PREFACE

Steel is the largest produced alloy (1808 million ton in 2018) in the world and India occupies 2nd rank (106.5 million ton) among top ten global steel producers. Steel plants use considerable amount of lime (lumps / fines) as fluxing agent during steel making. The major steel plants have their own lime kilns for preparation of fresh lime to be used in-situ. The calcined lime storage is avoided due to its hygroscopic nature. However, smaller steel units do not have such facilities due to economic reasons. These small steel units (Electric Arc Furnace (EAF) / Air Induction Furnace (AIF)) procure lime as per their requirements from local lime calcination units. The lime being hygroscopic in nature tends to weather during its transportation and storage.

The difficulty of procuring fresh lime and its use by small steel units in India, whose number is very large, attracted the attention of some researchers in past. These workers developed fluxed iron ore pellets (Hollow Pellet), Fluxed Hardened Pellets and Fluxed Direct Reduced Iron (DRI). The aim of such studies, conducted during 1975-2020, was to prepare weather resistant fluxing material for steel making containing high lime.

The present work is an extension of work done in the past on the preparation of fluxed DRI pellets. In the present study fluxed pellets with high basicity (2 to 8) were made using waste fines of iron ore and lime. The hardened fluxed pellets were then reduced in bed of coal to yield Fluxed Reduced Iron Ore Pellets termed Fluxed DRI. This Fluxed DRI has been used to make steel in Electric Arc Furnace and Induction Furnace to render study relevant to small steel units in India. The Plasma Arc Melting using Fluxed DRI has been done for academic interest. In addition the fluxed DRI prepared in this study was tested for its weather resistant behavior also. All these studies are described in this thesis comprising seven chapters.

Chapter-1 comprises of a brief introduction on the Indian production of steel, iron ore and lime-stone. The generation of finer fraction of iron ore in large quantity is the driving force to promote iron ore pellet making. The generation of lime fines in steel plants during lime calcination has also been indicated. The extensive literature survey of studies made globally to utilize such solid waste (iron ore and lime fines) revealed that work has not been done extensively in the following areas:

- Lime fines utilization in iron ore pellets with basicity more than 2.
- Lime fines utilization in reduced pellets.
- Highly fluxed reduced pellets melting in (EAF) / (AIF)
- Weather resistance properties of highly flux hardened / reduced (DRI) pellets

In light of above information, the plan was made for present studies as:

a. Procurement and Characterization of raw materials e.g. Iron ore fines, Lime fines and coal.
b. Preparation and characterization of hardened pellets with high lime contents (Basicity-2, 4, 6 and 8)
c. Preparation of fluxed DRI with different %R from hardened iron ore fluxed pellets of different Basicity 2, 4, 6 and 8 followed by their characterization
d. Characterization for weathering behavior of highly fluxed hardened & reduced DRI pellets.

e. Utilization of different % reduction (R) fluxed DRI for removal of impurities from pig iron melt to make steel using (EAF) and (AIF) melting. Some melts made under Nitrogen plasma and Hydrogen plasma environment.

Chapter-2 deals with the characterization of the raw materials. In the present work, typical iron ore and lime fines, coal and pig iron were procured as raw materials for this study. The iron ore fines and coal fines were crushed and ground to 72 mesh (210µm) size and analyzed for particle size distribution. The chemical and phase analysis of iron ore fines were investigated using XRF and XRD. Data of the mineralogical composition indicated that the gangue is mainly present in the form of alumina (3.70 wt. %) and silica (2.94 wt. %). Proximate analysis of coal fines was done to determine the fixed carbon, volatile matter, moisture and ash content. Chemical analysis of lime was done by using XRF. The various studies resulted following observations:

Hematite present as the major phase (92.5 wt. %) in the iron ore with Silica (2.94 wt. %). Particle size of the iron ore is (<210 µm) with D_{10}-40µm, D_{50} -70µm, D_{90} -140µm values. CaO presents as major chemical constituent (95 wt. %) in the lime powder. Coal fines contain Carbon (62.5 wt. %), Volatile matter (14.7 wt. %), moisture (8.1 wt. %) and ash content (14.7 wt. %). These materials were used to prepare green pellets for further study.

