CHAPTER - 2

REVIEW OF LITERATURE

This chapter deals with the literature review pertaining to composite pellets and smelting reduction processes / technologies. It discusses about the preparation, reduction kinetics, advantages, and uses of composite pellets in smelting reduction processes. A comprehensive review of various promising smelting reduction processes, their relevance and current status, foaming slag characteristics, and kinetics of smelting reduction of composite pellets in liquid metal bath is done.

2.1 Review on Composite Pellets

The term composite pellet is being employed here to mean pellet containing mixture of fines of iron bearing oxide and carbonaceous material (coal/coke/char) which has been imparted sufficient green strength for subsequent handling by coal bonding techniques [8]. The pellet should have sufficient strength to withstand high temperatures and stresses during reduction in a furnace.

Interest in iron ore-coal composite pellet technology had been there for many years without any significant successful application in iron making. The principal technological problem was to produce such composite pellets at low cost. Advances in coal bonding technology have brightened the prospects. It has been well known for a long time that reduction of iron oxide is faster, if the pellet contains mixture of oxide fines and carbon fines. Use of such composite pellets will also lead to utilization of blue dust/iron ore fines and coal/coke fines [5]. Therefore, technological relevance of iron ore-coal/coke composite pellets has been recognized. As composite pellets have been used partially or fully as burden material in cupola, rotary kiln and even blast furnace, some studies [8, 12-23] have been conducted on preparation and reduction characteristics of composite pellets as well. Composite pellets can be used as feed material in smelting reduction. Rate of production is expected to be much higher with composite pellets due to high degree of pre-reduction in smelting reactor.

2.1.1 Preparation of composite pellets

Pelletization is far more popular than any other processes for agglomeration of fines [24]. Traditional pellet making is costlier process due to the need of hardening in furnace at near fusion temperature of 1473 to 1573 K, using mostly oil-fired furnace. Therefore, production cost of these indurate 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 [25].

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 a suitable binder having hydraulic setting properties and pelletizing the blend. 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. Binders are widely used in agglomeration operation such as briquetting and pelletization to assure that the agglomerate possesses desired properties with regard to subsequent handling, transportation and processing. These properties depend on the requirements of a particular operation and installation [26]. In certain instances, the binders may perform a chemical function as well as a physical one.

2.1.1.1 Criteria for binders and cold bonding of pelletization

Binders must satisfy the following requirements [26]:

i) 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.

ii) Chemical composition: A good binder should bring no environmentally and metallurgically harmful elements such as P, S, As etc into product pellets. It should not increase impurities such as silica.

iii) Metallurgical performance: A good binder should maintain pellet's excellent metallurgical properties such as reducibility, swelling and pressure drop during reduction.

iv) Processing behaviour: Adding, mixing, dispersion of binder, green ball preparation, pellet drying etc should not be complicated or essentially change conventional pellet production circuit.

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

Advantages of cold bonding pelletization process

Cold bonding pelletization process offers the following advantages over the conventional pelletization process [25]:

i) the cold bonding process is quit 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 fully 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.

A composite pellet contains iron oxide and carbon fines. Iron ore-coal/coke composite pellets can be prepared only by cold bonding technology. When the composite pellets, which contain iron oxide and carbon fines, are introduced into a furnace for heat hardening, firstly carbon will burn-off before the oxide particles get a chance to develop strength through sintering due to oxidizing atmosphere around. Moreover, hydrocarbons will be liberated. All these result into loss of reductant. Secondly, evolution of gases would cause disintegration of pellets. Thermal stresses due to heating would be aggravating this tendency. Therefore, to increase green strength of composite pellets, binders are required to be added to bind the particles at room temperature or at somewhat elevated temperature (maximum 500 K or so). General requirement for good quality agglomerates includes sufficient strength for handling, transportation and outside storage as well as complete reduction in furnaces without degradation or excessive swelling [26].

2.1.1.2 Using inorganic binders

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

George and Boardman [12] made an attempt 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.

Hatarasen and Dian [13] prepared composite pellets with 2 pct bentonite as a binder. Three types of oxides were used viz. mill scale, Indian iron ore, and tail concentrates. Pellets were made with 15 pct coke dust. Xi-Lun [14] employed sponge iron fines as binder for ore-coke composite pellets. He 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.

Goksel et al [15] at Michigan Technological University (MTU), USA developed 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 to hot metal in cupola.

Ganguly and Patalah [16] employed sponge iron fines as binder to enhance the crushing strength of cold bonded iron ore-coal composite pellets for subsequent use 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 pct 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 use 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.

Takahashi [17] prepared pellets having 87 pct iron ore, 5 pct char coal (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).

Dutta and Ghosh [5] 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.

Wang et al [18] made an attempt to find out the optimum condition for the commercial production of green pellets. They found the raw material size of -200 mesh, moisture content of 8.7 to 9.1 pct and 1.5 to 2.5 pct bentonite as optimum for commercial production of green pellets. The decrease in strength of green pellets with finer grinding was due to the more spherical shape of the feed material after regrinding.

2.1.1.3 Using 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 [19] developed a smelting process to treat the iron ore deposits of the Peace River district of Alberta, Canada. The unbeneficiated ore 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 [20] 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 prerequirement 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 [5] 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 [21] 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 pct starch based 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 [22] 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 decrepitation characteristics of the pellets.

2.1.1.4 Using combined binders

Dutta [8] 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 has 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 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 [23] 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.

2.1.2 Reduction of composite pellets

2.1.2.1 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 [9].

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 gas fuel, carbon dioxide and steam. The gas fuel consists of large amount of hydrocarbons and small amounts of H_2 and CO. Above 973 K, the hydrocarbons are quickly cracked into hydrogen and carbon. Hence, pyrolysis of coal generates reducing gases such as hydrogen and carbon monoxide. So, the reduction of iron oxide is due to reaction with these reducing gases. It is well established [27] that reduction of iron oxide by carbon occurs as a combination of the gas-solid reactions as follows:

$$3\,Fe_2O_3\,(s) + H_2 / CO\,(g) = 2\,Fe_3O_4\,(s) + H_2O / CO_2\,(g) \quad .....(2.1)$$

$$Fe_3O_4\,(s) + H_2 / CO\,(g) = 3\,FeO\,(s) + H_2O / CO_2\,(g) \quad .....(2.2)$$

$$FeO\,(s) + H_2 / CO\,(g) = Fe\,(s) + H_2O / CO_2\,(g) \quad .....(2.3)$$

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

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

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

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

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

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. The following topics are very briefly reviewed.

i) Pyrolysis of coal, and
ii) Kinetics of carbothermic reduction and gasification reaction.

2.1.2.2 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 the volatile matter and represent 4 to 45 pct of the weight of the coal, depending on its type [28a]. Pyrolysis is accompanied by a change in the structure of the coal, leading to a marked variation in its thermophysical properties. Coal is a complex natural organic substance. The heating of coal causes thermal rupture of bonds, and volatile fragments escape from the coal. The 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 vapourized and transported outside of the coal grain. Simultaneously, the decomposition of the functional groups gives rise to the evolution of light gases, principally CO_2, H_2O, CH_4, and aliphatic C_2 compounds. Cracking, which occurs beyond 823 to 873 K, causes the liberation of CO and H_2. In the course of 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 [28b]. 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 [28a]:

i) heat transfer from the outside towards the surface of the grain,
ii) conduction of heat within the grain,
iii) kinetics and the heat effect of the devolatilization reactions,
iv) transport of the volatile matter from the inside to the outside of the grain,
v) heat exchanges between the volatile matter and the solid during its internal transport,
vi) secondary cracking reactions of the volatile species during their internal transport,
vii) swelling and cracking of the grain, and
viii) increase in the pressure within the grain due to the formation of gases.

Cypres and Soudan-Moinet [29] studied the influence of iron oxide additions on coal pyrolysis by thermogravimetry and the analysis of the evolved gases. They blended 70 pct bituminous coal with 30 pct of either hematite or magnetite and heated them from room temperature to 1273 K at the rate of 3.2 K/min. They observed 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 - 873 K, the weight loss of the coal-magnetite mixture was due to the coal devolatilization only. Magnetite was not reduced below 873 K. Between 673 and 823 K, Fe_2O_3 was reduced to Fe_3O_4, with loss of water and a little CO_2. They also observed that the yields of tar and gaseous hydrocarbon slightly decreased in the presence of iron oxides, mainly Fe_2O_3. In the secondary devolatilization zone, the reduction of iron oxides decreased H_2 yield and increased those of CO, H_2O and CH_4.

They [30] further studied the pyrolysis of coal and iron oxide mixture to establish the relationship between the release of volatile matter from coal and the reduction of iron oxides by thermogravimetry and 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 [27].

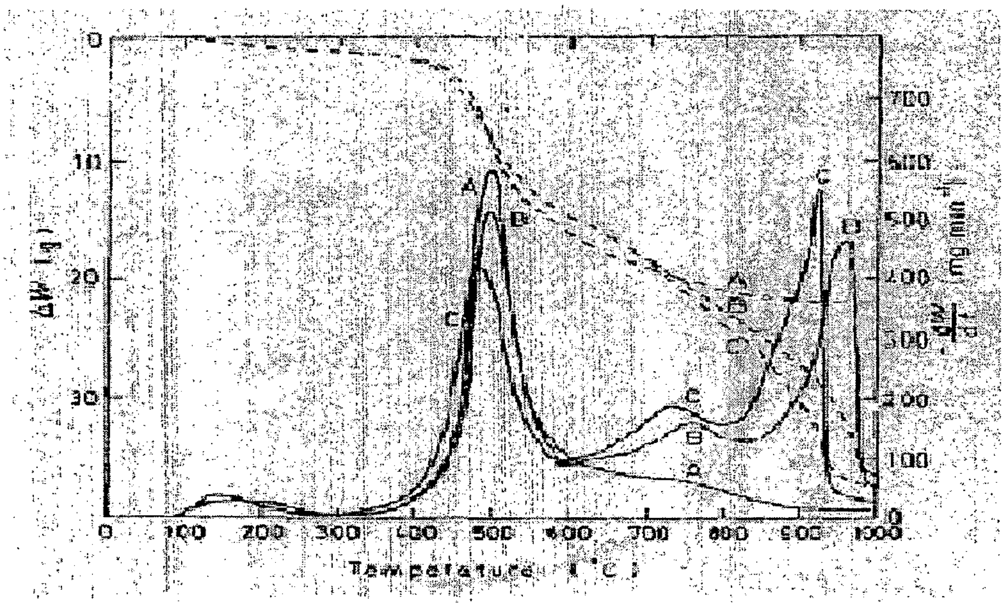


Fig. 2.1: Thermogravimetric curves, TGA (-----) and DTG (—–), of carbonization of coal and coal/iron oxide mixtures, A - coal; B - Coal + Fe_3O_4 (30 wt pct); C - Coal + Fe_2O_3 (30 wt pct).

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 773 K, but hidden in thermogravimetric 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 [30].

2.1.2.3 Kinetics of carbothermic reduction and gasification reaction

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 pellet then this is wholly carbothermic reduction. If, on the other hand, coal is used then reduction will be partly by gases evolved (due to pyrolysis of coal) especially H_2 and CO [27, 30]. 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 400 kJ/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 [31]. 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 in nature [32].

2.1.2.4 Brief review on reduction of composite pellets by previous investigators

Seaton et al [33] investigated the reduction kinetics of hematite/magnetite plus coal/char composite pellets in the temperature range of 1073 to 1473 K. They observed that at lower temperature (1273 K) hematite pellets reduce 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 $Fe_3O_4 \rightarrow FeO$ 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 [20] 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.

Takahashi [34] carried out reduction experiments for cold bonded pellets containing char using a pressurized moving bed reactor on laboratory scale. They found that the crushing strength of the pellet decreased remarkably in the moving bed during reduction up to the degree of reduction of 20 pct. However, the reduction of pellets proceeded without much change in shape and volume.

The reduction behaviour of the MTU-PelleTech cold bonded pellets [35], prepared from iron ore fines with 15 to 20 pct carbonaceous fines of 15 to 20 mm diameter, shows 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.

Seaton [36] used petroleum coke (also known as flexicoke) as a solid reducing agent for iron oxides in the manufacturing of cold bonded composite pellets. They found that the flexicoke used as a solid reductant gave reduction in excess of 90 pct and degree of metallization of approximately 85 pct.

Sharma [37] 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 1173-1473 K in oxidizing atmosphere. The effect of Fe_2O_3/C ratio, heating time, and heating rate on the reduction behaviour were studied. At the optimum reduction time, 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 total carbon, 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 determined 68.52 kJ/mol.

Dutta and Ghosh [27] carried out the non-isothermal reduction of composite pellets by thermogravimetry and demonstrated that reduction in a composite pellet occurs not only by carbon, but also significantly by H_2. Degree of reduction, volume change, and compressive strength of the pellets upon reduction were measured subsequently. Degree of reduction ranged from 46-99 pct. The gases, liberated during heating to high temperature, reacted with carbon and hydrocarbon to generate additional quantities of H_2 and CO, 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. No significant difference was found in degree of reduction.

Huang and Lu [38] 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 didn't 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 [22] 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 pct metallization, the residence time in the kiln was observed only 60 minutes as compared to 200-240 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 0.90-1.70 pct as compared to 0.20 pct in the case of lump iron ore.

Nascimento et al [39] analyzed all the steps of the reduction of self-reducing cold bonded composite pellets bearing hematite and charcoal in the range 1223 to1423 K. They observed transgranular cracks during $Fe_2O_3 \rightarrow Fe_3O_4$ reduction stage. This may 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 to1423 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 [40] 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. He also studied the effect of volume change on the reduction kinetics. The kinetics of reduction showed good agreement with Ginstling-Brounshtein model which showed that the diffusion of Fe^{2+} may be considered to be the rate controlling step. The kinetics of change in volume was interpreted using Johnson-Mehl equation. The apparent activation energy value of 68 kJ/mol was obtained for the reduction. He observed that swelling increased the rate of iron oxide reduction because of the formation of highly porous reduction products.

Dutta [41] 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 ($0.175\ K.s^{-1}$) and high heating rate ($0.35\ K.s^{-1}$). He observed that while carbon was the major reductant, reduction by H_2 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 reactions.

Wang et al [42] 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 [43] also studied the reduction kinetics of iron ore-coal pellets during fast heating at temperatures of 1323-1573 K. The effect of heat transfer on the reduction process and also the effect of volatiles on reduction were studied. They summarized the following:

i) The reduction by volatiles is negligible owing to their almost complete release in the initial period of heating.
ii) The reduction by carbon can be treated as a non-elementary homogenous reaction according to $Fe_xO_y + C = Fe_xO_{y-1} + CO$ and the reduction rate may be measured by the weight loss method.
iii) The reduction rate and the final reduction degree increase with an increase of test temperature.
iv) During fast heating of the pellet, the reduction was controlled by a chemical reaction in the initial period of heating and by heat transfer in the later period.
v) In the stage controlled by a chemical reaction, the reduction may be controlled by reduction by CO.
vi) In the stage controlled by heat transfer, the reduction rate was found very slow and was independent of the furnace temperature and the type of coal used.
vii) The apparent activation energy measured under the isothermal temperature condition (92.03-114.57 kJ/mol) was larger than that for the non-isothermal temperature condition (68.95-82.61 kJ/mol).

Takahashi et al [44] investigated the possibility of carbon-contained briquette of oxidized iron-scrap like 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 [45] 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 - 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 [46] investigated the reduction behaviour of iron ore-fuel oil composite pellets in both isothermal and non-isothermal conditions in the temperature range 1023 - 1273 K. They calculated the activation energies of 18.81 - 28.42 kJ/mol for non-isothermal reduction of composite pellets in nitrogen atmosphere, and 22.86 - 47.11 and 32.35 - 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 [47] reported the reduction behaviour of double layer composite pellet under isothermal condition in the temperature range of 1273 K to 1473 K. The variables studied were reduction temperature, carbon/iron-oxide ratio, and reduction time. They concluded that with increase in temperature (1273 K to 1473 K), C/Fe_2O_3 ratio (3 to

5), and reduction-time (20 to 40 min) the degree of reduction of iron ore increases. 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 jhamma coal, coke, and char.

