Preface

India primarily has two principal iron ores: Hematite (Fe_2O_3) and Magnetite (Fe_3O_4). Hematite is preferred chiefly over Magnetite for ironmaking due to its comparative ease of reducibility. The reduction of Hematite (Fe_2O_3) to Iron (Fe) proceeds through the following intermediate stages: $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$ and leads to a swelling of about 25%. This swelling is due to the change in crystal structure from Hexagonal (Fe_2O_3) to cubic (Fe_3O_4). Meanwhile, the reduction of cubic Magnetite (Fe_3O_4) to cubic Iron (Fe) leads to swelling of just 7-12%. However, the quality and quantity of hematite ores are decreasing in India. Thus, magnetite and other low-grade iron ores must be utilized to decrease the cost incurred on imported hematite ores. One such magnetite ore, found in Tuensang district of Nagaland, India, is unique as it contains a significant amount of Chromium (up to 5%) and Nickel (up to 1%). If extracted simultaneously, these metals would need fewer additions of costly ferrochrome and ferronickel during steelmaking, thereby cost would be reduced. The mining of this multimetallic magnetite ore would lead to generation of fines. Pelletization is one of the many methods to agglomerate the fines of this multimetallic magnetite ore (MMO) for two specific reasons: (a) conversion of hematite to magnetite and (b) conversion of intrinsic chromite to sesquioxide phases. The current study explores the pelletization and reduction studies of multimetallic magnetite ore fines.

Chapter 1 provides a brief overview of the Indian raw materials scenario, focusing on the pelletization of multimetallic magnetite ore (MMO), the significance of binders in pelletization, and a literature survey. It highlights the low utilization of magnetite ores, the generation of a high quantity of fines during mining, and the advantages of utilizing pelletization as an agglomeration technique for MMO. Furthermore, the chapter discusses the scarcity of prime coking coal and elucidates the benefits of using hydrogen as a substitute for carbonaceous reductants in ironmaking processes. An extensive literature survey was conducted, covering studies related to MMO in Nagaland, the use of various binders in pelletization, and the reduction processes of iron ores, chromite ores, and other multimetallic ores. The survey reveals a lack of substantial research on this specific type of iron ore. Towards the end of the chapter, the research gaps and objectives of the present investigation are outlined, laying the foundation for further exploration and analysis in subsequent chapters.

Chapter 2 presents the chemical composition of the MMO fines, different binders and reductants used along with the details of sample preparation for various studies. This chapter also covers the details of the sieve analysis, chemical analysis, phase analysis and proximate analysis using various characterization techniques. The details of pellet preparation, induration; determination of green strength, dry strength, cold crushing strength (CCS), tumbler index, shatter index, and abrasion index of pellets is also included in this chapter. Experimental details of carbothermic reduction, hydrogen reduction of hardened MMO pellets and oxyacetylene flame melting of DRI are also included in this chapter.

Chapter 3 deals with the preparation of hardened pellets from the MMO fines. Four sets of green pellets per binder (dosage:0.5 wt.%, 1 wt.%, 1.5 wt.%, 2 wt.%) were prepared. The drop number and green strength of the pellets were determined. The green pellets were air-dried overnight and oven-dried for 24 hours. The dried pellets were indurated at four temperatures (1000 °C, 1100 °C, 1200 °C, 1250 °C) for two hours to determine the effect of firing temperature on the strength of fired pellets. Every composition except 0.5 wt.% CMC and 0.5 wt.% dextrin gave sufficient green strength, drop number, and dry strength. Only pellets made with at least 1.5 wt.% colemanite gave industrially acceptable CCS. Thus, the most optimum binder dosage was fixed to be 1.5 wt.% colemanite as it provided sufficient CCS of 297 Kg/pellet and a porosity of 25 vol.%. The optimum firing temperature was fixed at 1250 °C. A high firing temperature coupled with a nonacidic, low melting point, and high boiling point binder like colemanite was necessary for the pellets made from this MMO. XRD and SEM analysis indicated that sintering and transformation of magnetite to hematite are responsible for high CCS values.

