

“REOXIDATION OF SPONGE IRON IS AN EXOTHERMIC PROCESS DUE TO REMOVAL OF HYDROGEN”

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Abstract— In the present era scarcity of high grade coal, high valuable process of coke production is a headache. So to get release from this problem huge amount of electric arc furnace and sponge iron production is increased. Sometimes Sponge iron transportation is a problematic situation, because during transportation chances of spontaneous burning of sponge iron are found, that is the effect of re-oxidation of sponge iron. Re-oxidation of sponge iron phenomenon refers to oxidation of metallic sponge iron in moisture condition. Metallic iron forms a strongly bonded $Fe(OH)_2$ compound which causes increase in mass of sponge iron. The re-oxidation phenomenon is an exothermic process. Sponge iron is spongy in structure having large in porous area. Thus it is very much reactive and seeks for high oxidation. So the sponge iron produced is highly susceptible to re-oxidation. So it is important to study the kinetic of sponge iron re-oxidation.

Keywords—Sponge iron, Iron ore, Coal, Dolomite, Power unit for initial power consuming unit.

INTRODUCTION

The conventional route for making steel consists of sintering/pelletization plants, ovens, blast and basic oxygen furnaces. Such plants need huge capital expenses and raw materials as they are the stringent requirements. The integrated steel plants having production less than one Million tons annually are generally not considered economically. Along with that the coke ovens and sintering plants in an integrated steel plant are highly polluting. On the other hand installations of highly complex and expensive pollution-control systems make this route highly capital intensive. Taking into account all the above mentioned demerits a new process known as Direct Reduction of Iron (DRI) process has been developed for

Iron making. This process is widely accepted by almost all the developing nations. The generation of scrap was less in comparison to the requirement of steel and also steel produced by recycling process is found to follow the more economic pathway than its production via Blast furnace –Basic oxygen furnace (BF-BOF) process. The coal base DRI rotary kiln used for the production of sponge iron with increased quality and product ability needs careful operations throughout the process. Number of DRI processes came up which are more economic. DRI production and consumption are influenced by a range of regional controls which include employment costs, power and gas prices, coal availability and quality, iron ore reserves, infrastructure and the availability as well as prevailing prices of prime scrap. Some of them have re-emerged in slightly different form. As touched upon earlier, sponge iron is mainly produced from ore by two different routes –

- (a) By reducing gases (CO and H_2) in a shaft furnace
- (b) Through direct treatment with coal in a rotary kiln.

Sponge Iron:-

Sponge iron is the metallic product formed by the reduction (removal of oxygen) of iron ore at temperature below the fusion point of iron while it is still in solid state. It is also called direct reduced iron (DRI). Direct-reduced iron (DRI) is produced from direct reduction of iron ore (In the form of lumps, pellets or fines) by a reducing gas produced from natural gas or coal. The reducing gas is a mixture of majority of hydrogen (H_2) and carbon monoxide (CO). This process of directly reducing the iron ore in solid form by reducing gases is called direct reduction. Hematite and magnetite are found on in earth crust as oxide form. Containing more than 27% oxygen. Oxygen particle occupy space in solid ore body in compound form in nature. In solid state reduction oxygen is removed from ore body making number of holes or cavities in the solid. During direct reduction, oxygen is removed from iron ore in solid state. This procedure results in a spongy structure of the product makes "sponge iron", with a high porosity. The manufacturing of sponge iron is highly sensitive to raw material characteristics. Depending on the raw material and the reduction process applied, apparent product density is approx. 2 g/cm^3 associated with a very high specific surface area. The latter is typically around $1\text{ m}^2/\text{g}$. The external shape of the ore is retained with 30% reduction in weight due to oxide reduction resulting in change in true density from 4.4 gm/cc to 7.8 gm/cc in this product.



Fig – 1, Sponge Iron

Sponge iron is the product created by heating an iron ore at a temperature high enough to burn off its oxygen and carbon content but below iron's melting point.

Concept of Sponge Iron:-

The appearance of iron ore is completely changed when it gets converted to sponge iron of its composition. The hematite iron ore is most suitable ore whose chemical formula is Fe_2O_3 is most suitable raw material for DRI. Composition of hematite iron ore as follows Fe, O_2 , SiO_2 , Al_2O_3 , CaO, MgO, Pb, Cu, Zn, V, S, P, LOI

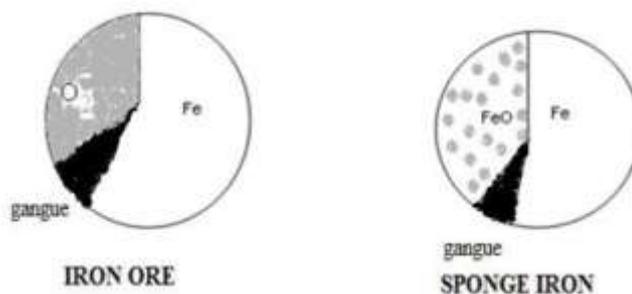
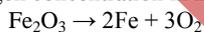


Fig – 2, Reduction & unredution

The oxygen concentration in hematite iron ore is as follows:



When hematite iron ore of 65% Fe oxygen combined is calculated as follows 111.70 parts Fe combined with 48 part O_2 , So 1 part of Fe combined 48 / 111.70

65 part Fe combined $48 \times 65 / 111.70 = 27.93$ part O_2

During reduction reaction only O_2 and LOI are removed and all other element remains intact. After reduction reaction the hematite ore is called DRI /sponge iron and the weight of the product becomes lighter due to removal of O_2 and LOI. The chemical composition of 65% Fe hematite iron ore is supposed to be as follows:

So like scrap the Fe iron content in sponge goes high depending on Fe % in ore.