Santos and Mourao [48] 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 obtained varied from 46 - 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 [49-52] 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_2 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 [49]. 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 pct reduction of iron oxide [50]. 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 [51]. They [52] 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. Their main findings were as follows:

i) wustite reduction rates become comparable to rates of carbon oxidation at higher temperatures, and
ii) graphite was as reactive as wood charcoal at higher temperatures, possibly due to the catalysis of graphite or its higher temperature dependence.

Aota et al [7] studied the reduction of cold bonded iron ore-coal composite pellets (cylindrical in shape having approximately 20 mm diameter and 20 mm height produced by vibration slip casting). The average point 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 [53] 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 70 to 50 in length and thereby the cost efficiency could be dramatically increased.

2.1.3 Advantages of composite pellets [9]

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

i) very fast reduction due to intimate contact between reductant and oxide particles,
ii) because of their uniform size and convenient form pellets can be continuously charged into the furnace leading to higher productivity,
iii) reduction in energy consumption because cold bonded composite pellets do not require induration,
iv) utilization of fines, which are cheap and are being generated in large quantities awaiting suitable disposal and utilization, and pollution control,
v) consistent product quality as the chemical composition of composite pellets (input material) does not change, and
vi) promising prospect for ironmaking at small scale with higher production rate.

2.1.4 Prospects of iron ore-coal composite pellets in smelting reduction processes

Metallurgical coking coal is costly and India has limited reserves of it (18.3 pct of the total reserves). Coke making in coke oven is a major source of environmental pollution whereas non-coking coal is widely available and cheapest reducing agent for iron oxide. On the other hand, Indian has vast reserves of non-coking coal (87.10 pct of the total reserves) and is most widely available [6]. It 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) [54]. 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 physico-chemical changes of the binder at low temperature [5].

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 [55]. The intimate mixing enhances gaseous diffusion rate significantly.

Iron ore-coal composite pellets have 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 40 tph) with a charge of 5 to 100 pct composite pellets are also available. Most of the trials were carried out with a charge consisting of 70 pct composite pellets and 30 pct scrap [56].

The advantages of cold bonded composite pellets as a feed material in cupola / rotary kiln / blast furnace are as follows [57]:

i) shortage of pig iron/scrap can be avoided by replacement of pig iron/scrap with composite pellets,

ii) 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,

iii) instead of large size cupola coke (100 x 150 mm) the cheaper small size blast furnace coke (50 x 75 mm) can be used,

iv) composite pellets are uniform in size as compared to any other iron-bearing charges used,

v) adjusting the carbon and basicity of the composite pellets can control sulphur content of the melt,

vi) efficient reduction behaviour of composite pellets leads to a drastic reduction in the retention time in rotary kiln, thereby improving productivity many folds, and

vii) improved product quality of rotary kiln due to increased carbon content (0.5 to 1 pct) in the sponge iron with good metallization.

2.2 Review of Smelting Reduction Processes

2.2.1 Introduction and historical development

Direct smelting has been the *holy grail* of iron and steel making for a long time. For the traditional blast furnace route the combination of sintering and coke making is becoming increasingly untenable from economic and environmental point of view. Smelting reduction is a much sought-after prize. Many have tried to develop direct smelting technologies, but the challenge appears to be particularly difficult, certainly more so than one might expect. Why is this so, and what does it take to break through? Any new technology is typically measured against the cost of pig iron from blast furnace. Modern integrated blast furnaces also happen to be fairly energy-efficient, and this ensures there is no easy solution [58].

Reduction of iron ore into iron is the first step in the production process of steel. It is also the most energy intensive step. The iron ore is reduced to iron at a high temperature. The iron is subsequently converted into crude steel, cast into semi-finished products and rolled and shaped 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 [59]. 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 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 [54]. 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 modern 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 [60].

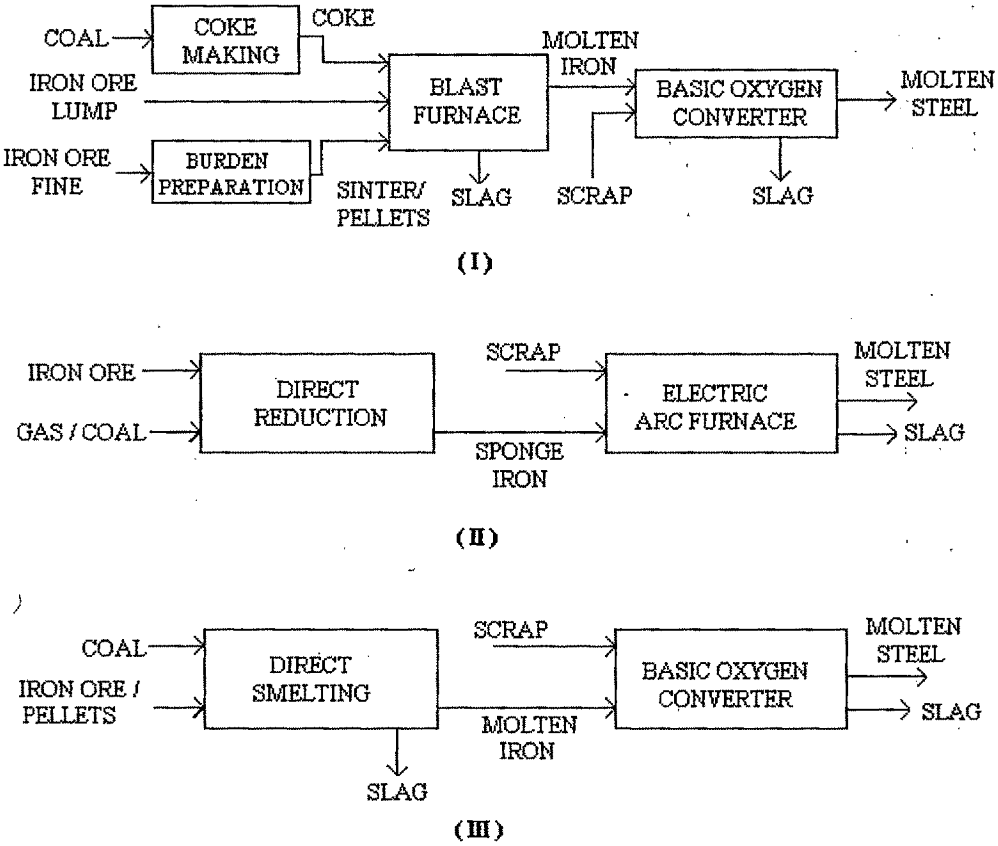


Fig. 2.2: Block diagram of various steelmaking process routes.

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. A number of processes based on natural gas and non-coking coal using iron oxide lump/pellets of fines as feedstock were developed, a few of which matured to the stage of commercial exploitation. In 1990, about 3.5 pct of the worldwide iron production was based on DR technology. In 2002, the share has increased to about 7.4 pct [59]. Advantages of sponge iron, as feed material, are well known. Even though DR technology could eliminate some of the inherent drawbacks of the blast furnace, it had its own limitations, the major ones being its solid product, small module size, product pyrophoricity, low productivity etc. Location of the DRI or HBI plant is limited to regions where natural gas is available at a reasonable price. Coal based DR processes have also been adopted for commercial production but they have their own limitations, the important ones are lower levels of productivity, low carbon content in the product, inability to use fines, ring formation in the kiln and its solid state [54]. Coal based DRI is not suitable for high capacity operation due to restriction in module capacity.

Energy experts had forecasted (in 1980s) that in coming decade the cost of high grade coking coal would rise at a much faster rate than electricity and non-coking coal [61]. That was true; the price of metallurgical coke in the international market had gone up to $360 per ton (i.e. Rs. 16200 per ton) in January 2004 from $150 per ton (Rs. 6750 per ton) in July 2003. Similarly, the price of steel scrap has also doubled to $320 per ton from $160 per ton in July 2003 [62].

The rapid growth of electric arc furnace steelmaking in last two decades (1980s and 1990s) has created growing demand for steel scrap. Significant improvement in steel plant's yield from 82 pct to 94 pct due to continuous casting technology has decreased the amount of in-plant generated scrap [63]. 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 the country and to take advantage out of large price differences between imported metallurgical coal and non-coking steam coal. The scenario forced innovators to look for alternative coal-based iron production routes [64].

In order to overcome the above, scientist and technologists have been working for quite sometime specially in the second half of this century to develop suitable process of ironmaking, called smelting reduction (SR) process, using non-coking coals and iron ore fines [65]. Smelting reduction technology was conceived in late 1930s. The history of the development 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 [66]. However, serious efforts started from 1980 onwards. In late 1950s and early1960s, steel manufacturers were interested in developing a technology that could convert iron ore into crude steel in just one step. In late seventies and early eighties, concerted efforts were made in many parts of the world to develop a process of making liquid iron similar to blast furnace using non-coking coal [59]. 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 [64].

2.2.2 Fundamentals of smelting reduction technology

Smelting reduction technology is a coal-based ironmaking process and thus different from the conventional coke-based blast furnace technology. Smelting reduction is a generic name for a gamut of oxy-coal liquid ironmaking technologies each of which have characteristic process features. The terms smelting reduction refers to a process where reduction of iron ore is carried out at high temperature to obtain liquid iron using non-coking coal and oxygen with a substantial part of the reduction taking place in the liquid oxide phase. In most smelting reduction processes, a certain fraction of oxygen is removed by solid state reaction and the rest is removed in the liquid state. Ideally, a SR process should have near 100 pct reduction of iron oxides in the liquid state in one step in a single reactor. SR technology exploits the principle that coal can be gasified in a bath of molten iron. The primary objective of all SR processes is to overcome the existing problems of BF and DRI technologies [54]. The basic approach is to produce liquid iron in a reactor using molten bath where iron-bearing materials are reacted with non-coking coal and oxygen to produce liquid hot metal. The reactor off-gases are used to pre-reduce the burden before it is fed to a smelting unit. In Indian context, these processes have great relevance as there is a need to conserve scarce coking coal. Further, the need of an alternative ironmaking technology arises to complement and supplement Indian blast furnace technology in order to produce hot metal of international quality at competitive price [67].

2.2.2.1 Concept of smelting reduction process

Carbon dissolved in molten iron in the temperature range of 1573 to 1873 K forms a strongly reducing medium. If air or oxygen is blown into a molten iron/carbon bath, the reaction, between the gas and the dissolved carbon to form almost 100 pct carbon monoxide, is very rapid. In addition, molten iron has a high affinity for carbon and if coal is added to the iron bath its carbon content can be effectively dissolved while any volatile components react with the bath yielding hydrogen. The concept of simultaneously dissolving coal in a molten iron bath and oxidizing the dissolved carbon by oxygen injection yields an iron bath coal gasification process. If iron ore or partially reduced iron ore is injected into the bath the process becomes an iron producer [68]. The basic process concepts can be engineered in a number of ways to produce:

i) gas as a primary product,
ii) gas generation with ironmaking, or
iii) iron production with minimal gas production.

2.2.2.2 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 [69].

The overall reaction is:

$$(FeO)_{slag} + C_{(s)} \text{ or } [C]_{in\,Fe} \rightarrow [Fe] + CO_{(g)} \qquad \ldots\ldots(2.7)$$

There is a general agreement that the above reaction takes place in two stages.

1st stage; slag-gas reaction:

$$(FeO)_{slag} + CO_{(g)} \rightarrow [Fe] + CO_{2\,(g)} \qquad \ldots\ldots(2.8)$$

2nd stage; carbon-gasification reaction:

$$C_{(s)} + CO_{2\,(g)} \rightarrow 2CO_{(g)} \qquad ....(2.5)$$

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

The following four possible rate-limiting steps may be visualized for this reaction between FeO in molten slag and solid carbon [70]:

i) mass transfer of FeO (i.e., Fe^{2+} and O^{2-} ions) 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).

2.2.2.3 Pre-reduction and post-combustion in smelting reduction

For developing an efficient SR process, it is essential to optimize the use of oxygen and non-coking coal, which act both as a reductant and source of heat energy. In order to realize an efficient SR process, it is important to [71]:

i) carry out the post-combustion of the bath gases at high level with high heat transfer efficiency for thermal compensation of iron ore reduction in the smelting reduction furnace (SRF),
ii) make direct use of the off-gas from the SRF for the pre-reduction of iron ore in the pre-reduction furnace (PRF), and
iii) maintain the stable operation of these two furnaces.

Post combustion refers to the burning of the partially oxidized gases generated as a result of the reduction reactions (i.e. CO to CO_2 and H_2 to H_2O) by oxygen/air in slag layer or above slag layer. The degree of post-combustion (PCD) is defined as [72]:

$$PCD(\%) = \frac{[(\%CO_2) + (\%H_2O)]}{[(\%CO) + (\%CO_2) + (\%H_2) + (\%H_2O)]} \times 100 \qquad .....(2.9)$$

The degree of post-combustion is used for the evaluation of the heat generation potential of the SRF, and also means the reducing potential of off-gas in the PRF. Practically, it is determined by the off-gas analysis.

Some of the heat generated in the SRF leaves without participation in smelting. Another parameter should then be introduced. That is the heat transfer efficiency (HTE), which is defined as the ratio of the heat effectively used for smelting to the total heat generated in the SRF. HTE, $\eta_{PC,}$ can also be represented as:

$$\eta_{PC}\,(\%) = \left(1 - \frac{\text{super heat of exhaust gas}}{\text{heat generated by post combustion}}\right) \times 100 \qquad .....(2.10)$$

Super heat of exhaust gas is the difference between the amount of input heat and that of output heat calculated under the assumption that the temperature of exhaust gas is equal to the temperature of the melt. Both PCD and HTE are important indices to evaluate the potential for intensive smelting in the SRF [72].

If PCD is high, the exit gas coming out of the smelting reduction unit will have more of CO_2 and H_2O thereby decreasing its potential as a reducing gas. It is observed that with about 50 pct post-combustion and a pre-reduction level of 25 - 30 pct, the efficiency of the smelting reduction is the same as achieved in a blast furnace. Ideally, any smelting reduction process should have 100 pct reduction of iron oxide in the liquid state in one step in a single reactor [67].

High PCD leads to utilization of fuel value of CO and H_2 more in the smelting reactor itself. Hence, it lowers coal consumption. The combination of low PCD (< 50 pct) and high degree of pre-reduction (PRD) [>30 pct] yields unnecessary excess process gas energy than that of required at the integrated steelworks. When higher PRD than 30 pct is desired, PCD should be kept lower than 30 pct to secure reduction potential for the pre-reduction. This results in a substantial increase of required process gas for the PRF, much larger than the energy required in the subsequent plants. Therefore, the combination of intensive post combustion (PCD $\geq$ 50 pct) and the light pre-reduction is considered to be reasonable as the alternative process [71]. For better fuel efficiency, it is also necessary that the heat generated in post combustion is effectively transferred to slag and metal to sustain endothermic reactions there and counter heat losses. This requires high heat transfer efficiency. HTE above 85 pct has been attained in second generation processes [55].

Hoffman [60] suggested that for any smelting reduction process to be successful, the optimum has to be found between the six elements of smelting reduction and the interaction amongst them. These elements are listed as follows:

i) degree of pre-reduction (PRD),
ii) post-combustion ratio (PCR),
iii) reaction kinetics (RK),
iv) heat transfer efficiency (HTE),
v) cost of production (COP), and
vi) environmental demands (ED).

In the case of iron ore reduction, the reaction kinetics or reduction rates could be increased by coal injection, increased carbon in slag, increased FeO in slag, high degree of pre-reduction and foaming slag. For the process to be energy efficient, it is necessary to have a high degree of post combustion (of the order of 50 pct). This high degree of post combustion or high oxidation potential could reduce the reduction rate and less CO and H_2 are available for pre- reduction. For high heat transfer efficiency, PCR should be high. This, however, leads to a high volume of gas generation, e.g., for a typical coal, 33 pct PRD and 50 pct PCR, over 1000 m^3 (STP) of gas is generated per tonne of metal. High PCR also results in high free-board temperature with consequent detrimental effect on refractories [60].

Katayama et al [72] calculated the heat transfer by radiation and gas convection and compared the same with actual data. They concluded that radiation and convection accounted for only 20 - 30 pct of total HTE. It may be emphasized now that high PCD and HTE are being aimed at to cut down coal consumption and not to enhance productivity. As a matter of fact, productivity tends to suffer at high PCD.

