Chapter 2: Materials and Experimental Methods

2.1. Introduction

The chapter offers a comprehensive overview of the multimetallic magnetite ore, binders, and reductants utilized in the study, detailing their chemical compositions and the procedures undertaken to prepare them for pelletization and reduction studies. It meticulously outlines the series of tests conducted to assess the potential industrial applicability of multimetallic magnetite ore pellets, encompassing factors like drop number, green and dry strength, Cold Crushing Strength (CCS), porosity, reducibility, metallization, as well as tumbler, abrasion, and shatter tests. Moreover, it extensively describes the various characterization tools and techniques applied, such as proximate analysis, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), X-Ray Fluorescence (XRF) and Optical Emission Spectrometry (OES), to thoroughly analyze the materials involved.

2.2. Raw Materials

The multimetallic magnetite ore (MMO) was obtained from National Metallurgical Laboratory (NML), Jamshedpur, India in the form of lumps of size 150 ± 10 mm. Non coking coal and coke were purchased from a local supplier in the form of lumps having a size of 60 ± 10 mm. The ore, non coking coal and coke were crushed and ground according to methods mentioned in Section 2.4.1, to obtain fines with particle size less than 210 micron. The particle size distribution of the obtained MMO fines was determined according to section 2.4.2 and the details are shown in **Table 2.1**. The MMO fines had a D10 of 38.68 µm, D50 of 60.41 µm and D90 of 142 µm as shown in **Figure 2.1** (determined according to methods detailed in Section 2.4.2).

Table 2.1: Particle Size distribution of the prepared MMO fines

Sieve no (BSS)	Sieve aperture (µm)	Wt. of powder passing through the sieve(gm)	Wt. of powder retained on the sieve(gm)	Cumulative undersize percentage
72	210	100	0	100
120	125	87.5	12.5	87.5
240	63	53	34.5	53
300	53	41.38	10.97	41.38
350	45	24.11	17.27	24.11
400	37	6.24	17.87	6.24
pan	--	0	6.24	0

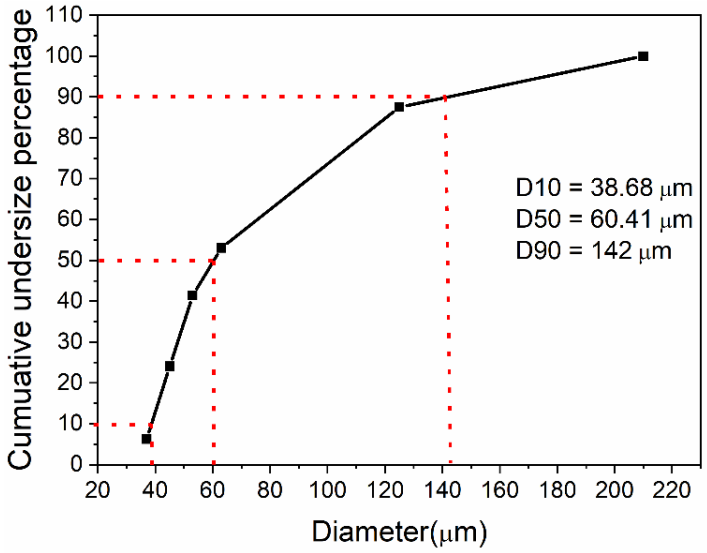

Figure 2.1: Sieve analysis of prepared MMO fines

The inorganic binder, colemanite was procured from a local supplier in Gujarat in the form of a powder having particle size -75 µm. The organic binders namely dextrin, carboxymethyl cellulose (CMC), and cornstarch were procured locally in the form of powders having particle size -60 µm. **Dextrins** $(C_6H_{10}O_5)n$ are a group of low-molecular-weight carbohydrates produced by the hydrolysis of starch or glycogen. Dextrins are a white, yellow, or brown powder that is partially or fully water-soluble, yielding optically active solutions of low viscosity [29]. **Corn starch** ($C_{27}H_{48}O_{20}$) or maize starch is the starch derived from the corn (maize) grain. **Carboxymethyl cellulose** (CMC) has widespread use in many industrial fields such as the food industry,

pharmacy, textile, and architecture. It is a crucial cellulose derivative with carboxymethyl groups (-CH_2\COOH) bound to some of the hydroxyl groups of the glucopyranose monomers that make up the cellulose backbone [38]. **Colemanite** ($Ca_2B_6O_{11}\cdot 5H_2O$) is a borate mineral found in evaporite deposits of alkaline lacustrine environments. Colemanite is a secondary mineral that forms by alteration of borax and ulexite. It has a melting point of 986 ℃ and forms boro-silicate bonding at relatively moderate temperatures [20, 30-32]. The chemical composition of the multimetallic magnetite ore fines and the inorganic binder colemanite was determined by XRF according to methods mentioned in Section 2.3.3 and is shown in **Table 2.2**.

Table 2.2: Chemical composition of multimetallic magnetite ore and colemanite

Multimetallic Magnetite Ore		**Colemanite**	
Component	**Wt.%**	**Component**	**Wt.%**
Fe_3O_4	62.20	Fe_2O_3	0.08
Al_2O_3	14.70	Al_2O_3	0.40
SiO_2	14.40	SiO_2	4.60
Cr_2O_3	4.95	MgO	3.00
MgO	1.41	SO_4	0.60
TiO_2	0.62	B_2O_3	40.00
NiO	0.59	Na_2O	0.35
MnO	0.45	SrO	1.50
P_2O_5	0.17	CaO	27.00
CaO	0.14	B	12.50
V_2O_5	0.09	LOI	9.97
SO_3	0.09		
Co_2O_3	0.05		
K_2O	0.03		
ZnO	0.03		
CuO	0.02		
ZrO_2	0.004		

Magnetite (Fe_3O_4) was the major constituent in the MMO followed by alumina (Al_2O_3) and silica (SiO_2). Chromium and nickel were also present in significant quantities in the form of CrO_3 and NiO. Colemanite contained B_2O_3 as the major constituent (40 wt.%) followed by CaO (27 wt.%) and free Boron (12.5 wt.%). Alumina and silica were found in very small quantities. The XRD analysis of the MMO fines is shown in **Figure 2.2**. Three major phases were observed, which include all the significant elements found in the chemical analysis. Some parts of iron are present as magnetite (Fe_3O_4), and the rest are combined with chromium in the form of chromite ($FeCr_2O_4$), Aluminum and silicon are combined as Kaolinite ($Al_2O_3.2\ SiO_2.2H_2O$).

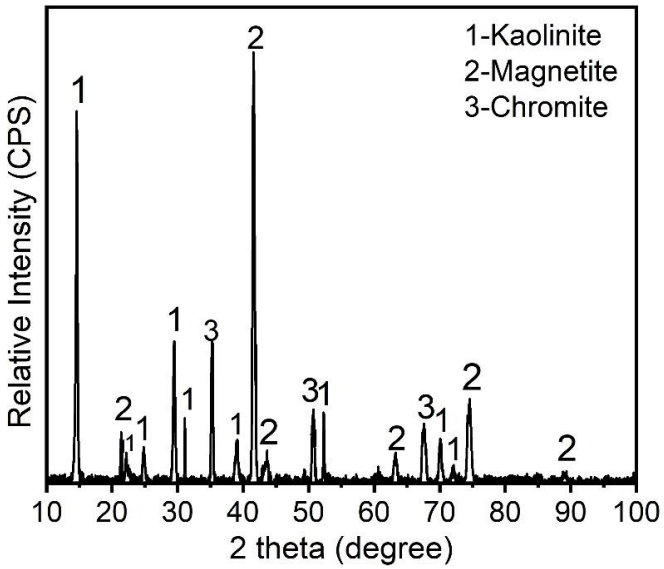

Figure 2.2: XRD analysis of the multimetallic magnetite ore fines

The proximate analysis of non coking coal (G4 grade) and coke was done according to section 2.4.3 and is shown in **Table 2.3**. Pure H_2 gas (99.99%) and pure N_2 gas (99.99%) for the gas-based reduction studies were procured locally.

