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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 behavior of impurities removal from melt. Results showed that the rate of removal of impurities (i.e. C, Si, Mn, P, S etc.) 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.

Keywords: *Fluxed DRI; Electric arc furnace; Desulphurization; Dephosphorization; Decarburization; Kinetics of steelmaking*

1. 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 are the main factors to improve in 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 compared 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% is produced by oxygen route; this is why DRI-EAF route is seen as an essential point of study in the Indian steel-making scenario [2–4]. Now, DRI becomes the main source of iron feedstock for steelmaking industries due to its inherent chemical and physical properties like virgin nature, low sulfur 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 50 years. 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 been adopted in the DRI-based steelmaking

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technology. Charging of hot DRI (pellets or briquettes) in EAF save 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 control these oxidation reactions; hence, a metallurgy process 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) is 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 sulfur as well tramp elements.[8] Compared 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 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 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 with ~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 would decrease adversely (pellets basicity~8) [13]. Fluxed pellets were hardened at 1180 ˚C to achieve sufficient compressive strength [22]. 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. The DRI was used to observe the effect of different fractional reduction on the removal of impurities from pig iron melt during EAF melting. Based on the results, three types of reduced flux DRI (30, 50, and 80% reduction) with 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.

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 varied with the change in the reduction level. As the percentage reduction of DRI (pellets) increased from 12 to 80%, the value of oxygen potential decreased. Value of oxygen potential inside the melt pool affected the removal of impurities. Based on the obtained result, 30, 50, and 80% reduced flux DRI were chosen for the kinetic study. For the 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.

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

After cooling, samples were prepared by cutting,

Table 2. *Charge mix used for different heats in melting25 minutes reaction time*