Based on the material and energy balance model developed by Research and Development Centre for Iron and Steel (RDCIS), Steel Authority of India Limited (SAIL), Ranchi the smelting reduction processes were analyzed for typical Indian raw materials. Analysis of these processes revealed that for Indian coals, having high ash and volatile matter, processes involving high PCD and high HTE either in single or two stages will be more appropriate [67].

2.2.2.4 Why is post combustion so important?

Production of hot metal requires heating of reactants to form a melt (with or without pre-reduction). In blast furnace, this heat is provided by combustion of carbon in coke. For any smelting reduction process, coal has to carry out the same functions. Heat is required within coal for heating of fixed carbon, volatile matter, ash, carbonization of coal, fluxing of ash, calcination of flux, and heating of associated flux. If calculations are carried out as per above requirements for a typical Indian coal (24 pct ash, 43 pct fixed carbon, and 29 pct volatile matter), we shall have a negative net available heat at zero PCD. Such coals are not suitable for processes, practicing low degree of post combustion, such as the Corex process. The RDCIS, SAIL, Ranchi has developed a mathematical model to represent smelting reduction process operating under different parameters [73]. Outputs presented in Table 2.1 have been obtained from that model.

Table 2.1: Net heat release from coal at different PCD

PCD (pct)	Heat release (Gcal/thm)
0	-0.107
30	0.929
50	1.620
70	2.311
90	3.002
100	3.347

(HTE = 85 pct, Wall heat loss = 5 pct, Slag basicity = 1.2)

At higher post combustion levels of about 45 pct the coal consumption is reduced to about 650 Kg/thm and the ore has to be reduced in the gaseous reduction only to the FeO state. In the case of ore fines, pre-reduction up to FeO state seems much easier than pre-reduction up to certain degree of metallization where sticking of the ore particles in large-scale plants is a major problem. So, at one end the use of low priced coal as an energy source can be made and on the other hand direct use of ore fines [74].

2.2.3 Foaming slag in smelting reduction processes

Foaming slag plays an important role in the smelting reduction processes. Considerable research activities were concentrated toward understanding the foaming behavior of slag in the past decade. Characteristics of foaming slag in smelting reduction processes are discussed in detail elsewhere [75].

The main functions of foaming slag are as follows [76]:

i) foaming agitates the bath and improves the transport phenomena associated with it,
ii) it provides a large interface between the slag and the gas to facilitate the reaction between FeO and CO and therefore the chemical reaction proceed more favourably,
iii) foam Shields the metal from the atmosphere and works as a thermal insulator for the process heat, and
iv) it acts as a medium for post combustion and heat transfer, which is the key to an energy efficient process. It plays an important role in heat transfer from the post combustion flame to the bulk slag in the reactor.

Some of the important parameters, which influence foaming of slag, are as follows [76]:

i) physical properties of slag such as density, viscosity and surface tension,
ii) composition and basicity of slag, which control the physical properties along with temperature,
iii) initial FeO content of slag, which also affects physical properties,
iv) presence of surface active agents such as S, P, CaF_2, MgO etc,
v) presence of solid particles, gas velocity and geometry of vessel,
vi) initial slag height, and
vii) reaction surface area i.e. the exposed bottom surface of the crucible.

2.2.4 Classification of smelting reduction processes

The smelting reduction processes can be broadly classified into two categories as follows:

i) processes utilizing coal and electricity, and
ii) processes utilizing oxygen and coal

2.2.4.1 Processes utilizing coal and electricity [10]

The smelting reduction processes utilize electricity and coal as the source of energy and reductant. These processes can be divided mainly into two types, namely, single-stage and two-stage.

i) Single-stage process

The reactor vessel is fed with cold iron ore without any pre-reduction and coal as reductant. In single-stage process, both reduction and smelting take place in the electric smelter. The off-gases from the electric smelter are used for internal generation of electricity as shown in Figure 2.3. The process offers greater flexibility compared with any other oxy-coal process.

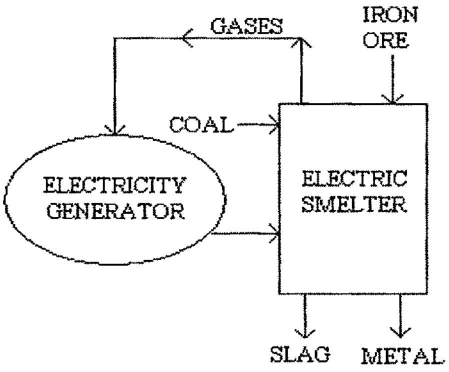


Fig. 2.3: Single-stage smelting reduction process.

ii) Two-stage process

The DRI produced in a reduction unit is smelted in the electric smelter. The off-gases from the reduction unit are used for internal generation of electricity as shown in Figure 2.4. This process offers greater flexibility compared with other oxy-coal processes.

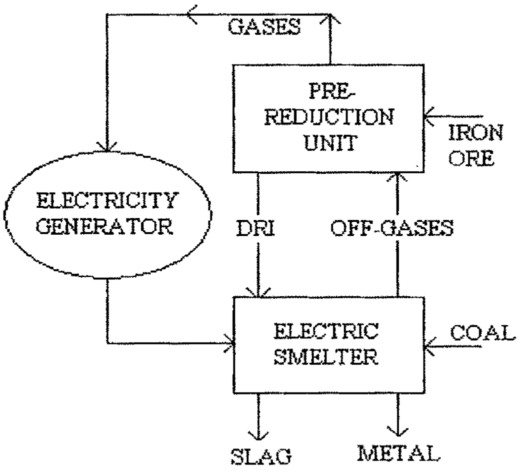


Fig. 2.4: Two-stage smelting reduction process.

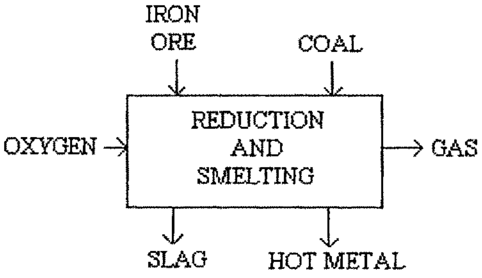
2.2.4.2 Processes utilizing oxygen and coal

The smelting reduction processes utilize oxy-coal combustion as the source of energy-cum-reductant. Based on the number of stages (i.e. according to their thermo-chemical configuration), these processes can be divided into three types as follows [10, 67]:

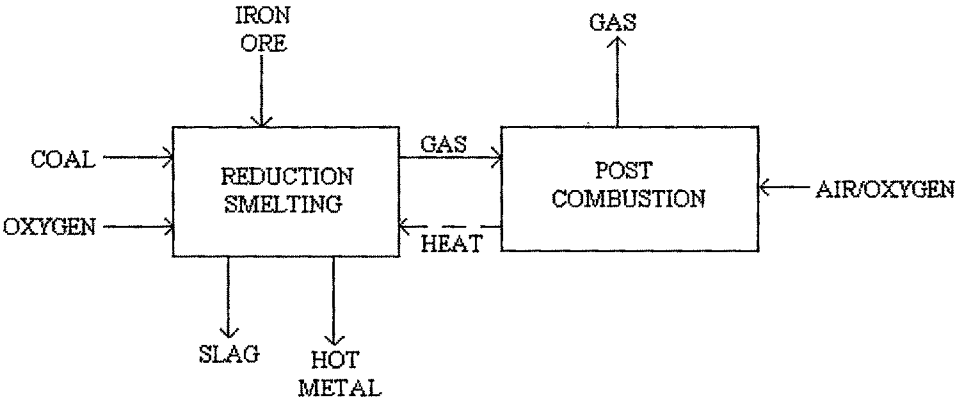
i) Single stage,
ii) Two stage, and
iii) Three stage processes.

i) Single-stage process

The single-stage process is the simplest of all the iron bath processes and theoretically represents the ideal smelting reduction configuration where hot metal is produced in a single reactor following reduction of the iron-bearing materials in liquid state. In single stage process, entire metallurgical reactions are carried out in a single reactor where iron ore, coal and oxygen are fed and the gases evolved from the molten bath are post combusted to a very high degree (around 70 pct) and the major portion of heat is transferred back to the molten bath. Refractory erosion is likely to take place and foamy slag is to be controlled during operation. The oxygen and coal requirements are higher compared with two-stage and three-stage processes. Romelt and Ausmelt processes belong to this category. Figure 2.5 shows the schematic diagram of the single stage process.



(a) Single-stage

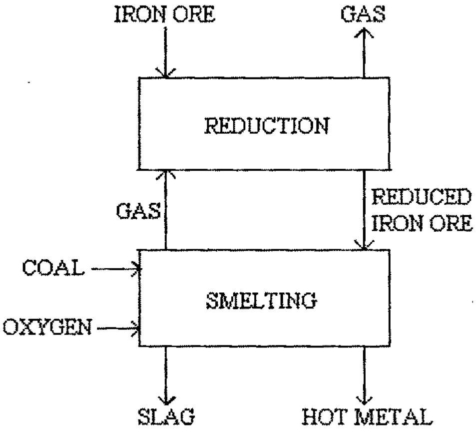


(b) Single-stage with post combustion.

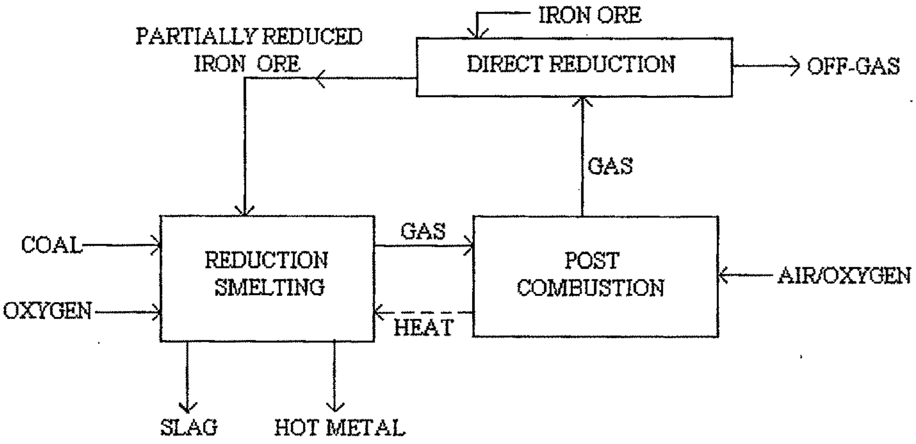
Fig. 2.5: Single-stage smelting reduction process.

ii) Two-stage process

In two stage processes, pre-reduced iron ore is smelted in separate reactor and most of the gas generated during the operation is utilized to pre-reduce the ore as well as to supply heat energy to the entire system through post combustion, e.g. Corex, HIsmelt, DIOS, AISI-DOE etc. Here, hot pre-reduced iron oxide generally having low degree of reduction is charged into smelting reactor along with coal and oxygen / pre-heated air. The gases evolving from the molten bath is post combusted by oxygen / pre-heated air to a moderate degree (around 50 pct) inside the smelter. The heat of the post combustion is efficiently transferred from the gas phase to the molten bath. HIsmelt process belongs to this category. Figure 2.6 shows the schematic diagram of the two stage process.



(a) Two-stage



(b) Two-stage with post combustion

Fig. 2.6: Two-stage smelting reduction process.

ii) Three-stage process

In three-stage process, a separate gasifier is coupled with the smelting unit and the pre-reduction unit to gasify coal producing CO, H_2, CH_4 etc. The process involves an additional step of gasification / gas reformation between smelting reactor and pre-reduction reactor. The presence of carbon in gasification zone helps in reducing the temperature of the melter off-gases without the loss of energy. Figure 2.7 shows the schematic diagram of the three stage process.

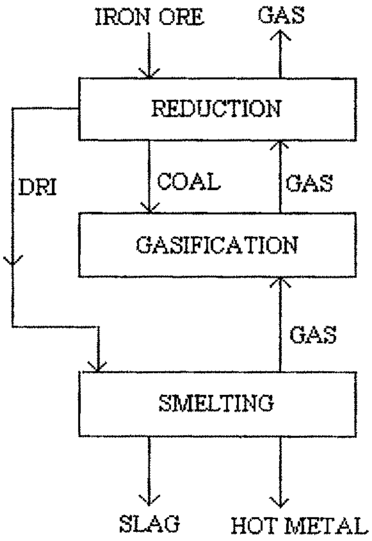


Fig. 2.7: Three-stage smelting reduction process.

2.2.5 Some popular smelting reduction processes

2.2.5.1 Corex process

Notable amongst those, which have succeeded to the point where multiple commercial plants have been built is Corex (Figure 2.8). The Corex process, developed and marketed by VOEST-ALPINE GmbH, Austria, is an example of first generation SR processes. It operates at low post combustion (<10 pct) and high pre-reduction (85-95 pct) with lump ore, pellets or sinter [64]. Corex developed from an initial pilot plant in Brazil (Korf Stahl, late 1970's) to a development plant at Kehl in Germany (60,000 tpa, 1981-1989). From there, it progressed to a demonstration plant in South Africa [C1000, rated at 0.3 million tonnes per annum (Mtpa), 1986-1998]. The first true commercial C2000 plant (Pohang, Korea) was commissioned in 1995. Corex took around 30 years to get from concept trials to full commercial C2000 operation [58]. The salient features of this process are given in Table 2.3.

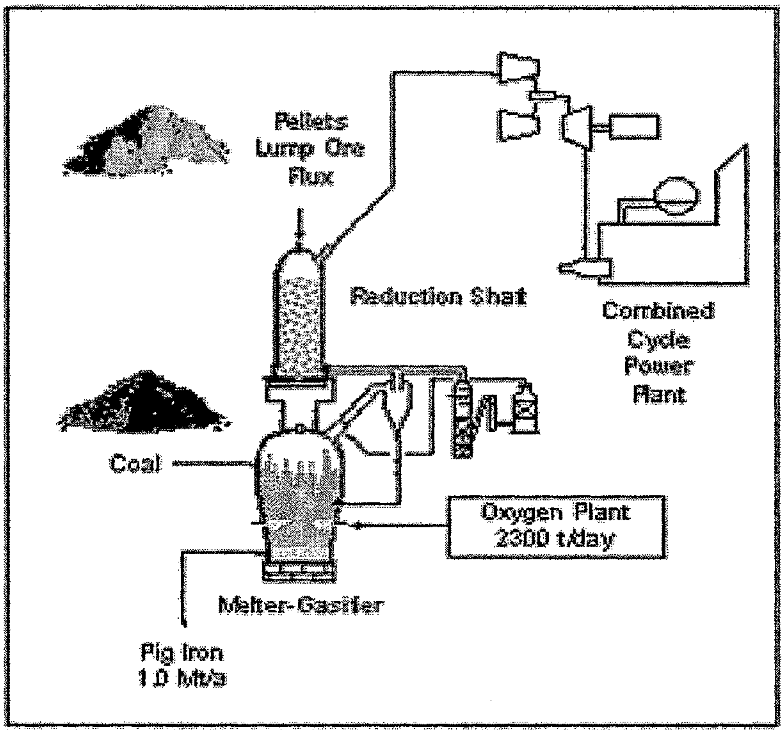


Fig. 2.8: Corex C3000 process.

Corex is the first commercially established and technologically proven two stage smelting reduction process based on non-coking coal. Presently, Corex commercial plants are in operation at POSCO, Pohang Works, South Korea; Saldanha Steel, South Africa; HANBO Steel Corporation, South Korea; ISCOR, Pretoria Works, South Africa; and JSW Steel Ltd, Vijayanagar Works, Karnataka, India [77]. Two Corex units, each having rated capacity of 0.8 Mtpa hot metal, are in operation at JSW Steel's Vijayanagar Works. ESSAR is constructing two Corex units at ESSAR Steel Works, Hazira, Gujarat, India. The first unit will be commissioned in January 2009 and second will be in March 2009. As per plan, 1.74 Mtpa hot metal will be produced from both Corex units. Most of the equipments are imported from INI (HANBO), South Korea [77a].

