## 3.1 INTRODUCTION

A major amount of iron ore and lime fines generation gives an opportunity to make a suitable charge material used for the steel making. Fines as charge materials cannot be directly used either in iron making or steel making processes [84]. There is an appropriate size requirement to charge in the furnace for smelting. Fines which are greater than 3mm can be converted in to lump form by agglomeration process (i.e. sintering process). Fines which are less than 3mm converted into fines (powder) by grinding into desirable size for pellet making. Highly fluxed iron ore pellets can be made by using these fines material. Hardening is the process of heating the iron ore flux pellets at higher temperature without sticking each other for a optimum time to obtain desired properties. Strength and porosity are two important properties of the hardened flux pellets [86]. There are new phase emerges during hardening process in the presence of slag forming constituents like silica, alumina, lime etc. The strength requires for the transportation and porosity necessary for the reduction of pellets. Formation of different crystalline phases of iron silicates, calcium ferrite and phase transformation of iron which are responsible for the crushing strength and porosity in the pellets. For the production of desired quality pellets, it is necessary to know the types of bonds and crystalline phases emerged during the hardening process.

## 3.2 EXPERIMENTAL

In this section all experiments which were conducted to know the optimization parameter of hardening process is explained in detail. **Figure-3.1** shows the process flow chart for preparation and characterization of highly flux hardened iron ore pellets.

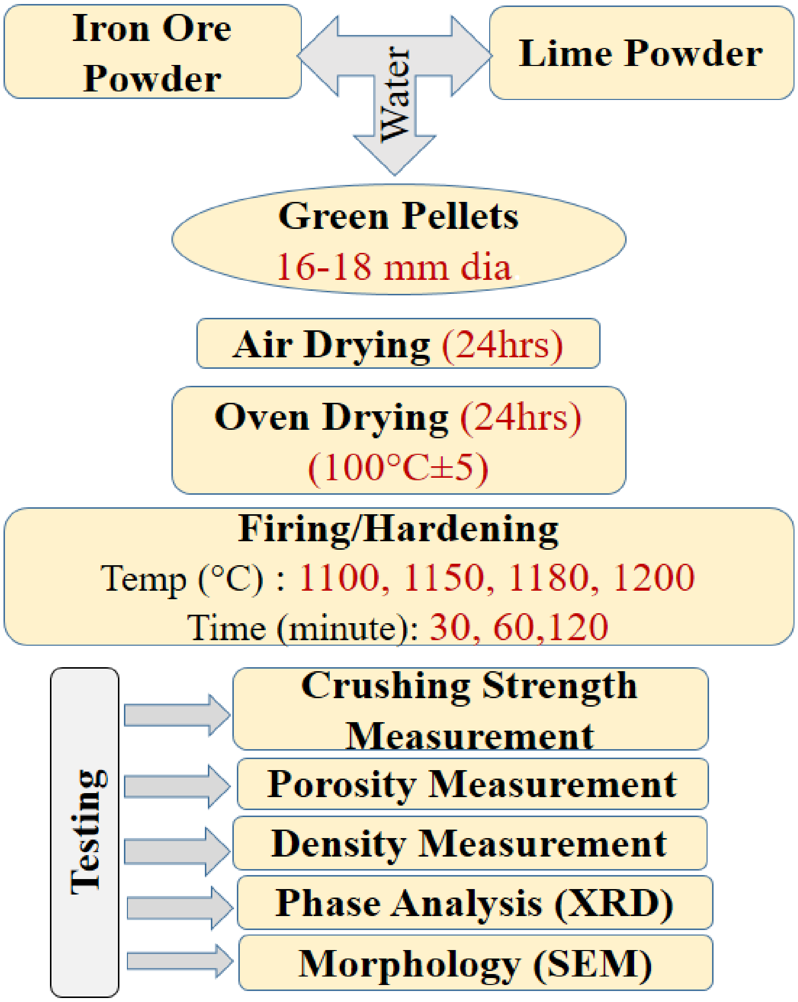

**Figure 3.1** Flow chart for preparation and characterization of highly flux hardened iron ore Pellets

### 3.2.1 PELLET PREPARATION

In the present work, iron ore and lime fines (-72 mesh/-0.2mm) were used as raw materials. There were several steps involved in the fluxed pellet making. Initially, the quantities of iron ore and lime fines were weighed separately according to obeying quantity mentioned in **Table 3.1** for the required basicity (i.e. 2, 4, 6, and 8). Before mixing, the lime was heated up to 1000°C temperature for eliminating residual carbonates and volatile constituents. The theoretical composition of the iron ore flux pellets with different basicity is shown in **Table-3.1.**

**Table-3.1** Theoretical Composition of the iron ore flux pellets

| Basicity ($CaO/SiO_2$) | Wt. % | ~2 | ~4 | ~6 | ~8 |
|---|---|---|---|---|---|
| Lime (g) | - | 6 | 11 | 15 | 20 |
| CaO (g) | 95 | 5.7 | 10.45 | 14.25 | 19 |
| Iron Ore (g) | - | 94 | 89 | 85 | 80 |
| $SiO_2$ | 2.94 | 2.76 | 2.61 | 2.5 | 2.35 |
| $Fe_2O_3$ (g) | 92.5 | 86.95 | 82.33 | 78.63 | 74.00 |
| $Fe_2O_3$/ CaO | - | 15.25 | 7.88 | 5.52 | 3.89 |

After weighing the raw materials, water was mixed in the lime to make cold slurry and then mix thoroughly with iron ore fines. In the final stage, pellets were made by rolling in hand. Hand rolled pellets were spherical having an approximate 18 mm diameter. **Figure-3.2** shows air dried flux iron ore pellets of ~18mm diameter.