Chapter 4 deals with the carbothermic reduction of the hardened pellets**.** Carbothermic reduction of hardened 1.5 wt.% colemanite pellets was performed at five temperatures, i.e. 950 °C, 1000 °C, 1050 °C, 1100 °C, and 1150 °C. A reduction temperature of 1100°C and a reduction time of 90 mins were found suitable to achieve the desired metallization of greater than 85% for pellets reduced with non-coking coal. On the other hand, pellets reduced with coke achieved a maximum % R of 76% and maximum % Fe_M of 83% at 1100°C, with a reduction time of 120 mins, which fell below industrial standards. The kinetic model $[(1-\alpha)^{-1/3}-1]^2 = kt$ was observed to be the best fit for the reduction of MMO pellets irrespective of the reductant used. The activation energy was found to be ~165.38 KJ/mole for pellets reduced with non coking coal and ~220.195 KJ/mole for pellets reduced with coke.

Chapter 5 deals with the hydrogen reduction of hardened pellets. Hydrogen reduction leads to faster reduction at lower reduction temperatures. The 1.5 wt.% colemanite bonded pellets were reduced at three temperatures of 700°C, 800°C, and 900°C, and reduction time varied from 1-60 mins. Three different gas flow rates were investigated: 0.25 L/min, 0.5 L/min, 1 L/min. A temperature of 900 °C, reduction time of 45 mins, and flow rate of 0.25 L/min gave optimum % R of 90, % Fe_M of 89%, and % H_2 utilization of 42%. In comparison, similar values of % Fe_M were achieved at a higher reduction time of 90 mins and an elevated temperature of 1100 °C when coal was used as reductant. Pellet cracking was observed at the optimized reduction parameters, and the pellets' CCS dropped drastically. SEM studies indicated that the cracking of pellets and a drop in CCS were due to the large-scale nucleation of reduced phases in the form of needles and spherical particles in a brittle slag phase. The effect of gangue constituents like Al_2O_3, MgO and SiO_2 was also investigated by preparing synthetic pellets. It was observed that the porosity and drop in CCS of pellets after reduction increased with the addition of Al_2O_3 & MgO and decreased with the rise in SiO_2 content. Complete removal of SiO_2 led to deterioration of CCS after reduction from 186 kg/pellet to 22 kg/pellet. Complete removal of Al_2O_3 gave a porosity of just 3.6 vol.% and a %R of 20%. SEM studies also confirmed that the porosity of pellets dropped with a rise in SiO_2 content and improved with a rise in Al_2O_3 content. Thus, proper control of the gangue oxide content in low-grade ores could maintain the porosity and CCS after reduction of H_2-reduced pellets without compromising reducibility.

Chapter 6 deals with the exploratory melting studies of the reduced MMO pellets. The MMO pellets were melted under a reducing flame of an oxyacetylene torch, and the effect of melting time was investigated. The melting time was varied from 4-10 mins. The metallic yield obtained was increased from 34.8 % to 40.2 % when H_2-reduced MMO pellets (H_2-DRI) were used instead of C-reduced MMO pellets (C-DRI). Using H_2-DRI, the Fe and Cr content in metal increased to a maximum of 97 wt.% and 1.2 wt.% with increase in melting time. The C, Si, and S content simultaneously decreased to 0.069 wt.%, 0.0108 wt.%, and 0.0166 wt.%, respectively. The initial % Fe_M of H_2-DRI (89%) was higher than C-DRI (85%); thus, it had a more pronounced effect on the recovery of iron and chromium. The metal produced from C-DRI has higher S and C contents than H_2-DRI because of use of non coking coal in the reduction process. The metal produced from C-DRI had higher Si contents than H_2-DRI. The results from this exploratory melting give subtle hints of the benefits of using H_2-DRI to recover metal from this multimetallic ore.

Chapter 7 presents the major conclusions drawn from the present investigation alongwith suggestion for future work.