Chapter 2 Literature Review

2.1 Iron ore

Iron ore deposits are distributed in different regions of the world under diversified geological conditions, mineralogical (geological) formations, and periods. Based on mode of occurrence and origin, the iron ore deposits are divided into five groups:[46]

(i) Banded Iron ore Formation (BIF),
(ii) Sedimentary Iron ore deposits of sideritic and limonitic composition,
(iii) Lateritic ore derived from sub-aerial alteration of gneiss, schist etc.,
(iv) Ti-V-magnetite deposits and
(v) Fault and Fissure filling deposits.

Table 2.1: Iron bearing Minerals and its properties[46]

Sr. No.	**Mineral**	**Composition**	**Iron content (pct Fe)**	**Specific gravity**	**Hardness (Mohs scale)**	**Colour**
1	Hematite (alpha) and Martite	α-Fe_2O_3	70	4.9-5.3	5.5-6.5	Steel grey to red
	Hematite pseudomorphous after magnetite					
2	Turgite	$2Fe_2O_3.H_2O$	66.1	4.2-4.6	6.5	Brown to red
3	Goethite	$Fe_2O_3.H_2O$	62.9	3.4-4.2	5-5.5	Brown to red Brown to yellow
4	Limonite	$2Fe_2O_3.H_2O$	60	3.4-4.2	5-5.5	
5	Lepidocrosite	$Fe_2O_3.H_2O$	62	4.09	5	Brown to reddish brown
6	Ilmenite	$FeTiO_2$	36.8	4.5	5-6	Black to brownish black
7	Maghemite	γ- Fe_2O_3	69.9	4.88	5	Brown
8	Magnetite	Fe_3O_4	72.4	5.17	5.5-6.5	Black, blue or brown black
9	Siderite	$FeCO_3$	48.2	3.7-3.9	3.5-4.5	Ash grey to brown
10	Pyirte	FeS_2	46.6	4.8-5.1	6-6.5	Brass yellow
11	Marcasite	FeS_2	46.6	4.9	6-6.5	Light brass yellow

12	Pyrrhotite	FeS_2	61.6	4.4-4.65	3.5-4.5	Bronze yellow
13	Chamosite	$(Mg.Fe.Al)_6(Si.Al)_4O_{10}(OH)_8$	33.42	3-3.5	3	Green to light yellow

Among these, the largest concentration of economic deposits is found to associated with volcano-sedimentary Banded Iron Formation (BIF) of Precambrian age. Banded Iron Formations are chemically precipitated enigmatic rocks constituting alternate iron-rich and iron-poor (amorphous silica rich) layers. This dichotomous compositional dowering is usually expressed on several scales at any given outcrop, from fine sub-millimeter-scale varve (*a pair of thin layers of clay and silt*) like lamina to meter scale bands. Surprisingly, the boundary between the ferruginous and siliceous layers is distinctly observed at a microscopic scale.[47]

During mining operations, generally three types of material are generated from the mineralized iron ore zones.

Type 1: Marketable or saleable grade (*above a certain cut-off Fe grade*)

Type 2: Sub or low-grade ore (*between cut-off and threshold Fe grade*)

Type 3: Mining waste (*below threshold Fe grade*)

The sub-grade or low-grade ores that are produced from mineralized zones may not conform to the present specifications of marketable ores as applicable to a particular region or period at the present stage of technological development and economy but may have a scope to make them saleable in future through advanced mining, beneficiation, and utilization techniques. The threshold value is a component of mineral conservation, which decides the lower limit of sub-grade ore in a mineral deposit and the upper limit of mining waste. The cut-off grade is the lower limit of the marketable or saleable ores as applicable to a particular region or period depending on the technological advancement. Hence, these ores are part of the mineralized mass, which is above the threshold value and below the required cut-off grade.[48]

IBM has revised the threshold value of minerals regularly under sub rule 7 of rule 12 by Mineral Conservation and Development Rules, 2017 which is in the interest of systematic development of mineral deposits and conservation of minerals. The threshold values for the iron ore are given below Table 2.2:[49]

Table 2.2: Threshold values of iron ore

Mineral	**Threshold Value** *(Fe pct in ore)*
Iron Ore	(i) Hematitic Ore - 45 pct Fe (Minimum) (ii) Hematitic Siliceous Ore - 35 pct Fe (Minimum) (iii) Magnetite Ore-15 pct Fe (Minimum)

With high grade iron ore reserves under the threat of depletion despite the revision of the threshold value of iron ores to 45 pct Fe & 35 pct Fe (from hematite ore & siliceous hematite ore respectively), it is obligatory on the part of the Mining Industry to consider exploitation and utilisation of low / lean grade iron ores which hitherto were sidelined as waste for effective utilisation. The fresh exploration strategy would have to be drawn with cut-off / threshold grade ores as a target.[46]

The geological assessment of the in situ low-grade iron resources is difficult because of their heterogeneous distribution in the mineralized zone. Further, these have different chemical, mineralogical, and textural characteristics though iron grade may be similar and the assessment of such subtype resources becomes more complex.[48]

The problems of Indian iron ore are:[50] i) highly friable in nature, ii) high alumina and silica content, c) poor liberation of alumina even at finer size, d) 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 the 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) the high amount of milling operations due to softness and poor liberation of the ore.

2.2 Specification of Iron ore

General end-user specifications of iron ore lumps, fines & concentrates used in making pellets / sinters for iron making is presented in

Table 2.3.[46]

Table 2.3: End-use graded specification for hematite

Lumps, Fines & Blue dust	**Chemical Constituents**			
	Fe (pct)	**SiO_2 (pct)**	**Al_2O_3 (pct)**	**P (pct)**
High grade	+65	2 max.	2 max.	-
Medium grade	62-65	3 max.	3 max.	0.1 max.
Low grade	60-62	4.5 max.	4 max.	0.1 max.
Unclassified	The range of minimum and maximum value of chemical constituents is too wide to be fitted in to any of the above grade.			

Increasing demand for the production of steel worldwide and advanced steelmaking techniques have necessitated the use of low-grade as well as finely disseminated iron ores. The country is not endowed with high-grade requisite iron ore resources. Therefore, it is imperative to achieve the best use of available low-grade iron ore resources through scientific methods of mining, beneficiation and pelletization.[51]

Over the past decade, it may be observed that there has been a phenomenal increase in the production of iron ore in India. Apart from the production of high-grade ores, many industries are exploring the possibility of beneficiation of low-grade ores for the production of iron and steel. Hence, utilization of low-grade iron ore is crucial for the optimization and conservation of the ore minerals. Also, during the operation of mining and beneficiation of iron ores a large quantity of fines as well as slime are generated. Generation of such fines and slimes may contribute to the loss of minerals to the extent of 30 pct of total value minerals.[52]

In recent times, the ratio of high grade / low grade in the deposits is coming down; fines – disregarded as waste, are becoming a valuable product considering the pelletization capacities in India. Modern beneficiation processes allow for the effective and low-cost upgrading of lump, fines and ultra fines.[53]

2.3 Mineralogical studies

The mineralogical characterization is very important in the study of these types of ore which will provide information about the mineralogy and different textural attributes to decide upon the right choice of beneficiation practices. The selection of suitable beneficiation processes depends on the physical characters of iron minerals and quartz[47]. The mineralogical characterization plays a vital role in the development process flowsheet to make upgradation of iron values in beneficiation concentrate. The detailed mineralogical characterization provides information on the quantitative percentage of mineral phases with the help of microscopic study, heating cycle and chemical analysis of the ores.[51]

Roy and Venkatesh[54] have studied geological complexities and mineralogical behavior of the Banded Iron Formation (BIF) and associated iron ores of Jilling–Langalata iron ore deposits, Singbhum-North Orissa Craton. Collected Iron ore samples represent Banded Hematite Jasper (BHJ), massive ore, hard laminated ore, soft laminated ore, martite-goethite ore, blue dust, flaky-friable ore and lateritic ores along with three types of shales from fresh exposures and mine faces from the ore deposits. Phase identification, morphology and texture of ores were revealed by the reflected light microscope and SEM. Principal iron ore minerals (i.e. magnetite or hematite) are associated with secondary iron ore mineral phases (such as martite or goethite)as well as gangue minerals –SiO_2 (Major), Al_2O_3, TiO_2, MgO and CaO. Table 2.4 shows chemical analyses and nature of ores.

Table 2.4: Chemical analyses and nature of iron ore

Sr. No.	Type of ores	Fe_2O_3 (pct)	SiO_2 (pct)	Al_2O_3 (pct)	Nature
1	BHJ	40-60	30-50	1-3	Alternate layer of hematite and jasper (quartz)
2	Laminated	85-95	01-10	1-4	Colour - Steel gray, hard and high grade
3	Lateritic	50-80	5-20	5-15	Relatively rich in goethite and kaolinite mineral, highly spongy and porous in nature.
4	Martite-goethite	85-90	4-5	3-4	Minerals – Martite and goethite, having voids and cavities.