**Figure-3.2** Air dried fluxed iron ore pellets

### 3.2.2 HARDENING OF PELLET

Hardening is a cycle of heating, holding and cooling. **Figure-3.3** shows the hardening cycle used in the current study.

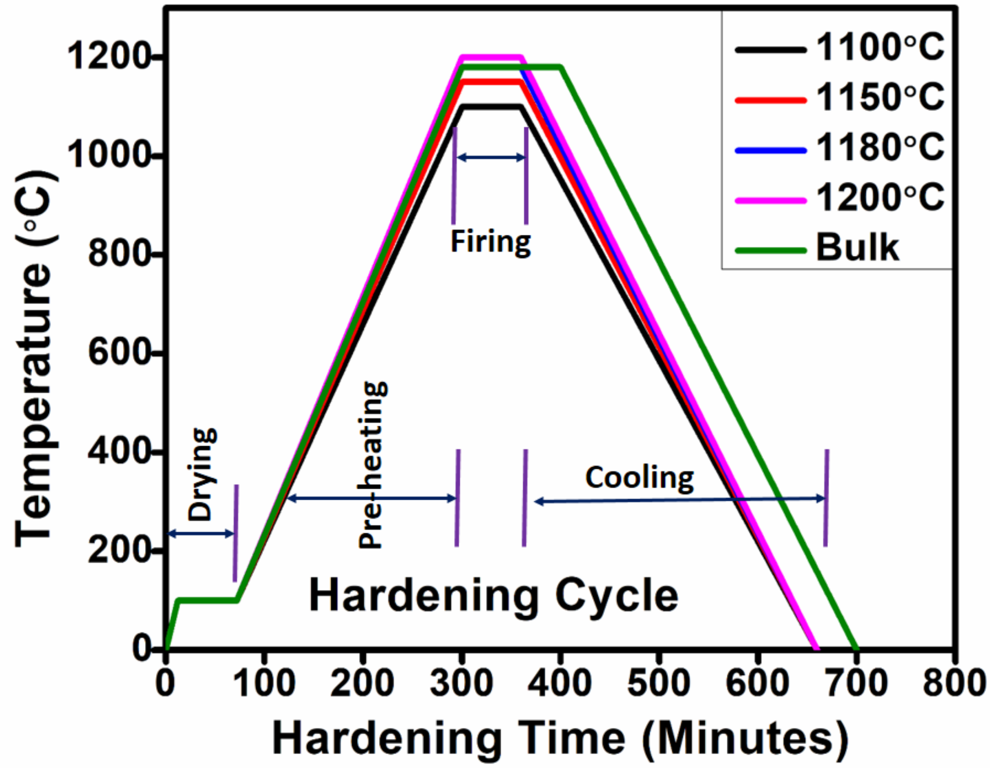

**Figure-3.3** Hardening cycle used for fluxed iron ore pellets

For the removal of moisture, green flux pellets were air dried for one day and then put in the oven for 24 hours at 100±5°C. The oven dried pellets were hardened to 1100°C, 1150°C, 1180°C and 1200°C separately for one hour inside a muffle furnace to obtain required properties in hardened flux pellets. Hardened pellets were taken out after furnace cooling. During hardening, no sticking was observed up to 1180°C, but pellets got agglomerated and stuck with each other and with inner surface of crucible when hardened at 1200°C. Hardening in bulk quantity (1Kg) was also performed in big crucible to obtained sufficient hardened flux pellets for further studies (i.e. for reduction studies). **Figure-3.4** shows the physical changes in the pellets before and after hardening process. Colour of the pellets changes from reddish brown to greyish black.

