dephosphorization

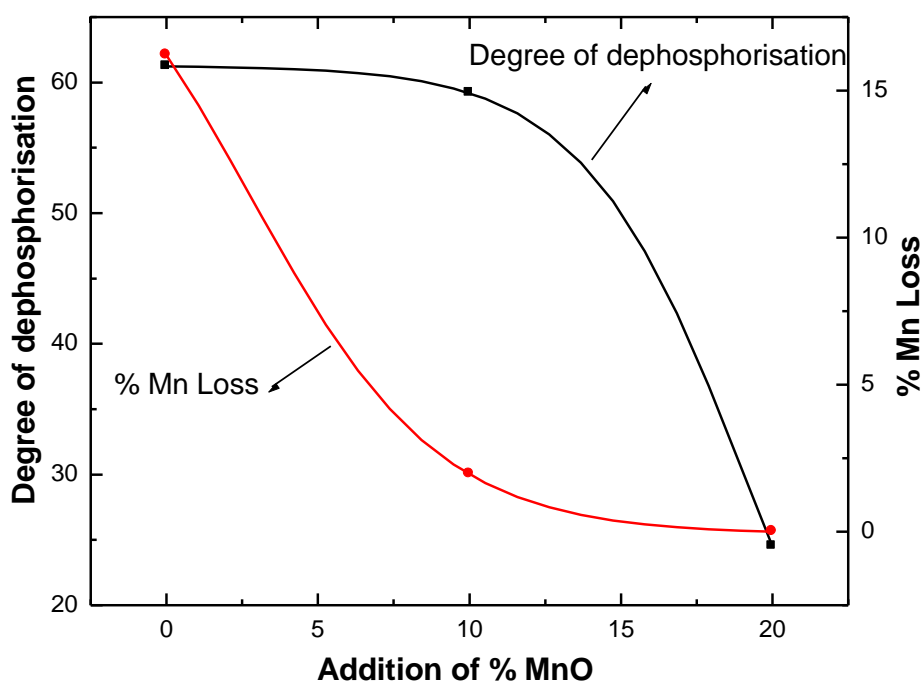| Test No.	Temp ^{0}C	Flux Wt. (10%wt) Flux Composition* (%)			Deg. of dephosphorization $\eta = \dfrac{P_f - P_i}{P_i} X100$	Mn Loss
		BaO	BaF_2	MnO	%	%
T1	1350	52	34	00	57.0	13.5
T2	1367	59	24	00	61.0	16.0
T3	1350	54	21	10	59.0	2.0
T4	1308	48	19	20	24.5	Nil

*Balance Impurities

Basis of flux composition calculation:

(i) Reagent grade $BaCO_3$ & commercial grade BaF_2 were used for tests.
(ii) Percentage of different constituents has been calculated with respect to other impurity constituents present in $BaCO_3$ & BaF_2.
(iii) % BaO has been calculated from the amount of $BaCO_3$ added assuming complete conversion of $BaCO_3$ to BaO.

Initial tests (Test Nos T1&T2) were carried out using calcined $BaCO_3$-BaF_2 flux pellets with 10%flux weight in the temperature range of 1350-1367^{0}C. There was significant phosphorus removal (61% - 57%) but the Mn loss was extremely high (16%). The reason of high manganese loss is perhaps the insufficient calcination of $BaCO_3$-based green pellets. XRD patterns results of the calcined pellets indicated that it contained only about 60% BaO. As there was no proper storage facility for storing the calcined pellets, part of BaO formed possibly got converted to $BaCO_3$ by picking moisture from the atmosphere. This may have created high oxygen potential in the bath, contributing to higher manganese loss. In order to reduce the Mn loss, addition of MnO in the flux was considered as one of the desirable options. But if the MnO is added, melting of flux becomes difficult near the melting temperature of ferromanganese alloy because of its high melting point (1785^{0}C). It was observed that melting of BaO based flux was possible at 1350^{0}C when the MnO content was 10% (Test No T3), which facilitated 59% phosphorus removal and also reduced the Mn loss to less than 2% (Fig-1). However, when MnO content was increased to 20% (Test No T4) in flux pellet, lot of black solid particles were found floating on the melt surface, which created difficulty in melting and resulted in poor phosphorus removal. Therefore, a flux composition consisting of 54% BaO, 21% BaF_2 and 10% MnO was selected for conducting subsequent tests to study the effect of other parameters.

Fig-1: Variation of degree of dephosphorization & %Mn loss with Addition of % MnO in flux
[Precision in the range of 0.04 to 0.4%]

b). **Quantity of flux:** The effect of change in flux weight on degree of dephosphorization is shown in Table 2.

