**Iron Making and Steel Making**
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Module - 01
**Lecture - 04**
Thermodynamics of BF Ironmaking

In this lecture, we will discuss the Thermodynamics of blast furnace Ironmaking. It is little elaborate compared to what I talked about the basic thermodynamics during the Iron Making Steel Making in the 1st lecture.

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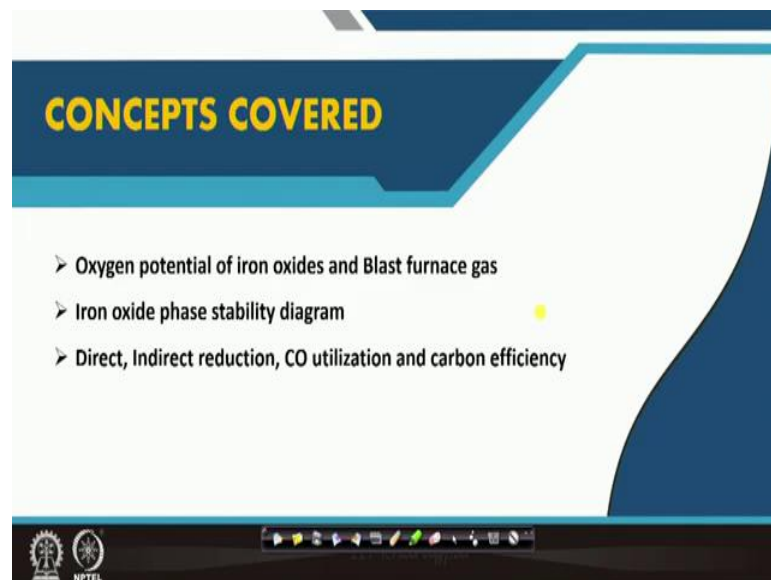
So, the concept covered here will be the oxygen potential of iron oxides and the blast furnace gases and their correlation and then iron oxide phase stability diagram, direct, indirect reductions, CO utilization and carbon efficiency.

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Courtesy: A.K. Biswas [1]
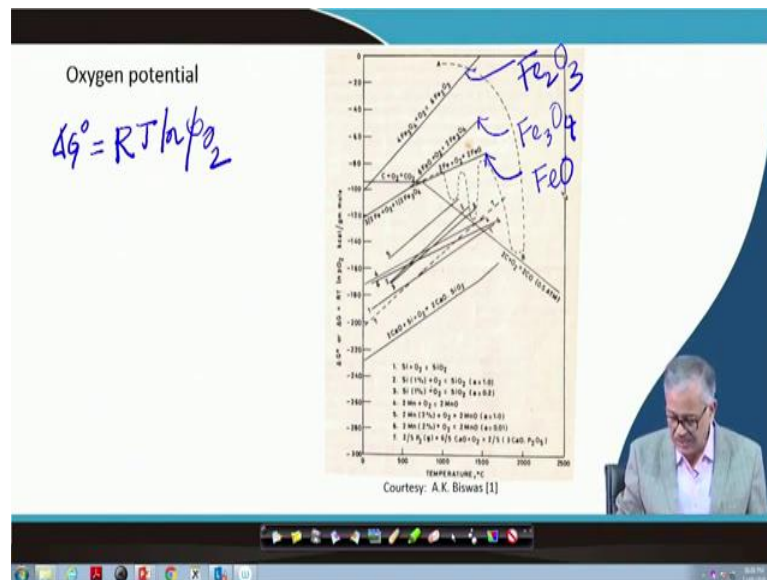
This is the Ellingham diagram, which I projected earlier also. So, basic features of Ellingham diagram, you already know. To recapitulate, it gives the relative stability of various oxides in their pure states. The y axis gives the standard free energy change, which is equivalent to oxygen potential of the respective oxides, $RT \ln(p_{O_2})$. The diagram also depicts the variation of oxygen potential with temperature.