Raw materials:-

Following are the key raw materials required for the formation of sponge iron.

• **Iron Ore:**

The iron ore used is hematite having Fe content 62-66%. Earlier the initial days the iron ore size was kept at 5-20 mm and was washed in a scrubber, but presently it has become a standard norm to use 5-18 mm ore as feed for a large kiln without scrubbing and/or washing. This has resulted in reducing the cost of iron ore fed to the kiln. The consumption of iron ore has also decreased from about 1600 kg per ton of sponge iron to 1500 kg levels mainly due to a better understanding of the process, improvements of the equipment and increased levels of automation. Two

main types of iron ore used for iron making are magnetite (Fe_3O_4) and hematite (Fe_2O_3). Common iron ores include:

Hematite - Fe_2O_3 - 70 percent iron
Magnetite - Fe_3O_4 - 72 percent iron
Limonite - $\text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$ - 50 percent to 66 percent iron
Siderite - FeCO_3 - 48 percent iron

Reductant Used	Reactor Design	Process	Charging Type
Reducing gas produce from natural gas or Neptha	Static bed	HYL	Sized lump/pellets
	Continuous retort	MIDREX	do
		PUROFER	do
		ARMCO	do
	Fluidised bed	Hi Iron	Sized Ore
		Esso Fior	Briquettes
		Nu Nron	
		HIB	
Solid & Liquid or gaseous	Rotary kiln	SN/RN	Sized lump/pellets

- **Coal:**

Non-coking coal is being used having certain important parameters considered necessary for the direct reduction of iron ore viz. reactivity, ash softening temperature, caking and swelling indices and sulphur content, etc. The industry has successfully adopted measures to utilize lower grade coals through better process control, installing raw material heating systems, shale picking belts and coal washing plants. With these measures the coal cost has been reduced by nearly 20-30% when compared with the usage of high grade coal.

- **Dolomite:**

Dolomite is mainly used as a desulphurising agent to prevent the pickup of sulphur by the sponge iron from the sulphur released by the burning of coal inside the furnace. The initial specifications for dolomite were 1-4 mm, later it was found that 4-8 mm dolomite was for more suitable by which the consumption can be reduced by 50%. This was mainly due to the fact that lot of dolomite fines were being lost to waste gases and with 4-8 mm fraction this loss was minimized.

- **Power:**

The initial plants were high power consuming units due mainly to the wet waste gas cleaning. The power consumption levels used to be 110-130 units per ton of sponge iron, with the advent of a dry gas cleaning system (electro-static precipitator), programmable logic operated drives and computers replacing the giant panels, the power consumption has been curtailed to 80-90 units per ton of sponge iron.

Processes for sponge iron making:

There are broadly two categories of producing sponge iron. Such as:

1. Coal-based processes
2. Gas-based processes

Coal based process:-

This process utilizes non-coking coal as reducing agent along with lumpy rich grade iron ore. The reduction is carried out in an inclined horizontal rotary kiln, which rotates at a predetermined speed. A temperature profile ranging from 800-1050°C is maintained along the length of the kiln at different zones and as the material flows down due to gravity and ore is reduced.