Chapter-3 describes in detail for the preparation of green flux pellets, its hardening and characterization. There were five steps involved in the preparation of fluxed hardened pellets. Initially, iron ore and lime fines were weighed separately according to the required basicity (2, 4, 6, and 8). After weighing the raw materials, water was mixed in the lime to make a slurry and then it was mixed thoroughly with iron ore fines for making green pellets. In the 3rd step, pellets were made by hand rolling. Hand rolled pellets were spherical having approximately 18±1 mm diameter. The green pellets were air dried for one day for the removal of moisture and then put in the oven for 24 hours at 100 ± 5° C for drying (to remove surface moisture)A. The oven dried pellets were heat hardened in the muffle furnace at different temperature ie.1100°C, 1150°C, 1180°C and 1200°C separately for 1 hour. The hardened pellets thus made were tested for their properties as below:

The heat hardened pellets were tested for cold crushing strength test by using 100KN Instron Universal Testing Machine (Model UTM Instron: 4206, strain rate=0.1mm/minute). The pellet porosity and density were measured by Archimedes' Principle using the kerosene oil as a liquid media. Scanning Electron Microscope (SEM) study of pellets was done by using SEM Model ZEISS EVO-18, OXFORD instrument with software INCA ENERGY 300, acceleration voltage=20kV, beam current~5mA) used to identify the microstructure of the samples. X-Ray Diffraction (XRD) analysis of pellets was done with XRD unit (Model Rikagu Miniflex-600 model with Dtex ultra detector and Cu-Kα radiation λ=1.54nm, acceleration voltage=40kV, current=15mA) was used to determine the phases formed in the hardened pellets. Samples were scanned at the rate of 2 degree per minute from 15° to 90°.

From the various studies conducted on the preparation of green and hardened pellets following observations were noted:

Formation of calcium ferrite phases appeared to be responsible for strengthening of heat hardened fluxed pellets at 1100-1200°C temperature. The high basicity (Basicity-8) pellets with more than 100 kg/pellet crushing strength and 44% porosity were possible by firing at 1180°C for 60 minute. Higher firing temperature (1200°C for present study) rendered pellets with high strength (500kg/pellets) with poor (5%) porosity which may be undesirable for use.

These hardened pellets were used to study their reduction behavior which describe in the following Chapter-4.

Chapter-4 deals with the reduction behavior of hardened pellets to yield fluxed DRI. On the basis of pellets hardening study result (optimum strength-porosity combination), pellets hardened at 1180°C were chosen for the reduction study. The coal was used as a reductant. The experiments were carried out at four different reduction temperature (i.e. 900, 950, 1000 and 1050°C) for 30, 45, 60, 90 and 120 minutes reduction exposure time, respectively. Each experiment was performed for a single pellet in a single crucible under isothermal condition. Each highly fluxed hardened iron ore pellets was weighed and placed separately inside the bed of coal held in the GI (galvanized iron) crucible (60 mm height and 25mm inside diameter) which was covered with grog (crushed refractory powder) to prevent firing with coal. The crucibles containing pellet were kept inside the resistance furnace at the predetermined reduction temperature. After reduction, the crucibles were taken out from the furnace after a fixed interval of time. The same procedure was followed for all set of experiments. The degree of reduction (%R) was calculated using formula based on the weight loss obtained for the different set of experiments respectively. Scanning Electron Microscope (SEM) used to identify the microstructure of the fluxed DRI. X-Ray Diffraction (XRD) was used to determine the phases present in the fluxed DRI. Samples were scanned at the rate of 2°/ minute from 20° to 110°. The various studies resulted the following observations:

It is possible to prepare highly fluxed (8 Basicity) and reduced DRI (>80%R) when heated in coal bed at 1000°C reduction temperature for 60 minute time. Reduction temperature and pellet basicity both affected the reduction process. Higher reduction percent could be achieved by increasing the temperature (900-1050°C) with required reduction time for pellets having basicity (2 to 8). The fluxed DRI pellets were tested for its weathering behavior and described in Chapter 5.

Chapter-5 deals with weathering behavior of highly fluxed hardened / DRI. In this study fluxed hardened / reduced DRI pellets with 4, 6 and 8 basicity and 65-98 %R were selected. The pellets were first weighed and the diameters of each hardened/DRI pellet were measured. Then, these pellets were placed on glass dishes having identity code number. Glass dishes with hardened/DRI pellets were kept in a tray under ventilated cover to protect pellets from the dust. Room humidity and temperature were measured by hygrometer and thermometer. Weight and diameters of all pellets were measured at scheduled time interval up to 30 days. The moisture gain by fluxed hardened/DRI was noted by its weight gain and volume change was estimated by diameter change. The study resulted following observations:

Highly fluxed DRI could be stored for 30 days in open humid atmosphere (80±5% humidity at 30±5°C temperature) without pellet swelling or breaking. The maximum gain of weight by fluxed DRI due to moisture did not exceed 2% in 10 days open air (80±5% humidity 30±5°C) storage. Highly reduced DRI (basicity-8) indicated cracked after 30 days of prolonged storage. Hardened flux pellets can be stored for more than 60 days without any problem of cracking and swelling in an open humid atmosphere (80±5% humidity at 30±5°C temperature).

