CHAPTER 2

REVIEW OF LITERATURE

This chapter deals with the literature review pertaining to utilization of steel plant wastes, especially dust and sludge. It discusses about the various methods of beneficiation of low-grade iron ores for upgradation. A comprehensive review of utilization of dusts and sludge is done. It also discusses about the composite pellets and smelting reduction processes/ technologies. A comprehensive review of different methods, used by investigators in past, for binder selection is done. Further composite pellet making is discussed by using several inorganic and organic binders. It discusses about preparation, reduction kinetics, advantages and uses of composite pellets. A fundamental knowledge of physical, mechanical and thermal behaviour of composite pellets, 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.

2.1 Sources of Steel Plant Waste

In a steel industry several manufacturing processes are employed involving use of various raw materials and in-process materials, and hence many valueless substances are generated which are termed as waste materials. Due to inferior quality of raw materials, Indian Steel Plants generate 1.2 tonne of solid waste by-products per one tonne of steel; compared to 0.55 tonne of that practicing in abroad [22]. The various solid wastes in the form of slags and sludges that are emerged from steel plants; such as blast furnace slag, blast furnace flue dust and sludge, Linz–Donawitz (LD) converter slag, LD sludge, LD dust, mill scale, mill sludge, etc. If these wastes are not properly utilised, it is bound to cause huge revenue loss, environmental degradation and ecological imbalance. By the application of suitable technology, the generation of waste can be minimized and used effectively elsewhere.The major wastes produced in integrated steel plants include BF slag, steel melting shop (SMS) slag accounting for nearly more than half a tonne for each tonne of steel produced in Indian steel plants. Utilization of BF slag was 95.89 pct, utilization of BOF slag was 55.94 pct and utilization of total solid waste was 85.17 pct in India during 2018-2019 [22].

The aspect of waste management at various levels from mines to smelter are working simultaneously for sustainable development. Today the waste generations are so much at various level, their disposal have become an international issue. Waste management involves management of such materials which have apparently no value. But prior to its management, proper characterization of wastes through physical, mineralogical and chemical analysis are very important, because if the composition is not exactly known,*Eco-saving* to be gained by the utilization of rejects can be lost [23]. With the scenario changing, on passage of time and with the technologies getting regularly upgraded, there is need for use of such waste materials continuously being produced in large quantum through conversion of work materials to either by-products or in-process material for recycling.

Generation of solid waste from process units mainly depends on quality of raw materials and technology adopted. The primary reason for high waste generation in Indian steel Industry is the poor quality of raw materials, i.e iron ore and coke. High ash content of coke leads to increased coke consumption in blast furnace causing increased slag generation. Further, higher ash content of coal leads to increased fly ash generation in power plant. The high alumina content of iron ore increases the coke rate in blast furnace. Technological and operational discipline can bring down hot metal’s silicon and sulphur level, which will in turn reduce the slag rate per tonne of crude steel. Other technological improvements like high blast furnace temperature, higher top pressure; use of prepared burden, injection (oxygen, coal,lime etc.) into blast furnace will reduce the coke consumption rate which will ultimately reduce the slag volume. Similarly, continuous charging technologies for electric arc furnaces can reduce the volume of dust discharge by as much as 40 pct [23]. Scrap in the pre-heater traps the dust and returns it to the furnace thereby increasing the steel yield. By adopting Electric Arc Furnace (EAF) of steel making the solid wastes generated from blast furnace process will be drastically reduced, which constituting major quantum of solid waste generation from an integrated steel plant.

Types of solid waste generates in an integrated steel plant is shown in Figure 2.1. For easy understanding, the steel plant solid wastes have been broadly classified into two categories [24]:

a. Solid waste generated from process units.
b. Solid waste generated from pollution control equipment.

Solid wastes generated from process units are generally characterized by their uniform size and composition, low moisture content and high levels of Fe, Ca, C etc., which makes thesewastes suitable for recycling within the plant or to be sold out to consuming industries.

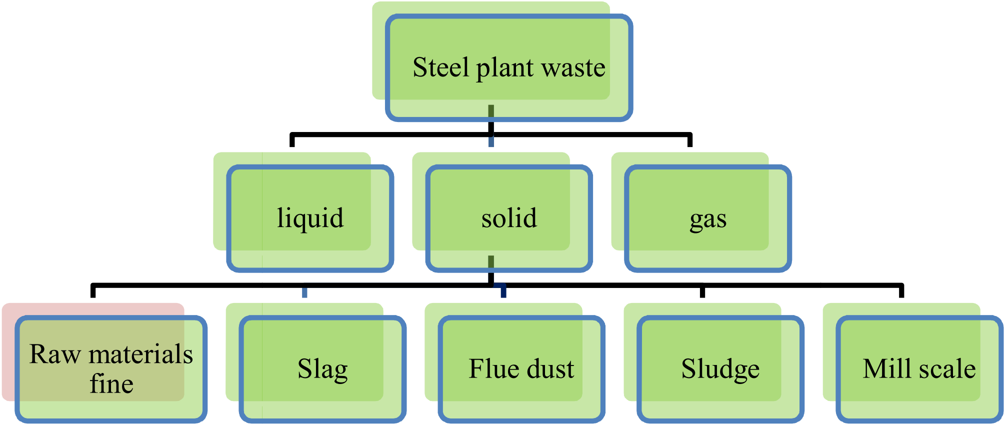


Fig.2.1: Type of waste generates in steel plant

Solid waste generation from pollution control equipment mainly depends on type of control equipment i.e. dry/wet, efficiency of the equipment and quality of raw materials. To improve the work zone air quality, highly efficient deducing systems have been installed to capture secondary emissions that were previously discharged to the environment. This environmental protection measures relating to air and water lead to the accumulation of sludge and dusts rendering their reuse cumbersome [23].

These dusts and sludge coming out of the pollution control equipment are grouped under hazardous waste. Pollution control measures can make the recycling of certain substances impossible due to their fine to ultra-fine particle size. Dusts and sludge generated from flue gas and pollution control units vary in size and composition. Quantity of various types of waste materials are generated differ from one steel plant to another depending upon: i) the adopted steel making process, and ii) installed pollution control equipment.

Details of solid wastes generated in an integrated steel plant are shown in Figure 2.2.

Table 2.1 shows the particle size, shape and chemical analysis of Steel Plant solid wastes.

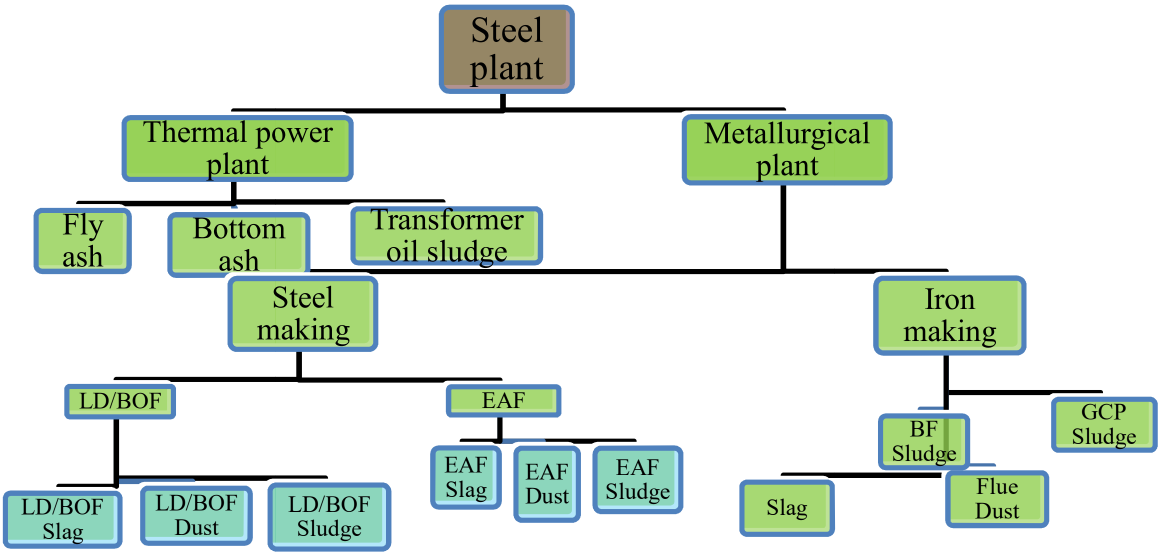


Fig.2.2: Types of solid wastes generated in an integrated steel plant

Table 2.1: Steel Plant Solid Waste Particle Size, Shape and Average Analysis [25]

Properties	Waste							
	Iron Ore	Blue Dust	Flue Dust	Mill Scale	Dry Sludge	Coke Breeze	BF Slag (Solidified)	Steel Slag (Solidified)
Shape & Size	Dust 100–500μm	Dust 100–500μm	Dust 0.1–1 mm	Chips 1–10 mm	Dust 100–500μm	Granular –3 mm	Lumps 10–500 μm	Lumps 10–500mm
Chemical Analysis, wt% :								
Fe (total)	55–60	68–69	28-34	68–69	30–34	-	-	16–20
SiO_2	6.5	1.0	10-13	0.5	10–11	8–9	30–32	10–16
Al_2O_3	2.1	0.5	~ 2	0.2	2.–3	4–5	20–22	-
CaO	-	-	7–9	0.2	2.–3	0.5–0.6	32–35	47–52
MgO	0.6		2–4	0.1	8	0.6	9	2–5
P_2O_5	-	-	-	-	-	-	-	1–3
C	-	-	31-38	-	4–5	80	-	-
Applications	Pellet for DRI/ Micro nodules for	Additive to pellet and sinter plant	Used in sinter plant	Sinter plant, Steel making and Thermit	Dumped as Waste	Sinter Plant and Power Plant	Cement, Slag wool and Road making	Fertiliser, Road ballast and Building Blocks

	sinter plant			Welding				

Apart from that, mill scales are the industrial by-product, which are produced due to hot working processes. Mill scales are produced in large amount by various processes like hot rolling, forging, heat treatment of steels etc. Most of these mill scales, which are combined with lubricant or oil, are treated as waste materials. Most of the slimes and mill scales are thrown away as waste for land filling and create pollution to the environment, which are not desirable.The huge quantities of iron ore slimes (containing 55 to 60% iron, size < 0.15 mm) are also 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[11].

2.1.1 Slag

2.1.1.1 Blast Furnace

More than 400 million tonne of iron and steel slag is produced each year [26]. Slag is a mixture of silica, calcium oxide, magnesium oxide, aluminium oxide and iron oxide. During smelting, slag forming agents i.e. fluxes (mainly limestone or dolomite, lime) are added to the blast furnace or steelmaking furnace to remove impurities from the iron ore, steel scrap, and other ferrous feeds; as well as from ash of coke. The slag protects the liquid metal from outside oxygen and maintains temperature by forming an insulating cover. As the slag is lighter than the liquid metal, they float and can be easily removed.

Air-cooled slag is hard and dense, it is especially suitable for use as construction aggregate. It is also used for ready-mixed concrete, concrete products, asphaltic concrete, road bases and surfaces, fill, clinker raw material, railroad ballast, roofing, mineral wool (which use as insulation) and soil conditioner [27].

Granulated slag forms sand-sized particles of glass, which is primarily used to make cementitious material. Concretes in corporations of granulated slag generally develop strength more slowly than concretes contain only Portland cement, which is the most common type of cement, but can have better long-term strength, release less heat during hydration, have reduced permeability, and generally exhibit better resistance to chemical attack [26].

Pelletized slag has a vesiculartexture (like volcanic rock) and is most commonlyused as a lightweight aggregate. If finely ground, it also has cementitious properties.Recyclability issues/barriers BF slag has a low intrinsic value depending on the method used to cool it and therefore most cannot be transported economically for long distances; however, this has not been an impediment to almost full consumption by various industrial customers. The sulphur content is a source of concern due to risk of release of odours and/or leaching when used for road construction [28].

2.1.1.2 Steelmaking

Different kinds of slags arise during the steelmaking processes. During the oxygen blow in LD/BOF, impurities in the metal (carbon, silicon, manganese, and phosphorus) as well as some iron are oxidized to form the largest portion of the slag, that is known as primary slag. Secondary slags are produced from the pre-treatment processing of hot metal and from secondary steelmaking operations which is known as ladle treatment of molten steel.

