DEVELOPMENT OF A PROCESS FOR DEPHOSPHORISATION OF HIGH CARBON FERROMANGANESE

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ABSTRACT

The bulk of high carbon ferromanganese produced in India continue to have more than 0.35% phosphorus since they are produced by carbothermic reduction process. The low phosphorus manganese ores are depleting fast and ferromanganese manufacturers will have no option but to use medium and low grade ores having high phosphorus content resulting in high phosphorus in the product. A systematic study was taken up at NML to solve this problem. Initially, a thermodynamic analysis was carried out for which Ba-P-O ternary predominance diagrams were constructed at several temperatures to predict the most suitable conditions for selective removal of phosphorus from high carbon ferromanganese. These conditions required a usage of a flux having a high level of basicity, moderate oxygen potential as well as low melting temperature. The experimental results showed that it was possible to remove phosphorus from high carbon liquid ferromanganese 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 subsequent study carried out at the laboratory scale 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 was felt that the handling of pellets under plant conditions would be easier and also eliminate the loss of flux as a dust, which occurs when powder is added. These pellets were forced towards the bottom of the melt for better efficiency. For this purpose, a plunging system was designed and fabricated in-house that helped in reducing the flux consumption to less than 5% and also improved the kinetics of the process. The desired results were achieved within 10 minutes of the addition of the flux. The know-how is ready for transfer to interested parties and authors are willing to conduct large scale trials with them.*

1. INTRODUCTION

Amongst the ferroalloys produced in India, ferromanganese constitutes almost half of the total production because of its extensive use in iron and steel industry [1]. Ferromanganese is used as deoxidizing and alloying agent in steel making but is one of the main sources of phosphorus contamination of steel. The detrimental effect of phosphorus on the mechanical properties of steel is well known [2,3]. The high phosphorus content (0.35-0.50%) of high carbon ferromanganese originates from the manganese ores, majority of which contain significant amount (~0.2%) of phosphorus which is reduced almost completely during smelting reduction from its oxides. In India, low phosphorus ores are depleting fast and the high carbon ferromanganese produced will continue to have phosphorus content more than 0.4%. Situation is no better in other parts of the globe. Research and development work to reduce the phosphorus content in the ferromanganese to desired levels (<0.20%) has been going on at several well established R&D centers [4-13] but there is no economically viable process to be used by the ferromanganese industry.

Several methods for dephosphorization could be possible theoretically, as mentioned below. Phosphorus removal by mineral beneficiation techniques was found not suitable since phosphorus is intimately associated with manganese [12,13]. Gaseous dephosphorization is not suitable because the partial pressure of manganese is higher than that of phosphorus at smelting temperatures. The reaction product of dephosphorization under reducing conditions is phosphide, which produces toxic phosphene in contact with moisture [5,8]. Therefore, all the methods mentioned above suffer from serious practical limitations.

In view of the difficulties associated with various routes as discussed above, the oxidizing conditions were considered as favorable choice for removal of phosphorus provided the Mn loss is prevented from high carbon liquid ferromanganese. Amongst the various reagent systems reported in the literature, the BaO based reagents were considered most effective because of their high phosphate capacity [5]. The dephosphorization reaction under oxidizing conditions using BaO based fluxes may be represented as follows:

$$\frac{3}{2}BaO(s)+P(1\%Sol^{n})+\frac{5}{2}MnO(l)=\frac{5}{2}Mn(l)+Ba_{3/2}PO_4(s) \qquad (1)$$

$$\Delta G^{\circ}=-136713+89.3T J/mol \quad [9]$$

A systematic study was taken up by NML to remove phosphorus from high carbon ferromanganese using $BaCO_3$ based fluxes [13-17]. Initially, a thermodynamic analysis using predominance area diagrams was carried out to identify the suitable conditions for selective removal of phosphorus from high carbon liquid ferromanganese

The activities of Mn, MnO and $Ba_3\ (PO_4)_2$ were calculated as 0.3, 0.5 and 0.1 for effective dephosphorization ([P]<0.2%) at 1573 K. This requires the oxygen partial pressure PO_2 to be below $3.0\ X10^{-17}$ atm as indicated by the hatched area in Figure.1.Experimental conditions were selected to achieve the desired values of activities. A graphite crucible was used to obtain a_{Mn}=0.3, as reported in the literature [18], the $BaCO_3$ based flux having a high phosphate capacity of the order of 10^{29} was selected to achieve a $_{Ba3\ (PO4)2}$ = 0.1 and the composition of the slag selected in such a way to obtain $a_{Mn}O$ >0.5 [19].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% [15,17]. Also the time taken to reach desired value of phosphorus was more than 15 minutes, which was not feasible to implement in the industry.

