Chapter 1:

Introduction and Literature Survey

1.1. Introduction

The iron and steel industry stands as one of the fundamental pillars of modern civilization, providing the essential materials needed for infrastructure, manufacturing, and countless other applications. The production of iron and steel not only fuels industrial growth but also serves as a barometer of a nation's industrial prowess and economic strength. The iron industry in India has a rich history that spans centuries, deeply intertwined with the country's economic development. From ancient times to the present day, iron has played a vital role in India's growth story, contributing significantly to its industrialization and infrastructure. India's crude steel production capacity has been expanding, in both public and private sector steel companies investing in modernization and capacity enhancement projects. This has led India to occupy 2nd position in crude steel production globally in 2023. With a production of 128.2 Mt of crude steel (World Steel Association) [1], iron and steel industry contributed to 2.5 % of India’s GDP in 2023 (Ministry of Steel, Govt. of India) [2] . Such a large production volume was only possible due to the significant resources of iron ore and other important raw materials like coal. However, rising raw material costs, energy constraints, stringent environmental regulations, and fluctuating market dynamics pose significant hurdles to sustainable growth. Moreover, the ironmaking industry is increasingly exploring alternative raw materials and process technologies to mitigate risks associated with traditional inputs and address sustainability concerns. These alternatives include the utilization of direct reduced iron (DRI), iron ore pellets, and scrap steel, as well as the development of innovative processes such as hydrogen-based direct reduction and bio-based reducing agents. Understanding the intricate relationship between ironmaking and the raw material scenario is essential for navigating the challenges and opportunities facing the industry.

1.2. Raw Materials for Iron Making: Indian Scenario

1.2.1. Iron ore

India ranks 4th in iron ore production as per the Annual Report (2021-22) by the Ministry of Mines, Govt. of India. With total resources of over 33.276 billion tonnes of hematite (Fe_2O_3) and magnetite (Fe_3O_4), India is among the leading producers as well as exporters of iron ore in the world[3]**(Figure 1.1a).** The production of Iron ore consisting of lumps, fines, and concentrates was 204.48 million tonnes (Mt) in 2021, of which lumps constituted 61.59 Mt (30.12%), fines constituted 141.70 Mt (69.30%), and concentrates constituted 1.19 Mt (0.58%) [3]**(Figure 1.1b)**. Odisha was the leading producer of iron ore, accounting for 52% of total production, followed by Chhattisgarh (18%), Karnataka (17%), and Jharkhand (10%). Iron ore production was also reported from Andhra Pradesh, Goa, Madhya Pradesh, Maharashtra, and Rajasthan.

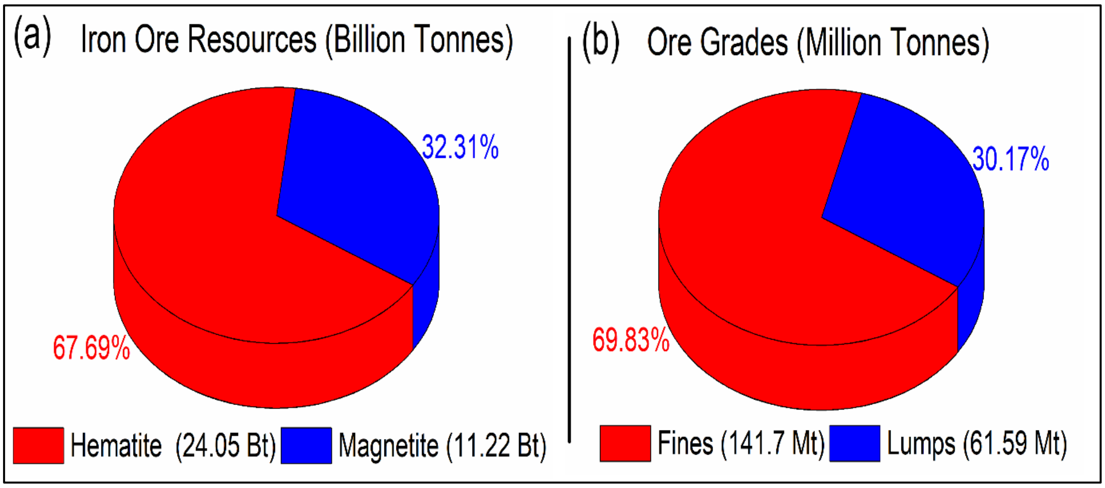

Figure 1.1: (a)Iron Ore resources in India (b) Classification of Ore grades produced in India in 2021.

1.2.1.1. Hematite

Hematite is one of the most important iron ore from which iron is extracted. Due to its high grade and availability, hematite is considered superior for ironmaking. Hematite, α- Fe_2O_3, is the oldest known iron oxide mineral and is widespread in rocks and soils. It is a common rock-forming mineral found in sedimentary, metamorphic, and igneous rocks worldwide. Although it was once mined at thousands of locations worldwide, today, almost all of the production comes from a few dozen large deposits where significant equipment investments allow companies to mine and process the ore efficiently. As per Indian Minerals Yearbook 2022 [3], the total resources of hematite are estimated at 24,057 Mt, of which 6,209 Mt (25.8%) constitute the ‘Reserves' category and the balance 17,848 Mt (74.2%) are under the 'Remaining Resources' category. The state wise distribution of hematite ore in India is shown in **Figure 1.2**. By grades, lumps constitute about 45%, followed by fines (26%), lumps with fines (13%), and the remaining 15% are black Iron ore, Unclassified, Not-known, and other grades.