BOF slag contains primarily Calcium silicates combined with fused oxides of iron, aluminium, manganese, calcium, and magnesium. Components in the hot metal from the blast furnaces, such as carbon, silicon, manganese, and phosphorus, as well as some of the iron are oxidized during the oxygen blow; whereas the oxidized carbon leaves as CO (converted to CO_2 above the slag), the other elements form oxides that enter the slag together with some of the sulphur in the hot metal and in the scrap. BOF slag has a higher basicity than blast furnace slag (lime/silica ratio of 2.5 to 4.0), higher FeO content approximately 25 to 35 pct, and is far more variable in chemical composition [28].

The EAF process has changed markedly during the last few years with the more intensive use of chemical energy (using hot metal as partial charge material), high power transformers, DC in place of AC power sources, and large portions of pig iron and of pre-reduced HBI and DRI in the charge. The result has been a dramatic shortening of heat cycle times (a 45 to 50 minutes tap-to-tap is not uncommon), decreased use of electrical energy, but increased volume of slag and baghouse catch. The latest trend, in Japan, Europe, United States and India, is the charging of hot metal from mini-blast furnace or a smelter to EAF. This practice can reduced electrical power requirements to the 200 to 250 kWh/t range and shorten heat cycles to less than 45 minutes

[28a]. This cause marked changes in the nature (i.e., amounts, composition) of the process by-products, slag and dust.

In EAF steelmaking, specific grades of steel scrap are selected and charged into the furnace along with varying amounts of other iron-bearing materials and fluxes. Charging typically takes place through the furnace roof from the basket. During the steelmaking process, one to three large cylindrical carbon electrodes (depending on type of furnace, AC or DC) are lowered through openings in the roof to melt the charge.

For every tonne of steel produced in electric arc furnaces, about 56 to 90 kg furnace slag are generated. In addition, ladle treatment facilities generate about 9 kg/t slag [28a]. In total, about 3 to 4 Mt of EAF slags are generated annually. These slags are somewhat different from those generated in BOF shops in terms of composition, commercial usage options, and recyclability issues. Important differences from BOFproduced slags exist due to factors related to process needs: EAF slags have lower basicity, i.e., lime/silica ratio (to permit foaming), and higher FeO and P_2O_5 contents. There is a lack of in-house reuse opportunities, and often the shipping costs to a potential industrial customer is too great to permit the sale of these low value materials for commercial consumption.

Disposal or utilization of steelmaking furnace slags present challenges due to their low intrinsic cash value. Significant quantities are landfilled in some plants. In integrated plants, the natural in-house customers for these slags are the sinter/blast furnace operations. However, their use is restricted by required limits of phosphorus levels in the hot metal. As a result, plants with sintering facilities consume 40 pct of BOF slag internally. The practice of recycling steelmaking slag internally has declined (from 30 pct about ten years ago) as a result of increased demand for low-phosphorus steels. The rate of slag recycling is higher in Canada, Europe and Japan in part due to economics and environmental regulations [28].

In the past, the presence of large amounts of free lime (up to 7 pct) made external sale difficult [28]. The existance of free lime required hydrating by exposing the slag to the elements. Improved BOF and EAF steelmaking practices have limited the content of free lime so that current steelmaking slags have many commercial applications, with room for development of others. Presently, most slags find applications as road aggregate and in the manufacture of Portland cement. For the latter application, a portion of the MgO and FeO contained within the slag are of benefit; however, high concentrations limit its use. Some more applications include anti-skid material for icy roads and landfill daily cover.

Few steelmaking slag can be used as a starter fluxing agent in steelmaking furnaces and is used extensively outside the steel works. It is used for road construction, where it gives excellent anti-skid properties, and in the cement industry. Part islandfilled while opportunities for sale to the cement industry remain to be capitalized.

2.1.2 Flue Dust and Sludge

2.1.2.1 Blast Furnace

The flue dust and sludge fromblast furnace are generated as a result of scrubbing and cooling the flue gases generated during the ironmaking operation. These off gases produced in the blast furnace are exhausted through the top of the furnace. These gases are cleaned, cooled, and then burned in the stoves to preheat the cold air for the blast furnace, or are used as fuel in other parts of the plant. Generally, cleaning the flue gases involves the removal of large particulates by a dry dust collector (yielding blast furnace flue dust) followed by a wet gas cleaning system for fine particulate removal (yielding blast furnace sludge). They are primarily composed of oxides of iron, calcium, silicon, magnesium, aluminium, as well as carbon in the form of coke breeze.

Two new technologies have been implemented for utilization of the iron units contained in blast furnace dust and sludge: cold bonding (briquetting) of the fine particles to make them suitable for use as a raw material in ironmaking and reduction in a rotary hearth furnace (RHF) [28]. While some steel plants have been successful in recycling the briquetted blast furnace residues to the blast furnaces, degradation problems occur while the briquetted residues are heated during descent in the furnace. This causes a loss in permeability of the burden resulting in loss of production.

The limits for maximum allowable zinc levels vary from steel plant to steel plant, but the control level of zinc (maximum) charged into the blast furnace is generally about 0.5 pound/net ton of hot metal. This experience-based limit is set to prevent zinc related build-ups in the blast furnace stack (which have been linked to catastrophic instances of internal scaffolding and slips) as well as damage to refractories by penetration of zinc followed by condensation of zinc chlorides. Currently dust and sludge are used as minor iron and carbon sources for sintering operations. Some plants use dust and sludge by mixing them with other residues, briquetting and recycling back to the blast furnace. Some plants landfill the dust and sludge.

Key barriers to the recycling of the dust directly back to the blast furnace include its size distribution (95 to 99 pct minus 20 mesh). Barriers to sludge recycling include its size distribution, moisture and chemistry which adversely affects blast furnace operation and refractory life.

BOF steelmaking dust and sludge is generated as a result of the cleaning of the off gases emitted from the oxygen-steelmaking processes. The off gases are exhausted through the top of the furnace. In most shops, the gases, which contain nearly 90 pct CO, are combusted with entrained cold air, then cooled, cleaned, and released into the atmosphere through a stack. In some shops, the gases are cooled with water sprays upon leaving the furnace and vented through a flare stack. In Japan, which has much higher energy costs, some shops make use of the energy in the off gases by adding them to the plant energy grid. In either situation, the primary cleaning is normally achieved by washing the gases with water and, in a few cases, by means of a dry system (electrostatic precipitators).

The wet gas cleaning system is generally a two-stage process. In the first stage, the gases are cooled, and the coarse dust is separated. During the second stage, the fine dust fraction is washed out of the gas. After settling in a sedimentation basin or thickener, the fine slurry fraction is dewatered by means of vacuum filters or centrifuges. The coarse slurry fraction is normally treated separately in drag classifiers. Modern steel works are also equipped with secondary collection systems, which collect dry dust during vessel charging and tapping operations.

One internal recycling development is briquetting of BOF dust and sludges for recycling back to the BOF. This approach uses the BOF as a reduction vessel, reducing scrap melting and consequently steel output. Additionally, vessel slopping is often observed when using these briquetted materials, resulting in environmental problems and yield losses. Another recycling method that has been investigated extensively is the separate treatment of the low zinc-containing coarse fraction, which can be recycled directly to a sinter plant or agglomerated and recycled. Unfortunately, the coarse fraction accounts for only 10 to 30 pct of the total dust or sludge produced; in-plant recycling of the fine fraction has not typically been possible without further processing to remove the zinc. Wet classification processes and selective chemical leaching tend to be ineffective due to the fineness of the material and the form in which the zinc is present, zinc ferrite (oxide) particles[28].

BOF steelmaking dust and sludge generally contains 50 to 65 pct iron and between 0.3 and 12 pct zinc on a dry basis. Size consist is to 97 to 100 pct minus 20 mesh with a significant portion finer than 5µm. For steelmaking sludge, the moisture content is 25 to 45 pct.

Steelmaking dust and sludge have been used in the production of Portland cement and as a colouring agent for concrete. At present, less than half of the steelmaking dust and sludge generated is being re-used, very little (one plant in the U.S.) internally in sinter plants due to the deleterious effect the contained zinc would have on blast furnace operation. A few plants recover the contained iron units by incorporating the dust/sludge in cold agglomerated briquettes as a charge in the BOF but at a penalty in steel output due to the decrease in scrap melting capability. A new technology, Rotary Hearth Furnace reduction, has been introduced to recover the iron and zinc units separately for return into their respective flow sheets [28]. Barriers to the recycling of steelmaking dust and sludges directly to the blast furnace or the steelmaking furnace are size distribution, moisture, and chemistry.

Researchers have also been looking into the possibility of reusing BOF steelmaking dusts and sludges as raw materials in the electric arc furnace. These studiesare based on the idea that by recycling EAF dust into the furnace, zinc and lead can be enriched in electric arc furnace dust to a level that makes it more economically attractive to treat for recovery of these elements.

An interesting opportunity exists to utilize the Fe values in BOF dusts in the cement industry to satisfy the iron oxide requirements for Portland cement. In one case in the Chicago area, payment for the iron units nearly covers the cost of transportation, and landfilling is avoided. Zinc contents typical of BOF dusts (2 to 10 pct) are not considered a problem for this application, but as in landfilling, the zinc values are lost.

2.1.2.3 Pollution Control Units

Dusts and sludge are obtained from pollution control units. Iron bearing dust and sludge can be a source of raw materials in the steel industry. The dusts differ from iron ore in its process of formation. The former in its process of formation received high temperature impulse in reducing and oxidizing atmospheres and sludge the same in wet condition. As a result of this, their structure, composition and properties are greatly affected and differ from the initial raw materials. In most cases steel plant dust and sludge is characterized by high level of disparity in sizes. Currently, the application of the available technical know-how of iron ore treatment to reclaim dust and sludge is ineffective in some plants and a huge quantity is either dumped or stored [24].

Blast furnace flue dust is a solid waste material from the integrated steel plant. Theflue dust is a mixture of oxides expelled from the top of the blast furnace, whose majorcomponents are iron oxides and coke fines. It also contains silicon, calcium, magnesiumand other minor elemental oxides in lesser amounts. The direct recycling of flue dust is not generally possible since it contains some undesirable elements (like zinc, lead and alkalimetals etc.) that can cause functional difficulties in the blast furnace. In many cases, the particlescontain substantial amount of Zn and Pb as the volatile impurities. It is mainly due to the Pb–Zncontaining scrap that is added into the blast furnace. Furthermore, in many cases the dustcontains toxic elements (Cd, Cr and As), which make it hazardous and non-acceptable forlandfill. Therefore, proper characterization followed by a suitable beneficiation method hasto be evaluated in order to recycle within the plant[8].The performance of blast furnace is strongly affected for presence of alkali due to reducing the softening and melting temperature of iron ore and sinters. Alkaline elements accumulate in blast furnace due to cyclic reactions and hinder the normal operations, loss of permeability of the burden, cracking of refractory bricks, etc. In addition to that alkali cyanides are likely to be formed cause environmental problems which is to be taken seriously. Zinc has been regarded as a problem because it forms a circuit in the furnace resulting in extra coke consumption. The volatility of zinc and its condensation in cooler region of blast furnace cause serious problems [16].

Investigations of dust in other metallurgical processeshave shown that there are different mechanisms for dustformation[29- 31]. The so-called mechanically formed dustconsists of solid or liquid particles that are transported withthe process gas. Chemically formed dust is formed byvaporization followed by condensation from the process gasat lower temperatures. Mechanically formed dust showedcoarser diversified particle size compared to chemicallyformed dust which had a particle size of approximately 1mm[32].

The dust is generally recycled through sinter making in more advanced countries. TheInstitute of Gas Technology, USA has developed a fluidized-bed process for recoveringdirect reduced iron from blast furnace flue dust. Up to 95 pct of the iron oxides containedin the waste stream could be reduced to elemental iron. The yield of iron depends uponthe quantity of iron oxide present in the flue dust and generally ranges from 20 to 30 pct of the waste stream [33].