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

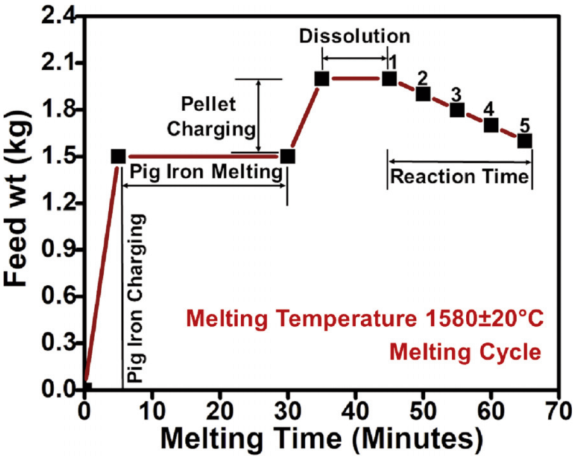

Figure 2. *Melting cycle used for the experiment*

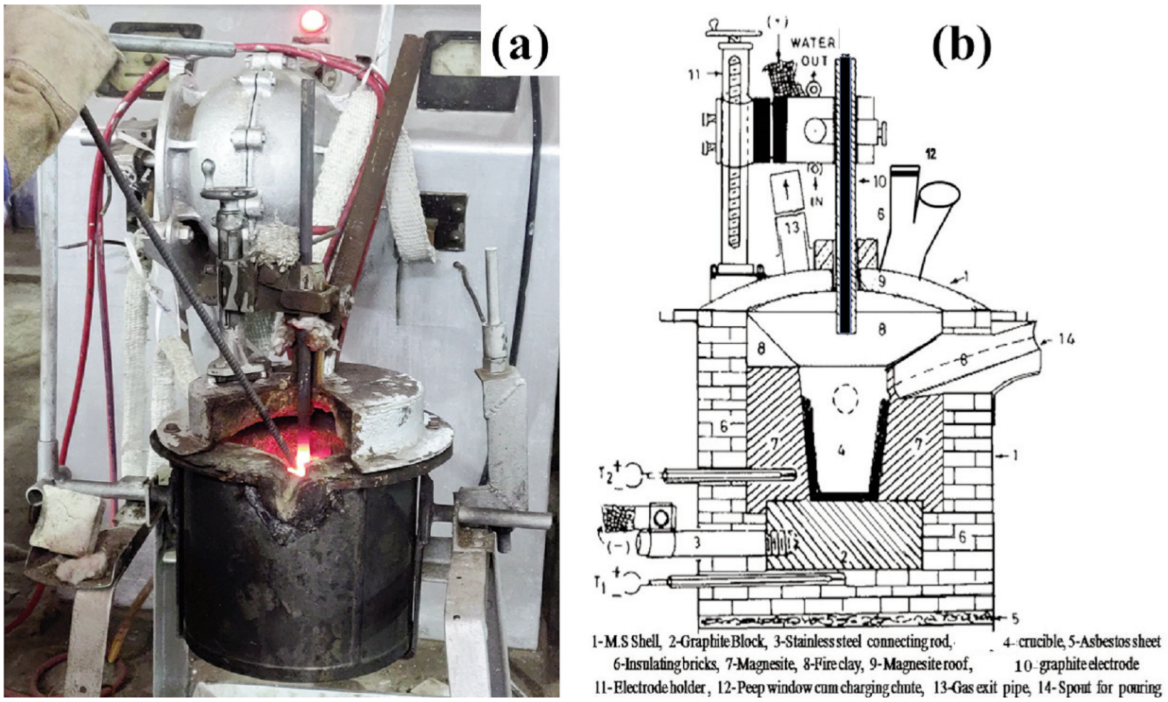

Figure 1. *Diagram of furnace used to melt the material: a) isometric diagram, b) schematic diagram of cross sectional view*

grinding, and polishing for their chemical analysis. Results are shown in Table 3.

3. Results and Discussion

3.1. 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.

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

It is evident from the Figure 3 that %R values greatly influenced the removal of impurities. In the case of low reduced DRI (12 and 18 %) excess FeO containing slag was formed due to the 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%. Based on the 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.

3.2. Silicon removal

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

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

Due to highly oxidizing nature of melting chamber, Si reacted with the oxygen, which was combined with iron (iron oxide form) in the slag, and enriched the melt pool with iron and transfer Si to slag varied quickly as silicon dioxide from the metal pool [21].

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

Elements	Pig Iron	Heat-1 (30%R-DRI)		Heat-2 (50%R-DRI)		Heat-3 (80%R-DRI)	
	(wt.%)	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

