ABSTRACT

TITLE : ' A PROCESS FOR PRODUCTION OF LOW SULPHUR DIRECTLY REDUCED IRON FROM WASTE IRON ORE SLIME INCLUDING REJECTED COAL CONTAINING MORE THAN 50% ASH '

This invention relates to a process for the production of highly metallaized directly reduced iron (DRI) with low sulphur contents from waste iron ore slime and rejected coal containing more than 50% ash. The iron ore slime pellets of 12 – 20 mm were made by the conventional method of pelletizing, utilizing – 70 to -200 mesh size iron ore slime fines. The green iron ore slime pellets were dried in the normal atmosphere and kept in the bed of mixture of rejected coal and desulphurizing agent of size range between -50 to -200 in a crucible. The pellets kept in the bed of rejected coal in a crucible were reduced between 900°C to 1200°C for 1 – 6 hours to get highly metallized low sulphur directly reduced iron via reduction. After reduction, crucible were removed from the furnace and allowed to cool from reduction temperature to about 600°C to 500°C temperature in the normal atmosphere maintaining reducing atmosphere inside the crucible to avoid re-oxidation and then separated from the residue of rejected coal and desulphurizing agent. Process parameters were optimized with respect to reduction temperature, time, amount of desulphurizing agents and rejected coal required for reduction to yield highly metallized low sulphur directly reduced iron (DRI), suitable for iron and steel making. This invention is particularly useful for converting mining waste, iron and steel plant wastes and low grade raw materials such as low grade iron ore, fines, slime, coking or non coking coal having low carbon high ash into a value added product.

{ FIGURE 1 }

WE CLAIM :

1. A process for production of low sulphur directly reduced iron from waste iron ore and includes rejected coal containing more than 50% ash comprising the steps of:

(i) grinding and screening waste iron ore slime to an optimum size range between – 70 to – 200 mesh and pelletizing to get pellets of diameter ranging between 12 to 20 mm;

(ii) optimizing moisture content in the iron ore slime pellets (12 – 20 mm size) by a known method to obtain a green strength of the pellets ranging between 8 to 15 N per pellet without any binder for safe handling and further processing;

(iii) grinding and screening rejected coal in a size range between – 70 to -200 mesh in order to use as a reducing agent during the reduction;

(iv) grinding and screening a desulphurizing agent (dolomite) to size ranges between – 70 to -200 mesh for application as a desulphurization agent during the reduction;

(v) mixing the rejected coal and the desulphurizing agent (dolomite) in a weight ratio of 1:0.05 to 1: 0.15;

(vi) locating the iron ore slime pellets in a static bed of the mixture of rejected coal and the desulphurizing agents for reduction in a weight ratio of 1: 0.3 to 1: 0.6; wherein a plurality of crucibles containing the iron ore slimmer pellets in the bed of mixture of rejected coal and desulphurizing agent is provided for reduction in a temperature range of 900°C to 1200°C for a time period of 1 to 6 hours ;

(vii) removing and cooling the crucibles containing the reduced iron ore slime pellets from said reduction temperature to a temperature range of 600 to 500°C in an ambient atmosphere (reducing atmospheres inside the crucible) to eliminate re-oxidation of the reduced iron ore slime pellets including cooling of the pellets to room temperature; and

(viii) separating the reduced iron ore slime pellets from the bed of residue of the mixture of rejected coal and desulphurizing agent.

2. A process as claimed in claim 1, wherein the waste iron ore slime comprises a compositional range:

Fe	: 40 – 58%
LOI	: 4 - 11%
$Si0_2$	: 8 - 15%
Al_20_3	: 4 - 8 %
P	: 0.12 – 0.18%
S	: 0.006 – 0.01%

3. A process as claimed in claim 1 or 2, wherein the iron ore slime fines comprises a size range between – 70 to -200 mesh.

4. A process as claimed in claim 1, wherein the iron ore slime pellets has a size range between 12 to 20 mm.

5. A process as claimed in any of the preceding claims, wherein the iron ore slime pellets comprise a green strength between 8 to 15 N per pellet.

6. A process as claimed in any of the preceding claims, wherein the waste rejected coal comprises a following compositional range:

Fixed carbon : 25 – 35% Volatile Matter: 8 – 15%
Moisture: 0.5 – 3% Ash :50 – 65%.