Table2: Effect of quantity of flux on degree of dephosphorization

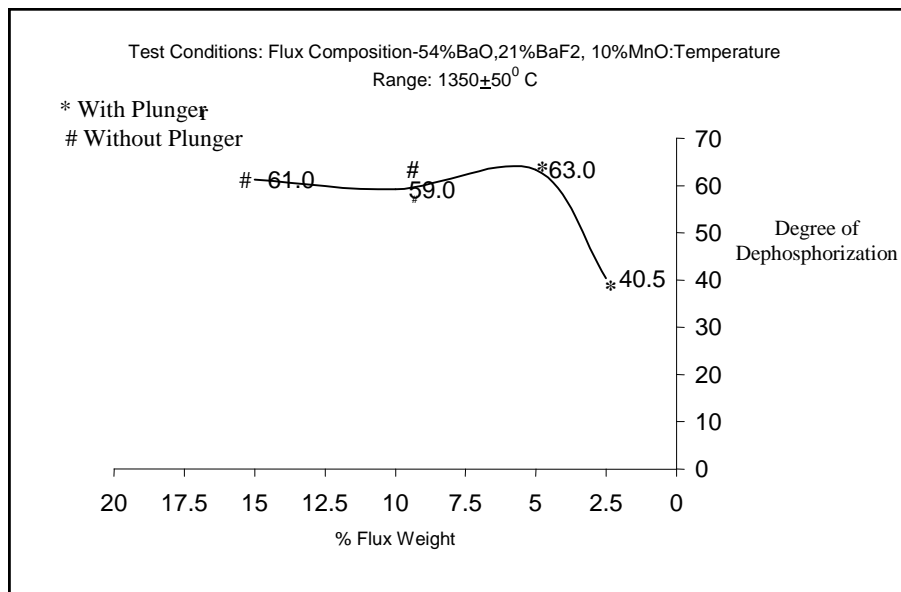| Test No.	Temp ^{0}C	Flux (%) Composition			$\eta = \dfrac{P_f - P_i}{P_i} X100$ (Dephos.Degree)	Mn Loss
		BaO 55	BaF$_2$ 21	MnO 10		
		Flux	Weight	(%)	(%)	(%)
T3	1350	10			59.0	2.0
T5	1312	15			61.0	2.0
T7	1400	5			63.0	3.5
T9	1292	2.5			40.5	2.0

Test Nos T5 to T9 were carried out to study the effect of change in flux quantity on the degree of dephosphorization. The flux weight was varied from 15% to 2.5% of the alloy weight in order to optimize the flux consumption without affecting the degree of dephosphorization. To increase the extent of phosphorus removal, the flux weight was first increased from 10% (Test No T3) to 15% (Test NoT5), but there was no significant improvement in the phosphorus removal. At this point it was decided to use a plunger for increasing the efficacy of flux used, which may decrease the flux consumption. Accordingly, for Test No T7 the flux quantity was reduced to 5% while using the improved mode of addition of flux. It was possible to hold the flux for 2-3 minutes at the bottom of crucible with the help of the plunger. The result showed a 63.0% phosphorus removal, but with a manganese loss of 3.5% (Table2). This higher manganese loss was apparently due to an incomplete calcination of BaCO$_3$ based green pellets. The XRD analysis of calcined pellets has confirmed the presence of BaCO$_3$ along with BaO, MnO and BaF$_2$ (Table3). Due to the presence of BaCO$_3$, the oxygen potential of the bath appears to be have gone up beyond the desirable range and may be responsible for higher manganese loss. In the next test (Test No T9), the flux consumption was further reduced to 2.5% using the same mode of addition (Fig2); however only 40.0% phosphorus was removed, indicating that 5% BaO–based flux is perhaps the optimum weight for more than 60% phosphorus removal.

Table3: XRD analysis represents the likely phases present in calcined pellets

No.	Angle	Counts	D$_{space}$	Rel I	Phases Present
2	25.08	313	4.12	35	MnO
3	27.83	841	3.719	93	BaCO$_3$, MnO$_2$
4	28.32	570	3.656	63	BaCO$_3$
5	30.20	473	3.434	52	BaCO$_4$
7	32.34	903	3.212	100	BaO
8	33.58	330	3.097	37	BaCO$_3$, BaCO$_4$, BaO
9	34.58	316	3.01	35	BaCO$_3$
10	35.92	294	2.901	32	BaCO$_4$
11	36.82	293	2.832	32	BaO
12	38.00	232	2.747	26	BaO
15	40.44	342	2.588	38	MnO, BaO
16	44.42	212	2.366	23	MnO
19	47.54	207	2.219	23	BaF$_2$, MnO
21	49.98	306	2.117	34	MnO$_2$
23	51.80	313	2.048	35	MnO
24	52.68	322	2.016	36	BaF$_2$
26	54.96	417	1.938	46	BaF$_2$, BaO
27	57.56	216	1.858	24	BaF$_2$
29	63.46	175	1.701	19	BaF$_2$
32	66.60	182	1.629	20	MnO
41	86.26	138	1.308	15	MnO, BaF$_2$
42	87.50	146	1.294	16	MnO

