

CHAPTER II LITERATURE REVIEW

2.1 Iron Ore

The most useful metal in the world, Iron, is extracted from an iron ore. It is the rock from which metallic iron can be economically extracted. Iron ore is a mineral substance in which, when heated in the presence of a reductant, will yield a metallic iron (Fe). The iron ore is usually very rich in iron oxides. Iron ores are mostly dark grey to rusty red in color and of high specific gravity. (SOLUTION, 2008)

2.1.1 Types of Iron Ore

Two main types of iron ore used for iron making – Magnetite (Fe_3O_4) and Hematite (Fe_2O_3). Common iron ores include:

> Hematite - $Fe_2O_3 \sim 70$ percent iron Magnetite - $Fe_3O_4 \sim 72$ percent iron Limonite - $Fe_2O_3 + H_2O \sim 50$ percent to 66 percent iron Siderite - $FeCO_3 \sim 48$ percent iron

2.1.2 Grades of Iron Ore

Iron ore is typically classified as High grade (+65% Fe), Medium grade (+62 – 65% Fe) and Low grade (< -62% Fe).

Lumpy/Fine Ore: Iron Ore is traded in lumps (i.e. sized ore) or in fines. Production/availability of lumps is limited by virtue of the natural occurrence and also because of the generation of fines during the crushing of large lumps present in the run-of-mines (ROM).

Natural Pellet: It is a term coined by producers in some Asian counties, to designate sized iron ore used directly in the Sponge Iron production.

Blue Dust: Blue Dust is the name given to naturally occurring, extremely friable, high grade Hematite Iron Ore powder. (Ranawat, 2008)

2.2 ITmk3 Technology

ITmk3, which stands for "Ironmaking Technology Mark Three," is the last coal-based direct reduction technology, called "Heatfast," which was developed and tested by National Steel Corp. Mark 1 is the first generation known as the blast furnace ironmaking, and Mark 2 is the gas-base direct reduction, including the MIDREX Process.

ITmk3 is a unique process technology since it ventures into a new area in the Fe-C diagram (see Figure 2.1). In this area, carbon composite pellets are reduced and melted at a relatively low temperature of 1,350 °C and the hot metal is easily separated from the slag. The ITmk3 reaction can be seen in the solid/liquid co-existence phase, which is different from the traditional ironmarking processes. Melting occurs after a reduction, and the residual FeO is less than 2 percent. Therefore, there is no FeO damage to the refractory. (Negami, 2001).



Fe-C Phase Diagram

Figure 2.1 Fe-C Phase Diagram.

ITmk3 provides a number of benefits versus the conventional ironmaking technologies:

- Reduction and slag separation occur within one step
- Super heated temperatures are not needed
- There is no FeO attack to the refractory
- Slag is cleanly separated from the metal
- Fine ore and low grade ore and coal can be used

2.2.1 Reactions in ITmk3 Process

The final goal of ITmk3 is to produce a molten iron directly from a fine ore and a coal through a one-step process. In the reduction stage, two reactions take place inside the pellet:

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2 \qquad Eq. 2.1$$
$$CO_2 + C \rightarrow 2CO \qquad Eq. 2.2$$

Reaction (2.2) is endothermic, activated at temperatures over 1,000°C. While the reduction is most active over 1,000°C, the required reaction heat balances the heating rate from the furnace, so that the pellet temperature is kept constant. When the reduction degree reaches 95 percent or above, a temperature drop in the iron is observed. This is a good indication that the carburization and the melting are proceeding. Using this reaction mechanism and a FASTMET-type RHF reactor with a carbon composite iron ore pellet as the raw material, ITmk3 produces an iron nugget product in a solid form which is similar to the pig iron. (Negami, 2001).

2.2.2 ITmk3 Process Flowsheet

From a process standpoint, ITmk3 has many advantages, including simple process, low investment cost, low production cost, flexible iron ore material selection and flexible reducing agent selection. The ITmk3 process flowsheet is shown in Figure 2.2. (Lehtinen, 2003).

- 1. A pulverized iron ore, a pulverized coal, and a binder are agglomerated into ball-shaped pellets.
- 2. The pellets are fed into a rotary hearth furnace. Reduction, melting and slag separation occur.
- 3. The resulting product is high-grade iron nuggets.