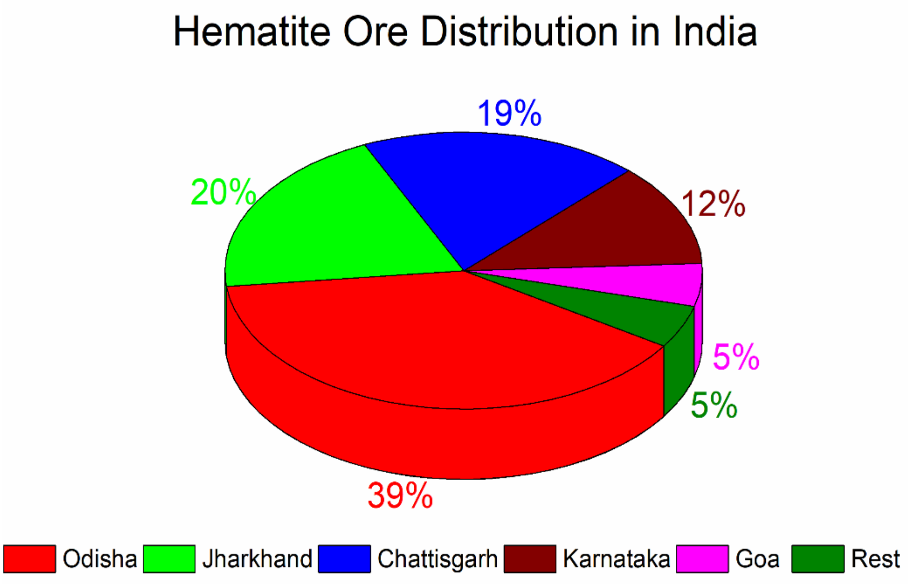

Figure 1.2: Hematite Ore distribution in India

1.2.1.2. Magnetite

Magnetite (Fe_3O_4) is a black, ferromagnetic mineral containing both Fe^{2+} and and Fe^{3+}. It has an inverse spinel structure. Magnetite is a heavy black mineral with its characteristics metallic lusture and contains about 72.4% iron in the pure form. As per Indian Minerals Yearbook[3], the total resources of magnetite are estimated at 11,227 Mt, of which 'Reserves' constitute a mere 202 Mt while 11,024 Mt are placed under 'Remaining Resources.' The state wise distribution of magnetite ore is shown in **Figure 1.3**. Classification based on grades shows that 21% of resources are of Metallurgical grade, while 79% belong to grades categorized as unclassified, unknown, and others. Based on mode of occurrence and origin, India's magnetite iron ore deposits are divided into five groups, viz. Banded Iron Ore Formation, Sedimentary iron ore deposits of sideritic and limonitic composition, Lateritic ores derived from sub-aerial alteration of gneiss, schists, etc. Titaniferous and Vanadiferous magnetite deposits and Fault and fissures filling deposits, but the largest concentration of economic deposits are associated with volcano-sedimentary Banded Iron Formation (BIF) of Precambrian age. The BIF, mainly comprising of banded hematite quartzite / banded hematite jasper (BHQ/ BHJ), contains 25 – 40% iron. By supergene enrichment, the iron content of this BHQ/BHJ has, in many places, gone up to about 55 – +65%, making them excellent quality ore. Magnetite dominant deposits are generally associated with banded magnetite quartzite (BMQ) and contain about 25 – 40% iron.