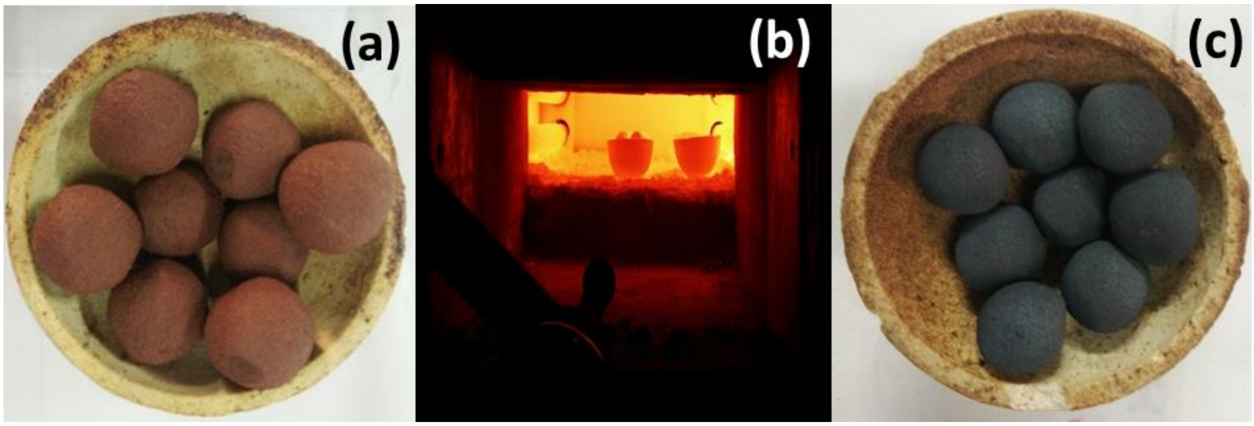

**Figure-3.4** Physical changes of iron ore pellet: a) Before hardening (Oven dried pellets); b) During hardening (In the Furnace); c) after hardening (Hardened pellets).

### 3.2.3 TESTING PROCEDURE OF HARDENED PELLETS

Now, hardened flux pellets are tested to optimize their different properties. The testing procedures are described in the following sub-section:

#### 3.2.3.1 Cold Crushing Strength

Crushing strength test was performed on a 100 KN screw-driven Instron Universal Testing Machine (Model UTM Instron: 4206, strain rate=0.1mm/minute) in the Mechanical Metallurgy Division of Department of Metallurgical Engineering, Indian Institute of Technology (BHU).Varanasi, India. 5 pellets of each hardening temperature were chosen for the cold crushing strength. There was no specific sample preparation methodology used for the crushing strength test. Pellet kept in the sample holder directly one by one under load. The average value of crushing strength is presented in Table 3.2.

#### 3.2.3.2 Porosity and Density Measurements

Porosity and density of pellets were measured by Archimedes' Principle using the kerosene oil as a liquid media in the Industrial Metallurgy Division, Department of Metallurgical Engineering, Indian Institute of Technology (BHU), Varanasi, India. 5 pellets of each hardening temperature were chosen for the study. First pellet is weighed in air (W1) then dipped in the kerosene oil for 24hrs. The kerosene oil action will cause expansion of air bubbles trapped in the pores and cause their expulsion. Kerosene oil enters into the pores to fill it. The weight (W2) of the kerosene oil-saturated sample is taken while dipped fully under kerosene oil. The pellet is now taken out and surface kerosene oil is removed by soaking with a cotton cloth. The weight of kerosene oil-saturated pellet is taken out in the air (W3).

Now, the weight of the kerosene oil absorbed in the open pores = (W3-W1)

The volume of kerosene oil absorbed in the pores = (W3-W1) /$\rho_{\text{kerosene oil}}$

Loss in weight of pellet due to buoyancy while being dipped in kerosene oil = (W3-W2)

Volume of pellet = (W3-W2) /$\rho_{\text{kerosene oil}}$

Hence,

Apparent porosity (%) = [(W3-W1)/(W3-W2)]*100

Apparent Density = W1/(W3-W2) g/cc

Average value of porosity and density of pellets given in Table 3.2

### 3.2.3.3 SEM Analysis

Scanning Electron Microscope (SEM) (Model ZEISS EVO-18, OXFORD instrument with software INCA ENERGY 300, acceleration voltage=20 kV, beam current~5mA) was used to identify the microstructure of the hardened highly flux iron ore samples. SEM analysis performed in Central instrument facility, Indian Institute of Technology (BHU), Varanasi, India. Broken piece of pellet after the compressive test was used to know the morphological changes with basicity and hardening temperature. Piece of the broken pellet was taken and flatted with the soft grinding. After grinding sample was coated with gold using sputter. This coating prevents charging of the specimen, which would otherwise occur because of the accumulation of static electric fields. It also increases the number of secondary electrons that can be detected from the specimen's surface in the SEM and therefore increases the signal to noise ration.

### 3.2.3.4 Phase Analysis

X-Ray Diffraction (XRD) (Model Rikagu Miniflex-600 model with Dtex ultra detector and Cu-Kα radiation λ=1.54nm, acceleration voltage=40 kV, current=15mA) was used to determine the phases present in the hardened highly flux iron ore pellets. Samples were scanned at the rate of 2 degree per minute from 15° to 90°. *Expert High Score* and *PCPDF* Software used to determine the phases of the material. XRD equipment was used for testing in the Structural metallurgy division of Department of Metallurgical Engineering, Indian Institute of Technology (BHU), Varanasi, India. Broken pellet after the compressive test was used for the XRD test. Broken pieces of pellets were crushed to make 200 mesh size powder. This fine powder was used to know the phases present in the hardened pellets.