Figure 2.2 ITmk3 process flowsheet.

Itmk3 can process either a magnetite or a hematite. Since the process separates metal and slag in one step, the process also depends on the iron ore quality. This opens the possibility of utilizing a lower grade iron oxide such as very fine tailings from beneficiation plants. However, the energy consumption per ton of iron nugget increases when processing a lower grade ore. All the iron contained in the oxide is converted into metallic Fe. ITm3 is also very flexible regarding carbon sources; the process can use coal, petroleum coke, or other carbonaceous material (Negami, 2001), (KOBE STEEL, 2007).

2.2.3 Product Features

The nuggets produced in ITmk3 have many beneficial features: slagfree pure products, a controllable carbon content, no re-oxidization, no fines generation, easy handling and transportation. The carbon level is controllable by the input of carbon and the heating. The contents of silicon, manganese and phosphorus in the product depend on the raw materials selection. The product sulfur level also depends on the sulfur contained in the coal; however, the process gas a good chance to reduce the sulfur level remaining in the nugget to the acceptable range.

The ITmk3 process provides a flexible, economical, and environmentally friendly technology for producing a high quality iron product. ITmk3 nuggets can be discharged cold for merchant sale, or hot, for charging to adjacent EAFs or BOFs for high quality steelmaking. ITmk3 plants can be located at mine sites, port facilities or in steelmaking facilities. Considering the importance of sustainable development, ITmk3 presents a great opportunity. (Negami, 2001).

2.3 Direct Reduction

ZHU De-qing *et al.* (2000) were successful in developing an innovative process of the direct reduction of cold-bound pellets from iron ore concentrate with a coal-based rotary kiln, in comparison with the traditional direct reduction of fired oxide pellets in coal-based rotary kilns. The process possesses several advantages: a shorter flowsheet, a lower capital investment, a greater economic profit, a good quality of direct reduced iron. The key technologies, such as the composite binder and corresponding feasible techniques were employed in practice.

Donskoi and Mcelwain (2003) studied the major physical parameters associated with the direct reduction in iron ore/coal composites, including heats of reactions, specific heats, composition, porosity, density, shrinkage, swelling, and thermal conductivity. Where estimates were not available, new formulae were given. In particular, this article focused on the temperature dependence of certain parameters, since this was required for the development of mathematical models.

Donskoi *et al.* (2003) developed the mathematical modeling of the rates of reduction, the coal gasification, and the devolatilization of coal in iron/ore coal

composites which were reviewed and critically analyzed. The effect of different parameters on the overall process was discussed. The concepts of a local rate of reduction and gasification and an integrated rate of reduction were introduced, and the rate-controlling steps in each case were reviewed. Current approaches to modeling coal pyrolysis were also described. This review, with the estimates, data, and analysis was related to the modeling rates of the reduction, the gasification, and the pyrolysis.

S. Roy and A. Das (2008) studied a detailed characterization followed by a beneficiation of low-grade iron ore slime from Jilling Langalota deposit, India, The work involved separating the gangue minerals viz. quartz and kaolinite to form ironbearing minerals, mostly hematite and goethite, as identified using XRD analysis to produce a suitable concentrate for downstream processing. The feed slime sample assayed 37.86% total Fe, 19.08% silica, and 14.4% alumina. A substantial amount of the sample was below 20 mm in size. The finer fraction contained a larger amount of gangue while the coarser fraction was richer in iron. Considering the characterization data, two flow sheets were conceptualized for the beneficiation of the slime sample with two- and four-stage processing, respectively. In the two-stage operation, the grade of the slime could be improved to 60.26% Fe, 4.45% silica, and 3.98% alumina with an overall yield of about 20%. The results from the four-stage operation showed that it is possible to upgrade the iron value to 66.97% with a yield of 14.4% while reducing the silica and alumina contents down to 1.7% and 1.52%, respectively.

