Iron Making and Steel Making
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Module - 01
Lecture - 05
Thermodynamics of BF Ironmaking (Continued)

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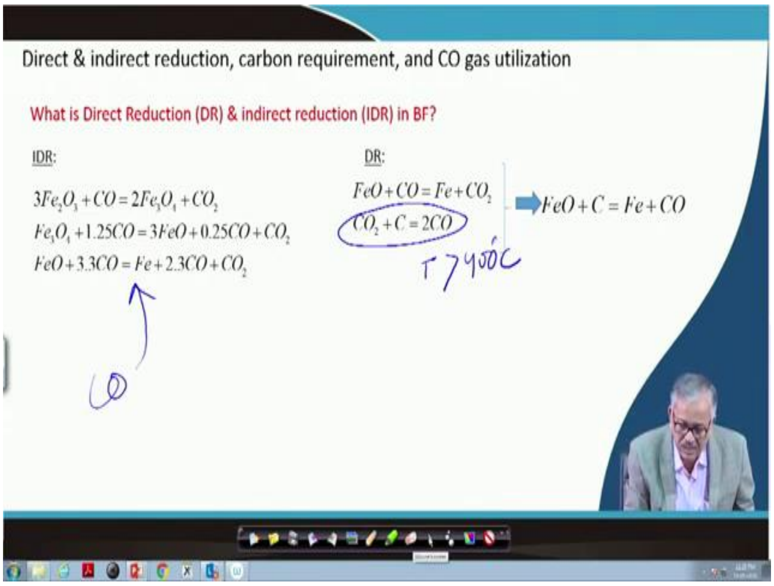

Direct & indirect reduction, carbon requirement, and CO gas utilization

What is Direct Reduction (DR) & indirect reduction (IDR) in BF?

IDR:

$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$

$Fe_3O_4 + 1.25CO = 3FeO + 0.25CO + CO_2$

$FeO + 3.3CO = Fe + 2.3CO + CO_2$

CO

DR:

$FeO + CO = Fe + CO_2$

$CO_2 + C = 2CO$

$T > 400^\circ C$

$\Rightarrow FeO + C = Fe + CO$

Now, we will discuss about the direct and indirect reduction in blast furnace. It is a very important concept; as we will see an optimum partitioning between the direct and indirect reduction plays a great role on the carbon efficiency as well as CO utilization. Now, what is direct Reduction and why it is called so?

Direct reduction of FeO may be represented as: $FeO(s) + C(s) = Fe(s) + CO(g)$ (1)

Direct reduction is a misnomer. Actually solid-solid reaction does not continue for long. As soon as the contact between these two solid particle diminishes the reaction stops. So basically this reaction, although it looks like two solid solid reaction, but actually it take place by gaseous intermediates like CO and CO_2. So, this reaction is basically a combination of two other reactions as shown below:

$FeO + CO = Fe + CO_2$ (2)

$CO_2 + C = 2CO$ (3)

Carbon participates in the reaction through the carbon gasification reaction (Equation 3) through in-situ generation of CO that subsequently reduce FeO and CO_2 generated is used up in the carbon gasification reaction. The combining this two reactions we get the equation (1), the conventional representation of direct reduction. Since carbon directly participate in the reduction process, such reduction is called direct reduction. Since, carbon gasification reaction is highly endothermic and takes place only at higher temperature (>900^oC), this reaction takes place only in the lower part of the furnace where temperature is high.