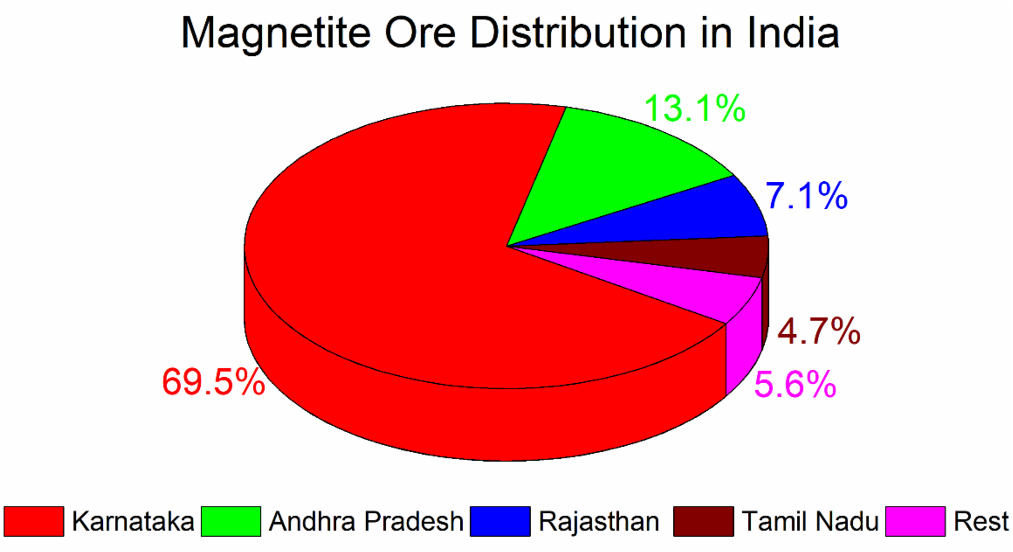

Figure 1.3: Magnetite Ore distribution in India

1.2.1.3. Iron Ore Fines

About 70 % of iron ores (~141.7 Mt) mined in 2021-22 and having a value of ₹ 29998 Crores are in the form of fines [3]**(Figure 1.1b)**. The mined ore having sizes >10 mm is considered as lumps. Lumps can be used directly in any ironmaking process. The ore having size < 10 mm are considered as fines. These iron ore fines cannot be directly used in most furnaces as they would clog the furnaces. The fines are thus converted to agglomerates like pellets and sinter with sizes (10-20 mm), and used in furnaces as raw materials.

1.2.2. Pellets and Sinter

Iron ore fines having a size of 4-10 mm are agglomerated to form sinter, and fines having a size < 4mm are agglomerated to form pellets. They are used extensively in blast furnaces and rotary kilns as they help to maintain raw material chemistry and bed porosity. The sintering process is used to agglomerate a mix of iron ore fines, fluxes, and coke breeze to produce a sinter having a size of 10-30 mm **(Figure 1.4a)**. There are about 39 sintering plants in operation in India, which have a total capacity of 96.13 million tonnes per annum[3]. The pelletizing process converts the iron ore fines, binder, and moisture to form soft spherical pellets of size 10-20 mm. A thermal treatment is done in a kiln to bake the soft raw pellet into hard spheres so that it can be used in furnaces **(Figure 1.4b)**. Currently, about 48 pelletization plants in India are in operation which have an annual capacity of 126.4 million tonnes[3].

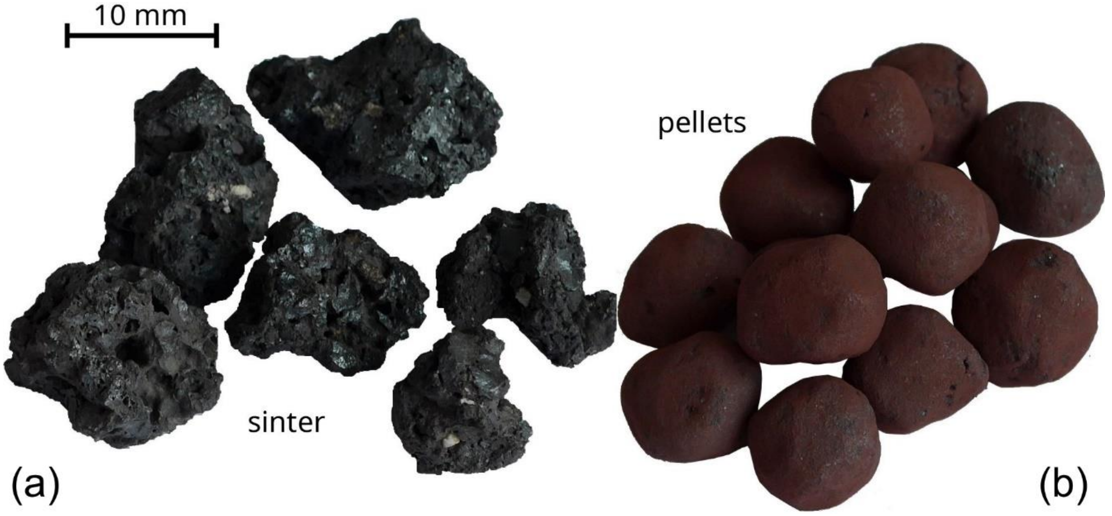

Figure 1.4: Representative image of sinter and pellet

1.2.3. Reductants

A reducing agent is a chemical species that reduces the iron oxides to metallic iron and itself gets oxidized. For example, Carbon reduces Fe_2O_3 to Fe, and itself gets oxidized to CO_2. Two types of reductants are used in ironmaking: Solid reductants (coal, coke) and gaseous reductants (Carbon monoxide, Reformed natural gas, Hydrogen). Most of the ironmaking in India is done with solid reactants. India has 352.123 Bt of coal resources, of which 177.179 Bt are proved resources and 146.949 Bt are indicated resources. Of the proven resources, only 5.313 Bt are of prime coking coal, 28.08 billion tonnes are of medium coking coal, and 317.026 Bt are of non-coking coal[3]. Thus, India has a shortage of prime coking coal and have very high reserves of non-coking coal. The coking coal deficit is maintained through imports, which adversely impacts the economy of the country.

