6.1 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 were the main factors to improve the modern steelmaking. In the world, extensive studies are in progress to produce hot metal outside the blast furnace. Smelting reduction of iron ore is one good step towards this goal. Smelting reduction process is economically feasible compared to blast furnace route with the possibility of utilization of iron ore fines in the form of agglomerates and non-coking coal instead of BF coke [27]. 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 total steel is produced by Electric route while 47% produced by oxygen route; therefore DRI-EAF route become an essential point of study in the Indian steel making scenario [95]. In the present chapter, utilization of different %R fluxed DRI in steelmaking is explained in detail. The present work signifies a relative study on the impurities removal from pig iron melt by addition of partially reduced highly fluxed direct reduced iron (DRI) in the form of pellets. The activity of FeO in slag was varied with the addition of different %R 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. Three different techniques of melting (Electric Arc melting, Induction melting and Plasma melting) were used for steelmaking in the current work. Principles of operation are different for each technique which are explained in subsequent section.

6.1.1 ELECTRIC ARC FURNACE

In the early phase of 19th century a number of people had attempted with electric arc as a tool to melt iron. First time Sir Humphrey Davy conducted an experimental demonstration in 1810 and in 1878-79, Sir William Siemens took out patent of electric furnaces of the arc type. But for the commercial use, in 1907 first arc furnace was established by Paul Heroult in United States. Electric arc furnace which is used for the steelmaking comprises a vessel lined with refractory. Vessel lines are usually water cooled and top of the furnace (roof) is covered with refractory brick’s. One or more (2/3) graphite electrodes enter the furnace through roof. In this furnace electrical energy is used to form an electric arc (in between two electrodes/electrodes-metal) which heats the metal by the radiant heat (Conduction, Convection) which is evolved during the arcing inside the furnace. Graphite/Carbon electrodes are mainly used to supply the power and create the arc between the metal bath and the electrode. The electric arc temperature reaches more than 3000°C [96]. A sectional view diagram of conventional type Electric Arc Furnace with charging and melting conditions is shown in **Figure-6.1.** There are mainly three types of electric arc furnace exist based on the arcing produced inside chamber of the furnace [96],[97]:

6.1.1.1 Direct Arc Type: In this process, Arc is formed between the electrodes & metal being heated/melted (i.e. Conventional EAF, Vacuum Arc Remelting-VAR).

6.1.1.2 Indirect Arc Type: In this process, an arc is formed in between two electrodes. Heat is conveyed to the metal by conduction, convection, radiation. If an arc burns under the cover of solid charge which surrounds the electrode used for making ferro-alloys which is known as submerged arc furnace.

6.1.1.3 Plasma Arc Type: In this process heat is evolved by passing diatomic gases (O, N, H, Ar etc. according to need during melting) through a hollow electrode from the top which ionized into the arc discharge zone at the bottom of the hollow electrode. In this process we can produce very high temperature along with creation of required environment inside the furnace (i.e. oxidizing /reducing /neutral /alloying by nitrogen etc.). This process can be used for melting special steels (especially N_2 bearing austenitic stainless steels using N_2 plasma as a source of arc) and extraction of pure metals from their ore.

Cold (Solid)

Hot Metal (Liquid)

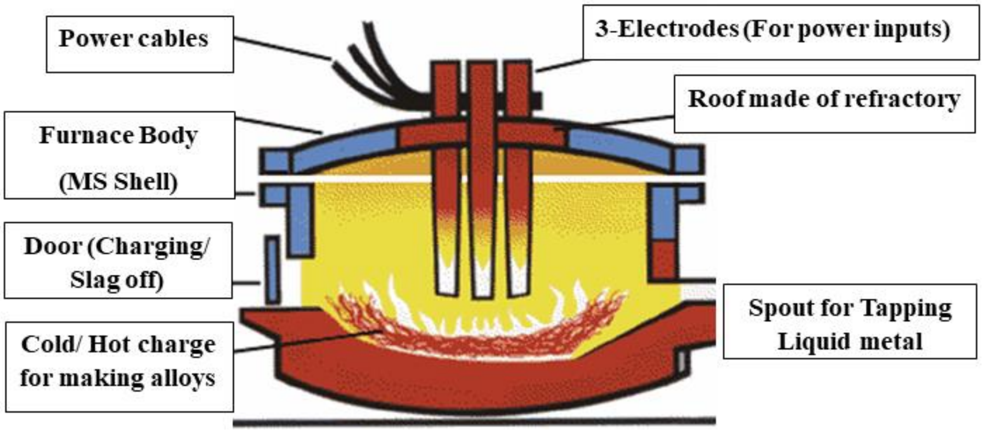

Figure 6.1 Sectional view of Electric arc furnace (Conventional Type)

6.1.2 INDUCTION FURNACE

Instead of arcing electricity can also be used for melting solid charge through induction. In small or medium scale steel plants air induction furnace normally plays significant role for making high quality steels, particularly stainless steel from stainless steel scrap. One beauty of air induction melting furnace is that chemistry of the melt can be adjusted very easily according to the requirement with the addition of mill scale and scrap of known chemistry. The use of sponge iron (DRI as lumps) in such furnace can be used to produce high quality steel by induction melting process. There are two coil system in the air induction furnace. In the primary coil an alternating current is supplied first, due to this current one magnetic field will be generated around the coil. Metallic charge works as secondary coil here. An electromotive force (emf.) is produced in the secondary circuit which creates heat in the charge material (i.e. $\mathbf{Q = I^2 R}$; Q-Heat, I- eddy current, R- resistance of metal) by the induced eddy currents (I) which passes through the resistance (R) of charge (metal) which can melt the charge material. This concept was given first by Michael Faraday of UK and in 1870 De Ferranti discovered the principle of electromagnetic induction, then First coreless induction furnace was made by Dr. E. F. Northrup in 1916 [96]. The induction heating allows a quick rise in temperature and can be easily controlled [2]. This process is being used as a melting tool so useful to produce steels with lower S and P by selecting proper raw materials. In this process metal can be deoxidized more easily. In this process loss of alloying elements is low and it ensures low non-metallic inclusions. A cross sectional view of conventional induction furnace and a Coil along with current induced arrangement is shown in **Figure-6.2.**

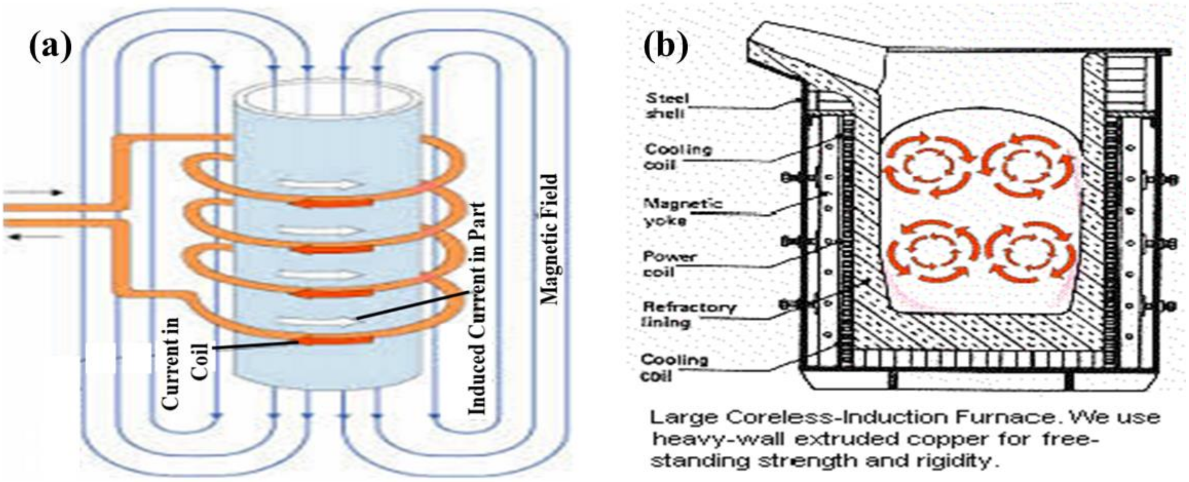

Figure 6.2 Conventional Induction Furnace; a) Coil along with current induced arrangement, b) Sectional view of conventional induction furnace.

From the above discussion, it is clear that each technique works in different manner to melt the material. Therefore, to know the effect of melting techniques (EAF, Ind. Furnace, and Plasma Furnace) using partially reduced fluxed DRI as pellets were selected for the present study. Simultaneously, bath environment definitely affects the melting conditions and removal of impurities from the melt, that's why, different plasma environment, i.e. reducing gas (hydrogen plasma), neutral gases (argon & nitrogen plasma) and air melting were adopted during studies. Further to study the effect of lime charging in the combined form (in-situ DRI) or free lime (powder form) were also studied in the current work. All experiments and results obtained are discussed in detail in this chapter one by one respectively.

6.2. EXPERIMENTS WITH ELECTRIC ARC MELTING

6.2.1. RAW MATERIALS AND THEIR PREPARATION

Raw materials used in the present study are lime powder, different %R fluxed DRI and pig iron which are shown in **Figure-6.3**. DRI was used to observe the effect of different fractional reduction on the removal of impurities (i.e. C, Si, Mn, S, P) from pig iron melt during EAF melting On the basis of obtained results, three different types of fluxed DRI (i.e. reduced up to 30, 50 and 80% R) pellets having 8-basicity 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-6.1**.

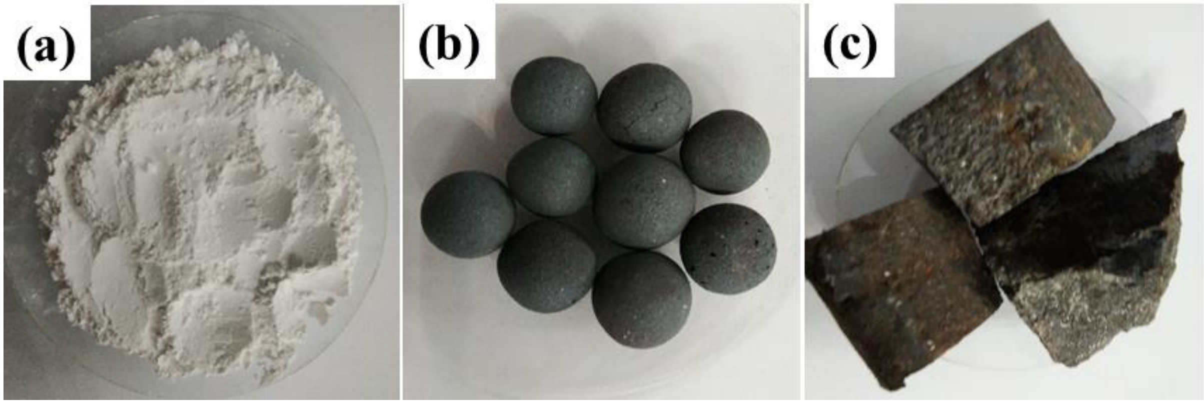

Figure-6.3 Raw materials used for the study: a) Lime powder; b) DRI; c) Pig-Iron

Table-6.1 Chemical composition of iron ore, lime and DRI

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 DRI (wt. %)								
Reduction (%)	**Fe_{Met}**	Fe_t	Iron Oxides	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- *(Iron Oxides-Fe_2O_3+Fe_3O_4+FeO), Fe_{Met}-Metallization (%), Fe_t-Fe Total*								

6.2.2. ELECTRIC ARC MELTING

Pig iron scrap of 1.5 kg was melted in the crucible of indigenously fabricated laboratory scale electric arc furnace (capacity 2kg). Diagrams of the furnace in different views are shown in **Figure-6.4**.

