

SYNOPSIS

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3. Date of Registration : 14th October, 2013
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6. Title of the Thesis : Upgradation of low-grade iron ore for Ironmaking
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9. Date of Synopsis submission : 11th November, 2019

There is tremendous increasing demand for steel due to rapid growth and development in recent past. The demand of steel can be fulfilled by the essential natural resources. India is fortunate regarding huge resources of iron ore. The basic reserve/recourse of the iron ore is about 33.28 Billion tonnes (Bt), out of which about 22.49 Bt of hematite and 10.79 Bt of magnetite, estimated by Indian Bureau of Mines (IBM), Nagpur as on 01st April 2015. Indian iron ore deposits are soft and friable in nature. Out of 22.49 Bt of hematite ore, approximately 33.92 pct (i.e. 7.63 Bt) ore is classified as **low-grade resources of iron ore**. In 2017-18, approximately 0.27 Bt i.e. 67.48 pct of total iron ore production (0.4 Bt) comes in the form of fines during mining operations itself.

In 2018, India is a second largest producer of crude steel in the world. Iron and steel industry's growth in India has been recorded exceptional in last 10 years. India produced 8.96 Million tonnes (Mt) of crude steel in September 2019, an increase of 1.58 pct compared to September 2018. India's crude steel production of year 2018 is 106.5 Mt. Correspondingly; the per capita steel consumption in the country was 71 kg in the year of 2018. As per National steel policy 2017 (NSP), estimated domestic steel production of 300 Mt will be achieved by 2030–31. Reaching out to this visionary aim, Indian steel plants must have to discontinue outdated technologies, increase their production capacities, uplift

the efficiency of operations, implement latest technologies, *utilize low-grade raw materials* as well as minimize waste generation.

The industrial development programmed of any country, by and large, is based on its natural resources. For producing 106.5 Mt crude steel required about 182 Mt of processed iron ore and 227 Mt run of mine ore. There are planning for about 300 Mt steel production by India in 2030, that will be required 513 Mt of processed iron ore and 639 Mt run of mine ore. The fast depletion of the high-grade iron ores and their increasing demand in steel industry put pressure on assessing the exploitation of lean ores. Low-grade iron ore is beneficiated to enhance its iron content up to the desired level of industrial specification required for different end uses. Due to scarcity of iron ore lumps and good quality of coking coal, alternatives route of iron and steel production are developed.

India has huge reserves of low-grade iron ore. Exploration and mining efforts of low-grade ores have not been adequate. Exploration strategy to mine ores with 45 pct total Fe grade as a target is on the anvil. Given the current stage of economic development, the present need is not only to explore new deposits but also to make use of low-grade ores. Towards future availability of iron ore for the domestic iron and steel industries and also for global business; attention for potential use of low-grade iron ores, especially fines are gaining momentum. About 33.9 pct of the total reserve of low-grade hematite iron ore (7.63 Bt) is available to meet the demand of Indian iron and steel industries.

Iron ore deposits are finite, non-renewable, unique and irreplaceable natural resource and with the fast depletion of high-grade ores, conservation of iron ore becomes our prime focus area to increase mine life. Iron ore resource has its own peculiar mineral characteristics requiring suitable beneficiation process to produce quality raw material. Mineralogical studies have become an integral part of mineral processing and beneficiation of an ore. Mineralogical studies are helpful to be familiar with the nature of association of gangue with the ore. In mineralogical studies, characterization techniques are such as Fluorescence Spectrometer (XRF), X-Ray Diffractometer (XRD), Scanning Electron Microscopy (SEM) and Energy Disperse Spectroscopy (EDS), helpful to determine different phases by qualitatively and quantitatively as well as their morphologies. The role of characterization studies is a vital to propose the process flow sheet for low-grade ores. As reflected in the National Steel Policy, Hematite iron ore

availability in the country will not last long. In order to ensure longer period of ore availability, it is very important that to use low-grade Banded Hematite Quartz (BHQ) and Banded Hematite Jasper (BHJ) iron ores after beneficiation. Looking at the present scenario, IBM has slashed the threshold value of iron ore at 45 pct Fe_(t).