In upper part of the furnace where temperature is low, inspite of its presence, carbon can not participate in the reaction by generating CO through gasification reaction. Therefore, reduction in the upper part of the furnace depends on the supply of CO from lower part of the furnace and all such reactions are called indirect reductions, which are shown below:

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2 \qquad (4)$$

$$Fe_3O_4 + CO = 3FeO + CO \qquad (5)$$

$$FeO + CO = Fe + CO_2 \qquad (6)$$

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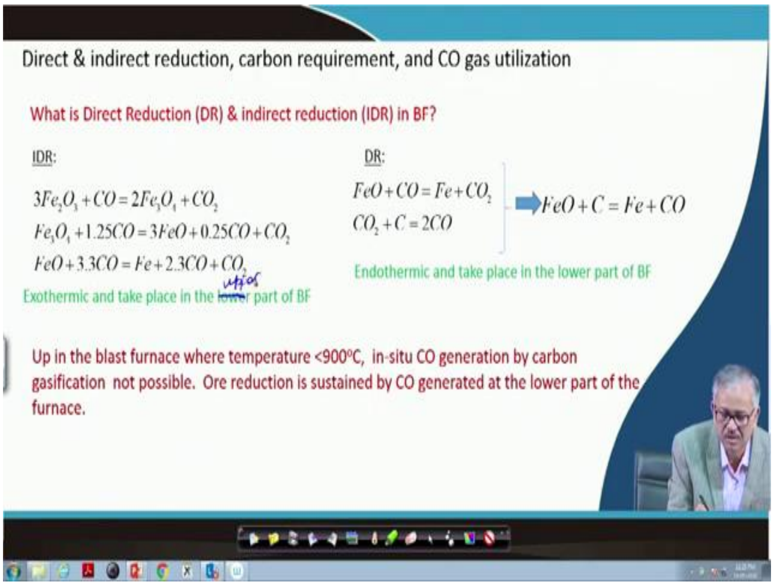

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Exothermic and take place in the ~~lower~~ upper part of BF

DR:

$$\left.\begin{array}{l} FeO + CO = Fe + CO_2 \\ CO_2 + C = 2CO \end{array}\right\} \Rightarrow FeO + C = Fe + CO$$

Endothermic and take place in the lower part of BF

Up in the blast furnace where temperature <900°C, in-situ CO generation by carbon gasification not possible. Ore reduction is sustained by CO generated at the lower part of the furnace.

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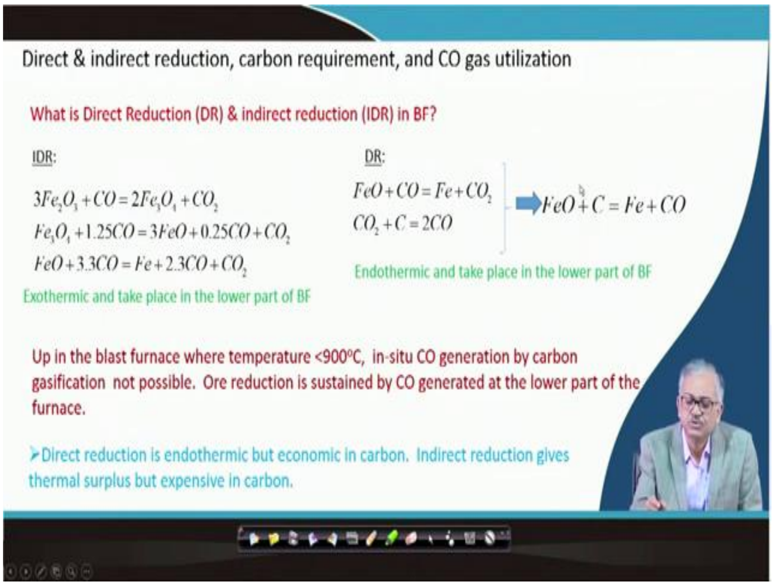

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Endothermic and take place in the lower part of BF

Up in the blast furnace where temperature <900°C, in-situ CO generation by carbon gasification not possible. Ore reduction is sustained by CO generated at the lower part of the furnace.

- Direct reduction is endothermic but economic in carbon. Indirect reduction gives thermal surplus but expensive in carbon.

