Iron Making
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Lecture - 33
Iron Making Lecture 33

But now we will talk about the alternative routes of iron making. So, in this lecture I would be talking some of the processes by which we make the iron in the solid form or in liquid form.

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Alternative Routes of Ironmaking

- Unavailability of high quality raw materials such as high grade iron ore and high ranking coke
- Environmental problems associated with blast furnace
- High capital cost related to blast furnace operations, etc.
- This led to the development of direct reduction, smelting reduction, mini blast furnace and other new emerging and future technologies

So, this alternate routes of iron making it came into existence mostly because, due to unavailability of high quality raw materials such as high grade iron ore and high ranking coke it. So, it many places due to depletion of high grade iron ore and generation of more points, I tried difficult to operate large furnace or some alternative route of iron making what thought to create. So, this low grade iron ore and the fines can be used and in fact, another driving force has been it is the absence of high ranking coke in many of the country, in some countries there is a depletion in the high ranking coal actually.

So, by which you can make the coke. So, these 2 were quite driving force and laterally environmental problem associated with the blast furnace and with many other industries beside iron and steel industries power industries and other has forced iron making companies to look for some alternative of each environment, the problem associated to it can be reduced.

So, green house emission of the cases can be reduced and third is a high capital costs related to the blast furnace operation and this is also an important factor when there is a small city or like that and you need the supply of the iron liquid iron and to make the steel, then 1 cannot afford to have a big blast furnace at a very high investment. So, that led to development again to another alternative routes of iron making. So, this led to the development of direct reduction is melting reduction, mini blast furnace and other new emerging and future technologies.

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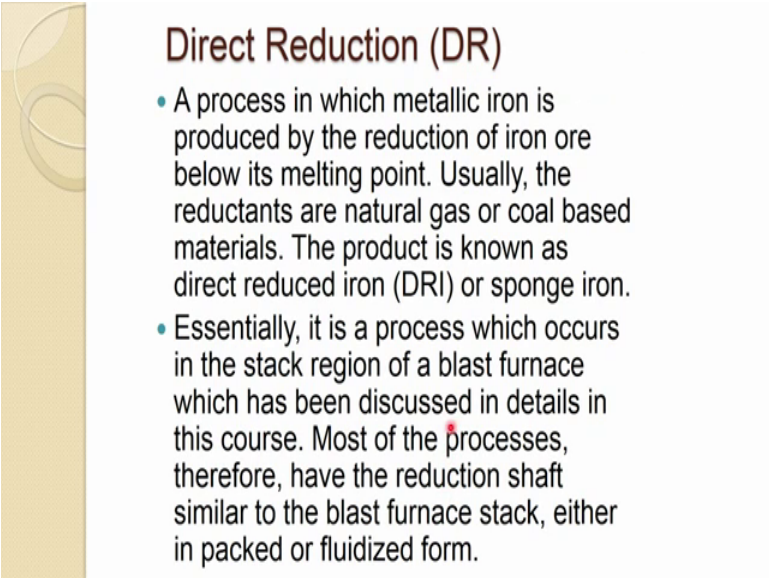

Direct Reduction (DR)

- A process in which metallic iron is produced by the reduction of iron ore below its melting point. Usually, the reductants are natural gas or coal based materials. The product is known as direct reduced iron (DRI) or sponge iron.
- Essentially, it is a process which occurs in the stack region of a blast furnace which has been discussed in details in this course. Most of the processes, therefore, have the reduction shaft similar to the blast furnace stack, either in packed or fluidized form.

So, this one we will be talking more about these technologies what have been come into existence until now. So, the first one which is quite all is direct reduction, so what in short from we called DR processes. So, a process in which metallic iron is produced by the reduction of iron ore below it is melting points. So, remember this is below it is melting point, so the product would be solid usually the reductants are natural gas or coal based materials the product is known as direct reduced iron or sponge iron.

So, DRI in salt what you call it is a direct reduced iron which is mostly in the solid symmetric form so because, it is done below the melting point of it essentially it is a process which occurs in this stack region of a blast furnace, which has been discussed in details in this course. So, you are already aware about the iron making in the blast furnace and in very detail we have discussed about the reaction which are occurring and the blast furnace in various zones.

But especially in this stack region where the reduction of iron oxide, in various form from hematite or magnetite to boostide occurs these those reaction are applicable even to the directly reduce direct reduction, because even in the upper part of the blast furnace in the stack region iron whatever is reduced it is still in the solid form and not in the liquid form and same thing happens even in direct reduction.

So, there is a big familiarity in not in terms of physical even the chemical reaction or physical chemical way whatever processes are occurring in the upper part of the blast furnace same thing can be applied to the direct reduction processes. So, most of the processes therefore, have the deductions are similar to the blast furnace is stack either in pack be d or fluidized form.

So, that is actually one difference so it can be either in a packed or fluidized form of where it is reduced into solid iron.

