Effect of partially reduced highly fluxed DRI pellets on impurities removal during steelmaking using a laboratory scale EAF

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Abstract

The present work represents a comparative study on the impurities removal from pig iron melt by addition of partially reduced highly fluxed direct reduced iron (DRI) to make steel in a 2 kg capacity electric arc furnace (EAF). Three types of fluxed DRI (30, 50, 80% Reduction (%R) with similar basicity-8) were used to maintain different level of oxidizing potential on the bath for studying the kinetic behaviour of impurities removal from melt. Results showed that the rate of removal of impurities (i.e. C, Si, Mn, P, S etc.) was increased initially up to 5 minutes of reaction time then decreased afterwards. Phosphorus (~64%), sulfur (~16%) and carbon (~94%) were removed simultaneously up to 25 minutes of reaction time using 30%R fluxed DRI. Similarly, phosphorus (~33%), sulfur (~50%) and carbon (~62%) were removed simultaneously using 50%R fluxed DRI while highly reduced (80%R) flux DRI removed sulfur (~58%), carbon (~56%) with a small fraction of phosphorus (~18%) from pig iron. It was observed in all the cases that silicon (>99%) and manganese (>80%) were removed. From the present study, it can be concluded that ~30%R DRI is favorable for effective phosphorus removal whereas ~80%R is favorable for sulfur removal. The significant removal of impurities could be achieved by charging ~50%R fluxed DRI in the pig iron melt.

Key Words: Fluxed DRI; Electric arc furnace; Desulphurization; Dephosphorization; Decarburization; kinetics of Steelmaking.

Introduction

The novel metallurgy of iron and steel is promising towards quality improvement, effectiveness and competitiveness of its production. The goal of all the steelmakers is to increase the yield with lining life of vessels at lower cost. Temperature control, hot metal to scrap ratio and enriched chemistry of feed were the main factors to improve the modern steelmaking. Worldwide extensive studies are in progress to produce hot metal outside the blast furnace or smelting reduction of iron ore. Smelting reduction process is economically feasible compare to blast furnace with the possibility of utilization of iron ore fines in the form of agglomerates [1]. In recent years, steelmaking processes are slowly shifting from BF (blast furnace) – BOF (basic oxygen furnace) to DRI (direct reduced iron) – EAF (electric arc furnace) route due to the involvement of enormous

investment, cost and scarcity of coke used in the blast furnace in India. In India, 53% of steel is produced by Electric route while 47% produced by oxygen route; that's why DRI-EAF route become an essential point of study in the Indian steel-making scenario [2–4]. Now, DRI became the main source of iron feedstock for steelmaking industries due to its inherent chemical and physical properties like virgin nature, low sulphur content, uniformity of composition, easy transport & handling, uniform density & shape [5–8]. Most of these DRI are used as a replacement of iron ore lump only but not as a blend of lime and iron oxide. A mixture of iron ore fines and lime powder in pre-fused condition (sinter/pellet) would be a better flux from dissolution (lower melting constituent) and refining point of view [6]. The scenario of DRI production has significantly changed in the last 50years. DRI production in the world increased from 0.8 million tons in 1970 to 99 million tons/year in 2018. India is the largest producer of DRI with 30 million ton production out of 99 million ton in the world [2]. In recent years, various advancements have adopted in DRI-based steelmaking technology. Charging of hot DRI (pellets or briquettes) in EAF saved the sensible heat of the DRI and reduce the energy consumption [9]. The massive generation of iron ore fines (~60%) and lime fine (~50%) during their mining and beneficiation process simultaneously increasing-price and demand of scrap encourage the production of fluxed DRI in India [10–13]. The removal of phosphorus and sulfur from the melt depends on the slag basicity, its oxygen potentiality and bath temperature [14–16]. Lime (CaO) is an essential ingredient for steelmaking. Lime can work as a fluxing agent during steelmaking as well as a binder in pellets making [17]. In earlier days, lime was charged in the form of lump as limestone ($CaCO_3$). Lump form consumed a lot of heat energy from the liquid metal during its dissociation, which resulted to decrease the temperature of bath [15,18]. To overcome this problem, charging as burnt lime in the form of powder/lump has been started [19]. The powder charging practice creates many environmental challenges like the generation of fumes which is hazardous for health and also a considerable amount of lime is lost through the exit off-gasses. Lime could not be used directly in the pure form due to its high melting point ~2973K (2700°C). Addition of iron ore with lime is done to reduce the melting point of pure lime up to 1503K (1230°C) [18]. Steelmaking process involves the oxidation of impurity elements therefore the activity of oxygen in the metal and activity of FeO in the slag are major factors which controls these oxidation reactions; hence, in process metallurgy elucidation of the governing parameters is essential [10]. Refining slag, oxidation potential still attract more and more interest of researchers and producers as well [16]. The use of DRI decreases the level of phosphorus, sulfur and other impurities in liquid melt by dissolution technique [20]. At the same time, the addition of lime in DRI works as flux and favors the higher removal of impurities from the melt in the slag form. Partially prefused synthetic flux (PSF) was used to remove the impurities from the melt in basic oxygen furnace (BOF). PSF dissolve very fast and enhance the rate of removal of carbon and phosphorous from the melt [21]. Partial replacement of scrap with DRI was studied in Induction furnace. Such type of steel can be produced with low amount of sulphur as well tramp elements.[8] Compare to the other source DRI provides clean bath to the steelmakers. Continuous charging of DRI can minimize the time and energy of the process.[22]

The present work experimentally measures the removal of impurities from the pig iron melt by addition of highly fluxed DRI which has different percentage of reduction during melting in electric arc furnace. Activity of FeO in slag was varied with the addition of differently reduced fluxed DRI which influenced the oxidation potential of bath during steelmaking. In this study an effort was made to establish a correlation ship between removal of impurities and amount of oxygen content as oxides of iron (FeO) in fluxed DRI.