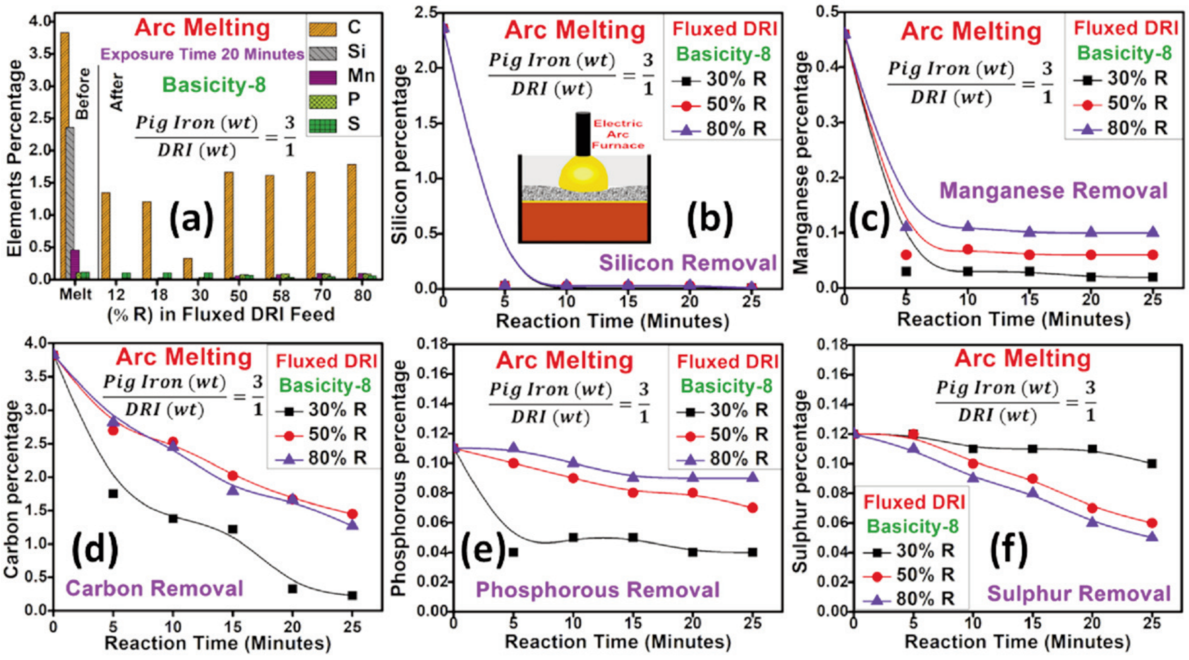

Figure 3. *Behavior of removal of impurities with reaction time under different conditions during electric arc melting a) for 20 minute exposure time b) silicon c) Manganese d) Carbon e) phosphorus f) sulfur*

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

$$(CaO)+(SiO_2)=(CaO.SiO_2); \quad \Delta G^0=-83453-3.4T\ J\cdot mol^{-1} \tag{2}$$

As the silica came into slag phase, it reacted with available lime according to the above reaction and formed a stable phase. From the above two reactions, it is obvious that some amount of oxygen was 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 that %R value did not have any effect on the removal of silicon. The same trend was observed for all values of %R, which meant that silicon reacted first with the available oxygen and made silicon oxidize that combined with calcium oxide and went into the slag.

3.3. Manganese removal

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

$$(FeO)+[Mn]=(MnO)+[Fe]; \quad \Delta G^0=-123516+56.40T\ J\cdot mol^{-1} \tag{3}$$

Removal of manganese was 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 was higher under conditions 30%R compared to 50 and 80%R value fluxed DRI due to availability of higher value of total FeO content in slag.

3.4. 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]

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

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

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 was not supplied to the hot metal; therefore, chances of this reaction were 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 forms CO which improves heat transfer, slag-metal interaction, and compositional homogeneity of the bath. In the case of 30%R DRI removal of carbon was higher for any time interval compared to 50 and 80%R DRI. Carbon removal became 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.

3.5. 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]

$$2[P]+5(FeO)+3(CaO)=(3CaO\cdot P_2O_5)+5[Fe]; \quad \Delta G^0=-767\,990\ +\ 103.2T\ J{\bullet}mol^{-1} \tag{6}$$

The capacity of dephosphorization depended on the thermodynamic behavior of phosphorus, oxygen in metal, and the content of P_2O_5 & FeO in the slag. These parameters changed with reaction time due to the change in composition and temperature. Furthermore, the free energy change for the reaction (Eqn.6) indicated that dephosphorization was more favorable at a lower temperature. Thus, the conditions for good dephosphorization were 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 had both iron oxide and CaO in the combined form which dissolved quickly in the metal bath and formed a highly basic oxidizing slag with a low melting point. In the 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 contained 94% FeO and 6% Fe_3O_4 while increasing reduction level, Fe_3O_4 phase was abolished from the DRI and Fe metallic increased. The 50%R DRI contained 70.83% FeO and 29.7% Fe metallic, therefore, oxygen potential of bath decreased with increasing metallic content, which was responsible for the low phosphorous removal compared to 30%R DRI. Dephosphorization was minimal in the case of 80%R value DRI because it contained only 29.75% FeO with 70.25% Fe. This amount of FeO was consumed by the other impurities elements to form their oxides which became slag and created the reducing condition in the bath. Therefore, the amount of oxygen, basicity, and temperature should be optimum for phosphorus removal.

3.6. Sulfur removal

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

$$CaO + FeS = CaS + FeO; \qquad (7)$$

$$\Delta G^0 = -4615 - 0.205T\ J{\bullet}mol^{-1}$$

Or

$$\left(O^{2-}\right) + \left[S\right] = \left[O\right] + \left(S^{2-}\right)$$

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, and $W_{\sum FeO}$ = wt of FeO in slag phase.