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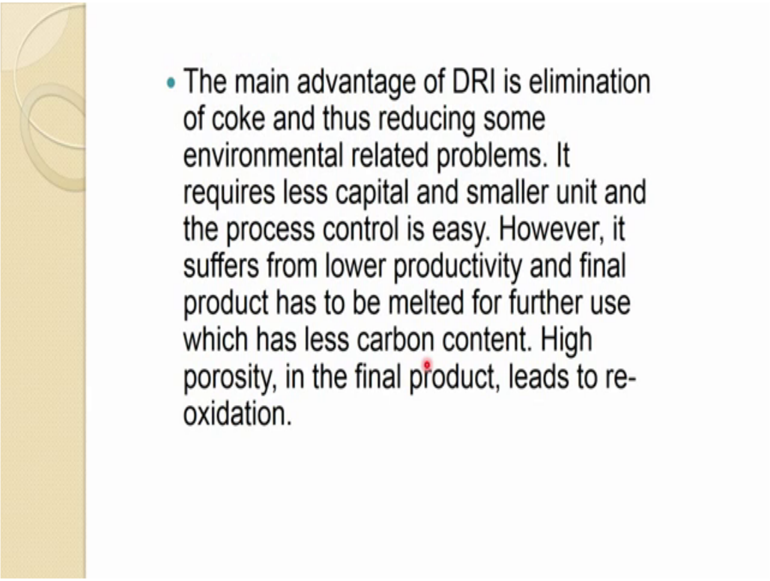

- The main advantage of DRI is elimination of coke and thus reducing some environmental related problems. It requires less capital and smaller unit and the process control is easy. However, it suffers from lower productivity and final product has to be melted for further use which has less carbon content. High porosity, in the final product, leads to re-oxidation.

So, the main advantage of DRI is elimination of coke and thus reducing some an environmental related problem. So, you must be aware that coke linking is a very nasty or dirty process which involves polarization of called the coke oven and that curies lots of environmental problems. So, this is the biggest advantage of DRI that you do not need coke as a reductant, but you can use the coal for that purpose and in that video also they do some environmental related problem and it is much more advantageous when in especially in those countries where the high ranking coal is not there. So, one can use the coal and can make the DRI, so it requires less capital and a smaller unit and the process control is easy because unit is a small they are not much complication.

So, process control become quite easy however, it suffers from lower productivity naturally it is a small unit and few other problems the productivity is low and final product has to be melted for further use which has less carbon content. And if you remember we talked already about melting point and other impurities which can affect the melting point of iron. So, if the less carbon in there melting point usually becomes quite high.

So, carbon reduce the melting point of iron quite substantially, so here in DRI director reduce arm you have a less carbon. So, you need then more energy to melt it later high porosity in the final product and this leads to the re oxidation; so due to because it is the form of in this pond more porosity is there it is get reduced. So, due to that lots of porosity is there in the reduced solid iron and when it comes out, so that time 1 had to be very careful it should not be exposed to the air otherwise it may re oxidized and it is not only that even a storage problem in transfer during transportation it may lead to the re oxidation. So, these are some associated problem with the dri, but it can be easily handled.

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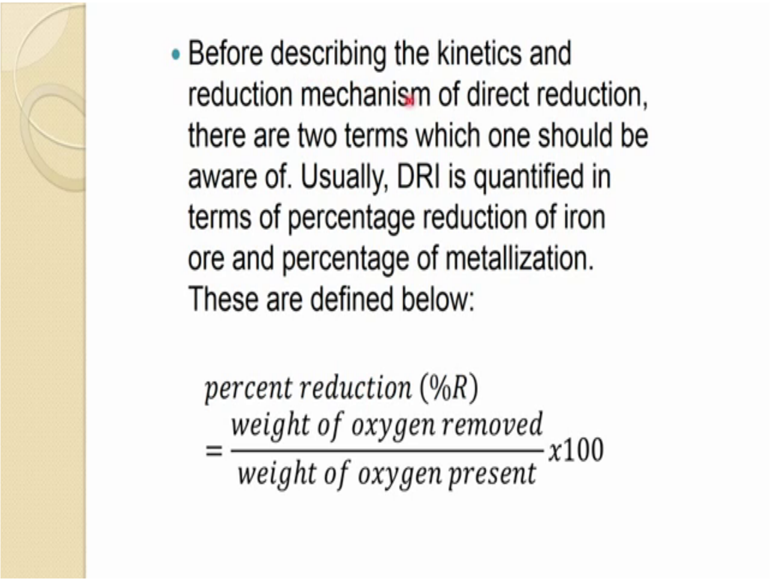

- Before describing the kinetics and reduction mechanism of direct reduction, there are two terms which one should be aware of. Usually, DRI is quantified in terms of percentage reduction of iron ore and percentage of metallization. These are defined below:

$$percent\ reduction\ (\%R) = \frac{weight\ of\ oxygen\ removed}{weight\ of\ oxygen\ present} x100$$

So, before describing the kinetics and reduction mechanism of direct reduction there are 2 terms, which 1 should be familiar and usually DRI is quantified in terms of percentage reduction of iron ore and percentage of metallization sometimes you call it degree of metallization, so these are defined below.

So, when you say percent reduction it is actually nothing it is a ratio of weight of oxygen removed from the ore and weight of oxygen present in it in to 100. So, that gives you the percentage reduction. So, whatever oxygen is removed from the ore and the total oxygen which is present in it divide by that and multiply by 100 will give you percent reduction.