7. A process as claimed in any of the preceding claims, wherein the desulphurizing agent is a commercially available industrial grade dolomite having following compositional range:

8. A process as claimed in any of the preceding claims, wherein the rejected coal is mixed with dolomite in a weight ratio of 1:0.05 to 1:0.15.

9. A process as claimed in any of claims 1 to 8, wherein the arrangement of iron ore slime pellets in the static bed of rejected coal has a ratio of 1: 0.4 to 1: 0.8.

10. A process as claimed in any of claims 1 to 9, wherein reduction temperature and time vary from 900°C to 1200°C and 1 to 6 hours respectively.

11. A process as claimed in any of claims 1-8, wherein cooling of the crucible is carried out in a temperature range of 600°C to 500°C to avoid re-oxidation of reduced pellets.

12. A process as claimed in any of claims 1 to 9, wherein separation of the reduced iron ore pellet from the residue of rejected coal and desulphurizing agent is carried out below 500°C to room temperature depending upon the requirement.

Dated this 22nd day of November 2013

(P.D. GUPTA)
OF L.S.DAVAR & CO
APPLICANTS AGENTS

TATA STEEL LIMITED
COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH (CSIR)

1 - SHEET
SHEET - 1

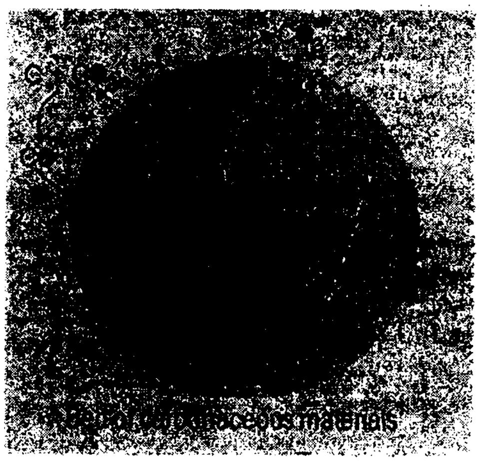

Fig-1

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FIELD OF THE INVENTION

The present invention generally relates to a process for production of highly metallized directly reduced-iron (DRI) with low sulphur contents. More particularly, the present invention relates to a process for production of highly metallized direct reduced iron pellets from waste iron or slime and rejected coal containing more than 50% ash.

BACKGROUND OF THE INVENTION

A number of gas and solid based processes for production of directly reduced iron (DRI) are known in the art. All these gas based and solid based processes of making DRI mostly requires iron oxide in the form of lump, fines, pellets or composite pellets and reducing agents in the form of gas or solid to convert these iron oxide into a metallic iron. It is interesting to note that, all the solid based DRI processes require coking or non coking coal having less than 20% ash as the reducing agent to convert iron oxide into a metallic iron. In contrast to the requirement, the worldwide shortage of coking coal in particular a limited reserves of coking coal with low ash contents especially, in India, forced the iron and steel makers to find a way to use coking or non coking coal having high ash content for iron and steel making. In addition to the limited reserve of coking coal with low ash content, a huge quantity of coal gets rejected during beneficiation and washing which interalia remains unutilized due to low carbon and high ash content. Similarly, during beneficiation and washing of iron ore, more than 30% slime is generated which remains unutilized. These iron ore slimes and rejected coals are although stored in massive water ponds, however they possess enormous problem for disposal and causes environmental hazards. The beneficiation/safe disposal of iron ore slime and rejected coal or converting the slime into a value added produce thus remains a challenging task for iron and steel industry. It may be noted that none of the prior art processes is capable to convert these waste iron ore slime and rejected coal containing more than 50% ash in a value added product.

The non-patent literatures by J. Feinman et al (Direct Reduction and Smelting Processes, Iron Making Volume, Chapter – 11, pp 741-780. The SISE Steel Foundation 1999) and by All hasanbeigi et al (Ernest Orlando Lawrence Berklye national Laboratory Report on "Emerging Energy – Efficiency and Carbon Dioxide Emissions – Reduction Technologies for the Iron and Steel Industries:

January, 2013, p.26 – 44), discussed about the historical development of directly reduced iron (DRI) making processes as well as emerging highly energy efficient iron making technology respectively, such as Midrex, HYL, Purofer, Finmet, Circored, Krupp-CODIR, SL/RN, DRC, OSIL, Fastmet, Technored, ITmk3, Coal based HYL process, Coal based MIDREX etc.