2. Experimental

2.1. Raw materials and their preparation

Raw materials used in the present study are pig iron, lime powder and highly fluxed DRI. Green fluxed pellets having ~18 mm diameter were prepared by mixing 20% lime in iron ore fines with the addition of optimum moisture content. Use of lime was restricted to 20% as beyond this green strength of pellets decreases adversely (pellets basicity~8) [13]. Fluxed pellets were hardened at 1180˚C to achieve sufficient compressive strength [23]. For the reduction, hardened fluxed pellets were kept in the bed of coal fines in a mild steel crucible. The crucibles were kept inside the electric resistance furnace at 1000˚C for various time intervals to obtain pellets of different degree of reduction. DRI was used to observe the effect of different fractional reduction on the removal of impurities from pig iron melt during EAF melting. On the basis of results, three types of reduced flux DRI (30, 50 and 80% reduction) having same basicity (8) were selected for studying the kinetics of impurities removal from the pig iron melt by producing a different oxidizing environment in the bath. Chemical composition of iron ore, lime and DRI is shown in Table-1.

Table-1 Chemical composition of iron ore, lime and fluxed DRI (pellets)

Chemical composition of iron ore and lime (wt. %)								
Iron Ore (Dry)							Lime (Dry)	
Fe_2O_3	Al_2O_3	SiO_2	MnO	P_2O_5	SO_3	Others	CaO	LOI
92.50	3.70	2.94	0.09	0.35	0.12	0.25	95	5
Theoretically calculated Chemical composition of fluxed DRI (pellets) (wt. %)								
Reduction (%)	Fe_{Met}[a]	Fe_t[b]	Iron Oxides[c]	Al_2O_3	MnO	SiO_2	CaO	Rest
30	0.58	0.43	73.57	2.96	0.07	2.35	20	0.62
50	29.17	21.59	52.41	2.96	0.07	2.35	20	0.62
80	72.05	53.32	20.68	2.96	0.07	2.35	20	0.62
Note- **a** - *Metallization (%)*, **b**-*Fe Total*, **c** - *$Fe_2O_3+Fe_3O_4+FeO$)*								

2.2. Melting

Pig-iron melt (1.5 kg) was prepared in the electric arc furnace (capacity 2kg). Diagram of the furnace used for melting process is shown in figure-1.
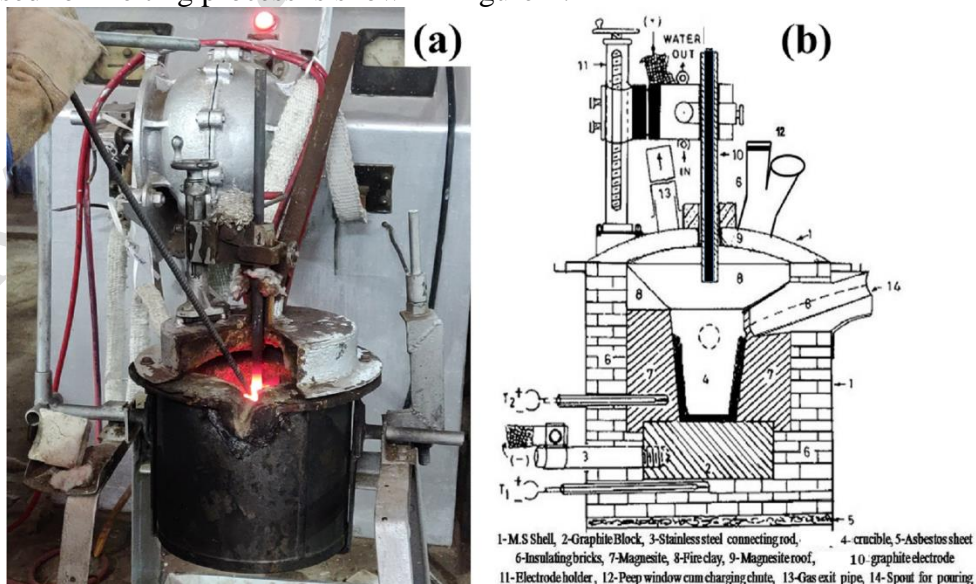

1-M.S Shell, 2-Graphite Block, 3-Stainless steel connecting rod,   4- crucible, 5-Asbestos sheet
6-Insulating bricks, 7-Magnesite, 8-Fireclay, 9-Magnesite roof,   10- graphite electrode
11-Electrode holder, 12-Peep window cum charging chute, 13-Gas exit pipe, 14-Spout for pouring

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Figure-1. Diagram of furnace used to melt the material: a) isometric diagram, b) schematic diagram of cross sectional view

Addition of reduced flux DRI (0.5 kg) in the ratio of 3:1 was used for the removal of impurities (i.e. silicon, manganese, carbon, phosphorus and sulfur) from the melt in 20 minute exposure time. Table-2 shows the details of charge mix composition used for the different heat. In all the heats, the input of CaO content (basicity) was the same. The quantity of FeO was varied inside the charge by the addition of reduced fluxed DRI (pellets) of different level reduction (12, 18, 30, 50, 58, 70 and 80%R). Oxygen potential of the pellets varies with the change in the reduction level. As the percentage reduction of DRI (pellets) increases from 12 to 80%, the value of oxygen potential decreases. Value of oxygen potential inside the melt pool affect the removal of impurities. Based on the result obtained, 30, 50 and 80% reduced flux DRI were chosen for kinetic study. For kinetic study, samples were withdrawn from the melt at regular interval of 5 minutes after complete dissolution of reduced flux DRI in the melt pool.