The fine solid particles recovered after wet cleaning of the gas emerging fromLDconvertersin the sludge form are termed as LD sludge. During this process the furnace emits veryfine iron oxide particles that are removed from the waste gases by a wet scrubbing process.This waste may contain high levels of CaO, Zn, Pb, etc. depending upon the type of limestoneand chemistry of scrap used during the process of steel making. At steel plants, the highmoisture content of the LD sludge (35–40 pct) is a major obstacle in its recycling to the sinterplant. It becomes sticky and forms agglomerates after long exposure to the atmosphere.Therefore, LD sludge must be optimally dried and made handleable before recycling.

In order to meet the strict environmental requirements, it has become necessary for steelplants to develop a process of recycling this waste material. The sludge contains appreciablequantities of iron and lime and is therefore quite suitable for recycling in the sinter plant [8].Due to very high iron and appreciable amount of CaO content, it is a good raw material for recycling to iron and steel industries. It has been observed that the Al_2O_3 contentis far lower than iron ore is an added advantage to reuse in steel plant.

In order to maximize the use ofLDsludge in sinter making, pre-pelletization ofLDsludgeis highly essential. Pilot plant trials successfully demonstrated the viability of recyclingmillion of tonne of steel plant dusts and sludge that are now typically land filled, and typicallyconverting them into useful products, i.e., hot metal for steel production, zinc-rich rawmaterial for the non-ferrous metal industry, and slag for road bed and cement production.The pilot plant trials and subsequent feasibility study showed that steel plant waste oxidescould be smelted in an environmentally sound manner for an attractive return on investment [34].

The carbothermic reduction of sludges without addition of coal under nitrogen atmosphere for conversion to metallic iron has been reported [35]. The results indicated that increasingthe weight ratio of sludge, size of solid sample, carbon content, density of solid sample orreaction temperature could increase the reduction rate. However, fordirect use of this type of sludge briquetting or pelletizing is important to agglomerate thefines.

2.2 Waste Management

A forestation, waste dump management, top-soil management, management of sub-grade minerals, mechanical beneficiation, dust suppression, monitoring of water and air quality, vibration survey, publicity and propaganda are some common environmental restoration efforts pursued by all mechanised and semi-mechanised iron ore mines. Mining and beneficiation of ores carried out on large-scale cause environmental problems. A specific problem in iron ore mining is the disposal of tailings and other deleterious silica minerals and phosphorous. To safeguard the environment and prevent ecological degradation, thrust has been laid on green belt development, solid waste management, monitoring of liquid and air effluents and other crucial environmental parameters [36].

Management of various types of solid waste in a steel plant is complex one. Though the basic approach is to explore the possibilities of recycling, enrichment and additional treatment within the production system, it is often not easy to integrate these in a well-established process flow sheet.

2.3Methods of Beneficiation

The basic principle of mineral beneficiation has not change for many years. The techniques have been improved, but are still essentially the same, using either a materials weight, density shape or magnetic susceptibility to enable separation. Further the approach to solve the problem of alkali management should be taken to recycle the material as such in sinter making to a great extent. Gas cleaning plant sludge is having about 50 pct total Fe and reported to be used as lime sludge briquette without beneficiation [37].The basic methods of beneficiation can be used for increasing metallic value of the dust and sludge. The selection of methods of beneficiation for reclamation of the waste in terms of cost for processing, no use of chemicals, eco-friendly and to be used at the site of waste storage is very critical.

Beneficiation(as applied to iron ore) defined as operations of milling (crushing and grinding); washing; filtration; sorting; sizing; gravity concentration; magnetic separation; flotation; and finally, agglomeration (pelletizing, sintering, briquetting, or nodulizing). Although the literature suggests that all these methods have been used to beneficiate iron ore, information provided by members of the American Iron Ore Association indicates that milling and magnetic separation are the most common methods used. Gravity concentration is seldom used at existing U.S. facilities. Flotation is primarily used to upgrade concentrates from magnetic separation by reducing the silica content of the concentrate[38].

Most beneficiation operations will result in the production of three materials: a concentrate; a middling or very low-grade concentrate, which is either reprocessed (in modern plants) or stockpiled; and a tailing (waste), which is discarded. Table 2.1 compares the percentage of total domestic iron ore treated by each beneficiation methods in 1990. A more detail of methods are described in later stages.

Table 2.2: Total Domestic Iron Ore Treated by Beneficiation methods[38]

S. No	**Beneficiation Method**	**Percentage of Iron Ore Treated**
1	Magnetic Separation	41.6
2	Flotation following Magnetic Separation	51.2
3	Flotation	6.3
4	Gravity Concentration	<1
5	Total	100

Before describing beneficiation methods/practices, it should be noted that the iron ore industry uses large amounts of water. The beneficiation of iron ore typically occurs in a liquid medium. In addition, many pollution abatement devices are used for treated water to control dust emissions. At a given facility, these techniques may require between 600 and 7,000 gallons of water per tonne of iron concentrate produced, depending on the specific beneficiation methods used. Much of the water is recycled from plant operations. Industry has indicated that an average of 95 pct of the water appropriated by iron ore facilities is recirculated and reused according to the Iron Mining Association of Minnesota.

2.3.1 Milling

Milling operations are designed to produce uniform size particles by crushing, grinding, and wet or dry classification. The cost of installation and operation costs of milling equipment are high. For this reason, economics plays a large part in determining the use of comminution equipment and the degree of crushing and grinding performed to prepare ore for further beneficiation. Other factors measured in determining the degree of milling include the value concentration of the ore, its mineralogy, hardness, and moisture content. Milling procedures are vary widely both between mills and within individual mills depending on these variables.

Milling is a multistage process and may use dry or wet ore. Typically, primary crushing and screening take place at the original mines site. Primary crushing is proficient by using gyratory and cone crushers. Primary crushing yields chunks of ore ranging in size from 15 to 25 cm. Oversize material is passed through additional crushers and classifiers to achieve the desired particle size. The ore is then crushed and sized at a secondary milling facility [38].

Secondary milling (comminution) further reduces particle size and prepares the ore for beneficiation processes that require finely ground ore particles. The product resulting from this additional crushing is usually less than 25 mm (actually 13 to 19 mm). Secondary crushing, if necessary and economical, is performed by using standard cone crushers followed by short head cone crushers. Also Gyratory crushers may be used.

Subsequent fine grinding further reduces the ore particles to the consistency of fine powder (325 mesh, 0.44 microns). The choice of grinding circuit is based on the density and hardness of the ore to be ground. Although most operations employ rod and/or mill grinding, a few facilities use autogenous or semi-autogenous grinding systems. Autogenous grinding uses coarse pieces of the ore itself as the grinding media in the mill. Semi-autogenous operations use metallic balls and/or rods to complement the grinding action of the ore pieces. Autogenous grinding is best appropriate to weakly cemented ores containing some hard material. The benefit of autogenous grinding is that it is less labour and capital intensive. Semi-autogenous grinding eliminates the need for a secondary crushing. Rod and ball wear, the principal maintenance cost of traditional grinders, is also eliminated with this method [38].

Between each grinding unit, hydro-cyclones are used to classify coarse and fine particles. Coarse particles are send back to the mill for further size reduction. Milled ore in the slurry form is pumped to the next beneficiation stage. If the ore being milled is to be send for flotation activities, chemical reagents to be used during the process may be added to the slurry at this time. To obtain a uniform product, many operations blend ores of several different grades, compositions, and sizes. The mixing of ore materials is typically attained through selective mining and hauling of ore.

2.3.2 Magnetic Separation

Magnetic separation may be carried out in either a dry or wet environment, though wet systems are more common. Magnetic separation operations can be categorized as low or high intensity. Low intensity separators use magnetic fields in the range from 1,000 and 3,000 gauss (gauss is the unit of induced magnetic field). Low intensity techniques are generally used on magnetite ore as an inexpensive and effective separation method. This method is used to capture only highly magnetic material, such as magnetite. High intensity separators employ fields as strong as 20,000 gauss. This method is used to separate weakly magnetic iron minerals, such as hematite, from nonmagnetic or less magnetic gangue material.

Low intensity wet processes typically involve conveyors and rotary drum separators using permanent magnets and are primarily used on ore particles 10 mm in diameter or less. In this process, ore is fed by conveyor into the separator where magnetite particles are attracted and held to sides of the drum until they are carried out of the magnetic field and transferred to an specific concentrate receiver. The nonmagnetic or week magnetic gangue material remains and is sent to a tailings pond. Low intensity dry separation is sometimes used in the trial stage of the separation process [38]. High intensity wet separators produce high magnetic field gradients by using a matrix of shaped iron pieces that act as collection sites for paramagnetic particles. Balls, rods, grooved plates, expanded metal, and fibres may be the shapes. A detailed description can be seen elsewhere [38].

The primary wastes from this type of operation (i.e. magnetic separation) are tailings made up of gangue in the form of coarse and fine-grained particles, and wastewater slurry in the case of wet separation. Particulate wastes from dry separation can also be slurried. After separation of solids in a thickener or settling pond, solids are sent to a tailings impoundment and the liquid component are recycled to the mill or discharged if water quality criteria are as per norms.

2.3.3Flotation

Flotation is a method where particles of one mineral or group of minerals are made to adhere preferentially to air bubbles in the presence of a suitable chemical reagent. This is accomplished by using chemical reagents that preferentially react with the desired mineral. Several factors are important to the accomplishment of flotation activities. These include uniformity of particle size, selection of reagents compatible with the mineral, and water conditions that will not interfere with the association of the reagents to the mineral or air bubbles.

Flotation is primarily used to upgrade concentrates recieved from magnetic separation. Over 50 pct of all domestic iron ore is upgraded using this technique. Flotation, when used alone as a beneficiation method, accounts for approximately 6 pct of all ore treated. Chemical reagents of following groups may be used in flotation. A description of the function of each group as follows:[38]

- Collectors/Amines→They cause adherence between solid particles and air bubbles in a flotation cell.
- Frothers→They are used to stabilize air bubbles by reducing surface tension, thus allowing collection of valuable material by skimming from the top of the cell.
- Antifoams→They react with particle surfaces in the flotation cell to keep materials from remaining in the froth. Instead, materials fall to the bottom as tailings.

Several factors are important, when conditioning ore for flotation with chemical reagents. These include thorough mixing and dispersal of reagents through the pulp, repeated contact between the reagents and all of the relevant ore particles, and time for the development of contacts with the reagents and ore particles to produce the desired reactions [39].

Reagents may be added in a number of forms including solid, immiscible liquid, emulsion, and solution in water. The concentration of reagents must be closely controlled during conditioning; adding more reagent than is required may retard the reaction and reduce efficiency [39].

There are various beneficiation methods available which can be used for iron enrichment. But the criteria for selection of proper beneficiation route for all type of dust and sludge is very critical because of the following reasons:

- All wastes are having unique physical characteristics depending upon the process involved,
- All wastes are having different chemical composition, and
- All wastes are having different surface characteristics.

2.4 Utilization of Steel Plant Wastes

Management of waste in an integral component of management of environment, as much as an important part of business opportunities. Metallurgical industries are energy intensive and mostly environment subversive. Life cycle assessment of an typical product from any metallurgical industries reveals significant environmental impacts. Though SAILplants in some way or other, did practice waste management (mainly through recycling). Other integrated plants in India also have similar arisings.What is a needed is common strategy to be adopted by the main steel producers to find viable outlet for the bulk categories of the solid wastes [40].The issue of *waste* in the steel industry is relevant because it is becoming a key variable for companies throughout the world. Indeed, governments and public opinions are demanding *cleaner* production to protect the environment, while the rising cost of raw materials isan incentive for companies to try and close material loops. Thus, the steel industry offers opportunities to re-engage social sciences with the materiality of production and waste.