US Patent No. 6,284,017 B1 discloses a production process of DRI using iron oxide and solid reductant. In this prior-published invention, fine iron oxide and powdered solid reductant is mixed and compacted into a sheet form using rollers. These compacted sheets are charged in a reduction furnace at a temperature of more than 1100°C for reduction. The directly reduced iron (DRI) thus produced is further charged into a shaft furnace or in a bath smelting furnace for melting at high thermal efficiency. However, the DRI produced by this process, requires more reductant and suffers from the quality requirement for steel which does not allow an economic use this DRI for steel making.

US Patent No. 6,036,744 teaches method and apparatus for production of DRI using iron oxide and carbonaceous material. The iron oxide and a carbonaceous reductant are compacted together and exposed to heat for reduction to obtain a metallic iron. During the reduction, a shell composed of the metallic iron is generated and grown on the surface of the surface of the compact including the slag aggregates inside the shell. Further, heating is performed to melt the reduced compact and subsequently, metallic iron is separated from the slag to get a highly metallized iron. Although the metallic iron thus produced has high metallization. However, this metallized iron finds very limited use for steel making due to high process cost and lack of quality requirements of steel.

US Patent No. 5,849,063 discusses a process for production of DRI or pig iron from industrial waste streams. The DRI or pig iron is produced from the electric arc furnace (EAF) and blast furnace dust stream, involves magnetic separation or floatation of iron containing material followed by briquetting and reduction in a suitable furnace. The reduced iron obtained from the above process however contains several other elements which do not allow economical use of produced DRI in the steel making process.

US Patent No.8182575 B2 teaches utilization of iron ore dust generated in the iron making process. The iron bearing materials are separated from the group of raw material and dried . These iron bearing materials are mixed with known reducing agents to get a mixture which is subjected to drying. Pulverizing of the mixture is carried out to obtain 80% minus sieve to have a particle diameter of 70 μm to 500 μm; the mixture is kneaded after the moisture content of the mixture is subjected to the kneading step to be agglomerated, and reducing the agglomerates in a rotary hearth furnace to produce direct reduced iron (DRI). The DRI thus produced contains very high gangue minerals due to mixing of reducing agents with the iron bearing materials. Hence, this prior art process/product did not find the market for production of iron and steel.

US Patent No. 3,443,931 teaches agglomeration of pulverized iron ore and pulverized coal mixture, drying of the agglomerated mass, and pre-induration between 872°C – 982°C temperature. The pellets are then subjected to reduction through application of a radiant heat source between 1260°C to 1425°C yielding reduced iron. The reduced iron obtained using the above mentioned process is charged into an electric arc furnace as a source of metallic iron. This method, however does not involve any low grade / lean iron ore fines and coal fine which narrows the selection of source of raw material for making the iron. Moreover, the pre-induration of agglomerates was carried to get optimum dry strength for handling and processing including reduction at high temperature to get a DRI. Thus, the process is a techno-economical process.

To overcome the problem of pre-induration at higher temperature a process for production of metallized briquette is disclosed in US Patent No. 4,701,214, which describes a method mixing iron oxide fines and coal fines with a known binder to form a mixture which is agglomerated by palletizing to form pellets. These pellets were charged into a rotary hearth furnace to get pre-reduced pellets and finally melted in a smelting reduction furnace in presence of carbon to get a metallized briquette. The smelting reduction of these pre-reduced pellets requires an additional carbon and extra energy for reducing and smelting, making the process a high energy consumption process.

US Patent No. 5, 637,133 discloses a process for manufacturing of sponge iron with low sulphur content. In the particular process, a superposed layer of finely divided iron oxide is deposited on a moving hearth and another layer made up of a mixture of solid reducing agent and a desulphurizing agent. These charge mix is heated externally above 900°C by using a burner, where the iron oxide is reduced by carbon monoxide (CO) and the gaseous compound of sulphur is fixed by desulphurizing agents yielding a solid cake of the sponge iron which is separated from the residue of the reducing materials containing sulphuring agent. The reduced solid cake contains huge quantity of impurities which restricts the use of this sponge iron in an electric steel making.

Thus, the known process as discussed hereinabove, have several drawbacks which can be summarized as under:-

(1) In all the above processes, high grade iron ore in form of fines, lumps and agglomerates of iron ore and coal fines are used.