Table-2 Charge mix used for different heats in melting

Constituents	Heat Number		
	Heat-1 (30%R-DRI)	Heat-2 (50%R-DRI)	Heat-3 (80%R-DRI)
Pig Iron (gm)	1500	1500	1500
Fluxed DRI (gm)	500	500	500
CaO in DRI (gm)	100	100	100
Reduction (%)	30	50	80

Melting cycle used for the experiment is shown in figure-2. A similar procedure of sampling was followed in all heats.
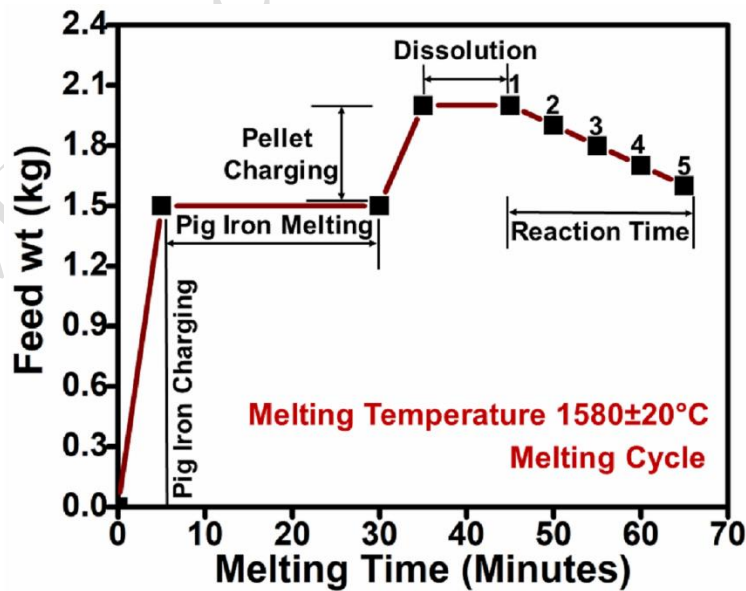

Figure-2 Melting cycle used for the experiment

After cooling, samples were prepared by cutting, grinding and polishing for their chemical analysis. Results are shown in Table-3.

Table-3 Chemical analysis of different heat products after 25 minutes reaction time

Elements	Pig Iron (wt.%)	Heat-1 (30%R-DRI)		Heat-2 (50%R-DRI)		Heat-3 (80%R-DRI)	
		Final (wt.%)	Removal (%)	Final (wt.%)	Removal (%)	Final (wt.%)	Removal (%)
C	3.83	0.23	93.99	1.45	62.14	1.66	56.66
Si	2.36	0.01	99.57	0.01	99.57	0.01	99.57
Mn	0.46	0.02	95.65	0.06	86.96	0.10	78.26
P	0.11	0.04	63.64	0.07	36.36	0.09	18.18
S	0.12	0.10	16.67	0.06	50.00	0.05	58.33

Results and Discussion

Effect of %R value of fluxed DRI on the removal of impurities

Figure-3 (a) shows the effect of fraction (%R) values of DRI on the removal of impurities from the pig iron for 20 minutes reaction time.
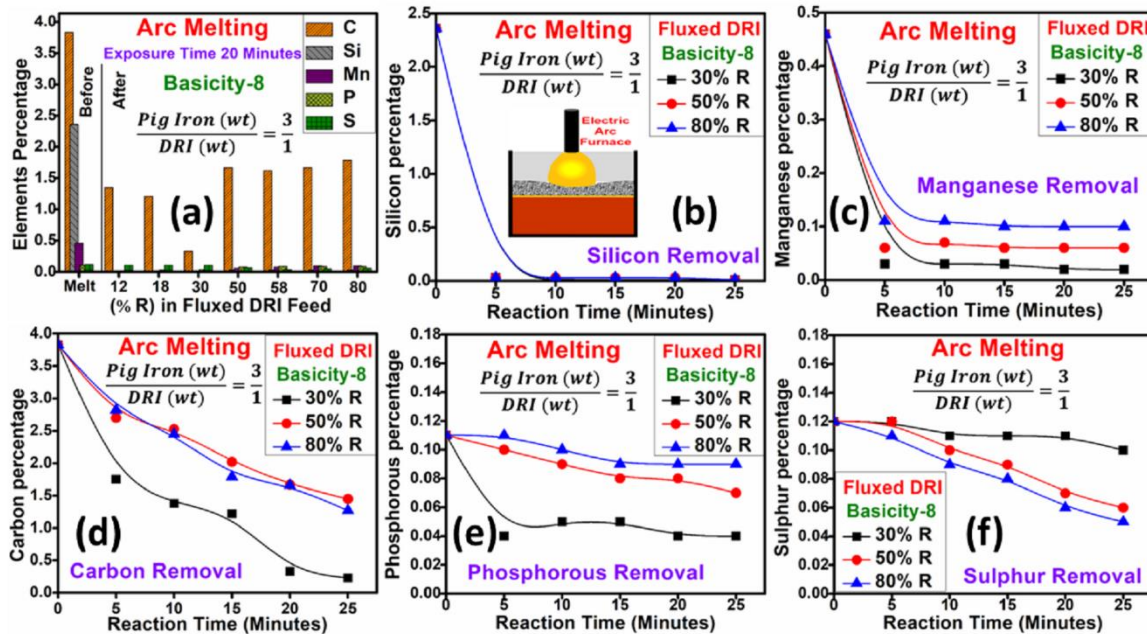

Figure-3 Behaviour of removal of impurities with reaction time under different conditions during electric arc melting a) for 20 minute exposure time b) silicon c) Manganese d) Carbon e) phosphorus f) sulphur

Chemical composition analysis of samples which were taken after 20 minutes reaction time is given in Table-4.

Table-4 Chemical analysis of different heat products using different %R value fluxed DRI

Chemical Composition after 20 minutes reaction time (wt. %)								
Elements	Pig Iron	12%R	18%R	30%R	50%R	58%R	70%R	80%R
C	3.83	1.35	1.21	0.33	1.67	1.62	1.67	1.79
Si	2.36	0.01	0.01	0.01	0.03	0.03	0.03	0.03
Mn	0.46	0.02	0.02	0.02	0.06	0.08	0.10	0.10
P	0.11	0.02	0.03	0.04	0.08	0.09	0.09	0.09
S	0.12	0.11	0.11	0.11	0.07	0.04	0.05	0.05

It is evident from the figure-3 that %R values greatly influence the removal of impurities. In the case of low reduced DRI (12 and 18 %) excess FeO containing slag formed due to that slopping occurred in laboratory scale (2kg) furnace which did not provide good and efficient results. In the case of 30%R fluxed DRI, exciting results were observed. All the impurities were removed to a significant level. Fascinating results were found on increasing the level of %R of DRI beyond 30%. On the basis of results 30, 50 and 80%R DRI were chosen to study the effect of %R value of DRI and reaction time on the removal of impurities from the pig iron melt.