Direct reduction is endothermic, but economic in carbon because 1 gram atom of carbon takes out one gram atom of oxygen. Most of the indirect reduction are mildly exothermic and supply heat. But those are expensive in carbon. For example, in case of indirect reduction, especially for FeO to Fe conversion, 3.3 moles of CO or 3.3 gram atom of carbon is required to extract one gram atom of FeO oxygen at 900^{o}C. Similarly, to extract one gram atom of oxygen from magnetite by indirect reduction, 1.25 gram atom of carbon is required at 900^{o}C. Therefore, although indirect reduction give thermal surplus, those are non-economic in carbon.

Higher oxides of iron, namely hematite and magnetite undergoes indirect reduction in the upper of the furnace. In the lower part of the furnace only wustite or FeO exists as iron oxide and it undergoes both direct and indirect reduction. So, if the oxygen in FeO is partitioned between direct and indirect reduction in such a way, that CO generated by direct reduction of FeO, is just sufficient to take out the rest of the FeO oxygen by indirect reduction, CO utilization and the carbon efficiency will be maximum.

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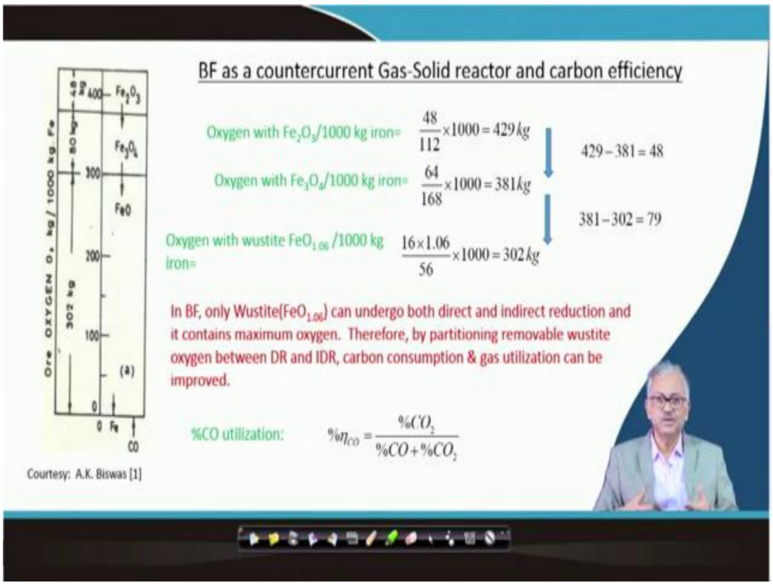

BF as a countercurrent Gas-Solid reactor and carbon efficiency

Oxygen with Fe_2O_3/1000 kg iron= $\frac{48}{112} \times 1000 = 429\,kg$

Oxygen with Fe_3O_4/1000 kg iron= $\frac{64}{168} \times 1000 = 381\,kg$

Oxygen with wustite $FeO_{1.06}$ /1000 kg iron= $\frac{16 \times 1.06}{56} \times 1000 = 302\,kg$

$429 - 381 = 48$

$381 - 302 = 79$

In BF, only Wustite($FeO_{1.06}$) can undergo both direct and indirect reduction and it contains maximum oxygen. Therefore, by partitioning removable wustite oxygen between DR and IDR, carbon consumption & gas utilization can be improved.

%CO utilization: $\%\eta_{CO} = \frac{\%CO_2}{\%CO + \%CO_2}$

Courtesy: A.K. Biswas [1]

Blast furnace is a counter current gas-solid reactor and this is a boon for sequential reduction for iron oxides in blast furnace. Blast furnace gas is rich in CO at the lower part of the furnace, and as the gas moves up its reduction potential decreases, especially in the upper part of the furnace where lower temperature does not promote carbon gasification and weaken the reduction potential of gas. And since higher oxides of iron have higher oxygen potential, or in other words, can be reduced with lower reduction potential of reducing gas; so, higher oxides get reduced at the upper part of the furnace and wustite appear in the system only at the lower part of the furnace where reduction potential gas is higher suitable for its reduction.