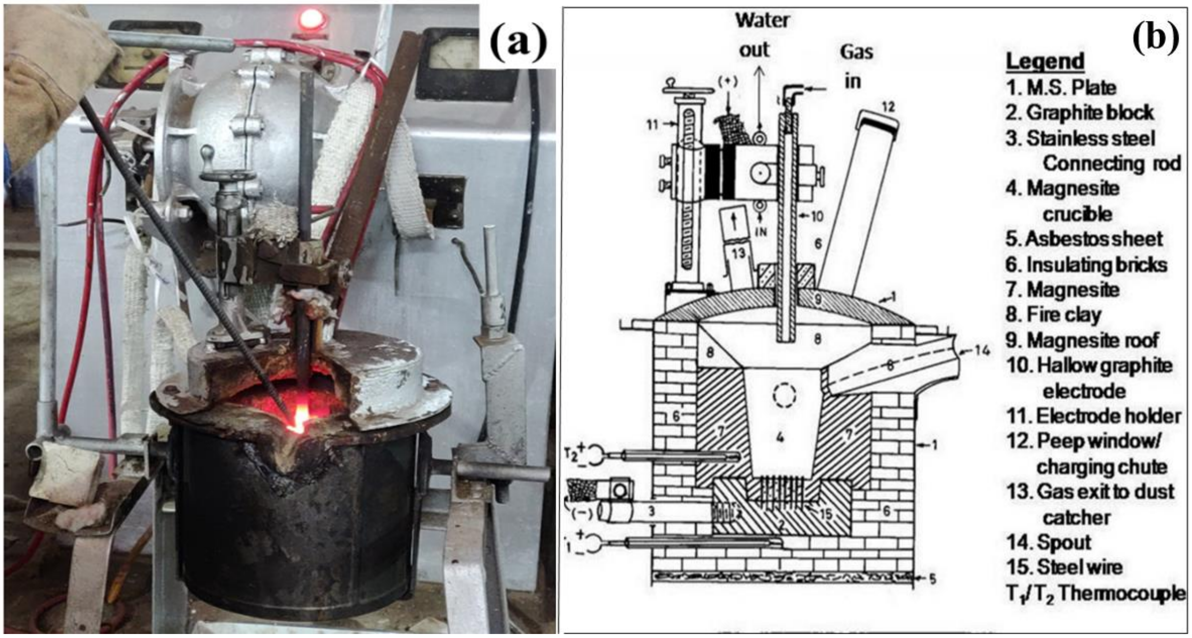

Figure-6.4. Diagram of furnace used to melt the material: a) Isometric diagram, b) Schematic diagram of cross sectional view

Addition of reduced flux DRI (0.5 kg) as pellets of different %R (i.e. 12%, 18%, 30%, 50%, 58%, 70% and 80%) in the ratio of 3:1 (Pig iron: DRI) was used in each heat to know for the removal of impurities (i.e. silicon, manganese, carbon, phosphorus and sulfur) from the pig iron melt for 20 minute exposure time after complete melt down of DRI in pig iron melt. **Table-6.2** shows the typical charge mix composition used for the different heat.

In all heats, the input of CaO content (basicity) was kept the same level. 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). **Table 6.3** gives the composition analysis report of these heats for 20 minutes exposure time. Based on the above melts result (from **Table 6.3**), only 30, 50 and 80% R fluxed DRI were selected for the kinetic study of impurities removal from the pig iron melt.

Table-6.2 Typical 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

For kinetic study, samples were withdrawn respectively at an interval of 5 minutes after complete dissolution of fluxed DRI in the melt keeping constant melt's temperature up to 1580±20°C. Melting cycle used for all experiments is shown in **Figure-6.5**.

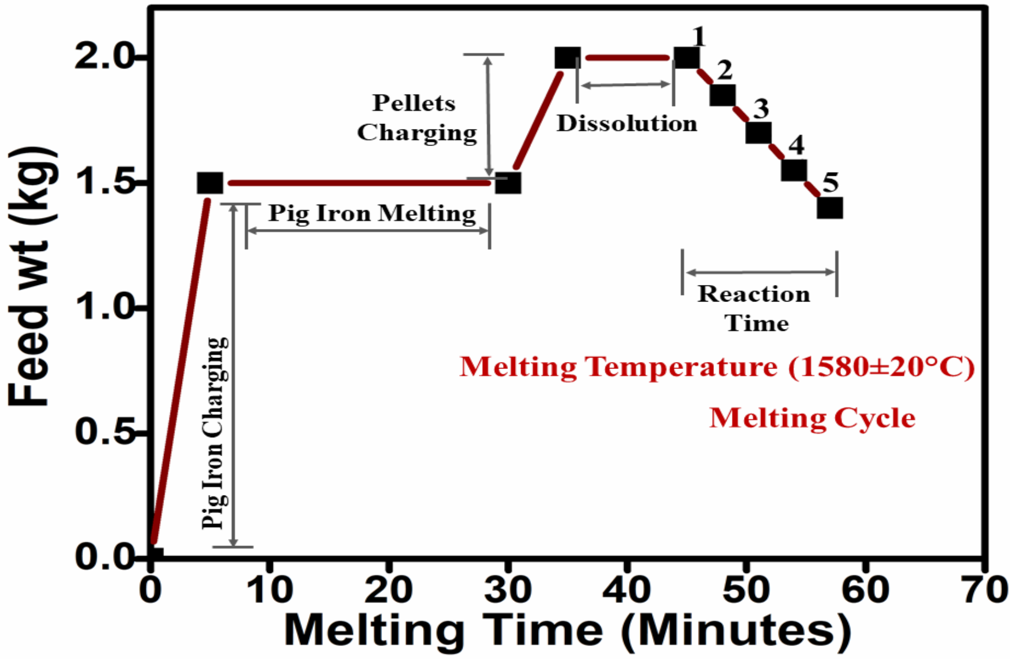

Figure-6.5 Melting cycle used for the experiment

Similar procedure for melting and sampling was followed in all heats. After cooling samples were prepared by cutting, grinding and polishing for their chemical analysis using Foundry Master Spectroscope/ Optical Emission Spectroscopy. Results are shown in **Tables- 6.3** and **6.4** respectively for 20 & 25 minutes exposure time.

6.3 RESULTS AND DISCUSSION

6.3.1 EFFECT OF %R FLUXED DRI ON REMOVAL OF IMPURITIES

Figure-6.6 (a) shows the effect of %R fluxed DRI on the removal of impurities from the pig iron for 20 minutes reaction time. Chemical composition analysis of samples which was taken after 20 minute reaction time is given in **Table-6.3.**

Table-6.3 Chemical analysis of different heat products using different %R fluxed DRI

Chemical Composition after 20 minute 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

Chemical composition analysis of samples for 30%, 50% and 80%R fluxed DRI addition was taken after 25 minute reaction time is given in **Table-6.4.**

Table-6.4 Chemical analysis of different heat products after 25 minute 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

It is evident from the **Tables (6.3 & 6.4)** that %R values greatly influence the removal of impurities. In the case of low reduced fluxed DRI (i.e. 12 and 18 %) excess FeO containing slag formed during melting is responsible for slopping in laboratory scale (2kg) furnace which did not give 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. Significant changes were found in the results on increasing level of %R fluxed DRI beyond 30%. On the basis of obtained results, 30, 50 and 80%R fluxed DRI were selected for studying the effect of %R fluxed DRI and reaction time on the removal of impurities from the pig iron melt.

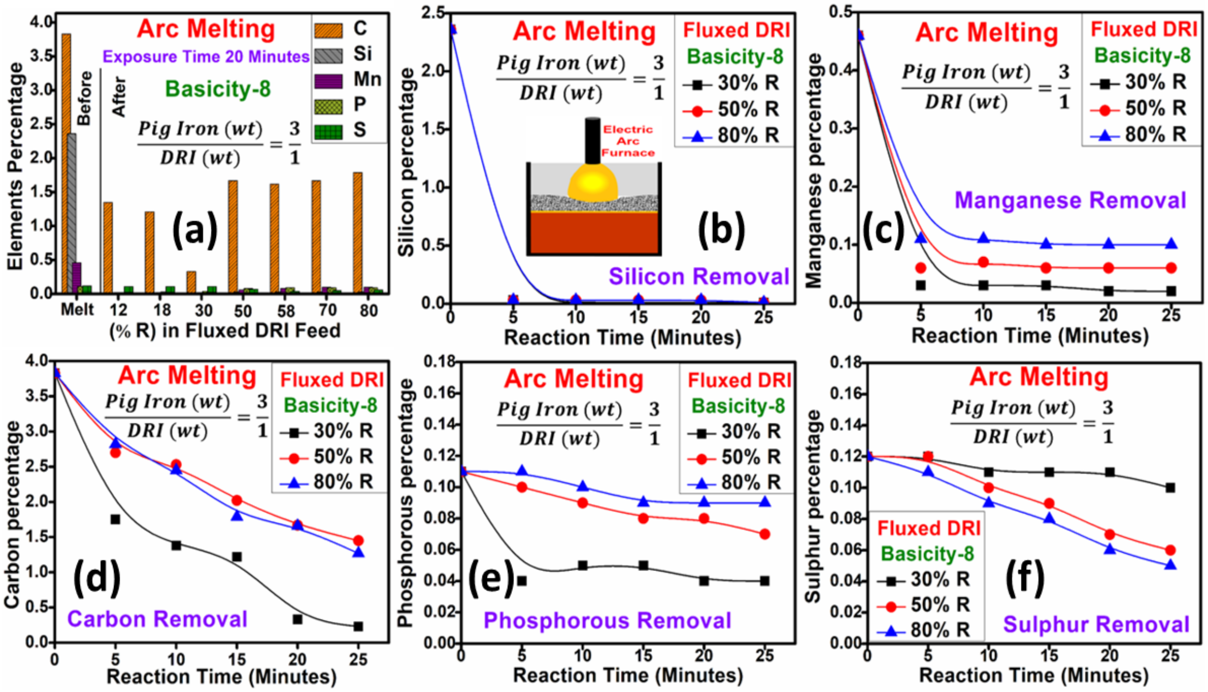

Figure-6.6 Behavior of removal of impurities with reaction time under different conditions during electric arc melting: a) for 20 minute Exposure time; b) Silicon; c) Manganese; d) Carbon; e) Phosphorus; f) Sulphur

6.3.1.1 Silicon Removal

Removal of Si mainly takes place at the slag-metal interface as per the following reaction [9]:

$$[Si] + 2(FeO) = (SiO_2) + 2[Fe] \qquad ; \ldots\ldots \quad (6.1)$$

Due to highly oxidizing nature of the melting chamber, Si reacts with the oxygen of iron oxide (FeO) exists along with lime (CaO) as slag (CaO. FeO) which enriches the melt pool with iron (liberated from FeO) [as per **equation 6.1**] and Si transferred towards slag (CaO. SiO_2)[as per **equation 6.2**] very quickly as Si-oxide from the metal pool [9].