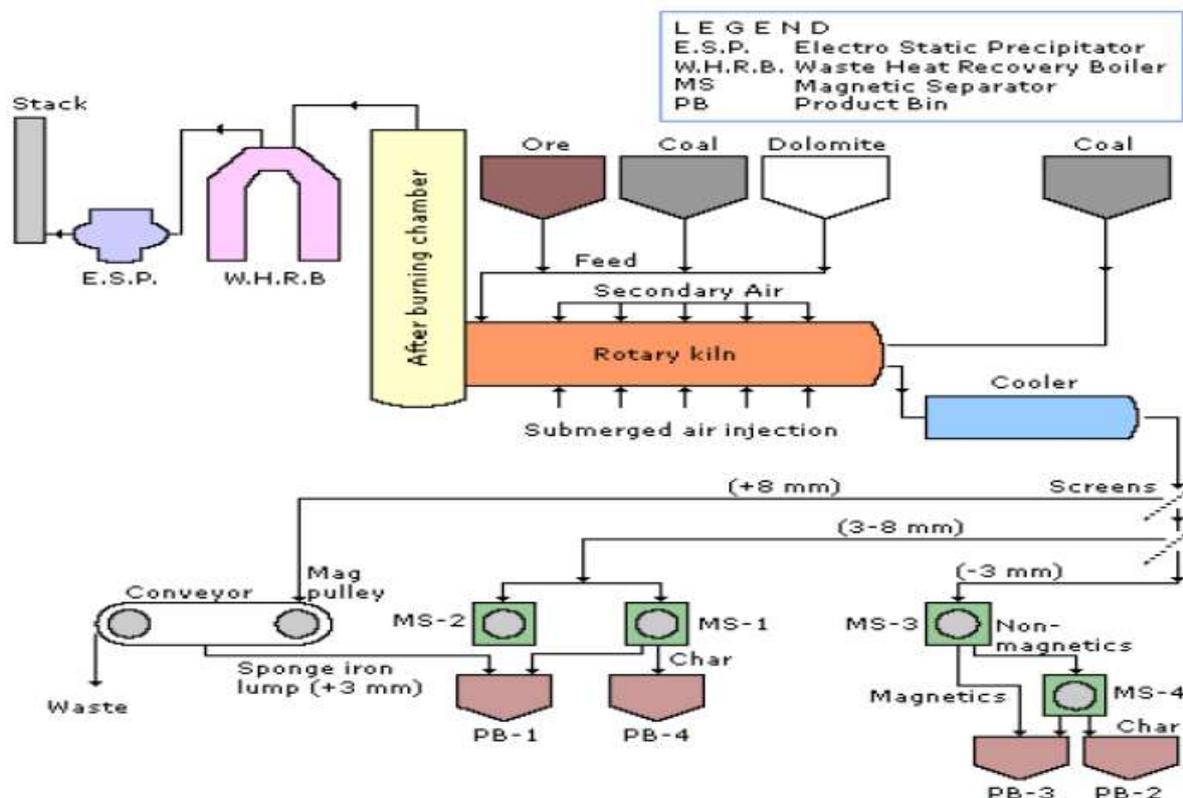


Fig 3 – Process flow diagram for coal based sponge iron

The hot reduced sponge iron along with semi-burnt coal, discharged from kiln is cooled in water-cooled cylindrical rotary cooler to a temperature of 100–200°C. The discharge from cooler consisting of sponge iron, char other contaminations are passed on through magnetic separators so that sponge iron can be separated from other impurities. Later the sponge iron is screened into two size fractions i.e. –3 mm & +3 mm. +3 mm fraction directly goes for usage, -3 mm fraction can be either used directly where ever it is possible or is to be briquetted by using molasses and hydrated lime as binders.

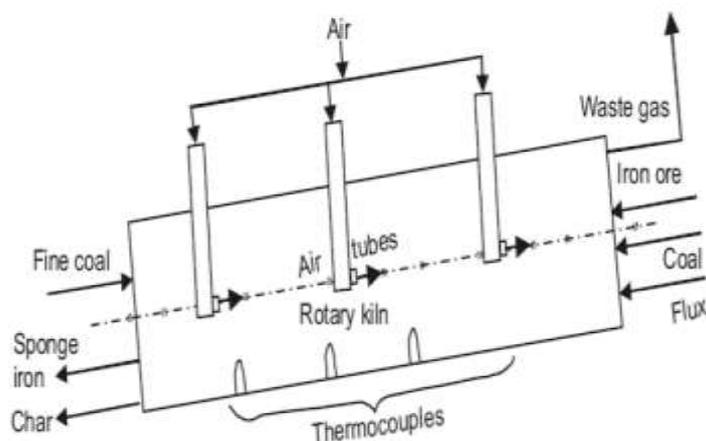


Fig – 4 Essential features of a reduction kiln in rotary kiln sponge iron plant

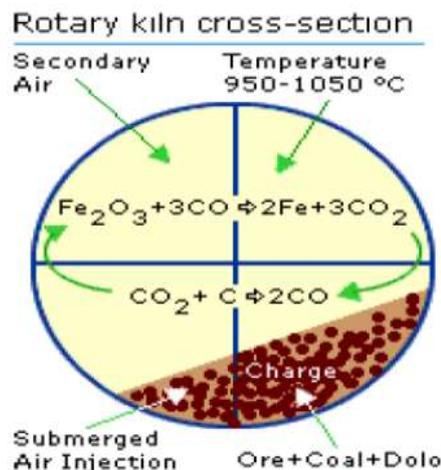
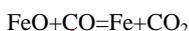
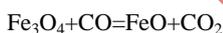
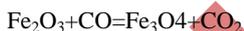
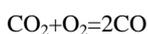
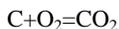


Fig – 5, DRI Rotary kiln cross section

The process built up on solid state reduction of iron ore by using sub-bituminous coal as a reductant under controlled atmosphere at desired temperature and pressure. The rotary kiln of more than 80m length and more than 4m dia, is designed in such a manner that solid feed stock move under kiln bed in touch with gaseous atmosphere throughout the length of the kiln.

In a rotary kiln carbon is used as reducing agent and reaction takes place mostly through CO intermediate. The reduction reaction of solid iron ore in rotary kiln is heterogeneous in nature. In rotary kiln where solid and gas phase are separated, the atmosphere is almost stagnant. For reducible reaction the reducing must get in touch with the interface otherwise reaction cannot be completed. Some of rate determining factor in iron ore reduction are associated with the nature of the reaction are associated with nature of reaction system and contact between the reducing phase while others are associated with nature of ore. The latter determine the ease with oxygen can be removed from the oxide in ore by the reducing gases.

Reaction:



Typical Analysis of Sponge Iron Produced from Coal Based Process

- Total iron 91 - 93 %
- Metallic iron 80 - 84 %
- Metallisation 90 - 92 %
- Gangue 3 - 4 %
- Carbon 0.25 %
- Sulphur 0.02 - 0.03 %
- Phosphorous 0.035 - 0.05 %

KINETICS OF IRON ORE REDUCTION

It is reduction reaction that iron oxide over come during transformation of phases under Pressure and temperature in the kiln at reducing atmosphere. Rate at which reduction is complete, determines the rate of reduction in the kiln. The reaction of metal oxide by carbon start at a temperature at which the line for free energy of CO formation resumes. This indicates that at 1000°C carbon can reduce all common metal oxide except Mn, Si, Ti, Mg and Ca. In the reactor large number of iron ore granules (used in lumpy form) is exposed to reductions. The large gaps between the granules are known as macropores and smaller gaps with in groups are known as

micropores. The reduction gas flow between the macropores and micropores of lumps of ores and hence boundary layer is formed around the individual lump. So, the gaseous reaction continuous as follows

The Reduction Mechanism for Iron Ores:

1. Diffusion of the hydrogen and CO gas across the
2. boundary, macropores and Micropores in the ores.
3. Phase boundary reaction.
4. Diffusion of water vapour through the micro pores and macropores
5. Diffusion of water vapour across the boundary layer migration of Fe^{++} and $2e$ to the iron nucleolus.