So, the sequence in which reduction takes place is Fe_2O_3 to Fe_3O_4 to FeO to Fe as shown in the figure above. As the CO gas moves it will first encounter FeO and subsequently Fe_3O_4 and Fe_2O_3. Simple stoichiometry shows that total oxygen to be removed from hematite per ton of iron produced is 429kg. Out of which 48 kg of oxygen will be relieved during hematite to magnetite conversion, 79 kg of oxygen will be removed during magnetite to wustite conversion and majority of oxygen is associate with wustite, i.e. 302 kg, which will be relieved during final conversion of wustite to iron.

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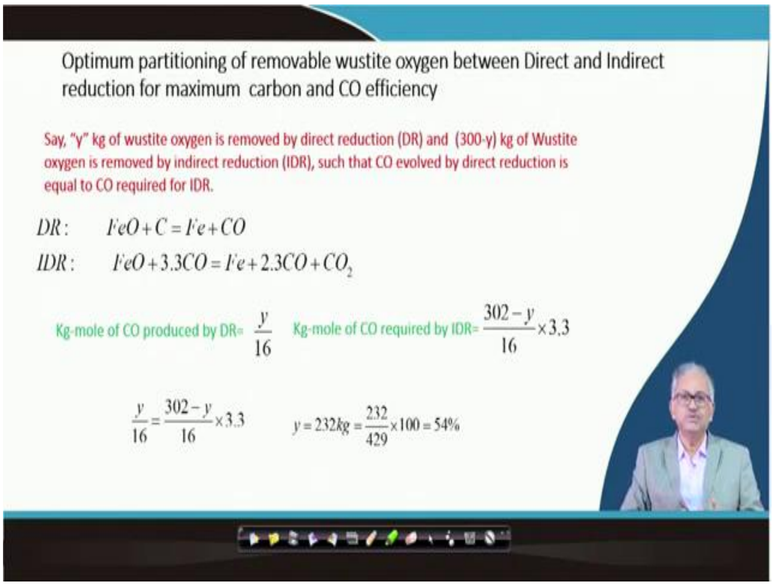

Optimum partitioning of removable wustite oxygen between Direct and Indirect reduction for maximum carbon and CO efficiency

Say, "y" kg of wustite oxygen is removed by direct reduction (DR) and (300-y) kg of Wustite oxygen is removed by indirect reduction (IDR), such that CO evolved by direct reduction is equal to CO required for IDR.

$$DR: \quad FeO + C = Fe + CO$$

$$IDR: \quad FeO + 3.3CO = Fe + 2.3CO + CO_2$$

Kg-mole of CO produced by DR= $\frac{y}{16}$ Kg-mole of CO required by IDR= $\frac{302-y}{16} \times 3.3$

$$\frac{y}{16} = \frac{302-y}{16} \times 3.3 \qquad y = 232kg = \frac{232}{429} \times 100 = 54\%$$

Let us now calculate for optimum partitioning of wustite oxygen for direct and indirect reduction for maximum CO utilization. CO utilization can be measured as the percentage of CO_2 produced out of initial CO present in the system. Let us consider out of 302 kg of wustite oxygen, y kg is removed by direct reduction such that the CO evolved from direct reduction is just sufficient to remove the rest (302-y) kg of wustite oxygen by indirect reduction.

Now, moles of CO generated by removing y kg of wustite oxygen, or y/16 kg-atom of wustite oxygen by direct reduction ($FeO + C = Fe + CO$) is y/16 kg-mole.

Now, CO required to remove (302-y) kg of wustite oxygen or, (302-y)/16 kg-atom of oxygen by indirect reduction ($FeO + 3.3 CO = Fe + 2.3 CO + CO_2$) is {(302-y)/16}×3.3 kg-mole

This sets up the following simple equation to calculate y.

$y/16 = \{(302-y)/16\} \times 3.3$

Solving, it yields y =232 kg, which 54% of the total oxygen content in the ore.