## 3.3 RESULTS AND DISCUSSION

Results of the above mentioned tests are explained in this section. **Table-3.2** shows the density, porosity and crushing strength of the hardened pellets at different hardening temperature from 1100° to 1200° C. **Figure 3.5** shows the effect of basicity and temperature on the crushing strength, porosity and density of flux hardened pellets. Trends of the compressive strength with varying basicity and temperature are shown in **Figure-3.5 (a)**. The strength of the pellets for a fixed basicity increases with increasing temperature. At the temperature 1100°C, the strength of pellets varies from 22.56 kg/pellet to 14.59 kg/pellet while at 1150°C it varies from 77.94 kg/pellet to 50.60 kg/pellets for increasing basicity of pellets from 2 to 8. It means, for temperature 1100°C and 1150°C, the strength of pellets decreases with increasing basicity but in the case of 1180°C and 1200°C, the trends are different. At 1180°C for six basicity pellets, the strength of 99.33 kg/pellet may be achieved due to sintering or localized incipient fusion between particles. At 1200°C, strength increases from 153.90 kg/pellet to 458.63 kg/pellet for 2 to 8 basicity pellets respectively. There is a drastic change observed in the behavior of strength at 1200°C with basicity 8 because at high temperature (~1200°C) a semi-liquid phase formation starts which creates the most densified structure and provides the maximum strength to the pellet. At temperature 1200°C with eight basicity pellets, most of the particles converted into uniform globular shape which may be another factor for outstanding strength of the pellets.

**Table – 3.2 Properties of hardened flux pellets for different hardening temperature**

| **Basicity** | **Properties** | **Temperature (°C)** | | | |
|---|---|---|---|---|---|
| | | **1100** | **1150** | **1180** | **1200** |
| **~2** | **Density (g/cm$^3$)** | 4.24 | 4.39 | 4.43 | 4.61 |
| | **Porosity (%)** | 41.02 | 37.22 | 36.08 | 33.17 |
| | **Strength (kg/pellet)** | 22.56 | 77.94 | 81.62 | 153.90 |
| **~4** | **Density (g/cm$^3$)** | 3.99 | 4.07 | 4.18 | 4.47 |
| | **Porosity (%)** | 45.62 | 40.82 | 38.02 | 34.87 |
| | **Strength (kg/pellet)** | 20.67 | 64.43 | 69.53 | 167.30 |
| **~6** | **Density (g/cm$^3$)** | 3.56 | 3.68 | 3.80 | 4.51 |
| | **Porosity (%)** | 49.92 | 45.31 | 40.84 | 35.41 |
| | **Strength (kg/pellet)** | 16.54 | 53.34 | 99.33 | 187.63 |
| **~8** | **Density (g/cm$^3$)** | 3.43 | 3.59 | 3.67 | 5.58 |
| | **Porosity (%)** | 51.65 | 46.83 | 43.65 | 4.57 |
| | **Strength (kg/pellet)** | 14.59 | 50.60 | 103.10 | 458.63 |

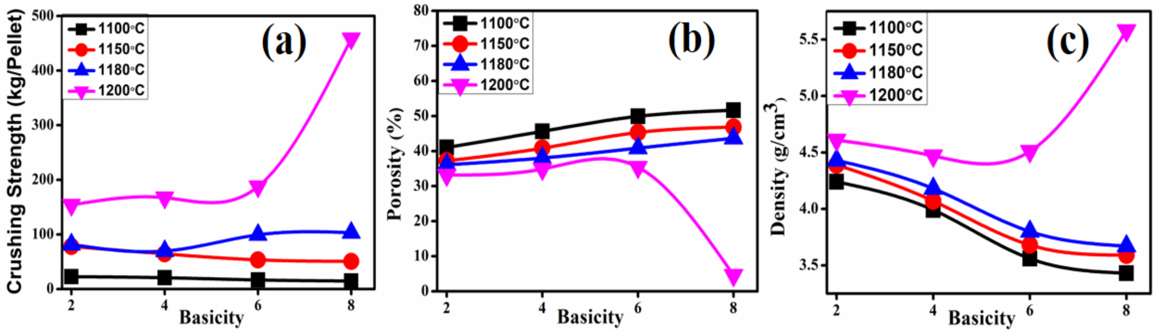

**Figure 3.5** Effect of basicity and temperature on properties of hardened flux pellets: a) Crushing strength; b) Porosity; c) Density

The trends of change in porosity and density with the basicity and temperature are shown in **Figure-3.5 (b) & (c)** respectively. The porosity of the pellets increases from 41.02% to 51.65% at the temperature of 1100°C for 2 to 8 basicity pellets. Similarly, at 1150°C and 1180°C temperature, porosity of pellets increases from 37.22% to 46.83% and 36.08% to 43.65% respectively. But in the case of hardening temperature at 1200°C, porosity trends of pellets are different. Initially, porosity of pellets increases from 33.17% to 35.41% with increasing basicity from 2-6, but afterwards porosity of pellets decreases drastically to 4.57% for basicity 8. Values of porosity decrease for all the basicity pellets on increasing hardening temperature. The density of the pellets decreases from 4.24 to 3.43 g/cm$^3$ at a temperature of 1100°C for basicity 2-8 while density observed 4.39-3.59 g/cm$^3$ at a temperature of 1150°C. At temperature 1180°C, density varies from 4.43-3.67 g/cm$^3$ but at 1200°C density changes from 4.61-4.51 g/cm$^3$ for basicity 2-6, and it suddenly increases up-to 5.58 g/cm$^3$ for the eight basicity. As conversed in the preceding section that, the formation of a more densified structure occurs with increasing temperature as well as basicity, is responsible for high density and low porosity. At the lower temperature, the removal of gases from the pellets takes place which creates the pores, but the increase in temperature leads to diffusion of elements of oxides, and they form the slag bond which decreases the porosity by shrinking.