Materials have a history of becoming wastes, but also of moving upwards ordownwards along a gradient of perceived complexity. For example, it is verysignificant that in an International Iron and Steel Institute(IISI) study in1987, the onlywastes were BF and BOF slags, which are not now seen as particularly difficult todeal with, and actually have many commercial applications that make them valuablematerials rather than wastes. In a later study in 1994 by IISI, the list of materials wasmuch longer, and much less straightforward to deal with, for example, with thepresence of toxic substances. However, this study still contained assertions that areunacceptable today, such as EAF dust being simply spread on fields as a zinc supplement[41]. This shows how fast the social, political and economic definitions ofwaste evolve, although they do not always necessarily intersect. The IISI was conducting further study in 2009, that took an even broaderperspective as it strived to analyse the production of steel in a life-cycle perspective,i.e. it took into account all the environmental outcomes of the production andapplications of the metal from *cradle to grave.*

Das et. al. [16] investigated on the effective utilization of blast furnace flue dust samples collected from the two integrated steel plants at Rourkela and Jamshedpur. The samples essentially contained unburnt coke and iron rich grains as the value-added products. Flotation technique was employed to recover the carbon particles present in the sample. They observed product containing around 80 pct carbon with more than 90 pct recovery from both the flue dust samples using diesel oil and MIBC as the collector and frother respectively. Iron rich grains (magnetite, hematite, wustite and iron metals) were recovered by low intensity magnetic separation technique. Magnetic separation of flotation tailings gave an iron concentrate of 61-64 pct Fe with 50-56 pct over all recovery. They also studied to remove the alkali content of the flue dust sample by scrubbing and washing, so that the material could be recycled for sinter making.

Deyet. al. [42] studied the washing and processing of iron ore slimes less than 0.15mm which were generated and discarded into the tailing pond. A typical iron ore slime sample containing 59.22 pct Fe, 4.76 pct SiO_2, and 4.57 pct Al_2O_3 was taken. The desliming operation was carried out by using Mozley hydro-cyclone. The process variables used to attain the optimum condition of desliming include the spigot opening, the feed pressure, and the diameter of the vortex finder maintaining the pulp density at 10 pct solid. The deslimed sample was treated by different techniques including an enhanced gravity separator to achieve iron concentrate with 65 pct Fe. The yield of the magnetic concentrate is about 46.8 pct with 65 pct Fe. To improve the yield, the overflow from hydro-cyclone and the rejects from magnetic separation were deslimed and processed to recover the iron values. The yield of final concentrate was 74 pct with 64.8 pct Fe, 1.76 pct SiO_2, and 1.8 pct Al_2O_3.

Duet. al. [43] investigated magnetic separation technology and studied recovery of iron values from iron ore washing plant slime tailing pond of Goa. The process comprising of particle size of -0.1 to +0.01mm fraction, further subjected to vertical pulsating high intensity high gradient magnetic separation at 8000 gauss background intensity with/ without a cleaner step, yielded a concentrate assaying >62 pct Fe at 25-30 pct yield both from clay and siliceous slime tailing with significant amount of -0.01mm content. The process enhanced the overall plant productivity by 4-6 pct and reduced the land requirement of tailing pond by ~25 pct. The implementation of desliming, vertical pulsating high gradient wet high intensity magnetic separator of Longi magnet, China reduced the operating power cost by 50 pct and capital cost significantly without sacrificing the metallurgy and productivity.

Johnet. al. [44]carried out investigation to utilize iron ore slime from the slime ponds of Joda and Noamundi region, India. They worked on the application of flotation to obtain the hematite and goethite concentrate with low gangue content from iron ore slimes. With flotation of silicates by using cationic collector and starch as a depressant for iron ore, starch adsorption occurred on quartz particles covered by iron oxides and on minerals which contain, Fe (II), Fe (III), and Al ions in their structure. An entire flotation of mineral complex was possible if the collectors used were mineral surface specific and hence using reverse and direct flotation accordingly.

Lal et. al.[45]investigated a low-grade magnetite ore of mine reject from Jharkhand area for beneficiation to assess the possibility of upgrading the iron content to the maximum possible extent, so that it may find the better place in industrial use. By beneficiation of low grade magnetite ore could enhance the Fe(T) upto 67.42 pct Fe(T) with a recovery of 64.8 pct. Specific gravity obtained over 4.7 with high magnetic susceptibility which requirement of the industrial specification for heavy media separation and possesses the quality of media reclamation at low intensity magnetic separation.

Vijayakumar et. al.[46]worked on screw classifier overflow slimes from an iron ore washing plant for the recovery of iron values by means of reverse cationic flotation as an alternate to direct anionic flotation. Chemically different cationic collectors were used in reverse flotation and for further optimization of other flotation process parameters. In the optimization, the main variables investigated were percent solids, collector and depressant dosage. An increase in the iron content of the concentrates was obtained with subsequentreduction in SiO_2 and Al_2O_3 levels.

Anupam et. al. [47] carried out experiments to beneficiate banded hematite quartzite samples collected from two different states of the country viz. Karnataka and Orissa by different techniques such as jigging, magnetic separation and using hydro-cyclones after their characterisation.They also proposed that beneficiated samples can be used to mix with high-grade haematitic iron ores. This would be helpful in conservation and utilisation of rich grade ores. Characterisation studies indicated that both the ores required fine grinding to a size of 200mesh to achieve effective liberation. They achieved an upgradation of iron content from a feed value of 42.8 pctiron to a maximum of 56.8 pctiron by magnetic separation with a yield of around 41 pct. Similarly, Bellary-Hospet sector ore indicated that it was 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.

Matiolo et. al. [48]suggested ore desliming followed by column flotation at laboratory scale. The complex low grade compact itabirite ore sample from Carajás province, Brazil with 35.9 pct Fe, 45.1 pct SiO_2 and 0.57 pct of Al_2O_3 was treated previously by magnetic separation and grounded to 97 pct< 20 μm.The cationic reverse flotation without desliming was tested the selectivity of the process was very low and did not meet the concentrate metallurgical goals of the pellet feed product. However, when desliming was applied prior to flotation, a concentrate product with chemical characteristics of the pellet feed was obtained. They could achieve iron metallurgical recovery of 72 pct with Fe grade in the concentrate of 66.5 pct Fe and 2.1 pct SiO_2 using starch as depressant for the iron oxides minerals at 1200–1500 g/t and an amine as the quartz collector at 100 g/t concentration at constantpH(10.5). It was proposed that the desliming stage was key in the separation of the iron bearing particles and has a high potential for the flotation process of this type of ores.

Zheng et. al. [49]worked on oolites which were bonding of hematite and other small gangue. They utilized coarse grinding to avoid sliming and to remove most of the apatite and quartz of coarse fraction. Both gravity separation and magnetic separation was giving low separation efficiency because of fine-grained dissemination and the traditional flotation flowsheet was not effective to separate this ore for the reason of severe slime. Coarse grinding and flotation tests had been used to remove the coarse gangue as possible, a stage grinding and stage flotation processing flowsheet is proposed finally after intensive sieving analysis, the concentrate Fe grade enriched to 57.52 pct from 45.43 pct and Fe recovery 77.34 pct .

Bhartia et. al. [50] proposed some beneficiation routes considering the nature of the iron ore deposits in the country. They suggested to involve crushing and screening, wet washing systems including scrubbing, jigging, slime beneficiation etc. They also suggested that depending on the grade of ore available the limits of washing can be decided and equipment for lump ore beneficiation such as jigs could be incorporated into the washing circuit. Scrubbing of ore either before washing or selectively scrubbing the lumps could be necessary. Very low-grade ore and jig rejects would be required to be totally ground and beneficiated for the production of pellet feed in order to utilize the iron ore resources entirely.

Indian hematite ores are typically rich in iron but contain unusually high alumina (as high as 7 pct) and in some cases, problem of high phosphorous content is also noted. The current practice of iron ore washing in India results in three products, namely coarse ore lumps, directly charged to blast furnace, the classifier fines, (3-5 pct alumina) which with or without beneficiation are fed to sintering plants and the slimes (6-10 pct alumina) which are currently discarded as waste[51]. Iron ores are being beneficiated all around the world, including at Kudremukh in India. Several techniques such as spirals, floatex density separators, jigs, multi-gravity separator, low and high intensity magnetic separator, conventional as well as column flotation, selective dispersion flocculation are all part of current industrial practice. Recent advances include Batac jigs, packed flotation column, packed column jigs and centrifugal concentrators like Falcon Concentrator Kelsey jigs Knelson Concentrator for the beneficiation of iron ore slimes. Processing of haematitic ores in India at present, however, does not involve any beneficiation except for whatever rejection of silica (and to some extent alumina) occurs during washing and classification of crushed ores. Several commendable efforts have been made by Tata Steel to come up with an economically viable beneficiation flow sheet for processing classifier fines. Two beneficiation plants had been set up to process sinter fines for value addition.

Seifelnassr et. al. [52]investigated the effectiveness of gravity and magnetic concentration techniques for the beneficiation of a Sudanese iron ore, which was a low-grade type of ore with high silica content, more than 45 pct SiO_2, and an average iron content of about 35 pct Fe. Since there were appreciable differences in specific gravity and magnetic susceptibility between the desired iron minerals and the gangue minerals, they suggested that gravity separation and/or magnetic separation to be useful for concentration. These two techniques were adopted for the beneficiation of the low-grade iron ore. As a result of the fine dissemination of the iron minerals and the most abundant gangue mineral, quartz, the optimum degree of grinding was around 150 μm. The rougher tests of both the gravity separation and magnetic separation produced concentrates of about 44 pct Fe. Each of these two concentrates was cleaned in a second stage of processing using high intensity magnetic separator. Final iron concentrates, assaying about 64 pct Fe at a recovery of about 70 pct, were reported.

Demircia, Turana and Yücel [17] investigated the direct reduction of the mill scale. Iron oxide layers (as mill scale) formed on the surface of continuouscasting and hot rolling steel products. They conducted experiments with the charge of the pelletized mill scale and solid reductant mixtures into the rotary kiln. They investigated the effect of temperature (1050 to 1150 °C), reductant type (anthracite coal and metallurgical coke) and the amount of reductant (150 pct and 200 pct stoichiometrically carbon) at different duration times during the reaction.The highest metallization degree was obtained as 97.4 pct at 1150 °C with anthracite coal (200 pct of thestoichiometriccarbon).

Zhang andXin[18]summarized and analysed the quantities of wastes were generated from the stainlesssteel processes. According to the characteristics, the stainless steel wastes could be classified into two categories: slags and dusts. They usually contained considerable quantities of valuablemetals and materials. A review of several methods for treating the various stainless steel wastes was done. It was veryessential not only for recycling the valuable metals and mineral resources but also for protecting theenvironment.

Nikitinet. al. [53] used small-scale wastes from some subdivisions of the plant for investigation. Wastes similarin granulometric and chemical composition to thematerials used in blast-furnace smelting were selected. To improve hearth operation and the gas permeabilityof the lower part of the blast furnace, chunk wastes were supplied in amount amounts corresponding to 0.3–2.5 pct ofthe total ironore consumption in the batch. Before,charging, the chemical composition of the materials were determined, and the <5 mm and >100 mm fractions are removed.

2.5Pelletization

Pellets are agglomerated from very finely (minus 200 mesh size) iron ore concentrates to which a small quantity of binder have been added. The process of pelletization consists of formation of green balls (5-20 mm size) by rolling of moist iron ore fines with binder in disc/drum pelletizer.

Binders play a very important role in the pelletization process. Binder is that material which serves as a bridge between the particles and thus increases the green or dry strength of the bonded particles. Binders accomplish two very important functionsin iron ore palletization [54]:

- 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.

Before selecting the binder, binder must satisfy the following requirements:

1. Mixing behavior: It should be spread out uniformly over the surface of particles.
2. Mechanical properties: A good binder should maintain good mechanical properties of pellets, including green, dry and fired pellets, e.g. deformation under load, resistance to fracture by impact and by compression, resistance to abrasion.
3. Chemical composition: A good binder should bring no environmentally and metallurgically harmful elements such as S, P, As etc. into product pellets. It should not increase impurities such as silica, alumina etc.
4. Metallurgical behavior: A good binder should maintain pellet's excellent metallurgical properties such as reducibility etc.
5. Processing behavior: Adding, mixing, dispersion of binder, green ball preparation, pellet drying, etc should not be complicated or essentially change conventional pellet production circuit.
6. Toxic factor: It should be harmless to the operating personals.

7. Cost factor: Price of binder should be acceptable for iron ore pellets production. It should be cheap and easily available in the market.