The problems of Indian iron ores are i) highly friable in nature, ii) high alumina and silica, c) poor liberation of alumina even at finer size, d) high alumina to silica ratio, e) low utilization of low-grade iron ores and lumps and f) difficulties in dewatering of slimes for water re-circulation. The quality of iron ore plays an important role in production of iron and steel and the cost of steel in the market. Indian iron ore suffers two basic problems: i) the softness of the ore and ii) high amount of milling operations due to its poor liberation nature of the ore.

Crushing and milling generate very high contributions to the total processing costs. Hence the cost applied to the final product will be extremely important as a low grade ore would yield a small ultimate product tonnage both due to the low content of the desired mineral(s) and the typical reduced recovery that is related to the low grade compared to richer ores. Pre-concentration, i.e. removal of coarse low grade waste may become very important. Electronic machine sorting, heavy media separation, jigging and coarse magnetic separation methods offer possibilities to minimize volume of ore that must be finely ground in order to adequately liberate the desired minerals.

India is endowed with large reserves of high-grade hematite ore. However, steady consumption of these iron ores is now a concern forcing to develop beneficiation strategies to utilize low-grade iron ores. In India, iron ores are generally washed to remove the high alumina containing clayey matter. Conventionally, after washing, the lumps are directly fed to blast furnace and the fines are used after agglomerating them into sinter. However, the slimes are being rejected in the tailing ponds. These slimes in most cases contain substantial iron values in the range of 54–58 pct Fe. Therefore, it is imperative to recover iron values from these slimes because of high demand on the good grade iron ores day-by-day.

The reserve of good quality ores is dwindling sharply, and the major iron ore resources that would be available in future are limited to lean ores, such as banded hematite quartzite (BHQ), banded hematite jasper (BHJ), and banded magnetite quartzite (BMQ). Banded iron formations (BIFs) are highly debatable Precambrian chemical

sedimentary rocks; characterized by the commonly alternating layers of iron-rich and silica-rich (Quartz or Jasper). Banding is best preserved in low-grade metamorphic occurrences, but even high-grade metamorphosed BIFs retain relict banding. These ores contain averagely 30-40 pct $Fe_{(t)}$. The formation of these ores is the result of residual concentration of iron contained in banded iron formation either through replacement of silica by iron or by leaching of silica in suitable oxidation-reduction conditions. Such processes, acting over a long period of time, have given rise to massive ore bodies, occupying the crust of the hills and elevated plateaus. The BHQ ores contain generally 35-40 pct $Fe_{(t)}$, 40-45 pct SiO_2 and 0.5-2.5 pct Al_2O_3 . The associated minerals in this low-grade iron ore is mostly hematite and quartz with little quantities of magnetite, martite and goethite. Large reserves of such iron ore deposits are available in India, which are currently not being exploited. With respect to magnetite and hematite, goethite iron ores have a reasonably least share as a raw material in extraction of iron. Their use is restricted mainly due to the observed spalling nature during firing. Due to the forecasted depletion of the available high-grade iron ores, a steady growth of the goethite share could be anticipated.

Concentrated efforts are being made to utilize the low-grade iron ore by organized mineralogical, beneficiation and agglomeration techniques. The utilization of low-grade iron ore is always challenging due to its complex mineralogy and accordingly constructing of flow sheet for beneficiation. For iron and steel making, valuable utilization of BIFs and goethite iron ore can be promising one just after upgradation of them. In India, there is also huge shortage of coking coal. Vast amount of coal fines and coke breezes are generated during coal mining and coking of coal respectively. By incorporating non-coking coal fines or coke breezes with up-gradated iron ore in cold bonded iron ore-coke/coal composite pellets which can be reduced the metallurgical coke requirement in the blast furnace. Due to scarcity of iron ore lumps and good quality of coking coal, alternatives route of iron and steel production are developed.

In the cold bonding concept, the fines of iron bearing oxides and carbonaceous materials are mixed with a suitable binder and optimum quantity of moisture. The mixture is then briquetted into the appropriate size of cylindrical shape. The composite briquettes are hardened due to physio- chemical changes of the binder in ambient conditions or at slightly elevated temperature (400 to 500 K). The challenges in cold bonding are to find a

suitable binder that ensures the proper physical and mechanical properties of the composite briquette.