$(CaO) + (SiO_2) = (CaO.SiO_2)$; …… (6.2)

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 the removal of silicon some amount of oxygen is necessary in the melt. **Figure-6.6(b)** shows the removal of silicon from the pig iron melt using 30, 50 and 80% R flux DRI. The results showed %R fluxed DRI do not have much effect on the removal of silicon after 10 minutes exposure time, but follows same trends of removal. It means silicon reacts first with the available oxygen and make silicon oxide which combined with calcium oxide and goes into the slag.

6.3.1.2 Manganese Removal

Removal of Mn mainly takes place as per the following reaction [9].

$[Mn] + (FeO) = (MnO) + [Fe]$; …… (6.3)

Removal of manganese is preferred at low basicity and high FeO content in slag. The results of Mn removal as a function of time under different %R fluxed DRI is shown in **Figure-6.6(c)**. It is obvious that Mn removal is higher under conditions 30%R compared to 50 and 80 %R fluxed DRI due to availability of more oxygen as FeO content in the slag. Although basicity of these DRI was fixed as mentioned previously.

6.3.1.3 Carbon Removal

Removal of Carbon as a function of time under different %R fluxed DRI materials is presented in **Figure-6.6(d).** Carbon removal mainly takes place as per the following reactions [9].

$[C]+ \frac{1}{2} O_2 (g) = CO (g)$; …… (6.4)

$[C] + (FeO) = CO\,(g) + [Fe]$; …… (6.5)

Equation (6.4) is a gas/metal reaction. It is happened when blowing of oxygen gas into metal bath where it directly reacts with carbon of the metal bath at high temperature. But, in the present work, oxygen is not supplied to the hot metal, hence chances of this reaction is negligible. **Equation (6.5)** is a slag-metal reaction. Here oxygen of iron oxide in slag reacts with bath carbon at the slag/metal interface. Heat transfer, slag/metal interaction and compositional uniformity of the bath can be improved by evolution of CO which is generated by the reaction of carbon with oxygen present in the FeO of partially reduced pellets. In the case of 30%R fluxed DRI removal of carbon is higher for any time interval compared to 50 and 80%R fluxed DRI. The removal of Carbon becomes almost constant after 20 minute reaction time for 30%R fluxed DRI while for 50 and 80% R fluxed DRI feed it was continuously decreasing up to 25 minute exposure time. Effective removal of carbon may be achieved either by increasing oxygen potential in bath or increasing exposure time.

6.3.1.4 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 [9].

$2[P] + 5(FeO) + 3(CaO) = (3CaO \cdot P_2O_5) + 5[Fe]$; …… (6.6)

$\Delta G^0 = -683\,000 + 580T\ J \cdot mol^{-1}$ …… ;…………..… (6.7)

The capacity of dephosphorization depends on the thermodynamic behavior of phosphorus & oxygen in metal and P_2O_5 & FeO in the slag. These parameters change themselves with reaction time due to change in composition and temperature of the melt. Furthermore, the free energy change **Eqn. (6.7)** for the reaction **(Eqn.6.6)** shows that dephosphorization is much favorable at a lower temperature. Thus, the conditions for good dephosphorization are: high oxygen potential as (FeO), high basicity of slag and lower bath temperature. Dephosphorization as a function of time under different %R fluxed DRI is presented in **Figure-6.6(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 on 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 observed least 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 to join the slag and creates the reducing condition in the bath. Therefore amount of oxygen, basicity and temperature should be optimum for phosphorus removal.

6.3.1.5 Sulphur Removal

Removal of Sulphur may take place mainly in the slag/metal interface as per the following reaction [9].

$CaO + FeS = CaS + FeO$;… …… (6.8)

Or

O^{2-} (liquid slag) + S (liquid iron) = (O liquid Iron) + S^{2-} (liquid slag)

Where, the modified equilibrium constant $k_S = (W_{(S)} / W_{[S]}) \cdot W_{\sum FeO}$. The composition of slag has significant effect on activity coefficients of sulfur and iron oxide in the slag. The values of activity coefficients (k_S) decreases with decreasing basicity of the slag. Temperature has an inverse effect, therefore value of k_S increases marginally with growing temperature. Thus, high basicity and low temperature with minimum amount of FeO in the slag favors higher degree of elimination of sulphur from the melt. Removal of sulphur as a function of time under different %R fluxed DRI is presented in **Figure-6.6(f)**. The percentages sulfur removal in the three conditions are 16%, 50% and 58% for 30%R, 50%R and 80%R fluxed DRI respectively, which have been calculated from initial and final metal analysis given in **Table-6.4**. In the case of 30%R fluxed DRI, considerable amount of sulphur was not removed from the melt because 30%R fluxed DRI contains high amount (~74%) of iron oxide which favors the formation of oxidizing slag in the bath. On increasing the %R fluxed DRI, Sulphur removal also increased due to the unavailability of oxygen. All the reactions (i.e. Si, Mn, C, P) took place before the start of Sulphur removal from the bath; therefore, oxygen supplied by iron oxide consumed in the removal of Si, Mn, C and P as their respective oxides. In the case of 30%R fluxed DRI amount of oxygen was sufficient to react with impurities of melt; 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 favours the removal of sulphur. For 80%R fluxed DRI oxygen amount was very least which was consumed by the Si, Mn and C consequently it created a neutral 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 substitute the charging of the iron ore and lump lime in EAF, because it enhances the smooth refining process without making the problem of foaming/slopping and also reduces the energy consumption as well due to presence of lower melting constituents in fluxed DRI.

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 making specific grades, i.e. AISI 1132, AISI 1137, AISI 1140 and AISI 1141 alloy steel by adjusting composition as per specification given in **Table-6.5** with the addition of ferro-alloy during melting.

Table-6.5 Comparative study of the present work product with 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

6.3.2 EFFECT OF REACTION TIME ON REMOVAL OF IMPURITIES

On the behalf of results shown in **Figure-6.6(b-f)** where 30, 50 and 80%R fluxed DRI were chosen to know the effect of reaction time on the removal of impurities (i.e. Si, Mn, C, P, S) from the pig iron melt. **Figure-6.6(b)** shows the trends for 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 of iron oxide in the initial stage to make stable silicon oxide and join with CaO. Manganese removal follows the similar trends like silicon which shown in **Figure-6.6(c),** but increasing value of %R fluxed DRI effect the removal. Most of the manganese removed in five minutes, afterwards it becomes constant. In the case of carbon, trends were different. It was evident from **Figure-6.6(d)**, 30%R fluxed DRI removes carbon up to 20 minutes afterwards it becomes constant but for 50 and 80%R fluxed DRI feed, it was decreasing continuously up to 25 minute reaction time. It may be decreased to a lower extent value either by increasing reaction time or oxygen potential in slag. Removal of Phosphorus and Sulphur was quite interesting. **Figure-6.6(e)** shows the trends of phosphorous removal. Phosphorus removed in early 5 minutes reaction time for 30%R fluxed DRI due to availability of sufficient oxygen while in the case of 50 and 80%R fluxed DRI it continuously removed slowly up to 25 minute reaction time due to insufficient amount of oxygen. **Figure-6.6(f)** shows the trends of Sulphur removal in which there was no significant changes observed in the removal of Sulphur for 30%R fluxed DRI up to 25 minute reaction time. Sulphur removal was observed after 5 minutes reaction time for 50%R fluxed DRI feed because up to 5 minutes exposure time amount of oxygen available as FeO was consumed by the removal of Si, Mn, P and carbon. In the case of 80%R fluxed DRI, Sulphur was observed removing continuously up to 25 minute reaction time. In this case the amount of oxygen is very less compare to other two feed materials, therefore, it was consumed in the early stage of the reaction and melt’s environment become neutral (means oxygen free, i.e. became reducing condition) that favored the removal of Sulphur from the pig iron melt. **Figure-6.6(e)** & **(f)** showed the reverse behavior. In the case of 30%R fluxed DRI phosphorus removed effectively with a negligible amount of Sulphur, while in the case 80%R fluxed DRI Sulphur removed effectively with a negligible amount of phosphorus. For 50%R fluxed DRI similar trend as 80%R was observed after 5 minute reaction time. This is a clear cut indication of the effect of oxygen potential on the removal of Sulphur and Phosphorus. Kinetics of dephosphorization somehow related to the decarburization process. During the decarburization

CO bubble formation takes place which goes inside the slag and make it foamy. The kinetics of elimination of impurities can be improved in the foamy slag therefore longer residence time of droplets favors the refining reaction and improve rate of dephosphorization. But on the other hand CO formation consumes oxygen and retards the oxygen potential of the bath at similar time which is necessary driving force for the dephosphorization.

6.3.3 EFFECT OF EXPOSURE TIME ON RATE OF REMOVAL OF IMPURITIES

Figure-6.7 shows the rate of elimination of impurities from pig iron using different %R fluxed DRI for 25 minute reaction time. **Figure-6.7(a)** is the schematic diagram of arc and melt conditions.