5	Blue dust	90-95	1-4	0.5-2	Colour - Steel gray
6	Shale	15-50	15-45	15-40	Prominent minerals are quartz and kaolinite, variable proportion of minerals

Mohanty et al.[47] studied mineralogical properties of banded iron ore samples from the Orissa region with the help of different techniques such as optical microscopy, X-Ray diffraction, electron microscopy, etc. In iron ore samples, there is a distinction between them due to the mineralogy of iron ore minerals (hematite / magnetite / goethite) and quartzite phases (jasper / quartz / clay), degree of metamorphism and effect of weathering. Such distinction is clearly observed by texture and banded formation of iron rich minerals and quartzite (silica rich) minerals in iron ores by naked eye observation as well as optical microscopy. The microscopic study revealed that the ores are mainly composed of iron oxide-hydroxide phases in different proportions with varying amounts of quartzite minerals like quartz and clay. Hematite, magnetite and goethite are the major iron minerals. Goethite, the major mineral in iron ore samples from the Hirapur area shows well-developed colloform (*involves the formation of distinct microcrystalline layers*) banding, a characteristic texture indicating colloidal precipitation.

Table 2.5: Occurrence of hematite iron ore and its characteristics

Sr. No.	**Type**	**Iron bearing minerals**	**Gangue minerals**	**Nature**
1	Massive	Hematite, goethite, martite and magnetite	Quartz, clay	Steel grey in colour, Specific gravity: >5, high crushing strength
2	Laminated	Hematite, goethite and limonite	Quartz, clay, gibbsite, chert	Laminated structure, Specific gravity: 4.2-4.7
3	Lateritic	Goethite, Limonite, Hematite, ochre	Quartz, clay, gibbsite	Dull luster, rich in alumina, Friable nature
4	Blue dust	Hematite, goethite	Quartz, clay	Generally blue/dark black or cherty red in colour, powdery form, Low alumina

Kotta et al.[55] have investigated on hematite iron ores from the regions of Odisha (03 samples) and Chhattisgarh (02 samples) for chemical, physical, thermal, textural and mineralogical studies. Comparative studies of ore samples were done for the viability of commercial exploitation. 04 samples have good quality with respect to world high-grade hematite iron ores. In optical microscopy, the fine (size <20μm) gangue minerals (i.e. Quartz and Kaolinite) are distributed in a matrix of hematite iron ores. SEM-EDS examination was carried out on the morphological and textural studies of ores. TG/DSC analyses found sequential endothermic reactions due to loss of moisture, dissociation of hydroxyl bonds (-OH) and decomposition of volatile substances / matters present in raw iron ores. The tumbler, abrasion and shatter indices of iron ores were in an acceptable range for iron making.

Ghosh et al.[56] reported the low-grade iron ore deposit from the Jharkhand-Orissa region, India into four categories. This noteworthy information about ore is helpful for mineralogical studies, quality of the ore and more importantly beneficiation studies. It has been categorized into:

(i) Grade –I with <45 pct Fe – containing shale rich type;
(ii) Grade –II with <45 pct Fe – containing BHJ rich type;
(iii) Grade-II with 45-55 pct Fe and
(iv) Grade-III with >55 pct Fe containing conventional flaky, hard, kanga, lateritic, shale and BHJ litho/ore types in varied proportions.

Rao et al.[11] have worked on mineralogical properties of low-grade iron ore from Bellary-Hospet sector, India. Major mineral is obtained hematite along with minor amounts of goethite, magnetite, martite and limonite with quartz and clay as gangue minerals in ore by microscopic investigation and similar results obtained in XRD studies. Authors advised detailed mineralogical characterizations on the complex nature of the ore. Furthermore, performance of mineral dressing operations is discussed on ore purposely.

Iron ore production was 201.43 Mt in 2017-18, out of which 134.46 Mt (66.75 pct) was produced in the forms of fines.[8] Further, 10-12 pct lumps become fines while handling, loading and unloading. The huge quantities of iron ore slimes (containing 55 to 60 pct iron, size -150 μm, in slurry, contains very fine particulate matter (iron ore) collected in tailing ponds, estimated to be 130 Mt (accumulate to the tune of around 10 Mt per year in

India) are not being utilized at present. Apart from that, most of the slime is thrown away as waste for land filling and creates pollution to the environment, which i not desirable.[57]

At the end of 2018, India has proved a coal reserve (mineable) of 101.36 Bt (9.6 pct) while the world's proved coal reserve is 1054.78 Bt. India has estimated coal reserves of about 326.5 Bt as of 1st April 2019. Out of this, coking coal is only 35.0 Bt (10.72 pct) which is mainly useful for blast furnace iron making, whereas the non-coking coal is 291.49 (89.28 pct). Large amounts of coal fines and coke breezes are generated during coal mining and coking of coal respectively.[58]

Around 60 pct of iron ore production comes in the form of fines (including concentrates) during the mining operations in India. Further, 10-12 pct lumps become fines while handling, loading/unloading operations and while converting them into calibrated lump ore for sponge/pig iron plants/exports. Thus, about 70-75 pct of the total production of India's iron ore is fines.[21] This enormous amount of fines is generated in Indian ore and coal mines due to mechanized mining and mineral dressing operations. A lot of coal fines and coke breeze are produced during coal mining and coking of coal respectively. Utilization of these fines for extracting metal is of vital concern for resource utilisation and pollution control.[59]

Low-grade iron ore, iron ore fines and iron ore tailings/slimes accumulated over the years at mine heads and generated during the existing washing processes, need to be beneficiated to provide concentrates of required quality to the Indian steel plants. However, these concentrates are too fine in size to be used directly in the existing ironmaking processes. For utilizing this fine concentrate, pelletization is the only alternative available.[60]

These fine concentrates cannot be processed in DRI reactors such as Rotary kiln, Midrex, HyL, and Rotary hearth.[21] Also, fines cannot be directly charged /used since do not allow proper gas flow through the furnace and are responsible for problems like fluidisation and flooding. The use of agglomerates is to allow ore fines to be utilised. While the optimum size range of lump ore is considered to be 10-30 mm, a large quantity of fines below 10 mm is produced, both during mining, subsequent beneficiation (if any) and handling. These fines can only be used after agglomeration. During agglomeration, fluxes can be added to produce pre-fluxed pellets or sinter. The use of pre-fixed pellets or agglomerates improves furnace performance.[61]

Pelletization plants generally involve huge capital investments and consume enormous of energy and fuel for grinding and pellet making. Hence, the capital investment and operating costs of pelletization plants are very high. Thus, the process of beneficiation followed by agglomeration will not only conserve the limited high grade lumpy iron ore but also will engender optimum utilisation of the available valuables from mine / process rejects. This will reduce the burden of stacking of tails/rejects that are kept for disposal and will be an effective measure to control environmental degradation. SAIL intends to incorporate pellets in their blast furnace burden and proposes a burden comprising of the 15 pct lumps, 15 pct pellets and 70 pct sinters in the near future. This strategy could open up the opportunity for the utilisation of low-grade iron ores, fines, and slimes which after beneficiation and transformation into pellets could find a larger scope for application.[46]

Although India has vast reserves of iron ore, lack of consistency with respect to the Al_2O_3/SiO_2 ratio makes these ores unsuitable to use directly in the metallurgical industries without prior beneficiation. It has also been established that the adverse effects of a high alumina-to-silica ratio (ideally it should be < 1) are detrimental to blast furnace as well as sinter plant productivity. Indian iron ores are being beneficiated by washing, scrubbing, hydrocyclone separation, gravity separation and magnetic separation. During sizing and washing operations the enrichment with respect to iron content is marginal and gangue reduction with particular reference to favourable Al_2O_3/SiO_2 is minimized.[11]

Only processed iron ores are used in the iron industry. Iron ore processing in the country is restricted to meet the physical standards, as it is inherently medium/high grade. Therefore, all the Integrated Steel Plants (ISPs) deploy multi-stage crushing, washing and sizing of ROM ore to produce lumps (-30 +10 mm) and sinter-feed size (-10 +0.15 mm) material. While, non captive sector supplying lumps to coal based Direct Reduced Iron (DRI) plants, resorts to multi stage crushing and screening to meet the feed size requirement. This practice generates large amounts of fines (-6 mm) and slimes (-100 mesh / 0.15 mm) which get unused at a mine site. Characteristically, Indian iron ores are soft & fragile in nature and mining and processing combined, generated a substantial amount of fines. The proportion of lumps & fines in fines in general is around **2:3.** Extensive R&D work was indeed carried out at various laboratories in India and at IBM's Ore Dressing Laboratory in particular on low-grade / sub-grade iron ore, iron ore fines (-10 mm) and classifier/tailing pond slimes (-100 mesh). The flow sheet developed on almost all types of ore reflects the possibility of producing concentrate suitable for sinter & pellet making. By and large, these flow sheets may offer a road map for the likely process route of beneficiation. By taking advantage of the same, the existing operations must look towards beneficiation as a means to overcome the crisis of supply of high grade ore and this is the need of the present time.[46]

Suthers et al.[23] have applied a comprehensive geometallurgical approach from the mining ore to processed product. Further, a framework has been developed based on this approach at CSIRO, Australia. The framework covers geology, mineralogy, beneficiation, processing of ore and metal production. Framework links between the nature of ore (*texture, mineralogy*), response of ore during beneficiation and product quality (*agglomeration*). The base of framework is ores group classification and the relationship of metallurgical properties with the group (as shown in Table 2.6). Correlation of ore properties helps to improve in prediction of ore response during unit operations – beneficiation and agglomeration.