1.3. Multimetallic Magnetite Iron Ore from ophiolite belt of Nagaland

Section 1.2.1 reveals that India possesses impressive hematite resources totaling 24,057 million tonnes (Mt), with 6,209 Mt categorized as reserves and 17,848 Mt as remaining resources [3]. Similarly, India boasts approximately 11,227 Mt of magnetite, with 202 Mt categorized as reserves and 11,025 Mt as remaining resources[3]. While 26% of hematite resources fall under the reserve category, only a mere 1.8% of magnetite resources receive the same recognition. Although India's hematite reserves currently suffice, it's crucial to tap into magnetite resources. According to the World Steel Association, global crude steel production reached 1,715.1 Mt as of December 2023, with India contributing 128.2 Mt [1]. India aims to produce 300 Mt of crude steel by 2030. Achieving such a monumental target necessitates the utilization of low-grade ores, of which India possesses vast reserves.

The discovery of the Nickel-chromium-cobalt-bearing magnetite deposit in Nagaland, particularly in Pokhpur within the Tuensang district, is a significant finding. This rare type of low-grade iron ore is crucial as India heavily relies on imports for strategic metals like nickel and cobalt. The utilization of this ore deposit holds promise as a potential contributor to the economic development of the North East region. Located in the north-eastern extremity of the Nagaland-Manipur ophiolite belt, part of the Indo-Myanmar ranges which include the Arakan Yoma, Chin, and Naga hills, the Pokphur magnetite deposit stands out. Its precise location is illustrated in **Figure 1.5** [4]. These magnetite ores manifest as sheet-like bodies across the ultramafic to mafic cumulate sequence [5].

Figure 1.5: Occurrence of magnetite ore in Nagaland [4]

Various characterization studies on the magnetite samples have been conducted by NEIST (formerly RRL) in Jorhat [6]**,** and IMMT (formerly RRL) in Bhubaneswar[7]. Additionally, preliminary investigations[8] on five different bulk samples were carried out at the National Metallurgical Laboratory in Jamshedpur to explore the potential for metal extraction from these ores. Notably, higher concentrations of Ni and Co were observed in sub-surface samples, particularly along the central zones of the boreholes.

The analysis revealed that magnetite comprised approximately 40 to 50 % of the specimens, with the remainder mainly consisting of silicates[9].

Moreover, studies on the multimetallic magnetite ores (MMO) have been undertaken to understand their mineralogical, chemical, and metallurgical characteristics. These investigations unveiled a mineral composition predominantly comprising magnetite, chromite, and hematite, alongside goethite, ilmenite, trevorite, pentlandite, and millerite[10]. Further characterization studies of the fines established that magnetite-rich regions contained between 35-65% Fe and 1-5 % Cr, while chromite-rich regions exhibited Cr concentrations of up to 30% and Fe concentrations ranging from 15-20%. Importantly, the beneficiation process resulted in minimal loss of Cr [11].

The MMO, ranging from 10-12.5 mm in size, were reduced in a gas-solid system at 900-1050 °C through indirect reduction using a mixture of reducing gases (30% CO +70% N_2). Additionally, MMO particles (0.59-5mm) were reduced in solid-solid systems through direct reduction in a horizontal tubular furnace at 900-1200 °C using petroleum coke and low ash coke as reductant. However, the inherent low reducibility of magnetite posed challenges in both solid-state and gas-based reduction methods, resulting in the formation of a dense product that hindered further reduction[10].

To tackle the challenge of low reducibility in fines, researchers investigated the efficacy of adding hydrogen to the reducing gas. A study conducted by Kuila et al. showcased promising results, revealing that MMO fines could be fully reduced in a pure H_2 gas atmosphere within just 25 mins at 900 °C, with a flow rate of 0.4L/min [12]. Furthermore, due to the low reducibility of the MMO lumps, direct melting of lumps in an arc furnace and induction furnace was investigated. This approach successfully extracted 97- 98% iron, 91 – 93% chromium, 95 – 96% nickel, 89 – 91% cobalt, 20 – 22% silicon, and 7.0 – 34% manganese present in the ore [13]. The reduction of chromium dictated the amount of carbon required for smelting reduction, with the oxides of nickel and iron being completely reduced prior to the reduction of chromium oxides [14]. Subsequently, a large-scale melting study was conducted at NML Jamshedpur, producing Ni-hard iron and abrasive-resistant cast iron from the ore, which were successfully tested as grinding media in cement kilns[15].

Despite extensive research on the mineralogy and reducibility of MMO lumps, there is a notable lack of studies on the utilization of fines. Considering that mining MMO in the future will generate fines, it was imperative to find proper utilization methods. Pelletization emerges as a viable agglomeration technique to utilize these fines effectively.

1.4. Pelletization of ore fines

Over time, the gradual depletion of high-grade iron ore deposits, coupled with growing environmental concerns regarding particulate emissions, has underscored the imperative for recycling and optimizing the utilization of iron ores. In response, pelletizing technology has emerged as a highly innovative approach to transform iron ore fines, traditionally considered as mine waste, into valuable pellets.

Unlike conventional agglomeration methods, pelletization offers the unique advantage of utilizing ultra-fine solid particles, thereby enabling better liberation and beneficiation. With pelletization, finer particles (<150 µm) are employed compared to other methods such as traveling grate sintering and briquetting (0.15 mm to 10 mm). This allows for the production of pellets characterized by homogenous chemistry, uniform shape, and a narrow size distribution, enhancing bed permeability within furnaces.