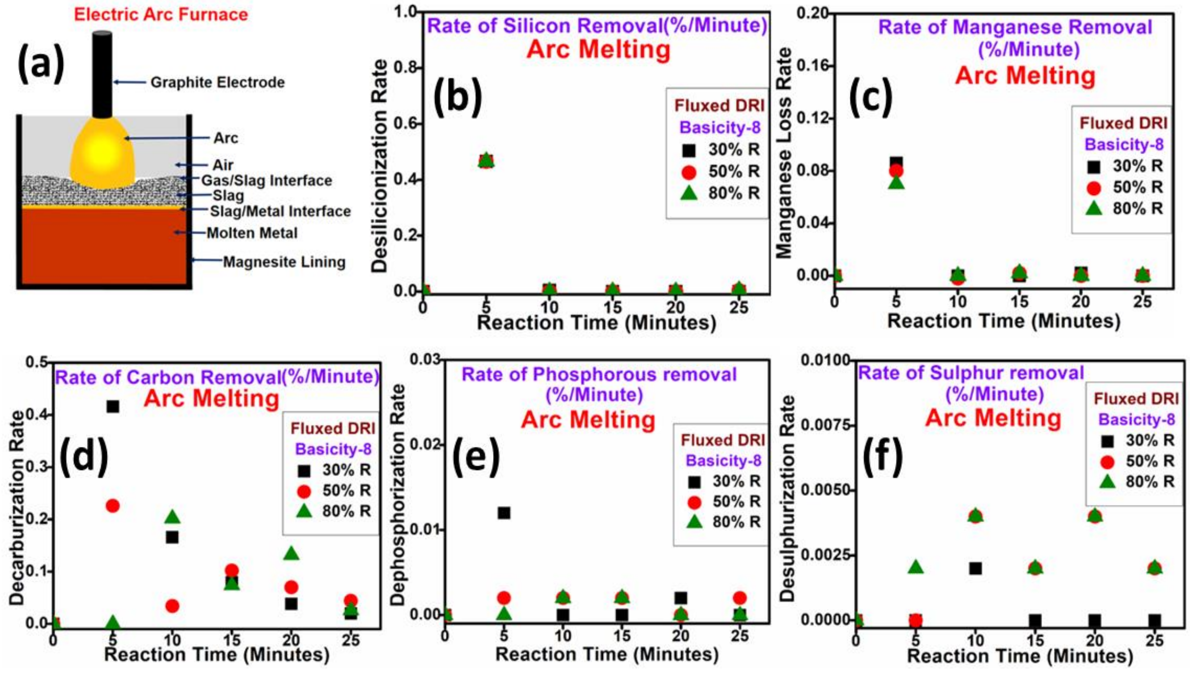

Figure-6.7 Rate of removal of impurities (%/minute): a) EAF; b) Silicon; c) Manganese; d) Carbon; e) phosphorus; f) Sulphur

Figure-6.7(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 time 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 time. **Figure-6.7(c)** shows the rate of removal of manganese. The rate of manganese removal follows the same trend as the rate of silicon removal. It was also observed the maximum rate obtained in five minutes afterwards it decreased. The rate of carbon removal shown in **Figure-6.7(d).** Rate of carbon removal for 30 and 50%R fluxed 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 goes to the maximum value in 10 minute total reaction time afterwards decreased. In the case of 30 and 50%R fluxed DRI the amount of oxygen available (oxygen potential in the bath) for the reaction is high compared to 80%R fluxed 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-6.7(e) & (f)** show the rate of removal of phosphorus and sulphur respectively. Rate of phosphorus removal was increased up to 5 minutes for 30%R fluxed DRI afterwards decreased while for 50 and 80%R fluxed DRI rate of phosphorus is minimal up to 5 minute reaction time. Rate of phosphorus removal starts to increase after 5 minute reaction time for 50 and 80%R fluxed 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 fluxed DRI while for 50 and 80%R fluxed DRI, it increased up to 10 minutes afterwards decreased.

6.3.4 EFFECT OF %R FLUXED DRI ON RATE OF REMOVAL OF IMPURITIES

Figure-6.8 shows the effect of %R fluxed DRI on the rate of removal of impurities from the pig iron. **Figure-6.8(a)** is the schematic diagram of arc and melt conditions. **Figure-6.8(b)** shows the rate of removal of impurities from the pig iron using 30%R 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.

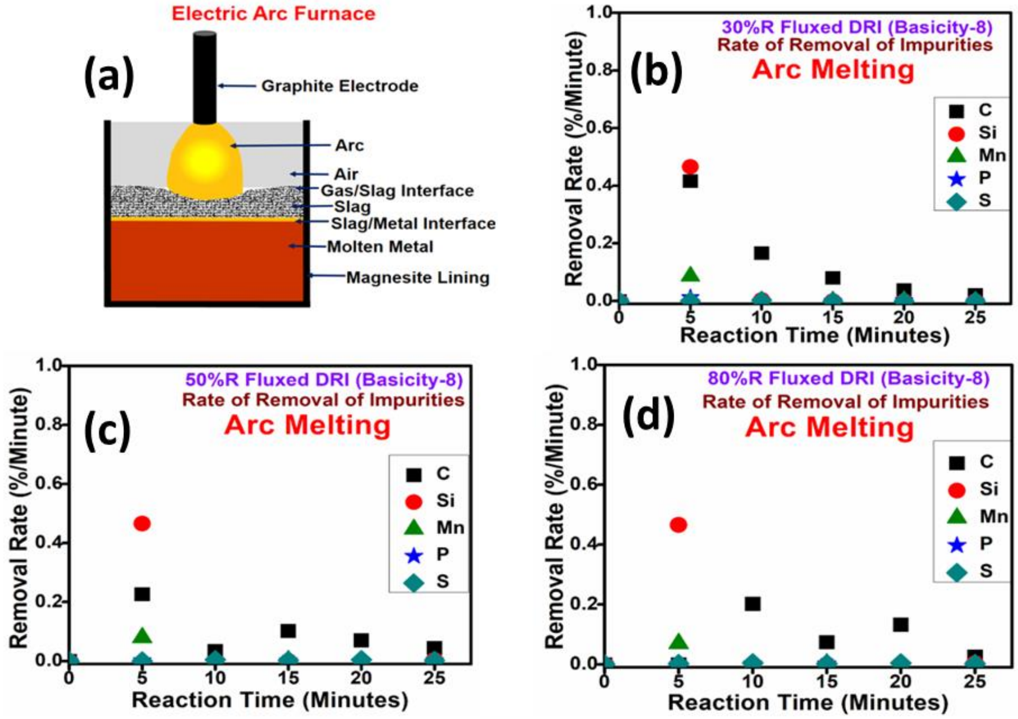

Figure-6.8 Rate of removal of impurities (%/minute) for different % R fluxed DRI feed: a) EAF; b) 30%R; c) 50%R; d) 80%R

Figure-6.8(c) shows the rate of removal of impurities from the pig iron using 50%R fluxed DRI. It was evident from the figure that the order of removal here similar to the 30%R fluxed DRI, but 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-6.8(d)** shows the rate of removal of impurities for 80%R fluxed DRI. In this case, trends in the rate were quite different. The rate of silicon and manganese removal was similar to previous heats, but the rate of Carbon, Phosphorus and Sulphur removal was different. In the presence of silicon and manganese the rate of carbon removal suppress. Due to the insufficient amount of oxygen the rate of phosphorus removal was observed negligible.

6.4 FINDINGS

The addition of different %R fluxed DRI in liquid pig iron melt studies resulted as following conclusions:

- Si and Mn were removed in the 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.
- The P removal occurred after silicon and manganese were removed, which may be due to availability of basic oxidizing slag.
- The carbon removal was delayed may be due to CO gas nucleation and growth occurring on furnace walls.
- Lowering of Sulphur 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 different %R fluxed DRI 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 fluxed 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 fluxed DRI.

6.5. EXPERIMENTS WITH AIR INDUCTION MELTING

In this section experiments was performed with air induction melting to know the effect of heating source on the removal of impurities.

6.5.1. RAW MATERIALS AND THEIR PREPARATION

Raw materials used in the present study are pig iron, lime powder and DRI pellets is shown in **Figure-6.3**. The chemical composition of raw materials was examined and reported in **Table 6.1**. Based on the results of the electric arc furnace melting, two types of reduced fluxed DRI pellets (i.e. 50% and 80% R) having 8- basicity were selected for attaining changed oxidizing atmosphere in the bath. In case of low reduced fluxed DRI, large amount of slag formation takes place which may create slopping/foaming problem in the induction melting due to its stirring/churning effect. Only lime powder is used to study the effect of in-situ lime and free lime charging on the elimination of impurities from the pig iron melt.

6.5.2. AIR INDUCTION MELTING

2kg pig iron scrap was melted in the air induction melting furnace (capacity 5kg). **Figure-6.9** shows the photographs of furnace for different operating conditions (cold charging, melting & sampling and tapping) used during melting studies. **Table-6.6** shows the details of typical charge mix composition used for the different heat.

Figure-6.9 Photographs of furnace used to melting studies: a) Isometric view; b) Cold Charging, Melting & Sampling; c) Pouring into crucible

Table-6.6 Charge mix used for different heats in melting

Constituents	Heat Number		
	Heat-1 (50%R-DRI)	**Heat-2** (80%R-DRI)	**Heat-3** (only Lime)
Pig Iron (gm)	2000	2000	2000
Fluxed DRI (gm)	800	800	-
Lime, insitu / free (gm)	160	160	160
Reduction (%)	50	80	-
Total Charge wt.(gm)	2800	2800	2160

Different %R fluxed DRI pellets were used to remove the impurities from the pig iron melt. In all heats, the input of CaO content was kept same. Melting cycle used in the present work is given in **Figure-6.10**.

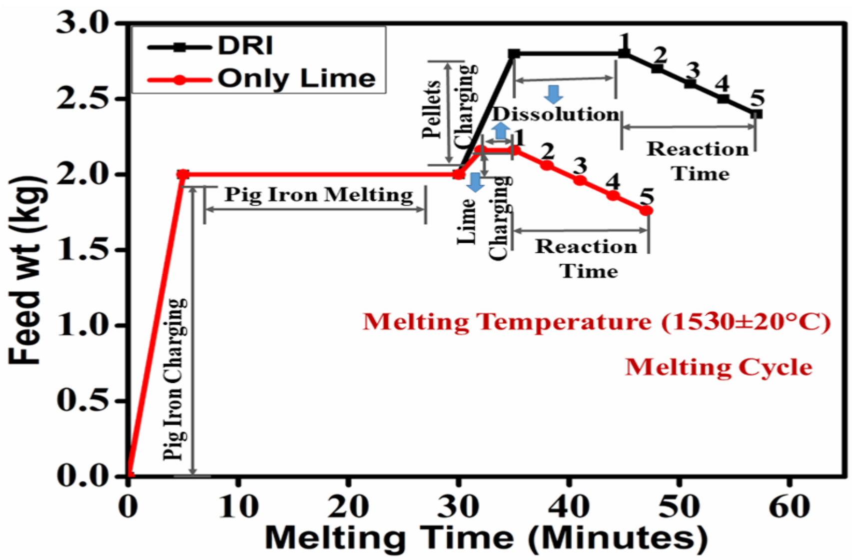

Figure-6.10 Melting cycle used for the experiment

First of all pig iron (2kg) was charged in the furnace to make a pool of molten metal. After complete melting of pig iron, fluxed DRI pellets (0.8kg) were charged continuously in the molten pool of pig iron. Fluxed DRI Pellets had taken ~10 minutes time for the complete dissolution in the pig iron melt. After complete dissolution of reduced fluxed iron ore pellets in the melt, samples were taken out at an interval of 3 minutes time up to 15 minutes exposure for kinetic study of impurities removal. A similar procedure for melting and sampling was followed in all cases of melting keeping constant melt‘s temperature 1530±20°C.