Sinha et al.[62] had investigated on impact of mineralogical studies on the sinter quality of Singhbhum Orissa iron ore by blending different grades of ores from this region. Microscopic studies by SEM and phase analysis by XRD were carried out for deletion of the effect of gangue minerals on sinter quality. Gibbsite grains have in the range of 10-50 µm in association with iron ore bearing minerals. 4-6 pct alumina is observed in iron ore with goethite which leads to increase in solid fuel consumption during sinter making. An adverse effect of alumina on sinter can be neutralized by mineralogical studies.

Coal types are discriminated according to their volatile matter content. Coking coal with volatile matter less than 1 pct is acceptable. Non-coking coal with, volatile matter less than 20 pct is preferred, but higher volatile matter coal can also be used. During iron making process, volatile matter of coal and other gases is burnt in the presence of oxygen from air and produces heat. So, the heat is also produced by burning volatile matter of coal. The reduction of iron oxide increased when non-coking coal is used as a reductant because it contains a considerable amount of volatile materials. If a higher amount of fixed carbon means lower volatile matter (VM), thereby lowering the char reactivity.[9], [36]

Below 623 K, most of the chemisorbed H_2O is evolved during the early stages of heating followed by the light gases of CO, H_2, CO, CH_4 and C_2H_6, which are developed in the range of 623-873 K. Above 873 K, complex hydrocarbons or tar consisting of large chains of carbon and hydrogen are released.[63] The released volatile is dissociated at higher temperatures to generate highly reducing gases like CO and H_2. For ore–coal composite pellets, the weight loss of the sample arises not only from oxygen and carbon losses, but also the loss of volatile matter and residual moisture present in pellet. Higher values of degree of reduction are obtained at lower temperature (600-700 K).[9], [21]

High ash content in coke or coal is necessitated washing treatment additionally which increase significantly cost values of coke processing and iron making process. The high ash coke creates operational problems such as high coke rate and low productivity in the iron making reactor. Thus, high ash content also increases phosphorus, sulphur or trace elements content in the hot metal. As the ash content increases, the available carbon of coke decreases, and subsequently, the heat supply to the furnace per unit weight of coke decreases. The ash is the inorganic residue after burning; ash contains refractory oxides, e.g. 55–60% SiO_2, 15–30% Al_2O_3, 4–10% Fe_2O_3, 2–3% CaO, 1–4% MgO, 2–8% Na_2O + K_2O and trace of TiO_2.[9]

Due to the presence of high ash content in coke, (a) the coke rate in BF will be high, 1% increasing of ash, coke rate increases 1–2%; (b) slag volume will be more; (c) productivity of BF will be low, due high volume of slag to low utilization of useful volume of BF, 1% increasing of ash, productivity decreases 2–3%; and (d) phosphorus in hot metal will be increased. Sulphur and phosphorus, usually present in coke in form of inorganic compounds, are later transferred into hot metal. Most of the sulphur and part of the phosphorus in hot metal comes from coke, and remaining phosphorus comes from the ore.[9], [36]

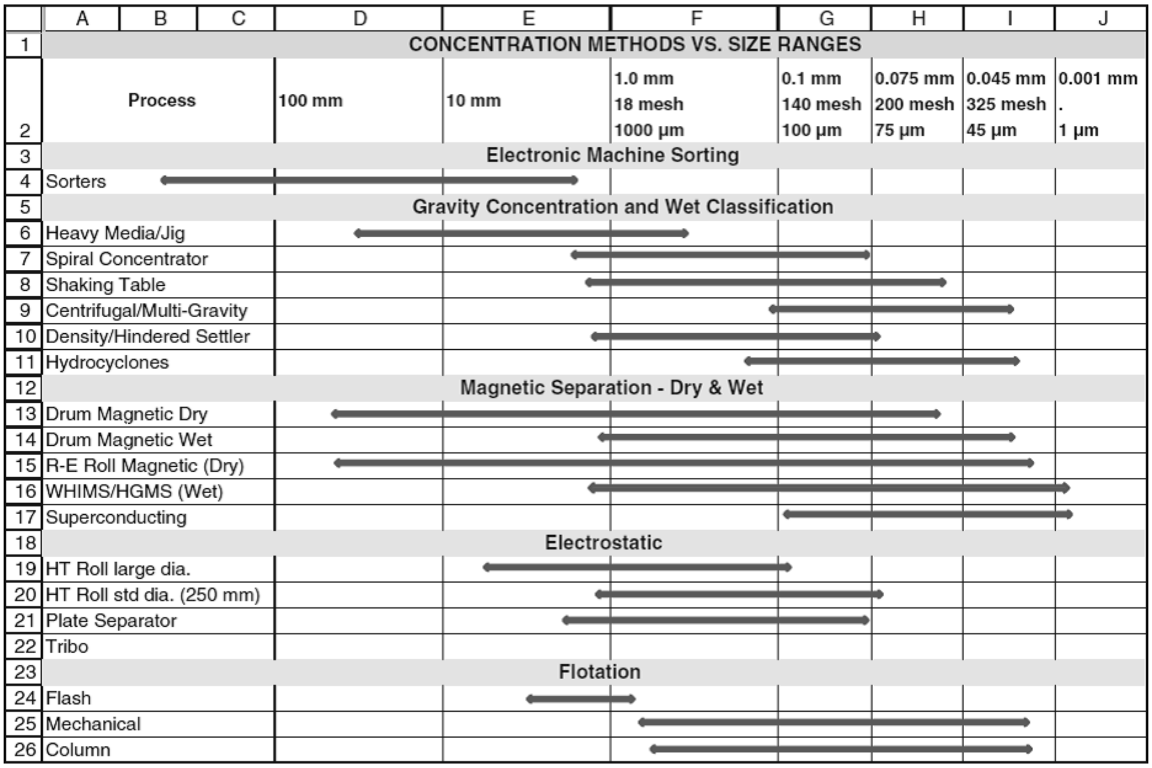
Table 2.6: Relative lump metallurgical qualities of common iron ore textural groups[23]

Sr. No.	**Ore group**	**Porosity**	**TI**	**AI**	**DI**	**RDI**	**RI**
1	Dense martite-hematite	very low	High	Low	low	Low	medium
2	Microplaty hematite	medium-high	low-medium	high-medium	very low	medium-high	high
3	Martite-goethite	Medium	medium	Medium	medium	medium	medium
4	Goethite-martite	High	low-medium	high-medium	medium	medium	high
5	Dense hematite / Martite / hydrohematite	Low	very high	Low	very high	Low	medium
6	Dense martite-goethite	Low	High	Low	high	medium	medium
7	Dense goethite-martite	Medium	medium	Medium	high	medium	medium
8	Microplaty hematite-goethite	Medium	medium	Medium	medium	high	high
9	Brown goethite	low-medium	medium	Medium	low-medium	low	high
10	Ocherous goethite	very high	Low	High	low	high	very high
11	Vitreous goethite	Medium	medium	Medium	medium	medium	high
** TI - tumbler index, AI - abrasion index, DI - decrepitation index, RDI - reduction degradation index, RI - reducibility index*							

2.4 Beneficiation of ore:

The prime function of beneficiation of iron ore is to improve the total Fe content and to decrease the alumina/silica ratio for smooth downstream utilisation. Challenges and solutions for upgrading Indian iron ore resources for long-term sustainability by using suitable beneficiation techniques. As the ore is heterogeneous in nature and characteristics of ore vary from place to place, an exclusive beneficiation flowsheet is needed for a particular ore.[51]

The typical size ranges that are agreeable for beneficiation methods are shown in Figure 2.1.[64]



	A B C	D	E	F	G	H	I	J
1	CONCENTRATION METHODS VS. SIZE RANGES							
2	Process	100 mm	10 mm	1.0 mm 18 mesh 1000 µm	0.1 mm 140 mesh 100 µm	0.075 mm 200 mesh 75 µm	0.045 mm 325 mesh 45 µm	0.001 mm . 1 µm
3	Electronic Machine Sorting							
4	Sorters							
5	Gravity Concentration and Wet Classification							
6	Heavy Media/Jig							
7	Spiral Concentrator							
8	Shaking Table							
9	Centrifugal/Multi-Gravity							
10	Density/Hindered Settler							
11	Hydrocyclones							
12	Magnetic Separation - Dry & Wet							
13	Drum Magnetic Dry							
14	Drum Magnetic Wet							
15	R-E Roll Magnetic (Dry)							
16	WHIMS/HGMS (Wet)							
17	Superconducting							
18	Electrostatic							
19	HT Roll large dia.							
20	HT Roll std dia. (250 mm)							
21	Plate Separator							
22	Tribo							
23	Flotation							
24	Flash							
25	Mechanical							
26	Column							

Figure 2.1: Typical size ranges for beneficiation methods

Jigging, the gravimetric technique is an appropriate process for the separation of iron ore lumps and fines at high separation densities. Jigs are divided into two types: (i) Lump ore jigs for size range from 38 mm to 10 mm and (ii) Fine ore for size range from 10 mm to 0.5 mm.[65] Rao et al.[66] concluded that jigging of fines is difficult when compared to lumps by using for Indian iron ores by apic jig.