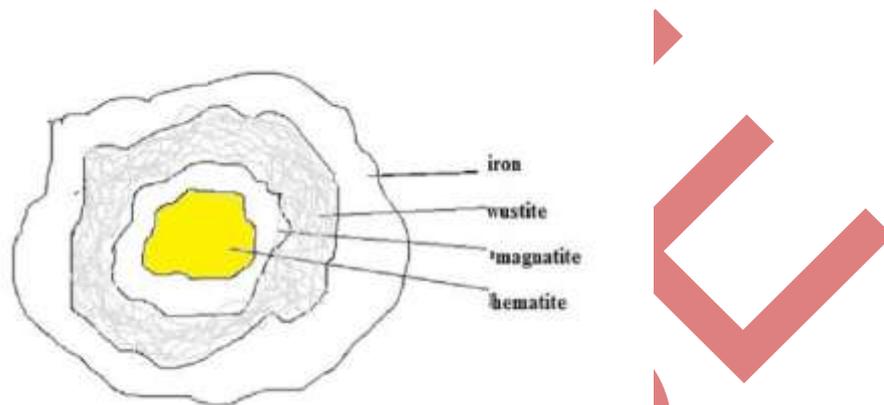


Fig – 6, Reduction section of iron ore

The diffusion of iron and electron the following pathway:



According to above mechanism O_2 is removed from the iron oxide at the iron wustite interface only. CO and Hydrogen diffuse inwards through the iron layers and the product gas CO_2 and water vapors diffuse outwards. The flow rate of gases through the bed of solid particles must be large enough so that a stagnant layer of gas cannot build up around each solid particle. For continuous effect of reaction, the reduction must get into the interface and solid may attain desired reduction. The coal gasification process

in air to CO_2 entirely depends on rate of removal of carbon or coal reactivity which mainly depends on pore structure of coal, particle size carbon concentration of active carbon, coal rank, ash of coal and other condition like charging.

Reducibility Factor of Sponge Iron:

This property of the iron ore depends on following factors:-

1. Nature of Iron Oxide

The major deposition of iron oxide in nature is mainly in the form of hematite & magnetite. The oxygen enrichment in hematite iron ore is more than the magnetite. Hematite iron ore is the saturation point of oxide ore which is more stable in nature. The purest hematite iron ore may contain maximum 1% of magnetic or magnetite in nature.

2. Ore Size

The deposition of iron ore in nature is usually in hard and massive form. But when the ore is considered for DRI process its size and shape are very much important for the of reduction reactions.

3. Porosity

The porosity of ore is one of the important factors which affect the reducibility. It is observed that the reducibility of soft hematite iron ore is greater than that of hard hematite and magnetite ore. The reducibility of natural ore show that for 90% reduction, reciprocal of time varied linearly with percentage porosity.

4. Nature & Composition of Gangue

It observed that natural ore contains gangue oxide of Si, Al, Cr, Ti etc. in different form. In some of the ores wustite is present as complex compound such as 2FeOSiO_2 , FeOAl_2O_3 , FeOCr_2O_3 where wustite exist in a state of low activity. These oxides tend to decrease the reducibility of iron ore in kiln in reducing atmosphere.

5. Swelling

Some ores show abnormal increase in volume at temperature between 900 to 1000°C. This is referred as swelling of ore. The cause of swelling has not been understood fully. Various investigators have in opinion that it is associated with mechanism of nucleation and growth having of wustite.

6. Temperature

The rate of reduction of iron oxide increases with increase in temperature of iron oxide. In solid gas reduction it is advantageous to use a temperature above 1000° C because boundary reaction is maximum for producing CO with CO_2 and C combination. It is observed that if iron ore is reduced to metallic iron at low temperature, this forms a layer of dense metallic iron on the ore body which affects reduction at higher temperature region.

7. Gas Compositions

The coal after gasification becomes a composition of CO_2 , H_2 , some water vapors, CO_2 etc. It is observed that by increasing the partial pressure of reducing gases the rate of reduction can be increased. It has been proved that hydrogen is better reducing gas than CO but at higher degree of reduction CO reduce iron oxide at faster rate.

8. Pressure

The increase in pressure is expected to increase the rate of reduction as increase the partial pressure of the reducing gas.

Grade of sponge iron

1) A Grade Sponge Iron

Sponge iron having total Fe more than 88% and metallization get up to 98% then sponge iron is called A grade sponge iron. .

2) B Grade Sponge Iron

Sponge iron having total Fe in between 80% to 87% and metallization get up less than 90% then sponge iron is called B grade sponge iron.

3) C Grade Sponge Iron

Sponge iron having total Fe is less than 80% and metallization less than 84% then sponge iron is called C grade sponge iron.

Properties of sponge iron:

1. Physical Properties:

There are several parameters to be monitored for improving the quality of sponge iron for steel making operation, these are listed below:-

(a) **Size** - A very fine sized material (1 mm to 2 mm) would be quickly oxidized during falling to the slag or may be lost in fume extraction system. Extremely large size (exceeding 30 mm) poses problem during continuous feeding. The size fraction less than 2 mm needs to be limited for continuous feeding and hence the size plays an important role.

(b) **Density** - Sponge iron after falling should have the ability to penetrate into the slag layer and reside at the slag/metal interface for effective heat transfer and chemical reaction. Sponge iron with lower density tend to float on the slag while, high density material readily penetrates into the metal. Hence, it is desirable to have the density of sponge iron in the range 4 - 6 gm/cc.

(c) **Unit Weight** – The transition time of the sponge iron pellets through the slag is dependent on the momentum. If the pellet stays in the slag layer for too long a time, the phenomenon of slag boiling occurs. Slag fluidity is highly important. However, a heavier sponge iron pellet does not require close control in slag fluidity.