After cooling samples were prepared by cutting, grinding and polishing for their chemical analysis using Foundry Master Spectroscopy/ Optical Emissions Spectroscopy. Result are shown in **Table-6.7.**

6.6. RESULTS AND DISCUSSION

6.6.1 EFFECT OF DIFFERENT %R FLUXED DRI ON REMOVAL OF IMPURITIES

Chemical composition analysis of samples which was taken after 15 minute reaction time is given in **Table-6.7.**

Table-6.7 Chemical analysis of different heat products after 15 minute reaction time

Elements	Pig Iron (wt.%)	**Heat-1** (50%R-DRI)		**Heat-2** (80%R-DRI)		**Heat-3** (Only Lime)	
		Final (wt.%)	Removal (%)	Final (wt.%)	Removal (%)	Final (wt.%)	Removal (%)
C	3.83	0.05	98.69	1.13	70.50	3.26	14.88
Si	2.36	0.01	99.58	0.02	99.15	0.46	80.51
Mn	0.46	0.04	91.30	0.09	80.43	0.36	21.74
P	0.11	0.05	54.55	0.09	18.18	0.11	0.00
S	0.12	0.07	41.67	0.04	66.67	0.02	83.33

Figure-6.11 shows the effect of different %R fluxed DRI on the elimination of impurities from the pig iron for 15 minutes reaction time. Reactions involved in the elimination of impurities from the pig iron is discussed in previous section (melting with electric arc furnace) from **Equations 6.1 to 6.8**. Similar types of reaction take place in all steel making technologies. The amount of removal depends on the provided condition during the operation and charged material. In the previous section only different %R fluxed DRI were used to study the removal of impurities. Here one more thing is added that is use of lime in free form to know the effect of in-situ lime (synthetic slag) and free lime on the removal of impurities.

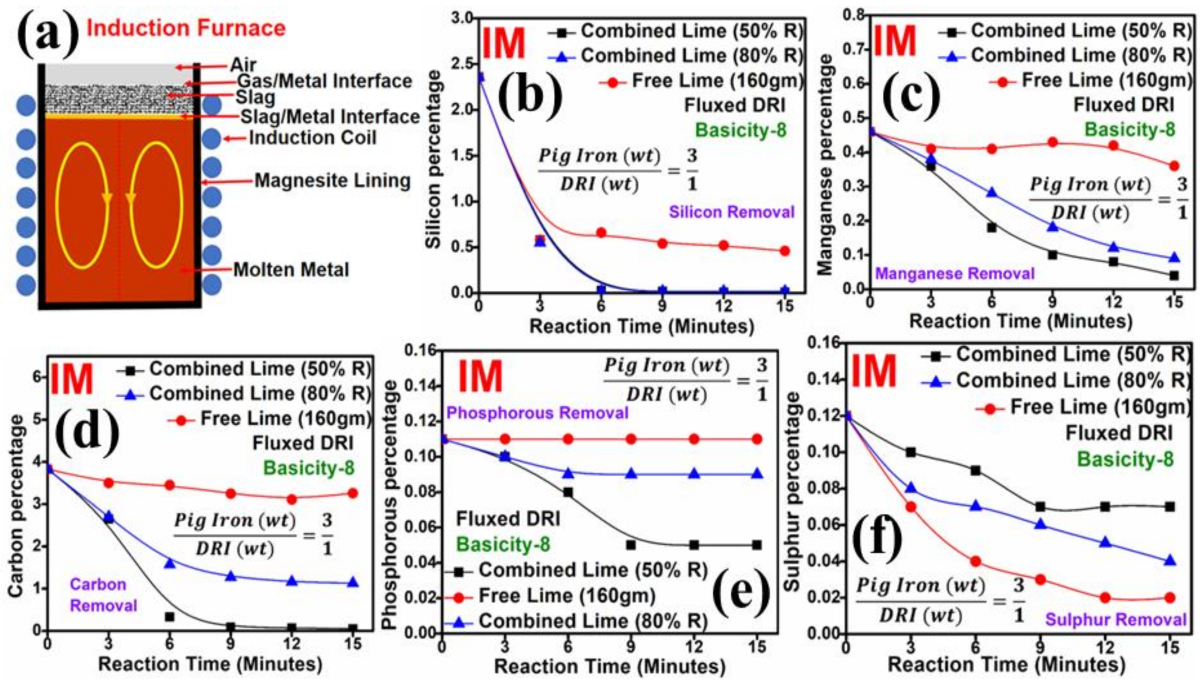

Figure-6.11 Behavior of removal of impurities with reaction time under different conditions during electric induction melting: a) Melting conditions; b) Silicon; c) Manganese; d) Carbon; e) Phosphorus; f) Sulphur

Figure-6.11(a) shows the theoretical separation arrangements of different layers in the air induction melting process. **Figure-6.11(b)** shows the removal of silicon from the pig iron melt. Trends of removal of silicon is similar for the 50 and 80%R fluxed DRI while it is different for the only lime charging. The silicon removal trends are similar to the melting in EAF. Partially reduced fluxed DRI have some amount of oxygen in the form of iron oxide which oxidizes silicon in to silicon oxide but in the case of only lime powder addition as such there is no source of oxygen available for the oxide formation, therefore silicon only reacts with oxygen of the open atmosphere exists above the melt which removed and rest remains in the melt. **Figure-6.11(c)** shows the removal of manganese. It is evident from the figure that partially reduced fluxed DRI is more favorable for the removal of manganese compared to the alone lime powder addition. In this case also similar behavior is responsible like silicon removal. **Figure-6.11(d)** shows the removal of carbon from the melt. Removal of carbon is observed highest in the case of 50% reduced flux DRI and it is negligible in the case of only lime powder charging. Here trends are different compared to the silicon and manganese because they can react with the oxygen of the environment but carbon cannot react with it. For the formation of carbon monoxide or carbon di oxide (gas bubble formation) some sites are required therefore it will take some extra time. In the case of 50%R fluxed DRI almost carbon is removed due to presence of sufficient amount of oxygen. One thing is very clear from this result that for the removal of carbon the presence of oxygen source is necessary without it carbon cannot be removed significantly. **Figure-6.11(e) and (f)** show very interesting results**.** **Figure-6.11(e)** shows the removal of phosphorous from the melt. In the case of only lime charging no phosphorous removal takes place it means only basicity is not responsible for the removal of phosphorous from the melt. The sufficient amount of oxygen as FeO in the melt is necessary with basicity. Removal of phosphorous is observed good enough in the case of 50%R fluxed DRI compared to two others melts because only lime creates oxygen deficient condition while 80%R fluxed DRI provides in sufficient amount of oxygen inside the bath. **Figure-6.11(f)** shows the removal of the Sulphur from the melt. It is observed from the figure that the removal of Sulphur is very effective in the presence of only lime charging it means there are no need of oxygen potential for the removal of Sulphur, only high basicity can remove Sulphur significantly from the melt. Increasing %R (i.e.>80%R) in fluxed DRI may be favorable for the removal of Sulphur in the presence of high basicity.

6.6.2 EFFECT OF REACTION TIME ON REMOVAL OF IMPURITIES

Figure-6.11 was also used to know the effect of reaction time on the removal of impurities (i.e. C, Si, Mn, S, and P) from the pig iron. **Figure-6.11(b)** shows the trends for removal of silicon from pig iron using different melting conditions. It was observed from the figure that silicon removed in the first six 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 shows different trends than silicon which shown in **Figure-6.11(c).** Removal of manganese is continuous for the partially reduced fluxed DRI charging while no manganese removal took place for charging only lime. In the case of carbon, trends were different. From **Figure-6.11(d)** it was evident, for 50%R fluxed DRI carbon removes up to 6 minutes afterwards it becomes constant but for 80%R fluxed DRI feed it decreased continuously up to 15 minute reaction time. It may be deceased to a lower extent value by increasing reaction time. The removal of carbon is negligible in the case of only lime charging even up to 15 minutes reaction time. The removals of Phosphorus and Sulphur were quite interesting. **Figure-6.11(e)** shows, phosphorus removed in 9 minutes reaction time for 50%R fluxed DRI due to availability of sufficient oxygen while in the case of 80%R fluxed DRI and only lime charging it is almost constant up to 15 minute reaction time due to insufficient amount of oxygen. **Figure-6.11(f)** shows, Sulphur removal was seen up to 9 minutes reaction time for 50%R fluxed DRI feed. In the case of 80%R fluxed DRI Sulphur removal was observed from the starting and it was continuously removed up to 15 minute reaction time. But, in the case of only lime charging, Sulphur almost removed up to 12 minutes reaction time. In this case amount of oxygen is negligible 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-6.11(e) & (f)** showed the reverse behavior. In the case of only lime charging Sulphur removed effectively with a negligible amount of phosphorous. This is a clear cut indication that the effect of oxygen potential in slag as (FeO) is there, responsible for removal of Sulphur and phosphorus.

6.6.3 EFFECT OF EXPOSURE TIME ON RATE OF REMOVAL OF IMPURITIES

Figure-6.12 shows the rate of removal of impurities from pig iron using different %R fluxed DRI and free lime addition respectively for 15 minute reaction time.