From the above figure, it might be observed that among the various oxides of iron, Fe_2O_3 has the highest oxygen potential, followed Fe_3O_4 and FeO and this potential values further increases with temperatures. Higher oxidation potential means higher dissociation pressure of oxygen indicating lower stability. In other words, to reduce Fe_2O_3, we would require lesser reduction potential of the gas compared to that required for Fe_3O_4 and FeO. This is a boon for counter current gas solid reaction in blast furnace because 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. So, higher oxides get reduced at the upper part of the furnace and wustite appear in the system at the lower part of the furnace where reduction potential gas is higher suitable for wustite reduction.
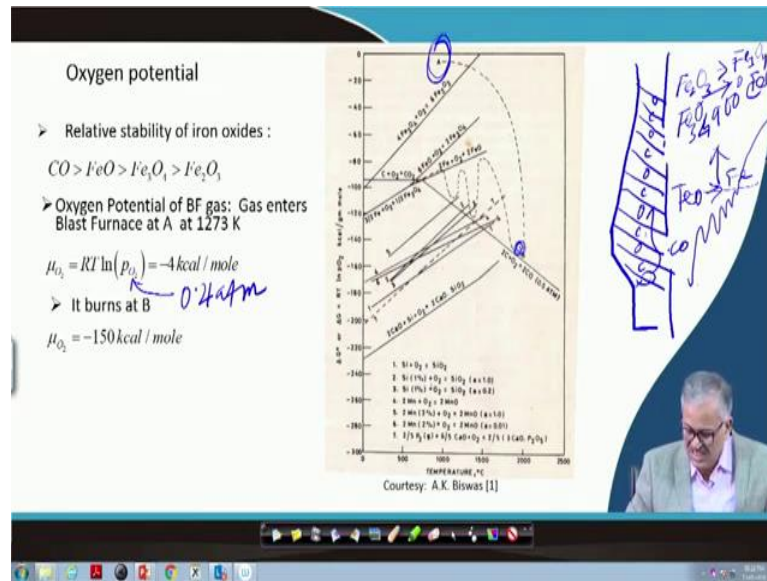
Now, let us see how the oxygen potential of the gas changes as it moves up into the blast furnace. The preheated air enters the blast furnace at point A (see the figure in slide). The temperature of the air blast as shown in the diagram is 1000^OC and thye partial pressure of oxygen in air at 1 atmosphere is 0.21. Therefore the oxygen potential of the gas at point A may be given as: $RT \ln(p_{O_2}) = \frac{1.98}{1000} \times 1273 \times \ln(0.21) = -3.9$ kcal/mole.

Next, the oxygen in air oxidize the carbon to CO (as I have mentioned that CO2 is not stable at high temperature in presence of carbon and therefore, if CO_2 forms initially it immediately gassify the carbon to finally produce CO) and the temperature raises to around 2000^OC and oxygen potential of the gas may be given by the line C-CO at 2000OC, as indicated by the point B in the figure and this value may be noted as -150 kcal/mole.

Now, let us see what happens as the gas moves up in the blast furnace. Blast furnace has alternate layers of ore and coke and therefore when the gas moves up after leaving the coke layer it will encounter the ore layer. In the ore layer in the layer part we have only FeO, so the oxidation potential of the gas will approach that of Fe-FeO line at comparatively lower temperature. So, the oxidation potential of the gas will increase as oxygen will flow to the gas from ore and the CO2/CO ratio in the gas will increase. Subsequently as the gas moves up its temperature will decrease and it will encounter another coke layer and its oxidation potential will decrease as the CO percentage in the

gas will increase by carbon gasification. This may be called the charging of the gas, as its reduction potential increases in presence of coke layer through carbon gasification reaction. Similarly, when tha gas further moves up its temperature further decreases and as it encounter ore layer its reduction potential decreases after reducing FeO and its may termd as discharging of the gas. Thus as the gas moves up its temperature progressively decreases due to gas solid heat exchange but its reduction potential increases and decreases as its encounters alternate coke and ore layers. So, the oxygen potential curve of the gas takes a spiral shape as shown in the diagram in the slide shown.

However, such fluctuation of oxidation potential of the gas diminishes beyond certain distance from the tuyere. The charging of the gas ceases when the furnace temperature become less than 900^OC, i.e., when gasification reaction weakens and therefore the oxidation potential of the gas steadily increases thereafter.