Table 2.3: Proximate analysis of the reductants used

Proximate Analysis				
Constituents(wt.%)				
	Moisture	**Volatile matter**	**Ash**	**Fixed Carbon**
Non coking Coal	6.96	9.91	13.37	69.76
Coke	1.73	2.10	37.40	58.77

2.3. Microstructural Characterization

The changes in phases of hardened pellets and Direct Reduced Iron (DRI) were analyzed by X-Ray Diffraction (XRD) method. The changes in morphology of the pellets after hardening/ reduction was examined under a Scanning Electron Microscope (SEM). The chemical composition of the MMO, colemanite and slag samples were determined by X-Ray Fluoroscence (XRF). The chemical composition of the metal obtained after melting was analyzed using an Optical Emission Spectrometry (OES).

2.3.1. X-Ray Diffraction

After drying and hardening, green pellets may undergo phase changes with respect to their initial state. Similarly, the Direct Reduced Iron (DRI) may exhibit different phases compared to the hardened pellets. These alterations significantly influence pellet properties. For analysis, ten pellets/DRI samples were ground into a powder (<210µm). This fine powder was subjected to X-Ray Diffraction (XRD) analysis using a PANalytical EMPYREAN HR-XRD instrument, with Co Kα radiation (λ=1.78901 nm), 40 kV acceleration voltage, and a 40 mA beam current. Scanning occurred at a rate of 2 degrees/min from 10 to 100 degrees. The resulting diffraction patterns were analyzed using Xpert High Score software to identify phases present in the samples.

2.3.2. Scanning Electron Microscopy

Following drying, hardening, and reduction processes, alterations in grain size, shape, and structure within the pellets may occur, consequently affecting their properties. To study these changes, a hardened multimetallic magnetite ore pellet/Direct Reduced Iron (DRI) was sectioned into two halves, and one half was subjected to Scanning Electron Microscopy (SEM) to assess morphology variations. The morphological changes in the pellets were examined using a SEM (ZEISS EVO-18 model, Oxford Instruments with INCA energy 300 software), operated at 20 kV acceleration voltage and 5 mA beam current. Additionally, Electron Dispersive Spectrometry (EDS) was employed to

determine the elemental composition of various areas and points within the sample, providing further insights into the structural alterations occurring within the pellets.

2.3.3. X-Ray Fluorescence

The chemical composition of the multimetallic ore, binder, and the slag resulting from melting studies of DRI was analyzed using X-Ray Fluorescence (XRF). These materials were ground in a ball mill to achieve a sample of particle size smaller than 210 microns. Subsequently, the ground sample was compacted into a cylinder of 40 mm diameter and 2 mm height to facilitate testing in the XRF machine (PANlytical Zetium). The elemental analysis was done using SuperQ software.

2.3.4. Optical Emission Spectrometry

It was necessary to evaluate the chemical composition of the metal produced when exploratory melting studies were conducted on Multimetallic DRI. This was done using an Optical Emmision Spectrometer (OES) named Foundry Master. Metallic samples having diameter 20 mm and thickness 2 mm were prepared for the OES analysis.

2.4. Raw Material Preparation

Figure 2.3 shows the flowchart for raw material preparation. The various steps are mentioned in following subsections.

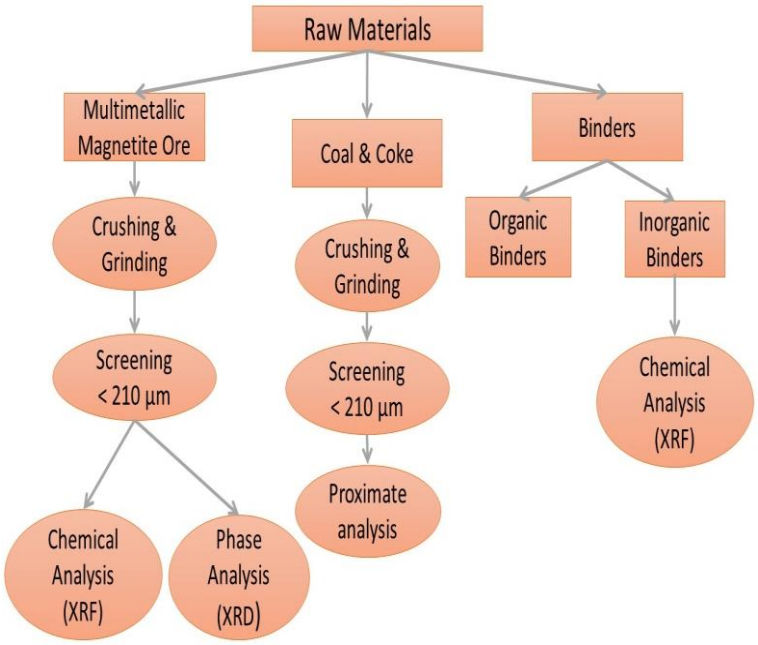

Figure 2.3: Procedure followed for preparation and characterization of raw materials

2.4.1. Crushing and Grinding

Crushing involves reducing the size of the ore from its initial size to less than 8 mm, while grinding further reduces the -8 mm fines to a powder form with particle sizes typically below 0.2 mm. The raw materials obtained were initially too large for pellet production, necessitating size reduction. **Figure 2.4** illustrates the steps involved in the crushing and grinding of MMO ores. Crushing occurred in two steps: first, ore lumps (>150mm) were crushed using a Jaw crusher to achieve a size of approximately <30mm. The -30mm lumps underwent further size reduction through a roll crusher, resulting in particles approximately <8 mm in size. Subsequently, the -8 mm fines were processed in a 20 kg capacity ball mill to convert them into a powder capable of passing through 72 mesh sieves (BSS standard), ensuring that the particle size of the fines was below the desired threshold of 210 µm.

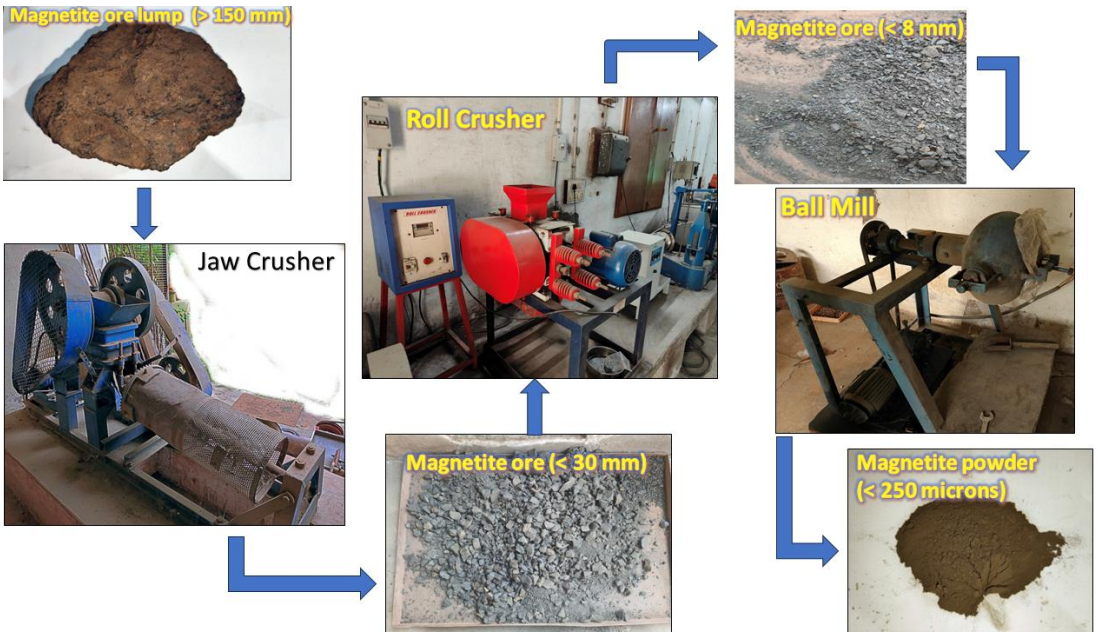

Figure 2.4: Procedure for preparation of fines of desired size from lump ore

2.4.2. Sieve Analysis

The -210 µm powder obtained from the ball mill contained particles of different sizes. Thus, it was necessary to define a particle size range. Hence, sieve analysis was done according to ASTM C136M [75]. Sieve analysis is a method in which the sample powder is passed through numerous sieves arranged in a stack. The sieve with the widest openings was placed at the top, and the size of the opening decreased down the stack. The stack was placed on a machine known as the sieve shaker, which gave the sieve stack a vertical juggling motion or, in other words, shook the sieve up and down continuously for a particular time. This ensured the segregation of the sample powder according to the particle size. A sample powder specimen of 100 gm of the ore was taken and put into the top sieve. **Figure 2.5** shows the setup used for sieve analysis.