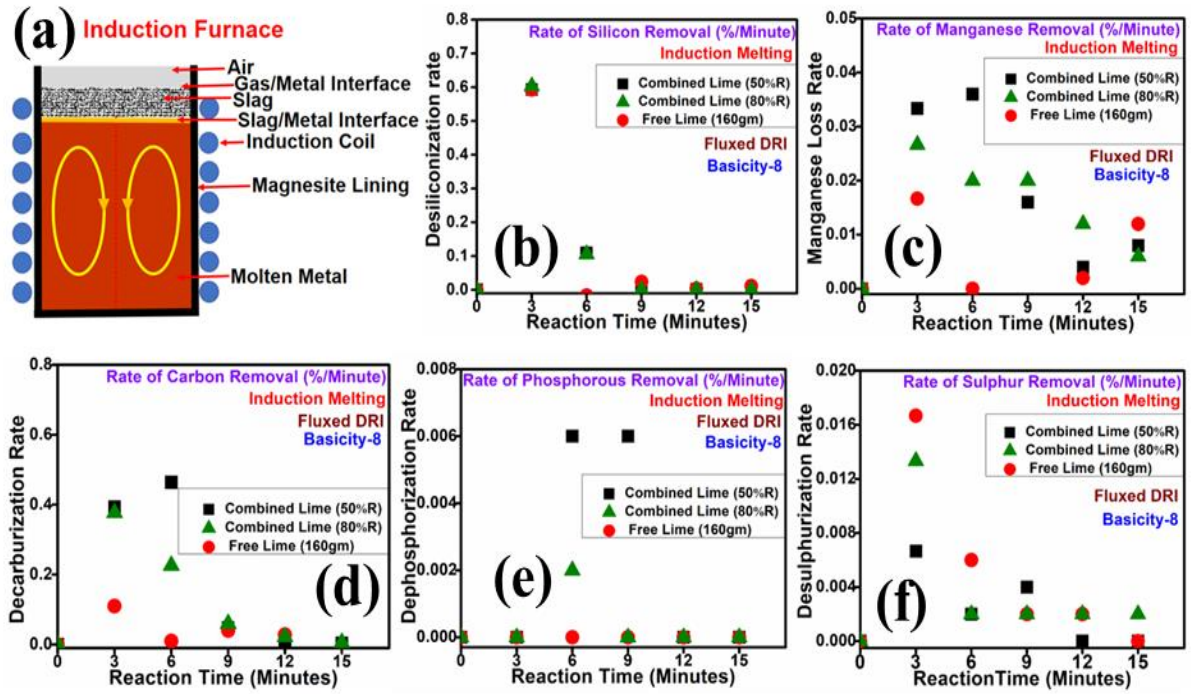

Figure-6.12 Rate of removal of impurities (%/minute): a) Ind. F/C; b) Silicon; c) Manganese; d) Carbon; e) Phosphorus; f) Sulphur

Figure-6.12(a) is the schematic diagram of melt's conditions during melting in induction furnace. **Figure-6.12(b)** shows the rate of removal of silicon. From the figure, it was evident that the rate of removal increased up to 3 minute reaction time afterwards it decreased. It means the maximum amount of silicon removed in three minutes. This reflects that silicon reacts instantaneously with the oxygen of the iron oxide phase and joins with 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 3-minute exposure time. **Figure-6.12(c)** shows the rate of removal of manganese. Rate of manganese removal doesnot follow a regular trend like silicon removal. It was observed that the maximum rate obtained in three minute exposure time during melting for the addition of only lime and 80%R fluxed DRI, afterwards it decreased. For 50%R fluxed DRI rate of removal of manganese is increased up to 6 minute reaction time afterward it decreased. It may be due to presence of oxygen in the partially reduced fluxed DRI.

Rate of carbon removal shown in **Figure-6.12(d).** The rate of carbon removal for only lime and 80%R fluxed DRI is maximum at 3 minutes afterwards it decreased. For 50%R fluxed DRI, rate of removal of carbon increased up to 6 minute reaction time afterwards decreased. Again it may be due to presence of sufficient amount of oxygen in the bath due to 50%R fluxed DRI. For the carbon reaction, some nucleation side is necessary; therefore, it will take a longer time in the case of 50%R fluxed DRI compared to 80%R fluxed DRI and only lime feed material. The rate of removals of phosphorus and sulphur are quite impressive. **Figure-6.12(e)&(f)** show the rate of removal of phosphorus and sulphur, respectively. Rate of phosphorus removal was increased up to 6 minutes for all heats afterwards decreased while for 50%R fluxed DRI rate of phosphorus is maximum up to 6 minute reaction time. Rate of sulphur removal is very sluggish for 50%R fluxed DRI while for 80%R fluxed DRI and only lime powder charging, it is very impressive in early 3 minutes afterwards decreased.

6.6.4 EFFECT OF %R FLUXED DRI ON RATE OF REMOVAL OF IMPURITIES

Figure-6.13 shows the effect of different %R fluxed DRI on the rate of removal of impurities from the pig iron melt for induction melting.

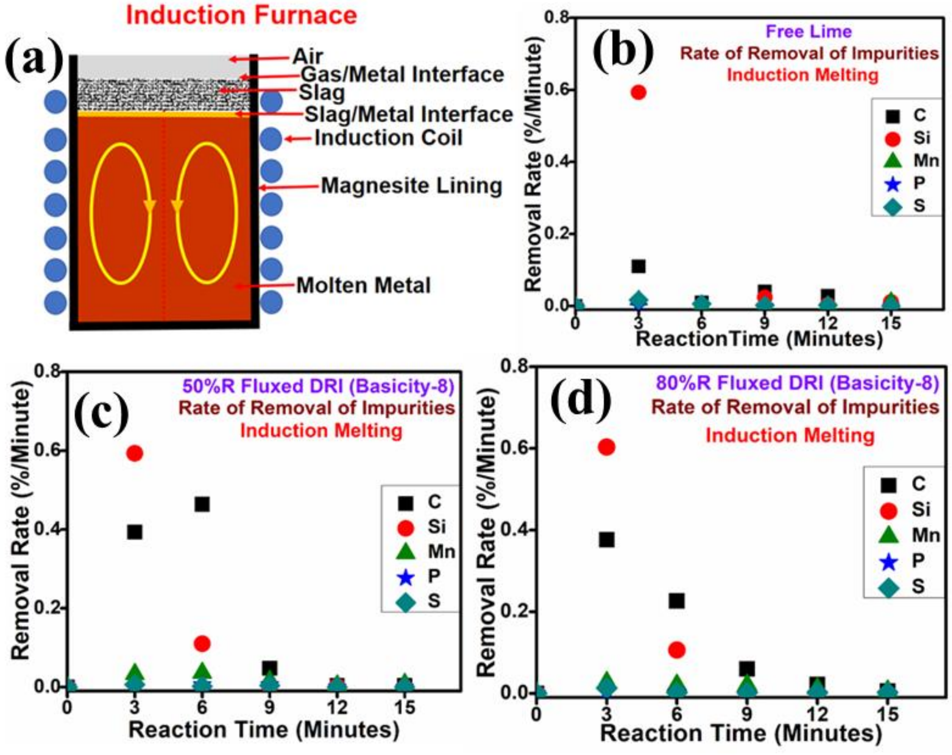

Figure-6.13 Rate of removal of impurities (%/minute) for different % R fluxed DRI feed: a) Ind. F/c; b) only free lime; c) 50%R fluxed DRI; d) 80%R fluxed

Figure-6.13(a) shows the systematic representation of melt's conditions of induction furnace during air melting operation. **Figure-6.13(b)** shows the rate of removal of impurities from the pig iron using only free lime addition as feed material. It was evident from the figure that the rate of removal of impurities increased up to 3 minutes afterwards decreased. The order of the rate of removals followed as Si>C>S>Mn>P. **Figure-6.13(c)** shows the rate of removal of impurities from the pig iron using 50%R fluxed DRI addition. In this case, the rate of removal of impurities (i.e. Si, Mn, S, P etc.) is maximum in 3 minutes except carbon removal. The rate of carbon removal increased up to 6 minutes reaction time it may be due to presence of sufficient amount of oxygen in the bath. It may be due to decrement in oxygen content of feed material or by increment in the metallic value of fluxed DRI. CO bubble formation required a nucleation site after that it become stable and grows, this process required some time because in the initial stage there were no interface available for the nucleation of CO gas. **Figure-6.13(d)** shows the rate of removal of impurities for 80%R fluxed DRI. In this case, trends in rate were quite different. The rate of silicon removal is similar to previous heats. But, the rate of carbon removal is maximum at 3 minute reaction time afterwards decreased, it may be due to presence of insufficient oxygen in the bath after 3 minutes. Due to the insufficient amount of oxygen in the bath, the rate of phosphorus removal was also observed negligible**.** Rate of manganese removal decreased as compared to the 50%R DRI feed but higher than the only lime charging heat. Rate of manganese also increased up to 3 minutes afterwards decreased. Rate of sulphur removal is higher in the case of 80%R DRI as compared to the 50%R DRI because of insufficient oxygen in the previous case. But rate of sulphur removal is almost similar in the case of only lime charging and 80%R fluxed DRI.

6.7. FINDINGS

Following conclusions may be drawn based on the present study:

- It can be found that, addition of lime in the melt effectively removes only sulfur while the addition of reduced fluxed iron ore pellets (DRI) can remove both sulfur and phosphorous simultaneously.

- Less reduced fluxed DRI pellets provide high oxygen potential as compared to high reduced fluxed pellets in the system which removes phosphorous efficiently as compared to sulfur.

- An effective removal of sulfur, phosphorous and carbon was observed in a single step of melting while using 50%R fluxed DRI pellets. This process needs to be optimized for the refining of pig iron melt for steel making.

6.8 EXPERIMENTS WITH PLASMA ARC MELTING

This work aims to study the influence of plasma environment and mode of lime charging on the removal of impurities from the pig iron during electric arc furnace steelmaking using fluxed DRI.

6.8.1. RAW MATERIALS AND THEIR PREPARATION

Raw materials used in the present study are lime powder, (80%R) fluxed DRI pellets and pig iron which are shown in **Figure-6.3**. The chemical composition of raw materials was analyzed and reported in **Table 6.1**. Details of the charge mix composition used for the present heats are shown in **Table-6.8.**

Table 6.8 Details of the charge mix composition used for different heats

Parameters	**Heat-1**	**Heat-2**	**Heat-3**	**Heat-4**
Pig Iron	1000	1000	1000	1000
Lime Mode for 8-Basicity	Fluxed DRI	Powder	Fluxed DRI	Fluxed DRI
80%R Fluxed DRI (g)	400	-	400	400
CaO (g)	80	80	80	80
Plasma Type	Nitrogen	Nitrogen	Hydrogen	Air
Total Charge wt. (g)	1400	1080	1400	1400

6.8.2 PLASMA ARC MELTING

There were total four heats were taken by using different plasma environment in an indigenously fabricated laboratory scale 2 kg arc furnace, including one heat by lime powder addition. **Figure-6.14** shows the melting cycle used in the current work. In all 4 heats, pig iron was used to prepare molten metal pool of 1kg in the first step followed by charging either 80%R fluxed DRI or lime respectively.