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Mohapatra and Patra (2009) studied chemical and physical properties, and the reduction behavior (in coal) of hematite iron ores, procured from ten different mines of Orissa., The study was undertaken to provide information to the iron and steel industries (sponge iron plants in particular). Majority of the iron ores were found to have high iron and low alumina and silica contents. All these iron ores were free from the deleterious elements (S, P, As, Pb, alkalies, etc.). The results indicated lower values of shatter and abrasion indices, and higher values of tumbler index in all the iron ore lumps except Serazuddin (previous) and Khanda Bandha OMC Ltd. For all the fired iron ore pellets, the degree of reduction in coal was more intense in the first 30 minutes after which it became small. Slow heating led to a higher degree of reduction in fired pellets than rapid heating. All the iron ores exhibited more than 90% reduction in their fired pellets in 2 hrs time interval, at a temperature of 900°C. Iron ore lumps showed a lower degree of reduction than the corresponding fired pellets.

Kumar and Patel (2002) studied on isothermal reduction kinetics (with F grade coal) in fired pellets of hematite iron ores, procured from four different mines of Orissa, in the temperature range of 850–1000°C to provide information for the Indian sponge iron plants. The rate of reduction in all the fired iron ore pellets increased markedly with a rise of temperature up to 950°C, and thereafter it decreased at 1000°C. The rate was more intense in the first 30 minutes. All iron ores exhibited an almost complete reduction in their pellets at temperatures of 900 and 950°C in < 2 hours' heating time duration, and the final product morphologies consisted of prominent cracks. Their overall rates were controlled by indirect reduction reactions. The carbon gasification reaction was the rate-controlling step.

2.4 Binder

Kawatra and Ripke (2001) studied binders which improve the pellet green strength. In this study, procedures were developed that took advantage of the ability of bentonite to form fibers, resulting in a dramatic decrease in the necessary bentonite dosage. When the mixing procedures were used that promoted fiber formation, the bentonite dosage needed to produce acceptable strength pellets was cut in half, from 14 (0.66%) to 7 (0.33%) lb/lt. In addition, bentonites that were previously considered of poor quality can have their performance enhanced by using this fiber development method, and be used successfully as iron ore pellet binders.

Forsmo *et al.* (2006) showed that a fundamental research during the past decade has been focused on understanding the role of viscous forces on agglomerate deformability and strength. In this work, they showed the variations in the plasticity and the strength of magnetite iron ore green pellets with varying liquid saturations and binder dosages (viscosities). For this purpose, a new measuring instrument was built to analyze the green pellet wet compression strength, the plastic deformation, and the breakage pattern. A new green pellet growth mechanism was suggested, based on the measured over-saturation. First, the green pellet plasticity needed to

exceed a minimum level to enable growth. This limiting plasticity defined the material-specific moisture content needed in balling. Secondly, it was suggested that the growth rate be controlled by the viscosity of the superficial water layer rather than by the mobility of the pore water.

Forsmo *et al.* (2007) studied the main binding force in wet iron ore green pellets which was the cohesive force of the viscous binder. The wet compression strength (wet-CS) in green pellets was, however, also influenced by the green pellet plasticity. A certain degree of plasticity was needed to sustain the green pellet growth rate. Too much plasticity resulted in a decreased bed permeability and production problems. As the plasticity increased, the wet-CS decreased. The amount of moisture needed to create a given degree of plasticity depended on particle properties and on the particle size distribution. A bentonite binder was used and the plasticity was adjusted to a constant level. Green pellets prepared of raw materials with narrow size distributions were just as strong as those with broader ones. This was because the main binding force was the cohesive force of the viscous binder. In green pellets was balled without the bentonite binder. Fineness, or rather the slope of the particle size distribution curve, had a major impact on the moisture content needed for the constant plasticity. If the slope increased, more water was needed to keep the plasticity on a constant level.

Forsmo *et al.* (2007) showed thermal volume changes and oxidation mechanisms in magnetite iron ore green pellets balled with 0.5% bentonite binder, as a function of raw material fineness and pellet porosity, are shown. When a pellet started to oxidize, a shell of hematite was formed around the pellet while the core still was magnetite. Dilatation curves were measured under non-oxidizing and oxidizing atmospheres to separately describe the thermal volume changes in these two phases. Dilatation measurements showed a contraction during oxidation between 330 and 900 °C by 0.5%. The extent of contraction was not influenced by the raw material fineness or the original porosity in pellets. Sintering started earlier in the magnetite phase (950 °C) compared to the hematite phase (1100 °C). The sintering rate increased with increasing fineness in the magnetite concentrate. A finer grind in the raw material would, therefore, promote the formation of duplex structures with a more heavily sintered core pulling away from the less sintered outer shell.