The main drawback of the above 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. In a recent study Liu et al.[10] also successfully melted BaO-based flux and were able to remove phosphorus to required level, but the time required to achieve this value was more than 30 minutes in a stagnant melt. Hence, another aim of this study was to reduce the time of reaction to a practical level for industrial application. For this purpose, a plunging system was designed and fabricated in-house that improved the kinetics of the process.

2. EXPERIMENTAL DETAILS

On the basis of results obtained in a previous study [17] 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 1050-11000C 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 ($1300\text{-}15000^{0}$C) under oxidizing conditions using calcined flux pellets. The following parameters were varied to study their effect on the degree of dephosphorization:

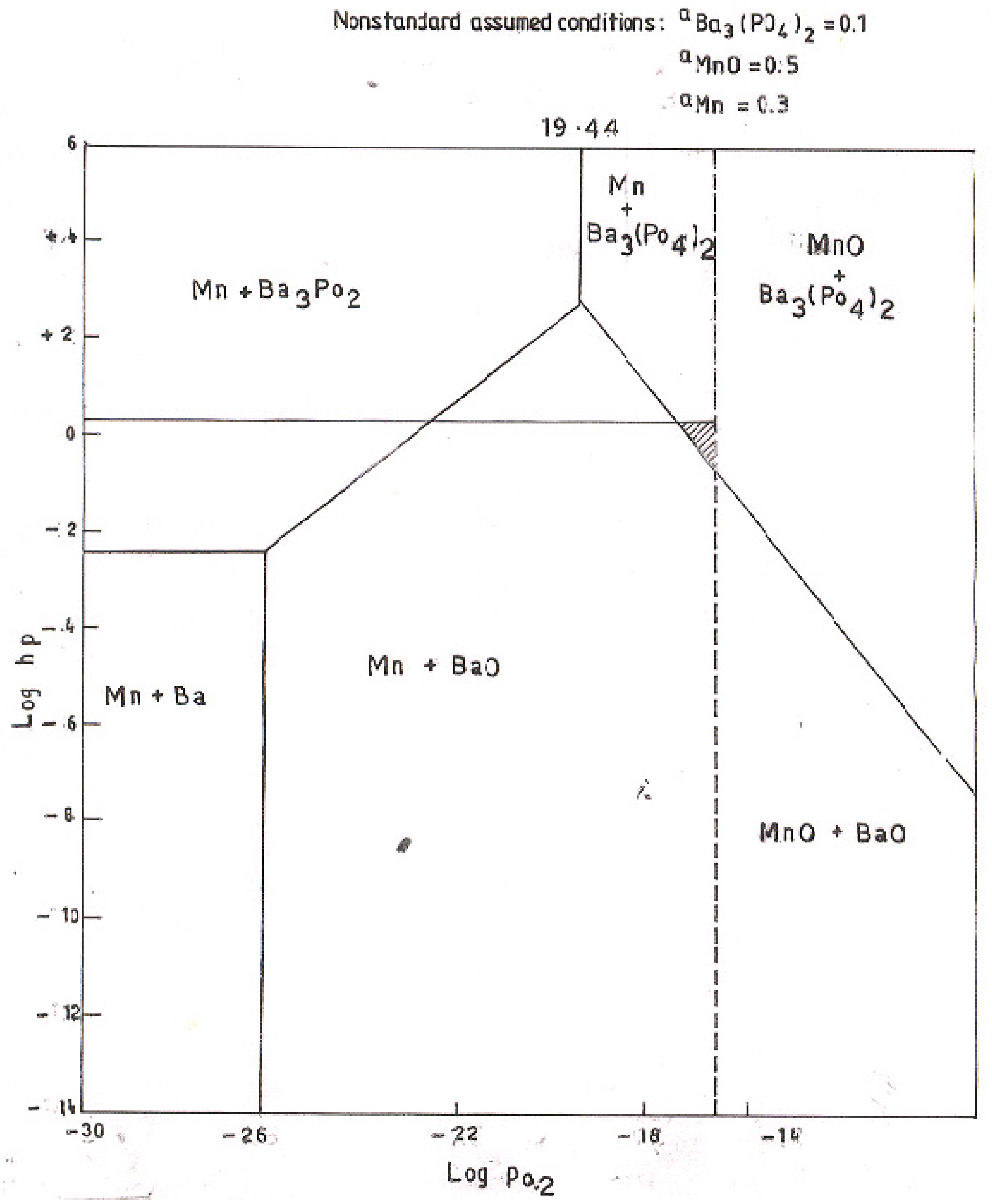

Figure 1: Predominance area diagram for Ba-P-O and Mn-O system at 1573K

1. Type of flux
2. Quantity of flux,
3. Effect of temperature and
4. The mode of addition.
5. Time

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.