All samples (hardened flux pellets of different basicity and temperature) for XRD analysis were prepared by crushing pellets into powder form (< ~200 mesh/-0.2mm). The results of the XRD analysis are shown in the **Figure-3.6**. Phase analysis reveals that there are only three main phases formed during the whole process i.e. Hematite ($Fe_2O_3$, Hexagonal Crystal Structure, Reference ID-9821101 and ICSD Collection Code-201101), Calcium Diferrite ($CaFe_2O_4$, Orthorhombic Crystal Structure, Reference ID-980016695 and ICSD Collection Code-16695) and Calcium Ferrite ($Ca_2Fe_{15.58}O_{25}$, Hexagonal Crystal Structure, Reference ID-980062328 and ICSD Collection Code-62328). At two basicity there are no changes in the peaks and intensity of the phases up-to 1180°C, but at 1200°C the intensity of calcium di-ferrite and hematite peaks decrease, and calcium ferrite emerges as highest intensity peak. On increasing the basicity from two to four, peaks of hematite starts disappearing at 1150°C while in the case of six and eight basicity hematite begins to disappear at 1100°C. For basicity 2, 4 and 6, family of calcium ferrite phases formed during the hardening process with fayalite. The amount of fayalite is significantly less, which cannot be detected with the help of XRD. While melting temperature of fayalite is less than 1200°C due to other impurities; therefore, it can get melted during hardening and provide sufficient strength to the pellets. For 8 basicity, the families of calcium ferrite phases, also get melted at temperature 1200°C with the fayalite phases and form a dense structure as shown in figure 3.9 [72]. For the basicity greater than 1.5 it contains hematite and ferrite phases in the form of calcium glass phases. Melt along with ferrite phase provides superior bonding in the pellets during induration which is responsible for the high crushing strength [60].

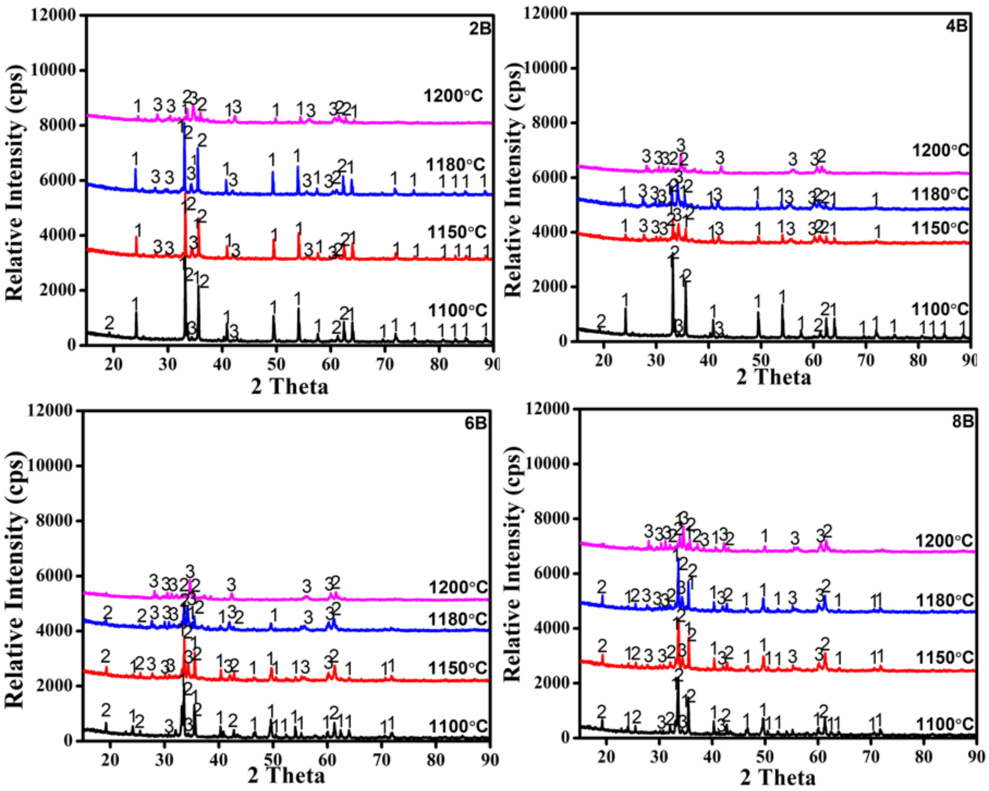

**Figure 3.6** Phase analysis of highly flux hardened pellets with basicity 2, 4, 6, 8. (1-Hematite, 2-Calcium Di-ferrite, 3-Calcium ferrite)

Crushing strength of the different phases given in **Table-3.3**. Hematite and calcium ferrite phases present in the hardened pellets. The presence of these phases may be responsible for the strengthening after reduction.

**Table-3.3** Crushing strength of different phases [3]

| S.No. | Phase | Strength (MPa) |
|---|---|---|
| 1 | Hematite | 267 |
| 2 | Di-Calcium ferrite | 142 |
| 3 | Calcium ferrite | 370 |

**Figure-3.7** shows the phase diagram of CaO-$Fe_2O_3$. The formation of different phases at different temperature for different composition of lime and hematite are mentioned in the figure.