Let us calculate the %CO utilization.

Now, (429-232) =197 kg of ore oxygen, or 197/32 =6.15 kg-mole of ore oxygen will be removed by indirect reduction. As far as CO_2 production is concerned, all indirect reduction may be represented as $CO + 1/2O_2 = CO_2$. Therefore, CO_2 produced = 6.15×2 = 12.3 kg-mole.

Total CO evolved from direct reduction was 232/16 = 14.5 kg-mole.

Therefore %CO utilization = (12.3/14.5)×100 = 84%.

Therefore, if 54% of ore oxygen is removed by direct reduction and rest 46% by indirect reduction, maximum % CO utilization can be achieved at 85%.

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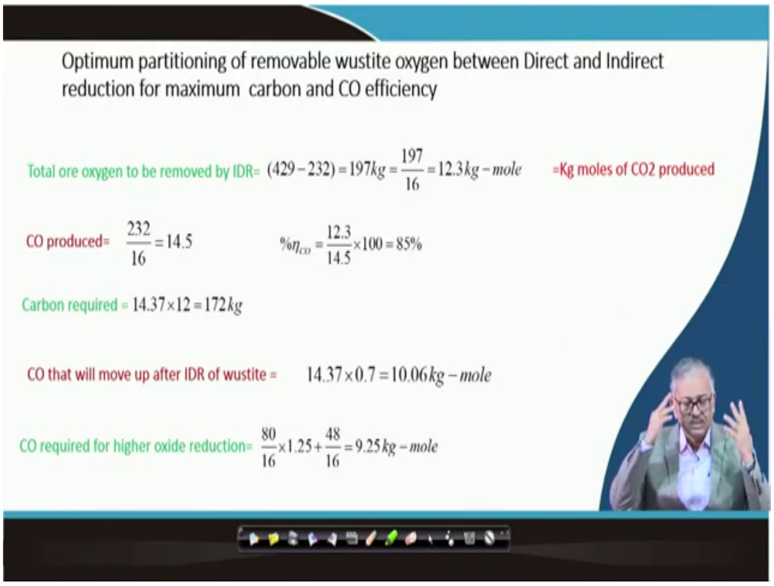

Optimum partitioning of removable wustite oxygen between Direct and Indirect reduction for maximum carbon and CO efficiency

Total ore oxygen to be removed by IDR= $(429-232)=197kg=\frac{197}{16}=12.3kg-mole$ =Kg moles of CO2 produced

CO produced= $\frac{232}{16}=14.5$ $\%\eta_{CO}=\frac{12.3}{14.5}\times100=85\%$

Carbon required = $14.37\times12=172kg$

CO that will move up after IDR of wustite = $14.37\times0.7=10.06kg-mole$

CO required for higher oxide reduction= $\frac{80}{16}\times1.25+\frac{48}{16}=9.25kg-mole$

Let us calculate the carbon required under this condition. Total carbon required in this case is equivalent to the CO generated by direct reduction = 14.5 kg-mole = 14.5 ×12 =174 kg, i.e the minimum possible carbon required.

Now let us see CO that move up after wustite reduction is sufficient to take out the rest of the oxygen from higher oxides. After indirect reduction of wustite, CO available will be given by 70% of the CO required for indirect reduction of wustite = 0.7×3.3×{(302-232)/16}=10.1 kg-mole. Now let us see how much CO is required to remove 79 kg of oxygen from magnetite and 48 kg oxygen from hematite. CO required to remove 79 kg magnetite oxygen = 1.25×(79/16)=6.17 kg-mole, at 80% CO utilization at 900^{o}C. CO required to remove 48 kg hematite oxygen = (48/16)=3 kg-mole at 100% CO utilization.

So, total CO required to remove oxygen from higher oxides = 9.17 and the available CO after wustite reduction is 10.1 kg-mole, which is sufficient to remove the oxygen from higher oxide at the maximum carbon efficiency. Therefore, CO available from wustite reduction will always meet up the CO requirement for removal of higher oxides.