Fig-2: Variation of flux weight on degree of dephosphorization

[Precision in the range of 0.1 to 0.4%]

Test Conditions: Flux Composition-54%BaO,21%BaF2, 10%MnO:Temperature Range: 1350$\pm$50^0 C

* With Plunger
\# Without Plunger

This investigation showed that with the use of plunger for addition of flux, it is possible to achieve similar results with 5% flux weight compared to 16% used earlier [6].

  c). **Effect of temperature**: The effect of temperature on degree of dephosphorization and % manganese loss is shown in Table4.

Table4: Effect of change of temperature on degree of dephosphorization and manganese loss

Test No.	Temp ^{0}C	$\eta = \dfrac{P_f - P_i}{P_i} X100$ (Dephos.Degree) (%)	Mn Loss (%)
T5	1312	61.0	2.0
T8	1350	53.0	2.0
T7	1400	63.0	3.5
T6	1450	-	Nil
T10	1560	20.5	-

On the basis of results obtained at different temperatures, it appears that the degree of dephosphorization appears to reach a maximum at about 1400^{0}C (Test No T7) (Fig3). This may be due to the fact that while oxygen partial pressure at slag/metal interface (for a fixed slag composition) increases with temperature and the phosphate capacity of flux decreases with increasing temperature. The result obtained at 1560^{0}C (only 20.5% phosphorus removal) is expected in view of a lower value of K at higher temperature (1560^{0}C) as per the Eq No (1). Table No 4 also shows the effect of change in temperature on Mn loss. The Mn loss was 2-3% when temperature was below 1400^{0}C and was reduced to almost nil when the temperature was increased to 1450^{0}C. This is expected because the oxidation of Mn is a highly exothermic reaction [11]. However, precise control of temperature was difficult for the tests carried out in the induction furnace.

[Precision in the range of 0.1 to 0.4%]

Test Condition: Calcined Pellets of Composition
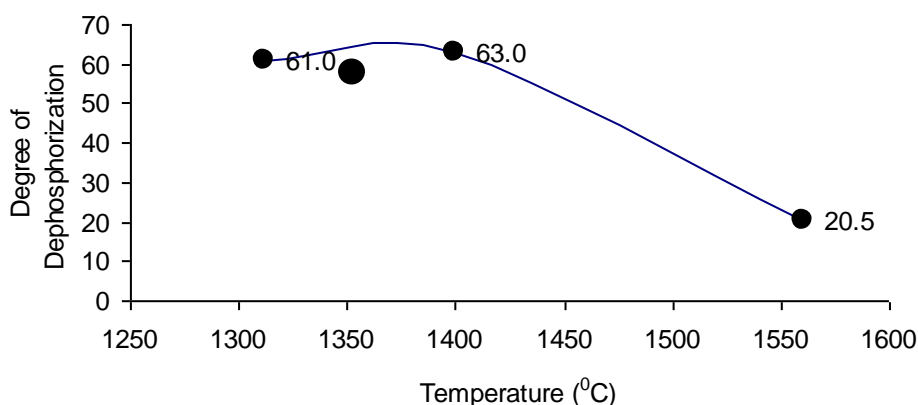$54\%BaO, 21\%BaF_2, 10\%MnO$

Fig-3: Variation of temperature on degree of dephosphorization

d). **Effect of residence time**: It was observed that lower temperatures required longer residence time for the pellets in the melt for better phosphorus removal. Samples collected after 10-15 minutes of the addition of the flux have shown adequate phosphorus distribution ratio in the temperature range of 1350^0C to 1450^0C. It was also observed that at temperatures in the range of 1450^0C to 1550^0C, the phosphorus distribution approached a stable value within 10 minutes and after that there was no significant change in the phosphorus removal.

5. CONCLUSIONS

1) A process has been developed at laboratory scale, which shows that more than 60% removal of phosphorus selectively from high carbon ferromanganese melts with the use of a BaO-MnO-BaF_2 flux.
2) An amount of 10% MnO was found to be suitable for melting the flux at moderate temperatures ($1300-1400^0C$) and removal of phosphorus.
3) The process restricts the manganese loss to less than 2%.
4) The drop in temperature of liquid ferromanganese after the addition of BaO-based flux was not significant. Therefore, it may be possible to use these flux pellets for treatment of liquid metal in the ladle after the metal is tapped.
5) A plunging system improved the efficacy of added flux. This helped in optimizing the flux consumption to 5%.

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