Silicon removal

Removal of Si mainly takes place at the slag-metal interface as per the following reaction [21]

$[Si] + 2 (FeO) = (SiO_2) + 2[Fe]$; …… $\Delta G^0 = -501500+120.2T$ J·mol^{-1} (1)

Due to highly oxidizing nature of melting chamber, Si reacts with the oxygen which is combined with iron (iron oxide form) in the slag and enrich the melt pool with iron and transfer Si to slag vary quickly as silicon dioxide from the metal pool. [21]
$(CaO) + (SiO_2) = (CaO.SiO_2)$; …… $\Delta G^0 = -83453-3.4T$ J·mol^{-1} (2)

As the silica come into slag phase, it reacts with available lime according to the above reaction and form stable phase. From the above two reactions, it is obvious that some amount of oxygen is necessary to remove silicon. Figure-3(b) shows the removal of silicon from the pig iron melt using 30, 50 and 80% R flux DRI. The result showed %R value does not have any effect on the removal of silicon. It follows the same trends for all values of %R, it means silicon reacts first with the available oxygen and make silicon oxidize which combined with calcium oxide and goes into the slag.
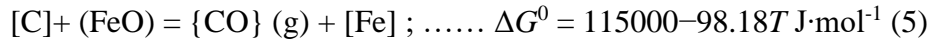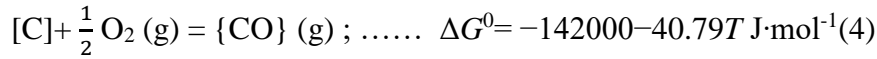
Manganese removal

Removal of Mn mainly takes place as per the following reaction [21]

$(FeO) + [Mn] = (MnO) + [Fe]$; …… $\Delta G^0 = -123516+56.40T$ J·mol^{-1} (3)
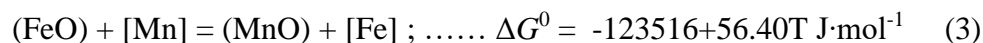
Removal of manganese is favored at low basicity and high FeO content in slag. Results of the Mn removal as a function of time under different %R values fluxed DRI are shown in Figure-3(c). It is obvious that Mn removal is higher under conditions 30%R compare to 50 and 80%R value fluxed DRI due to availability of higher value of total FeO content in slag.

Carbon removal

Removal of Carbon as a function of time under different %R value fluxed DRI materials is presented in Figure-3(d). Carbon removal mainly takes place as per the following reactions [21]

$$[C] + \frac{1}{2} O_2 \text{ (g)} = \{CO\} \text{ (g)} ; \ldots\ldots \ \Delta G^0 = -142000 - 40.79T \text{ J·mol}^{-1} \quad (4)$$

$$[C] + (FeO) = \{CO\} \text{ (g)} + [Fe] ; \ldots\ldots \ \Delta G^0 = 115000 - 98.18T \text{ J·mol}^{-1} \quad (5)$$

Equation (4) is a gas-metal reaction, where oxygen gas during blowing, directly reacts with bath carbon at high temperature. In the present work, oxygen is not supplied to the hot metal; therefore, chances of this reaction are negligible. Equation (5) is a slag-metal reaction. Here iron oxide in slag reacts with bath carbon at the slag metal interface. Reduced pellets have sufficient amount of oxygen in the form of FeO which reacts with carbon present in the molten bath and form CO which improves heat transfer, slag-metal interaction and compositional homogeneity of the bath. In the case of 30%R DRI removal of carbon is higher for any time interval compare to 50 and 80%R DRI. Carbon removal becomes almost constant after 20 minutes reaction time for 30%R DRI while for 50 and 80%R DRI feed it was continuously decreasing up to 25 minutes. Carbon content may decrease too much lower values by increasing either oxygen potential or reaction time.

Phosphorus removal

The reaction of dephosphorization is very critical in steelmaking. Removal of phosphorus takes place mainly at the slag-metal interface as per the following reaction [21]

$$2[P] + 5(FeO) + 3(CaO) = (3CaO \cdot P_2 O_5) + 5[Fe]; \ldots\ldots \ \Delta G^0 = -767\,990 + 103.2T \text{ J·mol}^{-1} \quad (6)$$

The capacity of dephosphorization depends on the thermodynamic behaviour of phosphorus, oxygen in metal and the content of P_2O_5 & FeO in the slag. These parameters change themselves with reaction time due to change in composition and temperature. Furthermore, the free energy change for the reaction (Eqn.6) indicates that dephosphorization is much favorable at a lower temperature. Thus, the conditions for good dephosphorization are high oxygen potential, high basicity and lower bath temperature. Dephosphorization as a function of time under different %R value fluxed DRI is presented in Figure-3(e). In all cases, fluxed DRI added have both iron oxide and CaO in the combined form which dissolves quickly in the metal bath and form a highly basic oxidizing slag with a low melting point. In case of 30% R value DRI, dephosphorization was significant due to presence of highly basic oxidizing bath environment. According to theoretical calculation 30%R DRI contains 94% FeO and 6% Fe_3O_4 while increasing reduction level, Fe_3O_4 phase abolished from the DRI and Fe metallic increases. 50%R DRI contain 70.83% FeO and 29.7% Fe metallic therefore oxygen potential of bath decreases with increasing metallic content, which is responsible for the low phosphorous removal compare to 30%R DRI. Dephosphorization was minimum in the case of 80%R value DRI because it contains only 29.75% FeO with 70.25% Fe. This amount of FeO consumed by the other impurities elements to form their oxides which becomes slag and creates the reducing condition in the bath. Therefore amount of oxygen, basicity and temperature should be optimum for phosphorus removal.