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 the high demand for good grade iron ores day by day.[19]

Alumina in Indian iron ore fines or slimes are obtained in the form of two distinct mineral constituents namely, gibbsite *(hydrated aluminium oxide*) and kaolinite (*having clay minerals in minor quantities*).[67]

Nayak et al. [68] processed the Indian slime from 54.70 pct Fe to 66.46 pct by the Mineral dressing operations. (Hydrocyclone » Wilfly table » Magnetic Separator » Flotation)

Lal et al.[6] had worked on the beneficiation of low-grade magnetite ore from Jharkhand. They achieved a high Fe value 67.42 pct Fe with a Fe recovery of 64.8 pct from as received sample (i.e. 25.73 pct Fe) and specific gravity over 4.7 with high magnetic susceptibility which meets the industrial specification for heavy media separation and possess the quality of media reclamation at a low intensity magnetic separation. (Jigging » Tabling » Magnetic separator)

Aupam et al.[69] studied on BHQ samples from two different states of the India viz. Karnataka and Odisha by different beneficiation techniques. The tests conducted on Barbil area, Odhisha - BHQ sample resulted in an upgradation of iron content from a feed value of 42.8 pct Fe to a maximum of 56.8 pct Fe by magnetic separation with a yield of around 41 pct. (DHIMS » WHIMS) Similarly, Bellary-Hospet sector - Karnataka ore has indicated that it is possible to increase the iron content from a feed assay value of 35 pct iron to as high as 55 pct iron with a yield of 20–24 pct. (WHIMS *with hard Bond Work Index*)

Seifelnassr Ahmed et al.[70] had investigated the effectiveness of gravity and magnetic concentration techniques for the beneficiation of a Sudanese iron ore, from the Wadi Halfa iron ore deposit, North of Sudan. Recovery achieved 70 pct (from 35 pct Fe to 64 pct Fe). Subsequently, the silica content lowered down from the ore by using beneficiation techniques. (Tabling » Magnetic separator)

Srivastava and Kawatra[24] attempted to simplify a conventional ironmaking route by eliminating of energy intensive processes such as blast furnace and coke ovens while adding more flexible processes such as rotary hearth furnace (RHF) and wet high-intensity magnetic separation (WHIMS) which can be processed a low-grade iron ore (27.32 pct Fe). Low-grade iron ore is characterized by several mineralogical techniques. Pellets were prepared by iron ore, coal (*reducing agent*) and bentonite (*binder*). Pellets were fired at 1698 and 1723 K for the firing time of 20 and 30 min. Nuggets (*fired pellets*) achieved a density of ~7 g/cm^3 and pct iron recovery in the range of 90-95. Upgraded ore had achieved 45.24 pct Fe.

Pani et al.[71] had done a beneficiation investigation on lean grade iron ore from Kiriburu (West Singhbhum, Jharkhand, India) based on size-grading. Gravity separations (jigging and spiral concentrator) were ineffective on lean grade iron ore due to gangue minerals association with iron bearing minerals which were insignificant in the impact of density differences. Desliming operation followed by wet high intensity magnetic separator achieved pellet grade concentrate iron ore (64.86 pct Fe) with a yield of 35.85 pct.

Subrata Roy[72] studied goethitic-lateritic ore (GLO) from Eastern India. Mineralogical studies revealed that iron ore porous and friable oxides and hydroxides of iron. Hematite and goethite are the main iron-bearing minerals while kaolinite and gibbsite are the major gangue mineral constituents in ore. Due to the friable nature of ore, significant amounts of ore are lost as fines in the jigging and wilfley table operations. In place of as mentioned operations, multi gravity separator (MGS) has been effectively worked to reduce ore fines in tailings and increase in recovery values of iron. So, the nature of ore is a critical factor for choosing of effective gravity separation technique.

Chaurasia and Nikkam[73] have used a multi-gravity separator (MGS) by optimization of data for low-grade iron ore from Jilling mines of Barbil, Orissa. Low-grade ore is beneficiated from 50.74 pct to 65.11 pct with a recovery of 71.88 pct. MGS can be processed 400-500 µm range of gangues. Although, this MGS has constraints on several operating parameters like ore characteristics, feed rate, fluid flow rate, etc to achieve a higher recovery value of iron.

Rao et al.[74] have checked amenability of multi-gravity separator (MGS) on sub grade iron ore. Ore is having a composition of 40.80 pct Fe, 40.90 pct SiO_2, 0.24 pct Al_2O_3 and 0.20 pct LOI. By mineralogical studies, ore was identified as BHQ type with few bands of jasper. Ore has as an area distribution of 46 pct for ore minerals and 54 pct gangue minerals. By varying several parameters of MGS equipment had achieved optimum yield in the range of 53 – 55 pct of a concentrate and with 53-56 pct Fe and 12-16 pct SiO_2 with a recovery of 66-75 pct Fe.

Vidyadhar et al.[75] have attempted to upgrade low-grade iron ore – BHQ type from Meghatuburu mine, India. BHQ ore contains 37.52 pct Fe, 42.23 pct SiO_2, 0.82 pct Al_2O_3 and 1.83 pct LOI. Mineralogical studies revealed that a reasonable amount of degree of liberation is achieved only below 150 µm size. Ore is upgraded by using multiple techniques in sequence from hydrocyclone, falcon concentrator, Low Intensity Magnetic Separator (LIMS), Wet High Intensity Magnetic Separator (WHIMS) to floatation. -210 µm fine size iron ore achieved of enrichment of 63.7 pct Fe and 9.35 pct SiO_2 with a yield of 28 pct.

Haran et al.[76] have beneficiated sub-grade iron ore from Kenojhar District, Orissa, India containing 57 pct Fe, 7.7 pct SiO_2, 4.8 pct Al_2O_3, 0.4 pct TiO_2, 1.3 pct Mn and 4 pct LOI. The beneficiation process involved a cyclone separator, tabling and followed by a Wet High Intensity Magnetic Separator (WHIMS). The upgrade iron ore achieved 65 pct Fe, 2 pct SiO_2, 1.8 pct Al_2O_3, 2 pct Mn and 0.9 pct LOI with a recovery of 60.1 pct Fe. (Cyclone Separator » Tabling » WHIMS)

Jyoti et al.[77] studied on low grade iron ore from Gua mines, Jharkhand-Orissa region, India. The iron ore fine is de-slimed using a hydro cyclone and the underflow product was subjected to reverse flotation. Ore was upgrade from 57.6 to 64.7 pct Fe by using hydro clone and froth floatation. Results of these studies show that froth flotation can be used for beneficiation of low grade iron ore to produce a concentrate suitable for pellet feed for iron making. (Cyclone Separator » Froth floatation)

Filippov et al.[78] studied beneficiation of iron ores by reverse cationic flotation process. This process is more advantageous to magnetic separation and anionic floatation. Hard water can be used for floatation process. Depressant can be replaced but a universal reagent regime for iron ore beneficiation can be proposed due to the variations in the mineral composition of different iron ore deposits. Further development of the reverse cationic flotation of iron ores requires a more detailed consideration of the nature of iron-bearing gangue minerals and the application of original approaches for the selective removal of these species.

Guanghui Li et al.[79] have attempted to eliminate high amounts of Al_2O_3 from limonite iron ore by roasting and followed by leaching treatment. Roasting conditions were 1000 ºC for 15 min with 14 pct (wt.) Na_2CO_3. The amount of Al_2O_3 lowered from 8.16 pct to 2.13 pct and the amount of Fe increased from 48.92 pct to 63.21 pct in concentrated ore.

Kyoung-oh Jang et al.[80] have investigated on low-grade goethite ores from Australia which is categorized as *difficult-to-process ore*. In this beneficiation studies, chemical and mineral transformations of goethite ores were studied by reduction roasting and magnetic separation. Transformation of goethite ores into iron oxide or iron can be explained by following sequential reactions:

$$2\alpha - \mathrm{FeOOH}_{(s)} \rightarrow \alpha - \mathrm{Fe_2O}_{3(s)} + \mathrm{H_2O}_{(g)} \quad \text{...... (2.1)}$$

$$3\alpha - \mathrm{Fe_2O}_{3(s)} + \mathrm{CO}_{(g)} \rightarrow 2\mathrm{Fe_3O}_{4(s)} + \mathrm{CO}_{2(g)} \quad \text{.....(2.2)}$$

$$\mathrm{Fe_3O}_{4(s)} + \mathrm{CO}_{(g)} \rightarrow 3\mathrm{FeO}_{(s)} + \mathrm{CO}_{2(g)} \quad \text{.....(2.3)}$$

$$\mathrm{FeO}_{(s)} + \mathrm{CO}_{(g)} \rightarrow \mathrm{Fe}_{(s)} + \mathrm{CO}_{2(g)} \quad \text{.....(2.4)}$$

2.5 Agglomeration of iron ore with carbonaceous materials:

The feed to any furnace should form a permeable bed of material, permitting gas to flow through it uniformly at a high rate. Fine iron ore concentrates are not suitable in their as-produced form, both because fines tend to pack into a non-permeable bed and because the fine particles are likely to be carried away as dust by the high blast flow rates. The fine ore must therefore be agglomerated into larger particles that will improve the permeability of the furnace burden, increase the rate of reduction, and reduce the amount of material blown out of the furnace as dust. Four basic processes have been developed for agglomerating iron ores: sintering, nodulizing, pelletizing and briquetting.[81]

Briquetting consists of compressing fines into lumps of regular shape using high pressure such as rolls, punches, extruders or similar devices. Out of these four basic processes, briquetting has salient features:

- Agglomerate (*i.e. briquette*) is prepared by cold-bonded process.
- It requires a relatively few amount of binder.
- It doesn’t require induration treatment.
- Overall process time (*preparation » making » drying*) is much less than others.
- The compressive strength value of a briquette is higher than the other agglomerates.
- Due to compaction, the least amount of fines is generated during the process.
- Due to uniformity and consistency in size and shape of briquettes which help to better reduction rate.