(2) The carbonaceous material used in prior art as a reducing agent for production of directly reduced iron (DRI) contains high fixed carbon (> 65%) and low ash (<20%).

(3) In all the processes, iron ore fines are agglomerated with carbonaceous material leading to increased gangue content in the reduced iron yielding poor metallization with high level of impurity.

(4) Increased gangue content in the directly iron (DRI) requires more fluxes during melting, resulting in decrease in the rate of production.

(5) The DRI produced from the conventional routes pickup more sulphur and other elements from the coal during reduction which disallows economical use of the produced DRI for iron and steel making.

(6) All the known DRI processes require pre-indurated pellets (indurated at 1250 to 1350°C) for reduction which interalia require additional energy and increases the process steps for production of the DRI.

(7) No process has been developed till date to utilize the waste iron ore slime and rejected coal containing more than 50 % ash for production of the DRI.

OBJECTS OF THE INVENTION

It is therefore an object of the present invention to propose a process for production of low sulphur directly reduced iron from waste iron ore and includes rejected coal containing more than 50% ash which eliminates the drawbacks of the prior art.

Another object of the present invention is to propose a process for production of low sulphur directly reduced iron from waste iron ore and includes rejected coal containing more than 50% ash which ensures use of the rejected coal for complete reduction of the waste iron ore slime pellets to produce highly metallized low sulphur reduced iron suitable for iron and steel making.

A still another object of the present invention is to propose a process for production of low sulphur directly reduced iron from waste iron ore and includes rejected coal containing more than 50% ash which avoids the sulphur pickup in the produced DRI during reduction.

Yet another object of the present invention is to propose a process for production of low sulphur directly reduced iron from waste iron ore and includes rejected coal containing more than 50% ash which provides optimum size of the iron ore slime pellets, for complete reduction of iron ore slime pellets.

Another object of the present invention is to propose a process for production of low sulphur directly reduced iron from waste iron ore and includes rejected coal containing more than 50% ash which reduces the pellets by utilizing only optimum amount of rejected coal.

A further object of the present invention is to propose a process for production of low sulphur directly reduced iron from waste iron ore and includes rejected coal containing more than 50% ash in which an optimum reduction temperature and reduction time is used to get highly metallized low sulphur reduced iron with high cold crushing strength applicable for blast furnace and electric steel making processes.

SUMMARY OF THE INVENTION

Accordingly, the present invention provides a process for the production of highly metallized low sulphur directly reduce iron from waste iron ore slime and rejected coal which comprises :

(i) Grinding and screening of waste iron ore slime to an optimum size range between – 70 to – 200 mesh and palletizing to get pellets of diameter ranging between 12 to 20 mm.

(ii) Optimizing the moisture content in the iron ore slime pellets (12 – 20) mm size) by known method to get the green strength of the pellets ranging between 8 to 15 N pellet without binder for safe handling and further processing.

(iii) Grinding and screening of waste rejected coal in the size range between – 70 to -200 mesh to be used as a reducing agent during reduction.

(iv) Grinding and screening of the desulphurizing agent (dolomiter) in the size ranges of – 70 - -200 mesh to be used as a desulphurizing agent during reduction.

(v) Mixing of rejected coal and desulphurizing agent (dolomite) in the weight ratio of 1:0.05 to 1:0 0.15.

(vi) Technique for arrangement of iron ore slime pellets in the static bed of mixture of rejected coal and desulphurizing agents for reduction in the weight ratio of 1:0.3 to 1:0.6.

(vii) Arrangements of crucible containing iron ore slime pellets in bed of mixture of rejected coal and a desulphurizing agent for reduction in the temperature range of 900°C to 1200°C for 1 to 6 hours reduction time.

(viii) Removal and cooling of crucible containing reduced iron ore slime pellets from reduction temperature to a temperature range of 600 to 500°C in the normal atmosphere (reducing atmospheres inside the crucible) to avoid the re-oxidation of reduced iron ore slime pellets and thereafter cooling to room temperature.

(ix) Separation of reduced iron ore slime pellets from the bed of residue of mixing of rejected coal and a desulphurizing agent.