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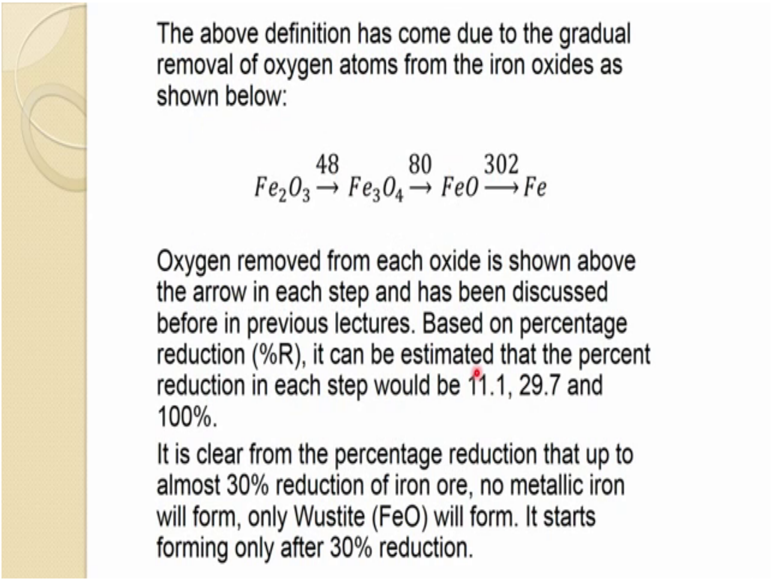

The above definition has come due to the gradual removal of oxygen atoms from the iron oxides as shown below:

$$Fe_2O_3 \xrightarrow{48} Fe_3O_4 \xrightarrow{80} FeO \xrightarrow{302} Fe$$

Oxygen removed from each oxide is shown above the arrow in each step and has been discussed before in previous lectures. Based on percentage reduction (%R), it can be estimated that the percent reduction in each step would be 11.1, 29.7 and 100%.

It is clear from the percentage reduction that up to almost 30% reduction of iron ore, no metallic iron will form, only Wustite (FeO) will form. It starts forming only after 30% reduction.

Then so the above definition also has come due to the gradual removal of oxygen atoms from the iron oxide as shown below. So, as he said it is a removal of oxygen from the ore and the total oxygen present. So, if you look at the way all our iron oxide is present in any of the iron ores, first one it is hematite with which you are already aware. So, when it goes to hematite to magnetite it actually removes about 48 atoms of a what 3 8 sort of oxygen is removed, whether you can tell moles or kg moles or gram mole.

So, that that much oxygen is removed from hematite to magnetite and when from magnetite to wustite it is reduced 80 1 sort of oxygen is removed in terms of 10 tones or kgs when you do it and from our. So, pertain basis so if we take it 48 kg 80 kg and from wustite to iron about 302 kg of oxygen 1 has to remove, then you get iron to do you can see from wustite to iron the maximum oxygen is removed.

So, oxygen removed from each oxide is shown above, the arrow in each step and has been discussed before in previous lectures. So, if you go the physical chemical behavior of the iron oxide in the blast furnace where we discuss in detail about the reaction kinetics reduction of iron oxide in various way and even the optimization and that one all these things have been described.

So, I would encourage you to go to those lecture and in brief I will also take it again here. So, based on percentage reduction it can be estimated that the percent reduction in each step would be 11.1. So, from Fe2 O 3 to Fe3 or 4 it would be 11.1 from every 3 or 4 to FeO is 29.7 and from FeO to Fe 100 percent reduction.

So, it is clear from the percentage reduction that up to almost 30 percent, if you look at to here up to almost thirty percent reduction and or no metallic ion is formed only wustite will form. So, it starts forming only after 30 percent reduction. So, therefore one has to define a degree of metallization of our percentage of materialization in a different way because, only after 30 percent of reduction the metallic ion coming to the picture.

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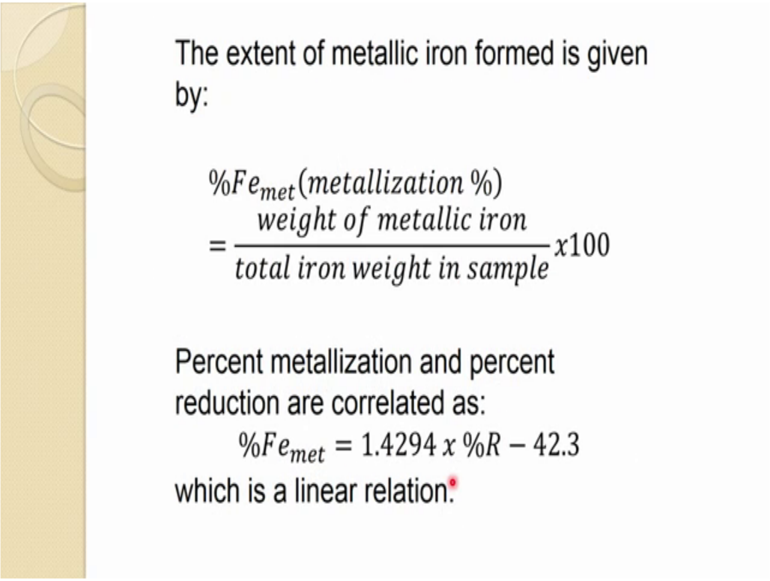

The extent of metallic iron formed is given by:

$$\%Fe_{met}(metallization\ \%) = \frac{weight\ of\ metallic\ iron}{total\ iron\ weight\ in\ sample} x100$$

Percent metallization and percent reduction are correlated as:

$$\%Fe_{met} = 1.4294\ x\ \%R - 42.3$$

which is a linear relation.