Moreover, the pellets produced through this process can be efficiently stored and transported over long distances, serving as input ferrous burdens for iron and steel manufacturers worldwide. These designer pellets, with precisely controlled chemistry, contribute to reduced coke consumption and optimize slag chemistry compared to conventional burdens. Consequently, pelletization has evolved into a self-sustaining economic activity, gaining traction as a preferred charge mix in sponge iron production and blast furnaces alike [16].

1.5. Binders and their role in Pelletization

A binder, or binding agent, serves as a vital component in iron ore pelletization, facilitating the formation of cohesive pellets from raw materials. Broadly defined as any material that promotes cohesion through mechanical, chemical, or adhesive means, binders are typically liquid or dough-like substances that solidify during chemical or physical processes. They are further categorized as organic (such as bitums, animal and plant glues, and polymers) or inorganic (including lime, cement, gypsum, and liquid glass), with variations based on the main material's nature, ranging from metallic, ceramic to polymeric compositions. In iron ore pelletization, binders fulfill two crucial functions:

- **Nucleation and Agglomeration**: The binder imparts plasticity to the moist ore, facilitating the formation of nucleation sites from which pellets grow at a controlled rate. This phase ensures the consolidation of particles into cohesive agglomerates.
- **Particle Cohesion and Sintering**: During drying, the binder maintains particle cohesion within the agglomerates. As water is removed, the binder continues to bind the particles until the pellet undergoes sufficient heating to sinter the grains together, forming a solid pellet structure[17].

The suitability of a binder is assessed based on its effectiveness in performing these functions while avoiding contamination or sintering issues. Binders are utilized to enhance various pellet properties, including:

- Balling of Iron Ores: Binders promote and facilitate the balling process in pelletizing drums or discs, ensuring uniform pellet formation.
- Strength Improvement: Binders enhance the strength of green, dry, pre-heated, and fired pellets, contributing to their durability during handling and transportation.
- Heat Sensitivity Mitigation: Binders help overcome issues associated with heat-sensitive balls during the drying stage, such as increased shock temperature of green balls.
- Lower Temperature Attainment: Binders enable the production of high-quality pellets at lower temperatures, optimizing energy efficiency and reducing production costs.
- Quality Enhancement: Binders improve the properties of fired pellets, including their mechanical strength, porosity, and metallurgical performance[16].

In essence, binders play a pivotal role in iron ore pelletization, facilitating the production of high-quality pellets with desirable properties while ensuring process efficiency and product quality. The pellets produced by any kind of binder must satisfy certain industrial standards (IS 11092 and IS 6495) as mentioned in **Table 1.1**. The properties in **Table 1.1** are explained in more detail in Section 2.

Table 1.1: Desirable properties of pellets for ironmaking

Property	Typical Values
Dry Strength	2.2 kg/pellet
Cold Crushing Strength (CCS)	200 kg/pellet
Abrasion Index	<5%
Shatter Index	85-95%
Tumbler Index	>94 %

1.6. Pelletization of Multimetallic Ore and its benefits

Apart from the benefits outlined in section 1.4, pelletization of this multimetallic ore offers additional advantages unique to its composition. The pelletization process typically involves two key steps: green ball formation and induration. In the case of this ore, the induration step holds particular significance. During induration, the magnetite present in the ore can be oxidized to hematite, thereby enhancing the ore's reducibility. This conversion transforms the reduction process from $Fe_3O_4 \rightarrow Fe_xO \rightarrow Fe$ to a more favorable $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe_xO \rightarrow Fe$ process. This three-stage reduction causes significant expansion (about 25%) due to a change in crystal structure from hexagonal hematite to cubic magnetite[18]. Furthermore, the induration process facilitates the oxidation of chromite to a complex sesquioxide. Preoxidation of chromite ores has been shown in various studies to improve their reducibility [19-21]. The reduction of chromite in this ore is crucial in determining the amount of reductant required.

Bentonite is a commonly used binder due to its affordability, high water adsorption capacity, and dry film strength [22]. However, the high silica and alumina content in the multimetallic ore, like many low-grade iron ores, renders bentonite unsuitable as it would introduce additional silica and alumina into the pellet mix. Physical beneficiation to reduce silica and alumina is not feasible as it would also decrease the nickel content, some of which is associated with the non-magnetic fraction and would be lost during beneficiation [13]. Therefore, alternative binders must be explored for this ore. Ideally, the chosen binder should contain additives such as borates, fluorides, SiO_2, CaO, MgO, and Al_2O_3, as these additives have been shown to positively impact chromite reducibility [23-26]. By selecting binders with these additives, the pelletization process can maximize the ore's potential while maintaining its valuable composition.

1.7. Alternative binders for pelletization of multimetallic magnetite ore fines

Numerous studies have explored alternative binders for pelletizing iron ores, aiming to move beyond conventional options like bentonite. For instance, Shaik et al. investigated colemanite, an inorganic binder rich in boron, achieving the required compressive strength (CCS) with a dosage of 0.4%. The strength enhancement was attributed to the formation of borosilicate slag bonds [27]. In another study, Kotta et al. examined molasses and dextrin as binders for hematite pelletization, with pellets containing 4% molasses and 1% dextrin meeting industrial standards at a firing temperature of 1250 °C [28, 29]. Similarly, Devashayam et al. explored cold setting binders (binders which can produce required CCS at room temperatures) like epoxy resin and periglue for hematite ore pelletization, achieving pellets with CCS of 407 kg/pellet [30].