The general requirement for good quality agglomerates includes sufficient strength for handling, transportation and outside storage as well as a complete reduction in iron and steel furnaces without degradation or excessive swelling.[82]

Mining and processing of Indian iron ore generate huge amounts of fines. Besides, there are huge deposits of naturally occurring iron ore fines (blue dust) with 60–65 pct total iron content. These fines need to be agglomerated for use as burden material. Fines cannot be directly charged / used since do not allow proper gas flow through the furnace and are responsible for problems like fluidisation and flooding. While the optimum size range of lump ore is considered to be 10-30 mm, a large quantity of fines below 10 mm is produced, both during mining, subsequent beneficiation (if any) and handling. These fines can only be used after agglomeration. During agglomeration, fluxes can be added in order to produce pre-fluxed pellets or sinter. The use of pre-fixed pellets or agglomerates improves furnace performance.[61] It is a well-established fact that if iron ore fines are intimately mixed with carbonaceous fines (coke / coal / charcoal), the rate of reduction can be speeded up by a factor of an order of magnitude compared to that for ore lumps and reductant kept separately in the charge.[25]

When the composite pellets are introduced into the furnace for heat hardening, firstly carbon will burn off before the oxide particles get a chance to develop strength through sintering due to the oxidizing atmosphere around them. Moreover, hydrocarbons will be liberated. All these result in a loss of reluctance. Secondly, the evolution of gases would cause the disintegration of pellets. Thermal stresses due to the heating would aggravate this tendency. Therefore, to increase the green strength of composite pellets binders are required to be added to bind the particles at room temperature or a somewhat elevated temperature (maximum 773 K). The general requirement for good quality agglomerates includes sufficient for handling, transportation and outside storage as well as sufficient strength for handling or excessive swelling.[28]

Interest in iron ore-coal composite pellets / briquettes has grown since the 1980s because of the following advantages:[26]

- Utilization of cheaper recourses such as iron-bearing fines, carbonaceous fines, etc. which are cheap and are being generated in large quantities awaiting suitable disposal and control pollution;
- Rapid reduction of pellets due to intimate contact between iron oxide particles and reductant (*carbonaceous*) fines;
- Reduction in energy consumption, as cold-bonded composite pellets do not require induration (*high temperature heating*);
- Promising prospects for iron making - steel making at a small scale with less capital investment;
- Because of their uniform size and convenient form, pellets can be continuously charged into the furnace, leading to higher productivity; and
- Consistent product quality as the chemical composition of composite pellets (*feed material*) does not change.

Composite pellet containing iron oxide and carbon fines can be prepared only by cold-bonding technology. Cold bonding process is preferred because:[83]

- The briquettes are hardened in a cold bonding process due to physic-chemical changes of the binder at low temperature, the free ore grains remaining intact. This benefits the reducibility of the briquettes.
- It is an energy saving process for briquette and hence is becoming more popular.
- If composite briquettes are fired or hardened, simultaneously their reduction also occurs due to the presence of carbon. Hence instead of getting fired oxide briquette, some metal from due to reduction within the composite briquette and hardening of briquette does not take place.

The ore-coal composite briquettes can be prepared by cold-bonding technology. Figure 2.2 shows the flow diagram for composite briquette making.[84] Cold bonding of briquettes involves the mixing of iron ore fines and coal fines of suitable size with a suitable binder having hydraulic settling properties. The briquettes are hardened in a cold bonding process due to physico-chemical changes of the binder in ambient conditions or at slightly elevated temperature. A binder is a material that serves as a bridge between the particles and thus increases the green or dry strength of the bonded particles. Binders are widely used in agglomeration operations such as briquetting and pelletization to assure that the agglomerate possesses desired properties regarding subsequent handling, transportation and processing. These properties depend on the requirements of a particular operation and installation.[85] In certain instances, the binders may perform a chemical function as well as a physical one.

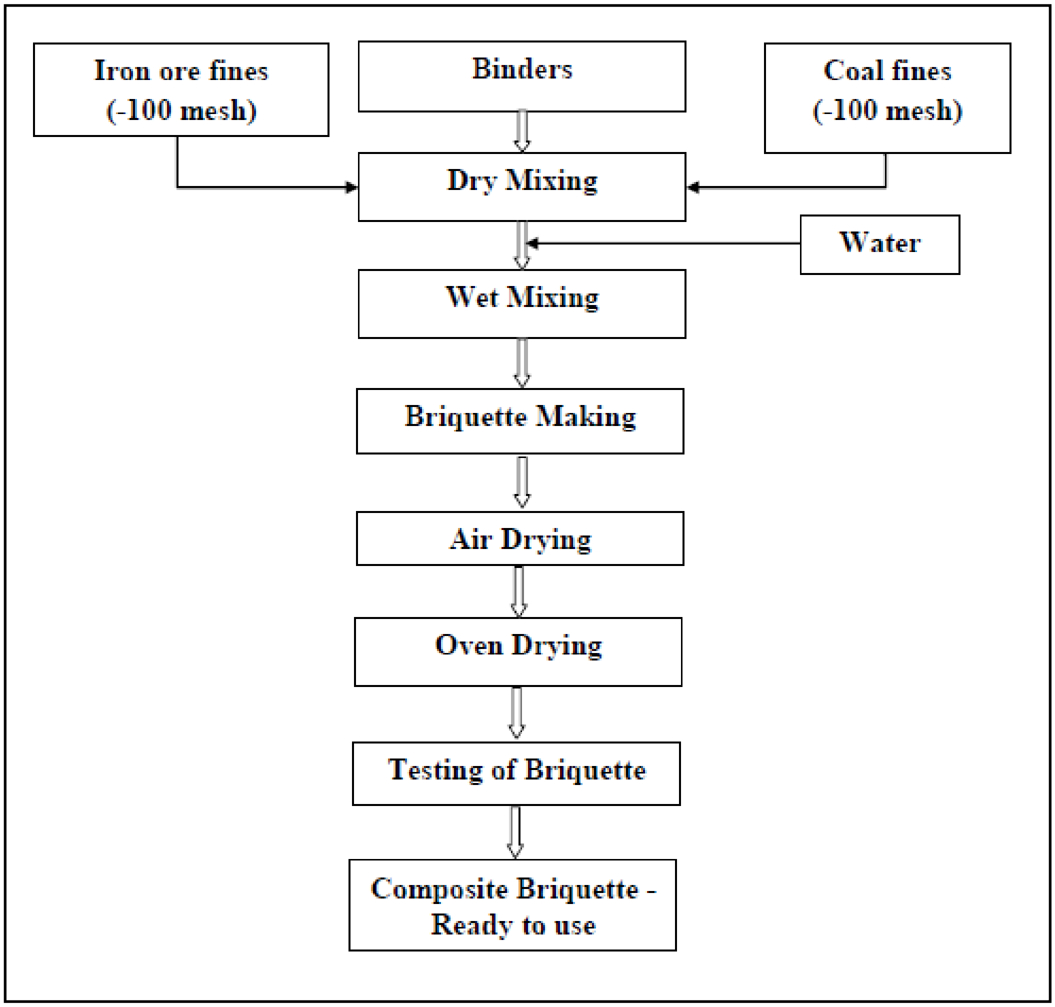


Figure 2.2: Flow diagram of iron ore-coal composite briquette

Functions of a Binder: It accomplishes two most important functions in iron ore agglomeration:[86]

- The binder makes the moist ore plastic so that it will nucleate seeds that grow at a controlled rate into well-formed pellets.
- During drying, the binder holds the particles in the agglomerates together while the water is removed and continues to bind them together until the pellet is heated sufficiently to sinter the grains together.

Types of Binders: Research workers have tried to prepare iron oxide/ore and coke/coal/charcoal composite pellets/briquettes, using various organic or inorganic binders and as well as combining of them. Binders used to prepare composite pellets are classified as:[21], [84]

1. **Inorganic binders**: Bentonite, cement, sponge iron powder, lime, burnt lime, $Ca(OH)_2$, silica, water glass, fly ash, fly ash and lime, boron compounds, sodium polyacrylate (SPA) etc.
2. **Organic binders**: Dextrin, dextrose, thermosetting resin (TSR), starch based binder, molasses, polyvinyl alcohol (PVA) etc.
3. **Combined binders**: Different combinations of organic and inorganic binders such as dextrin, TSR, molasses, lime, $Ca(OH)_2$, etc.

A binder used in the briquetting process can be divided into an inorganic binder, organic binder and compound binder, and all of them have respective advantages and disadvantages:[30]

1. The inorganic binder such as bentonite has a long history and mature experience of use and it has a significant effect on the performance of briquettes, however, due to its impurities, the appropriate control of supplying amount is necessary, such as the 1.5 pct–2.0 pct mass fraction of bentonite is appropriate.
2. Adding organic binder will not increase the content of harmful elements in the briquettes, but its performance at high temperature is poor, which has a great influence on the decrepitation temperature of briquettes, and the binder’s price is high.
3. The use of compound binder can reduce the supplying amount of inorganic binder, reduce the cost of briquettes, improve the quality of briquettes, and get better performance of briquettes.