The term composite briquette is employed here to stand for that the briquette containing mixture of fines of iron bearing oxide and carbonaceous material (coal / coke) which has been imparted sufficient green strength for subsequent handling by cold bonding technique. The prepared cold bonded briquette should have sufficient mechanical strength to withstand high temperature and stresses in reduction furnaces.

An encouraging attention in composite pellets/briquettes has grown from the decade of 1980s because of the following advantages:

1. Utilization of cheaper resource and pollution control,
2. Very fast reduction rate due to intimate contact between a reducing agent and oxide particles,
3. Reduction in energy consumption for production because cold bonded composite pellets/ briquettes don't require induration treatment,
4. Promising prospect for iron making at small scale with higher production rate,
5. Because of their uniform size and convenient form, pellets/briquettes can be continuously charged into the furnace, which is leading towards higher productivity, and
6. Consistent production quality as the chemical composition of composite pellets/ briquettes does not change.

The concept of Smelting Reduction (SR) process of iron ore, an alternative to blast furnace technology was initiated around 1970. The SR processes involving both reduction and smelting are very similar to blast furnace in which all the reactions takes place in a single reactor. Most of the smelting reduction processes involve by removal of oxygen from the iron ore in the solid state (initially) followed by further removal of remaining oxygen in the liquid phase reduction reaction. Ideally, a smelting reduction process should have 100 pct reduction of iron oxides in the liquid state in a single stage in a single reactor.

There is a shortage of coking coal all over the world in general and in particular in India. On the other hand, India has vast reserves of non-coking coal, which is widely available and cheapest reducing agent for iron oxide. Hence, non-coking coal based iron making technology has special relevance for country like India. In fact, the need to make

non-coking coal based iron making units economically viable has resulted in the development of SR processes, which do not face sticking problem at high temperature. The SR process exploits faster reduction kinetics at higher temperature due to enlarged specific contact area between reactants in a dispersed phase and increased mass transport rates due to convection and thereby improves productivity. The process makes use of non-coking coal in a broad range of composition and accepts a wide range of materials including iron ore fines, plant wastes such as dusts and sludge or inferior grade ore directly. Their process control is relatively simple and they work out economically at small scale operation catering to varying demands of the market. The process is environmentally acceptable keeping the demands of coming years in view. Some of the upcoming SR processes are Corex, Romelt, HIs melt, Ausmelt, DIOS, Fastmet, Finex, ITmk³ etc. Amongst these Corex, Fastmet/ ITmk³ have already been established at commercial scale.

In smelting reduction technology, upgraded iron ores can be utilized with coal / coke fine as the feed material in the form of composite briquettes. Rate of production is expected to be higher with composite briquettes due to high degree of pre-reduction to the smelting reactor. There have been limited research activities on the use of upgraded iron ore directly in the steel making process. However, the productivity is not significant enough to use them directly. Looking into the above aspect, the objective of present study is twofold:

1. Mineralogical and beneficiation studies of low-grade iron ore by using several techniques and constructing an appropriate route for beneficiation with good recovery of iron.
2. Utilization of composite briquettes in liquid metal bath for steel making. As well as auxiliary studies as backup investigation with emphasis on isothermal reduction kinetics.

The thesis consists of six chapters covering all the relevant information about the low-grade iron ore, mineralogical studies, beneficiation processes, composite briquettes, smelting reduction processes and the work that had been done on utilization of iron ore fines by beneficiation, agglomeration and reduction smelting to produce steel.

The first chapter briefly discusses about the importance of low-grade iron ore and its beneficiation. It also discusses the about mineralogical studies. Further chapter covers a

definition and advantages of cold bonded composite briquettes. Outlines of the objectives and plan of work are also presented.

The second chapter covers the literature review related to utilization of low-grade iron ore – BIF and goethite. It discusses about the various methods of beneficiation of low-grade iron ores for upgradation. A broad review on beneficiation of Indian iron ore is done. Chapter covers about the composite briquettes and smelting reduction technologies. A detailed literature review is done on composite briquette making by using several types of binders. This part discusses about preparation, reduction kinetics, advantages and uses of composite briquettes. A fundamental knowledge of physical, mechanical and thermal behavior of composite briquettes, concept of cold bonding, smelting reduction process concepts and understanding of mechanism and kinetics of smelting reduction processes are of utmost importance before advancing through the intricacies of the present study.