In one embodiment of the present invention, the waste iron ore fines used may be iron ore slime or low grade iron ore fines collected from iron ore mines or iron ore beneficiation / washing pond having a composition in the range of :

Fe	:40 - 58%
LOI	:4 - 11%
SiO_2	:8 - 15%
Al_2O_3	:4 - 8%
P	:0.12 – 0.18%
S	:0.006 – 0.01%

In still another embodiment of the present invention, the waste rejected coal or other coal from coal mines or coal washery used in the process may have the composition in range of :

Fixed carbon :25 – 35%	Volatile Matter: 8 - 15%
Moisture: 0.5 – 3%	Ash :50 – 65%

In still another embodiment of the present invention, the size range of iron ore slime pellets vary from 12 mm to 20 mm for reduction in the bed of a mixture of rejected coal and desulphurizing agents or other carbonaceous materials.

Yet another embodiment of the present invention, the size, shape and materials of the crucibles used in the process is selected according to the furnace design and mode of heating source.

In a further embodiment of the present invention, reduction of iron ore slime pellets is carried out in a temperature rang between 900°C to 1200°C in the bed of said mixture of rejected coal and a desulphurizing agent.

In a still further embodiment of the present invention, reduction of the iron ore slime pellets is carried out for a time period of 1 to 6 hours.

BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWING

Figure 1 – shows a schematic of reduction mechanism according to the invention.

The produced highly metallized low sulphur DRI of the present invention can be charged into electrical arc furnace, induction furnace, and basic oxygen furnace without further processing for steel making as a substitute of scrap.

DETAIL DESCRIPTION OF THE INVENTION

The present invention is a process for reduction of waste iron ore slime pellets in a bed of mixture of rejected coal and a desulphurizing agent to produce highly metallized low sulphur reduced iron directly applicable in a blast furnace, electric arc furnace, induction furnace and basic oxygen furnace for iron steel and steel making. The following examples are given by way of illustration and should not be construed to limit the scope of the invention.

EXAMPLE 1

75.1 grams iron ore slime pellets (12 – 20 mm diameter) of composition:
Fe 48.5 %, L0I:9.46 %, $Si0_2$:13%, Al_20_3: 7.5%, P: 0.18%, S: 0.01% was kept in the bed of mixture of rejected coal and a desulphurizing agent in a crucible and reduced at 900°C for 1 – 6 hours in a reduction furnace. At the reduction

temperature, the gasification of rejected coal produced $C0_2$ which immediately reacted with the carbon present in the bed of rejected coal which gives rise to Co. The CO thus generated is highly reducing in nature and reacted with iron ore slime pellets (iron oxide) kept in bed of rejected coal to produce metallic iron. The process of gasification and reduction is continued till the completion of carbon for gasification or complete reduction of pellets. This process is not only limited to the rejected coal but can be extended to the other carbon bearing material such as low reactive coal, Jhama coal and middling coal etc. The reduction mechanisms taking place during reduction are shown in Figure 1. The details of reactions taking place the during the reduction step is illustrated hereinbelow:

Reactions	Remarks
$C+0_2 = CO_2$	Gasification of carbon
$C+C0_2 = 2O$	
$C+½\ 0_2 = CO$	
$3Fe_2O_3 + CO = 2Fe_3O_4 + C0_2$	Indirect Reduction
$Fe_30_4 + C0 = 3Fe0 + C0_2$	
$Fe0 + C0 = Fe + C0_2$	
$Fe_2O_3 + 3CO = 2Fe + 3CO_2$	
$2Fe_2O_3 + 3C = 4Fe + 3CO$	Direct Reduction

After reduction, the crucible is removed from the furnace and allowed to cool from a reduction temperature to 500°C in normal atmosphere (reducing crucible atmosphere) to avoid re-oxidation of the reduced pellets and thereafter separated from the residue of the mixture of rejected coal and the desulphurizing agent. The samples collected from different reduction time were analyzed for their percentage reduction and found that up to 77.72 %, the reduction is achieved at 900°C 4 fours reduction time. After 4 hours reduction, the complete gasification of carbon occurs and further increase in reduction times leads to a re-oxidation of the reduced pellets.

The percentage reduction achieved at 900°C for different reduction time is given in the table 1.