(d) **Crushing Strength** - Sponge iron should possess good crushing strength to prevent generation of large amounts of fines.

(e) **Weather Resistance** - Sponge iron is prone to oxidation and heat builds up in contact with atmosphere. The storage of sponge iron for long periods of time affects its metallization, partially due to surface re-oxidation caused by the porous structure of sponge iron pellets or lumps.

(f) **Carbon Contents** - During continuous feeding, an active carbon oxygen boil is necessary to shield the arcs. It has been observed that to achieve the aforesaid, sponge iron should possess a minimum of 0.60% carbon.

(g) **Metallization** - High metallization helps in lower power consumption but severely reduces the bath activity and results in flat bath conditions. For low metallization levels, increased carburization is required to compensate for the extra oxygen in sponge iron.

2 Chemical Properties:

1. The sponge iron retains the size as that of iron ore and contains no oxygen.
2. Little amount of oxygen as FeO.
3. It is attracted by magnet and looks black with metallic lusture.
4. It picks up little carbon during process.
5. Highly reactivity with moisture.



Effect of Moisture on Sponge Iron Material

Main reason of high sensitivity of DRI towards rapid re-oxidation is because of its high porosity leading high surface to volume ratio. The chemical reaction involved in oxidation of DRI with air moisture leads to heat formation. The presence of hydrogen gas (if due to moisture) compounds the problem.

Advantages of using sponge iron in steel making:

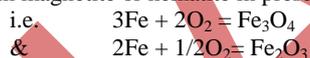
Use of sponge iron:

- Increases productivity through shorter tap-to-tap time and refining time.
- Simultaneous melting and refining with continuous charging.
- Faster metallurgical reactions and Improved as well as more stable power consumption
- Less electrode consumption due to stable power.
- More precise of steel compositions and quality advantages.
- High degree of metallization (up to 92%) and consistent chemical composition.

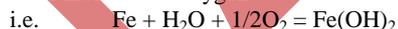
II Reoxidation:-

Sponge iron is produced in that iron ores are directly reduced by means of reducing gas, which consists of carbon monoxide & hydrogen & reduces iron oxide to metallic iron. The material in this process remains solid. *The metalized end product has high porosity i.e. it has a very large surface area to weight ratio. Thus it is very much chemically reactive & easily oxidized. So the sponge iron produced is highly susceptible to reoxidation.* The term reoxidation includes

1. Oxidation to form magnetite or hematite in presence of oxygen



2. Rusting in presence of moisture & oxygen



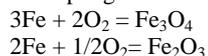
The re-oxidation of the metalized product means a high loss in quality because it decreases degree of metallization i.e. Fe metal/Fe total which is a measure of the quality of sponge iron. The iron oxide which has been formed by the re oxidation is either lost in the slag when sponge iron is melted to produce steel or must be reduced,

Mechanism of re-oxidation:

Sponge iron is utilized in the steel making industry as a basic raw material source for the production of steel. Generally speaking, sponge iron is produced by exposing hematite iron ore in comminuted form to a reducing gas environment at temperatures somewhat below blast furnace temperatures. Typically, the components of sponge iron are metallic iron, iron oxide, gangue and possibly carbon. Metallic iron is iron which has been totally reduced by the reducing gas environment. Gangue is the term used in the industry to refer to all non-ferrous material, except carbon contained in the ore. Gangue may include silica, alumina, lime, magnesia, phosphorus, sulfur and possibly other materials. A deposit of carbon on the outside surface of the sponge iron particulate will be described in greater detail hereinafter. In all of the iron ore reduction processes just referred to, freshly produced sponge iron as found in the final step of the process may be at a temperature of 300°F. or, in some cases, significantly higher. The freshly produced sponge iron must be moved from the reactor to some type of storage location or be immediately utilized in a steel producing process. In the past, it was more typical that the freshly produced sponge iron be used rather quickly in the production of steel. However, in the last few years, this situation has changed. There are more and more iron ore reducing plants being built in various parts of the world entirely removed from steel producing facilities. Therefore, it has become necessary that sponge iron be stored and even shipped long distances. Freshly produced sponge iron is not a stable material. In fact, such sponge iron is pyrophoric and subject to degradation through oxidation by exposure to air or water. There are two mechanisms by which sponge iron is believed to reoxidize.

Oxidation mechanism:

□ In the first mechanism sponge iron will react with dry air i.e. oxygen to form a magnetite by the following reaction:



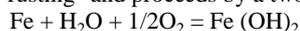
□ This reaction is very exothermic and can generate enough heat to spontaneously ignite adjacent sponge iron particles. Reoxidation presents a particularly aggravated problem when the sponge iron is already at high temperatures such as when it is removed from the reduction furnace.

□ Three stages of oxidation are identified, a rapid initial stage, an intermediate stage in which the rate of re-oxidation decreases significantly, and a final stage, in which the rate of oxidation is very low. The length of each stage and the rate of re-oxidation are related to temperature and to the status of raw materials.

□ The problem of pacifying freshly produced sponge iron against re-oxidation conventionally involves cooling it to a safe temperature. Attempts to at least partially cool the sponge iron to a safe temperature are found in the prior art. It is known that freshly reduced sponge iron must be cooled down significantly. Some cooling has been incorporated into the reduction process. Generally, this initial cooling occurs while the sponge iron is still in the reduction reactor. A separation and cooling process by which sponge iron may be better pacified against reoxidation.

Rusting mechanism:

□ A second mechanism by which sponge iron is believed to reoxidize involves its reaction with water vapor and air. This process is referred to as "rusting" and proceeds by a two stage reaction as follows:



□ The hydrated ferric oxide formed by reaction may undergo yet another reaction to liberate water and hydrogen. The "rusting" process not only results in the loss of pure iron which presents a serious economic loss over long periods of storage estimated loss to rust may be as high as 1.5% by weight per month. It also presents a dangerous shipping problem since hydrogen is generated as a by-product of the rusting reactions.