The third chapter deals with the mineralogical studies and beneficiation of low-grade iron ores which include characterization of raw materials (i.e. iron ores, coke, charcoal), sieve analysis of raw materials, proximate analysis of coal, chemical analysis of etc. Beneficiation methods, an attempt was made to find suitable upgradation technique for increase in total Fe percent; thereby developing a proper beneficiation route for iron ore.

For these studies of raw materials, iron ores were collected from mines of (i) Bonai ranges of Jharkhand - Odisha sector and (ii) Red and Yellow ochre from Bhilwara – Rajasthan state. Charcoal and coke were procured from local market of Vadodara and Rajkot respectively. Initially, mineralogical studies were carried out to gather the information related to mineral phases which have been helpful in beneficiation studies.

For the mineralogical studies; chemical analysis, mineral phases, texture, surface morphology, phase identification, phase – size and shape with help of XRD, XRF, SEM-EDS, hand mineralogy and ore microscopy. Mohs hardness and density of ore were also measured. (i) Odisha ore (53 pct Fe_(t), 8.50 pct SiO₂, 7.30 pct Al₂O₃) is having hematite (100-150 μm) as major phase, goethite and quartz (50-75 μm) are as minor phases (i.e. BHQ type in nature). Ore's Density and Mohs hardness are 3.6 and ~ 4.0 respectively. (ii) Rajasthan ore (33 pct Fe_(t), 24.12 pct SiO₂, 13.23 pct Al₂O₃) is having goethite (70-100 μm) as major phase, quartz and kaolinite (20-50 μm) as minor phases. Ore's Density and Mohs hardness are 2.8 and ~ 3.0 respectively.

For beneficiation studies, Odisha iron ore crushed and grinded as per the requirement of beneficiation methods. Different sized ore were beneficiated using various methods like jigging, Wilfley table (Tabling), air classifier and hydraulic classifier. After beneficiation trials, the two methods were finalised. The process route using two beneficiation methods is finalised where jigging was used in the first stage and followed by the Wilfley table. The concentrate and middling were mixed for further utilization. Total Fe 59.75 pct recovery was achieved. In jigging operation, Fe total was upgraded to 59.02 pct. In tabling operation, Fe total was upgraded to 62.13 pct. Based on total Fe percentage increase the two stage beneficiation route is used.

For beneficiation studies, Rajasthan iron ore crushed and grinded as per the requirement of beneficiation methods. Different sized ore were beneficiated using various methods like jigging, Wilfley table (Tabling). Satisfactory results were not achieved in the conventional beneficiation operations. So, magnetic roasting process was applied to upgrade this lean grade ore. Several trials were taken with different parameters (particle size of ore, time and temperature). Magnetic roasting was carried out with two different carbonaceous materials like coke fines and charcoal fines for stoichiometric reactions. Best results obtained for roasting operation at 1173 K for 120 minutes. After roasting process, roasted ore is further upgraded by wet magnetic separation. By using coke fines, 34.6 pct total Fe of roasted ore was achieved which was further upgraded to 49.1 pct by wet magnetic separation. Recovery of total Fe 91.9 pct was achieved. Similarly, by using charcoal fines, 38.0 pct total Fe of roasted ore was achieved which was further upgraded to 49.6 pct total Fe by wet magnetic separation. Recovery of total Fe 90.29 pct was achieved.

The fourth chapter discusses the briquettes preparation, experimental setup for isothermal reduction studies; smelting reductions, apparatus and procedure are also discussed. Characterization and testing of materials are discussed in this chapter. The testing techniques, measurement of degree of reduction and activation energy are calculated.

Upgraded ore (Rajasthan) was agglomerated (i.e. making composite briquette) with carbonaceous materials (either charcoal or coke fines) for the utilization of these in smelting reduction process. Two different cylindrical shaped briquettes were prepared: (i) for isothermal reduction studies: Diameter 10 mm and height 12-13 mm and (ii) for smelting reduction: Diameter 25 mm and height 24-25 mm. Binder (10 pct PVA) was used for the preparation of briquettes and their properties were tested. It was observed that

compressive strengths of 10 mm and 25 mm diameter briquettes were 1170 N/briquette and 380 N/briquette respectively. Variation in compressive strength was observed mostly by ± 15 pct of the average value.