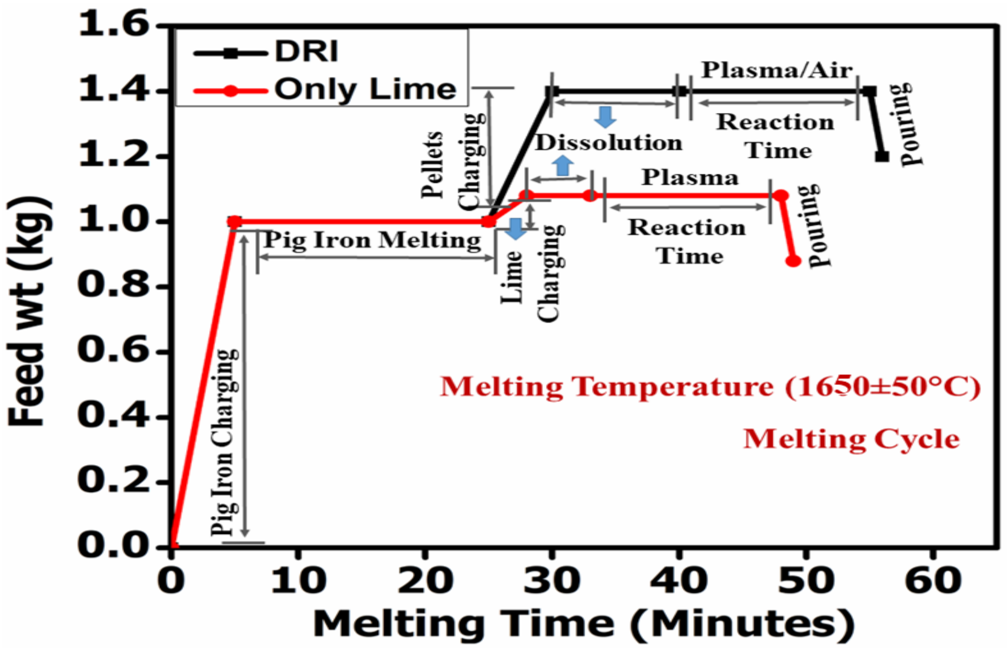

Figure-6.14. Melting cycle used for the present study

In the first step small pieces of pig iron scrap was charged batch wise in the crucible of electric arc furnace to prepare molten metal pool of 1 kg each for all four heats separately. Solid graphite electrode was used only to melt down the pig iron and fluxed DRI/Lime charged in the crucible of the furnace. Solid graphite electrode was changed after melting of pig iron and fluxed DRI/Lime by replacing it with hollow graphite electrode where gas (i.e. N_2, H_2) is passed through it for generation of plasma environment at the bottom near arc zone over the metal pool.

Figure-6.15 shows the schematic diagram of plasma setup and different interphases formed during steel making. It was taken 20 minutes time to melt 1 kg pig iron in normal arc condition of EAF.

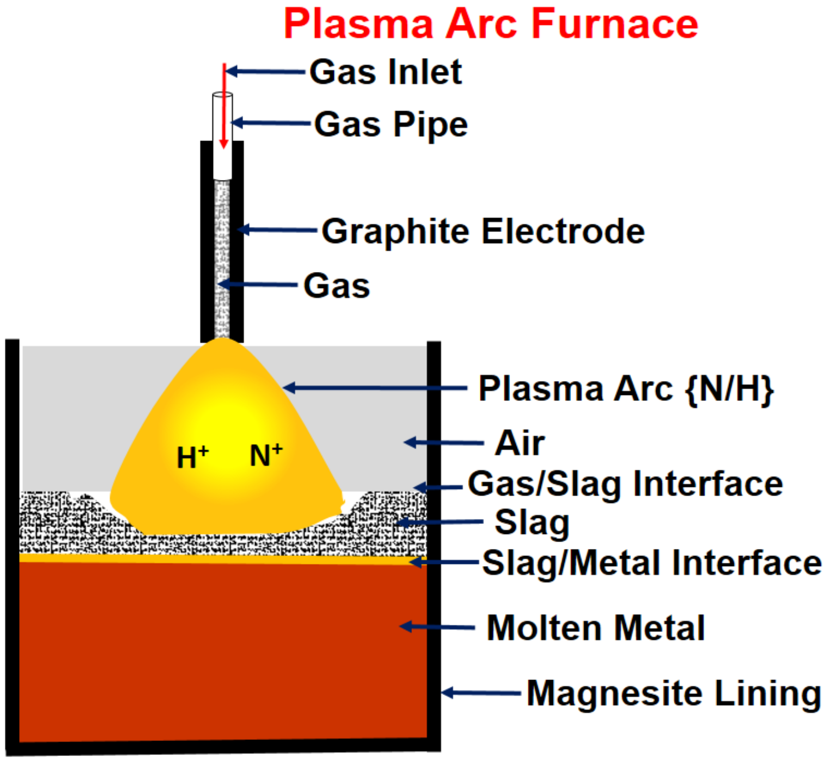

Figure-6.15. Schematic diagram of plasma arc furnace setup and Different interphases arrangements during steelmaking

After complete melting of pig iron, in the first heat 80%R fluxed DRI was charged continuously in the molten metal pool and completed the melting operation.

After complete melting of 80%R fluxed DRI, nitrogen plasma was created inside the furnace by changing solid graphite electrode with hollow graphite electrode as shown in **Figure-6.15**. Due to creation of plasma (i.e. ionization of gas molecules) it increases the temperature of the bath up to 1600±50°C (1873±50°K). This process was continued up to next 15 minutes and afterwards melt was poured in to mold of graphite block. Finally, an ingot of the required shape was obtained.

In the second heat, similar procedure was adopted to make molten metal pool of pig iron. Free lime was charged in the powder form at the place of fluxed DRI in the molten metal pool followed by nitrogen gas flow and rest other steps were similar to first heat. In the third heat again molten metal pool of pig iron was made by similar procedure. 80%R fluxed DRI was charged in the molten metal pool followed by hydrogen gas at the place of nitrogen gas for the plasma formation. In the fourth heat molten metal pool of pig iron was prepared by adopting similar procedure. 80%R fluxed DRI was charged in the molten metal pool without any plasma atmosphere. Reaction time in all four heats was maintained constant i.e. 15 minute. In all the heats, the input of CaO (either free or combined) and FeO content (in DRI) was the same, but different environments above the molten pool were maintained inside the furnace by passing different plasma gases (i.e. nitrogen, hydrogen) and open atmosphere respectively. After cooling samples (ingots from graphite mold) were prepared by cutting, grinding and polishing for chemical analysis using foundry master (model WAS, 01J0054).

6.9. RESULTS AND DISCUSSION

Elemental analysis of each heat was done with the help of foundry master and given in **Table-6.9.**

Table 6.9 Initial and final elemental analysis of samples (wt. %)

Elements	Pig Iron	Heat-1, Nitrogen (80%R DRI)		Heat-2, Nitrogen (Lime Powder)		Heat-3, Hydrogen (80%R DRI)		Heat-4, Air (Normal Arc) (80%R DRI)	
		Final	**Removal (%)**	**Final**	**Removal (%)**	**Final**	**Removal (%)**	**Final**	**Removal (%)**
C	3.83	2.02	47.26	3.49	8.88	1.16	69.71	2.45	36.03
Si	2.36	0.01	99.57	0.20	91.52	0.01	99.57	0.03	98.72
Mn	0.46	0.03	93.48	0.31	32.6	0.08	82.61	0.10	78.26
P	0.11	0.11	0.00	0.11	0.00	0.11	0.00	0.09	18.18
S	0.12	0.02	83.33	0.01	91.67	0.02	83.33	0.08	33.33

6.9.1 EFFECT OF PLASMA ENVIRONMENTS ON REMOVAL OF IMPURITIES

Behavior of removal of impurities after 15 minute plasma exposure time under different plasma conditions during melting in electric arc furnace, is shown in **Figure-6.16.**

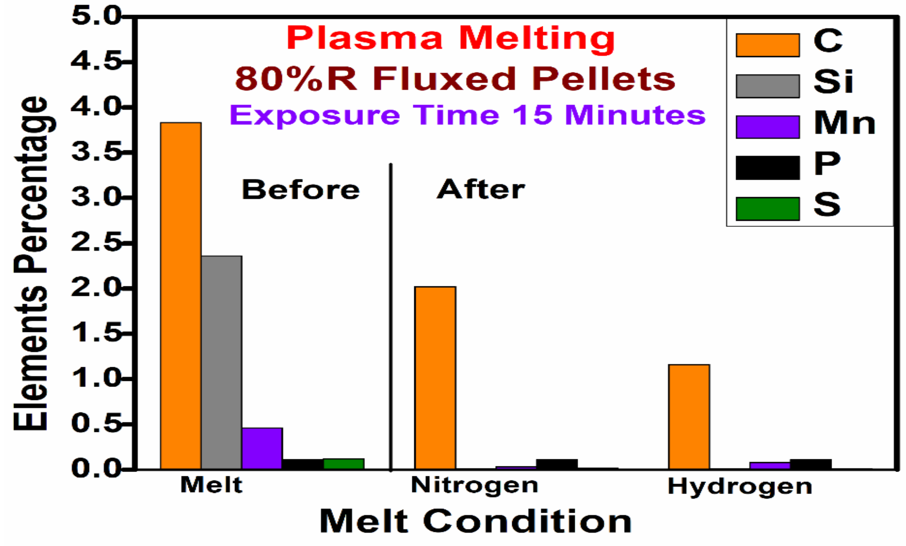

Figure-6.16. Behavior of removal of impurities under different plasma conditions during melting in electric arc furnace

In this figure chemical composition of pig iron before and after addition & exposure of melt are shown. In this figure effect of plasma environment on the removal of impurities from the pig iron melt using 80%R fluxed DRI (in-situ lime charging) is shown. From the figure, it is depicted that the removal of carbon is higher in the case of hydrogen plasma as compare to nitrogen plasma. It may be due to formation of some hydrocarbons in the presence of hydrogen plasma gas. Removal of Sulphur is very high in both cases. It may be due to the deficiency of oxygen content above the melt due to presence of hydrogen (reducing) and nitrogen (inert) plasma environment as well as the presence of high basicity with the addition of 80%R fluxed DRI. Nitrogen gas provides the inert atmosphere above the melt and stops the contact of furnace chamber’s oxygen to the melt and hydrogen creates reducing conditions which are very prompt for the removal of Sulphur. Silicon is removed about 99% in both the cases it means silicon reacted with the atmospheric oxygen during pig iron melting before DRI charging due to its high affinity towards oxygen. Silica may be combined with lime of the fluxed DRI to form stable slag phase. Similar type of trends is observed in the case of manganese removal. Dephosphorization is not found in both cases, because of higher temperature of melt in the presence of plasma and deficiency of oxygen potential in the bath, which are necessary factors for phosphorous removal. Heat number-4 was taken in the open atmosphere (normal arc) to compare the results with others. In this case, neither phosphorous nor Sulphur removed significantly in 15 minutes reaction time. It was found from the comparative study that in all plasma exposure heat results were obtained far well than exposure of open atmosphere during melting.