Sieves of the following sizes were used: BSS 72(210 µm), BSS 120(125 µm), BSS 240(63 µm), BSS 300 (53 µm), BSS 350 (45 µm), BSS 400 (37 µm). After the sieve shaking operation, the sieves were separated from each other, and the weight of the powders retained on different sieves was measured. A graph was plotted with

cumulative undersize percentage on the y-axis and particle size in μm on the x-axis. From the graph, D10, D50, and D90 were calculated by drawing intercepts on the x-axis from the plotted curve, which corresponded to 10%, 50%, and 90%, respectively, of the cumulative undersize percentage on the y-axis.

D10 = 10% of the particles are smaller than this diameter.

D50 = 50% of the particles are smaller than this diameter.

D90 = 90% of the particles are smaller than this diameter

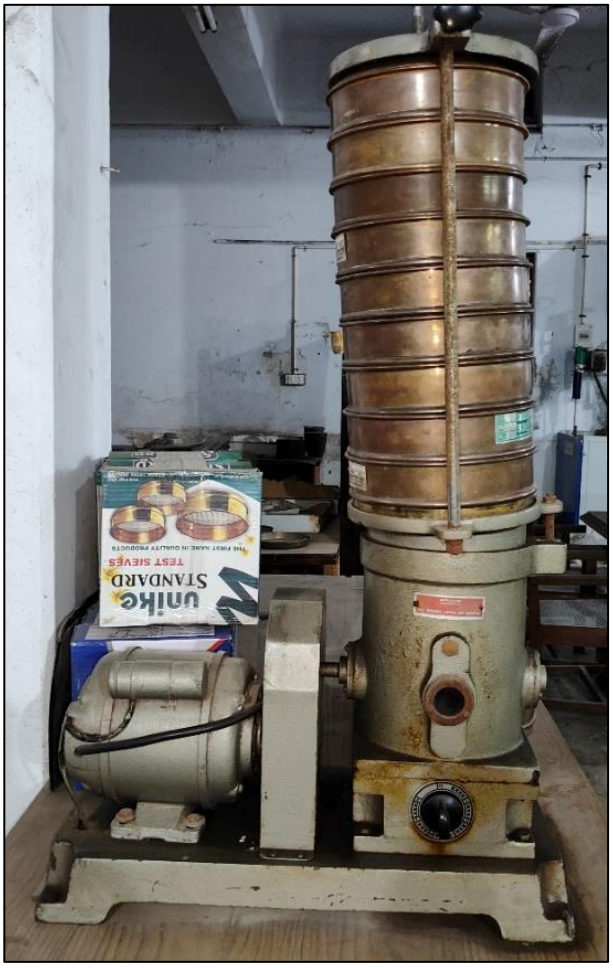

Figure 2.5: Setup used for sieve analysis of multimetallic magnetite ore fines

2.4.3. Proximate analysis of coke and non coking coal

Proximate analysis of coal and coke is a technique to determine the amount of volatile matter, ash, moisture, and fixed carbon, which could help in evaluating the potential

usage of coal and coke. An average of four experiments was reported. The various constituents are determined as follows

2.4.3.1. Moisture Content

The change in the weight of the sample after heating the weighed sample of coke/coal for one hour at 110 °C gives an estimate of the moisture content of the coal/coke sample. One gm of fine powdered (-210 μm) non coking coal/coke was taken in a glass dish of 50 mm dia and 10 mm depth with a lid, and the weight. of the sample (coal/coke fines + glass dish +lid) was recorded. Then, the sample without the lid was exposed to temperatures of 110 ± 5 °C for one hour in an oven. After one hour, the sample was taken out of the oven, and the lid was again put back and cooled in a desiccator to prevent reabsorption of moisture. The sample (coal/coke fines + glass dish + lid) was again weighed [76]. The moisture content in weight % was calculated as

% Inherent moisture = (Change in wt. of sample/ Initial wt.) × 100……(2.1)

2.4.3.2. Ash content

One gm of fine powdered (-210 μm) coal/coke was taken in a silica dish of 50 mm dia and 10mm depth without a lid, and the weight. of the sample (coal/coke powder + silica dish) was recorded. The sample was heated in a muffle furnace at 400±5 °C for 30 mins to oxidize all the sulphur and part of carbon. The sample was then transferred to another furnace held at 800±5 °C and kept there for 1 hour. To ensure complete combustion, this second step was repeated numerous times till the weight. of the residue becomes nearly constant across numerous iterations. Then, the sample was weighed again, and this weight. of the residue was termed as ash content [76]. The ash content in wt.% was calculated as

% Ash content = (Wt. of residue / Initial wt. of sample) × 100……(2.2)

2.4.3.3. Volatile matter

One gm of fine powdered (-210 μm) coal/coke was taken in a specially designed silica crucible of 22 mm dia and 32 mm depth with a lid. The depth of the crucible was kept large so that the coal/coke fines can be heated in the absence of air whenever the crucible was used in conjunction with the lid. The sample (crucible+ lid + non coking coal/coke fines) was placed on a nichrome wire tripod to keep the crucible about 5 mm above the furnace bed. Before putting it into the furnace, the weight. of the sample plus the tripod was noted. The sample with tripod was heated in a furnace at 925 ± 5 °C. After 7 mins, the sample+ tripod was taken out from the furnace, and reweighed. The weight. difference also included the moisture content, which needs to be subtracted from the total weight. loss [76]**.**

The volatile matter (%VM) was calculated as

% VM= (Change in wt. of sample / initial wt.) × 100 - % inherent moisture...(2.3)

2.4.3.4. Fixed Carbon

Fixed carbon (%FC) was estimated indirectly by the following formula [76]

% FC= 100 - (%VM + % Inherent moisture + % Ash content)……(2.4)

2.5. Preparation and characterization of Hardened pellets

The multimetallic magnetite ore fines underwent pelletization and subsequent characterization as outlined in **Figure 2.6**. The MMO was mixed with a single binder in the required proportion. The dosage of the binder was varied from 0.5 to 2 wt. %. This process was repeated with all the other binders, and thus, four sets of pellets (14-19 mm dia) were made with each binder, each corresponding to a particular dosage in wt.% (0.5, 1, 1.5, 2). Colemanite was calcined at 550 °C for 1 hour before being added to the green pellet mix as the water of crystallization present in colemanite may lead to the spalling of pellets at higher temperatures [22, 77]. The other binders were added

without any pre-treatment. **Figure 2.7** shows the prepared green pellets using colemanite binder.

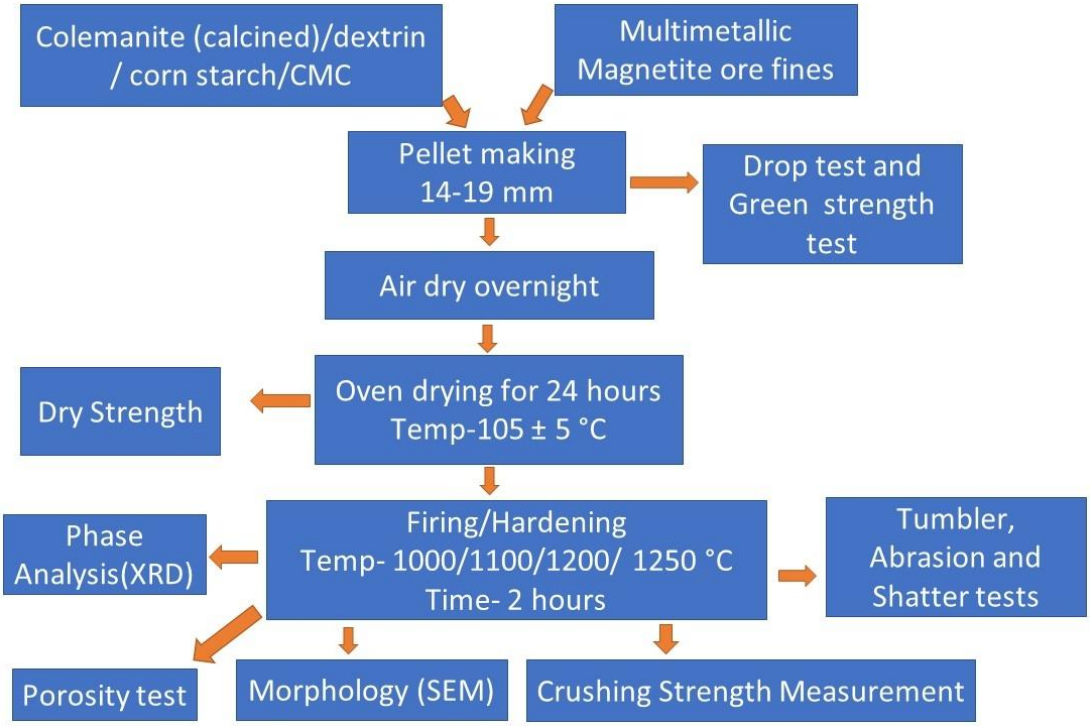

Figure 2.6: Procedure for preparation and characterization of hardened pellets

Figure 2.7: Green pellets prepared with different dosages of colemanite.