At constant porosity in green pellets, the oxidation time became longer as the magnetite concentrate became finer, because of the enhanced sintering. In practical balling, however, the increase in fineness would necessitate the use of more water in the balling, which resulted in an increase in the green pellet porosity. These two opposite effects leveled out and the oxidation time became constant when green pellets were balled at a constant plasticity. Combining the results from the oxidation and dilatation studies revealed new information on the rate limiting factors in oxidation of iron ore pellets. At 1100 °C, the diffusion rate of oxygen was limited by sintering in the magnetite core, taking place before oxidation rather than by the diffusion rate of oxygen through the oxidized hematite shell, as has been claimed in earlier literature. The oxidation rate was at maximum at around 1100 °C. At 1200 °C, the rate of oxidation substantially decreased because both the hematite shell and the magnetite core showed heavy sintering at this temperature.

2.5 Iron Nugget Production by ITmk3

Anameric *et al.* (2004) studied the production and properties of pig iron nuggets. The nuggets were produced from pellets consisting of a mixture of iron oxide, coal, flux, and a binder, which were heated to 1450°C. These pellets then self-reduced to produce a solid, high-density, highly metallized (96.5% Fe) pig iron. During the nugget production process, a separate slag phase formed that cleanly separated from the metal. The physical and chemical properties of the pig iron nuggets were similar to the pig iron produced by blast furnaces, which were distinct from the Direct Reduced Iron (DRI).

Anameric *et al.* (2005) studied the carburization effects on pig iron nugget making. Three chemically and physically distinct products were produced after the reduction of magnetite to iron, as a function of furnace residence time. At a constant temperature of 1425°C, the residence time was varied. As the furnace residence time increased the amount of carbon diffused into metal increased, lowering the melting point of the metal phase.

Anameric *et al.* (2007) studied transformation mechanisms of self reducingfluxing dried greenballs into pig iron nuggets. The pig iron nuggets, which have similar chemical and physical properties with the blast furnace pig iron, were produced by a single step heat treatment of self reducing–fluxing dried greenballs. During this single step heat treatment, the transformation of self reducing fluxing dried greenballs into pig iron nuggets did not take place instantaneously. Rather, it was composed of three transformation stages, (1) transformation of self reducing, (2) transformation of DRI into TDRI, and (3) transformation of TDRI into pig iron nuggets.

Anameric *et al.* (2007) showed conditions for making a direct reduced iron, transition direct reduced iron, and pig iron nuggets in a laboratory furnace temperature-time transformations. Throughout the heat treatments, DRI, TDRI and pig iron nuggets were produced. The furnace temperatures and residence times corresponding to their production are shown in Figure 2.3.



Figure 2.3 The corresponding experimental furnace temperatures and residence times.

Anameric *et al.* (2007) studied the iron nugget production form ITmk3 process at a laboratory scale and compared the reduction product with the blast furnace pig iron. Pig iron nuggets were characterized utilizing apparent density measurements, optical microscopy, scanning electron microscopy with energy dispersive spectroscopy, and bulk chemical analysis. It was determined that pig iron nuggets had high apparent density (6.7–7 g/cm³); had high iron content (95–97 %); and exhibited microstructures similar to a white cast iron, which is essentially the same as pig iron from a blast furnace.

Iwasaki *et al.* (2009) developed a method and a system for producing metallic nuggets providing a reducible mixture of reducing materials (such as carbonaceous material) and reducible iron bearing material (such as iron oxide). They were arranged in discrete portions, such as mounds or briquettes, on at least a portion of a hearth material layer (such as carbonaceous material). A coarse overlayer of carbonaceous material was provided over at least some of the discrete portions heating the reducible mixture to 1420°C, 1400°C and 1375°C. This resulted in a formation of an intermediate product of one or more metallic iron nuggets,

which had a sulfur content of less than 0.03%, and slag, which had less than 5% mass MgO, were the ratio by weight percentage of sulfur in the slag and in the metallic nuggets was between 12 to 15.