6.9.2 EFFECT OF MODE OF LIME (IN-SITU/FREE) ADDITION ON REMOVAL OF IMPURITIES

Figure-6.17 shows the influence of the mode of lime charging, i.e. combined form

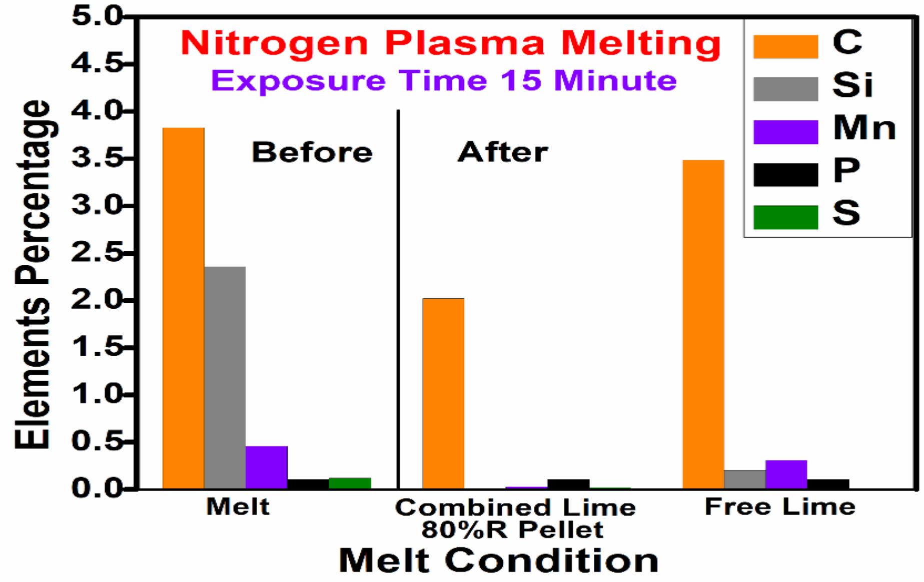

Figure-6.17. Behavior of removal of impurities under different mode of Lime charging during melting in electric arc under N2 Plasma furnace

(In-situ fluxed DRI) and free form (lime powder) on the removal of impurities from the pig iron in the presence of nitrogen plasma during EAF steelmaking.

It is observed from the results that in the case of free lime charging removal of carbon and phosphorus is negligible with significant removal of silicon and Sulphur. For the removal of phosphorous highly oxidizing conditions required inside the bath with low temperature. On charging lime in the powder form there was no oxygen available inside the bath therefore negligible removal of carbon and phosphorous was observed. From **Table-6.9** it is apparent in the case of combined lime (fluxed DRI), Sulphur was removed up to 83.33% while in the case of free lime powder addition it removed up to 92%. Removal of Sulphur and silicon were very effective in both cases. The removal of Sulphur may be due to the presence of high basicity, low oxygen potential and high temperature due to plasma which are necessary conditions for the desulphurization. In the case of 80%R fluxed DRI removal of carbon and manganese also significant with silicon and Sulphur. It may occur due to the presence of oxygen inside the 80%R fluxed DRI which were available in the combined form. Si>Mn>C>P>S, this is the sequence of deoxidizing capacity of the elements present in the molten bath. Silicon is the strongest deoxidizer amongst the all present elements therefore it reacted first with the available oxygen in the bath and make its stable oxide after that manganese and carbon reacted and make their respective oxides afterwards bath became oxygen deficient which favors the removal of sulphur from the melt.

6.10 FINDINGS

The variation of plasma gases and lime charging mode in liquid pig iron melt studies resulted following conclusions:

- Plasma environment is a beneficial technology to remove silicon and Sulphur from the pig iron melt by using highly reduced (>80%R) fluxed DRI.
- Mode of lime charging definitely affects the process of steelmaking during EAF.
- Sulphur could be removed to a deficient level (0.01%) using highly reduced fluxed (≥80%R) DRI of basicity (B-8) in the hydrogen plasma atmosphere.

6.11 TENTATIVE MECHANISM FOR THE REMOVAL OF IMPURITIES FROM PIG IRON DURING MELTING

Based on the above explanations, possible reactions and a tentative mechanism involved in different set of experiments for the removal of impurities during steelmaking process 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.) **Figure-6.18** shows the hypothetical diagram of distinct layers/interfaces which formed during the refining of steelmaking in open atmosphere melting.

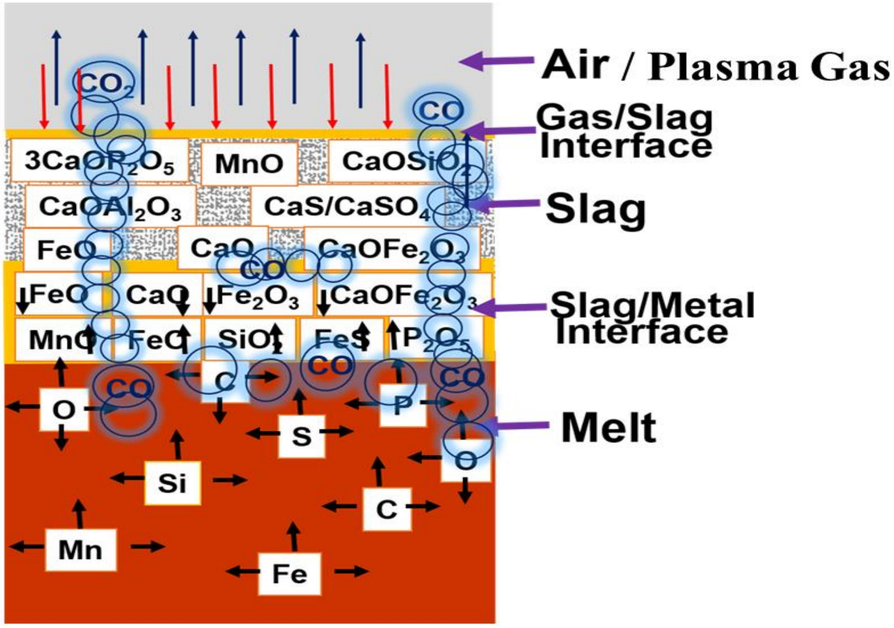

Figure-6.18: Schematic diagram of an imaginary distinct layers/interfaces, elements and reactions involved during removal of impurities from pig iron in an EAF.

Bulk Metal phase, Bulk Slag phase and Bulk Gas phase are present as layers in the melt chamber. There are some interfaces, like Metal/Slag interface, Slag/Gas interface and metal/slag/ crucible surface interface. The reactions happened at interface due to transfer of reacting species (reactants) from the bulk towards interface and products of reactions transferred towards bulk where product species absorbed by the different bulk (i.e. Metal, Slag and Gas). The presence of different reacting species (reactants) and products of reaction are in:

Pig iron Melt Phase: The presence of reacting species in pig iron melt are Fe, Si, Mn, C, S, and P.

Slag Phase: The presence of reacting species in fluxed DRI are CaO, FeO, Fe_2O_3, Fe_3O_4, SiO_2, Al_2O_3, CaS.

Gas Phase: O_2, N_2, H_2

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. 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. After silicon, manganese reacts with iron oxide to form manganese oxide and this combine with silica to make a slag phase. Carbon reacts in some different manner. During the removal of silicon and manganese, there were some nucleation sites for CO formation developed in the melt because without nucleation site gas bubbles cannot be formed therefore, carbon removal started after removal of silicon and manganese. Here whole liquid (metal/slag) is in contact with rough surface of crucible which provides nucleation sites for gas bubbles formation. Carbon removed in the form of gas (i.e. CO/CO_2) 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 be accelerated. Phosphorus also reacts with the oxygen of iron oxide to make its oxide (P_2O_5). These oxides joined lime to make its stable slag phase ($CaO.P_2O_5$). High oxidation potential is required in the bath for the removal of phosphorous in the presence of high basicity at lower temperature. According to literature amount of phosphorous removal increases up to 15% FeO amount in the slag afterwards it decreases. Therefore the presence of iron oxide phase in the slag is essential condition for the phosphorous removal. In the present study phosphorous removal was observed in the case of reduced iron ore charging only. There were no phosphorous removal was observed in the case of lime charging due to absence of iron oxide phase in the slag phase. The affinity of Sulphur towards iron is very high therefore, Sulphur found with iron in the melt. Iron sulphide reacts with calcium oxide slag to make a stable calcium sulphide slag phase. Highly reducing conditions is required in the bath for the removal of sulphur in the presence of high basicity at higher temperature. Sulphur removal is very effective in the case of only lime charging and highly reduced pellets (>80%R DRI) because there were oxidation potential is negligible due to insufficient amount of iron oxide present in the DRI while in the case of lower reduced DRI (30 and 50%R) removal of sulphur decreases due to presence of oxygen potential at higher temperature which is not favorable condition for the sulphur removal. 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 %R fluxed DRI as feed material. Conventionally, oxygen combined with the iron to form iron oxide (FeO) in the case of oxygen injection used during refining process, but in the present studies, there was no need for iron oxide formation during process, because it presents in the fluxed DRI. In the oxygen steelmaking technology first oxygen reacts with iron to form iron oxide which goes towards slag phase to make it oxidizing nature for removal of impurities. This iron oxide reacts with different impurities to form their respective oxide based on the removal conditions exist in the melt, but in the current study, iron oxide directly supplied in the form of DRI. 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 form of lump that took energy and time for dissolution, but in the current study lime was charged in the form of calcium ferrite, i.e. low melting constitute phase which will dissolve faster than lumpy lime therefore by charging lime in the form of fluxed DRI can minimized dissolution time which will again reduce the energy consumption and cost of the process.

6.12 MAJOR CONCLUSIONS ARE DRAWN FROM DIFFERENT MELTING STUDIES:

The addition of different %R fluxed DRI in liquid pig iron melt studies using different melting techniques resulted as following conclusions:

- Highly %R fluxed DRI pellets may be useful feed material for the removal of impurities from the pig iron.
- 30 and 50%R fluxed DRI pellets may be useful feed material for the removal of phosphorous with other impurities except Sulphur. Presence of oxygen in the form of iron oxide is favorable for creating oxidizing potential as well as high basicity in the bath which are responsible for the phosphorous removal.
- 80%R fluxed DRI pellets and only lime powder feed material are useful for the efficient sulphur removal with other impurities except phosphorous. 80%R fluxed DRI contains high amount of iron in the metallic form which may dissolve the present impurities and only lime creates the high basicity and neutral condition in the bath which is necessary for the sulphur removal.
- Presence of plasma gases changes the environment over the melt in the furnace, therefore it effects the removal of impurities from the pig iron. Sulphur could be removed to a deficient level (0.01%) using highly reduced (≥80%R) fluxed DRI which contains high basicity (B-8) in the hydrogen plasma atmosphere.
- Techniques of melting (Arc/Induction/Plasma) all follow the same pattern of the removal of impurities, only rate of removal of impurities varies with the melting techniques.