Sulphur removal

Removal of sulphur may take place mainly in the slag-metal interface as per the following reaction [21]

CaO + FeS = CaS + FeO; …… $\Delta G^0 = -4615 - 0.205T$ J·mol^{-1} (7)

Or

$(O^{2-}) + [S] = [O] + (S^{2-})$
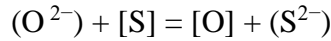
Where, the modified equilibrium constant $k_S = (W_{(S)}/W_{[S]}) \cdot W_{\sum FeO}$.

k_s = modified equilibrium constant, $W_{(S)}$ = wt of sulfur in slag phase, $W_{[S]}$ = wt of sulfur in metal phase, $W_{\sum FeO}$ = wt of FeO in slag phase

Effect of slag composition on activity coefficients of sulfur and iron oxide in the slag is that k_S decreases with decreasing basicity of the slag. Also, the value of k_S increases slightly with increasing temperature. Thus, the degree of desulphurization increases with increasing basicity, decreasing total FeO content of the slag and increasing temperature of the bath. Removal of sulphur as a function of time under different %R value fluxed DRI is presented in Figure-3(f). The percentages sulfur removal in three conditions is 16%, 50% and 58% for 30%R, 50%R and 80%R value of fluxed DRI respectively, which have been calculated from initial and final metal analysis given in Table-3. Since the slag was oxidized (94% FeO content) in case of 30%R value DRI; therefore, not much sulphur removal was observed. On increasing the %R value of DRI, sulphur removal also increased due to the unavailability of oxygen. All the reactions took place before the sulphur removal inside the bath; therefore, oxygen supplied by iron oxide consumed by Si, Mn, C and P first to make their respective oxides. In the presence of oxidizing environment in the bath sulphur cannot be removed because as the amount of oxygen will increase the amount of FeO in the slag will increase which inhibit the removal of sulfur from metal to slag phase. Thermodynamically, other impurities except sulphur can be removed in oxidizing environment favorably. In the case of 30%R value DRI amount of oxygen was sufficient to react with impurities; that's why the bath was always oxidized. Hence, phosphorus removed effectively with a negligible amount of sulphur. In the case of 50%R value DRI the value of FeO decreases from 94% to 70.83% which is responsible for the removal of sulphur compare to 30%R DRI. In the case of 30%R DRI consumption of oxygen have taken time compare to 50%R DRI that's why after an interval of time oxygen available in the bath consumed by impurities in the case of 50%R DRI and bath become reducing/neutral and favors the removal of sulphur. For 80%R value DRI oxygen amount was very least which was consumed by the Si, Mn and C consequently it created a reducing environment with basic slag which favor the effective removal of sulphur with a negligible amount of phosphorus. Thus, the use of the highly fluxed DRI has the potential to replace the charging of the iron ore and lump lime in EAF and enhance smooth refining process without creating the problem of foaming.

The use of fluxed DRI in electric arc furnace resulted high degree impurity removal (C-94%, Si-99%, Mn-96%, P-64% and S-16%) resulting in the preparation of steel with very low metalloid content (C-0.23%, Si-0.01%, Mn-0.02%, P-0.04% and S-0.10%). Such melt could be used for preparing specific grade i.e. AISI 1132, AISI 1137, AISI 1140 and AISI 1141 alloy steel by adjusting composition as per specification given in Table-5 with the help of ferro-alloy addition.

Table-5 Comparative study of the present work product and established alloy

Alloy	C	Si	Mn	P	S
Present Study (30%R)	*0.23*	*0.01*	*0.02*	*0.04*	*0.10*

AISI/1132	0.27-0.34	0.10	1.35-1.65	0.04	0.08-0.13
AISI/1137	0.32-0.39	0.10	1.35-1.65	0.04	0.08-0.13
AISI/1140	0.37-0.44	0.10	0.7-1.00	0.04	0.08-0.13
AISI/1141	0.37-0.45	0.10	1.35-1.65	0.04	0.08-0.13

Effect of exposure time (reaction time) on the removal of impurities

On the behalf of result shown in figure-3(a); 30, 50 and 80%R value fluxed DRI were chosen to know the effect of reaction time on the removal of impurities (i.e. C, Si, Mn, S, P) from the pig iron. Figure-3(b) shows the removal of silicon from pig iron. It was observed from the figure that silicon removed in the first five minutes exposure time for all three heats, afterwards it becomes constant. It means silicon reacts with oxygen/iron oxide in the initial stage to make stable silicon oxide. Manganese removal follows the similar trends like silicon which shown in figure-3(c) but here %R value effect the removal. Most of the manganese removed in five minutes, afterwards it becomes constant. In the case of carbon, trends were different. From figure-3(d) it was evident, for 30%R value DRI carbon removes up to 20 minutes afterwards it becomes constant but for 50 and 80%R value DRI feed it was decreasing continuously up to 25 minutes reaction time. It may decrease to a lower extent value by increasing reaction time. Removal of phosphorus and sulphur was quite interesting. Figure-3(e) shows, phosphorus removed in early 5 minutes reaction time for 30%R value DRI due to availability of sufficient oxygen while in the case of 50 and 80%R value DRI it was continuously removing slowly up to 25 minutes reaction time due to insufficient amount of oxygen. Figure-3(f) shows, there were no significant change observed in the amount of sulphur for 30%R value DRI up to 25 minutes reaction time. Sulphur removal was seen after 5 minutes reaction time for 50%R DRI feed because up to 5 minutes amount of oxygen was available which was consumed by the Si, Mn, P and carbon. In the case of 80%R value DRI sulphur removal was observed from the starting and it was continuously removing up to 25 minutes reaction time. In this case amount of oxygen is very less compare to other two feed materials, therefore, it was consumed in the early stage of the reaction and environment become neutral that favored the removal of sulphur from the pig iron melt. Figure-3(e) & (f) showed the reverse behaviour. In the case of 30%R value DRI phosphorus removed effectively with a negligible amount of sulphur, while in the case 80%R value DRI sulphur removed effectively with a negligible amount of phosphorus. This is a clear indication of the effect of oxygen potential on the removal of sulphur and phosphorus. There is collective agreement on some aspects of dephosphorization kinetics associated with decarburization. Firstly, droplet swelling, caused by CO formation inside the droplet increases the droplet residence time in the slag. Secondly, longer residence time favors refining reactions, especially for dephosphorization which can only take place at a significant level when metal is in contact with slag. Thirdly, decarburization will suppress dephosphorization by competing for oxygen, thereby lowering the interfacial oxygen potential, which controls the driving force for dephosphorization. Finally, because of droplet swelling, the slag/metal interfacial area will change with time this must be accommodated in the rate equation.