Therefore, considering the development in direction of binders, organic binder and organic-inorganic compound binder have become the focus of research and development. Extensive research work is carried out on binder development for iron ore-coal composite pellet/briquette by several research groups all over the globe. Dutta and Chokshi[21], [84], [87], [88] have worked with several organic and inorganic binders like fly ash, lime, slaked lime, calcium hydroxide, dextrose, molasses, cement, polyvinyl alcohol (PVA), Sodium polyacrylate (SPA) as an individual or combination of different proportions for cold bonded iron ore-coal composite briquette / pellet. Table 2.7 shows a summary of research works for strengthening of cold bonded iron ore-coal composite briquette / pellet.

Eisele and Kawatra[86] broadly reviewed several binders used in iron ore pelletization. Binders are classified based on binding mechanisms which help to understand the binder’s competence with raw materials. Binding mechanisms of binders and binder combinations were discussed with distinction in properties. Standard tests for significant binder characteristics were mentioned with crucial results. Bentonite is a prime binder in iron ore pelletization. Industrial wastes, like coal fly ash, have been shown inspiring results. Organic binders – synthetic chemicals to low value waste products have been shown promising results among all binders. Such binders don’t contain silica or alumina which is highly favourable conditions for ironmaking. A major drawback of this group of binders is that these burn away before hardening treatment. Cold-bonding process has potential to replace the conventional pelletization process. It can be replaced hardening treatment of pellets which is energy intensive and expensive step of pelletization. The Cold bonding process relies majorly on binder use for particular raw materials. A Combination of binders (such as organic and inorganic binders) has been attempted to decrease the deficiencies of one binder with another one and improve in pellets’ properties. Due to these, a combination of binders is always advantageous for the cold bonding process.

Table 2.7: Research work carried out on iron ore-coal composite pellet / briquette

Sr. No.	Research group	Type of agglomerate	Iron ore / oxide / waste	Carbonaceous material	Binder (pct)	Compressive strength (N / agglomerate)	Remarks
1	George and Boardman[89]	Pellet	Solid waste – mill scale, dust, sludge	Coke breeze	10 pct Portland cement	>200	
2	Ganguly and Patalah[90]	Pellet	Blue dust	Coal	6-15 pct Sponge iron fines	50-900	5 pct NaCl solution is sprayed as moisture during pelletization.
3	Takahashi[91]	Pellet	Ore	Charcoal	8 pct Portland cement	1000-1300	12-14 mm diameter
4	Dutta and Ghosh[25]	Pellet	Ore	Coal	8 pct Cement + 2 pct Lime	202	-100 mesh of binder
					-do-	357	-325 mesh of binder
					4 pct Thermosetting Resin (TSR)	329	
					3 pct TSR + 1 pct Dextrin	339	
5	Shivaramakrishna et al.[92]	Pellet	Ore	Coal	5 pct Starch based	250	
6	Agrawal et al.[93]	Pellet	Ore	Coal	Dextrin	~300	
7	Raval & Dutta[94]	Pellet	Ore	Coal	SPA	976	
8	Dutta et al.[95]	Pellet	Ore	Coal	Slaked lime, molasses, dextrose	110-607	CO_2 treatment

Sr. No.	**Research group**	**Type of agglomerate**	**Iron ore / oxide / waste**	**Carbonaceous material**	**Binder (pct)**	**Compressive strength (N / agglomerate)**	**Remarks**
				Coke	Slaked lime, molasses, dextrose	245-1600	CO_2 treatment
9	Sah & Dutta[85]	Briquette	Ore	Coal	Lime + Dextrose	357	
10	Dutta & Chokshi[87]	Briquette	Ore	Coal	Fly ash + slaked lime + molasses	404	
					PVA	978	binder as a solution
11	Dutta & Chokshi[88]	Pellet	Ore	Coal	Fly ash + slaked lime + molasses	216	
					PVA	362	binder as a solution
12	Han et al.[30]	Briquette	BF dust and iron oxide	BF dust (*32.21 pct C*)	1-5 pct of (Corn starch + Sodium silicate)	44-69	at 473 K
						1295- 2075	at 1523 K
13	Ye et al.[96]	Pellet	Ore	Biochar (*from oak tree*)	2.5 pct Bentonite	33.9	Core-shell type
						33.2	Homogeneous
14	Ammasi and Pal[97]	Pellet	Ore	BF Flue dust (*33 pct C*)	Bentonite	2515	Indurated at 1553 K; 10 min.

2.6 Reduction studies on cold bonded composite briquette / pellet:

2.6.1 Theory of Reduction

If the pellet contains a mixture of oxide and carbon fines then the reduction rate of iron oxide is much faster. The reduction kinetics is expected to be enhanced due to the presence of reductants in situ which causes shortening of diffusion distances of reductants and the availability of the large number of reaction sites.[26]

During the reduction of iron ore-coal composite pellets, the evolution of volatile matter takes place due to the pyrolysis of coal. The volatile matter comprises mainly gas fuel, carbon dioxide and steam. The gas fuel consists of large amounts of hydrocarbons and small amounts of H_2 and CO. Above 973 K, the hydrocarbons are quickly cracked into hydrogen and carbon. Hence, pyrolysis of coal: generates reducing gases such as hydrogen and carbon monoxide. So, the reduction of iron oxide is due to a reaction with these reducing gases. It is well established that the reduction of iron oxide by carbon occurs as a combination of the gas-solid reactions as follows:[98]

$3Fe_2O_{3\,(s)} + H_2 / CO_{\,(g)} = 2Fe_3O_{4\,(s)} + H_2O / CO_{2\,(g)}$ ..... (2.5)

$2Fe_3O_{4\,(s)} + H_2 / CO_{\,(g)} = 3FeO_{(s)} + H_2O / CO_{2\,(g)}$ ..... (2.6)

$FeO_{(s)} + H_2 / CO_{\,(g)} = Fe_{(s)} + H_2O / CO_{2\,(g)}$ ..... (2.7)

Volatile matters in the coal evolve during heating and the decomposition of hydrocarbons also occurs at high temperature, according to the reaction:

Higher hydrocarbons (g) → Lower hydrocarbons (g) + H_2 (g) + C(s) ..... (2.8)

Gasification of carbon by CO_2 (*Boudouard reaction*) and H_2O takes place as follows:

$C(s) + CO_2(g) = 2\,CO(g)$ ..... (2.9)

$C(s) + H_2O(g) = CO(g) + H_2(g)$ .....(2.10)

CO and H_2 gases thus generated again act as reductants for iron oxides present in the ore. It is to be noted that if only carbon is employed as a reductant, then gasification of carbon by CO_2 and reduction of iron oxide by CO are the only reactions of concern. Therefore, carbothermic reduction and gasification of C by CO_2 are often discussed together in fundamental kinetic studies in the laboratory. The following topics are very briefly reviewed.

i) Pyrolysis of coal, and

ii) Carbothermic reduction and gasification reaction.

2.6.1.1 Pyrolysis of Coal

Pyrolysis of coal refers to the heating of coal, in the absence of air (or inert atmosphere), to understand its thermal behaviour. It is an initial step in the coal thermal decomposition process. When coal is subjected to pyrolysis, various physico-chemical changes occur at different temperatures. The pyrolysis of coal leads to the formation of three classes of product namely coke, tar and gases. Coke is the solid residue of the transformation process and is richer in carbon than coal. The tars and gases are the volatile matter and represent 4 to 45 pct of the weight of the coal, depending on its type**.**[99] Pyrolysis is accompanied by a change in the structure of the coal, leading to a marked variation in its thermophysical properties. Coal is a complex natural organic substance. The heating of coal causes thermal rupture of bonds, and volatile fragments escape from the coal. The weakest chemical bonds begin to break at 300 to $400^{o}C$ (573 to 673 K), producing molecular fragments, in a process termed depolymerization. These fragments can lead to the formation of tars, paraffin, olefins etc. if they are small enough to be vapourized and transported outside of the coal grain. Simultaneously, the decomposition of the functional groups gives rise to the evolution of light gases, principally CO_2, H_2O, CH_4, and aliphatic C_2 compounds. Cracking, which occurs beyond 550 to $600^{o}C$ (823 to 873 K), causes the liberation of CO and H_2.

During the pyrolysis of coal, substantial weight loss occurs because of the evolution of volatile matters. The amount and type of volatiles that evolve varies with the rank and heating rate of the coal as well as the conditions prevailing in a reaction chamber. The extent to which the coal devolatilizes varies greatly (less than 5 pct to over 60 pct) as a function of final temperature. The proportions of various products change with changes in pyrolysis temperature.[100]

The mechanisms liable to influence the pyrolysis process in a coal grain are as follows:[99]

i) Heat transfer from the outside towards the surface of the grain,
ii) Conduction of heat within the grain,
iii) Kinetics and the heat effect of the devolatilization reactions,
iv) Transport of the volatile matter from the inside to the outside of the grain,
v) Heat exchanges between the volatile matter and the solid during its internal transport,
vi) Secondary cracking reactions of the volatile species during their internal transport,
vii) Swelling and cracking of the grain, and
viii) Increase in the pressure within the grain due to the formation of gases.