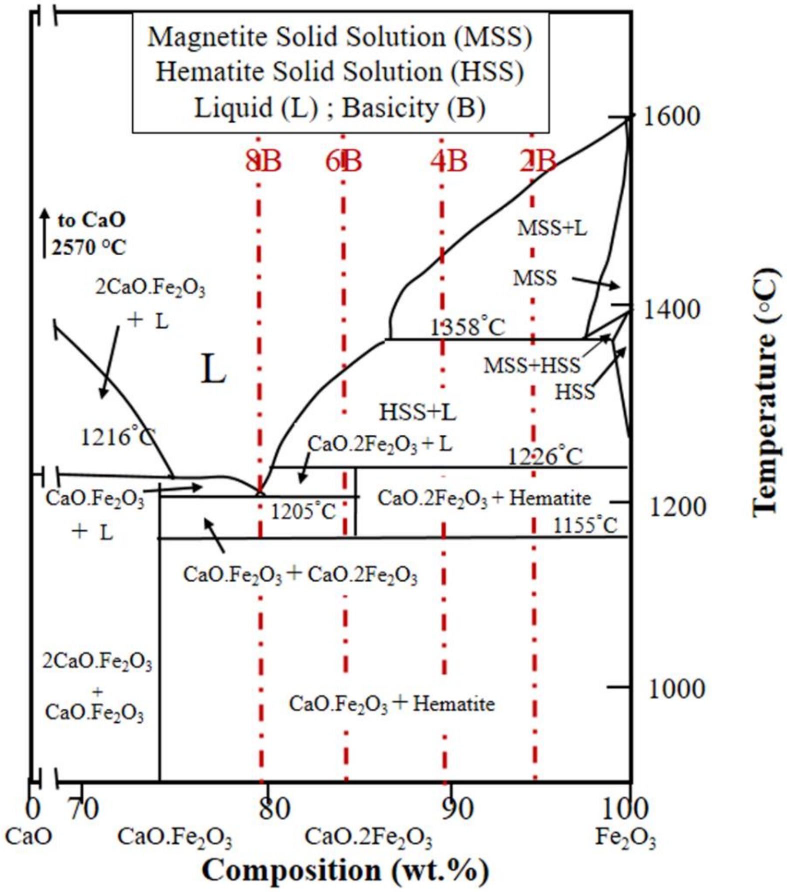

**Figure 3.7** Binary phase diagram of CaO and Fe2O3 [11]

From the above figure it can be seen that for ~80% $Fe_2O_3$ and ~20% CaO lower melting (~1200°C) constituent phase formed which is responsible for the sticking behavior above 1200°C hardening temperature.

The SEM was conducted on hardened flux pellets to determine the morphology of phases and porosity distribution. **Figure-3.8** explains the morphology of the newly form phases in the pellets. Morphology of the oven-dried pellets are similar; all images reflect the random distribution of the particles.