So, the extent of metallic ion formed is given by percentage of metallic iron equal to weight of metallic iron divided by total iron weight in the sample into 100 that will give to the percentage. So, weight of metallic iron which is formed divided by the total iron weight in the sample that will give you the metallization or degree of metallization. So, for percent metallization in percent reduction are correlated as. So, it is a empirical correlation which has been found between the degree of metallization and a cure for a reduction.

So, percent on metallization equal to 1.43 in to percent reduction minus 42.3. So, from this equation you can see this is a linear equation h there is a linear relation between the percent metallization and the percent reduction. So, when you a draw a line it will give you a straight line cutting on the x axis all, so and if you know the percent reduction you can probably from this relation calculate the degree of metallization.

So, once now you are familiar for this because this term usually degree of metallization and percentage reduction it is a quite useful in describing the efficiency of the DRI process and more than 90 percent degree of metallization it needed in direct reduction process, so 93 94 95 percent or so at some time even up to 90 67 percent.

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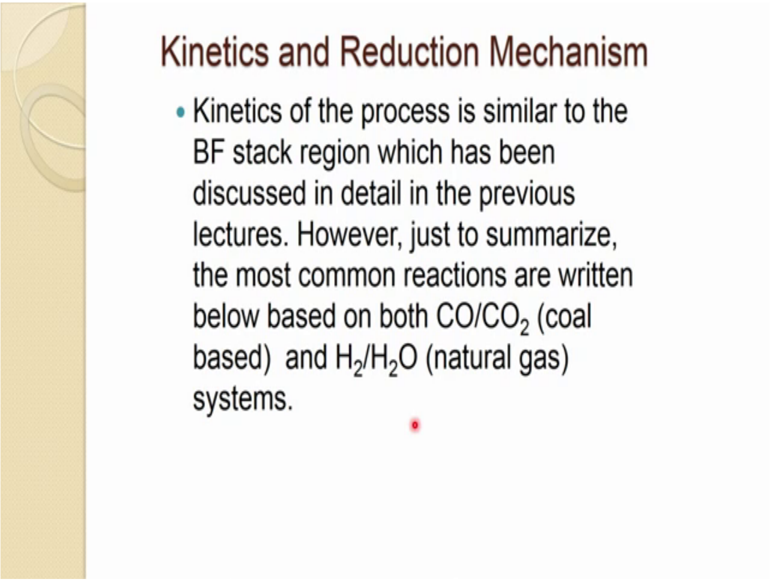

Kinetics and Reduction Mechanism

- Kinetics of the process is similar to the BF stack region which has been discussed in detail in the previous lectures. However, just to summarize, the most common reactions are written below based on both CO/CO_2 (coal based) and H_2/H_2O (natural gas) systems.

Now, it is about the kinetics and reduction mechanism which is again an essential part for any of the process or new process engine here. So, kinetics of the process is similar to the blast furnace is stack region, which has been discussed in details in the previous lectures. However, just to summarize the most common reaction are written in below. So, based on both CO CO 2 so this is CO CO 2 means mostly the coal waste reaction and H 2 H 2 O, so this is actually debate mostly from the natural gas based reaction. So, DRI directed reduction can occur by 2 of the process which we will discuss in detail later. So, these 2 processes are either a coal waste, so carbon is a reductant our natural gas. So, hydrogen is the reductant in combination with the carbon also CO plus H 2.

So, we have already discussed about this system iron carbon oxygen system, if you go back to our previous lecture and similarly about this we have discussed a bit in duration even to the discussing about injection of moisture as to oxygen, through the tuyere in order to increase the reduction efficiency of the gas and that time we discuss about this system also too I would encourage you to go through that.

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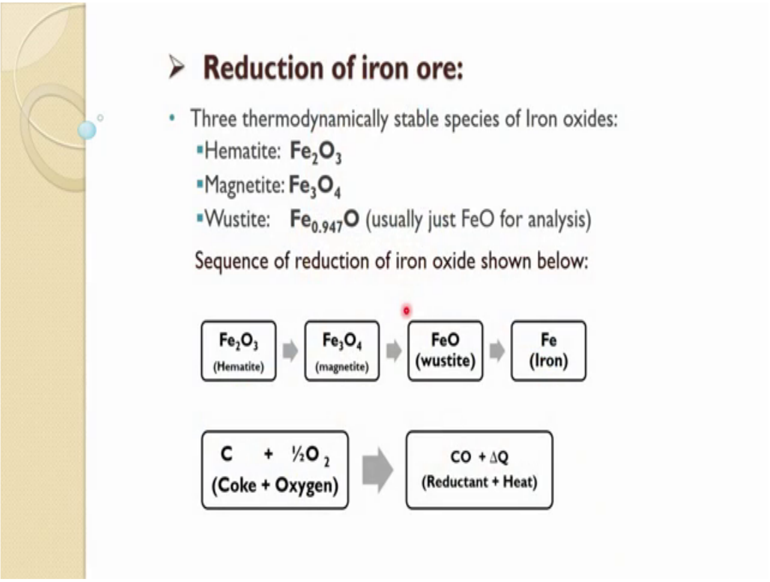