Effect of slag composition on activity coefficients of sulfur and iron oxide in the slag was that k_S decreased with decreasing basicity of the slag. Also, the value of k_S increased slightly with increasing temperature. Thus, the degree of desulphurization increased with increasing basicity, decreasing total FeO content of the slag, and increasing temperature of the bath. Removal of sulfur as a function of time under different %R value fluxed DRI is presented in Figure 3(f). The percentage of sulfur removal in three conditions was 16%, 50%, and 58% for 30%R, 50%R, and 80%R value of fluxed DRI, respectively, which were 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, not much sulfur removal was observed. On increasing the %R value of DRI, sulfur removal also increased due to the unavailability of oxygen. All the reactions took place before the sulfur removal inside the bath; therefore, oxygen supplied by iron oxide was consumed by Si, Mn, C, and P first to make their respective oxides. In the presence of oxidizing environment in the bath sulfur could not be removed, because as the amount of oxygen increased, the amount of FeO in the slag increased, which inhibited the removal of sulfur from metal to slag phase. Thermodynamically, other impurities except sulfur can be removed in oxidizing environment favorably. In the case of 30%R value DRI amount of oxygen was sufficient to react with impurities; this is why the bath was always oxidized. Hence, phosphorus was removed effectively with a negligible amount of sulfur. In the case of 50%R value DRI the value of FeO decreased from 94% to 70.83%, which was responsible for the removal of sulfur compared to 30%R DRI. In the case of 30%R DRI consumption of oxygen took more time compared to 50%R DRI. This is why after an interval of time oxygen available in the bath was consumed by impurities in the case of 50%R DRI and bath became reducing/neutral and favored the removal of sulfur. For 80%R value DRI oxygen amount was very low, which was consumed by the Si, Mn, and C and consequently it created a reducing environment with basic slag which favored the effective removal of sulfur with a negligible amount of phosphorus. Thus, the use of the highly fluxed DRI had the potential to replace the charging of the iron ore and lump lime in EAF and enhancing smooth refining process without creating the problem of foaming.

The use of fluxed DRI in electric arc furnace resulted in the 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

3.7. 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 was removed in the first five minutes exposure time for all three heats and afterwards it became constant. This meant that silicon reacted with oxygen/iron oxide in the initial stage to make stable silicon oxide. Manganese removal followed the similar trends like silicon which was shown in Figure 3(c), but here %R value effected the removal. Most of the manganese was removed in five minutes and afterwards it became constant. In the case of carbon, trends were different. From Figure 3(d), it was evident, for 30%R value DRI carbon was removed up to 20 minutes and afterwards it became 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 sulfur was quite interesting. Figure 3(e) shows that phosphorus was 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 removed 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 sulfur for 30%R value DRI up to 25 minutes reaction time. Sulfur 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 sulfur removal was observed from the start and it was continuously removed up to 25 minutes reaction time. In this case amount of oxygen was much lower compared to other two feed materials, therefore, it was consumed in the early stage of the reaction and environment became neutral that favored the removal of sulfur from the pig iron melt. Figure 3(e) & (f) showed the reverse behavior. In the case of 30%R value DRI phosphorus was removed effectively with a negligible amount of sulfur, while in the case 80%R value DRI sulfur was removed effectively with a negligible amount of phosphorus. This is a clear indication of the effect of oxygen potential on the removal of sulfur and phosphorus. There have been a collective agreement on some aspects of dephosphorization kinetics associated with decarburization. Firstly, droplet swelling, caused by CO formation inside the droplet, increased the droplet residence time in the slag. Secondly, longer residence time favored refining reactions, especially for dephosphorization which could only take place at a significant level when metal was in contact with slag. Thirdly, decarburization would suppress dephosphorization by competing for oxygen, thereby lowering the interfacial oxygen potential, which controled the driving force for dephosphorization. Finally, because of droplet swelling, the slag/metal interfacial area would change with time and this must be accommodated in the rate equation.