Corex consists of two reactors, the reduction shaft and the melter-gasifier [78]. The reduction shaft is located above the melter-gasifier and reduced iron bearing materials are extracted by a screw system. The volumes of the reduction shaft and melter-gasifier are ~600 and 2200 m^3 respectively. A reduction shaft is used to metallize incoming ore. Pellets, lump ore and fluxes are fed into the reduction shaft via a lock hopper system. About 5 - 6 pct of coke is also added to the shaft to avoid clustering of the burden inside the shaft, owing to sticking of ore/pellets, and to maintain adequate bed permeability. The iron bearing material is reduced to over 70-90 pct metallization in the shaft, and is termed DRI. The hot DRI at about 973-1073 K along with partially calcined limestone and dolomite is continuously fed into the melter-gasifier through downpipes for smelting. Non-coking coal is fed directly into the melter-gassifier. Pure oxygen, predominantly blown through the tuyeres, burns the fixed carbon/char of the coal and generates heat and reducing gases. The hot metal and slag formed in the process are collected in the hearth and tapped periodically. The hot gas generated in the melter-gassifier, containing about 70 pct CO and 25 pct H_2, is used as reducing gas in the shaft. The top gas from shaft and residual reducing gas is subsequently made available as a highly valuable export gas suitable for wide range of applications. Coal consumption rate of around 1000 kg/thm is significantly higher than that of a blast furnace (typically 700 kg/thm). The melter-gassifier operates in a strongly reducing mode (similar to a blast furnace), resulting in most of the phosphorus reporting to metal. The reduction shaft and melter-gassifier work at an elevated pressure of approx. 5 bar. Corex is heavily reliant on export gas credits to make the economics work. The melter-gasifier can largely be divided into three reaction zones namely gaseous free board zone (upper part or dome), char bed (middle part above oxygen tuyeres) and hearth zone (lower part below oxygen tuyeres). The efficiency of the melter-gasifier primarily depends on the following parameters:

i) size and chemical analysis of the raw materials; especially the coal,
ii) low CO_2 pct in the reduction gas so as to ensure higher metallization of the DRI,
iii) optimum distribution of oxygen between the tuyeres and dust burners,
iv) permeability of the char bed,
v) high system pressure, and
vi) high melting rate operation, i.e., large amount of hot metal produced per hour.

2.2.5.2 Finex process

In a joint research and development project POSCO, RIST and VAI are developing the Finex process; a fine ore based smelting reduction process. It is rated as the most advanced commercial ironmaking technology. The aims of the Finex process are [79]:

i) direct charging of sinter feed (less than 8 mm) without prior agglomeration stage,
ii) direct charging of coal,
iii) minimum coal consumption and high gas utilization, and
iv) same hot metal quality characteristics as from blast furnace or Corex process.

In Finex process, the fine ore is reduced to DRI in a three stage fluidized bed system. Melting, final reduction and carburization of the hot DRI to liquid hot metal is performed in the melter-gasifier.

POSCO completed construction of the 2000 tpd demonstration plant that utilizes a next generation environmental friendly ironmaking technology and entered into operation in May, 2003. The new plant has an overall capacity of 0.6 Mt. The Finex process is more advanced and the new plant produces molten iron directly using cheaper and abundant iron ore powder and bituminous coal (non-coking coal) [80]. The iron ore powder used for Finex is bountiful and cheaper. This results in the process being 15 pct cheaper in production cost than the blast furnace production method. In addition, Finex is being praised as an eco-friendly process because sulphur and nitrogen oxide emissions are reduced to 10 pct of the amount generated from the conventional blast furnace method.

2.2.5.3 Romelt process

It is a single stage process operating at sub-atmospheric pressure where liquid iron is produced in a molten slag bath reactor directly using iron-bearing materials and non-coking coal. It requires minimum preparation of raw materials and there is no limitation of size range and moisture content. It requires oxygen as the primary gasification medium. In this process, reduction of iron oxide takes place in foaming slag phase. It has simple design requiring fewer numbers of unit operations and unit processes compared to other processes under development [81]. It is environmentally more acceptable compared to the conventional routes. Higher post combustion (greater than 70 pct) with high heat transfer efficiency is the principal driving force of the process. The productivity of Romelt furnace basically depends upon achieving the post combustion level of the order of 70 pct. In Indian context, the process has significance in that it does not depend upon coking coal and is able to accept coal with high ash. The suitable charge material for the Romelt process is lumps-ore including fines (preferred size range 0-20 mm), mill scale, sludge, pre-reduced pellets, and coal as reductant (moisture content 10 pct max, volatile matter 20 pct max, ash < 20 pct, and preferred size range: 0 to 20 mm). Either lime (< 5 mm size) or limestone can be used as flux [67].

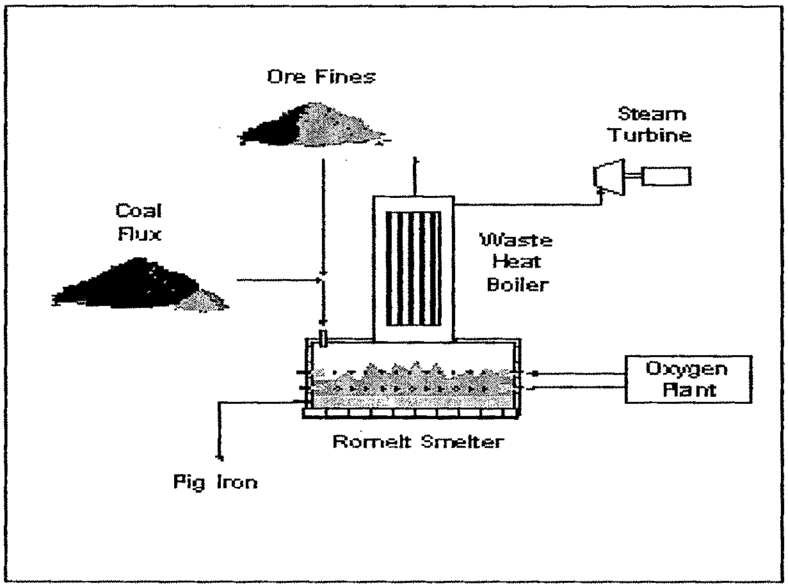


Fig 2.9: Romelt Process.

The process, shown in Figure 2.9, requires an additional element as a waste-heat boiler for recovery of heat from out going gases. In the waste-heat boiler, complete post-combustion of gases to carbon dioxide and water is accompanied with emission of respective amount of energy and recovery of sensible heat of waste gases, their temperature dropping from 1873 - 1973 K to 523 - 573 K. Therefore, the Romelt plant is power-cum-technological unit that may incorporate a power block for generation of electric power [82].

The salient features of this process are given in Table 2.3. Romelt is another such technology, which is now being offered for its commercialization and a Romelt plant is under installation near Jagdalpur, Chhattisgarh, India. The project involves producing 0.3 Mtpa hot metal from iron ore slimes. A key aspect of this project appears to be elimination of accumulated slimes, which could otherwise pose a significant environmental problem [77].

2.2.5.4 DIOS process

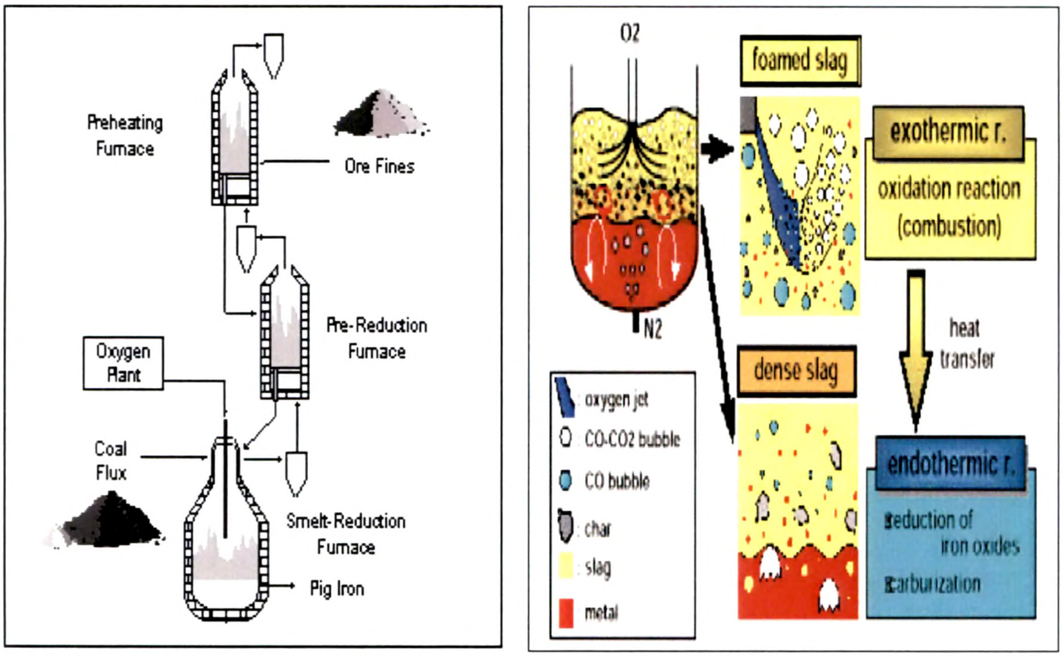
The process is a combination of smelting reduction furnace (SRF) and two-stage pre-reduction furnace (PRF). Iron ore fines of up to 8 mm size and coal up to 25 mm size are used. Iron ore fines are preheated at approximately 873 K in a fluidized bed preheater, then preliminarily reduced to 27 pct at 1053 K in a fluidized bed pre-reduction furnace. The DIOS process has the following characteristics [83]:

i) iron ore and coal fines can be directly used,
ii) coke is not used, so there are no restrictions on the kind of coal,
iii) process can be halted and restarted easily, affording excellent flexibility, and
iv) the intensity of bath stirring may be optimized for higher PCD and HTE.

The salient features of this pilot plant are given in Table 2.3. A 500 tpd (i.e. 0.15 Mtpa capacity) pilot plant has been successfully in operation at NKK, Keihin steel plant, Japan since1993. The pilot plant, located at NKK's Keihin works, Japan was essentially a modified 250 tonnes BOF [54]. Based on the pilot plane data, performance of a 6000 tpd commercial plant has been worked out and following benefits are envisaged with respect to similar capacity blast furnace [77].

i) reduction in construction cost by 35 pct,
ii) reduction in production cost by 19 pct,
iii) reduction in CO_2 emission by 4 - 5 pct, and
iv) reduction in net energy consumption by 3 - 4 pct.

The DIOS process operates at a pressure of 1 to 2 bar and uses top-feed of coal and ore as shown in Figure 2.10 (a). Unlike Romelt, it uses a top lance for oxygen injection and has a fluidized bed system for iron ore pre-reduction. In the smelter, most of the reduction occurs in a foamy slag layer. Theoretically, this combination can achieve the coal rates necessary to compete with a modern blast furnace. The calorific value of export gas is low (1100 kcal/Nm^3) compared to Corex process and can be used for power generation. Figure 2.10 (b) shows the physical images of SRF (DIOS).



(a) (b)

Fig. 2.10: (a) DIOS process and (b) SRF (DIOS).

2.2.5.5 HIsmelt process

This process was developed by CRA Ltd (Australia) and Midrex Corporation (USA) in co-operation with CSIRO (Australia), Klockner (Germany) and Davy McKee (UK) but presently it has been taken over by Rio Tinto Group. The original version of HIsmelt started out as a modification of bottom-blown K-OBM (steelmaking) process. Initial trials were conducted in the early 1980s on a 60 tonnes K-OBM converter at Maxhutte in Germany [84].

A rejuvenated version of HIsmelt based on top injection is shown in Figure 2.11. The salient features of the pilot plant are given in Table 2.3. The process uses iron ore fines directly with non-coking coal (less than 10 pct ash content preferred). A thick slag layer is situated above the metal bath. Upon contact with the iron bath, dissolution of the carbon in the coal occurs, which react with the oxides in the iron bearing feeds, forming carbon monoxide. Rapid heating of the coal also results in cracking of the coal volatiles releasing hydrogen. The CO and H_2 is post combusted with oxygen. The sensible and chemical energy in the off-gas can be utilized for preheating, pre-reduction and/or calcination of the metallic feed and fluxes. One of its most important achievements was demonstration of plant availability of around 99 pct. The phosphorous removal capacity of the process has been readily demonstrated with an average of 85-95 pct of the input reporting to the slag phase [84, 85].

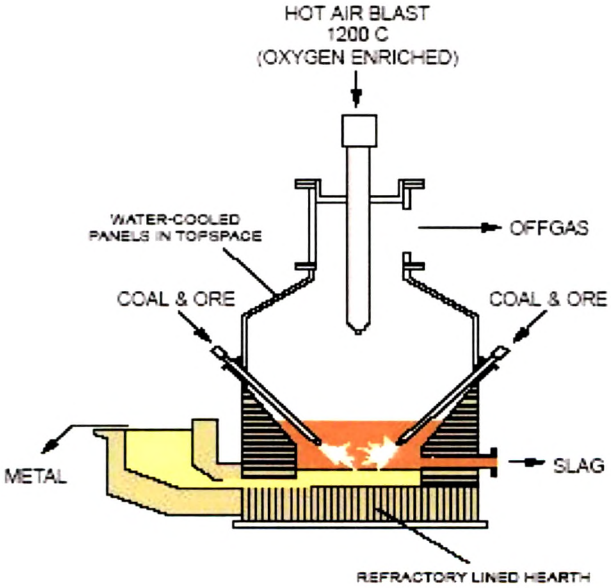


Fig. 2.11: HIsmelt process.

The major difference with respect to other SR processes is that this process uses oxygen-enriched air and the vertical SR vessel operates at pressure slightly below atmospheric pressure, thus there is no chance of leakage of gases. The hot metal does not contain any silicon, as silicon reduction does not take place during the process and, therefore, the hot metal is more suited for steelmaking. Based on the pilot plant data, two modules of commercialization have been designed (6 m and 8 m hearth diameter vessels for 0.5 and 1.5 Mtpa capacity respectively). It is economic at smaller scale (0.5-1.0 Mtpa) and meets future environmental standard [77].

The main advantages of the HIsmelt process are [86]:

i) economic at smaller scale (0.5-1.0 Mtpa),
ii) scaleable to single units producing 2 Mtpa and higher,
iii) uses a wide range of non-coking coal,
iv) direct use of low cost, readily available raw materials,
v) simple, flexibility and controllable,
vi) high energy efficiency and balanced energy flow sheet,
vii) high level of process intensity,
viii) high quality hot metal product,
ix) meets future environmental standards,
x) air based process and therefore no need for large oxygen production facility, and
xi) plant availability of greater than 99 pct.

After 20 years of development phase involving multiple pilot plants, HIsmelt has recently emerged as the only ferrous direct (bath) smelting process thus far to proceed to the commercial status. Rio-Tinto, together with Nucor Steel, Mitsubishi and Shougang Steel as joint venture partner, is now in the process of building a 0.8 Mtpa plant in Perth, Western Australia [58].

2.2.5.6 AusIron process

The process is developed by Ausmelt Ltd, Victoria, Australia and a 2 tph capacity pilot plant had been built at Whyalla in South Australia. It is a single stage process operated under sub-atmospheric pressure. The salient features of this process are given in Table

2.3. The developers have long experience in non-ferrous metallurgy using vertical injection lances [77].

The AusIron process is a bath smelting process which directly processes ferrous bearing feed materials to produce molten iron. The process, as shown in Figure 2.12 is based on top submerged lance technology where coal, ferrous feed, flux and oxygen are injected directly into the smelter slag bath. Ferrous materials rapidly dissolve in the slag bath, whilst the reductant coal reacts with iron oxides contained in the slag. The turbulence generated by submerged combustion provides efficient mixing, resulting in high smelting rates. CO produced by smelting reactions, together with coal volatiles, is post-combusted immediately above the slag bath using oxygen-enriched air delivered through a shroud around each lance. The evolution of gases from the lance tips generates a cascade of slag droplets above the bath providing a large surface area for efficient recovery of post-combustion energy. Complete combustion of the fuel gases is achieved within the furnace maximizing energy recovery and avoiding the production of difficult low calorific value fuel gases [87].