Table : 1. Percentage reduction of pellets at 900°C for different reduction time

Reduction time (hrs.)	1	2	3	4	5	6
% Reduction	47.7	52	47.67	77.72	66.12	62.34

EXAMPLE 2

24 sets of 100 grams iron ore slime pellets of compositions: Fe 55.94%, LOI: 4.96%, SiO_2: 9.14%, Al_2O_3 : 4.48%, P:0.172%, S: 0.008% was kept in the bed of mixture of rejected coal and a desulphurizing agent in a crucible and each set of crucible containing iron ore slime pellets were reduced in a reduction furnace at 900°C, 1100°C, and 1200°C for 1 – 6 hours. After reduction of pellets, crucibles were removed from the furnace at the interval of 1 hour and allowed to cool from reduction temperature of 500°C in normal atmosphere and thereafter separated from the residue of mixture of rejected coal and a desulphurizing agent. The samples collected from different reduction temperature and time were analyzed for their percentage reduction, cold crushing strength, % shrinkage and density. The kinetic study of the reduced pellets were carried out and it was found that, the 1100°C temperature and 3 hours reduction time was the optimum temperature and time for the reduction of iron ore slime pellets in the bed of mixture of rejected coal and a desulphurizing agent to get more than 98% reduction.

EXAMPLE 3

24 sets of iron ore slime pellets containing 100 grams of pellets in each set (crucible) in the size range of 10 – 15 mm diameter and another 24 sets of sets of iron ore slime pellets having diameter 16 – 15 mm size range were reduced in the bed of mixture of rejected coal and a desulphurizing agent at 900°C to 1200°C for 1 – 6 hours. After reduction of pellets, crucibles were removed from the furnace and analyzed for their properties such as percent reduction, percent metallization, sulphur contents, cold crushing strength and swelling shrinkage etc. It was observed that the pellets having size range between 10 15 mm diameter have shown more percent reduction compared to the pellets having size range between 16 – 20 mm diameter at lower reduction time (< 1 hr) at all the reduction temperature (900°C to 1200°C). The further increase in reduction time the present reduction of pellets having size range of 16 – 20 mm diameter reveals more reduction compared to pellets having size range 10 15 mm diameter up to 2 ½ hours reduction time. The further increase in the reduction time (more than 3 hours) the percent reduction of the pellets achieved more than 98 % in the all size range of the pellets.

EXAMPLE 4

The effects of sulphur pick up from the rejected coal into the reduced iron ore slime pellets during reduction between 900°C to 1200°C for 1-6 hours has been carried out by the addition of a desulphurizing agent in the rejected coal. Moreover, particularly dolomite was chosen as a desulphurizing agent due to its economically availability and efficiency to reacts with the gaseous compound to form solid compound. At reduction temperature, during gasification of rejected coal, the sulphur contents in the coal also formed the gaseous compound of sulphur which immediately reacted with the desulphurizing agents and remains in the bed of rejected coal. The addition of desulphurizing agent particularly dolomite decreases the sulphur diffusion in the reduced iron ore pellets from 0.168% to 0.006%. The addition of dolomite in the rejects coal has been optimized to get very low sulphur content which will influence the quality of steel made from the DRI produced. The addition of the desulphurizing agents was not only limited to dolomite but other low cost desulphurizing agents such as sodium carbonate, calcium carbonate etc and like wise can be used as a reducing agent.

The major advantages of the present invention are given here:

1. A process for production of low sulphur Directly Reduced Iron (DRI) utilizing waste iron ore slime and rejected coal.

2. Ability to utilize the waste or discarded slime or low grade iron ore fines or likewise from mines heat or beneficiation plant or waste from iron and steel plant up to -400 # mesh size with wide range of Fe content about 40-58%.

3. Ability to utilize waste or discarded carbonaceous material from coal beneficiation plant or coal washery containing low carbon and high ash (> 50 % ash) with wide range of size fraction.

4. Ability to get optimum green strength of pellets for handling and further processing without any binder.

5. The process has ability to use air dried pellets without any pre-induration.

6. The process requires only little excess amount of rejected coal than the stoichiometric carbon required for reduction compared to the existing conventional process which requires 1:0.8 to 1:1 ore to coal ratio.

7. The process utilizes cheap and economically available desulphurizing agents to avoid the sulphur pickup in the DRI during reduction.

8. The process has ability to produce DRI with as low as 0.006% sulphur.

9. The process requires only 1: 0.4 to 1: 0.6 ore to coal radio for complete reduction.

10. The process has ability to avoid the re-oxidation of the reduced pellets after reduction.

11. Ability to reduce iron ore slime pellets in the static bed of the rejected coal.

12. The DRI produced have very low sulphur content which makes it suitable to meet the quality requirement for production of all grade of steel.