3.8. Effect of exposure time on the rate of removal of impurities

Figure 4 shows the rate of removal of impurities

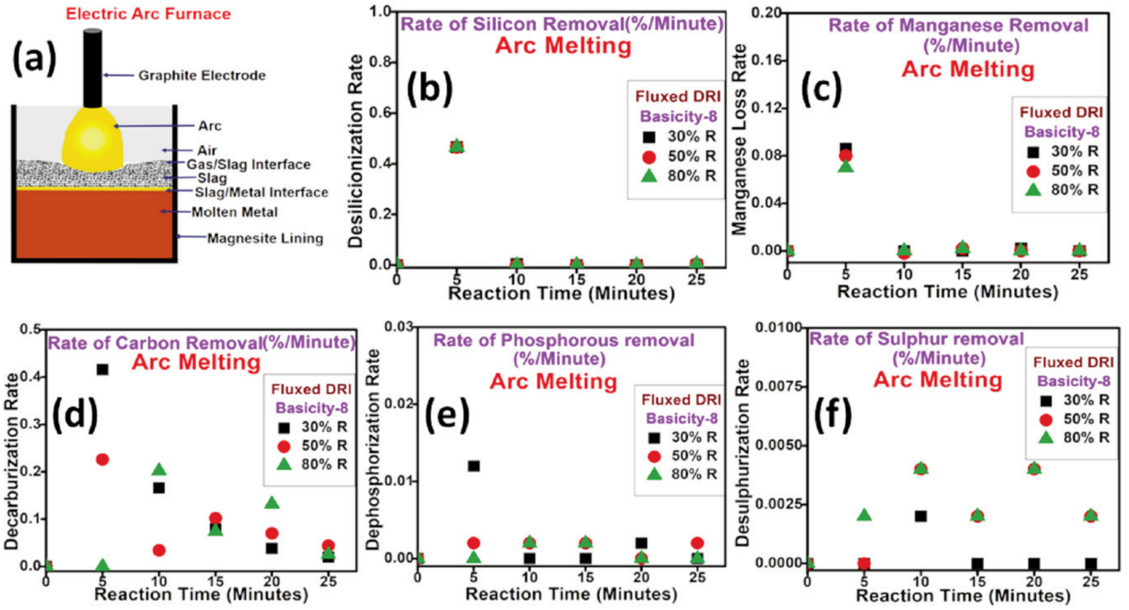

Figure 4. *Rate of removal of impurities (%/minute) a) EAF b) Silicon c) Manganese d) Carbon e) phosphorus f) Sulfur*

from pig iron using different %R value DRI for 25 minute reaction time.

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 was removed in five minutes. This reflected that silicon reacted instantaneously with the oxygen-rich iron phase and made a 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 was responsible for the decrement in the rate of removal after 5-minute exposure. Figure 4(c) shows the rate of removal of manganese. Rate of manganese removal followed the same trend as the rate of silicon removal. It was observed that the maximum rate was obtained in five minutes and afterwards it decreased. Rate of carbon removal is shown in Figure 4(d). Rate of carbon removal for 30 and 50%R value DRI was maximal at 5 minutes and afterwards it decreased. For 80%R value DRI, rate of removal of carbon up to 5 minute was negligible, and after 5 minutes it increased and obtained 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 was high compared to 80%R value DRI. For the carbon reaction, some nucleation side was necessary; therefore, it would take a longer time in the case of high metallized feed material compared to low metallized value feed material. Again the rate of removal of phosphorus and sulfur was quite impressive. Figure 4(e) & (f) show the rate of removal of phosphorus and sulfur, respectively. Rate of phosphorus removal was increased up to 5 minutes for 30%R value DRI and afterwards it decreased, while for 50 and 80%R value DRI rate of phosphorus was minimal up to 5 minute reaction time. Rate of phosphorus removal started to increase after 5 minute reaction time for 50 and 80%R value DRI and increased up to 10 minute reaction time and became constant for the next five minute reaction time and afterwards it decreased. Rate of sulfur removal was very sluggish for 30%R value DRI while for 50 and 80%R value DRI, it increased up to 10 minutes and afterwards it decreased.