To ensure sufficient structural strength and prevent breakage during transportation and handling, the green pellets underwent a series of heating treatments. Initially, the pellets were air-dried overnight and kept in a laboratory oven at 105±5 °C for 24 hours to remove moisture, thereby preventing cracking at induration temperatures.

Subsequently, the oven-dried pellets were placed in a laboratory resistance furnace **(Figure 2.8)** and indurated at four different temperatures: 1000, 1100, 1200, and 1250 °C. The pellets were indurated in the furnace for 120 mins after reaching the desired temperature to ensure complete slag bonding and particle sintering. Following this, the furnace was turned off, allowing the pellets to cool before removal. Notably, no sticking was observed at any of the hardening temperatures employed.

Figure 2.8: Resistance Furnace used for hardening of dry MMO pellets

Pellets prepared from iron ores must satisfy some criteria as mentioned in **Table 1.1**. Thus, various tests were conducted on pellets to determine their worthiness for the industry. The tests are described in detail in the following subsections.

2.5.1. Green strength test

Green strength of pellets is a very important property as it allows easy handling of pellets in wet conditions. The green strength of pellets was measured by the drop number and green crushing strength.

Drop number is measured to determine a pellet's ability to withstand certain number of drops from a fixed height. For obtaining drop number, a single pellet was dropped from a standard height of 450 mm, on a steel plate and the number of drops per pellet was counted until the pellet broke. Ten pellets per dosage per binder were taken and dropped. The acceptable drop number was 4.

Figure 2.9 illustrates the schematic diagram of the setup utilized for measuring green crushing strength [76]. The setup comprises a pan balance featuring a graduated bottle on the right-hand side (RHS) and a set of parallel plates on the left-hand side (LHS). The top plate was adjustable and can be moved vertically using the adjustable head. Conversely, the lower plate was fixed to the pan on the LHS. Initially, a pellet was positioned between the two parallel plates on the LHS of the pan balance. To balance the weight. of the pellet, water was added to the graduated water bottle placed on the RHS of the pan balance. The system was calibrated such that a 1 cm rise in water height in the graduated bottle corresponds to a load of 1 gm on the pellet. Once the proper balance was established, the adjustable head on the LHS of the pan was rotated until the top plate gently touches the pellet. The water level in the graduated bottle was then recorded. Subsequently, water was allowed to fill the graduated bottle, causing the RHS of the beam connecting the two pans to move vertically downwards. Consequently, the LHS pan starts to move vertically upwards, compressing the pellet between the two parallel plates until the compressive load reaches a specific value. The flow of water into the graduated bottle was halted upon the appearance of cracks on the pellet. The new water level was recorded, and the difference between the initial and final water levels provided the green crushing strength of the pellet. An average of ten pellets per dosage per binder was taken to determine the green crushing strength in gm/pellet.

Green crushing strength (gm)= (Final water level – Initial water level) ml × ρ…..(2.5)

where ρ = density of water in gm/cc

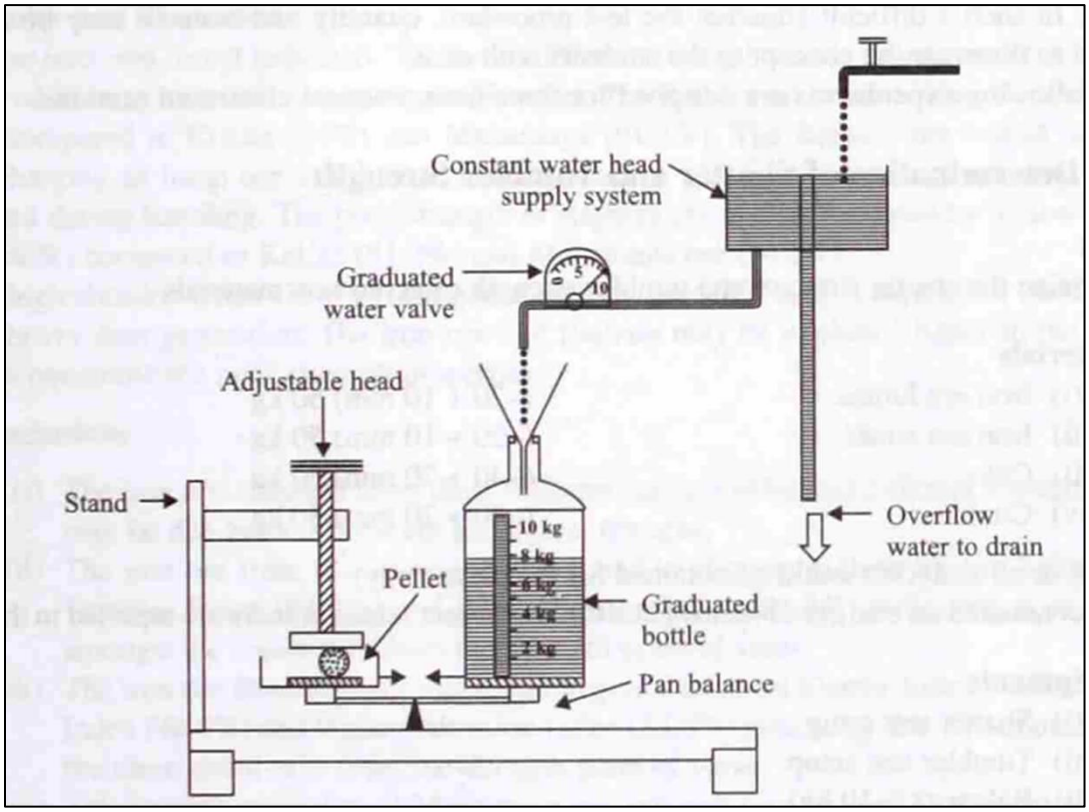

Figure 2.9: Apparatus to measure green crushing strength [75]

2.5.2. Dry strength and Cold Crushing Strength (CCS)

Dry strength of pellets refers to their ability to withstand mechanical stresses after drying but before undergoing further processing or heating steps. This property is crucial for assessing the pellets' resilience during handling, transportation, and storage in its dry state. Cold Crushing Strength (CCS) was another essential mechanical property used to evaluate pellet strength. It measures the resistance of pellets to compressive forces after induration. A higher CCS value indicates greater strength and durability, signifying the pellets can withstand higher loads without disintegrating into fines. The tests for dry strength and CCS were conducted using a 100-kN screw-driven Instron Universal Testing Machine (UTM) (model 4206) with a cross head speed of 0.1 mm/min, following ASTM E382 standards [78]. Typically, four pellets per binder per

dosage of each hardening temperature were tested, and the average was taken as the CCS (kg/pellet) of the pellets.

2.5.3. Measurement of Porosity

The porosity of pellets was measured by folowwing ASTM C20 [79] . 5 pellets per dosage per binder of each hardening temperature were chosen for this study. The dry pellets were first weighed in air. The pellets were then dipped in boiling water for 30 mins. The water saturated pellet was cooled and weighed while dipped fully under water. The pellet was then taken out of water and surface water was removed by soaking in cotton cloth. The weight of the water saturated pellet was then taken in air.