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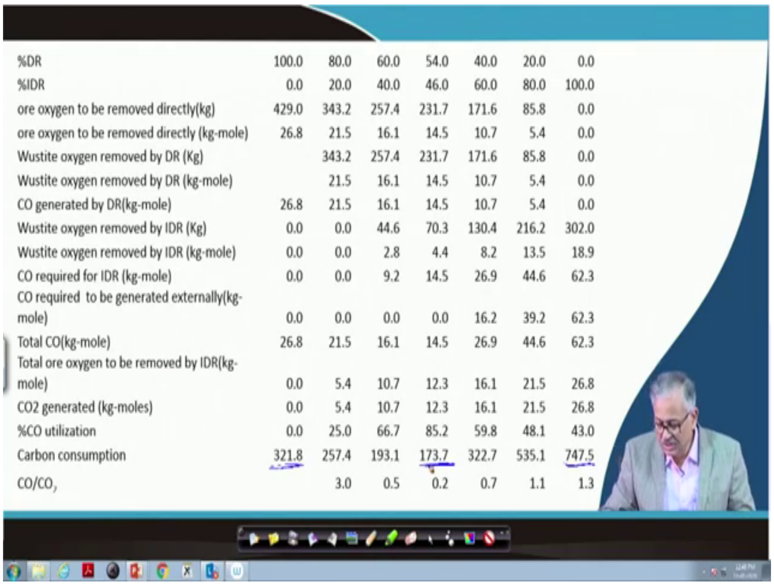

%DR	100.0	80.0	60.0	54.0	40.0	20.0	0.0
%IDR	0.0	20.0	40.0	46.0	60.0	80.0	100.0
ore oxygen to be removed directly(kg)	429.0	343.2	257.4	231.7	171.6	85.8	0.0
ore oxygen to be removed directly (kg-mole)	26.8	21.5	16.1	14.5	10.7	5.4	0.0
Wustite oxygen removed by DR (Kg)		343.2	257.4	231.7	171.6	85.8	0.0
Wustite oxygen removed by DR (kg-mole)		21.5	16.1	14.5	10.7	5.4	0.0
CO generated by DR(kg-mole)	26.8	21.5	16.1	14.5	10.7	5.4	0.0
Wustite oxygen removed by IDR (Kg)	0.0	0.0	44.6	70.3	130.4	216.2	302.0
Wustite oxygen removed by IDR (kg-mole)	0.0	0.0	2.8	4.4	8.2	13.5	18.9
CO required for IDR (kg-mole)	0.0	0.0	9.2	14.5	26.9	44.6	62.3
CO required to be generated externally(kg-mole)	0.0	0.0	0.0	0.0	16.2	39.2	62.3
Total CO(kg-mole)	26.8	21.5	16.1	14.5	26.9	44.6	62.3
Total ore oxygen to be removed by IDR(kg-mole)	0.0	5.4	10.7	12.3	16.1	21.5	26.8
CO2 generated (kg-moles)	0.0	5.4	10.7	12.3	16.1	21.5	26.8
%CO utilization	0.0	25.0	66.7	85.2	59.8	48.1	43.0
Carbon consumption	321.8	257.4	193.1	173.7	322.7	535.1	747.5
CO/CO_2		3.0	0.5	0.2	0.7	1.1	1.3

Let us now see, what will be %CO utilization, carbon required at different percentage of direct and indirect reduction. As can be seen from the chart above that as the direct reduction increases beyond 54% , the CO generated by direct reduction of wustite exceeds the CO requirement for indirect reduction of wustite and as a result the process become less efficient in terms of carbon consumption and % CO utilization. Again when the direct reduction goes below 54%, the CO generated by direct reduction of wustite fall short of CO required for the indirect reduction of wustite and that calls for extra CO generation externally, that increases carbon requirement as well as reduces the % CO utilization.