Reduction of iron ore:

- Three thermodynamically stable species of Iron oxides:
  - Hematite: Fe_2O_3
  - Magnetite: Fe_3O_4
  - Wustite: $Fe_{0.947}O$ (usually just FeO for analysis)

Sequence of reduction of iron oxide shown below:

Fe_2O_3 (Hematite) → Fe_3O_4 (magnetite) → FeO (wustite) → Fe (Iron)

C + ½O_2 (Coke + Oxygen) → CO + ΔQ (Reductant + Heat)

But in brief I am taking it again here, but I will not go much into the detail because, this has already been discussed before. So, 3 thermodynamically stable species of iron oxide as you are aware hematite magnetite and wustite this is stoichiometry this oxygen association or the percentage associated with iron changes. So, it is not a stable oxide which we said before also. So, hematite due to magnetize due to wustite and gives the iron and this is a partial oxidation of the carbon, which gives you the CO and heat is required for that, but for complete combustion you get the CO 2 and heat is lead in that when you produce more heat.

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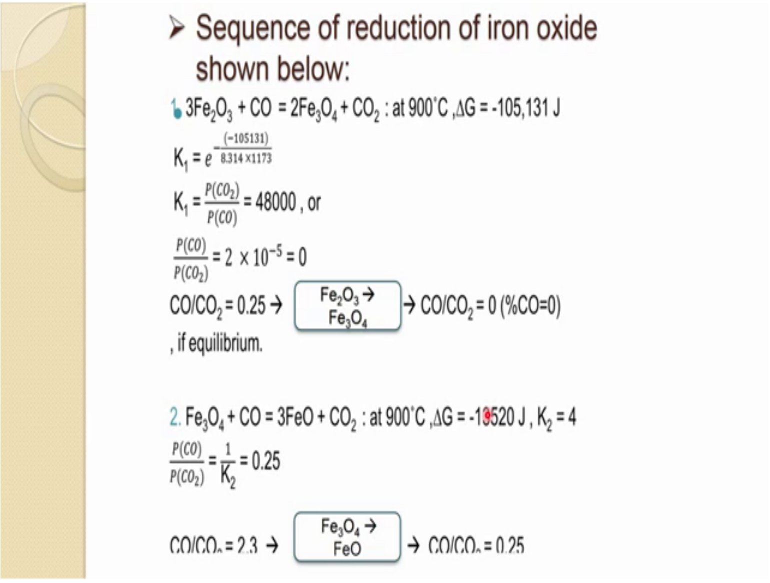

Sequence of reduction of iron oxide shown below:

1. $3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$: at 900°C, $\Delta G = -105{,}131$ J

$K_1 = e^{-\frac{(-105131)}{8.314 \times 1173}}$

$K_1 = \frac{P(CO_2)}{P(CO)} = 48000$, or

$\frac{P(CO)}{P(CO_2)} = 2 \times 10^{-5} = 0$

$CO/CO_2 = 0.25 \rightarrow \boxed{Fe_2O_3 \rightarrow Fe_3O_4} \rightarrow CO/CO_2 = 0$ (%CO=0)

, if equilibrium.

2. $Fe_3O_4 + CO = 3FeO + CO_2$: at 900°C, $\Delta G = -13520$ J, $K_2 = 4$

$\frac{P(CO)}{P(CO_2)} = \frac{1}{K_2} = 0.25$

$CO/CO_2 = 2.3 \rightarrow \boxed{Fe_3O_4 \rightarrow FeO} \rightarrow CO/CO_2 = 0.25$

And I if you look at the previous lecture and go through this we have already discussed about this reaction, how hematite converted into magnetite by CO at nine hundred degree centigrade.

So, we are here talking about the DRI which is usually the temperature is about nine ah. In fact, temperatures ranges from 700 to 1000 or sometime some term only to 1100 it may go. So, it is mostly in their trend, but usually this is sort of a temperature which is maintained in most of the reduction shaft in DRI or even in the fluidized bed about 750 or like that sort of temperature 700.

So, this all reactions and their kinetics is applicable even for RI, so hematite to magnetite at 900 delta g was given. So, if you look at the equilibrium constant it is a very high and that gives the percent of CO 2 utilization or and all my 0. So, it is very easily reduced which we discussed before and from magnetite to wustite it is your K 2 is low and it is about 0.25 this ratio comes.

So, that this still needs less CO, but can be reduced more comfortably ah, but of course harder than the magnetite and when it we go to the FeO to Fe and then get equilibrium constant value is very low.