2.5.1 Composite Pellets

Iron ore-coal composite pellet technology has been under development for last many years without its significant contribution in ironmaking. The principle technological problem is that to produce such composite pellet at comparatively lower cost. Of late, the development of cold bonded composite pellets at lower cost has brightened the prospects. Traditional pellet making is costlier process due to need of hardening in furnace at a temperature of 1200 – 1300°C. Cold bonded pellets do not require hardening treatment and hence constitute a potential alternative route for utilization of ore fines. Cold bonded iron ore-coal composite pellets also utilize cheap and readily available reductant such as coal fines, coke breeze, and char fines.

Composite pellets, containing iron oxide and carbon fines, should be prepared only by cold bonding technology.Cold bonding technology is preferred because [54]:

1. The pellets are hardened in cold bonding process due to physico-chemical change of the binder at low temperature, the free iron ore grains remaining intact. This benefits the reducibility of the pellets.
2. It is an energy saving process for pellets production and hence is becoming more popular.
3. If composite pellets are fired or hardened, simultaneously its reduction also occurs due to presence of carbon. Hence instead of getting fired oxide pellets some metal form due to reduction within the composite pellet and hardening of pellet does not take place; as well as carbon also loss from composite pellet.

The term composite pellet is applied here to mean pellet containing mixture of iron oxide bearing fines and carbonaceous material(coal/coke/char) which has been imparting sufficient green strength for subsequent handling by cold bonding techniques[13].

Interest in iron ore coal composite technology had been there for many years without any significant successful application in iron making. The technical problem was to produce the composite pellet at the low cost. Advances in the cold bonding technology have brightened the prospects. It has been well known for a long time that if there will be carbon particle with the iron oxide, the reduction will be faster. Use of such composite pellet will promote the utilization of dust, sludge and coal/ coke fines.Therefore, technological relevance iron ore coal composite pellets have been recognised. As composite pellets have been used partially or fully as burden material in cupola [55,56], rotary kiln [57-59] and even blast furnace [60]. Studies [13, 55, 58-71] have been conducted on preparation and reduction kinetics of the composite pellets as well. Composite pellets can be used as feed material in smelting reduction [72, 73]. Rate of production is expected to be much higher with composite pellets due to high degree of pre-reduction in smelting reactor.

2.5.2 Preparation of Composite Pellets

Pelletization is more popular than any other processes for agglomeration of fines [74]. Traditional pellet making is costlier process due to the need of hardening in furnace at near fusion temperature of 1200 to 1300^{0}C (1473 to 1573 K), by using oil. Therefore, production cost of these indurated pellets is increasing day by day due to the increasing price of oil. Alternative energy saving process is the cold bonding technology for pellet making which is becoming more and more popular now-a-day all over the world. The pellets are hardened in cold bonding process due to physico-chemical changes of the binder at low temperature; the free ore grains remain intact, which benefits the reducibility of pellets as well. The binder additions normally are 10 to 12 pct by weight of the iron ore constituent. To produce sufficiently strong bonding structure, the binder and the concentrate must have an extensive specific surface area.

The ore-coal composite pellets can be prepared by cold-bonding technology. Cold bonding of pellets involves mixing of iron ore fines and coal fines; of suitable size with suitable binder and water. The pellets are hardened in cold bonding process due to physico-chemical changes of the binder in ambient conditions or at slightly elevated temperature. Binder is that material which serves as a bridge between the particles and thus increases the green or dry strength of the bonded particles [74].

Cold bonded pelletizing technique has some specific advantages in contrast to the traditional pelletizing technique of iron ores[75]:

i. The cold bonding process is quite flexible and allows usage of metallurgical wastes like blue dust, coal/coke fines, steel plant dust, mill scale, sludge etc.,
ii. The cold bonding processes use coarser material for pelletizing and consequently the grinding costs and power requirements are considerably reduced,

iii. The cold bonding eliminates indurations in an oxidizing atmosphere,

iv. The usage of furnace oil is either eliminated or reduced considerably,

v. Chemical composition of the raw material does not change (unlike in conventional pelletization) and magnetite will not be oxidized to hematite,

vi. Cold bonded pellets can be self-fluxing,

vii. High temperature properties of cold bonded pellets have been found superior to indurated pellets in certain cases, and

viii. Capital and operating costs of cold bonded pellets are estimated to be only two third of indurated pellets.

2.5.3Binders for Composite Pellets

2.5.3.1 Inorganic Binders

There are different types of binders available for composite pellet making. Cement, bentonite,sponge iron powder, lime, hydrated lime, and silica have been employed as inorganic binders.

George and Boardman [60] tried to convert the waste materials produced at steel plant into a reusable product using Swedish Grangcold pelletization process. Composite pellets were prepared from 88.9 pct waste materials (e.g., basic oxygen furnace dust, mill scale, blast furnace dust and blast furnace sludge in 2.2 : 1.3 : 1 : 1 ratio) and 11.1 pct coke breeze along with 10 pct portland cement. The waste material pellets were much superior to sinter and exhibited higher reducibility and produced fewer fines when subjected to reduction test and tumbling test. The tests on the Swedish blast furnaces had indicated increased productivity when sinter was replaced by cold bonded pellets. Other advantages were the cost of disposal of steel mill waste materials and a cleaner environment.

Xi-Lun [59] employed sponge iron fines as binder for ore-coke composite pellets. It was found that the compressive strength of 100 to 200 N per pellet (8 to 10 mm diameter) was suitable for direct charging to rotary kiln. Ganguly and Patalah [61] also used sponge iron fines as binder to enhance the crushing strength of cold bonded iron ore-coal composite pellets for subsequent used in rotary kiln direct reduction or for smelting. They prepared pellets using 6, 8, 10 and 15 pct sponge iron fines to the charge mix (75 pct blue dust and 10 pct coal). The curing time changed from 1 to 4 days. Five percent NaCl solution (pH value 4) was sprayed as a moisture addition to the pelletizer. They found that the crushing strength of the pellet significantly improved as 50, 100, 400 and 900 N per pellet against the used of 6, 8, 10 and 15 pct sponge iron fines as binder respectively. On reduction, the strength of the pellets declined as expected but it was still within tolerable limit (500-1000 N per pellet) for use in kiln.

Goksel et. al. [55] developed at Michigan Technological University (MTU), USA the MTU-PelleTech cold bonding pelletization process. In this process, lime and silica flour were added to the mixture of iron bearing materials and coal/coke dust. The pellets were strengthened in an autoclave by steam curing for 1 to 2 hrs at 5.1 to 20.4 bar pressure. Compressive strengths of composite pellets were reported to vary from 952 to 2037 N per pellet (13 to 25.4 mm diameter). These pellets were found sufficiently strong for handling, storage, transportation and processing for hot metal in cupola.

Dutta and Ghosh [13] prepared composite pellets using inorganic binders with and without autoclaving. Without autoclaving, the dry strength of composite pellets was 202 N per pellet by using 8 pct cement and 2 pct lime (both -100 mesh size). By using -325 mesh size cement and lime, the strength of pellets was increased to 357 N per pellet. They also used lime and silica mix, $Ca(OH)_2$ and silica mix, and combined form of binders to prepare composite pellets using an autoclave. The pellets were hardened by high pressure steam in an autoclave (13 to 27 bar at temperature of 460 to 500 K) for 2,5 to 9.5 hrs. The strengths of 240 and 1030 N per pellet were obtained for ore-coal composite and ore-char composite respectively.

Takahashi [69] prepared pellets having 87 pct iron ore, 5 pct char coal (contained 98.4 pct fixed carbon) and 8 pct portland cement. After curing for 10 days at room temperature and drying at 773 K in nitrogen atmosphere, the strength of pellet was found 1000-1300 N per pellet (12 to 14 mm diameter).

2.5.3.2 Organic Binders

In contrast to inorganic binders, organic binders have the inherent advantage of being eliminated during firing and hence, do not contaminate the product. Starch based binders; dextrin, molasses, dextrose and oil-slush are some of the organic binders.

Gransden et. al.[56] developed a smelting process to treat the iron ore deposits of the Peace River district of Alberta, Canada. The ore, without beneficiated, was agglomerated with char using an asphalt binder and smelted in a cupola. The briquette composition was 73 pct iron ore, 11 pct char, 6 pct lime and 10 pct asphalt. The char reduced the iron oxides to iron and burning foundry coke provided process heat. The basicity of the slag varied between 0.5-0.7. Slag fluidity was not a problem during operation, except when the temperature was low (1588 K). The most important variable in trials was the ratio of briquette to coke in the charge (i.e. 3:1, 4:1, and 5:1). The sulphur content of the hot metal was found to decrease as the silicon content (and temperature in the cupola) increased. Around 75 pct of the iron in the agglomerate was recovered in the pig iron.

Ansari et. al. [70] studied the effect of the density of the bitumen-bonded magnetite pellets on crushing strength. The aim was to achieve high crushing strength in pellets without the pre-requirement of firing at high temperature. Another advantage of mixing bitumen with iron oxide is the fact that it supplements the reduction of iron oxide in hydrogen by about 17 pct at 1373 K. In contrast to many organic binders, bitumen is cheap and widely available either in its natural form or as residues from oil refining.

Dutta and Ghosh [13] also prepared composite pellets using organic binders like dextrin and thermo setting resin (TSR). The average compressive strengths of dry pellets obtained were 329 N per pellet for 4 pct TSR and 339 N per pellet for 3 pct TSR and 1 pct dextrin.

Shivaramakrishna et. al. [57] studied the possibilities of different organic binders for making ore-coal composite pellets. They investigated the relative importance of various process parameters like ore/coal ratio, choice of binders etc. Raw materials of -100 mesh size were taken and 5, 10 and 15 pct coal were added. Molasses, oil-slush and starch based binder were used as organic binders and bentonite, sodium silicate and lime as inorganic binders. Except starch based binder, no other binders yield sufficient strength. They observed that a starch based binder, used in even small quantities, resulted in more strengths than in all the other cases. Starch based binder was used 0.5 to 5 pct by weight. Maximum strength was reported as 250 N per pellet (8 to 12 mm diameter) with 5 pctstarchbased binder. They found that with a reduction time of 15 minutes at 1323 K for 5 pct coal in pellet, the degree of metallization was more than 84 pct. It was also observed that increasing coal content in composite pellets increased the degree of metallization and carbon percentage in reduced pellets. They found the use of ore-coal composite pellets advantageous over lump ores because of very low reduction time and superior product quality.

Agrawal et. al. [58] reported that the strength of ore-coal composite pellets increased up to 300 N per pellet by using dextrin as binder. Small amount of phenol- formaldehyde was employed successfully to improve the decrepitating characteristics of the pellets.

2.5.3.3 Combined Binders

Dutta and Ghosh [13] also tried different combination of organic and inorganic binders such as dextrin, TSR, sugar, dextrose, molasses, bentonite, lime and $Ca(OH)_2$. The strength of pellets was 317 N per pellet for combination of TSR, dextrin and bentonite. The strength of pellets was 369 and 235 N per pellet using $Ca(OH)_2$ plus sugar and lime plus sugar respectively. The research work had been carried out at M S University of Baroda, Vadodara since 1990 on the strengthening of composite pellets. Lime (CaO), $Ca(OH)_2$ or combination of lime and $Ca(OH)_2$ with molasses, dextrose or sodium-polyacrylate(SPA) were employed as binders. The pellets were strengthened by CO_2 treatment. The strength of composite pellets obtained was satisfactory (more than 500 N per pellet).

Raval and Dutta [62] studied the effect of several binders such as lime, cement and sodium-polyacrylate (SPA) on the compressive strength of cold bonded ore-coal composite pellets. Cement gave good strength but poor reducibility and lime gave poor strength but good reducibility. Both these binders produced large amount of slag. SPA, on the other hand, resulted in reasonable strength and reducibility with minimum amount of slag. The strength of pellets (372 N per pellet) and briquettes (976 N per pellet) bonded with 6 pct SPA were found quite above the acceptable values to be a burden material for cupola and direct reduction furnaces.