3.9. 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(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 and afterwards it decreased, except for sulfur. Rate of sulfur removal was 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

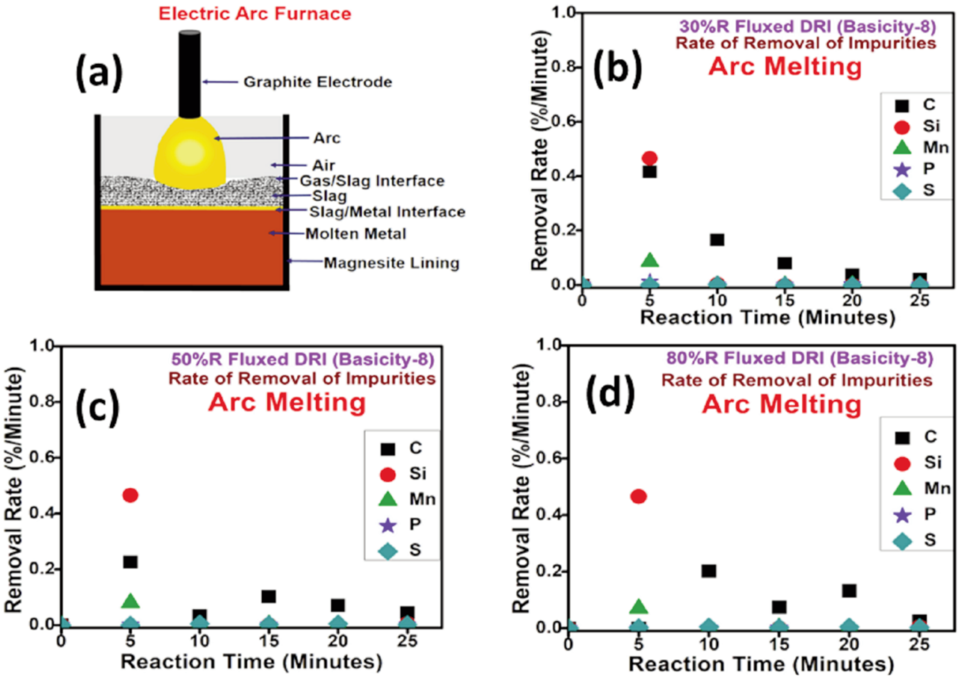

Figure 5. Rate of removal of impurities (%/minute) for different values of R fraction (%R) in fluxed DRI feed, a) EAF b) 30%R c) 50%R d) 80%R

the order of removal here was 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 compared 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 sulfur was different. In the presence of silicon and manganese rate of carbon removal was suppressedx. Due to the insufficient amount of oxygen rate of phosphorus removal was observed negligible.

3.10. 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.

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

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

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

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

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

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

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

$$[FeS]_y+(CaO)_x=Ca_xS_y+FexOy$$

(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 reacted first to form silica. Oxygen for the reaction of silicon was supplied by iron oxide. Some amount of oxygen could 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 would not take much time in the dissolution. During the dissolution, calcium combined with silica and formed a stable calcium silicate slag.

After silicon, manganese reacted with iron oxide to form manganese oxide and it combined with silica to make slag phase. Carbon reacted 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 could not be formed. Therefore, carbon removal

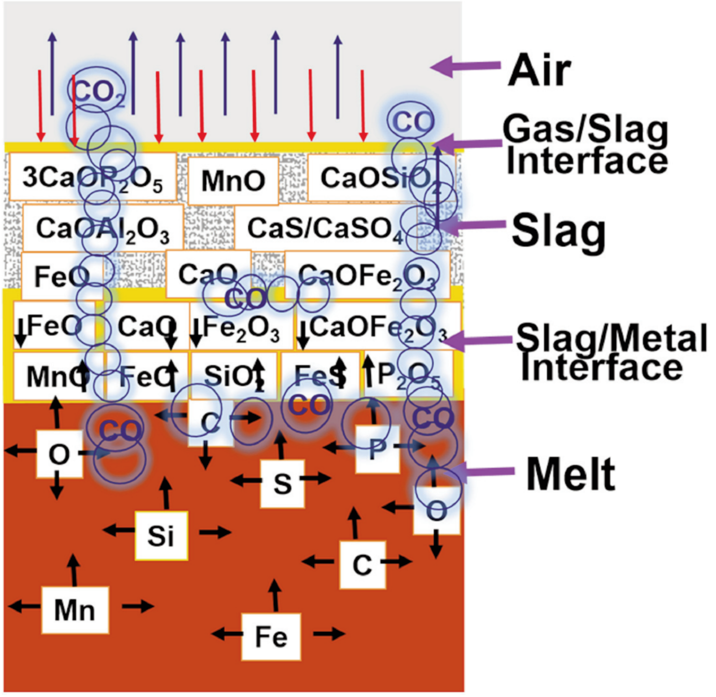

Figure 6. *Schematic diagram of an arrangement of different interfaces, elements and reactions involved during removal of impurities from pig iron in an electric arc furnace*