3. RESULTS AND DISCUSSION

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

3.1 Type of Flux

The effect of change in composition on the extent of dephosphorization is shown in Table1.

Table 1: Effect of change in flux composition on degree of dephosphorisaton

Test No.	Temp ^{0}C	Flux Wt. (10%wt) Flux Composition* (%)			Deg. of dephosphorization $\eta = \frac{P_f - P_i}{P_i} X100$	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

Basis of flux composition calculation:

1. Reagent grade $BaCO_3$ & commercial grade BaF_2 were used for tests.
2. Percentage of different constituents has been calculated with respect to other impurity constituents present in $BaCO_3$ & BaF_2
3. % 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 1350-13670^{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 [20]. 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,

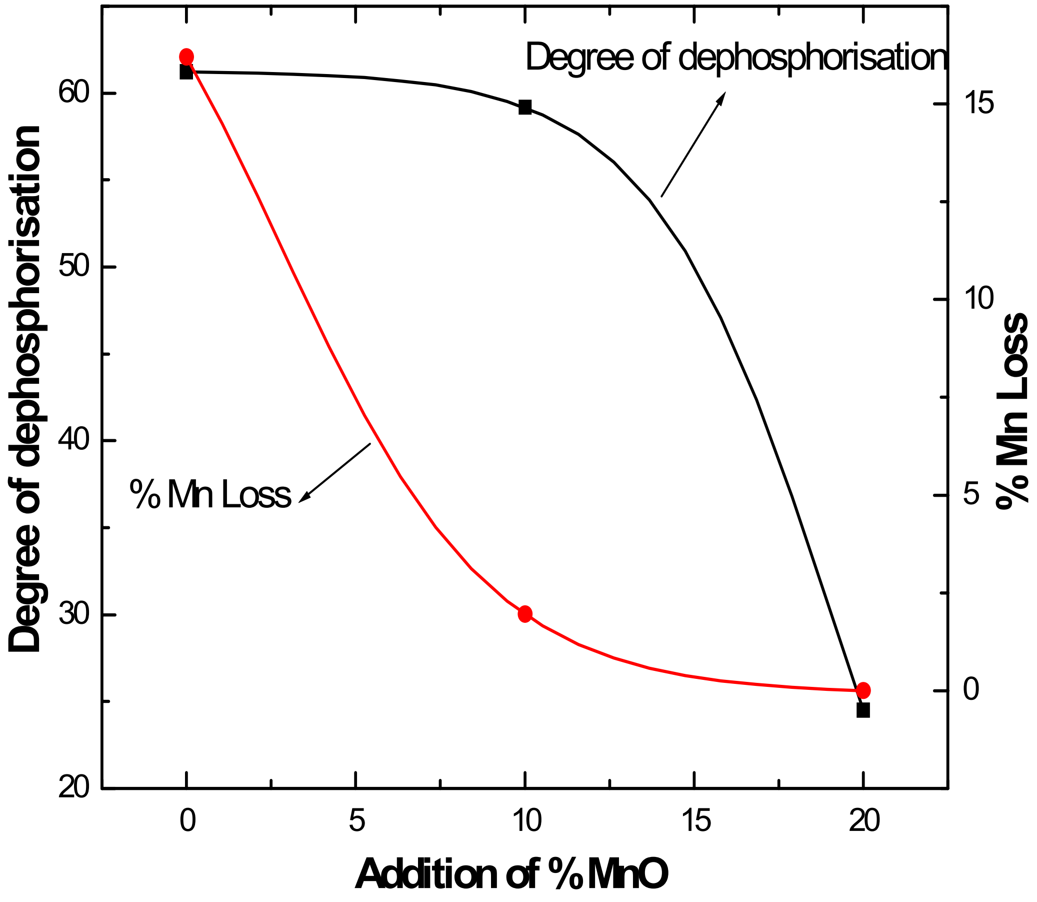

Figure 2: Variation of degree of dephosphorization & %Mn loss with Addition of % MnO in flux [Precision in the range of 0.04 to 0.4%]

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 13500^{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-2). 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.

3.2 Quantity of flux

The effect of change in flux weight on degree of dephosphorization is shown in Table 2.

Table 2: Effect of quantity of flux on degree of dephosphorization

Test No.	Temp ^{0}C	Flux Composition (%)			$\eta = \frac{P_f - P_i}{P_i} X100$ **(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 was carried out to study the effect of change in flux quantity on thedegree 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 [20].