Now, the **wt. of the water absorbed in the open pores (gm)** = wt. of water saturated pellet in air- wt. of dry pellet in air……..(2.6)

Or **volume of water absorbed in open pores (cm^3)** = wt. of the water absorbed in the open pores × ρ,…….(2.7)

where ρ= density of water

The loss in wt. of the sample due to buoyancy while being dipped in water = wt. of water saturated pellet in air – wt. of water saturated pellet while being dipped in water…….(2.8)

Or **volume of sample** = loss in wt. of the sample due to buoyancy while being dipped in water × ρ……...….(2.9)

Hence, **apparent porosity %** = (Volume of water absorbed in open pores/ volume of sample) ×100……...(2.10)

2.5.4. Tumbler Index, Shatter Index and Abrasion Index

The Tumbler Index (TI) is a measure of the physical properties of iron ore pellets, providing insight into their resistance to degradation during transportation and handling. Specifically, it quantifies the tendency of pellets to break or form fines when subjected to tumbling or rotation. The Abrasion Index (AI) is a measure of the resistance of iron ore pellets to abrasion or wear. It quantifies the ability of pellets to withstand frictional forces and mechanical abrasion occurred during transportation, handling, and processing. The Shatter Index (SI) is a measure of the susceptibility of a material to break upon impact. It provides a relative assessment of the material's resistance to shattering or fragmentation when subjected to sudden impacts (IS-6495).

5 kg of samples were prepared for the shatter test. The pellets were loaded into the shatter test setup and dropped four times on a thick steel plate from a height of 2 meters. Then, the material was sieved on a 10 mm screen, and the fraction retained on the 10 mm sieve was weighed. Similarly, a 5 kg sample was taken for the tumbler test. The samples were put into the tumbler drum, which was subjected to 200 revolutions at 25 rpm. After tumbling in the drum, the sample was taken out and sieved with 6.3 mm and 0.5 mm sieves. The samples retained on the 6.3 mm sieve and the fraction of sample passing through the 0.5 mm sieve were weighed [74].

TI = (Wt. of sample retained on 6.3 mm sieve / Initial wt. of sample) ×100…….(2.11)

AI = (Wt. of sample passing through 0.5 mm sieve / Initial wt. of sample) ×100…(2.12)

SI = (Wt. of sample retained on 10 mm sieve /Initial wt. of sample) ×100…….(2.13)

2.6. Reduction of Hardened Pellets

The reducibility of the hardened MMO pellets were investgated by employing both solid reductants (non-coking coal, coke) and gaseous reductants (H_2 gas). The details of the experimental methods have been explained in the following subsections

2.6.1. Solid-based reduction

The solid based reduction of hardened MMO pellets with carbonaceous reductants (non coking coal, coke) and the subsequent characterization studies were done according to the procedure shown in **Figure 2.10**.

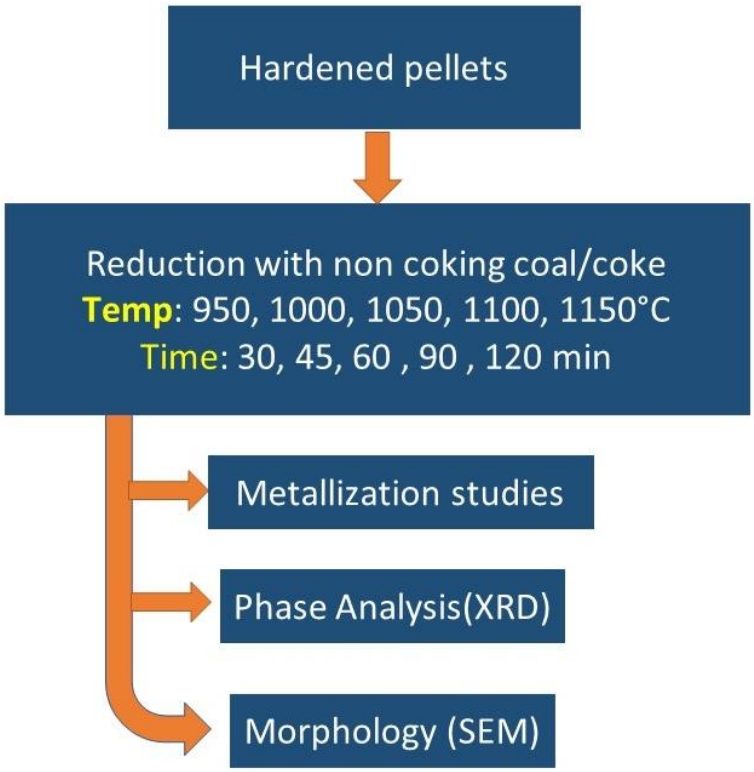

Figure 2.10: Procedure followed for the carbothermic reduction of Hardened MMO pellets

A pellet was placed in a reductant bed kept inside a galvanized iron crucible of 60 mm height and 25 mm inner dia **(Figure 2.11)**. Each crucible contained one pellet in the bed of solid reductants (non-coking coal and Coke). Grog (crushed refractory powder) and a top plate were placed to cover the crucible to maximize the time of interaction between the pellets and reducing gas. Five crucibles were placed inside a resistance furnace at a given temperature as shown in **Figure 2.12.**

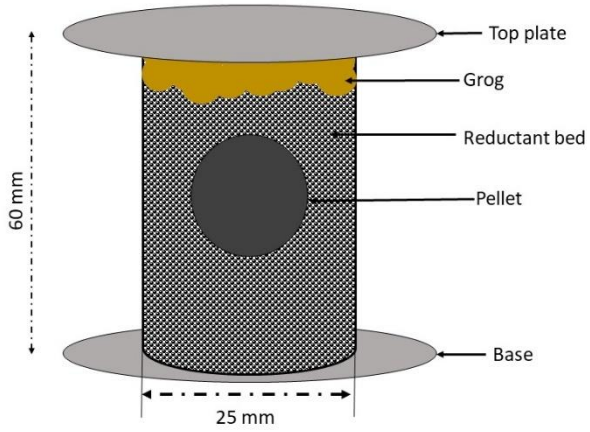

Figure 2.11: Crucible setup used for carbothermic reduction of MMO pellets

The reduction was carried out at five temperatures of 950 °C, 1000 °C, 1050 °C, 1100 °C, and 1150 °C. The crucibles were taken out of the furnace one by one at intervals of 30, 45, 60, 90, and 120 mins, respectively. Each reduction experiment was repeated for five times to ensure the reproducibility of results. The pellet's weight., and photographs before and after reduction were recorded to calculate the weight. change, and changes in physical appearance. The phase changes and morphological changes in the pellets were analyzed by XRD and SEM respectively.

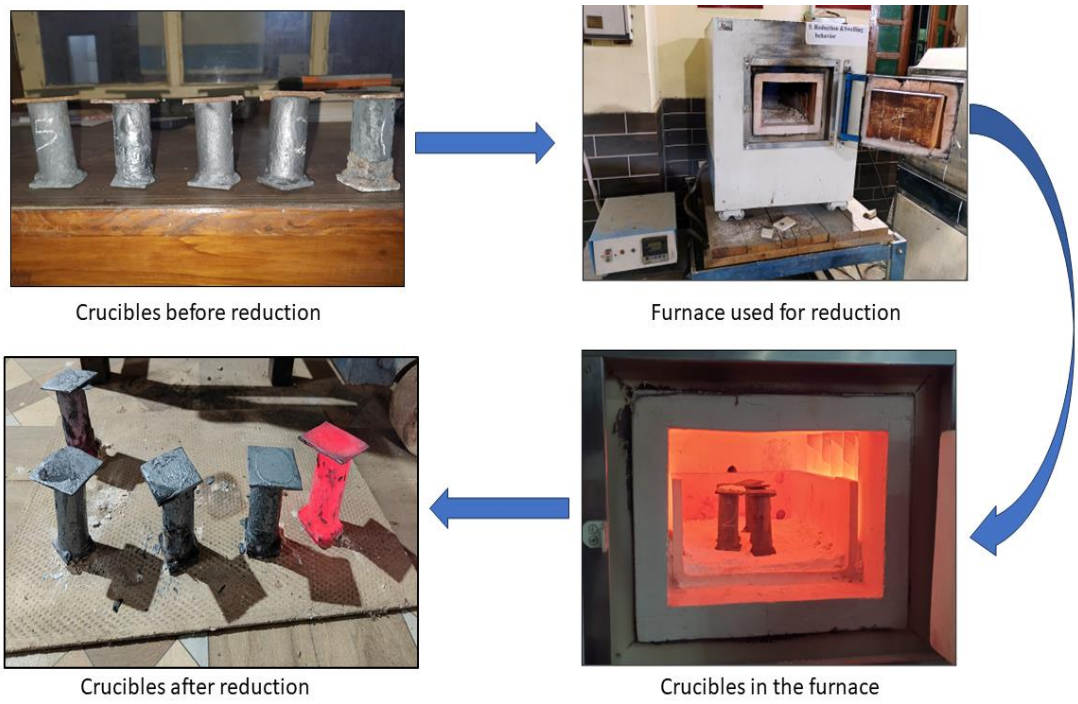

Figure 2.12: Different steps in the carbothermic reduction of pellets

2.6.2. Gas-based reduction

The gas-based reduction of hardened MMO pellets with hydrogen gas (H_2) and the subsequent characterization studies were done according to the procedure shown in **Figure 2.13.**