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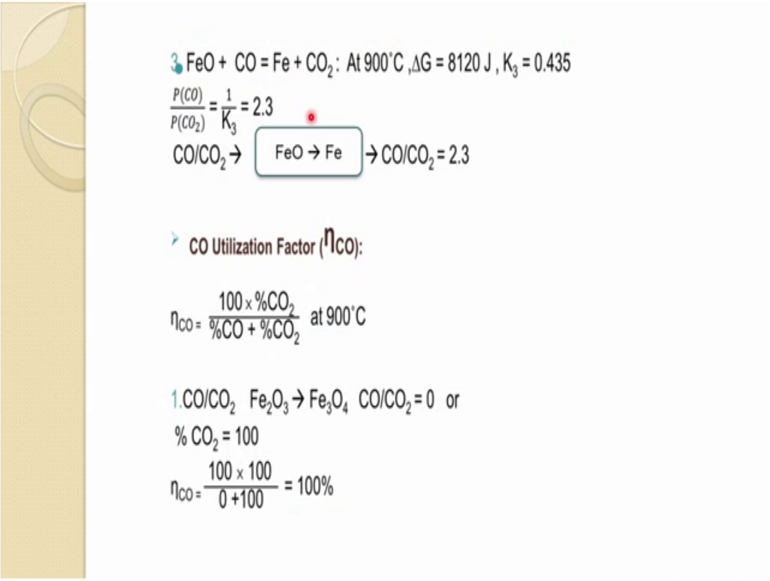

3. $FeO + CO = Fe + CO_2$: At 900°C, $\Delta G = 8120$ J, $K_3 = 0.435$

$$\frac{P(CO)}{P(CO_2)} = \frac{1}{K_3} = 2.3$$

$CO/CO_2 \rightarrow \boxed{FeO \rightarrow Fe} \rightarrow CO/CO_2 = 2.3$

- CO Utilization Factor (η_{CO}):

$$\eta_{CO} = \frac{100 \times \%CO_2}{\%CO + \%CO_2} \text{ at } 900^\circ C$$

1. CO/CO_2 $Fe_2O_3 \rightarrow Fe_3O_4$ $CO/CO_2 = 0$ or

$\% CO_2 = 100$

$$\eta_{CO} = \frac{100 \times 100}{0 + 100} = 100\%$$

So, you needed high rejection potential or a high reducing power of the gases. So, that is where do you have CO CO2 ratio up to 2.3 and it is clearly also we talked about the efficiency of the reaction and utilization of the CO factor. When we put it this ratio for respective of these 3 reaction we will find hematite to magnetite is almost 100 percent CO utilization and for others for magnetite to wustite it is about 80 percent utilization that factor. So, it decreases however because, here you really need a very high reduction potential and the utilization factor for from wustite to iron it is at about 30 percent.

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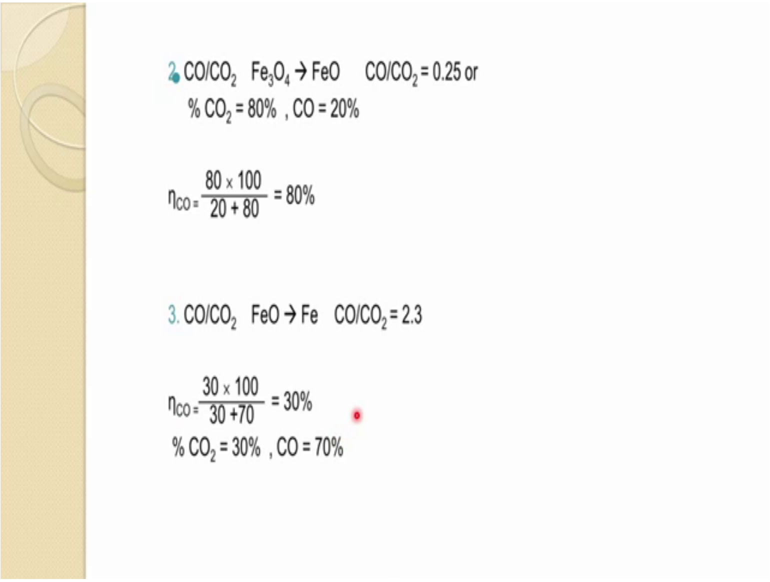

2. CO/CO$_2$ $Fe_3O_4 \rightarrow FeO$ CO/CO$_2$ = 0.25 or

% CO$_2$ = 80% , CO = 20%

$$\eta_{CO} = \frac{80 \times 100}{20 + 80} = 80\%$$

3. CO/CO$_2$ $FeO \rightarrow Fe$ CO/CO$_2$ = 2.3

$$\eta_{CO} = \frac{30 \times 100}{30 + 70} = 30\%$$

% CO$_2$ = 30% , CO = 70%

So, again which means you have to introduce a very high reduction potential cases from the bottom. So, FeO can reduce into iron and it is gen losses this reduction potential power so and which you do not need that much in the upper as it goes up, in the upper part of this table whether it is a blast furnace or directed reduction. So, it can easily reduce magnetite to wustite and then you need a very little CO presence or the reduction potential to convert hematite into magnetite. So, from the bottoms you send a high potential reducing cases ah, so it can reduce wustite to iron.