3.3 Mode of addition

Test No T7 was carried out with 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). The flux quantity was reduced to 5% This higher manganese loss was apparently due to an incomplete calcination of $BaCO_3$ based green pellets

This investigation has 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 [17]. The stable value was obtained within 10

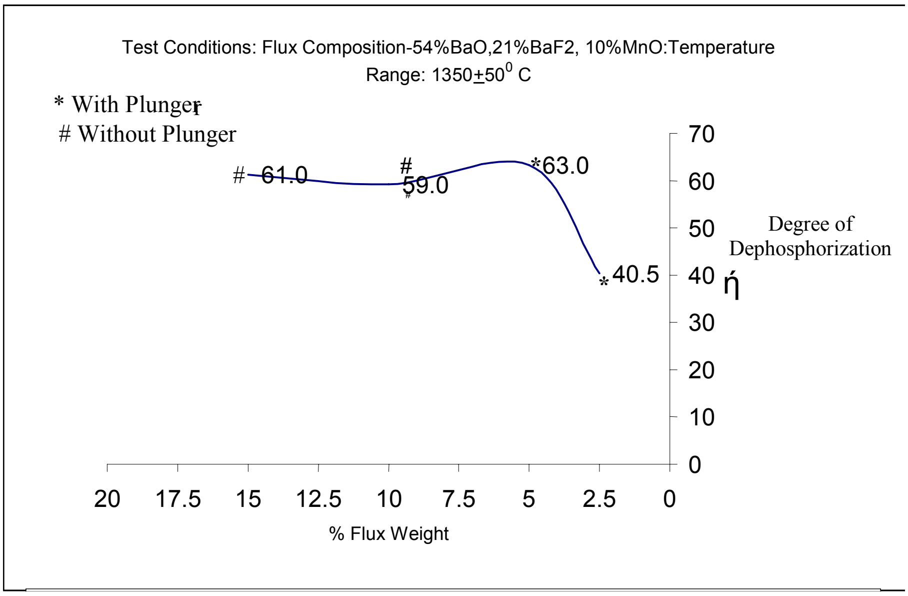

Figure3: Variation of flux weight on degree of dephosphorization [Precision in the range of 0.1 to 0.4%]

minutes of addition of flux. In a study carried out earlier the kinetic model predicted that it could be possible to remove almost 80% phosphorus at about 5 minutes of flux injection in the melt [21].

3.4 Effect of Temperature

The effect of temperature on degree of dephosphorization and % manganese loss is shown in Table4.

Table 4: Effect of change of temperature on degree of dephosphorization and manganese loss

Test No.	Temp ^{0}C	$\eta = \frac{P_f - P_i}{P_i} X100$ **(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) (Fig4). 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

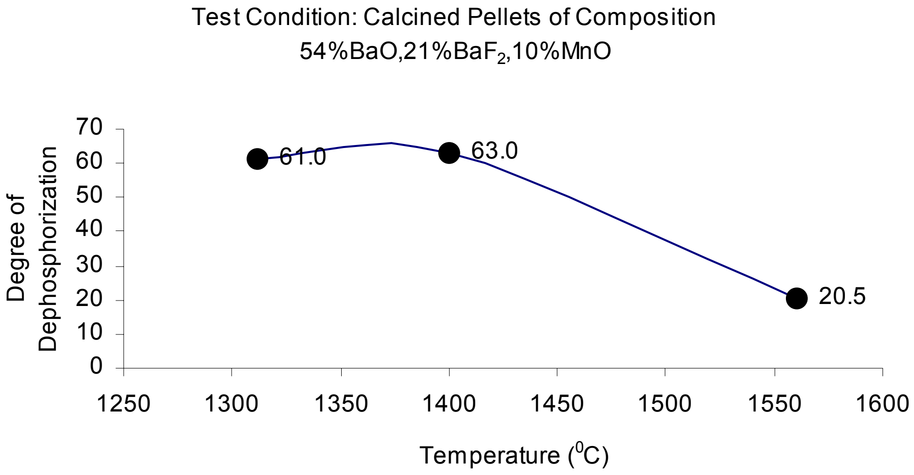

Figure 4: Variation of temperature on degree of dephosphorization [Precision in the range of 0.1 to 0.4%]

temperature was below 1400^0C and was reduced to almost nil when the temperature was increased to 1450^0C. This is expected because the oxidation of Mn is a highly exothermic reaction [16]. However, precise control of temperature was difficult for the tests carried out in the induction furnace.

3.5 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.

4. CONCLUSIONS

- 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.
- An amount of 10% MnO was found to be suitable for melting the flux at moderate temperatures (1300-1400^0C) and removal of phosphorus.
- The process restricts the manganese loss to less than 2%.
- 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.
- A plunging system improved the efficacy of added flux. This helped in optimizing the flux consumption to 5%.

5. ACKNOWLEDGEMENT

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