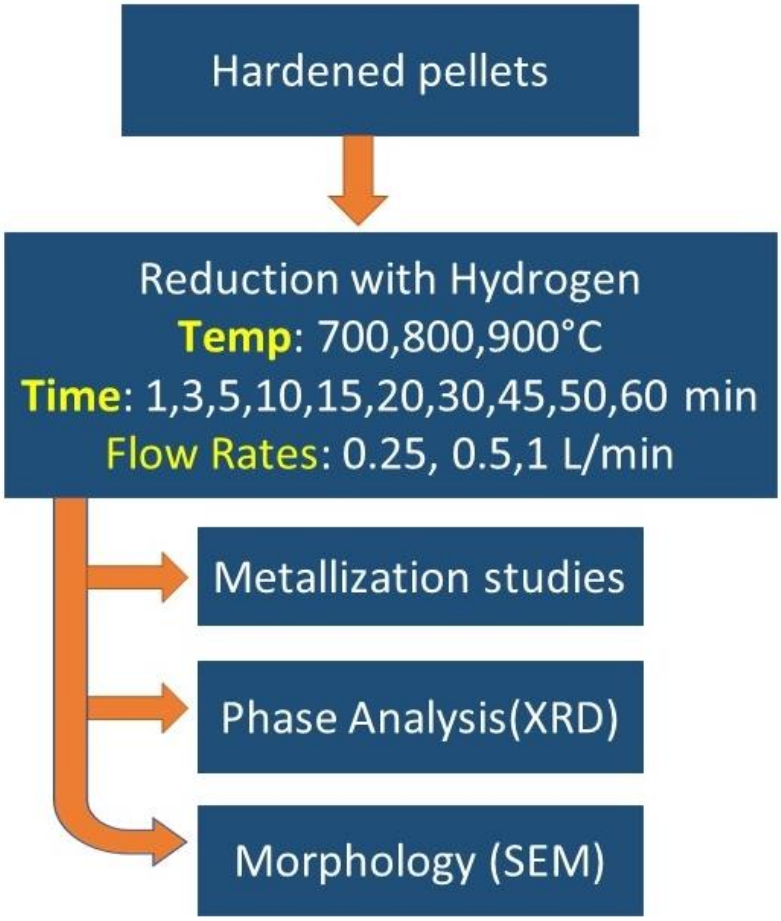

Figure 2.13:Procedure followed for the hydrogen reduction of Hardened MMO pellets

Figure 2.14 shows the experimental setup for hydrogen reduction in a tube furnace. Three spherical hardened pellets (diameter: 15-19 mm) were initially placed on a refractory boat **(**13**)**, and the boat was placed inside the quartz tube (9) at room temperature. The quartz tube was filled with nitrogen gas, and the outlet valve was closed to prevent leakage and maintain an inert atmosphere inside the furnace. The furnace was allowed to attain the desired temperature. **Figure 2.15** shows the placement

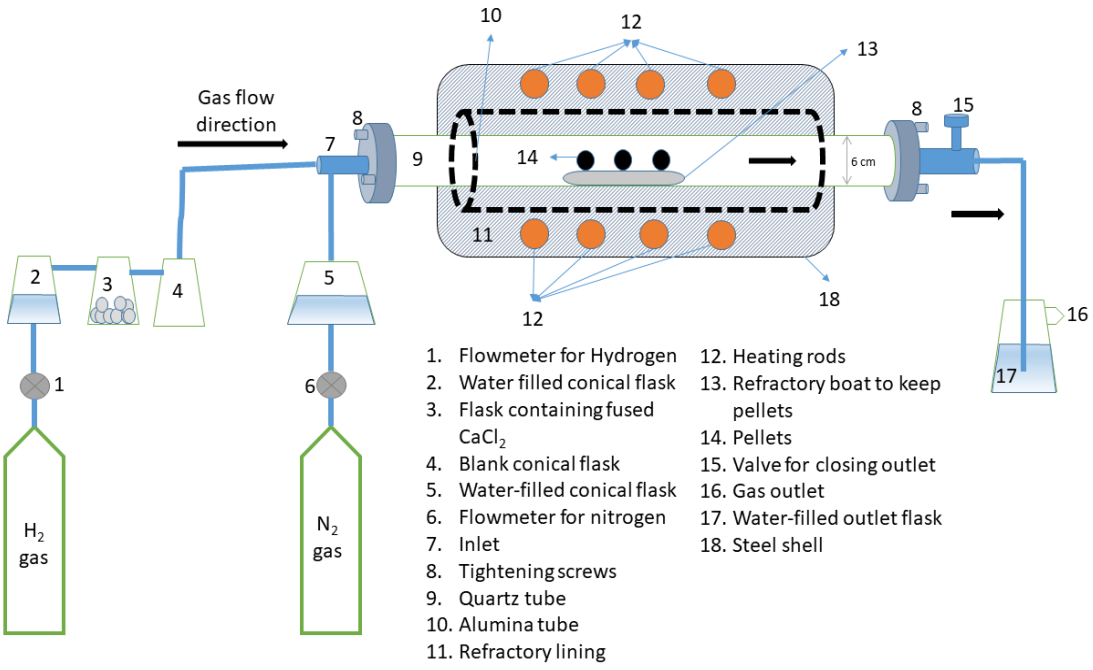

Figure 2.14: Experimental setup for hydrogen reduction

of pellets in the refractory boat. The reduction studies were carried out at three temperatures: 700 °C, 800 °C, and 900 °C. The variation in the temperature was ± 5 °C. Once the furnace attained the desired temperature, the outlet valve was opened, nitrogen was again passed into the furnace for 10 mins, and pure hydrogen was allowed to flow into the furnace at a predetermined flow rate for the desired reduction times.

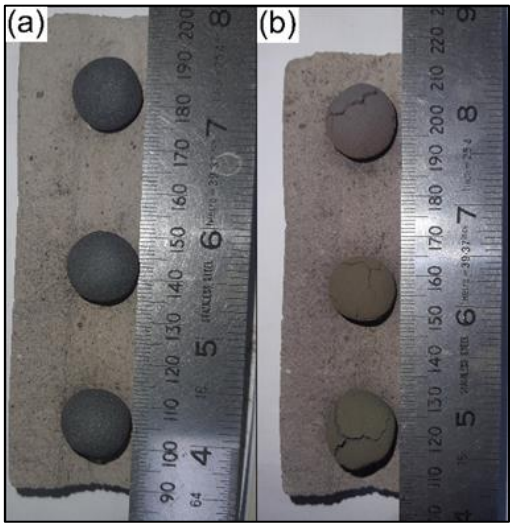

Figure 2.15: Pellets placed in refractory boat (a) before reduction (b) after reduction

Three different flow rates of 0.25L/min, 0.5 L/min, and 1 L/min were used to investigate the effect of flow rates on the reducibility. The pellets were kept in the

furnace for the reduction durations of 1 min, 3 mins, 5 mins, 10 mins, 15 mins, 20 mins, 30 mins, 45 mins, 50 mins, and 60 mins. After the completion of the reduction, the furnace was switched off, the hydrogen flow was stopped, and the nitrogen flow was commenced to drive out the remaining hydrogen gas inside the tube furnace. After about 10 mins, the outlet valve was closed, and the tube was again filled with nitrogen gas so that the pellets cooled down to room temperature in a neutral atmosphere. The boat and pellets were taken out of the furnace after the furnace cooled down to room temperature. All the experiments were repeated three times to ensure the reproducibility of the results. The weight of the pellets and photographs before and after reduction studies were recorded to determine the mass change and changes in the physical appearance of the pellets. The phase changes and morphological changes in the pellets were analyzed by XRD and SEM respectively.