PROCESSES & ANALYSIS OF RE-OXIDATION:

There are four processes are used study about re-oxidation. Those are:

- i. Thermo gravimetric Analysis
- ii. Microscopic examinations
- iii. X-ray diffraction
- iv. Surface area measurements.

Thermo gravimetric analysis:

Thermo gravimetric analysis of sponge iron is used to study the reaction kinetics or the degree re-oxidation of sponge iron. Here the iron ore which is reduced by reducing gases with 90 -95 % degree of reduction to sponge iron is analyzed. The reduced product is subjected to reoxidation in dry air. The rates of reoxidation at 473-1073 K as a function of time was studied. The kinetic analysis developed has been used to establish the reaction mechanism which is found to be essentially of first order

Microscopic examination:

Microscopic examination and porosimetric measurements were used to elucidate the kinetics and mechanisms of reduction and re-oxidation. During reduction of iron oxide, the rate was increased with temperature and the structure of sponge iron produced was temperature dependent. Three transition temperatures were identified during re-oxidation. Re-oxidation at the initial stages was controlled by interfacial chemical reaction whereas at both the intermediate and later stages, solid-state diffusion was the rate controlling step.

X-ray diffraction:

The structure of the oxide layers is examined by X-ray diffraction; generally, magnetite is observed as a main component, accompanying small amounts of hematite.

Surface area measurement:

As those sponge-irons are oxidized, their specific surface areas increase and then decrease gradually. Specific surface area is the surface area per unit weight of the sample.

FACTORS CONTROLLING RE-OXIDATION:

Re-oxidation degrees of sponge-irons could be considered to be controlled by these factors .Such as:

□ Specific Surface Area

With increase in specific surface area the chemical reactivity of sponge iron increases & it becomes more susceptible to re-oxidation.

□ Temperature

The sponge iron discharged at higher temperature is more susceptible to re-oxidation than at lower temperature. Again, temperature rises by the heat of re-oxidation. The factor of temperature is particularly important for low temperature re-oxidation.

CHARACTERISTICS OF RE-OXIDISED SPONGE IRON:

- Oxidation of sponge-irons proceeds very rapidly by exposure to oxidizing atmosphere and then proceeds slowly. The latter obeys logarithmic law.

- As those sponge-irons are oxidized, their specific surface areas increase and then decrease gradually.

- The early rapid re-oxidation is regarded as gaseous diffusion control and latter slow oxidation obeys the logarithmic oxidation law.

METHODS OF INHIBITION OF RE-OXIDATION:

□ Discharging the sponge iron at room temperature or at about 50-100°C from the DRI furnaces.

□ Storing the material in dry condition & in dry place.

□ Avoid any contamination of wet material to the dry sponge iron piece.

□ The reoxidation problem could be overcome if the sponge iron could be contacted with a substance which would coat and shield its active metal surfaces from contact with air or moisture

□ By using inhibitors such as; Benzylamine, ammonium benzoate, the commercial VCI etc.

□ Production of sponge iron in the form of Hot briquetted iron (HBI) has minimized the risk of ignition and substantially reduced reoxidation, making handling and transportation of DRI much easier, and enabled DRI to be used as a substitute for scrap in steelmaking by the electric furnace.

DISADVANTAGE OF REOXIDATION OF SPONGE IRON:

□ Re-oxidation may introduce large portion of oxygen into the metal structure & requires special treatment during steel making & other refining processes.

□ The oxidation process is exothermic & stored bulk sponge iron can show a spontaneous increase in temperature to 80 to 100°C even to the point of ignition. Such temperature rises are especially disadvantageous when the sponge iron is stored in a hold of a ship because of the thermal stresses on the hull or otherwise endanger this conveyance.

PRECAUTIONS TO AVOID RE-OXIDATION

It has been estimated that main conditions, which could eventually cause sponge iron re-oxidation is the sudden increase in the temperature of sponge iron to uncontrolled levels. In order to avoid this condition, the following general precautions must be followed.

Contact with heat sources:

Direct contact with the heat sources must be avoided such as heat surfaces, welding butts & heavy radiation sources. Sponge iron accumulation must be avoided over electric motor, electrode conduits, equipment bearings or any other potential source of thermal energy. Due to the low specific heat of the fine dust, a short contact with a hot source could start re-oxidation through the dust accumulated. A direct exposure to solar rays or heat received from the roof in a storage building shall not increase the sponge iron temperature to unstable levels.

Contact with water:

In general, direct contact of sponge iron with water has a detrimental effect on the product quality, because the re-oxidation rate increases when the product is wetted. If the dry product is piled over wet sponge iron, which tends to re-oxidize faster, the heat dissipation could not be sufficiently fast to avoid a sudden temp rise, due to low thermal conductivity of the product. If this happens, a spot of unstable material will appear & rest of the product will be spoiled if it is not separated on time.

IMPORTANCE:

Outcome of this investigation may be useful for devising means to protect sponge iron against rapid re-oxidation & spontaneous combustion. Since in many cases sponge iron facilities are located at great distances from steel mills, and often must be transported to such distant mills by sea transport, some method must be found by which its tendency to rapidly reoxidize upon contact with moisture in the air, with the consequential liberation of heat and hydrogen, can be eliminated or significantly reduced.