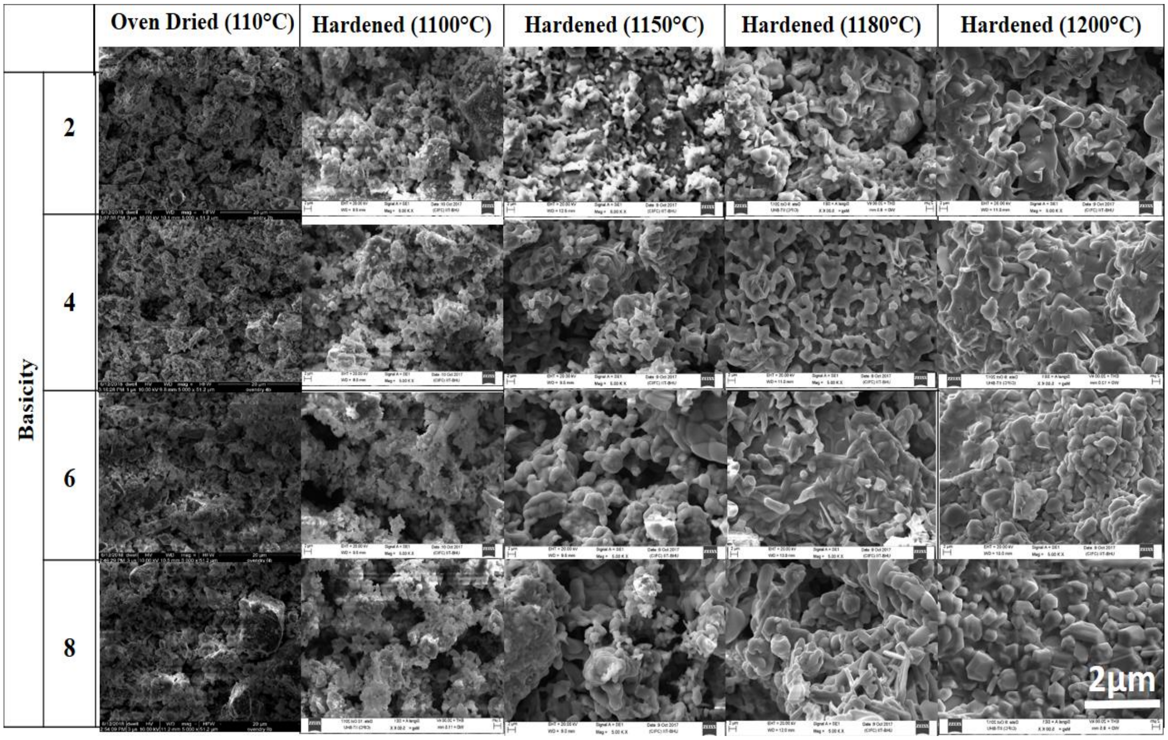

**Figure 3.8** SEM images of highly flux hardened pellets at 5000X magnification.

Change in morphology is observed on increasing temperature for all basicity; it means temperature have a significant effect on the properties from low to high basicity pellets. For all pellets, morphology was similar at 1100°C, but it is different from the oven-dried pellets. It means that there is no significant effect of the basicity on the properties in the lower hardening temperature.

**Figure-3.9** shows the distribution of loose particles, pores and cavity in the hardened pellets at different basicity and temperature. Loose particles were found for all basicity up to 1150°C.

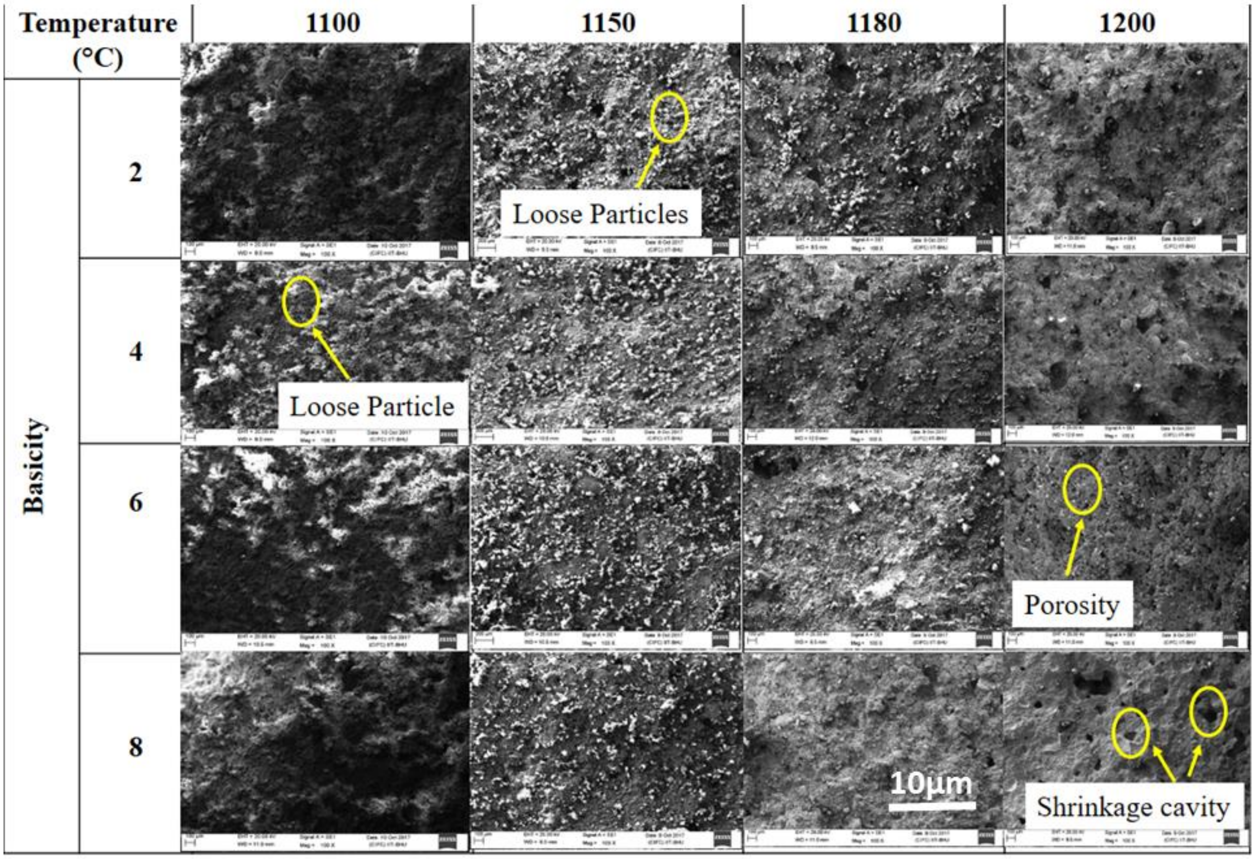

**Figure 3.9** SEM images of highly flux hardened pellets at 1000X magnification.

It decreased for 8 basicity and 1200°C hardening temperature. It was not found for all basicity at 1200°C hardening temperature.  A different type of pattern was observed for 6 and 8 basicity at 1180 and 1200°C hardening temperature. It is explained in **Figure 3.10**. **Figure 3.10** shows SEM images of hardened pellets at 1180°C&1200°C for basicity 6&8 to observe the densification pattern, pores, and cavity in the pellet hardened pellets. From the **Figure 3.10**, it is perceived that densification inside the pellets increased with growing temperature and basicity. The microstructure of eight basicity pellet hardened at 1200°C **(Figure-3.10d)** shows the maximum densification. **Figure 3.7** shows, 1206 °C is the eutectic point for basicity 8 (20% CaO), it means above this temperature the mixture of calcium ferrite and calcium di-ferrite will convert into the liquid phase. So, there may be a possibility to exist a semi-liquid phase (mushy zone) at boundary temperature (i.e.1200°C). A well sintered texture is observed in **Figure-3.10d**.