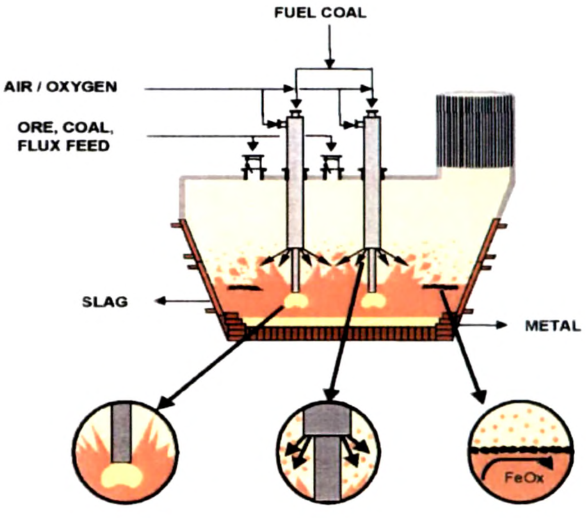


Fig. 2.12: AusIron process.

The key attributes of the technology are [87]:

i) low-grade lump-ore/fines and any grade of coal can be used and, therefore, no pelletizing or sintering is required,

ii) direct use of non-coking coals,
iii) it can use ferrous residues from mineral processing or steel plant waste products, as low cost feed to produce pig iron,
iv) typical hot metal chemistry is: 2.5 to 4.2 pct C, 0.02 to 0.04 pct Si, 0.02 to 0.08 pct S, and <0.08 pct P (high quality metal product is suitable for both electric and oxygen steelmaking),
v) unique feature of the process is production of low phosphorous and low sulphur iron from high phosphorous iron ore,
vi) an efficient single stage process not reliant on preheating or pre-reduction of ore feeds,
vii) the furnace operates at sub-atmospheric pressure allowing simple feeding and tapping arrangements,
viii) dust carry-over is low, typically less than 1 pct of the feed rate,
ix) the absence of coke ovens and sinter/pellet plants reduces environmental issues typically associated with ironmaking,
x) the use of a single stage, highly efficient smelter reduces capital requirements for new ironmaking capacity and permits effective use at smaller scales of operation than conventional processes,
xi) the lance based operations offer the ability to start, stop and idle the process easily, and
xii) a waste heat boiler system, directly coupled, can generate sufficient electrical power to supply the ironmaking facility and associated oxygen plant, with surplus power available for sale.

2.2.5.7 AISI-DOE process

American Iron and Steel Institute (AISI) and the Iron and Steel Division of HYLSA have developed this process. The concept was very similar to that for DIOS. The salient features of this pilot plant are given in Table 2.3. The process, as shown in Figure 2.13, uses iron ore pellets/fines and high volatile non-coking coal as feed material. A 5 tph pilot plant was built at Universal, Pennsylvania, USA and operated from1990 to1993. Other pilot scale (8 tph) trials were to start up in 1993. The major findings include [54]:

i) sulphur in hot metal from 0.05 to 0.25 pct,
ii) 10 to 20 pct less P in hot metal than that in BF hot metal for the same ore,
iii) smelting intensity as high as 8.5-9.7 $t/m^3/d$,
iv) heat transfer efficiency of 75-98 pct, and
v) post combustion ranging between 10-15 pct.

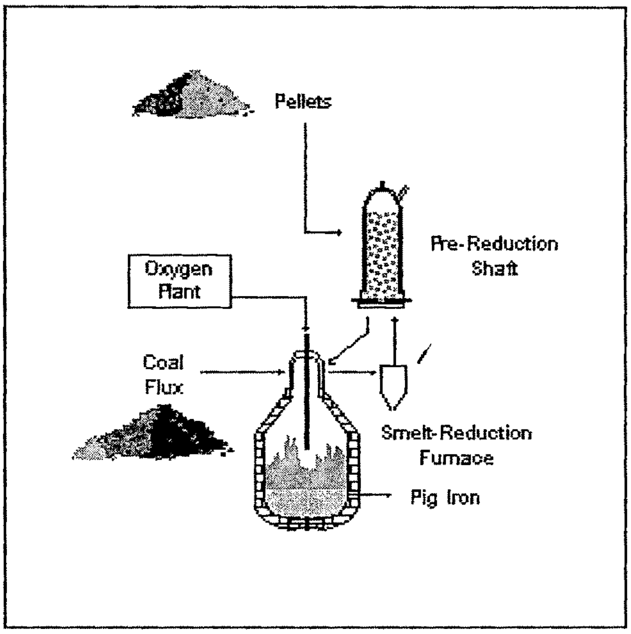


Fig. 2.13: AISI process.

The most noteworthy feature of the AISI-DOE process is that the product is semi-steel. The primary attempt at commercialization revolved around setting up a 0.25 Mtpa revert-based smelter using waste from several integrated steel plants.

2.2.5.8 Redsmelt Process

Demag's Redsmelt technology is capable of producing high quality DRI and hot metal suitable for integrated steel plants and EAF based mini steel plants. In the area of alternative ironmaking processes, Demag offers the rotary hearth furnace (DRHF) for hot DRI production and submerged arc furnace (SAF) to convert the DRI into hot metal. Iron bearing materials (iron ore, steel mill dust, mill scale etc.) and reductants (coal, coke, pet coke etc.) are, if necessary, ground below 200 microns and wet-mixed with organic and/or inorganic binders. This mix is then pelletized in a drum or on a disc to green pellets between 9 to 15 mm in size. The pellets travel on the rotary hearth for 10 to 18 minutes, where they are reduced to DRI. The hot DRI pellets are melted subsequently in a SAF. The demonstration tests in Ellwood City at Inmetco have proven the system on an industrial scale for direct reduction. Tests carried out by Demag have shown that the DRHF process is capable of producing pellets with mechanical and chemical properties suitable for blast furnace processing without noticeable losses due to degradation or re-oxidation. The coal rate is much lower than the other coal-based DRI processes. The electric power and natural gas consumption is also low in comparison to most other processes. Emission of off-gases (CO, SO_x, NO_x etc) and dust are at least one order of magnitude lower than that of blast furnace plant and can be further reduced by introducing commercially proven gas cleaning units. By re-using all the waste water within the plant (e.g., for mixing and pelletizing) the liquid emissions are close to zero. The chemistry of Redsmelt hot metal in pct is: C = 3.60, Si = 0.20, Mn = 0.60, S = 0.05 and S (after desulphurization) = 0.02 [88].

2.2.5.9 Iron Dynamics process

Iron Dynamics International (IDI) was established in 1996 to supply pig iron to electric arc furnaces at SDI's Butler, Indiana Works. The IDI process, as shown in Figure 2.14,

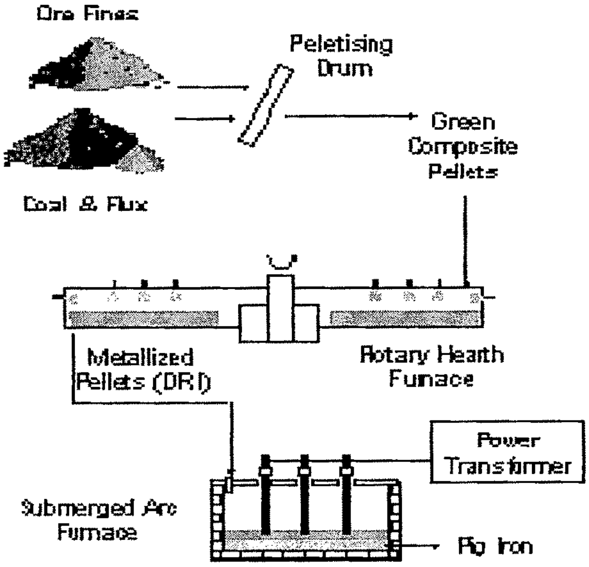


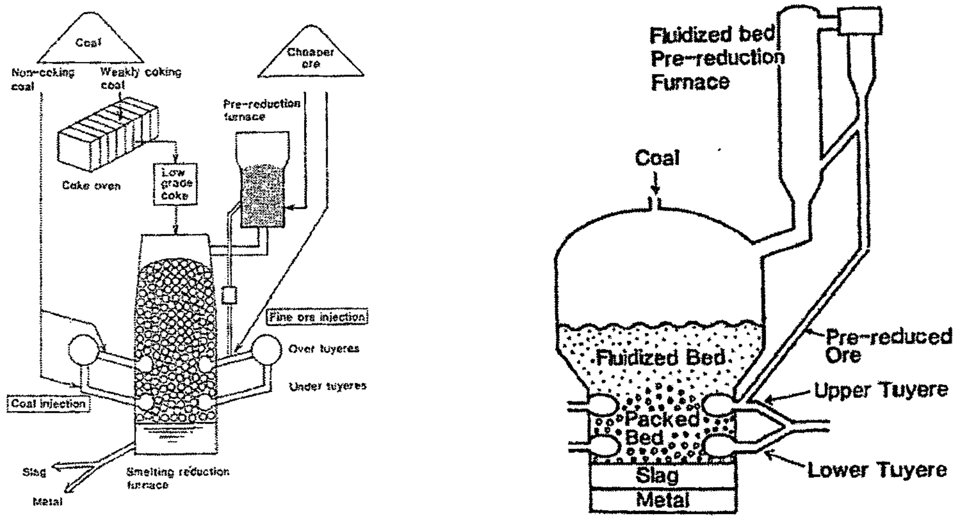
Fig. 2.14: IDI process.

uses a coal-ore composite pellet, which is fed to a rotary hearth furnace (RHF) to make DRI. This (hot) DRI is then fed to a submerged arc furnace (SAF) for melting. The IDI process was essentially a combination of two pre-existing technologies: a Mitsubishi RHF package coupled to a Demag's SAF [58].

2.2.5.10 Kawasaki STAR process

Kawasaki Steel, Japan has developed a new smelting reduction process (Kawasaki's STAR process) with a coke-packed bed for the production of pig iron or ferroalloys. The process uses low grade coke and ore fines. The Stainless Steel Advanced Reactor (STAR) process is characterized by [89]:

i) a coke-packed bed shaft furnace,
ii) installation of two-stage tuyeres,
iii) direct use of fine ore without agglomeration,
iv) a gravitational powder transportation and injection system (through tuyeres), and
v) a fluidized bed pre-reduction furnace for full utilization of a by-product gas.



(a) (b)

Fig. 2.15: (a) STAR process and (b) XR process.

STAR process is shown in Figure 2.15 (a). The 10 tpd capacity pilot plant has been used to produce pig iron and ferrochromium. Iron ore fines are pre-reduced in multiple fluid beds and transferred to a moving coke bed where further heating and reduction is accomplished by a hot air blast. The pilot plant tests were carried out successfully in 1986. Several kinds of metals such as iron and ferrochromium were produced using low grade coke and fine ores. Good fluidity of the slag is very important to maintain stable continuous operation. Good desulphurization was achieved in spite of the relatively low basicity, ranging from 1.0 to 1.2. Top gas temperature varied in the range of 973-1273 K, and was mainly dependent on the coke ratio. It is evident from the results of the pilot plant tests that the STAR process is preferable to conventional methods of producing ferroalloys such as ferrochromium. The use of coke in the furnace is a big process disadvantage.

Further development has concentrated on the Excellent Kawasaki Smelting Reduction (XR) process which uses coal rather than coke. The process is shown in Figure 2.15 (b). The smelting vessel appears similar to Corex. The main differences are the direct injection of pre-reduced fines into the smelting vessel and the use of a circulating fluid bed for fines reduction. A 10 tpd pilot plant has been built at the Chiba works.

2.2.5.11 Fastmet process

The success of rotary hearth furnace (RHF) based DRI technology has led to the development of Fastmet process. Midrex Technologies in partnership with its parent company, Kobe Steel Ltd, Japan have developed the Fastmet process as a carbon based reduction technology; applicable for processing iron ore as well as iron oxide containing materials such as steel mill wastes. From both economical and environmental points of view, Fastmet process is very attractive as a proven technology for dust recycling. The process shows excellent promise for application to Indian *blue dust* [90].

The Fastmet process converts iron oxide pellet feed, oxide fines and/or steel mill wastes into metallized iron in a rotary hearth furnace using pulverized coal or other carbon-bearing material as a reductant. The product can be cold DRI, hot DRI, HBI or hot metal depending on end use requirements. The RHF is a flat, circular refractory hearth rotating inside a high temperature, circular tunnel kiln. A water seal is used to 'seal' the interface between the rotating hearth and the tunnel kiln preventing air and flue gas leakage. Prepared feed for RHF typically consists of composite agglomerate (either pellets or briquettes) made from a mixture of iron oxide and a carbon source such as coal, coke fine, charcoal or other carbon bearing solid. The feed agglomerates are placed on the hearth evenly, one or two layers thick. Burners located above the hearth provide heat required to raise the feed agglomerates to reduction temperature and start the process. The burners are fired with natural gas, fuel oil, waste oil, or pulverized coal. Most of the heat required for maintaining the process is supplied by combustion of volatiles, which are liberated from the heated reductant, and combustion of carbon monoxide, which is produced by the reaction of carbon reducing metallic oxides. The agglomerates are fed and discharged continuously and stay on the hearth for less than one revolution, typically 6-12 minutes, depending on the reactivity of feed mixture and target product quality [91].

In 1995, Midrex and Kobe Steel built a demonstration-scale facility (2.75 tph) at Kobe Steel's Kakogawa Steel Works, Japan to demonstrate the commercial Fastmet operation. The first Fastmet commercial facility of 0.19 Mtpa DRI at Hirohata Works of Nippon Steel Corporation, Japan started production in April 2000. Typical degree of metallization of the product was 92.9 pct. The second commercial Fastmet plant for steel mill waste processing became operational at Kobe Steel's Kakogawa Works in May 2001. The DRI produced by Fastmet process is fed to an Electric Ironmaking Furnace (EIF), developed by EMC International, a sister concern of Midrex. This has led to the development of Fastmelt technology, an economical solution for production of high quality metal known as FastIron. Typical chemistry of FastIron in pct is: C = 4.54, Si = 0.47, Mn = 0.10, S = 0.013 and P = 0.036 [92].

Energy consumption is most important in today's era of high energy costs and environmental concern. Table 2.2 compares Fastmelt process with other ironmaking processes on an equivalent GJ per tonne of hot metal basis [91].

Table 2.2: Energy consumption in ironmaking processes

Energy (GJ per tonne of hot metal)	Fastmelt	HIsmelt	Corex	Redsmelt	Blast Furnace
Coal	12.24	19.47	30.87	14.85	
Natural gas	2.68	2.20	0.50	2.17	
Electricity	6.11	3.38	0.83	6.65	
Sub-total	21.03	25.05	32.10	23.67	23.36
Off-gas energy credit	4.56	3.38	13.20	5.10	5.35
Total Energy	16.47	21.67	18.90	18.57	18.01

2.2.5.12 Ironmaking Technology Mark 3 (ITmk3) process

ITmk3 represents the next generation of modern ironmaking technology. It is a unique technology developed and owned by Kobe Steel Ltd, Japan for smelting iron ore fines using non-coking coal to produce premium grade iron in the form of nuggets. The heart of the ITmk3 process is the rotary hearth furnace (RHF) where iron ore fins are reduced and smelted using pulverized coal. The process flow sheet, as shown in Figure 2.16, depicts various units and sub-units used in the ITmk3 process. The Mesabi Nugget demonstration plant, Japan commissioned in July 2004 achieved continuous, reliable production of iron nuggets under commercial operation conditions. Ten thousand metric tonnes of quality iron nuggets were produced during the four test campaign. These iron nuggets were consumed in the steelmaking operations at various North American locations [91].