Sah and Dutta [63]prepared iron ore – coal composite pellets by cold-bonding technique. Various binders such as lime, $Ca(OH)_2$, slaked lime, dextrose, molasses and SPA (sodium polyacrylate) alone or in combination in different proportions were employed for making composite briquettes. Slaked lime and dextrose in combination produced the highest strength (357 N per briquette) amongst the various binders employed for producing composite briquettes and therefore they selected for producing the composite pellets for the smelting reduction.The compressive strength values of 362 and 330 N per pellet were obtained for Bhilai coal (57.0% fixed carbon, 27.0% volatile matter, 1.33% moisture, and 14.67% ash) and Jharia coal (48.35%

fixed carbon, 15.65% volatile matter, 0.35% moisture, and 35.65% ash) composite pellets (Fe_{tot}/C_{fix} ratio at 4.0) respectively.

Dutta and Chokshi[71] observed that the average strength of briquette increased with increasing of molasses for fixed amount of fly ash and lime after CO_2 treatment. They observed that CO_2 treatment was helpful to increase the strength of the briquette, due to the formation of carbonate bond. The strength was 404 N per briquette was obtained with the binder combination of fly ash, slaked lime and molasses with CO_2 treatment. The maximum strength was 722 N per briquette was obtained with the binder of polyvinyl alcohol (PVA).

2.6 Reduction of Composite Pellets

2.6.1 Theory of Reduction

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 shortening of diffusion distances of reductant and availability of large number of reaction sites [66].During reduction of iron ore-coal composite pellets, evolution of volatile matter takes place due to pyrolysis of coal. The volatile matter comprises mainly of gaseous fuel, carbondioxide and steam. The gaseous fuel consists of large number of hydrocarbons and small amounts of $H_2$and CO. Above 973 K, the hydrocarbons are 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 reaction with these reducing gases. It is well established that reduction of iron oxide by carbonoccurs as combination of the gas-solid reactions as follows:

$$3Fe_2O_3(s) + H_2/CO\ (g) = 2Fe_3O_4(s) + H_2O/CO_2(g) \qquad \text{... (2.1)}$$

$$Fe_3O_4(s) + H_2/CO\ (g) = 3\ FeO\ (s) + H_2O/CO_2\ (g) \qquad \text{... (2.2)}$$

$$FeO\ (s) + H_2/CO\ (g) = Fe\ (s) + H_2O/CO_2\ (g) \qquad \text{... (2.3)}$$

Volatile matters in the coal evolved during heating and decomposition of hydrocarbons, thatoccurs at high temperature, according to the reaction:

$$\text{Higher hydrocarbons (g)} \rightarrow \text{Lower hydrocarbons (g)} + H_2\ (g) + C\ (s) \qquad \text{... (2.4)}$$

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

$C (s) + CO_2 (g) = 2CO (g)$ ... (2.5)

$C (s) + H_2O (g) = CO (g) + H_2 (g)$ ...(2.6)

CO and H_2 gases thus generated again act as reductants for iron oxides in the ore. It is to be noted that if only carbon is employed as 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. Hence, the pyrolysis of coal, kinetics of carbothermic reduction and gasification reactionare briefly reviewed.

2.6.2 Pyrolysis of coal

Pyrolysis of coal refers to the heating of coal, in absence of air (or inert atmosphere), to understand its thermochemical 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 the coal. The tars and gases are thevolatile matter and represent 4 to 45 pct of the weight of the coal, depending on its type[76]. Pyrolysis is accompanied by a change in the structure of the coal, leading to a marked variation in its thermo-physical 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 weak chemical bonds begin to break at 573 to 673 K, producing molecular fragments, in a process termed depolymerization. These fragments can lead to the formation of tars, paraffins, olefins etc, if they are small enough to be vaporized 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 carbon compounds. Cracking, which occurs beyond 823 to 873 K, causes the liberation of CO and H_2. During pyrolysis, the density of coal usually decreases due to swelling and the evolution of volatiles.

During pyrolysis of coal, a 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 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 [77]. The proportions of various products change with changes in pyrolysis temperature.

The mechanisms liable to influence the pyrolysis process in a coal grain are as follows [76]:

1. Heat transfer from the outside towards the surface of the grain,
2. Conduction of heat within the grain,
3. Kinetics and the heat effect of the devolatilization reactions,
4. Transport of the volatile matter from the inside to the outside of the grain,
5. Heat exchanges between the volatile matter and the solid during its internal transport,
6. Secondary cracking reactions of the volatile species during their internal transport,
7. Swelling and cracking of the grain, and
8. Increase in the pressure within the grain due to the formation of gases.

Cypres and Soudan-Moinet [78] studied the influence of iron oxide additions on coal pyrolysis by thermo-gravimetry 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 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 573 to 873 K, the weight loss of the coal-magnetite mixture was due to the coal devolatilization only. Magnetite was not reduced below 873K. Between 673 and 823 K, $Fe_2O_3$was reduced to Fe_3O_4, with loss of H_2O and a little CO_2. They also observed that 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 of CO, H_2O and CH_4 gases.

Cypres and Soudan-Moinet [79] 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 thermo-gravimetry and 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 (Figure 2.1). 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 1223K, 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 [64].

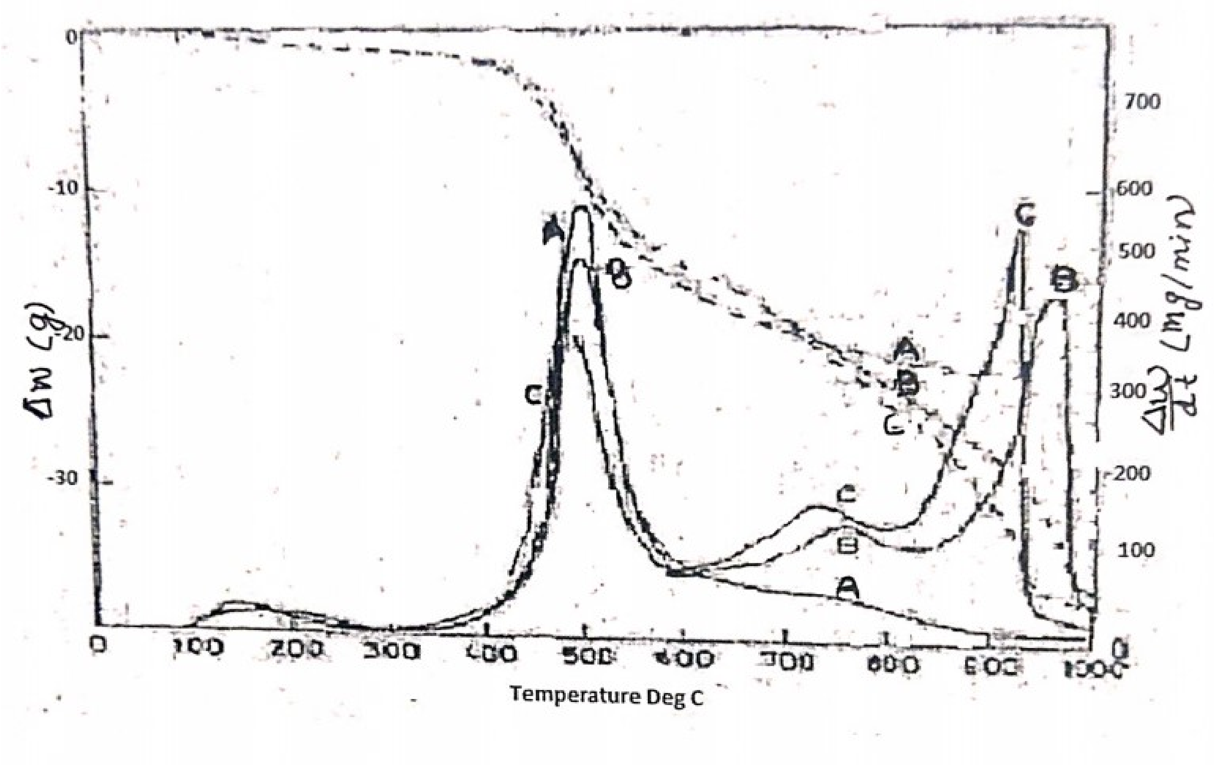


Fig. 2.3 TGA (-—) and DTG (—), of carbonization of coal and coal/iron oxide mixtures, A - coal; B - Coal + Fe_3O_4(30 wt pct); C - Coal + Fe_2O_3(30 wt pct).

Thermo-gravimetric 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).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 at between 673 and 773K but hidden in thermo-gravimetric measurements by primary volatilization of coal. X-ray diffraction confirmed that between 673 and 773 K, the hematite 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 reduced to iron [79].

2.6.3 Kinetics of Carbothermic Reduction

Kinetically, reduction of oxides in composite pellet is significantly by carbon in a mixture of iron oxide and carbon. If char or coke is used as reductant in composite pellets then this is wholly carbothermic reduction. On the other hand, if coal is used then reduction will be partly by gases evolved (due to pyrolysis of coal) especially H_2 and CO [64, 76-78]. 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 (2.1) to (2.3) and (2.5), i.e., through gaseous intermediates.

Kinetics of carbothermic reaction has been studied in past mostly by taking powder mixture of graphite, coke or charcoal with iron oxides or ores. Carbothermic reduction of iron oxides has generally been found to be controlled by gasification reaction. Such conclusion is based on two observations: firstly, higher activation energy (about 400kJ/mol) and secondly, the catalytic effect of freshly reduced metallic iron on the rate of carbon gasification and also reduction of iron oxides by carbon [80]. Both interfacial chemical reactions and 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 iii nature [81].

Seaton et. al. [82] investigated the reduction kinetics of hematite/magnetite and coal/char composite pellets in the temperature range of 1073 to 1473 K. They observed that at lower temperature (1273 K) hematite pellets reduced faster than the magnetite ones. The rate of reaction increased with increasing temperature, and the reduction of hematite appeared to be enhanced by increasing the lime content. They found that the reduction steps $Fe_2O_3 \rightarrow Fe_3O_4$ and

Fe_3O_4→FeO took place rapidly during early stages of reduction. The surface and centre temperatures of composite pellets were also measured. It was found that 15, 17 and 20 minutes were needed for the pellets to reach thermal equilibrium at 1273, 1373 and 1473 K respectively.

Ansari et. al. [70] also studied the reduction kinetics of bitumen-bonded magnetite pellets. At low temperatures (673-773 K), the overall reduction rate was found to be chemical reaction controlled. The reduction of pellets, at high temperature (973-1373 K), appears to be initially chemical reaction controlled and later on solid-state diffusion controlled.

The reduction behaviour of the MTU-PelleTech cold bonded pellets [83], prepared from iron ore fines with 15 to 20 pct carbonaceous fines of 15 to 20 mm diameter, showed that the largest portion of the carbon present in composite pellets was consumed in 15 minutes at a temperature exceeding 1366 K and the pellets were completely metallized in 5 to 15 minutes at higher temperature. Above 1700 K, heating of the pellets resulted in complete melting of the pellets with separation of the slag.

Sharma [84] studied the effect of non-coking coal quality on the reduction kinetics and physical properties of composite pre-reduced pellets under isothermal and non-isothermal conditions in the temperature range 1173 to 1473 K in oxidizing atmosphere. The effect of Fe_2O_3/C ratio, heating time, and heating rate on the reduction behaviour were studied. It was observed that the reduction rate of iron oxide increased with increasing temperature and increasing carbon content of the pellet. The highest reduction rate and highest crushing strength were obtained when non-coking coal (highest fi fixed carbon and volatile matters) was used as reducing agent. The reduction of iron oxide with non-coking coal in composite pellets followed first order reaction kinetics and the value of activation energy was obtained 68.52 kJ/mol.

Dutta and Ghosh [64] carried out the non-isothermal reduction of composite pellets by thermo-gravimetry and demonstrated that reduction in a composite pellet occurs not only by carbon, but also significantly by H_2 gas. Degree of reduction, volume change, and compressive strength of the pellets upon reduction were measured subsequently. Degree of reduction varied from 46 to 99 pct. The gases, liberated during heating to high temperature, reacted with carbon and hydrocarbon to generate additional quantities of H_2 and CO gases, which were responsible for a significant fraction of reduction. Also, the reduction behaviour of ore-coal composites was compared with those of ore-char composites under identical condition.