Sr. No	Du r. in da ys	Wt. of crucible	Initi al wt. of sam ple	Wt. after sun dry	Wt. diff	Rate of reoxi- dation	Wt after heating at 400° C	Wt diff.	Rate of reoxi- dation
1	1	38.638	50	89.7537	1.1157	0.0639	90.5202	1.88219	0.1078
2	2	21.571	50	72.8054	1.2344	0.0707	73.6348	2.06377	0.1182
3	3	37.97	50	89.8190	1.8490	0.1059	91.3887	3.41867	0.1958
4	5	20.556	50	73.2117	2.6557	0.1521	74.4845	3.9285	0.225
5	7	34.78	50	87.4793	2.6993	0.1546	89.3423	4.5623	0.2613
6	9	25.126	50	77.8375	2.7115	0.1553	79.7407	4.61468	0.2643

EXPERIMENTATION

RAW MATERIALS:

The raw material (coal based sponge iron) from " **Bhushan Power & Steel Ltd.**" used for the re-oxidation/rusting study has the following composition:

Fe (m) = 81.48%
Sulphur = 0.038%
Carbon = 0.015%
Others = 18.467%

FOR#20 MESH SIZE at 200°C:

APPARATUS REQUIRED

1. Electric weighing machine
2. Muffle furnace
3. Beaker
4. Crucible

PROCEDURE FOLLOWED

- A sample of sponge iron was taken and crushed into different mesh sizes through sieve analysis.
- The 230 mesh size & 20 mesh size of the sample were taken for experimental analysis. 50 gms of 20 mesh size samples were taken each in 6 beakers that are analyzed in day 1, day 2, day 3, day 5, day 7, day 9 etc. Similarly, 10 gms each of 230 mesh size & 20 mesh size sample were taken in 6 beakers & analyzed for those 6 consecutive days.
- The sample was kept in beaker by adding water of about 300 ml in which the sponge iron sample is dipped in.
- For day 1 the analysis is done in such a way that the water from the sample was poured away & the sponge iron sample in it are dried for 1-2 hour. The dried sample was then put inside muffle furnace at a temperature of 400°C for about 1 hour where reoxidation occurs. The weight gain in the sample due to re-oxidation was observed in electric weighing machine. This procedure is

OBSERVATION:

Sl. No	Duration in days	Weight of crucible	Initial wt. of sample	Wt. after sun dry	Wt. diff	Rate of reoxidation	Wt after heating at 400° C	Wt diff.	Rate of reoxidation
1	1	38.638	10	48.875	0.237	0.06802	49.049	0.411	0.11788
2	2	21.571	10	31.823	0.252	0.07228	32.018	0.447	0.12824
3	3	37.97	10	48.360	0.390	0.11193	48.667	0.697	0.19986
4	5	20.556	10	31.102	0.546	0.15657	31.358	0.802	0.22991
5	7	34.78	10	45.339	0.559	0.16019	45.717	0.937	0.26835
6	9	25.126	10	35.724	0.598	0.17139	36.066	0.940	0.26936

PLOT OF GRAPH

From above analysis the following graphs are plotted.

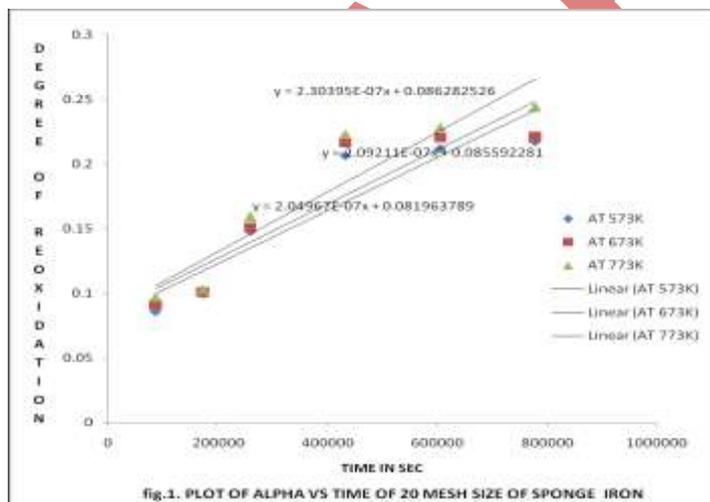


Fig.1. PLOT OF ALPHA VS TIME OF 20 MESH SIZE OF SPONGE IRON

Fig – 7, Plot of Alpha vs. time of 20 mesh size of sponge

Evaluation of Activation Energy:

We can determine the activation energy values (E) in several ways. Here, in the integral approach the plot of ln k vs. reciprocal temperature is made. This plot for the sponge iron oxidation has been shown in fig-2. The slope of this arrhenius plot provides the value of (-E/RT)

The E value can also be calculated using differential approaches. It may be noted that the rate of reaction is related to temperature & fractional conversion by the differential equation

$$(d\alpha/dt) = k f(\alpha) = A \exp^{-E/RT} f(\alpha) \text{ ----- (1)}$$

Considering a fixed value of α , one gets

$$\ln (d\alpha/dt) = \ln A + \ln f(\alpha) - E/RT \text{ ----- (2)}$$

Since $\ln f(\alpha)$ has a fixed value for a given α it follows that a plot of the left hand side against reciprocal temperature would be a straight line. The slope of this would yield the value of $(-E/RT)$