Chapter-6 deals with studies on use of fluxed DRI for Steelmaking. In this work, three type of melting techniques EAF/AIF/ Plasma Arc Furnace (PAF) were used to study the behavior of fluxed DRI in pig iron melt. On the basis of these three techniques this chapter is divided in three parts A, B and C, respectively. Higher basicity (B=8) fluxed DRI with different (%R) fraction were selected for the study. Fluxed DRI with 10, 20, 30, 50, 60, 70 and 80%R were used in the EAF melt. The steel making process involved making pig iron melt pool which contained 3.83% C, 2.36 % Si, 0.46 % Mn, 0.11 % P and 0.12 % S. The known weight of fluxed DRI pellets were charged in the pig iron melt pool and samples drawn out at schedule time interval. At the end remaining melt was poured out in the graphite mold. Steel samples prepared by cutting and grinding process was used for chemical analysis by Optical Emission Spectrometer. On the observation of these studies, 30, 50 and 80%R DRI were added to know the rate and kinetics of Si, Mn, C, P, S removal during electric arc steel making. The use of lower % R fluxed DRI resulted in high slag volume formed which may be a cause of slopping. In the case of Induction furnace melting free lime and combined lime present in the 50 and 80%R fluxed DRI were used. The net amount of lime charged was equal in both form. In plasma melting the nitrogen and hydrogen gases were used to create different type of environment (neutral and reducing) over melt pool. Mass balance and chemical analysis were done to know the effect of fluxed DRI on the removal of C, Si, Mn, P and S from pig iron melt. The addition of fluxed DRI in liquid pig iron melt studies resulted following observations:

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. The P removal occurred after silicon and manganese. The carbon removal was delayed may be due to CO gas nucleation and growth occurring on furnace walls. Sulphur was lowered in the melt may be due to dilution of melt by iron from fluxed DRI as well as absence of oxidizing slag. The quantity of fluxed DRI (%R) appeared to affect the kinetics of the removal of impurities significantly. Addition of fluxed DRI with lower %R rendered more oxidizing slag and promoted P removal while higher %R resulted more S removal. Use of plasma melt technique resulted more sulphur removal under hydrogen gas. Resulphurized grade steel can be directly produced by using 30%R fluxed DRI in electric arc furnace. The use of 30%R fluxed DRI pellets in electric arc furnace remove (C-98%, Si-99%, Mn-96%, P-66%, S-17%) while 50%R fluxed pellets remove (C-62%, Si-99%, Mn-87%, P-36%, S-50%) and 80%R fluxed DRI pellets remove (C-57%, Si-99%, Mn-78%, P-18%, S-58%). Use of 50%R fluxed DRI pellets in induction furnace remove (C-98.69%, Si-99%, Mn-91%, P-55%, S-42%) while use of 80%R fluxed DRI pellets remove (C-71%, Si-99%, Mn-80%, P-18%, S-67%) and only lime powder removes (C-15%, Si-81%, Mn-22%, P-0%, S-83%). Plasma furnace resulted high degree of sulphur removal from the melt. In case of 80%R fluxed DRI pellets addition with nitrogen plasma removal of sulphur is (83%), whereas for only lime powder charging it increases up to (S-92%). For the case of 80%R DRI pellets with hydrogen plasma and normal arcing condition the sulphur removal values are (S-83%) and (S-33%) respectively for 15 minute reaction time.

Chapter-7 describes achievements of the present studies as overall conclusions and scope of future works. The overall conclusions are:

- Waste iron ore and lime fines can be effectively utilized for preparing fluxed DRI pellets.
- The pellet heat hardening at 1180°C for 60 min provided optimum combination of strength and porosity which make it strong and reducible quality fluxed pellets.
- The hardened flux pellets could be reduced in the bed of coal to the different degree by providing required temperature and exposure time.

- The fluxed DRI pellets did not adsorbed more than 2% moisture when kept in humid atmosphere (80±5% humidity) at 30±5°C for more than 10 days. Thus, fluxed DRI proved a safe method for lime storage and transportation.
- Fluxed DRI quality (%R) affects the rate of C, Si, Mn, P & S removal from the pig iron.
- The preparation of low carbon (0.23%), Silicon (0.01%), Mn (0.02%), P (0.04%) and S (0.1%) steel was possible in this study using fluxed DRI pellets.
- Fluxed DRI pellets may be useful as flux feed in EAF & AIF steelmaking to provide basic slag.

The scopes of future work are:

1 Double fluxed DRI pellets charging practice may perform in the future for the effective removal of phosphorous and sulphur simultaneously from the melt. Pellets reduced less than 50%R favor the removal of phosphorous while >80%R can be used to control the sulphur. Thus, in the initial 50% reduced pellets could be charged, after removing slag than 80% reduced pellets should be charged in the melting pool.

2 Plasma technology may be a good scope for the future work. Results obtained during the plasma melting are very interesting. To study the kinetics of the removal of impurities from the melt during plasma melting, more experimental work is required in highly controlled way.

At the end of the thesis, references used in the text are presented in well-arranged way.