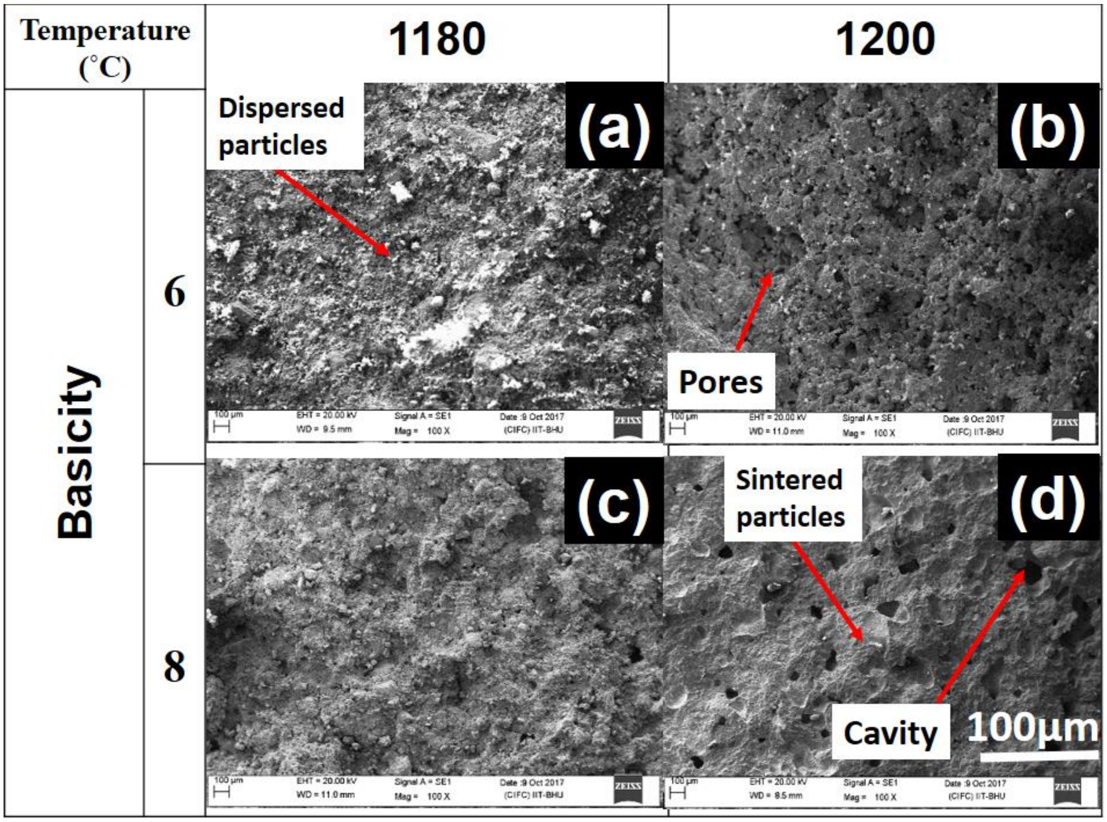

**Figure 3.10** SEM images of highly flux hardened pellets at 100X magnification: a) 6 basicity at 1180°C ; b) 6 basicity at 1200°C ; c) 8 basicity at 1180°C; d) 8 basicity 1200°C

It may be a reason for the formation of the densest microstructure at 1200C° for 8 basicity pellets, which is responsible for the drastic change in the crushing strength value (i.e. 458 kg/pellet), porosity value (4.57%) and density value (5.58 g/cm$^3$). Ulrika et al. also detected a similar relationship between strength and densification of microstructure [87]. It is observed from the **Figure-3.7** that melt formation temperature is decreased with increased basicity. At lower basicity, the possibilities of semi-liquid type phase formation are negligible therefore at 6 basicity less dense structure **(Figure-3.10b**) compared to 8 basicity **(Figure-3.10d)** at 1200°C hardening temperature and **(Figure-3.10a)** compared to **(Figure-3.10c)** at 1180°C hardening temperature formed which shows the decreasing value of crushing strength with decreasing value of basicity at same temperature.

## 3.4 FINDINGS

Based on the results of the experiment, the following findings may be drawn as follow:

- It is feasible to prepare highly fluxed (Basicity-8) iron ore pellets by using waste fines of iron ore and lime as a raw material.
- Formation of calcium ferrite phases appeared to be responsible for strengthening of fired pellets at higher 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 renders pellets with high strength (500 kg/pellets) with poor (5%) porosity which may be undesirable for further use.