Huang and Lu [65] investigated the reduction kinetics of ore-coal mixture at 1473 K. Thermocouples were installed in various locations of the mixtures, and temperature-time data were obtained. Considerable temperature gradient was observed in the sample especially in the beginning. Gases, which were generated in chemical reactions, played an important role in convective heat and mass transfer. For same degree of reduction, less carbon was consumed in interior regions due to indirect reduction by gaseous reductants from outer regions. Similarly, degree of reduction was found to be lower at interior than at surface. Reduction did not follow topochemical pattern in individual grains. Metallic iron, formed at low temperature regions, coexisted with magnetite and wustite. In this complex non-isothermal reaction system, based on temperature profiles and mathematical analysis, it was concluded that heat transfer was rate-limiting step.

Agrawal et. al. [58] studied the reduction of cold bonded ore-coal composite pellets for making sponge iron. Both laboratory and plant trials showed fast reduction of the pellets as compared to lump iron ore. They summarized that for 90 pet metallization, the residence time in the kiln was observed only 60 minutes as compared to 200 to 240 minutes for conventional iron ore. The requirement of coal decreased by 20 pct, kiln productivity increased almost two-fold and carbon content of sponge iron was 0.90 to 1.70 pct as compared to 0.20 pct in the case of lump iron ore.

Nascimento et. al. [85] analysed all the steps of the reduction of self-reducing cold bonded composite pellets bearing hematite and charcoal in the range 1223 to 1423 K. They observed trans-granular cracks during $Fe_2O_3 \rightarrow Fe_3O_4$ reduction stage. This might be explained by the formation of lamellae of magnetite. The microstructures of the step $Fe_3O_4 \rightarrow FeO$ were similar to the first step of reduction and the formation of superficial microcracks in the FeO phase was observed. Wustite was found porous presumably due to the gas evolution. The typical morphology between 1223 to 1423 K in the step $FeO \rightarrow Fe$ was that of iron whiskers. At 1423 K the morphology was a mixed one, i.e., a dense morphology (cluster of cone shaped whiskers) adjacent to a porous morphology of iron. The porous morphology of the metallic phase observed at 1423 K meant that it evolved from the wustite instead of from a dense layer of iron.

Goswami [86] studied the kinetics of iron oxide reduction by heating a central column of blue dust surrounded by a concentric layer of non-coking coal fines in the temperature range of 1173-1323 K. The loose column of blue dust got reduced, consolidated and sintered to produce directly reduced iron rod. The kinetics of reduction showed good agreement with Ginstling-Brounshtein model which showed that the diffusion of Fe^{2+} might be considered the rate controlling step. The value of 68 kJ/mol was obtained as apparent activation energy for the reduction.

Dutta [66] reported the kinetics and mechanism of iron ore-coal composite pellets that were heated from room temperature to 1273 K both at low heating rate (0.175 K per second) and high heating rate (0.35 K per second). He observed that while coal was the reductant, reduction by H_2 gas was also significant. The degree of reduction varied from 46 to 99 pct depending upon pellets composition and heating rate. For low heating rate, three stages of reactions (devolatilization of coal, reduction of iron oxide by volatile gases and H_2 gas, and reduction by CO gas) were observed whereas for high heating rate, two stages of reactions (simultaneous devolatilization of coal and reduction of iron oxide by volatile gases, and reduction by CO gas) were observed. The activation energy values, obtained for final stage reduction, varied from 183.1 to 268.5 kJ/mol, which meant that the overall reduction was controlled by gasification reaction.

Wang et. al. [67] carried out the reduction of iron concentrate with coal fines by thermogravimetry at heating rates of 20 K/min and 30 K/min. They observed that for reduction of 16-18 mm diameter magnetite-coal composite pellets at temperatures less than 1173 K, the effects of volatiles were significant but at higher temperatures (more than 1323 K) the effects were negligible. They also studied the reduction kinetics of iron ore-coal pellets during fast heating at temperatures of 1323 to1573 K. The effect of heat transfer on the reduction process and the effect of volatiles on reduction were studied. The activation energy obtained under the isothermal temperature condition (92.03 to 114.57 kJ/mol) was larger than that for the non-isothermal temperature condition (68.95 to 82.61 kJ/mol).

Takahashi et. al. [87] investigated the possibility of carbon-contained briquette of mill scale to be used as new raw materials for hot metal production. Three kinds of briquettes were prepared by the mixture of reduced iron, mill scale and different amount of coke breeze (7-20 pct) with a binder composed of syrup, slaked lime and starch. Reaction rates for the reduction of iron oxide, the gasification of coke, and the thermal decomposition of binder in oxidized iron-scrap briquettes containing pulverized coke were measured by the measurements of both changes of weight and gas volume under the conditions of elevating and fixed temperatures in the nitrogen atmosphere.

Kasai et. al. [88] studied the reduction of iron oxide-coal composite pellets i.e. single tablet reduction and packed bed reduction of the pellets, in the temperature range of 1473 to 1673 K, to examine the process feasibility. They observed that the metallization and degree of reduction of reduced pellets were increased with increase in mixing ratio of coal up to 22 pct. Beyond this value, increase of bed temperature facilitated reoxidation of the pellets. Increase in amount of CaO coating to the composite pellets led to increased metallization and degree of reduction.

El-Geassy et. al. [89] investigated the reduction behaviour of iron ore-fuel oil composite pellets in both isothermal and non-isothermal conditions in the temperature range 1023 to 1273 K. They obtained the activation energies of 18.81 - 28.42 kJ/mol for non-isothermal reduction of composite pellets in nitrogen atmosphere, and 22.86 to 47.11 and 32.35 to 40.67 kJ/mol at initial and final stages for isothermal reduction of composite pellets in hydrogen atmosphere respectively. They observed that initially the reduction was controlled by gaseous diffusion and at later stage by gaseous diffusion as well as chemical reaction. The non-isothermal reduction of composite pellets in N_2 atmosphere was not completed and stopped at different extents depending on temperature and fuel oil content. At the early stages, an incubation period was detected, and the reduction was controlled by the gaseous diffusion mechanism.

Sharma and Upadhyay [90] reported the reduction behaviour of double layer composite pellet under isothermal condition in the temperature range of 1273 K to 1473 K. They concluded that with increase in temperature (1273 K to 1473 K), C/Fe_2O_3 ratio (3 to5), and reduction time (20 to 40 min), the degree of reduction of iron ore were increased. They found that the effect of reduction temperature on degree of reduction was highest followed by reduction time and C/Fe_2O_3 ratio. Highest degree of reduction was obtained when non-coking coal was used as reducing agent followed by coke, and char.

Santos and Mourao [91] studied the reaction between iron oxides and carbon (thermogravimetric analysis) at temperatures higher than 1473 K employing solid carbon or carbon dissolved in liquid iron as reductant. The carbon was in the form of graphite, coke fines and charcoal. When composite pellets were heated at temperatures higher than 1473 K, it was observed that as the temperature increased the effect of the type of carbonaceous material on the reaction rate decreased, indicating that the reaction controlling mechanism is changing from carbon gasification to heat transfer. The activation energies calculated varied from 46 to 120 kJ/mol; well below the ones obtained at lower temperature ranges. They found that charcoal was the most effective reducing agent followed by graphite and coke fines.

Fruehan and co-workers [68, 92-94] investigated the reduction kinetics of iron ore-coal pellets or mixtures by volatiles present in coal in a rotary hearth furnace in the temperature range of 673- 1273 K. The kinetics of the reduction by H_2gas was found to be a complex mechanism, initially, nucleation and growth controlling the rate. They observed a catalytic effect due to the existing iron nuclei followed by a mixed control of chemical kinetics and pore diffusion. Up to 1173 K, reduction by H_2 was considerably faster than by carbon in the pellet/mixture or by CO [92]. Compared to hydrogen, the reduction by carbon was negligible at 1173 K and below. About 2 pct reduction was achieved at 1173 K and 19 pct reduction was achieved at 1273 K after 1000 seconds. Beyond 3000 seconds, reduction of as high as 56 pct was achieved. However, significant carbon oxidation of the iron oxide-graphite pellets by H_2O generated from the reduction of $Fe_2O_3$by H_2 was observed. The reduction was higher near the interface of coal/Fe_2O_3 due to the higher reducing potential. The volatiles caused about 20 to 50 pet reduction of iron oxide [93]. The reduction of pellets at the top layer by volatiles from the bottom layers of the three-layer pellet geometry in a rotary hearth furnace (RHF) was observed to be about 15 pct. The partially reduced layer showed mixed phases of iron oxides dispersed in the matrix of reduced layer, indicating the importance of the limited mixed control. From the morphological observations of partially reduced pellets and the computed rates of bulk mass transfer, volatile reduction appears to be controlled by a mixed-control mechanism of bulk gas mass transfer and the limited-mixed-control reduction kinetics [94]. They [68] proposed a process of ironmaking consisting of the combination of a rotary hearth furnace and a bath smelter employing wood charcoal as reductant and energy source. A combined reaction model considering the steps of carbon oxidation and reduction of the iron oxides was developed allowing the measurement of rate constants of carbon oxidation and wustite reduction. The analysis showed that wustite reduction can have a significant effect on the overall rate of reduction in composites at high temperatures.

Aota et. al. [12] studied the reduction of cold bonded iron ore-coal composite pellets (cylindrical in shape). The average strength of the pellets with alumina-cement binder was observed 500 N/pellet. The degree of metallization under argon atmosphere was 94 pct and good quality solid DRI was produced. The reducing action was observed to happen at the solid/solid interface between the carbon (coal) and the iron ore as opposed to the gas/solid reduction with lump ore or indurated pellets in the SL/RN rotary kiln process. They summarized that by increasing the temperature and heating rate; metallization can be achieved within an hour. Based on their [95] laboratory scale metallization results of cold bonded composite pellets, proposed a conceptual design of pilot scale rotary kiln process for producing 10,000 tpy DRI. The important feature of the process was the preheating of pellets in a preheater by the top gas from the kiln. The pellet preheater outlet temperature was set at 723 K to prevent coal devolatilization. Complete use of both the sensible and chemical heats in the process itself makes the process more energy efficient than that of Inmetco and Fastmet processes. In the SL/RN process, where there is no iron ore preheating step, about 70 pct of the kiln is used only for heating the feed. They concluded that in newly designed DRI process, the heating zone in the kiln can be reduced from 178 to 127 cm length and thereby the cost efficiency could be dramatically increased.

Sah and Dutta [96] investigated the effect of coal quality on the reduction kinetics of iron ore–coal composite pellets under non-isothermal condition in inert atmosphere. They also investigated the effect of Fe_{tot}/C_{fix} ratio in pellets, volatile matter in coal, and temperature on the reduction kinetics of iron ore–coal composite pellets using simultaneous thermogravimetric and differential thermal analyser (TG–DTA).

During non-isothermal reduction of composite pellets, they observed as follows:

(i) Reduction rate of iron oxide increases with increasing temperature,

(ii) Reduction rate increases with increase in porosity of pellets and

(iii) The computed values of activation energy (E) are lower during the initial stage of reduction (0.86–8.82 kJ/mol) than those in the later stages of reduction (12.37–38.32 kJ/mol).

(iv) These above values indicate that the initial stage reduction was controlled by gaseous diffusion mechanism and at final stage, mixed control reaction mechanism (i.e., both gaseous-diffusion and chemical reaction) was the rate controlling step.

2.7 Advantages and Disadvantages of composite pellets

The advantages of using cold bonded composite pellets as feed material are as follows [13]:

1. Very fast reduction due to intimate contact between reductant and oxide particles,
2. Because of their uniform size and convenient form pellets can be continuously charged into the furnace leading to higher productivity,
3. Reduction in energy consumption because cold bonded composite pellets do not require induration,
4. Utilization of fines, which are cheap and are being generated in large quantities awaiting suitable disposal and utilization, and pollution control,
5. Consistent product quality as the chemical composition of composite pellets (input material) does not change, and
6. Promising prospect for ironmaking at small scale with higher production rate.