Due to the explosive nature of H_2 gas a few safety arrangements were made in the experimental setup. Water filled conical flasks (2 and 5 in **Figure 2.14**) and blank flask (4 in **Figure 2.14**) were used to arrest any backfire of H_2 gas from the hot reaction zone. The gas emeging out of flask no 2 (**Figure 2.14**) would invariably contain some moisture. Thus, gas was made to pass through a flask conatining fused $CaCl_2$ to absorb the moisture. Water filled flask (no 17 in **Figure 2.14**) was used to dilute the exit gas.

2.6.3. Metallization studies

A minimum amount of metallization (~85%) in DRI is essential to make it fit for industrial use [80].The percentage metallization of Fe ($\%Fe_M$) in DRI was defined as:

$$\mathbf{\%Fe_M = (Fe(M) / Fe(T)) \times 100} \quad \text{,,(2.14)}$$

where Fe(M) = Wt. of Metallic Fe in Reduced sample

Fe(T) = Total wt. of Fe (unreduced+ reduced) in the sample

Fe(M) in the DRI was deduced by chemical methods according to IS 15774 [80] as shown in **Figure 2.16.**

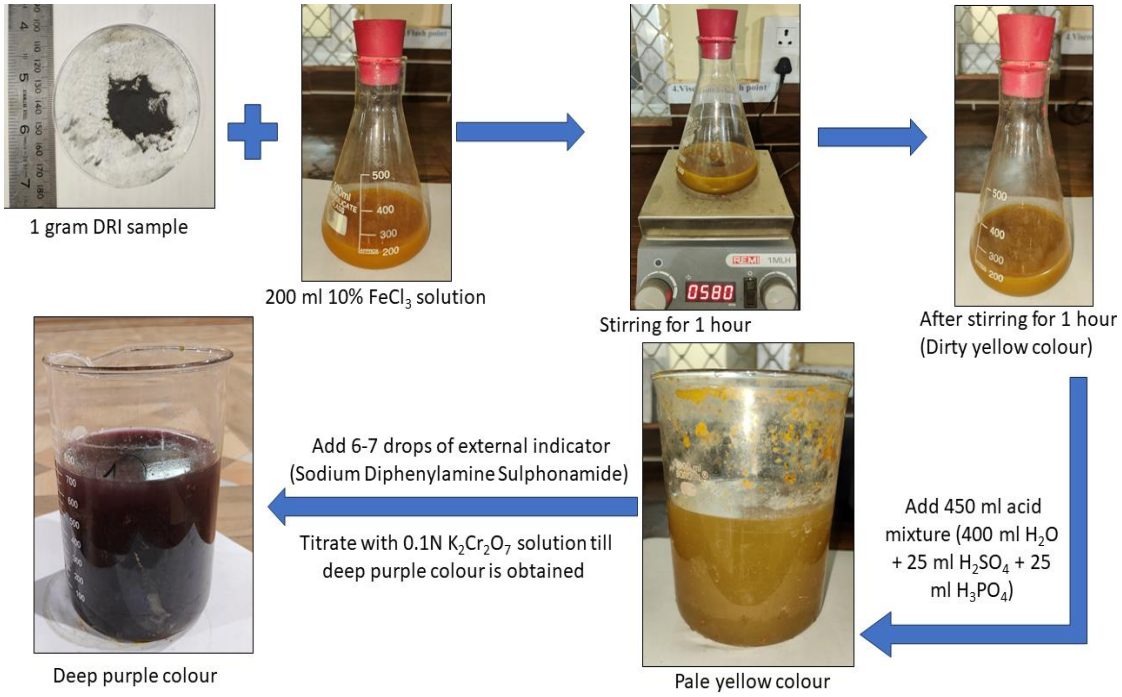

Figure 2.16: Metallization test procedure

The procedure to determine Fe(M) was as follows:

- 1 gm of DRI powder sample was taken in a 500 ml conical flask and 200 ml of 10% (m/v) Ferric chloride ($FeCl_3$) solution was added to it.
- The mouth of the flask was closed with a stopper and the solution was agitated with a polypropylene coated magnetic stirrer for 1 hour.
- The solution was filtered through medium texture filter paper and the filtrate was added to 1000 ml conical flask containing 400 ml distilled water, 25 ml analytical grade concentrated phosphoric acid (98%) and 25 ml analytical grade concentrated sulphuric acid (98%).
- Three to four drops of an external indicator, i.e., sodium diphenylamine sulphonate (SDPS) was added to the solution and then titrated with a standard 0.1N potassium dichromate ($K_2Cr_2O_7$) solution till the solution attains a deep

purple colour. The amount of potassium dichromate solution consumed gives a measure of the metallic iron present in the DRI by the following relation

1 ml 0.1 N $K_2Cr_2O_7$ = 0.001 862 gm of Fe(M)………(2.15)

Fe(T) is the measure of the sum total of reduced metal as well as of the iron present in the unreduced iron oxides. The amount of Fe(T) in 1 gm DRI can be approximated in the following manner.

- Total Fe_3O_4 present in the ore = 62.2 wt.%
- Fe(T) present in ore = 62.2 × (3 × 56) / (3 × 56 + 16 × 4) = 45.1 wt.%
- Fe(T) present in an initial hardened pellet in gm = 0.451 × initial wt. of pellet
- The DRI produced will have a weight less than that of the initial pellet but will contain the same amount of Fe(T) in gm which is **0.451 × initial wt. of pellet**.
- Now **Fe(T) % in DRI** = (0.451 × initial wt. of pellet /wt. of DRI produced) × 100.
- **Thus, Fe(T) in 1 gm DRI= (Fe(T) wt.% in DRI /100) × 1**……(2.16)

2.6.4. Preparation of synthetic pellets

It was essential to investigate the possible influence of gangue elements on the CCS and the reducibility of pellets. Thus, synthetic pellets were prepared by mixing commercially available magnetite powder (analytical grade) with different proportions of MgO, Al_2O_3, and SiO_2 (analytical grade), respectively, based on **Table 2.4**. The compositions of the pellets are varied in the following way. Let's suppose the multimetallic ore is subjected to any type of treatment to reduce the amount of Al_2O_3 from 14.7% to 0%. The weight of the input material will be more than that of the output material and the wt.% of Fe_3O_4 and other oxides in the output of the process will be higher than that of input material. Thus, mixtures corresponding to that of the output material were made and the compositions of those mixtures are mentioned in Table 5.1.

Table 2.4: Compositions of different mixtures used to prepare synthetic pellets

Mixture		Oxides(wt.%)									
		Fe_3O_4	Al_2O_3	SiO_2	CrO_3	MgO	TiO_2	NiO	MnO	CaO	P_2O_5
Al_2O_3 (wt.%)	**0**	72.92	0.00	16.88	5.80	1.65	0.73	0.69	0.53	0.16	0.21
	3	70.73	3.00	16.37	5.63	1.60	0.71	0.67	0.51	0.16	0.20
	6	68.55	6.00	15.87	5.46	1.55	0.68	0.65	0.50	0.15	0.20
	9	66.35	9.00	15.36	5.28	1.50	0.66	0.63	0.48	0.15	0.19
	12	64.17	12.00	14.86	5.11	1.45	0.64	0.61	0.46	0.14	0.19
	14.7	62.2	14.7	14.4	4.95	1.41	0.62	0.59	0.45	0.14	0.18
SiO_2 (wt.%)	**0**	72.66	17.17	0.00	5.78	1.65	0.72	0.69	0.53	0.16	0.21
	3	70.48	16.66	3.00	5.61	1.60	0.70	0.67	0.51	0.16	0.20
	6	68.31	16.14	6.00	5.44	1.55	0.68	0.65	0.49	0.15	0.20
	9	66.12	15.63	9.00	5.26	1.50	0.66	0.63	0.48	0.15	0.19
	12	63.95	15.11	12.00	5.09	1.45	0.64	0.61	0.46	0.14	0.19
	14.4	62.2	14.7	14.4	4.95	1.41	0.62	0.59	0.45	0.14	0.18
MgO (wt.%)	**0**	63.09	14.91	14.61	5.02	0.00	0.63	0.60	0.46	0.14	0.18
	0.3	62.90	14.87	14.56	5.01	0.30	0.63	0.60	0.46	0.14	0.18
	0.6	62.71	14.82	14.52	4.99	0.60	0.63	0.59	0.45	0.14	0.18
	0.9	62.52	14.78	14.47	4.98	0.90	0.62	0.59	0.45	0.14	0.18
	1.2	62.33	14.73	14.43	4.96	1.20	0.62	0.59	0.45	0.14	0.18
	1.41	62.2	14.7	14.4	4.95	1.41	0.62	0.59	0.45	0.14	0.18

Three groups with each having 6 sets of green pellets (20 pelllets in each set) were prepared. The first group contained 6 sets of pellets with each set corresponding to a different wt.% of SiO_2 (0, 3, 6, 9, 12, 14.4). Similarly, the second group also had 6 sets, each corresponding to a different wt.% of Al_2O_3 (0, 3, 6, 9, 12, 14.7). The third group also had 6 sets each corresponding to a different wt.% of MgO (0, 0.3, 0.6, 0.9, 1.2,

1.41). The green pellets containing 1.5 wt.% colemanite as binder were indurated at 1250 °C for 2 hours.