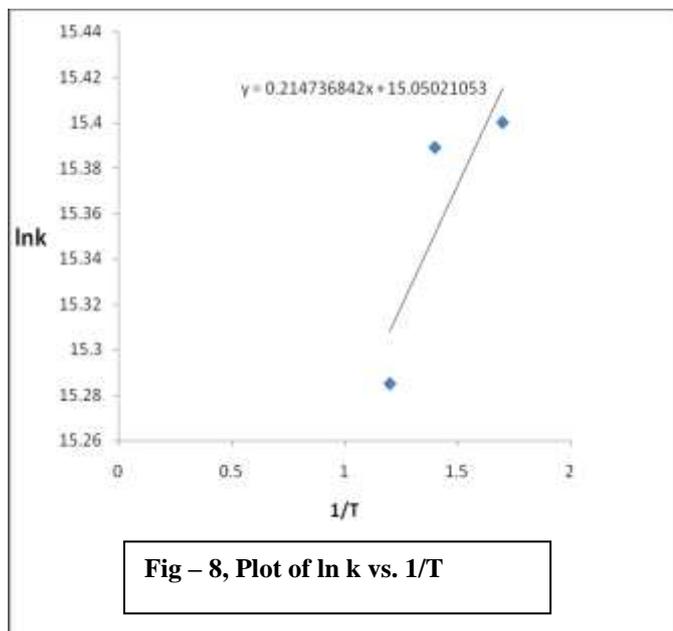
Equation – 1 can be written as

$$1/(A \exp^{-E/RT}) d\alpha/f(\alpha) = dt$$

So, at a given value of α , we can get

$$t_\alpha = (\text{Constant}/A) \exp^{-E/RT} \text{ ----- (3)}$$

So a plot of $\ln t_\alpha$ against reciprocal temperature should be a straight line & the slope would yield the value of activation energy (E).



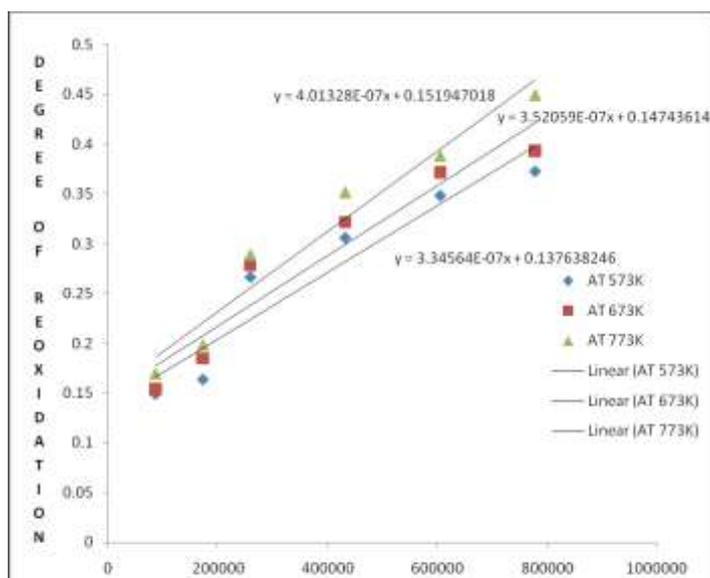


Fig – 9, Plot of Alpha vs. time of 20 mesh size of sponge iron

TIME IN SECS

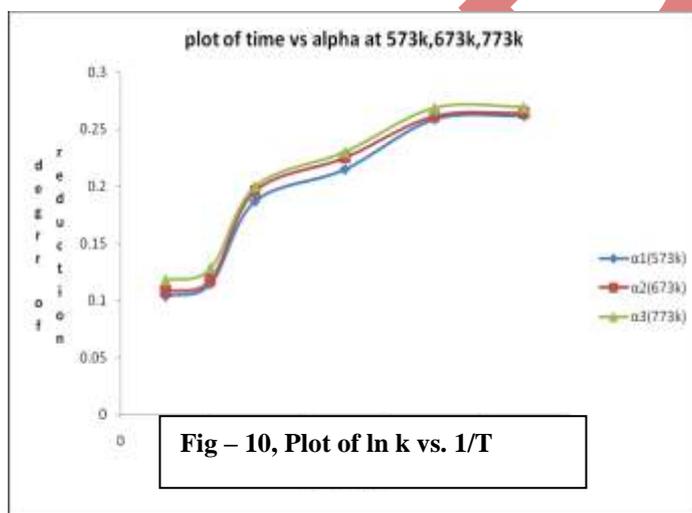


Fig – 10, Plot of ln k vs. 1/T

RESULT AND DISCUSSION

Reoxidation of sponge iron is an exothermic process due to removal of hydrogen. In this project first of all we collect the sample weight. Then we provide moisture atmosphere i.e.; the sample was dipped in water for various days interval. Then after some dry we weighted and collected the weight of samples in table 2, 3 4 and 5. The compound from this chemical reaction of sponge iron and moisture i.e Fe(OH)₂. So there is net mass gain in sponge iron from metallic iron to iron hydroxide product. This phenomenon is called rusting, which is an oxidation phenomenon. after heating at various temperature such as 300°C,400°C,500°C it is found that further increase in mass gain of sample taken, it is due to conversion of metallic iron to iron oxide form i.e.; Fe₂O₃ (hematite) . Assuming the sample (metallic sponge iron) was converted to hematite structure. We calculated the rate constant of oxidation from the graph α vs. time which is indicated in figure-7 and 9. The energy released in reoxidation phenomenon is derived in the figure-8 and figure-10.

CALCULATION OF DEGREE OF REOXIDATION:

In this sample percentage of metallic iron is 81.48%

Sample taken =10gm

In 10gm sample % of metallic iron =8.148 gm

Assuming all metallic iron is converted to Fe_2O_3

$2\text{Fe} \rightarrow \text{Fe}_2\text{O}_3$

112 gm of iron is converted to 160gm Fe_2O_3

So, in 112 gm of iron mass gain is 48gm

In 1 gm of iron mass gain is (48/112)gm

In 8.148gm of iron mass gain is 3.492gm

So, degree of reoxidation (α) = (practically weight gain/theoretical weight gain)

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