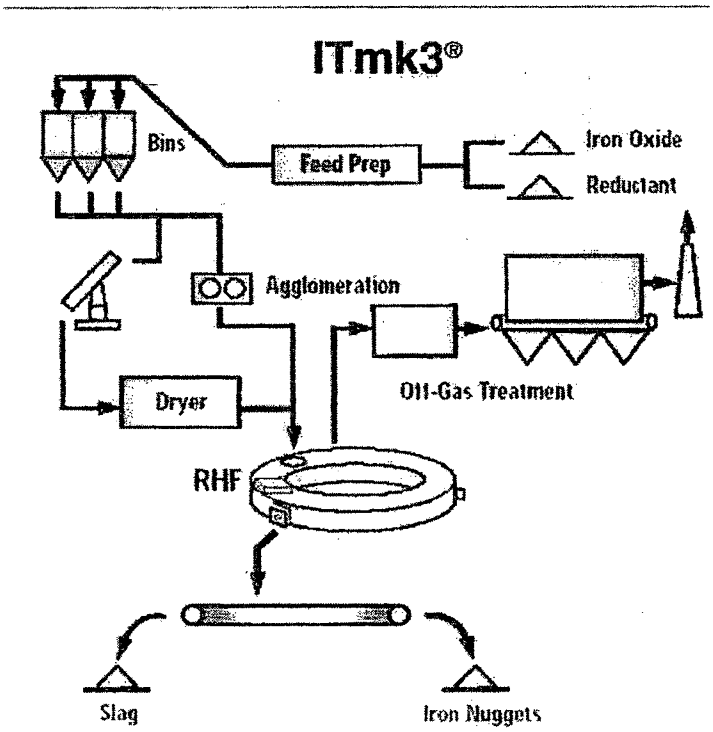


Fig. 2.16: ITmk3 process.

The ITmk3 process is an ideal vehicle for iron ore mining companies to supply pig iron grade nuggets directly to the EAF steelmaking industry. A typical composition of nuggets in pct is: metallic iron = plus 97, C = 2.0 - 2.5, S = 0.07 - 0.10 and P = 0.01 - 0.02. ITmk3 nuggets are a metallurgically clean and dust free source of alternative iron for high quality EAF steelmaking and foundry iron castings. The ITmk3 process emits 20 pct less CO_2 than blast furnace operations. These nuggets are not prone to reoxidation and do not require special handling during shipment. Because of their convenient form, these nuggets can be continuously fed to the steelmaking furnace for higher productivity and lower liquid steel cost. KWIKSTEEL, Japan represents an extension of modern ironmaking technology that combines the best of natural gas-based Midrex direct reduction with ITmk3-type technology.

2.2.6 Smelting reduction processes -- A comparative study

The characteristic features of some of the smelting reduction processes, which have gone up to pilot plant scale and are ready for commercialization (Corex process has already been commercialized almost nineteen years back in the year 1989) are given in Table 2.3.

Table 2.3: Characteristic features of some smelting reduction processes

Parameter	Corex	Romelt	HIsmelt	Ausmelt	DIOS	AISI-DOE
Developer	Korf Stahl, Germany and Voest Alpine, Austria	Mascow Institute of Steel and Alloy, Russia	Klockner Germany & CRA Ltd. Australia, Presently taken over by Rio Tinto Group	Ausmelt Ltd., Australia	Japan Iron and Steel Federation (JISF), and a consortium of eight Japanese Steelmakers.	American Iron and Steel Institute (AISI) and Iron and Steel Division of HYLSA
Pilot / Commercial plant size, tph	83 (commercial -ized)	18	14	2	21	5
Operating pressure, bar	5	<1	1.5 – 1.8	<1	3 – 4	1.7
Post combustion	5 – 10	50 – 70	60 – 80	100	> 45	> 40

degree, pct						
Heat transfer efficiency, pct	-------	60 – 70	95	70	85	75 – 98
Heat transfer medium	Via fixed bed	Foaming slag layer	Slag-metal transition zone	Foaming slag layer	Foaming slag layer	-------
Reductant / Energy	Non-coking Coal, Oxygen	Non-coking Coal, Oxygen	Non-coking Coal, Oxygen, Electricity	Lump/ powdered coal, Air/ Oxygen	Non-coking Coal, Oxygen, Electricity	Volatile coal, Oxygen, Electricity
Coal consumption, kg/thm	1060	800	700	1014	900	-------
Oxygen consumption, Nm^3/thm	586	695	300	740	520	-------
Type of reactor	Shaft reduction & Melter - gasifier	Horizontal rectangular reactor (water cooled)	Circulatory fluidized bed (water cooled vertical vessel)	Converter / Channel type	CBF or Bubbling bed (water cooled panels)	HYL Shaft
Smelting	In-bed melting of ore, gasification of coal	In-bath smelting	In-bath smelting	In-bath smelting	In-bath smelting	-------
Pre-heat temperature, K	> 1023	--------	> 1073	--------	> 1073	> 1073
Pre-reduction degree, pct	80 – 85	--------	< 30	--------	< 30	< 30
Ore type / Preferred size, mm	Lump ore, Sinters, Pellets (8–20 mm)	Fines, Lump (0–20 mm)	Fines	Lump ore, Fines	Fines	Pellets, Fines, Scraps
Total energy input, GJ/thm	-------	25.2	25.9	-------	25.7	-------
Energy recovered from turn off	11.76	2.8	7.6	7	10.2	-------

gas, GJ/thm						
Net energy, GJ/thm	15.5	22.4	18.3	-------	15.5	-------
Environmental evaluation w.r.t. Blast Furnace	Good	Fair	Fair	Good	Good	Good
Production cost w.r.t. Blast Furnace	11 pct more	1 pct more	-------	-------	-------	-------
Overall ranking based on techno-economic evaluation	III	IV	I	I	II	-------
Combustion medium	Highly O_2 intensive	Highly O_2 intensive.	Less O_2 intensive	Highly O_2 intensive	Highly O_2 intensive.	-------
Process response	3 – 4 hours	Fast	Very fast (seconds)	Fast	Fast	-------
Number of stages	Two stage (three steps) process	Single stage process	Single stage process	Single stage process	Two/Three stage process	-------
Reductant's characteristics	Blend of non coking coal; Moisture < 5 %, FC: 55 - 65 %, VM: 20-30%, Ash: 5-12%, S: 0.4-0.6%, Size range: 5-40 mm.	Non-coking coal; Moisture: 10 % max, VM: 30% max., Ash: < 25%. Size range: 0 - 20 mm.	Non-coking coal fines; FC: 50 -73 %, VM :10 - 38 %, Ash : 5 -12%, Size range: - 6mm	Non-coking coal; Use of low-grade non-coking coal is claimed.	Non coking coal; VM: up to 37%, Size: -25mm	Volatile coal
Oxygen	High purity O_2 >95%.	Mixed blast lower lance: 50% air+ 50% O_2, Upper lance:	Preheated 1200 °C, O_2 enriched air, O_2/Air fed into the	Use of O_2 enriched air (30-50%).	O_2 enriched air, High purity O_2 > 95%.	------

		100 % O_2, Purity >90%	vessel through a central lance.			
Process off-gas	Medium CV (prereduction and power generation)	Medium CV (power generation)	Low CV (Air based – high PC)	Medium CV (power generation)	Medium CV (power generation)	------
Quality of hot metal (chem. composition , pct)	C: 4.5 - 4.7, Si: 0.6 - 0.8, S: 0.01-0.02, P <0.10	C: 4.0 - 4.8, Si:0.01-0.10, S: 0.02-0.05, P: 0.05- 0.15	C: 4.0 – 4.5, Si: 0.0, S : 0.08, P < 0.05	C: 2.4 - 4.2, Si: 0.02-0.04, S : 0.02 -0.08, P < 0.08	C: 3.0 – 3.5, Si < 0.05, S < 0.05, P: 0.05 -0.10	------
Tapping	Hot metal and slag are periodically tapped through one tap hole at pressure	Separate tap holes for hot metal and slag, with free outflow	Vessel is equipped with four hearths for continuous tapping of hot metal	Hot metal and slag are tapped periodically through a tap hole	Hot metal and slag are tapped through a tap hole	------
Tapping temperature, K	1763 -1793	1623 -1773	1743 - 1773	1673 -1773	1773 - 1823	------
Refractory	Problem in tap-hole region	Extensive use of water cooled panel	Hearth area minimal wear	-------	High wear (High slag temperature)	------
Stop and go ability	Good	--------	Poor	-------	Fair	Fair

2.2.7 Advantages and limitations of smelting reduction processes

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 [64]:

i) lower capital cost due to lower economic scale of operation,
ii) lower operating cost primarily owing to the use of non-coking coal,

iii) higher smelting intensity with higher productivity (due to faster reaction kinetics, increased transport rate due to convection, and an increase in the convection rate due to enlargement of specific phase contact areas in dispersed phases),
iv) direct utilization of iron ore fines and coal fines,
v) no requirement of expensive coking coal,
vi) possible elimination of sinter / pellet and coke plants,
vii) decrease in manpower requirement and reduced operational cost,
viii) environmental friendliness (due to lower emissions),
ix) maintain the same level of hot metal quality as obtained in blast furnace,
x) better control over process parameters,
xi) flexibility in selection of thermo-chemical configuration,
xii) faster reduction,
xiii) recycling of existing stock-piles, in-plant dusts, sludge and other reverts wherever and to the extent possible, and
xiv) 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.

Limitations [64]:

i) consumption of large amount of oxygen, the generation of which requires high amount of power consumption (0.6 KWh / Nm^3 of oxygen),
ii) the process generates large amount of high calorific value export gas and the economic viability of the process depends on its efficient utilization,
iii) 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,
iv) pre-reduction of ore fines is mandatory, and
v) needs highly efficient post combustion necessary to meet the energy requirement of the smelting processes.

2.2.8 Kinetics of smelting reduction of composite pellets in liquid bath

Research and developments have been going on throughout the world to understand more about the mechanism and dynamic behaviour of bath smelting such as slag foaming, dissolution kinetics of carbon in liquid iron bath, reduction of iron oxide in slag, role of post combustion etc.

According to Bafghi et al [93], kinetic studies pertinent to the smelting reduction of iron oxide are mainly conducted in three fields:

i) reduction of molten iron oxide (pure or in slag) with solid carbon,
ii) reduction of molten iron oxide with solute carbon, and
iii) reduction of molten iron oxide with carbon monoxide.

Laboratory studies are essential to understand the important aspects of smelting reduction processes e.g. kinetics of FeO reduction and foaming of slag. Laboratory data not only relate to actual rector conditions but are also useful for reactor design. The foaming behaviour and reduction kinetics are interrelated and they are largely determined by slag properties, viz. density, viscosity, surface tension and temperature. Some of the important investigations by researchers in the field of smelting reduction are summarized below.

Kondokov et al [94] studied the reduction of liquid ferrous oxide in a graphite crucible in the temperature range of 1723-1923 K and established that the reduction rate increased with increasing pressure. They concluded that the carbon gasification reaction is the rate-controlling step because the activation energy measured for the FeO reduction (159.83 kJ/mol) was close to the activation energy for the carbon gasification reaction (125-270 kJ/mol).

Reeve and Walsh [95] investigated the reduction behaviour of composite pellets of wustite and carbon in the region of 1679-1725 K in argon atmospheres. Both wustite and carbon particles were screened to -325 mesh and experiments were done at carbon percentages between 14.3 and 20 pct. The composite pellets were prepared using approximately 5 pct bentonite. The activation energy for the reduction reaction was 87.86 kJ/mol. Gas chromatographic analysis result, after the reduction, showed the presence of both CO and CO_2 in the system. For wustite-carbon composite pellets, surrounded by a protective layer of carbon, reduced in oxidizing atmospheres a value of 62.76 kJ/mol was obtained for the activation energy. The same value was obtained for NiO-carbon composite pellets surrounded by carbon between 1711 and 1791 K in pure oxygen. Hematite composite pellets in pure oxygen gave activation energy of 104.6 kJ/mol. In all experiments, in pure oxygen, gas analysis showed only CO_2 as a reaction product, indicating complete burning of CO to CO_2.

Sato et al [96] worked on the rate of melting of cylindrical pellets in a carbon saturated melt. According to their work, the melting rate of the pellets was enhanced by increasing the carbon content of the bath, carbon content of the pellet and residual oxygen content of the pellet. Further, they measured the melting rate as a function of gas evolution from the pellet. They demonstrated that the melting rate increases with decreasing gangue content and decreasing melting point of the slag. The apparent activation energy for melting was found 138 kJ/mol; value from which they concluded that the process was controlled by the rate of heat transfer.

Sommerville et al [97] studied the kinetics of reduction of iron oxide in slag by carbon dissolved in iron. They found that the reduction rate was governed by the reaction occurring at the gas-metal interface for iron oxide content below 2.5 pct. Above this value, the gas-slag interfacial reaction might took over as the rate determining one. They [98] further observed that the presence of gas bubbles at the slag-metal interface played a very significant role in determining the mechanism of reduction of low concentrations of ferrous oxides in slag by iron carbon alloys. They concluded the gaseous decarburization of iron by CO_2 to be the rate controlling step.

Seaton et al [99] performed experiment on rate of dissolution of pre-reduced iron in molten steel. Reduced pellets from Midrex and HyL process and laboratory made pellets containing coal char were used. The melting tests were performed in an induction furnace using a 6 kg capacity magnesia crucible. The dissolution of the pellets was accompanied by continuous gas evolution and bath agitation which was due mainly to the reduction of iron oxides remaining in the pellets by the carbon within the system. They found that HyL pellets dissolved faster than Midrex and Midrex pellets dissolved faster than laboratory made pellets. This behaviour was attributed to the difference in composition and physical structure of these pellets. The rate of heat transfer from the bath to the pellet was found to increase with increasing gas evolution.

Sato et al [100] investigated the reduction rate of iron oxide in molten slag by carbon in molten iron. They found that the reduction rate was proportional to the second power of the iron oxide content in the molten slag except for the starting and the ending periods of the experiment. The rate constant of the slag-metal reaction in an alumina crucible was smaller than that in a graphite crucible. The maximum rate constant of the reduction of iron oxide in the molten slag by carbon in the molten iron was observed at slag basicity of around 1.5.

Yusheng and Ting [101] studied the kinetics of FeO reduction by solid carbon, solute carbon and carbon monoxide. They found that for slag containing 20-80 wt pct FeO, the reaction was of first order while it was of second order for slags containing FeO less than 20 wt pct with solid carbon as a reductant. The rate controlling steps were diffusion of FeO and convection of heat for slag containing FeO less than 80 wt pct. In case of reduction of molten FeO by CO, the rate of reduction was found proportional to the square root of flow of CO through melt and the rate controlling step was diffusion transport of FeO. The rate of reduction of molten FeO by solute carbon was found 10 to 100 times higher than that by solid carbon or carbon monoxide.

Basu [102] has reported that the reduction of iron oxide rich slags in a carbon saturated iron bath follows first order kinetics in the temperature range of 1573-1773 K. He also showed that the rate increases with increasing CaO/SiO_2 ratio, but after a value of 1.5, the rate decreases. He also used optical basicity as an additional kinetic parameter for study of reduction of FeO. The slag basicity keeps on changing due to changes in the percentage FeO content in the slag. This is automatically reflected in the optical basicity index since it is defined in terms of a ratio such as CaO/SiO_2.

Bafghi et al [93] studied the kinetics of the reduction of iron oxide in molten slag, held in alumina crucible under argon gas atmosphere. The composition of the primary slag was 20.5 pct Li_2O, 38.4 pct CaO, and 41.1 pct SiO_2. The initial concentration of iron oxide was changed between 3 pct and 12.5 pct. The experimental temperature was 1573 K. The reaction rate was largely affected by slag foaming. At higher FeO concentrations, the apparent rate constant was almost independent of the mechanical stirring. At lower FeO concentrations, the effect of rotation on the apparent rate constant was found to be small at lower speeds but tended to become larger at higher speeds. This was an indication that the melt was strongly agitated by CO gas bubble evolution. The rate of reduction is controlled predominantly by the mass transfer in the slag phase.

Min and Fruehan [103] investigated the reduction of Fe-C droplets (containing 2 to 5.5 wt pct carbon) in a CaO-SiO_2-FeO slag and found that the rate of reaction was proportional to the FeO content. The rate of reduction decreased with decreasing carbon content. It also decreased significantly with increasing sulphur content. They concluded that the diffusion of FeO in slag was rate controlling.

Katayama et al [72] reported the reduction of iron oxide in the smelting reduction process with a thick layer of slag through 5 t and 100 t experiments at 1753 ± 30 K. A large amount of carbonaceous material (coal or coke) was required in the slag layer for efficient smelting reduction in terms of reduction, recarburization, and heat transfer. They observed that the amount of slag and carbonaceous material, bath temperature and the intensity of bath stirring predominantly influenced the overall rate of reaction. The rate constant increased with increasing stirring intensity of metal bath and with an increasing amount of carbonaceous material. The apparent activation energy in 5 t and 100 t melt experiments were 117.15 and 75.31 kJ/mol respectively.