Cypres and Soudan-Moinet [101] studied the influence of iron oxide additions on coal pyrolysis by thermogravimetry and the analysis of the evolved gases. They blended 70 pct bituminous coal with 30 pct of either hematite or magnetite and heated them from room temperature to 1273 K at the rate of 3.2 K/min. They observed the devolatilization of coal in two stages: i) Primary devolatilization at 573 to 873 K, and ii) Secondary devolatilization above 873 K. They found that the presence of iron oxides reduced the primary devolatilization rate of coal between 573 and 873 K. They observed that below 523 K, the coal loses its moisture. Between 573 and 873 K, the weight loss is significant because of tar release. Above 873 K, weight loss of the coal is small as only gases are released. In the temperature range of 573 to 873 K, the weight loss of the coal-magnetite mixture was due to the coal devolatilization only. Magnetite was not reduced below 873 K. Between 673 and 823 K, Fe_2O_3 was reduced to Fe_3O_4, with a loss of water and a little CO_2. They also observed that the yields of tar and gaseous hydrocarbon slightly decreased in the presence of iron oxides, mainly Fe_2O_3. In the secondary devolatilization zone, the reduction of iron oxides decreased H_2 yield and increased those of CO, H_2O and CH_4.

They[102] further studied the pyrolysis of coal and iron oxide mixture to establish the relationship between the release of volatile matter from coal and the reduction of iron oxides by thermogravimetry and the analysis of gases. The pyrolysis of coal, especially beyond 873 K, produces reducing gases H_2 and CO. Between 873 to 1273 K, the rate of weight loss of the blends passed through two maxima: the first, a minor one, at around 1000 K, and the second, much more pronounced at around 1173 K (as shown in Figure 2.3). After the second maximum, the rate of weight loss decreased rapidly and the weight stabilized. For the coal-hematite blend, the reduction was completed at 1223 K, whereas for the coal-magnetite blend, it was necessary to carbonize to 1273 K. They also observed that the evolution of hydrogen was significant above 873 K, with a maximum at around 1073 K. The quantity of hydrogen evolved from the blends was reduced compared to coal alone, especially in the region of the maxima. Hydrogen, therefore, played an important role in the reduction of composite pellets below 1073 K. This was also observed by Dutta and Ghosh for iron ore coal / char composite pellets.[98]

There was a significant generation of CO and CO_2 from the blends in the reduction zone. A primary reduction by H_2 and CO of the hematite was observed between 673 and 773 K but hidden in thermo-gravimetric measurements by primary volatilization of coal. X-ray diffraction confirmed that between 673 and 773 K, the hematite was reduced to magnetite. In the two blends the reduction of magnetite started at around 873 K. From the onset of that reduction, in addition to wustite, a little iron was detected. At around, 1073 K the wustite reached its maximum percentage. Afterwards, it rapidly got reduced to iron.[102]

2.6.1.2 Carbothermic Reduction and Gasification Reaction

Kinetically, the reduction of oxides in composite pellets is significantly by carbon in a mixture of iron oxide and carbon. If the composite pellet used char or coke as reductant then this is wholly carbothermic reduction. If, on the other hand, coal is used then the reduction will be partly by gases evolved due to the pyrolysis of coal, especially H_2 and CO.[102] Kinetics of reduction by H_2 and CO would not be separately reviewed since its salient features are well established. Now it has been universally accepted that carbothermic reduction takes place via the reactions (2.5) to (2.7), (2.9) and (2.10) i.e. through gaseous intermediates.

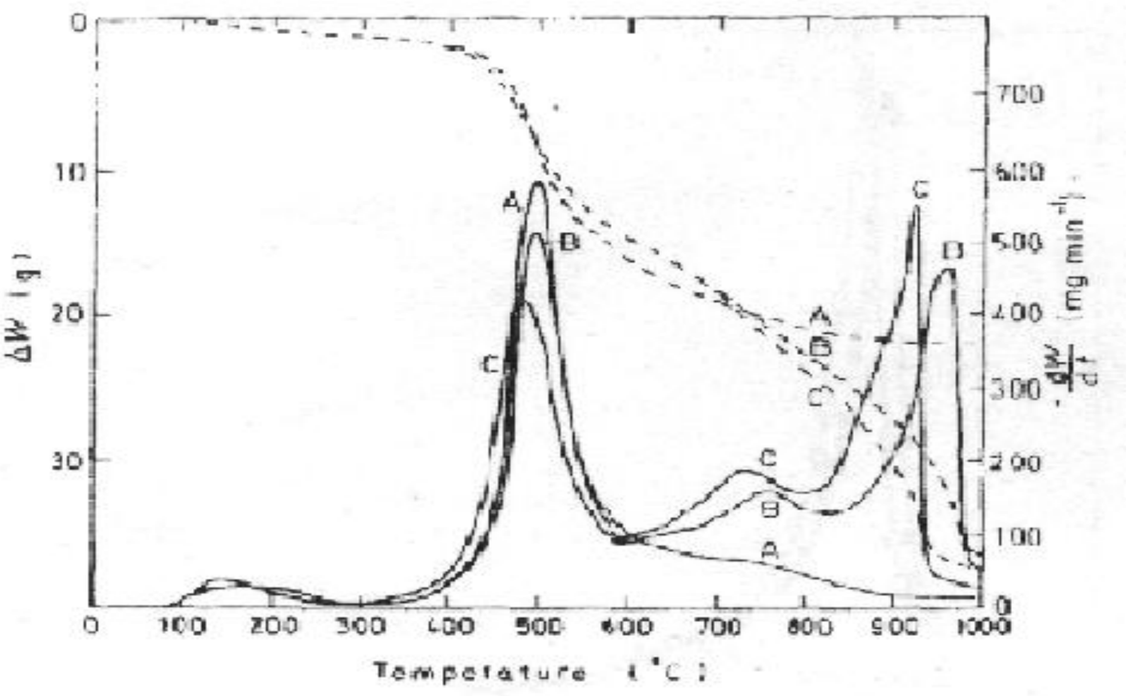


Figure 2.3 : Thermogravimetric curves, TGA (-----) and DTG (——), of carbonization of coal and coal/iron oxide mixtures, A - coal; B - Coal + Fe_3O_4 (30 wt pct); C - Coal + Fe_2O_3 (30 wt pct).

The carbothermic reduction of iron oxides has generally been found to be controlled by gasification reaction. Both interfacial chemical reactions, as well as mass transfer, have been found to control the rates of reduction reaction and gasification reaction. The overall rate is sometimes affected by the rate of heat transfer as well since it is endothermic in nature.[103]

2.6.2 Reviews on Reduction of Composite Pellet / Briquette

The carbothermic reduction of composite pellet / briquette has been prepared by iron ore / oxide and coke / coal / pet. coke / fuel / graphite powder. Isothermal and / or non-isothermal reduction studies were carried out in past. The degree of metallization / reduction of composite agglomerates are achieved reasonably better than conventional iron ore pellets. Reduction time is much less than the conventional ore pellets. Few research works are reported in Table 2.8.

Table 2.8: Reduction studies of composite pellet agglomerate

Sr. No.	**Research group**	**Type of agglomerate**	**Isothermal / Non isothermal**	**Degree of Reduction (pct)**	**Activation energy (kJ/mol)**	**Remarks**
1	Sharma[104]	Iron ore - Non coking coal -- composite pellet	Non-isothermal	---	68.52	
2	Dutta and Ghosh[98], [105]	Composite pellet	Non-isothermal	46-99	183.1-268.5	TG-DTA study
3	Agrawal et al.[93]	ore-coal composite pellet	Isothermal	90	---	Produced sponge iron
4	Goswami[106]	Iron oxide-blue dust-coal fines -- layered pellet	Non-isothermal		68	
5	Wang et al.[107]	Iron ore-coal composite pellet	Isothermal	---	92.03-114.57	
6	El-Geassey et al[108]	Iron ore-fuel oil composite pellet	Non-isothermal	---	68.95-82.61	
			Isothermal	---	18.81-28.42	
7	Santos and Mourao[109]	Iron oxide-carbon	Non-isothermal	---	46-120	TG DTA; upto 1473 K
8	Sohn and Fruhen[63]	Iron ore-coal composite pellet	Isothermal	56	---	1273 K; 3000 s
9	Sah and Dutta[59]	Iron ore-coal composite pellet	Isothermal	68-92		different Fe(T)/C_{fix} ratios
10	Man and Feng[110]	Iron ore-coal composite pellet	Isothermal		149.21 148.82	CO H_2

Ponomar et. al[111] have studied reduction kinetics by a transformation of hematite to magnetite by a gaseous reduction in the temperature range of 573-873 K. Ore is roasted in a single step process, which can be described using first order reaction model. The calculated activation energy for transformation is 41.9 kJ/mol.

Ammasi and Pal[97] investigated indurated iron ore - carbonaceous materials composite pellet of hematite ore with any one carbonaceous material - coal, coke or blast furnace flue dust. They also studied the effect of carbonaceous materials on properties of pellet. The properties of pellet like a reducibility index and reduction degradation index were decreased with an increase in quantity of all three different carbonaceous materials. Although cold crushing strength (CCS) of pellet is increased with increase of induration temperature.

Vining et al.[112] had worked on the briquetting of Australian hematite-goethite iron ore fines. Several parameters and tests were applied for the fired briquette to achieve best cold crushing strength value. Iron ore fine, flux - hydrated lime and moisture were used for briquette. Further briquette was fired in the temperature range of 1523 – 1623 K with time range of 01-30 min. *Feed moisture content* resulted one of the critical parameter for briquetting operations. 7.5 – 8.5 wt. pct moisture content briquette achieved density of 3.40 – 3.45 gm/cm3 and green strength of 4.0-5.5 kgf. Highest crushing strength of fired briquette was reported 478 kgf at 1623 K firing temperature for 10 min and with 1.22 basicity of flux.