Four different types of composite briquette ($\varnothing = 10$ and 25 mm) were prepared for smelting reduction. These are as follows:

- (a) Upgraded iron ore (Rajasthan) by coke + Coke
- (b) Upgraded iron ore (Rajasthan) by charcoal + Charcoal
- (c) Upgraded iron ore (Rajasthan) by coke + Charcoal
- (d) Upgraded iron ore (Rajasthan) by charcoal + Coke

The iron ore-coke/charcoal composite briquettes were prepared by using PVA as binder with $Fe_{(t)}/C_{fix}$ ratios as per stoichiometry and tested for their properties. The experiments for smelting reduction of composite briquettes were used. Smelting reduction of composite briquettes was done in an induction furnace of 4 kg capacity.

Brief discussion about the facilities such as experimental set-up for smelting reduction, Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Energy Dispersive X-ray Fluorescence (XRF) Spectrometer (OES) and TG-DTA are also discussed in this chapter. XRD test was carried out to identify the phases present in reduced briquettes. XRD test was carried out to identify the phases present in low-grade iron ore. SEM examination of low-grade ores was initially carried out to analyse the morphology (i.e., shape, size and distribution) of the particles. The isothermal reduction of composite briquettes was carried out in nitrogen atmosphere. Reduced briquettes were examined by SEM to observe the microstructure of the briquettes. XRD test was carried out to identify the phases present in reduced briquettes. For measurement of degree of reduction for composite briquette, the weight loss method was used. The loss in weight due to loss of oxygen, carbon and volatile matters were taken into consideration.

The fifth chapter deals with the analysis of experimental data generated on various aspects of the study in accordance with the scheme of experiments presented in previous chapter. The reduction studies of composite briquettes were analysed. Degree of reduction for 10 mm diameter composite briquette, (i) (upgraded iron ore + charcoal) is 73.13 pct and (ii) (upgraded iron ore + coke) is 75.36 pct. The thermal behaviour of carbonaceous materials and composite briquettes such as decomposition, weight loss, reduction etc was determined by TG-DTA. Smelting reduction of composite briquettes in liquid metal bath

is carried out at temperature 1873 ± 20 K. During smelting reduction, it was observed that the 25 mm diameter composite briquettes are completely dissolved within 40-45 sec. Smelting reduction of composite briquettes deals with the bulk dissolution of 25 mm diameter briquettes into the molten bath of steel and iron recovery is calculated in terms of yield. Overall, the yield is achieved 90-94 pct. For 20 pct composite briquette (upgraded iron ore + charcoal), yield was 94.7 pct. While, 20 pct composite briquette (upgraded iron ore + coke), yield was 94.18 pct. SEM photomicrographs of reduced briquettes revealed cluster of metalized iron, sintered structure and surface cracks due to thermal decomposition of the volatile matters. The hardness of the normalized steel was also measured in Rockwell hardness testing machine and observed in the range of 81 to 103 HRB (Rockwell B scale).

The sixth chapter contains the summary and conclusions of the present work, and suggestions for further work. The present investigation concludes that the low-grade iron ores could be upgraded by beneficiation processes. The Odisha iron ore can be upgraded from 53 pct $Fe_{(t)}$ to 59-62 pct by beneficiation (like jigging, Wilfley table). The magnetic roasting process was applied to upgrade Rajasthan iron ore (33 pct $Fe_{(t)}$); 38.0 pct total Fe of roasted ore was achieved which was further upgraded to 49.6 pct total Fe by wet magnetic separation.

Upgraded ore (Rajasthan) were agglomerated (i.e. making composite briquette) with carbonaceous materials (either charcoal or coke fines) for the utilization of these in smelting reduction process. Degree of reductions for 10 mm diameter composite briquettes obtained 73.13 pct (with charcoal) and 75.36 pct (with coke). Overall, the yield was achieved 90-94 pct for smelting reduction of composite briquettes which are noteworthy data at laboratory level research.