Moreover, lime addition, as investigated by El Husseiny et al. and Hu et al., proved beneficial in improving drop number and CCS of hematite pellets [23, 31]. Sivrikaya et al. conducted extensive research investigating various binders for both hematite and magnetite ores, including colemanite, dextrin, starches, carboxymethyl cellulose, different molasses, hemicellulose, corn starch, and proprietary binders like Ciba. Among these, colemanite, an inorganic binder, was found to enhance the cold crushing strength (CCS) of pellets. However, other organic binders provided satisfactory green and dry strength but exhibited limitations at high temperatures. To address these challenges, the researchers suggested employing a combination of organic and inorganic binders for both hematite and magnetite ores. This approach aimed to capitalize on the strength of each type of binder, leveraging the benefits of inorganic binders like colemanite for enhanced CCS, while organic binders contributed to green and dry strength [22, 32-36]. Similarly, carboxymethyl cellulose (CMC) was explored by Fan et al. and Haas et al., with varying results; while green strength and CCS of magnetite pellets improved, obtaining indurated hematite pellets with sufficient strength according to **Table 1.1**, proved challenging [37, 38].

Srivastava et al. investigated effect of nineteen binders on magnetite, of which hemicellulose, sodium lignosulphonate, and lactose monohydrate provided strong indurated pellets having CCS > 200 kg/pellet [39]. Furthermore, Moraes et al. explored multiple binders for magnetite like sodium hydroxide, sodium carbonate, sodium metasilicate, sodium tripolyphosphate, carboxymethyl cellulose. The best CCS was achieved with pellets made with 1.5% sodium silicate[40]. Additionally, waste products of steelmaking, such as LD sludge, were found to enhance the CCS, tumbler, and shatter index of hematite pellets in studies by Pal et al [41].

Overall, binder performance is influenced by the chemical composition of the iron ores used. While some binders like dextrin may not be effective for magnetite ores, they may perform well for hematite ores. Binders like sodium silicate and sodium lignosulphonate, although successful, cannot be used for certain ores due to their impact on pellet mix composition. Among all binders, colemanite and starches like dextrin, cornstarch, and carboxymethyl cellulose appear suitable for most types of ores.

1.8. Reduction of Multimetallic ores

There are two primary routes for ironmaking: blast furnace and Direct Reduction (DR). In India, the low reserves of prime coking coal have prompted the exploration of direct reduction of iron ores as an alternative. This approach leverages the abundant non-coking coal resources in the country, saving costs associated with importing expensive coking coal and converting it to coke. Direct Reduction (DR) encompasses various processes based on different feedstocks, furnaces, and reducing agents. Unlike the blast furnace method, which involves both solid and liquid state iron oxide reduction, DR involves removing oxygen from iron ores in the solid state. This technique offers flexibility, making it a preferred choice for processing multimetallic ores worldwide.

Both solid-based and gas-based reduction methods have been extensively studied for multimetallic ores like V-Ti Magnetite (VTM) and high chromium V–Ti magnetite (HCVTM). Sui et al. explored gas-based reduction of VTM pellets, achieving a maximum reduction of 94.1% in a H_2 atmosphere at 1050 °C for 60 mins. The reduction rate increased with higher temperatures and $H_2/(CO + H_2)$ ratio [42]. The carbothermic reduction of VTM and HCVTM ores has also been investigated, with studies showing enhanced reducibility by increasing volatile matter in coal. An increase in volatile matter increased the amount of hydrogen in the reducing gas [43, 44]. Samanta et al. achieved a maximum reduction rate of 78% for VTM lumps at 1200 °C using solid activated charcoal[45]. For HCVTM ore, reduction studies using H_2–CO–CO_2 gas revealed a 95% reduction in pellets within 40 mins at 1100 °C and the reduction increased with higher H_2 gas content[46]. Similarly, methane gas was utilized for solid state reduction of Fe–Ti–V–Cr ore, achieving full reduction of magnetite at 1100 °C after 60 mins[47].

The reduction of multimetallic ores is very complex in nature and the reduction usually proceeds by formation of intermediate complex oxides which lead to incomplete reduction. Cheng et al studied the reduction mechanism of preoxidised Cr-V-Ti-Fe ores and established the sequence of reduction of various oxides as follows: $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$; $Fe_2Ti_3O_9 \rightarrow Fe_2TiO_4 \rightarrow Fe_5TiO_8 \rightarrow FeTiO_3$; $V_2O_3 \rightarrow VO$; $(Fe_{0.6}Cr_{0.4})_2O_3 \rightarrow FeO.Cr_2O_3 \rightarrow Cr_2O_3$ [48]. In a study by Liu et al., it was found that complete reduction of VTM (V-Ti Magnetite) concentrates using solid reductants was not achievable due to the formation of complex phases during the reduction process [49]. The association of iron with vanadium and titanium in the reduction products decreased the separation efficiency of the metals[50].