2.7. Melting of DRI

The experiment was aimed at comparing the chemical composition and recovery of valuable elements produced by melting two types of direct reduced iron (DRI): H_2-DRI, produced through hydrogen reduction, and C-DRI, produced through non-coking coal reduction. Both types of DRI were melted under a reducing flame generated by an oxyacetylene torch. The process followed is depicted in **Figure 2.17**.

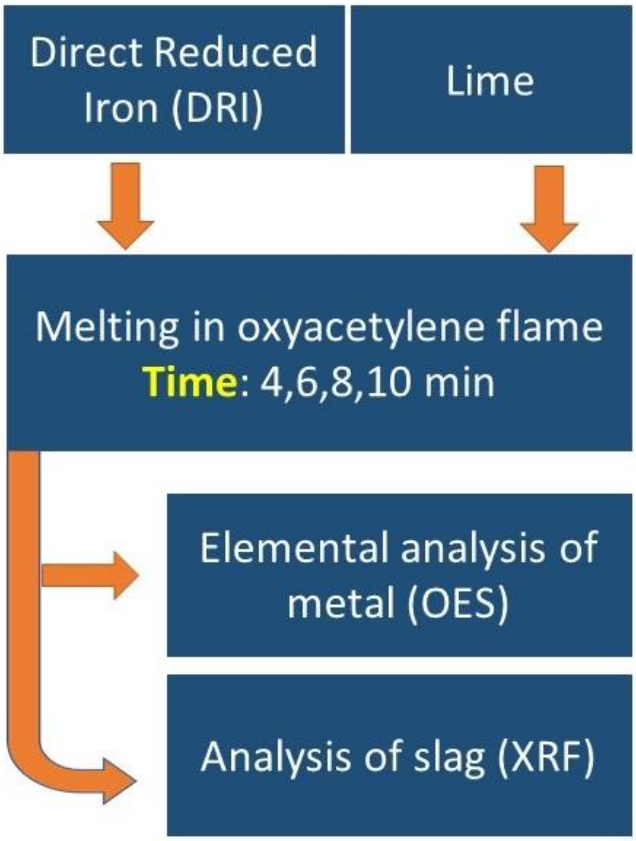

Figure 2.17: Process for melting of DRI and the characterization of the melting products.

Initially, lime (to maintain a basicity of 1) and 4-5 DRI were positioned within an alumina crucible, as depicted in **Figure 2.18**. The dimensions of the crucible are provided in **Figure 2.19**. Subsequently, a reducing flame was generated by adjusting the flow of acetylene and oxygen gas to achieve a ratio of acetylene to oxygen of 1.5:1.

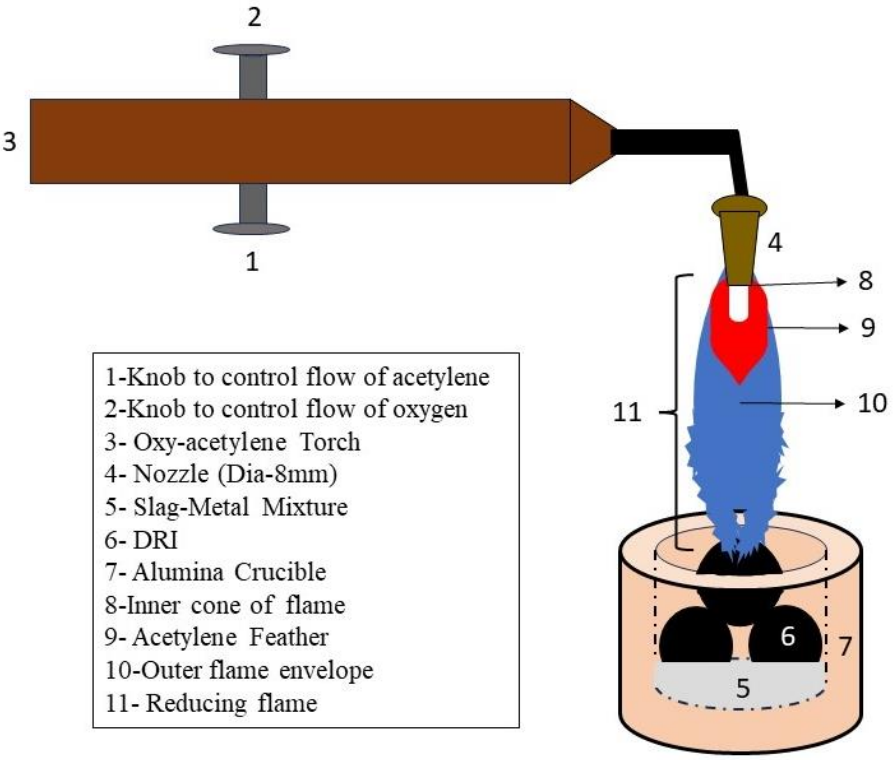

Figure 2.18: Setup used for Oxy-acetylene flame melting of DRI

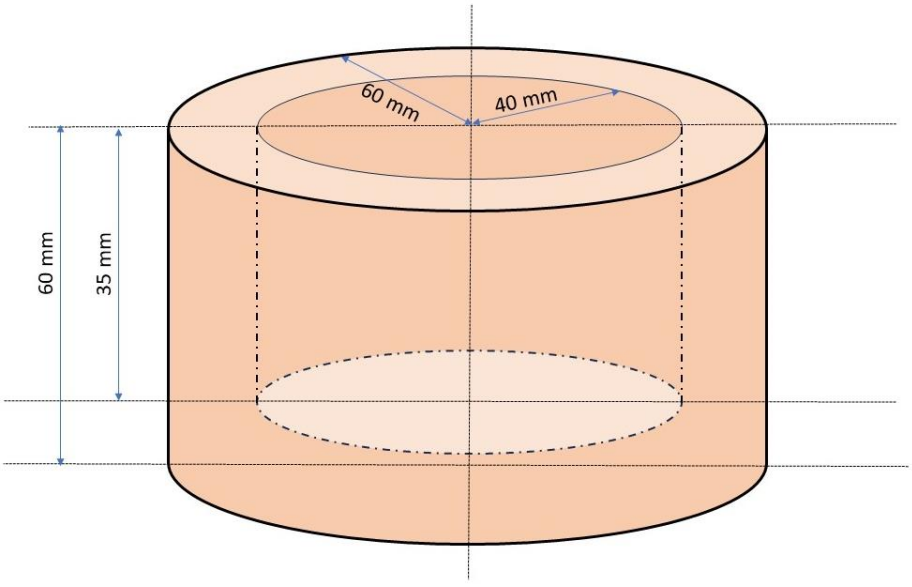

Figure 2.19: Crucible used for melting of DRI

The reducing flame was maintained in direct contact with the DRI, as illustrated in **Figure 2.18**, for the specified melting duration. This melting duration ranged from 4 to 10 mins, allowing for an exploration of the impact of melting time on both metallic yield and the chemical composition of the resulting metal. Following the predetermined melting time, the flame was extinguished, and the molten material was left to cool and solidify within the crucible. Subsequently, the metal in the form of nuggets, was extracted from the crucible and weighed to ascertain the yield. The yield was calculated as

Yield (%) = (Wt. of metal obtained/Wt. of DRI used for melting) ×100…….(2.17)

The metal nuggets were remelted in a neutral flame obtained from the oxyacetylene torch to fuse them into a single piece. The fused metallic sample was analyzed for its chemical composition by OES as described in Section 2.3.4. The slag was analyzed for its chemical composition by XRF as described in Section 2.3.3.