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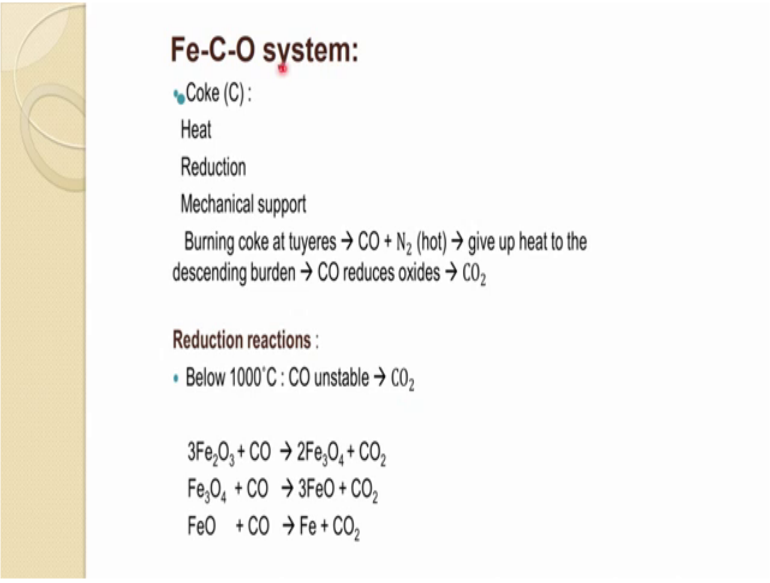

Fe-C-O system:

- Coke (C) :
  Heat
  Reduction
  Mechanical support
  Burning coke at tuyeres → $CO + N_2$ (hot) → give up heat to the descending burden → CO reduces oxides → CO_2

Reduction reactions :

- Below 1000°C : CO unstable → CO_2

$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$

$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$

$FeO + CO \rightarrow Fe + CO_2$

So, this is FeO CS carbon system of course, because these has been taken from the previous lectures. So, here this is not applicable because, this is a separate part of producing reducing gases in a indirectly reduction processes while in blast furnace it is in von drake that it is a part of it.

So, we will not so this is not relevant to the direct reduction process; however, these reactions are quite relevant to direct reduction processes that hematite to magnetite to wustite and wustite to iron and below thousand degree or nine it is CO it is a bit unstable and goes to CO 2.

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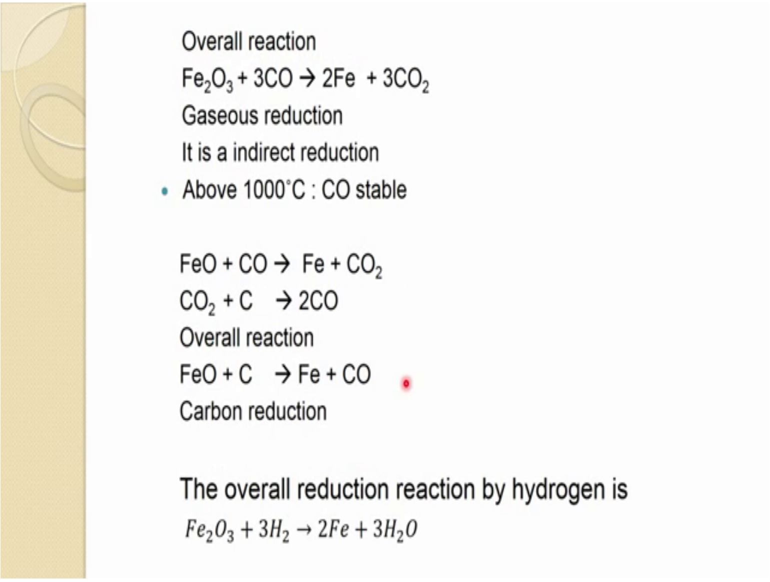

Overall reaction

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

Gaseous reduction

It is a indirect reduction

- Above 1000˚C : CO stable

$FeO + CO \rightarrow Fe + CO_2$

$CO_2 + C \rightarrow 2CO$

Overall reaction

$FeO + C \rightarrow Fe + CO$

Carbon reduction

The overall reduction reaction by hydrogen is

$Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O$

So, the overall reaction if want to give in the upper region then my case is written, it can be written in this way which is sort of indirect detection which has been discussed quite in detail previously and similarly the other variant form of the carbon whatever the overall reaction takes in this form with some you also called the direct detection. If it is lower part of the blast furnace, but this is not relevant to the director detection process and mostly this is the one which is more relevant and the overall reduction reaction but the hydrogen usually. So, this is monthly by carbon and this is mostly why hydrogen the way to keep overall reaction with the CO this overall reaction with hydrogen. Similarly, it is given by this reaction from hematite to iron the overall reaction.