Most studies have indicated that hydrogen is a superior reductant compared to solid carbon or carbon monoxide (CO), attributing this superiority to its small size and higher diffusivity. Overall, the reduction of multimetallic ores presents challenges due to complex phase formations, but the use of hydrogen as a reductant shows promise in overcoming these hurdles.

1.9. Hydrogen reduction: An eco friendly reduction approach

The flexible nature of DR process allows for the use of hydrogen gas as a reductant. Use of hydrogen gas as a reductant instead of carbonaceous material offers significant advantages like lower greenhouse gas (GHG) emissions, faster reduction at lower temperatures, and the absence of a complicated boudouard (C-O) reaction system. The iron and steel industry contributes about 7 % of the total carbon dioxide emission globally and about 35% of all CO_2 produced in the manufacturing sector[51, 52]. About 1.9 tonnes of CO_2 is produced per ton of crude steel[53, 54]. Use of green hydrogen can reduce the emissions of 2.3 gigatonnes of CO_2 annually and decrease global warming[55, 56]. The most important benefit would be the production of water as a

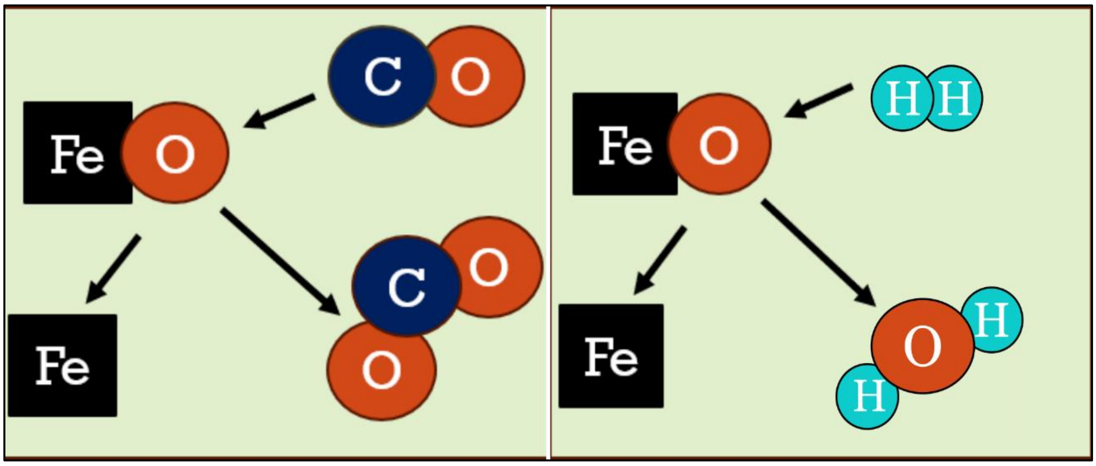

Figure 1.6: Difference in product with change in reductant

byproduct gas, which could reduce the carbon footprint of the iron and steel industry **(Figure 1.6)** [57]. As the hydrogen molecule size is smaller than that of CO, the diffusion rates into the pellet will be much higher than CO, which could lead to a faster reduction rate and enhanced metallization. Depending on the manufacturing method, there are three types of hydrogen: gray hydrogen, blue hydrogen, and green hydrogen. Gray hydrogen is the cheapest ($0.98-2.93 per kg), as it is produced from natural gas. Blue hydrogen is essentially gray hydrogen but uses carbon capture and storage technologies. Use of blue hydrogen reduces greenhouse gases at an added cost; thus, the production cost is $1.8-$4.7 per kg. The cleanest and most expensive at $ 4.5- $ 12 per kg is green hydrogen, produced by electrolysis of water using electricity generated from renewable sources. Though the current cost of hydrogen is high, it is estimated that in countries like Brazil, China, India, and Sweden, the cost of green hydrogen will become less than gray hydrogen by 2030[58, 59]. The reduced cost could make hydrogen a potent alternative to carbonaceous reductants in Direct Reduction (DR) processes.

The reduction rate of iron oxides (sinters, pellets, fines, lumps) with H_2 gas surpasses that observed for CO-based processes, as indicated by several studies [54, 60, 61]. Higher conversion of the raw material is usually achieved under H_2 atmosphere than in the CO atmosphere. Hematite Pellets (diameter 10-13 mm) for instance, were nearly entirely reduced to metallic Fe by H_2 at 800 °C, whereas only the edge and transition areas of the pellets were reduced by CO [62]. Similarly Iron ore-coal pellets (TFe:67%) were almost entirely reduced by H_2 gas at 1100 °C while they were only 87% reduced in a pure CO environment [63].

An increase in the hydrogen content of a reducing gas also enhances its reduction efficacy, as demonstrated in a study by Yi et al. on iron ore pellets (TFe:65%) with a diameter of 12.5-16 mm. In this study, the reduction time decreased from 25 mins to about 13 mins when the H_2:CO ratio was changed from 0.4:1 to 2.6:1 [64]. Similar results were also obtained in other studies[65]. This increase in reducibility can be attributed to the easy nucleation of magnetite and wustite, along with fast solid-state diffusion, which contribute to fast reduction kinetics [53].