Effect of exposure time on the rate of removal of impurities

Figure-4 shows the rate of removal of impurities from pig iron using different %R value DRI for 25 minute reaction time.
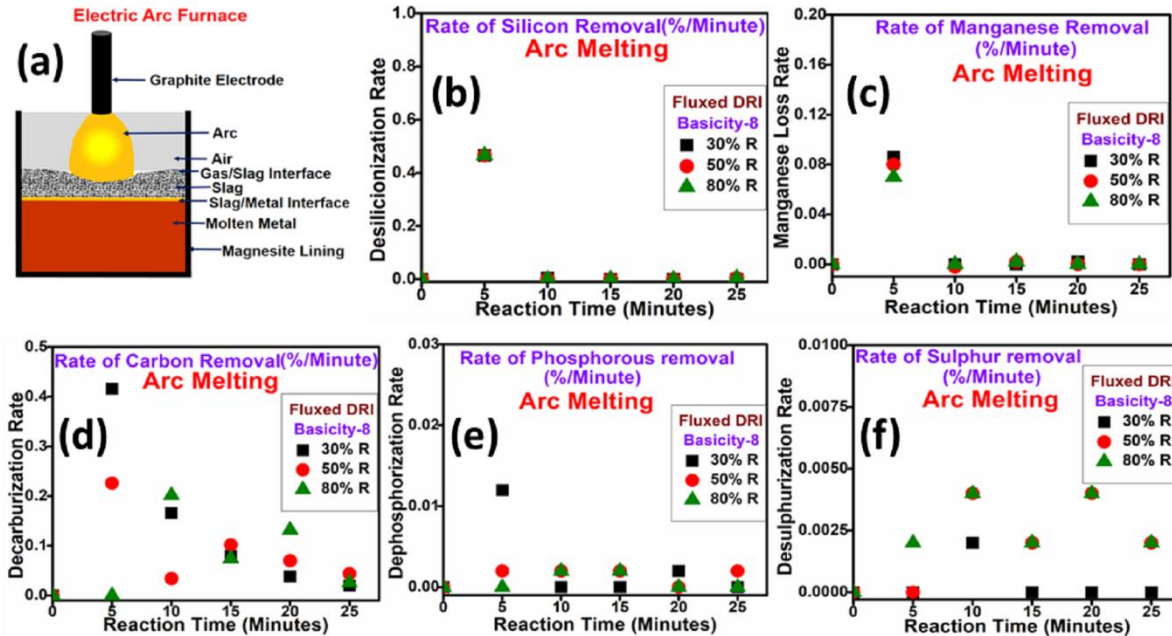
Figure-4 Rate of removal of impurities (%/minute) a) EAF b) Silicon c) Manganese d) Carbon e) phosphorus f) Sulphur

Figure-4(a) is the schematic diagram of arc and melt conditions. Figure-4(b) shows the rate of removal of silicon. From the figure, it was evident that the rate of removal increased up to 5-minute reaction afterwards it decreased. It means the maximum amount of silicon removed in five minutes. This reflects that silicon reacts instantaneously with the oxygen-rich iron phase and make stable slag phase. With increasing reaction time, the activity of silicon decreased in the metal phase with increasing activity of silica in the slag phase which is responsible for decrecement in the rate of removal after 5-minute exposure. Figure-4(c) shows the rate of removal of manganese. Rate of manganese removal follows the same trend as the rate of silicon removal. It was observed that the maximum rate obtained in five minutes afterwards it decreased. Rate of carbon removal shown in figure-4(d). Rate of carbon removal for 30 and 50%R value DRI is maximum at 5 minutes afterwards it decreased. For 80%R value DRI, rate of removal of carbon up to 5 minute is negligible, after 5 minutes it increased and go to the maximum value in 10 minute total reaction time afterwards decreased. In the case of 30 and 50%R value DRI amount of oxygen available (oxygen potential in the bath) for the reaction is high compare to 80%R value DRI. For the carbon reaction, some nucleation side is necessary; therefore, it will take a longer time in the case of high metallized feed material compare to low metallized value feed material. Again the rate of removal of phosphorus and sulphur is quite impressive. Figure-4(e) & (f) shows the rate of removal of phosphorus and sulphur, respectively. Rate of phosphorus removal was increased up to 5 minutes for 30%R value DRI afterwards decreased while for 50 and 80%R value DRI rate of phosphorus is minimal up to 5 minute reaction time. Rate of phosphorus removal start to increase after 5 minute reaction time for 50 and 80%R value DRI and increased up to 10 minute reaction time and become constant for next five minute reaction time afterwards decreased. Rate of sulphur removal is very sluggish for 30%R value DRI while for 50 and 80%R value DRI, it increased up to 10 minutes afterwards decreased.