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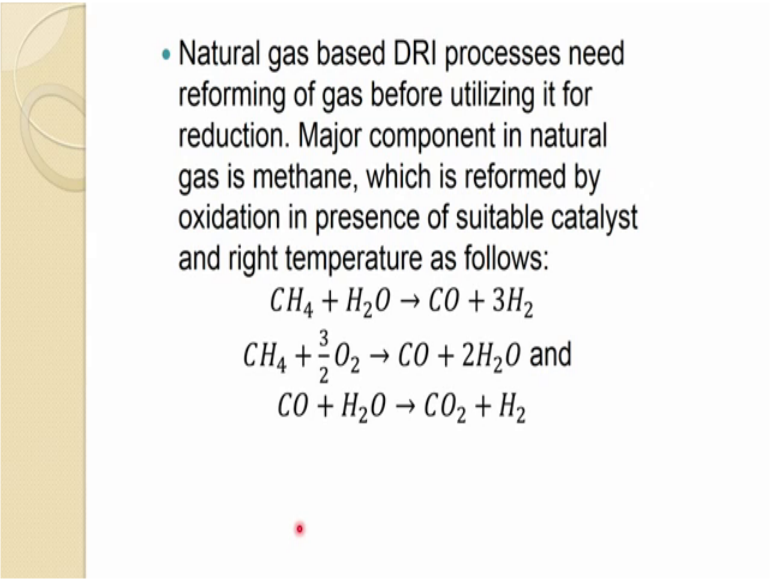

- Natural gas based DRI processes need reforming of gas before utilizing it for reduction. Major component in natural gas is methane, which is reformed by oxidation in presence of suitable catalyst and right temperature as follows:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

$$CH_4 + \frac{3}{2}O_2 \rightarrow CO + 2H_2O \text{ and}$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

Now, here hydrogen actually do get it through the natural gas. So, these are the gas based reduction whatever we discussed here, these are the cold wastes or solid sort of rate reactions through which you get the CO and this is the natural gas based the DRI reduction and usually in the natural gas methane is the major part of it.

So, you can use as such the natural gate. So, it needs reforming. So, before utilization of it so major component in natural gas is methane which is reformed by oxidation it is a methane ethane other 2 carbons. So, by oxidation in presence of suitable catalyst usually nickel we will talk a little later and the right temperatures. So, it keeps a mixture of hydrogen and CO, so by adjusting the temperature here at catalyzed pressure another parameter, so one can add j this ratio.

So, can have a high reduced highly reducing reducible cash from the reformer ah. So, natural gas first pass through the reformer and then these cases are used for the detection purpose. So, so in case of hydrogen get pure hydrogen the process usually is chemically controlled.

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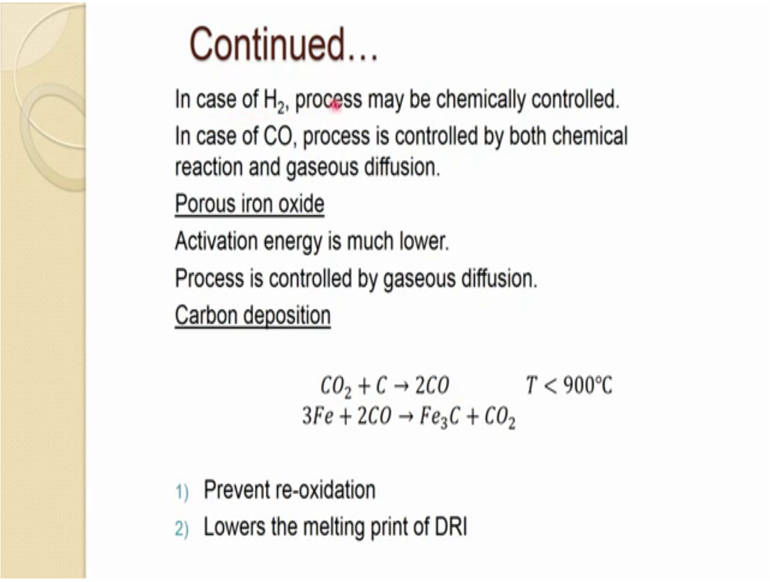

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In case of H_2, process may be chemically controlled.

In case of CO, process is controlled by both chemical reaction and gaseous diffusion.

Porous iron oxide

Activation energy is much lower.

Process is controlled by gaseous diffusion.

Carbon deposition

$$CO_2 + C \rightarrow 2CO \qquad T < 900°C$$
$$3Fe + 2CO \rightarrow Fe_3C + CO_2$$

1) Prevent re-oxidation
2) Lowers the melting print of DRI

Ah But in case of CO it is both chemical and diffusion controlled gas diffusion it could be even combination depends on many situations, porous iron oxide the activation energy much lower in porous iron oxide and process is controlled mostly by gaseous diffusion if iron oxide is fade if it is very porous, then even we will talk about that a little later. Now many times what have been carbon deposition occurs and this actually we had discussed again in the in terms of blast furnace that wustite reaction carbon deposition reaction in the action. So, that is also occurred at later nine hundred degree Celsius and sometimes the cementite is also found.

Sometime it is good in direct reduction it should reduce a the little melting point and not on only, that also it is react sedation of iron is prevented or at least is reduced by forming this iron carbide and this in one way also could when it is used as a feed. So, carbon percentage is increased in that way. So, prevent re oxidation lowers the melting point of DRI when this reaction occur at sometime it is needed to do this.