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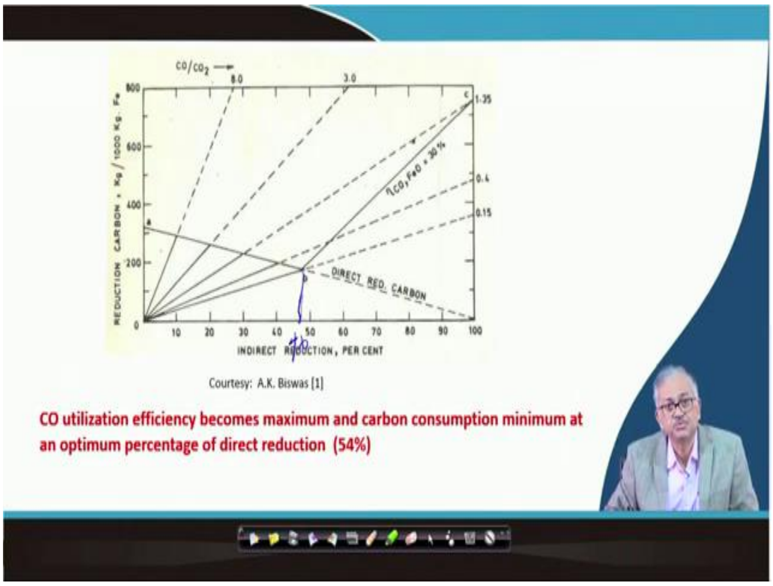

Courtesy: A.K. Biswas [1]

CO utilization efficiency becomes maximum and carbon consumption minimum at an optimum percentage of direct reduction (54%)

The above graph, graphically represent the calculation above. We can see, with 100% direct reduction the carbon requirement is around 321 kg. and as the indirect reduction increases, i.e. as the CO evolved is used for indirect reduction, carbon consumption decreases and it becomes minimum at 46% indirect reduction, when the CO evolved from direct reduction is just sufficient to support the indirect reduction. If indirect reduction increases further beyond 46%, then CO generated from direct reduction fall short that is required for rest of the indirect reduction and as a result extra carbon need to be burned to supplement the indirect reduction and this increases the carbon requirement. The carbon requirement becomes maximum at 100% indirect reduction, which may be calculated as: (302/16)×3.3×12= 748 kg.

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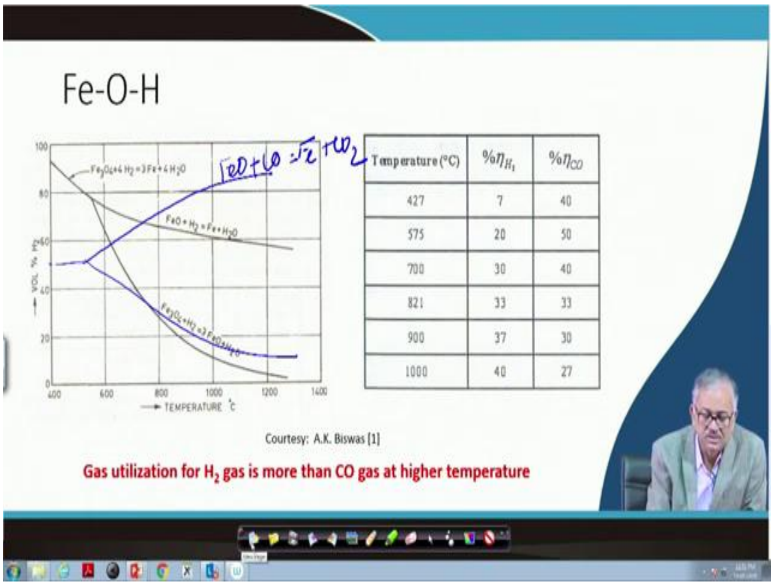

Fe-O-H

Temperature (°C)	$\%\eta_{H_2}$	$\%\eta_{CO}$
427	7	40
575	20	50
700	30	40
821	33	33
900	37	30
1000	40	27

Courtesy: A.K. Biswas [1]

Gas utilization for H_2 gas is more than CO gas at higher temperature

Hydrogen is also a reductant in the blast furnace, which is generated by hydrocarbon injection and humidification of air blast. Therefore, let us understand the thermodynamics of hydrogen reduction. In the above diagram the equilibrium lines for hydrogen reductions are superimposed on the Fe-C-O diagram.