started after removal of silicon and manganese. Carbon was removed in the form of gas, therefore, it did not join the slag phase, but due to formation of foamy slag in the presence of gases, kinetics of the removal of impurities was accelerated. Phosphorus also reacted with the oxygen of iron oxide to make its oxide. These oxides reacted with lime to make its stable slag phase. The affinity of sulfur towards iron was very high, therefore, sulfur combined with iron in the melt. Iron sulphide reacted 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 played 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 reacted with iron to form iron oxide. Then this iron oxide reacted with different impurities to form their respective oxides, but in the current study, iron oxide was directly supplied in the form of fluxed DRI (pellets). This way the amount of energy and reaction time can be minimized by eliminating one step during steelmaking. In steelmaking generally lime was charged in the lump form that took time for dissolution, but in the current study lime was charged in the form of calcium ferrite [22], i.e. low melting constituted phase which would 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.

4. 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 possibly due to CO gas nucleation and growth occurring on furnace walls.

Sulfur 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 sulfur and phosphorous simultaneously up to some extent.

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

Author's Contribution

R.K.Dishwar- Perform Experiments, Analysis of Result, Manuscript Writing and Communication, O.P. Sinha: Help in the design of the experiment, Results and discussion, Manuscript Corrections.

Conflict of Interest

There is no conflict of interest.

Data Availability

We cannot provide the data in raw form. It will be used for further research work. We can provide it on the special request.

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UTICAJ DELIMIČNO REDUKOVANOG VISOKO FLUKSOVANOG DRI PELETA NA UKLANJANJE NEČISTOĆA TOKOM PROIZVODNJE ČELIKA U ELEKTROLUČNOJ PEĆI U LABORATORIJSKIM USLOVIMA

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Apstrakt

Ovaj rad predstavlja uporednu studiju o ukljanjanju nečistoća iz rastopa sirovog gvožđa dodavanjem delimično redukovanog visoko fluksovanog direktno redukovanog gvožđa (DRI) za proizvodnju čelika u elektrolučnoj peći kapaciteta 2 kg (EAF). Tri tipa fluksovanog DRI (redukovanog 30, 50 i 80% (%R) sa sličnom baznošću – 8) korišćena su za održavanje različitog nivoa oksidacionog potencijala u rastopu da bi se proučilo kinetičko ponašanje prilikom uklanjanja nečistoća iz rastopa. Rezultati su pokazali da se brzina uklanjanja nečistoća (tj. C, Si, Mn, P, S i drugih) u početku povećavala tokom 5 minuta reakcionog vremena, a da se zatim smanjila. Fosfor (~64%), sumpor (~16%) i ugljenik (~94%) su uklonjeni istovremeno tokom 25 minuta reakcionog vremena kada je upotrebljen 30%R fluksovani DRI. Slično tome, Fosfor (~33%), sumpor (~50%), i ugljenik (~62%) su uklonjeni istovremeno kada je korišćen 50%R fluksovani DRI, dok je visoko redukovani (80%R) fluksovani DRI uklonio sumpor (~58%), ugljenik (~56%) i mali deo fosfora (~18%) iz sirovog gvožđa. U svim slučajevima je primećeno da su uklonjeni silicijum (>99%) i mangan (>80%). Na osnovu ovog istraživanja se može zaključiti da je ~30%R DRI pelet pogodan za efikasno uklanjanje fosfora, dok je ~80%R DRI pogodan za ukljanjanje sumpora. Značajno uklanjanje nečistoća iz rastopa sirovog gvožđa bi se moglo postići korišćenjem ~50%R fluksovanog DRI peleta.

Ključne reči: *Fluksovani DRI; Elektrolučna peć; Odsumporavanje; Odfosforavanje; Razugljenisavanje; Kinetika proizvodnje čelika*