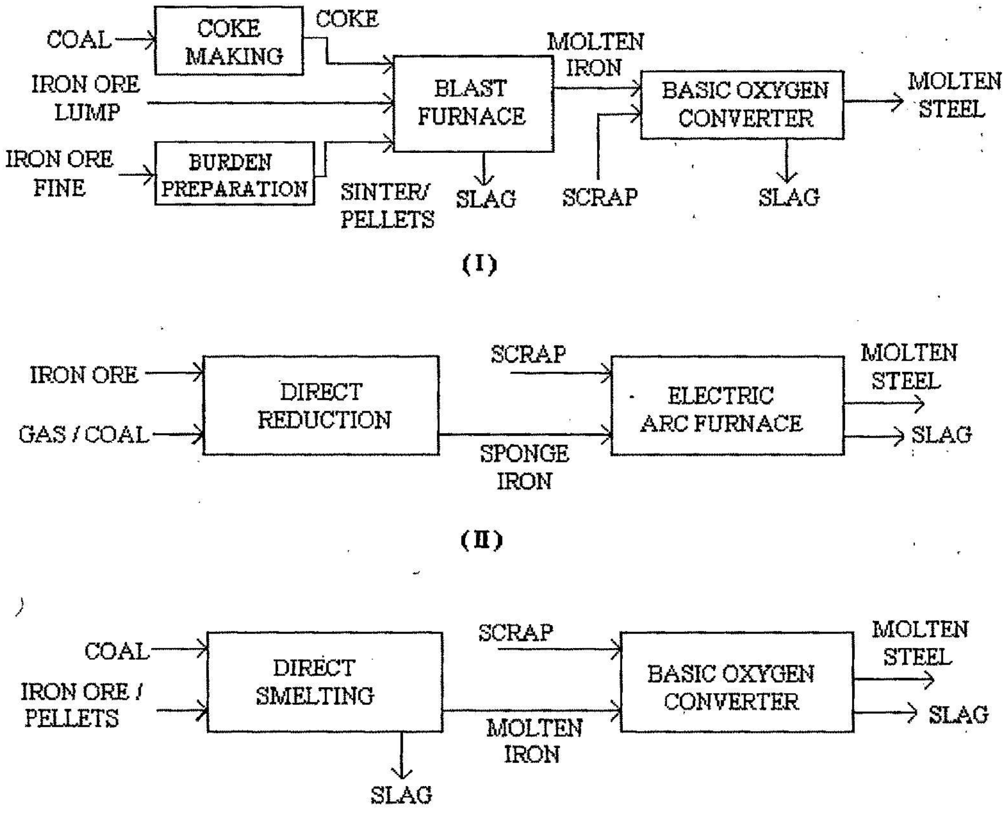
Thedisadvantages of using cold bonded composite pellets as feed material are as follows

1. Cost of binders for composite pellets are more than fired pellets.

2.8 Smelting Reduction Processes

The first step in the production process of steel isreduction of iron ore into iron . It is also the most energy intensive step. The iron ore is reduced to impure iron at a high temperature. The impure iron is subsequently converted into crude steel, cast into semi-finished products and further rolled into finished products. There are two major conventional routes for producing finished steel. Both routes play a role in the development of smelting reduction (SR) technology. The *first route* is an integrated steel plant where iron ore is reduced in a blast furnace (BF) and subsequently refined to steel [15]. A block diagram illustrating various process routes to steelmaking is shown in Figure 2.2.

For the past hundred years or so, blast furnaces have played a major role in producing hot metal/pig iron because of their high efficiency, mass production, and high degree of gas utilization. Such a long and sustainable track record arises out of continuous development in design, intensification of process technology, state-of-the-art instrumentation and control system including artificial intelligence system [97]. A new lease on life has been given to the BF by the use of oxygen instead of air, and coal injection to enable a high level of substitution of coke by coal. Continuous efforts have been made over the years to improve the overall process efficiency and as a result the modem blast furnace today is considered an extremely efficient metallurgical reactor. Recently, a new version of BF operations has been announced; the balanced oxygen blast furnace (BOBF). The essence of this process is to control the ratio of O_2 to N_2 in the blast. This allows the injection of a large amount of coal (300 kg/thm), which results in a decrease in coke rate [98].



(I)

(II)

(III)

Figure : 2.4 Block diagram of various steelmaking process routes

The *second route* is known as a mini steel plant. In most mini steel plants, recycled / purchased steel scrap and / or direct reduced iron (DRI) is melted in electric arc furnaces and further processed into final products. The mini steel plant route is considerably less energy-intensive than the traditional integrated steel plants. In mid-1960s, direct reduction (DR) technology was projected as the best possible alternative to the dominant BF technology route.

The rapid growth of electric arc furnace steelmaking in last two decades (1980s and 1990s) had created growing demand for steel scrap. Significant improvement in steel plant's yield from 82 to 94 pct due to continuous casting technology had decreased the amount of in-plant generated scrap. The need for an alternate ironmaking technology also arises out of the demand to conserve the depleting reserves of good quality coking coal, to make use of non-coking coal reserves dispersed across India and to take advantage out of large price differences between imported metallurgical coal and non-coking coal. The scenario forced innovators to look for alternative coal-based iron production routes. Coal-based direct reduction processes were developed.

In order to overcome the above problem, scientist and technologists had been working for quite some time specially in the second half of last century to develop suitable process of ironmaking, called smelting reduction (SR) process, using non-coking coals and iron ore fines [99]. Smelting reduction technology was conceived in late 1930s. The history of the progress of SR processes goes back to 1950s. The laboratory scale fundamental studies on the smelting reduction of iron ore were started first by Dancy in 1951. However, serious efforts started from 1980 onwards. In late 1950s and earlyl960s, steel manufacturers were interested in developing a technology that could convert iron ore into crude steel in just one step [100]. In late seventies and early eighties, concerted efforts were made in many parts of the world to develop a process of making liquid iron like blast furnace using non-coking coal [98]. In recent years, about twenty smelting reduction processes have been under development throughout the world. The basic principle of a SR process is to melt the pre-reduced iron ore/sinter/pellets with non-coking coal and oxygen or hot blast in a reactor. The aim of all the SR processes is to consume the least amount of coal and oxygen to make the process fuel-efficient [99].

2.8.1 Prospects of Iron Ore-Coal Composite Pellets in Smelting Reduction

Metallurgical coking coal is rarer material and India has limited reserves (19,082 Mt i.e.only 12.8 pct of the total reserves as on 1.4.2018) [6]. Coke making in coke oven is a major source of environmental pollution. On the other hand, Indian has vast reserves of non-coking coal(129,112 Mt i.e. 86.8 pct of the total reserves) and most widely available. Non-coking coal is the cheapest reducing agent for iron oxide.

A lot of iron ore fines and coal fines are generated during mining. India has hundreds of million tonnes of accumulated blue dust (e.g. Tata Steel's Noamundi mines itself has 48 Mt of blue dust) [101]. Recycling and 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. In the development of composite pellet technology, the principal technological problem was to produce such composite pellets at comparatively lower cost. Of late, the development of cold bonded composite pellets at low cost has brightened the prospects.

Traditional pellet making is a costlier process due to need of hardening in furnace at a temp of 1523 to 1623 K. Cold bonded pellets do not required hardening and hence constitutes a potential alternative route for utilization of ore and coal/char/coke breeze fines. The composite pellets are hardened in cold bonding processes due to physicochemical changes of the binder at low temperature [13].

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, 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 [72]. The intimate mixing enhances gaseous diffusion rate significantly.

Sah and Dutta [73] studied reduction smelting of iron ore-coal composite pellets in laboratory induction furnace. *They observed that (i) the time required for complete dissolution in liquid metal bath was very fast (83-90 seconds), (ii) the fraction of reduction for 40 seconds of immersion varied from 0.68-0.87 for Jharia coal pellets and 0.73-0.92 for Bhilai coal pellets, and (iii) the fraction of reduction increased with decreasing Fe/C ratio and increasing immersion period. X-ray diffraction (XRD) of reduced pellets revealed that the reduction occurred topochemically.*

Iron ore-coal composite pellets had been tested in cupola as burden material and results are reported to be encouraging. They could be reduced completely and melted within normal retention, time in the cupola. The test results of production size cupola (5 to 40tph) with a charge of 5 to 100 pct composite pellets were available [102]. Most of the trials were carried out with a charge consisting of 70 pct composite pellets and 30 pct scrap.

2.8.2 Advantages of Composite Pellets as Feed Material [103]

- Shortage of pig iron/scrap can be minimized by substitute with composite pellets,
- Price of the composite pellets is expected to be more stable than that of pig iron or scrap, which depends on demand and supply position of the market;
- Instead of large size cupola coke (100 x 150 mm) the cheaper small size blast furnace coke (50 x 75 mm) can be used,
- Composite pellets are uniform in size as compared to any other iron-bearing charges used, hence continuous charging is possible;
- By adjusting the carbon and basicity of the composite pellets can control sulphur content of the melt,
- Efficient reduction behavior of composite pellets leads to a drastic reduction in the retention time in rotary kiln, thereby improving productivity many folds; and
- Improved product quality of rotary kiln due to increased carbon content (0.5 to 1pct) in the sponge iron with good metallization.

2.8.3 Basic Principle of Smelting Reduction

The basic principle of a SR process is to melt the pre-reduced iron ore/pellets with non-coking coal and oxygen or hot blast in a reactor. SR technology consists of a pre-reduction unit and a smelting unit. In pre-reduction unit, ore/pellets/fines are partially reduced and pre-heated using the gas generated in the smelting unit. The partially reduced ore is injected or fed into the smelting vessel containing iron-carbon melt and slag [104].

The overall reaction is:

$$(FeO) + C\ (s)\ \text{or}\ [C] \rightarrow [Fe] + \{CO\} \qquad (2.7)$$

The above reaction takes place in two stages:

1st stage; slag-gas reaction:

$$(FeO) + \{CO\} \rightarrow [Fe] + \{CO_2\} \qquad (2.8)$$

2nd stage; carbon-gasification reaction:

$$C\ (s)\ \text{or}\ [C] + \{CO_2\} \rightarrow 2\{CO\} \qquad . \qquad (2.5)$$

Here, the parentheses denote the liquid slag phase, the square brackets denote the liquid metal phase and curly brackets denote the gas phase.

The following four possible rate-limiting steps may be visualized for this reaction between FeO in molten slag and solid carbon [105]:

i. Mass transfer of FeO from slag phase to slag-gas interface,
ii. Chemical reaction at slag-gas interface,
iii. Gas diffusion in the gas layer separating slag and solid carbon, and
iv. CO_2 - carbon reaction (chemical reaction at carbon-gas or metal-gas interface).

2.8.4 Advantages and Limitations of Smelting Reduction

2.8.4.1 Advantages

Smelting reduction processes have many advantages with respect to raw materials, energy cost, investment cost, economy of scale and environmental compatibility. The SR processes are expected to have the following advantages [106]:

1. Lower capital cost due to lower economic scale of operation,
2. Lower operating cost primarily owing to the use of non-coking coal,
3. Higher smelting intensity with higher productivity (due to faster reaction kinetics, increased transport rate due to convection, and an increase in the convection ratedue to enlargement of specific phase contact areas in dispersed phases),
4. Direct utilization of iron ore fines and coal fines,
5. No requirement of expensive coking coal,
6. Possible elimination of sinter / pellet and coke-oven plants,
7. Decrease in manpower requirement and reduced operational cost,
8. Environmental friendliness (due to lower emissions),
9. Maintain the same level of hot metal quality as obtained in blast furnace,
10. Better control over process parameters,
11. Flexibility in selection of thermo-chemical configuration,
12. Faster reduction,
13. Recycling of existing stock-piles, in-plant dusts, sludge and other reverts wherever and to the extent possible, and
14. Better energy economy, i.e., electricity generation from the off-gases. Some, smelting reduction processes yield rich off-gases which can be used for the generation of electricity.

2.8.4.2 Limitations

The SR processes are expected to have the following limitations [106]:

1. Consumption of large amount of oxygen, the generation of which requires high amount of power consumption (0.6 kWh / Nm^3 of oxygen),

2. The process generates large amount of high calorific value export gas and the economic viability of the process depends on its efficient utilization,

3. The maximum module size of a SR unit may be limited to 1 Mtpa and may not be the best alternative if large iron making capacities are to be generated,

4. Pre-reduction of ore fines is mandatory, and

5. Needs highly efficient post combustion necessary to meet the energy requirement of the smelting processes.