Sarkar et al.[113], [114], [115] had studied isothermal reduction kinetics on cold bonded composite briquette of titaniferous magnetite ore (TMO) (48.96 pct Fe, 23.23 pct TiO_2, 1.95 pct SiO_2, 3.8 pct Al_2O_3) with two different reductant - coke dust (79.46 pct C_{fix}, 4.01 pct VM, 16 pct Ash and 0.53 pct moisture) as well as lean grade coal (28.28 pct C_{fix}, 28.31 pct VM, 36.21 pct Ash and 7.4 pct moisture). For reduction kinetics studies, process temperature was varied from 1273 to 1473 K for 3-60 min. The maximum reduction of TMO-coal composite briquettes is completed at 1373 K within 30 min while TMO-coke reported its maximum reduction value at 1473 K for 60 min. So, lean grade coal took less time for reduction as compared to coke. Coal contains more than 25 pct volatile matter which liberates H_2 and CO gases during the reduction process. These gases take part actively in reduction which results in the maximum yield value of iron. Out of several gas–solid reaction mechanisms, a spherical mechanism is used for activation energy. Arrhenius equation is calculated as 59.52 KJ/mol for coke dust and 93.42 KJ/mol for lean grade coal.

2.7 Smelting Reduction Process

There is a shortage of coking coal all over the world in general and in India in particular. Enormous amounts of coal fines and coke breezes are generated during coal mining and coking of coal respectively. Incorporating non-coking coal fines / coke breezes in cold bonded composite pellets, the metallurgical coke requirement in the blast furnaces can be subsequently reduced by partially feeding the composite pellets in BF. Utilization of these fines for extracting metal is of vital concern for resource conservation and pollution control.[21]

It is well established that the reduction rate of iron oxide is much faster if the pellet contains an intimate mixture of oxide and carbon fines. The reduction kinetics is expected to be enhanced due to the presence of reductants in situ which causes particle-to-particle contact and availability of a large number of reaction sites.[26]

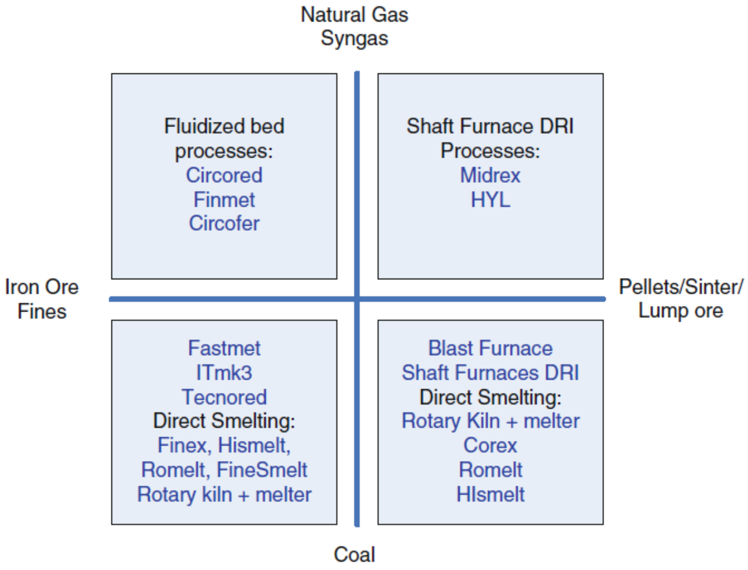


Figure 2.4: Classification of ironmaking processes

Over the globe, various ironmaking technologies are practised with an aim of extraction of iron efficiently from the ore. The nature and complexity of raw materials are the most critical factors in developing diverse ironmaking processes. Ironmaking processes can be classified based on raw materials (as shown in Figure 2.4):[116]

Iron and steel making processes can be broadly categorised into:

1. Conventional - Blast Furnace
2. Alternative processes – direct reduction (DR) and smelting reduction (SR).

The blast furnace is the dominant reactor and conventional route for Ironmaking. As of today, *Blast furnace Smelting* is the most economical iron making processes. However, it is now facing problems like a shortage of good quality coke and higher investment costs for the furnace and auxiliary types of equipment. The experts have forecasted that in the coming decade, the cost of high grade coking coal will rise at a much faster rate than electricity and non coking coal. The Blast furnace ironmaking has achieved near perfect maturity through intensive developments that have taken place around the globe. However, some of the threats to the blast furnace route are:[36], [37], [117]

- Stringent raw material requirements,
- High capital requirement,
- Lack of flexibility,
- Strict environmental policies,
- Coke is the biggest threat (Need of high grade coking coal and the environmental issues of coke making),
- Generation of air pollutants such as SO_x, NO_x and dust.

Alternative ironmaking processes that do not use the blast furnace and are not dependent on coke as the primary reductant, currently account for about 8 pct of the global iron production.[61] Alternative ironmaking is a collective name for all ironmaking production routes other than the blast furnace ironmaking route. The alternative ironmaking processes include processes using coal as well as natural gas and processes that produce either solid product (HBI/DRI) or liquid iron. To subdivide these production routes into smaller groups the type of ironmaking furnace / reactor can be used as a criterion.[37]

India does not have adequate scrap for steelmaking but has adequate reserves of iron ore. With respect to coking coal, the country does not have enough coking coal; and the available coking coal reserves are of inferior quality. Hence, there is a tremendous interest in iron making technologies to provide an alternative to the traditional blast furnace iron making process and to move away from using metallurgical coke as the prime reductant and fuel.[116]

SR processes are the latest development in pig iron production. The SR process emerged during the 1990s. In SR processes, iron ore and coal are added directly to a metal-slag phase where the ore is reduced. The SR process combines the gasification of coal with the smelting reduction of iron ore. All smelting reduction processes aim to produce hot metal, without using either coke or high-grade iron ore as a feedstock. However, it needs to be stressed that only a few conceptualized SR processes have reached the commercial scale till date. This has happened even though these new processes are one generation ahead of classical blast furnaces in terms of their intrinsic process versatility as well as superior environmental friendliness.

Iron ore uses as one of coolants in steelmaking. Coolants added to the basic oxygen furnace (BOF) absorb the released heat energy (*due to oxidation of impurities*) and control the temperature from overshooting. The coolants are chosen such that the absorbed heat energy is utilized economically and iron added gainfully during melting as much as possible.[118] This conventional coolant has been replaced by cold bonded iron ore slime briquette at the commercial scale of Tata Steel, Jamshedpur, India. 5-12 ton briquettes have been charged in 160 ton BOF heats. Briquettes have composition of 54.1 pct Fe, 4.73 pct SiO_2, 4.20 pct Al_2O_3, 5.38 pct CaO, 0.14 pct P. 4 pct lime + 4 pct cement used as binder for briquette making. This briquette helped into:[31]

- Better control of turndown temperature of heat – *obtained within range during heats,*
- Reduced oxygen blowing requirements – *slime gave part of oxygen,*
- Low P content- *lowered down P than the targeted value,*
- Lime requirement – *added as a binder,*
- Commercial viability – *Cost of briquette is much less than lump ore*.
- Sustainable development – *by consumption of slime and reducing the use of lump ore*

2.7.1 Feasibility of iron ore-coal composite pellet/briquette in smelting reduction processes

Coking coal is costly and India has limited reserves of it. Coke making in coke oven is a major source of environmental pollution whereas non-coking coal is widely available and the cheapest reducing agent for iron oxide. On the other hand, India has vast reserves of non-coking coal (i.e., approximately 87.1 pct of the total reserves) and is most widely available. It is the cheapest reducing agent for iron oxide.[119] A lot of iron ore fines and coal fines are generated during mining. India has hundreds of million tons of accumulated blue dust. Utilization of these fines for extracting metal is of vital concern for resource conservation and pollution control. Use of iron ore-coal/coke composite pellets will lead to utilization of fines of iron ore and coal.[87]

A basic dilemma in bath smelting processes is that a high degree of post combustion (PCD) does not allow more than 30 pct pre-reduction and hence adversely affects productivity. In this connection, the use of cold bonded ore-coal composite pellets may lead to significant improvements. It is now well known that reduction is much faster with composite pellets than the ordinary ore pellets or lump ore. When ore and carbon powders are intimately mixed, the rate of reduction is speeded by up to two orders of magnitude. The intimate mixing enhances the gaseous diffusion rate significantly.

Iron ore-coal composite pellets as burden material have been tested in cupola and encouraging results are reported. They could be reduced completely and melted within normal retention time in the cupola. The test results of production-sized cupola (5 to 40 tonne per hour) with a charge of 5 to 100 pct composite pellets are also available. Most of the trials were carried out with a charge consisting of 70 pct composite pellets and 30 pct scrap.[82]

Sah and Dutta[120] studied fundamental investigation on smelting reduction of iron ore-coal composite pellets in molten metal bath. Kinetics studies on smelting reduction of iron ore-coal composite pellets were carried out in an induction furnace at a temperature of 1723 ± 10 K. For 16 to18 mm diameter pellets, they observed that the time required for complete dissolution in a liquid metal bath is 83 to 90 seconds.