Effect of %R value in fluxed DRI on the rate of removal of impurities

Figure-5 shows the effect of %R value of fluxed DRI on the removal of impurities from the pig iron.
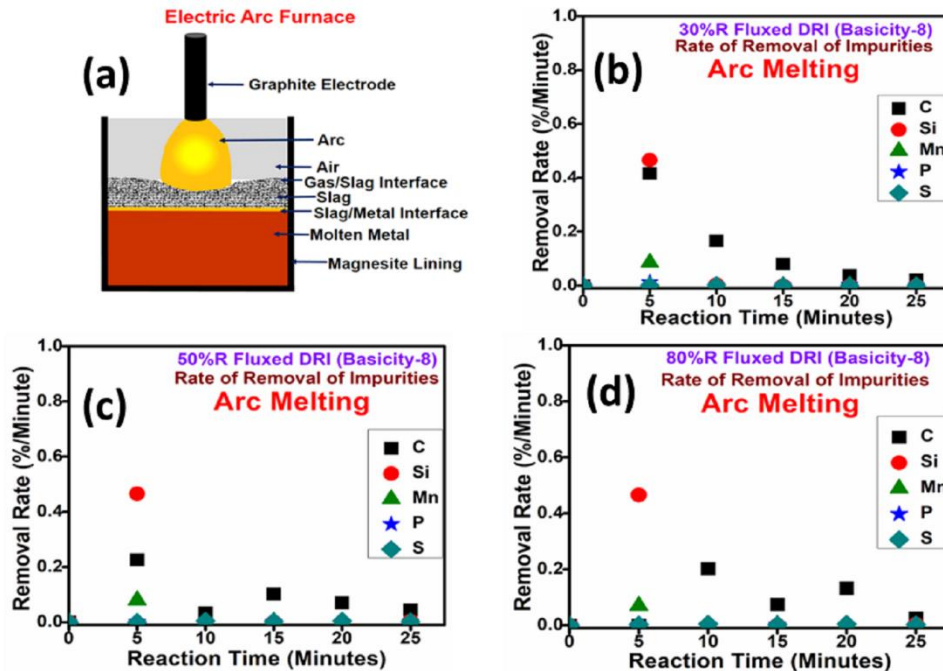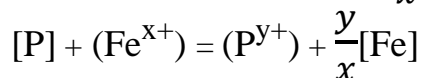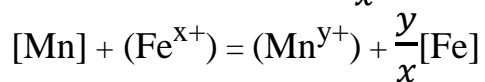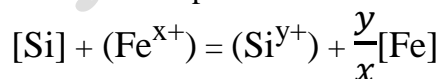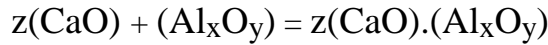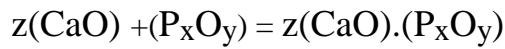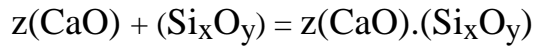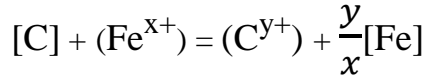

Figure-5 Rate of removal of impurities (%/minute) for different values of R fraction (%R) in fluxed DRI feed, a) EAF b) 30%R c) 50%R d) 80%R

Figure-5(b) shows the rate of removal of impurities from the pig iron using 30%R value fluxed DRI. It was evident from the figure that the rate of removal of impurities increased up to 5 minutes afterwards decreased except sulphur. Rate of sulphur removal is negligible due to oxidizing condition inside the bath. Order of the rate of removal followed as Si>C>Mn>P>S. Figure-5(c) shows the rate of removal of impurities from the pig iron using 50%R value DRI. It was evident from the figure that the order of removal here similar to the 30%R value DRI (figure 5b) but by the quantity wise, rate of removal was quite different. In this case, the amount of carbon removal decreased compare to the previous one. It may be due to decrement in oxygen content of feed material or by increment in the metallic value of fluxed DRI. Figure-4(d) shows the rate of removal of impurities for 80%R value DRI. In this case, trends in rate were quite different. Rate of silicon and manganese removal was similar to previous heats, but rate of carbon, phosphorus and sulphur was different. In the presence of silicon and manganese rate of carbon removal suppress. Due to the insufficient amount of oxygen rate of phosphorus removal was observed negligible.

Tentative Mechanism for removal of different impurities during EAF melting
Based on the above explanations, a tentative mechanism and possible reactions involved in the removal of impurities were written as below.

$$[Si] + (Fe^{x+}) = (Si^{y+}) + \frac{y}{x}[Fe]$$

$$[Mn] + (Fe^{x+}) = (Mn^{y+}) + \frac{y}{x}[Fe]$$

$$[P] + (Fe^{x+}) = (P^{y+}) + \frac{y}{x}[Fe]$$

$$[C] + (Fe^{x+}) = (C^{y+}) + \frac{y}{x}[Fe]$$

$$z(CaO) + (Si_xO_y) = z(CaO).(Si_xO_y)$$

$$z(CaO) + (P_xO_y) = z(CaO).(P_xO_y)$$

$$z(CaO) + (Al_xO_y) = z(CaO).(Al_xO_y)$$

$$[FeS]_y + (CaO)_x = Ca_xS_y + Fe_xO_y$$
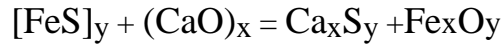
(Note: x and y are not constant. These are the oxidation state number. These are the function of temperature.)

From the previous discussion, it was very clear that silicon reacts first to form silica. Oxygen for the reaction of silicon was supplied by iron oxide. Some amount of oxygen can be achieved from the atmosphere of melting chamber of the furnace because the melting was performed in the open atmosphere. Figure-6 shows the hypothetical arrangement of the different layer/interfaces formed during the refining of pig iron in open atmosphere melting.