It can be seen that hydrogen reduction lines are moving downward with increase in temperature. Although at lower temperature hydrogen utilization is lower than that of CO, but as the temperature reduction increases beyond 600^{o}C, hydrogen utilization increases sharply over that of CO, especially for FeO-Fe reduction, the major reduction. So, hydrogen is definitely a better reductant, but only thing is that hydrogen reaction is endothermic, especially FeO-Fe reduction, which is exothermic for CO reduction. Otherwise thermodynamically hydrogen is a better reductant than CO.

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REFERENCES

- 1. A. K. Biswas: Principles of Blast Furnace Ironmaking, SBA Publicatio, Kolkata, 1984, P. 4,8

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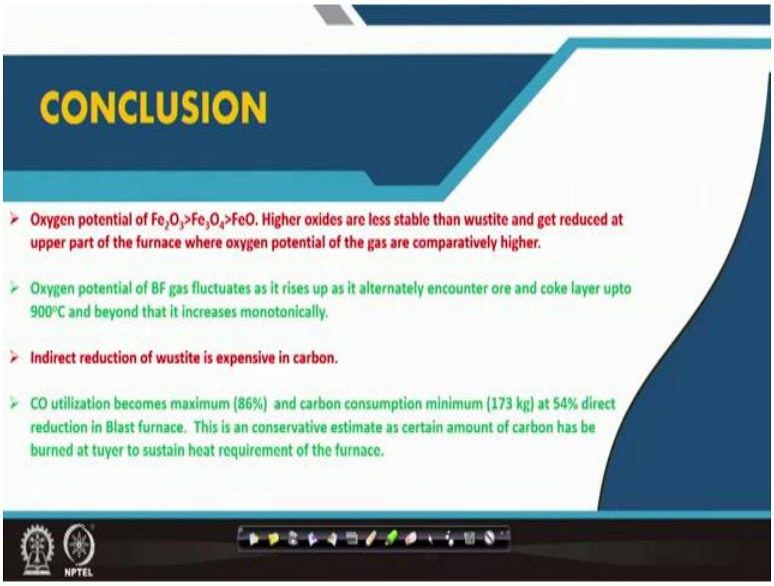

CONCLUSION

- Oxygen potential of Fe_2O_3>Fe_3O_4>FeO. Higher oxides are less stable than wustite and get reduced at upper part of the furnace where oxygen potential of the gas are comparatively higher.
- Oxygen potential of BF gas fluctuates as it rises up as it alternately encounter ore and coke layer upto 900°C and beyond that it increases monotonically.
- Indirect reduction of wustite is expensive in carbon.
- CO utilization becomes maximum (86%) and carbon consumption minimum (173 kg) at 54% direct reduction in Blast furnace. This is an conservative estimate as certain amount of carbon has be burned at tuyer to sustain heat requirement of the furnace.

To conclude, we have seen that higher oxides are reduced by indirect reduction at the upper part of the furnace. While, wustite reduction takes place at the lower part of the furnace both by direct and indirect reduction. Optimum partitioning of direct and indirect reduction for wustite oxygen can lead to maximum carbon efficiency and % CO utilization. The efficiency become maximum at 54% direct reduction with 174kg carbon/ton of iron produced and 85% CO utilization.

Thermodynamically, hydrogen is better reduction from the point of view of % hydrogen utilization. But hydrogen reductions are endothermic, while FeO-Fe reduction by CO is exothermic.

Thank you.