Krishna Murthy and Elliott [104] studied the reactions of Fe-C melts with wustite, hematite and partially metallized iron oxide pellets. They investigated the effects of pellet type, size, shape, and initial temperature as well as bath temperature. They found that the time for complete reaction (t_R) was the same for both wustite and hematite pellets of equal weight at or above 1723 K, but longer than that for partially metallized pellets. The shape of pellets did not show any noticeable effect on t_R. The initial pellet temperature also did not show any effect on the reduction rates. They [105] further investigated the mechanism of iron oxides reactions with Fe-C melts. They observed the reduction rates of iron oxides as a function of several operating variables. The time for complete reaction (t_R) of pure synthetic wustite and hematite decreased with increasing melt cross-section area. The agitation of the melts did not show any effect on the reaction rates. The reaction rate of commercial oxide pellets was several times lower than that of the pure synthetic oxide pellets.

Street et al [106] investigated the reduction and dissolution behaviour of composite pellets, prepared from ferruginous and organic wastes from an integrated steel plant, using bath smelting technology. Smelting of pellets occurred rapidly taking approximately 45 to 60 sec for dissolution at temperature of 1773 K. A short incubation period preceded pellet smelting, which lasted for few seconds, that was attributed to the formation of a slag crust on the pellet during initial contact with slag. Pellet dissolution appeared limited to the interface between the pellet and slag. Cross sectioning of the pellets revealed a diffused reaction front. Porosity was also increased during smelting. The reaction front indicated the existence of a temperature gradient within the composite pellet. X-ray diffraction and microscopy revealed that little metallic iron was produced in the early stage of smelting.

Prakash et al [107] studied the reduction kinetics of iron oxides in molten slag by dissolved carbon in liquid iron melt and the behaviour of phosphorous transport at the slag/metal interface during smelting of prereduced iron ore. The variables of their studies were: reduction time, temperature of the molten slag, and the major constituents in the molten slag. They observed that the reduction rate was enhanced by higher basicity and a lower degree of reduction, i.e. higher initial FeO content in molten slag. The reduction of FeO in molten slag by bath carbon is controlled by the chemical reaction at the interface.

Paramguru et al [70] worked on the reduction of FeO in molten $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}MgO\text{-}FeO$ slags by solid carbon in an extended-arc plasma reactor. They analyzed the effect of slag characteristics and consequent foaming behaviour on the rate of reduction of FeO by solid carbon. The reduction reaction was found to be controlled by mass transport of FeO in liquid slag. The CO gas generated in the process stirred the bath to establish a convective mass transport system. The CO gas generated also caused foaming and affected the reaction rate significantly. The foaming index (Σ) and the rate constant (k) can be expressed in terms of the slag characteristics such as viscosity (μ), surface tension (γ), and density (ρ) using a dimensionless analysis [$\Sigma = k\,\mu/(\rho\gamma)^{0.5}$]. They also examined the correlation using optical basicity as a kinetic parameter for reduction of FeO in CaO-FeO-SiO_2 slag by carbon saturated iron bath.

Lee et al [66] investigated the kinetics of the smelting reduction of iron ore by carbon in the graphite crucible and the carbon-saturated molten iron at high temperature ranging 1673 to 1823 K. They observed that the smelting reduction reaction proceeded by the following two stages: firstly, an initial quiet reduction without foaming, and secondly, a highly active reduction with severe foaming. They concluded that these two types of smelting reduction reactions of iron ore by the graphite crucible and by the molten iron are essentially the same. The overall reaction rate was controlled by carbon gasification reaction.

Min et al [108] studied the kinetics of smelting reduction of FeO in CaO-SiO_2-FeO slag by solid carbon by using the mass spectrometer technique. They observed that:

i) The reduction rate of FeO increased with increasing FeO activity in the slag.

ii) The rate of reduction decreased with decreasing carbon content and increasing sulphur content.

iii) The rate determining step would change from the mass transfer of FeO at a low FeO content (<5 wt pct) to the chemical reaction at a high FeO content (>30 wt pct). The diffusion of FeO in the slag was rate controlling.

Goswami et al [109] investigated the kinetics of smelting reduction of unreduced fluxed composite pellets and fluxed composite pre-reduced iron ore pellets in an induction furnace. The pellets were charged into the slag layer floating on the carbon saturated molten iron bath in a graphite crucible. The temperature of the slag was varied within the range of 1623 K to 1823 K for the pellets of basicity 2. Kinetic studies showed a mixed kinetic model of both diffusion and chemical reaction controlled. Although the kinetics of reaction increased with increase in temperature and basicity, the basicity dependence on the kinetics is not very significant.

Lee et al [110] studied the effect of various operational parameters such as bed height, carbon to oxygen (C/O) ratio, operating pressure, and steam injection ratio on the transport phenomena in the Corex melter-gassifier. Increase in bed height resulted in increase of temperature near the combustion zone. Operational pressures affect the rate of tar in the coal. The variation in the C/O ratio affected the heating rate of coal followed by a drastic change in the heat and mass transfer of solid and gas phases. The C/O ratio variation also changed the tar evolution rate, coal heating rate, overall reactor temperature, and the gas phase composition. From these considerations, the C/O ratio should be carefully controlled for the stable operation.

Sarma et al [111] investigated the reduction of CaO-SiO_2-Al_2O_3-FeO slags containing less than 10 pct FeO by solid carbonaceous materials such as graphite, coke and coal char at reactions temperature from 1673 to 1723 K. The rate of CO evolution from the system was measured using stationary and rotating carbon rods as the reductants. They measured reaction rates ranged from 3.25×10^7 mol cm^2 s^{-1} at 2.1 pct FeO under static conditions to 3.6×10^6 mol cm^2 s^{-1} at 9.0 pct FeO for a rotating rod.

Seo and Fruehan [112] studied the kinetics of the reaction of the blast furnace hearth slags, containing low amounts of FeO (less than 3 pct), with solid carbon. They found that the reaction rate of FeO is independent of the type of coal used. The rate of CO gas evolved increased with increasing FeO content. The overall rate is controlled by a series of processes such as the reaction of CO_2 with C, CO with FeO in slag, liquid phase mass transfer of FeO in slag, and gas phase mass transfer. For low FeO contents, the liquid phase mass transfer was found the rate controlling mechanism.

Jouhari et al [113] worked on the kinetics of FeO reduction in molten (synthetic) slag using a graphite crucible in a 50 kW dc capacity plasma reactor. The crucible surface served as reductant. The influence of initial FeO concentration in the slag, crucible diameter, basicity, initial slag height, and CaF_2 addition on reduction rate had been investigated. They observed that:

i) the diffusion of FeO in the slag phase controls the reduction rate,
ii) the rate constant increased with increase in FeO concentration and temperature, and
iii) the rate constant decreased with increase in initial slag height.

Galgali et al [114] studied the reduction behaviour of 5 to 20 wt pct FeO in a synthetically prepared slag by various reductants like coal, coke, carbon from graphite crucible and solute carbon in iron bath in a 35 kW dc extended arc plasma reactor. They reported that:

i) the rate of reduction increased with increase in initial FeO content of the slag,
ii) the slag height increased with increase in FeO concentration of the slag, and
iii) the reduction reaction follows first order reaction kinetics and is controlled by mass transfer.

Bhoi et al [115] investigated the reduction of FeO in CaO-SiO_2-FeO slag containing FeO in the range of 20-40 wt pct by solute carbon in pig iron and by solid carbon as pure graphite substrate in the temperature range of 1573-1773 K where CaO/SiO_2 ratio was fixed at one. They observed that the reduction of FeO by solute carbon in pig iron is much faster than that by solid carbon as pure graphite substrate. The reaction rate constant was found to increase with increasing FeO content in slag.

Molloseau and Fruehan [116] studied the reduction behaviour of FeO by carbon in iron droplets for CaO-SiO_2-MgO slags containing 3 wt pct to 35 wt pct FeO and temperature ranging from 1643 K to 1763 K. It was found that the behaviour of the metal droplets in the slag changed significantly with FeO content in the slag. They observed that below 10 pct FeO the droplets remained intact while reacting with slag and the reaction rate was controlled by dissociation of CO_2. But above 10 wt pct FeO concentration, the metal droplets became emulsified within the slag and increased the surface area and reaction kinetics tremendously. The reaction rate was controlled by mass transfer of FeO as Fe^{2+} and O^{2-} ions.

Li and Ratchev [117] worked on the rate of interfacial reactions between molten CaO-SiO_2-Al_2O_3-Fe_xO slags and CO-CO_2 at temperatures ranging from 1673-1873 K and 5 to 20 wt pct FeO. They observed that, at a given iron oxide concentration, the reduction rate constant increased significantly with an increase in the CaO/SiO_2 ratio.

List of laboratory experimental set-up adopted by various investigators in smelting reduction studies is well reviewed by Jouhari et al [118] and further updated by present author that is shown in Table 2.4.

Table 2.4: Laboratory experimental set-up adopted by various investigators in smelting reduction studies

Reference	Heating system	Crucible material	Remark
Fay Fun (1970), [119]	Induction furnace	Magnesia	Reduction of FeO by solid carbon (graphite rod)in CaO-SiO_2 slag
Lloyd et al (1975), [120]	Induction furnace	Alumina	Reduction of FeO by solid carbon
Borgianni (1978), [121]	Tammann furnace	Vitreous graphite	Reduction of FeO rich slag by coke
Sommerville et al (1980), [97]	SiC furnace	Alumina	Reduction of FeO in slag by solid carbon
Upadhyay et al (1980), [98]	SiC furnace	Alumina	Reduction of FeO in slag by solid carbon
Sato et al (1984), [100]	Tammann furnace	Alumina as well as Graphite	Reduction of iron oxide (FeO) in molten slag by carbon in liquid iron and solid carbon (graphite)
Ito and Fruehan (1989), [122]	Electric furnace	Alumina	Foaming of slag by argon injection
Jiang and Fruehan (1991), [123]	Induction furnace	Alumina	Foaming of slag by argon injection
Katayama et al (1992), [72]	BOF converter (5 t and 100 t capacity)	Magnesite and tarred dolomite lining	Reduction of iron oxide by solid carbon added from outside (bath having thick layer of slag)
Bafghi et al (1992), [93]	SiC furnace	Alumina	Reduction of FeO in slag by solid carbon
Min and Fruehan (1992), [103]	SiC furnace	Alumina	Reduction of FeO in slag by Fe-C drops
Kitamura and Okohira (1992), [124]	Tammann furnace	Graphite	Reduction of FeO by solute carbon

Ogawa et al (1992), [125]	SiC resistance furnace	Graphite	Reduction of iron oxide by solid carbon (graphite, coke, glassy carbon)
Utigard and Zamalloa (1993), [126]	SiC furnace	Alumina	Foaming of slag by argon injection
Krishna Murthy and Elliot (1994), [104, 105]	Induction furnace	Graphite	Reduction of FeO by solute carbon
Galgali et al (1997), [127]	Plasma reactor	Graphite (zirconia lined)	Reduction of FeO rich slag by coal, coke, carbon from graphite crucible and solute carbon in iron bath
Lee et al (1997), [66]	Electric furnace with SiC heating element	Graphite	Reduction of iron oxide by solid carbon and carbon saturated molten iron bath
Paramguru et al (1997), [70]	Plasma reactor	Zirconia lined graphite	Reduction of FeO in $CaO-SiO_2-Al_2O_3-MgO-FeO$ slag by solid carbon
Jouhari (1997), [128]	Plasma reactor	Graphite	Reduction of FeO in slag by solid carbon
Street et al (1997), [106]	DC arc furnace,	Magnesite lining	Reduction of steel dust-organic waste composite pellet in slag phase
	Induction furnace	Alumina	Reduction of steel dust-organic waste composite pellet in slag phase
Prakash et al (1997), [107]	Tamman furnace	Graphite	Reduction of FeO in slag by solute carbon in liquid iron and solid carbon from graphite crucible
	Submerged arc furnace	Alumina	Effect of bath carbon gradient on the reduction of FeO in slag
Goswami et al (1999),	Induction	Graphite	Reduction of FeO in slag by carbon

[109]	furnace		saturated molten iron bath
Bhoi et al (2002), [115]	Electric heated tube furnace	Platinum	Reduction of FeO in slag by solute carbon in pig iron bath and solid carbon from graphite substrate
Molloseau and Fruehan (2002), [116]	Induction furnace (Ar-atmosphere)	Magnesia	Reduction of FeO by carbon in iron droplets
Santosh and Maurao (2004), [48]	Induction furnace	Graphite	Reduction of iron oxide (FeO) by carbon dissolved in liquid iron
Bhoi et al (2006), [129]	Induction furnace	Graphite	Reduction of FeO in CaO-SiO_2-FeO slag by solid carbon
Bhoi et al (2006), [130]	Induction furnace	Alumina	Reduction of FeO in slag by solute carbon in pig iron bath

Bandyopadhyay et al [131] used five different types of carbons (nut coke, charcoal, pet coke, coal, and graphite) to study the effect of different physical properties of carbon on dissolution characteristics. They found that the ash content in the carbonaceous materials has very significant influence on the dissolution kinetics. Increase in temperature enhanced the dissolution rate. Surface active agent like silicon was found to promote the rate of dissolution. Preliminary results of a mathematical model indicated that the dissolution process is mass transfer controlled.

K. Ohno et al [132] studied the kinetics of the carburization phenomenon during smelting reduction. They observed the reaction between carbon, slag and iron at the ironmaking temperature by a laser scanning microscope coupled with an infrared image-heating furnace and a special assembly, where iron and carbon did not contact each other directly as molten slag was placed in between. They observed that:

i) the rate of Fe-C particles movement was very fast and the iron was carburized without a direct contact with carbonaceous materials during smelting reduction, and
ii) the amount of carbon supplied by Fe-C particles balanced with that diffused into the iron.

Roodsari and Conochie [133] investigated the influence of slag formed from gangue and ash content on the melting behaviour of ore-coal composites at 1583 K. The composite pellets with CaO/SiO_2 ratios of 0.13, 0.54 and 1.42 were used in the experiments. Alumina was kept constant at 15 wt pct of the total gangue and ash content. For each CaO/SiO_2 composition, the total gangue and ash content was 15, 10 or 5 wt pct of feed. They reported that:

i) the behaviour of ore-coal composites was dependent on slag composition,
ii) unreduced iron oxide in the core of the pellet played an important role in the melting behaviour of the pellets by lowering the melting point of the slag, and
iii) at low heating rates, the TG/DTA tests showed that the sample with the highest amount of lime ($CaO/SiO_2 = 1.42$) reduced to higher degree in the solid state.

Khanna et al [134] studied the dissolution rates of four different coal-chars (ash content ranging from 9.04 to 12.61 wt pct) in liquid iron at 1823 K by carburizer-cover method. Two-stage behaviour in carbon pickup by the liquid iron was observed; stage-I, with a short period of contact, showed a much higher rate of carbon dissolution as compared to stage-II. The slow rate of carbon dissolution in stage-II was attributed to high levels of interfacial blockage by reaction products. They concluded that the chemical reactions at the interface play an important role in determining the rate of char dissolution in liquid metal.

Carbon dissolution in liquid iron has been intensively studied with various carbonaceous materials due to its importance in future blast furnace ironmaking and alternative iron smelting processes. The rate of this reaction was conventionally considered to be limited by the mass transfer in liquid iron. When a solid carbon material contacts with liquid iron, the dissolution of carbon occurs through two elementary steps [135]:

i) dissociation of carbon atoms from solid structure into liquid at the solid-liquid interface, and
ii) mass transfer of carbon from the interface into liquid bulk.

When carbon dissolution is limited by mass transfer, the equilibrium of reaction will be achieved at the interface. The carbon dissolution rate is influenced by the solid-liquid contact area.

2.2.9 Kinetics of smelting reduction -- A comparative study

A summary of studies of reduction kinetics of iron oxides by carbonaceous materials by several investigators are presented in Table 2.5.