The advantages of hydrogen-based reduction also apply to iron ore fines. Oh et al. investigated the reduction of hematite particles (0.74μm) across a temperature range of 800-1300 °C and found that the reduction reaction duration with CO was approximately 5.7 times longer than with H_2 [66]. Similarly, Pineau et al. studied the reduction of hematite (TFe: 70%) powder (1-2μm) and magnetite (TFe: 63%) powder (1-2μm) in the temperature range of 220-680 °C and 210-950°C, respectively. It was observed that the reduction rate of both Fe_2O_3 and Fe_3O_4 was higher with H_2 compared to CO [67, 68].

In a study by He et al., hydrogen reduction of commercial Brazilian hematite ore fines was completed at 800 °C within 60 mins. The rate of reduction increased with the rise in temperature and H_2 gas content in the reducing gas[69]. Similarly, the reduction of magnetite concentrates was also enhanced by adding hydrogen to CO-CO_2

mixtures[70]. Furthermore, the ease of reduction with H_2 also leads to lower activation energies compared to CO reduction[71].

Hydrogen reduced pellets exhibit reduced swelling and cracking compared to carbon reduced pellets. The swelling and cracking of pellets decrease with an increase in the H_2 content of the reducing gases, with particle swelling typically observed in a CO atmosphere[66]. Yi et al. concluded that the volume swelling of pellets intensified with an increase in the CO / (CO + H_2) ratio [72]. Furthermore, research has demonstrated that adding H_2 to the CO-CO_2 gas mixture decreases swelling not only in magnetite concentrates but also in hematite pellets [70] [73].

The decreased swelling of the pellets contributes to improved reduction degradation properties, as measured by the Reduction Degradation Index (RDI). RDI is a quantitative measure of the amount of fines generated after the reduction of pellets, sinters, or lump ores. Generally, materials with lower strength tend to exhibit higher fragmentation and fine generation, with the RDI of sinters increasing with the amount of H_2 gas in the gas mix [74]. Therefore, H_2-based reduction offers advantages over carbon based reduction due to its faster reduction kinetics and decreased tendency for cracking in agglomerates and lumps.

1.10. Scope of present investigation

The literature on multimetallic magnetite ore (MMO) from the Pokhpur region of Nagaland highlights its unique composition, notably containing significant amounts of chromium (Cr) and nickel (Ni). Various studies have been conducted to determine the mineralogical, chemical, and metallurgical characteristics of these ores. Additionally, extensive research has explored different techniques such as smelting reduction, solid-based, and gas-based reduction methods for the ore lumps. However, despite thorough investigations into ore lumps, there is a noticeable scarcity of studies on the utilization of fines of the MMO. Future mining operations are expected to generate substantial quantities of fines, necessitating the adoption of agglomeration techniques for effective processing. Among these methods, pelletization stands out due to its ability to control raw material chemistry, maintain uniform bed permeability, and enhance reducibility through the conversion of hematite to magnetite and chromite to sesquioxide.

The success of pelletization hinges on selecting an appropriate binder to produce pellets with adequate low and high-temperature strength, along with specific physical properties outlined in **Table 1.1**. Bentonite, a commonly used binder, is unsuitable for the multimetallic magnetite ore due to its high silica and alumina content. Consequently, alternative binders such as colemanite, starches, and carboxymethyl cellulose have been explored in numerous studies and found suitable for various types of iron ores. However, as agglomeration studies specific to MMO fines are lacking, there is a significant scope for investigating different binders to determine the most suitable one for successful pelletization of these fines. This research gap presents an opportunity to optimize the pelletization process for MMO fines by identifying the most effective binder tailored to their unique composition and properties.

In addition to meeting specific physical properties, pellets must also exhibit adequate reducibility to facilitate further ironmaking and steelmaking processes. Currently, the majority of iron ore reduction relies on carbonaceous reductants such as coke or coal. However, concerns about the high emissions of greenhouse gas CO_2 are expected to make the use of carbonaceous reductants increasingly challenging in the future. Consequently, there is a growing need for hydrogen reduction of multimetallic magnetite ore pellets. However, there is a notable scarcity of research articles on both the carbothermic reduction of multimetallic magnetite ore pellets and the hydrogen reduction of low-grade ores. Therefore, there is significant scope for investigating the carbonaceous and hydrogen reducibility of multimetallic magnetite ore pellets to address this gap in knowledge.

There have been no attempts to recover various metals from reduced MMO pellets, indicating a significant research gap. Therefore, there is a scope to explore methods for recovering precious metals from MMO pellets. With the ore's unique composition, such exploration could unlock considerable value.

1.11. Objectives

The objectives of the present investigation are:

a) To determine the best binder for pelletization and optimal conditions for the induration of MMO pellets.

b) To identify the best solid reductant for the reduction of indurated pellets and determine optimal conditions for carbothermic reduction of pellets made from MMO fines.

c) To establish optimal conditions for the reduction of MMO pellets using hydrogen gas.

d) To explore methods for the recovery of valuable metals from the reduced MMO pellets.