Lime was present as readymade slag in the form of iron silicate and calcium ferrite inside the fluxed DRI therefore, it will not take much time in the dissolution. During the dissolution, calcium will combine with silica and form a stable calcium silicate slag.
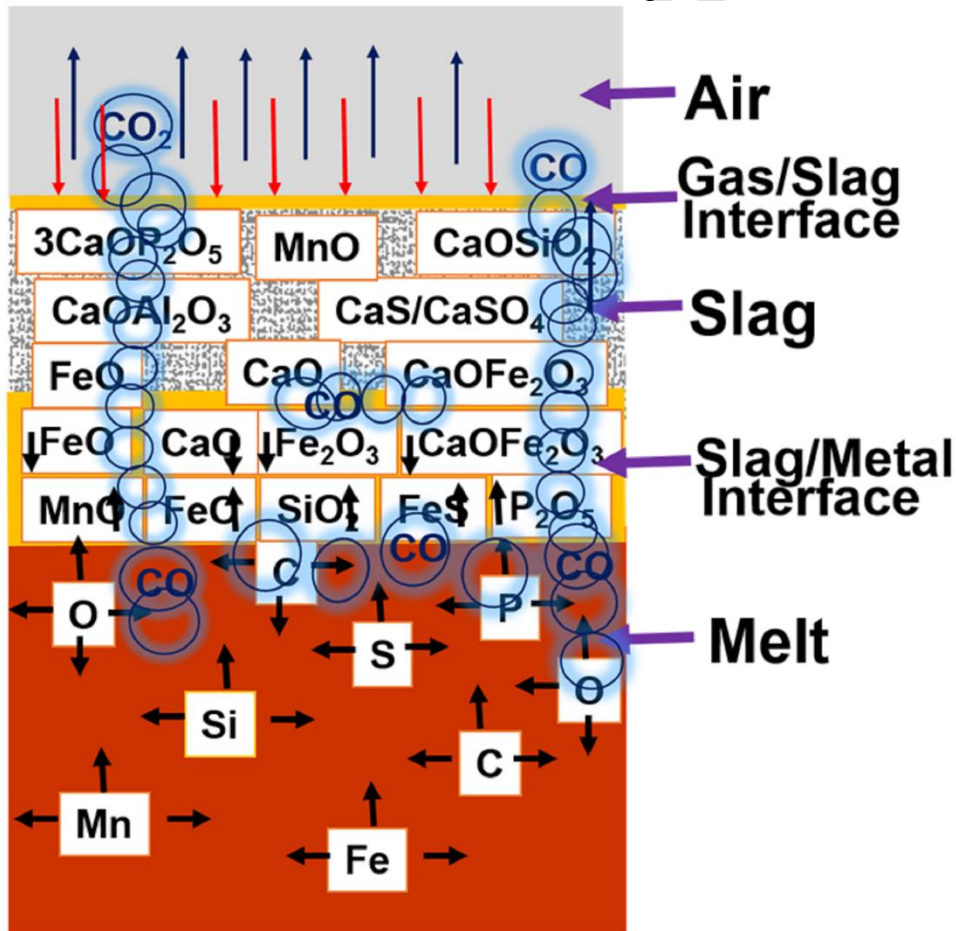

Figure-6 Schematic diagram of an arrangement of different interfaces, elements and reactions involved during removal of impurities from pig iron in an electric arc furnace

After silicon, manganese reacts with iron oxide to form manganese oxide and this combine with silica to make slag phase. Carbon reacts in some different manner. During the removal of silicon and manganese, there were some sites for CO nucleation developed in the melt because without nucleation site gas bubbles cannot be formed therefore, carbon removal started after removal of silicon and manganese. Carbon removed in the form of gas therefore, it will not join the slag phase, but due to formation of foamy slag in the presence of gases, kinetics of the removal of impurities will accelerate. Phosphorus also reacts with the oxygen of iron oxide to make its oxide. These oxides reacts with lime to make its stable slag phase. The affinity of sulphur towards iron is very high therefore, sulphur combined with iron in the melt. Iron sulphide reacts with calcium oxide to make a stable calcium sulphide slag phase.

From the above discussion, it was evident that the activity of oxygen and amount of lime play a key part in the elimination of impurities from the molten metal. In this study amount of oxygen was varied with the help of using different level of reduced flux DRI as feed material. Initially, oxygen combined with the iron as iron oxide therefore, there was no need of iron oxide formation in this process. In the oxygen steelmaking technology first oxygen reacts with iron to form iron oxide. Then this iron oxide reacts with different impurities to form their respective oxides, but in the current study, iron oxide directly supplied in the form of fluxed DRI (pellets). In this way amount of energy and reaction time can be minimized by eliminating one step during steelmaking. In steelmaking generally lime charged in the lump form that had taken time for dissolution, but in the current study lime was charged in the form of calcium ferrite [23] i.e. low melting constitute phase which will dissolve faster than lumpy lime. Therefore by charging lime in the form of fluxed DRI, dissolution time can be minimized which will again reduce the energy consumption and cost of the process.

Conclusions:

The addition of fluxed DRI (pellets) in liquid pig iron melt studies resulted as following conclusions:

- Si and Mn were removed in first 2-5 minutes followed by carbon removal. The P and S were also minimized under certain conditions.

- The rate of removal of Si and Mn were high in first 2 minutes which may be due to oxidizing slag provided by addition of fluxed DRI (pellets).

- The P removal occurred after silicon and manganese were removed, which may be due to basic oxidizing slag availability.

- The carbon removal was delayed may be due to CO gas nucleation and growth occurring on furnace walls.

- Sulphur was lowered in the melt may be due to dilution of melt by iron from fluxed DRI as well as absence of oxidizing slag.

- The quality of fluxed DRI (%R) appeared to affect significantly. Addition of fluxed DRI with lower %R rendered more oxidizing slag and promoted P removal while higher %R resulted in more S removal. 50%R DRI could be used to remove sulphur and phosphorous simultaneously up to some extent.

- Resulphurized grade steel can be directly produced by using 30%R DRI.

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Figure-1. Diagram of furnace used to melt the material: a) isometric diagram, b) schematic diagram of cross sectional view.

Figure-2. Melting cycle used for the experiment

Figure-3 Behaviour of removal of impurities with reaction time under different conditions during electric arc melting a) for 20 minute exposure time b) silicon c) Manganese d) Carbon e) phosphorus f) sulphur

Figure-4 Rate of removal of impurities (%/minute) a) EAF b) Silicon c) Manganese d) Carbon e) phosphorus f) Sulphur

Figure-5 Rate of removal of impurities (%/minute) for different values of R fraction (%R) in fluxed DRI feed, a) EAF b) 30%R c) 50%R d) 80%R

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