Table 2.5: Published work on direct reduction of iron oxides by carbonaceous materials

References	Ore (form, size)	Carbonaceous material (form, size)	Specimen (form, size, oxide to carbon ratio)	Temperature, K	Atmosphere	Reduction measurement	Activation energy (E), kJ/mol	Rate controlling steps
Otsuka and Kunii [136]	hematite powder, -100 to 325 mesh	graphite, -65 to -325 mesh	packed bed, 16 x 20 mm dia., 80/20 by wt pct	1323 to 1423	nitrogen	micro-balance	for F<1/3: 230, 260 and 272; for F>1/3: 60 and 98	carbon gasification; for F >1/3 influenced by size of Fe_2O_3
Ghosh and Tiwary [137]	hematite ore, -60 mesh	lignite coke, -60 mesh	pellet, 19.1 mm dia., Fe_2O_3/C : 85/15 to 65/35 wt pct	1173 to 1373	self generated	weight	average 78.2	FeO reduction
Rao [138]	hematite ore, -325 mesh	amorphous carbon, -48 to -325 mesh	pellets, 7.9 x 12.7 mm dia., Fe_2O_3/C: 1/1.5 to 1/9 by mole	1123 to 1360	argon	weight	301.2	carbon gasification
Fruehan [139]	hematite powder,	graphite, coal char,	pellets packed bed, pellet dia: 6x6 to	1173 to 1473	argon, helium	micro-balance	293 - 335	carbon gasification

	FeO, -200 mesh	charcoal, coke, -200 mesh	14x14, bed depth: 5 to 20 mm, Fe_2O_3/C : 84/16 wt pct for hematite					
Srinivasan and Lahiri [140]	hematite ore, -300 mesh	graphite, -300 mesh	pellet, 9 to 12 mm diameter, Fe_2O_3/C : 1/3 to 1/8 by mole	1200 to 1333	nitrogen	micro-balance	F dependent, 417 (for F= 0.2), 285 (for F=0.6), 56 (for F= 0.8).	carbon gasification in final stage of FeO reduction
Sommerville et al (part-I) [97]	iron oxide	carbon dissolved in molten iron	pellets of iron oxide and master slag (Reduction of FeO in slag phase)	1673 to 1723	self generated	-------	-------	chemical reaction at gas-metal and gas-slag interface
Sommerville and Upadhya (part II) [98]	iron oxide	carbon dissolved in molten iron	pellets of iron oxide and master slag (Reduction of FeO in slag phase)	1683	self generated	-------	-------	gaseous decarburization of iron by CO_2
Seaton et al [33]	hematite, magnetite ore, 80 pct pass -325 mesh	coal char , -325 mesh	pellet, 14 mm diameter, hematite 80.4/19.6, wustite 82.8/17.2 by wt pct	1073 to 1473	nitrogen	weight	hematite: 125-239, magnetite: 159	carbon gasification, heat transfer

Seaton et al [99]	iron ore fines	coal char	pellets (Midrex, HyL reduced pellets, and Lab made pellets)	induction furnace melting	-------	-------	-------	key factors: gas evolution from the pellet & heat transfer through solid-liquid interface
Sato et al [100]	FeO in powder form	carbon in molten metal bath & graphite crucible	reduction of FeO in molten slag	1593 to 1893	nitrogen	chemical analysis	163.2 to 246.9	reduction rate of FeO is proportional to the square of FeO concentration
Bryk and Lu [141]	magnetite ore, -75 µm	high volatile coal, graphite, -75 µm to -1400 µm	packed bed, diameter: 19 to 43 x 90 to 132, 80.7/19.3 to 70/30 wt pct, graphite: 84.8/15.2	1173 to 1573	argon, air	Chemical analysis	-------	heat transfer
Mookherjee et al [142]	iron ore, -500 +250 µm	coal or coalchar, -500 +250 µm	Iron ore surrounded by carbon materi-al; 15x 30 mm diameter; 1:1, 1:2 wt. ratio	1123 to 1323	self generated	chemical analysis	F dependent, 130.7 (F=0.2), 152.1 (F=0.3), 144.7 (F=0.6), 146.3 (F=0.7)	carbon gasification
Roman-	iron ore	Coal char	C_{Fix}/Fe = 0.16 to 0.32	1073 to	self	-------	116.4 (for	follows first order

Moguel et al [134]	(90 to 358 µm)	(-180 +90 µm)		1273	generated		reduction of wustite by CO)	reaction kinetics
Mazumdar et al [144]	iron ore (-100 mesh)	noncoking coal (-2 +1 mm)	pellets of iron ore, 8 mm diameter	1123 - 1323 (steps of 50 K)	self generated	weight	176.6 (with coal), 208.6 (with char), 200.3 (char gasification)	diffusion controlled
Prakash and Ray [145]	iron ore, -10 + 6 mm, -6 +3 mm	non- coking coal, -10 + 6 mm, -6 +3 mm	packed bed, 85 x 75 mm diameter, 1:0.6 to 1:1 weight ratio	1073 to 1273	self generated	chemical analysis	90.9 to 111.2 (isothermal reduction), 72.7 to 75.7 (nonisothermal reduction)	--------
Reddy et al [146]	iron ore, -150 µm	coal, -150 µm	pellets, 14 mm diameter, fixed carbon 1: 0.97 to 1.94 by mole	1173 to 1373	self generated	weight	108.2 (initial stages), 93.2 (later stage)	chemical reaction controlled
Haque et al [147]	iron ore, -250 +180 µm	coal, -500 +353 µm	fluidized bed, coal/ore ratio =2, Air flow rate: 2.5 lit/min,	1173 to 1273	reducing	chemical (total iron) analysis	155	carbon gasification, follows first order reaction kinetics
Haque et al	iron ore, -	coal,	packed bed, 30 x 38 mm	1223 to	reducing	chemical	148 to 151	-------

[148]	0.75 to 2.4 mm	-0.75 to 2.4 mm	diameter, 1:0.7 to 1:0.9 weight ratio	1323		analysis		
Haque et al [149]	iron ore fines, -2 +1 mm	coal char fines, -2 +1 mm	packed bed, C_{Fix}/Fe_{Total} ratio : 0.40, 0.50, 0.56	1223 to 1323	reducing	weight	33 for iron ore, 145 for carbon gasification	carbon gasification, follows first order reaction kinetics
Katayama et al [72]	iron ore pellet (10-15 mm)	coal (10-25 mm), coke (10-25 mm)	-------	1723 to 1773	self generated	-------	117.15 for 5 t furnace, 75.31 for 100 t furnace	-------
Sharma [37]	iron ore fines (-75 µm)	non-coking coal (-75 µm)	spherical composite pellets (5 - 6 mm), After coating with iron ore (10 mm)	1173 to 1473	self generated	weight	68.52	follows first order reaction kinetics
Huang and Lu [38]	iron ore (magnetite), 0.3 to 0.044 mm	pulverized coal (high volatiles)	pellets, ore/ coal ratio: 80/20 by wt, density of ore-coal mixture: 2.1 g/cc	1473	self generated	weight	-------	heat transfer, reduction does not follow topochemical pattern
Prakash [150]	iron ore (-0.140 + 0.105 mm)	non-coking coal (-0.140 + 0.105 mm)	ore-coal mixture, non-isothermal reduction	1273 maximum	self generated	weight	12 – 80	follows first order reaction kinetics

Krishna-Murthy et al [104]	hematite & wustite fines, -325 mesh	graphite (from crucible)	spherical / oval shape pellets of iron oxide, 14 mm diameter, weight: 5 - 6 g	1473 to 1923	self generated	-------	76.2 ± 27.7	order of reaction: 0.3-0.4, follows n^{th} order reaction kinetics
Street et al [106]	steel dust	cellulose, sewage sludge	composite pellets, 15 mm dia and 7 to 10 mm height, weight: 3 g, density: 1.38 g/cc	1473 (reduction temp), 1773 (smelting temp)	argon/ self generated	weight (TGA)	-------	crackling core model was proposed
Goswami [40]	blue dust (-200 mesh)	noncoking coal (-1 mm)	cylindrical column of blue dust	1173 to 1373	self generated	weight	68	diffusion controlled
Lee et al [66]	iron ore (2.75 to 4 mm)	carbon from graphite crucible as well as C in molten iron bath	smelting reduction of 30 pct reduced iron ore in C saturated molten iron bath	1673 to 1823	self generated	-------	100.83 (for graphite), 95.81 (carbon saturated molten iron bath)	-------
Wang et al	iron ore	hard and	pellets, 16 to 18 mm	1173 to	nitrogen	weight and	initial stage 68.95 to 82.61,	initial stage: chemical reaction,

[43]	fines	soft coal fines	diameter, Fixed C in iron oxide 1.0	1573		chemical analysis	and later on independent of temperature	later on heat transfer
Nacsimento et al [151]	iron ore, 80 pct under 100 μm	charcoal, 95 pct under 100 μm	pellets, 9.1 to 15.3 mm diameter, 1:3 to all carbon in mole	1273 to 1423	argon	weight	for FeO →Fe stage: 146 for 9.1 mm pellet, 91 for 15.3 mm pellet	for 9.1 mm C gasification and heat transfer, for 15.3 mm heat transfer
Goswami et al [109]	blue dust, -200 mesh	noncoking coal, -2 00 mesh	spherical pellets (iron ore: coal: lime :: 60: 30: 10),	1273 (reduction temp), 1623 to 1823 (bath temp)	self generated	chemical analysis	42.01 (for FCRIP), and 60.75 (for FCP)	initially diffusion controlled, later on chemical reaction controlled
Min et al [108]	FeO	solid carbon	reaction between solid C and FeO containing slag (CaO-SiO_2-FeO slag)	1723 to 1823	self generated	chemical analysis (Mass spectro-meter)	251 for 10 wt pct FeO in slag	carbon gasifica-tion (at $a_{FeO}>$ 0.50), mixed steps of carbon gasification and mass transfer (at $a_{FeO} < 0.50$)
Seo and Fruehan [112]	FeO prepared from reagent grade	coal char	smelting reduction of FeO in CaO-SiO_2-Al_2O_3 -FeO slag	1723	self generated	chemical analysis	-------	liquid phase mass transfer of FeO in slag, carbon gasification, reaction of CO

	hematite		containing 40 pct FeO (slag basicity = 1)					with FeO in slag
Kasai et al [45]	iron ore (hematite)	graphite (11 to 21 wt pct)	tablets (18 mm dia, 11 mm height), weight of tablet: 6 g, tablets coated with $CaCO_3$	1473 to 1673	argon	weight (TG-DTA)	-------	-------
Takahashi et al [44]	reduced iron, mill scale	coke breeze	briquettes (ρ= 3.2 g/cc), major axis: 40 mm, shape: oval	1270 to 1500	nitrogen	weight, gas flow rate	-------	follows first order reaction kinetics
Kasai et al [45]	hematite (-0.105 mm)	pulverized coal (-0.105 mm)	pellets (12-20 mm), slurry coated pellets [$Ca(OH)_2$/coal powder ratio : 80/20]	1473 to 1573	self generated	chemical analysis	-------	-------
El-Geassy et al [46]	iron ore (< 74 µm)	fuel oils (5 to 20 pct)	pellets, both isothermal and non-isothermal reduction studies,	1023 to 1273 (in steps of 50 K)	nitrogen, hydrogen	weight	18.81 to 28.42 (for non-isothermal); 22.86 to 47.11 in initial stage) and 32.35 to 40.67 in final stage for isothermal	gaseous diffusion (initial stage), gaseous diffusion and chemical reaction (final stage)

Jouhari et al [113]	iron ore (-2 + 0.5 mm)	graphite (from crucible)	iron ore fines added in synthetic molten slag	1823 ± 25	self generated	chemical analysis	153	mass transport in slag phase
Bhoi et al [115]	FeO in powder form	solute carbon in iron bath, graphite	reduction of FeO in CaO-SiO_2-FeO slag containing 40 pct FeO (slag basicity = 1)	1573 to 1773	self generated	chemical analysis	101.4 (for reduction by solute carbon), 66.5 (for reduction by graphite	follows first order reaction kinetics
Zhang et al [152]	iron ore, 0.35 to 0.50 mm	H_2-CH_4-Ar gas mixture	Fixed bed reactor	873 to 1198	self generated	weight	78.47 (magnetite to wustite), 86.13 (wustite to metallic iron)	-------
Bandyopadhyay et al [131]	electrolytic iron, sponge iron	nut coke, charcoal, pet coke, coal and graphite	cylindrical samples of graphite	1823 to 1923	argon	chemical analysis	41.84 (for dissolution of carbon in liquid iron bath)	boundary layer mass transfer
Santos and Maurao [48]	iron oxide (reagent grade hematite), <-100 µm	graphite, coke, charcoal, <-100 µm	pellets, 12 mm (cold bonded pellets), 10 mm (fired pellets)	1223 to 1623 and 1561 to 1912	argon for TGA, self generated for smelting	weight	46 to 120 for comp. pellets in 1473 – 1623 K using TG set-up	heat transfer (at high temperature)
Shalini et al	iron ore	coal	spherical pellets of iron	1173 to	self	weight	59.386	diffusion

[153]	fines	(-72 mesh)	ore (10 mm diameter)	1323 (steps of 50 K)	generated			controlled (isothermal reduction)
Dutta et al [27, 41]	blue dust, -200 mesh	coal fines, -200 mesh	pellets, $Fe_{(total)}/C_{(fix)}$ = 5.5	1273 ±5	argon	temp. and gas composition as function of time	183.1 to 268.5 (for low heating rate), 183.1 to 244.1 (for high heating rate)	carbon gasification (non-isothermal reduction)
Sohn and Fruehan (part-I) [49]	iron ore (-100 +200 mesh)	coal fines	composite pellets, thermogravimetric set-up	673 to 1273	argon	weight	-------	mass transport and chemical reaction
Sohn and Fruehan (part-II) [50]	porous analytical hematite (-100 + 200mesh)	graphite, coal-char (-100 +200 mesh)	composite pellets, 16 to 18 mm dia, thermogravimetric set-up	1173 to 1273	argon	weight	-------	mass transport and chemical reaction
Fortini and Fruehan [52]	taconite concentrate, reagent grade hematite (-200 mesh)	wood charcoal, reagent grade graphite (-200 mesh)	composites of iron oxide and carbon, sample wt : 0.10 to 0.70 g	1213 to 1473	argon	weight	368.2 (for wood charcoal-wustite from taconite), 443.5 (for graphite-wustite from hematite)	-------

Bonalde et al [154]	iron oxide (hematite)	pure H_2, pure CO, Midrex gas mixture	pellets (9.5 to 12.7 mm)	1123	self generated	weight	-------	chemical reaction (initial stage), and diffusion (later stage)
Donskoi et al [155]	hematite (90 pct passing 40 µm)	charcoal (< 105 µm), coal (< 105 µm)	composite pellets, 18 mm dia., C/Fe ratio on dry basis = 2.72	1423 to 1523 (nonisoth-ermal reduction)	preheated nitrogen	weight	-------	-------
Bhoi et al [129]	FeO in powder form	carbon from graphite crucible surface	reduction of FeO in CaO-SiO_2-FeO slag (basicity =1)	1673 to 1873	self generated	chemical analysis	118	mass transport of FeO in slag

2.2.10 Concluding remark

From the literature review, it is clear that composite pellets have been successfully produced. Test results have also established that they can be used as feed material in cupola, rotary kiln and even blast furnace. ITmk3 process uses composite pellets to produce almost pure pig iron nuggets. However, it has not yet picked up commercially in a significant way. This is due to the cost of production of pellets where selection of a suitable binder plays very crucial role. Local conditions, future trends and developments are going to dictate economics. Review on kinetics and reduction mechanism of composite pellets indicates that the reaction mechanism in composite pellet is very complex because of the participation of many phases, gases and occurrence of several reactions simultaneously and not yet fairly understood.

Review of smelting reduction processes / technologies indicates that not much work is done on fundamental studies on reduction smelting of iron ore-coal composite pellets to make the composite pellets acceptable as feed material. There have been a few investigations reported in the literature on smelting reduction of iron oxides in contact with Fe-C melts (mostly in slag phase) under various operating conditions. However, fundamental studies on smelting reduction of iron ore-coal composite pellets in liquid metal bath are not available in published literature.