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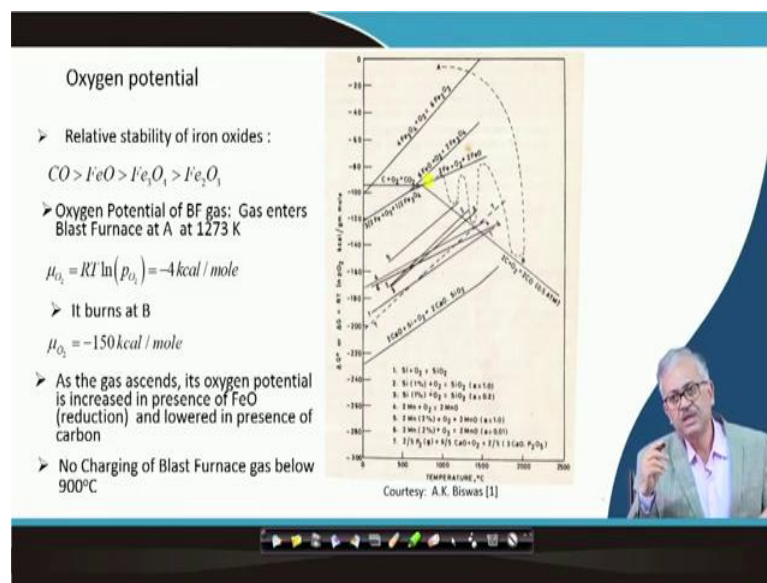
So, no charging of blast furnace gas below 900^OC; no charging means its reduction potential will never further be increased because below 900^OC, there is no insitu CO generation. So, the reduction in the upper part of the furnace will take place by utilizing CO that will move up after its utilization in the lower part of the furnace, which is called the indirect reduction.

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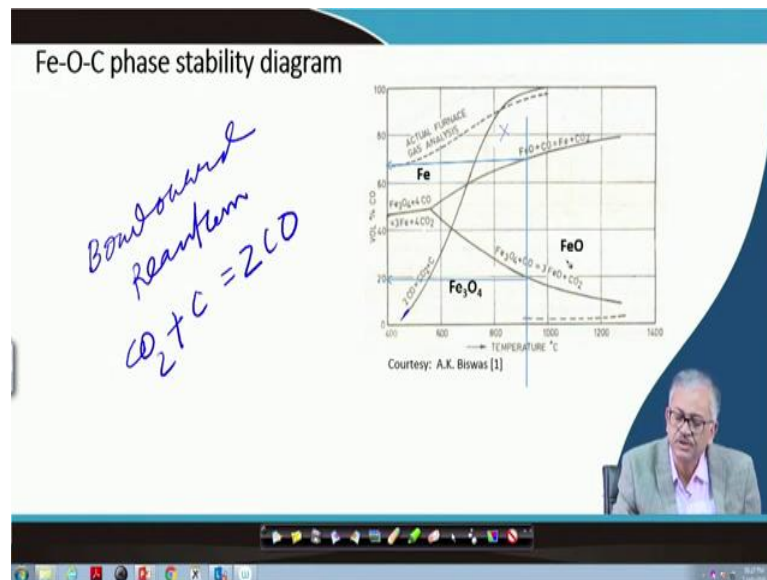
Now, we come to the Fe-C-O phase stability diagram. This is a very important diagram because I was discussing the process in terms of oxidation potential. And I think, it is better to describe the process in terms of the volume percent of CO into the blast furnace gas. It is the ratio of CO and CO_2 in the gas that decides its oxidation, or reducing potential and therefore, oxidation potential is an indirect or derived parameter. CO, CO_2 can be measured directly. At the tuyere level everything is CO and as the gas moves ups, it take up the ore oxygen forming some amount of the CO_2; CO get oxidized to CO_2 and iron ore get iron ore get reduced to the iron.CO_2 again gassify carbon to CO and thus the ratio of CO and CO_2 changes in the BF gas, deciding its oxidation or reducing potential. The equilibrium gas composition of the blast furnace can be given by the carbon gasification reaction: $CO_2 + C = 2CO$. This reaction is also known by the Boudouard reaction. The BF gas composition is dictated by this reaction, because it is the slowest reaction compared to the ore oxidation.

In the phase stability diagram, you can find all three iron oxides equilibrium lines. The hematite to magnetite line ($3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$) is shown by dotted line below. Similarly, magnetite to wustite ($Fe_3O_4 + CO = 3FeO + CO_2$) and wustite to iron equilibrium line ($FeO + CO = Fe + CO_2$) are also shown. The boudouard line is also superimposed. The region of various stable phases are indicated in the two dimensional domain of temperature and volume percentage of CO in the gas. So it means if the

boudouard line is above any oxide equilibrium line, that oxide is likely to be stable. For example, the point indicated by cross in the figure, the equilibrium gas composition as indicated by Boudouard line is above that required for FeO-Fe equilibrium. Indicating Fe will be stable. There is a large region encapsulated by FeO-Fe and Fe_3O_4-FeO lines, indicating the satble zone for FeO.

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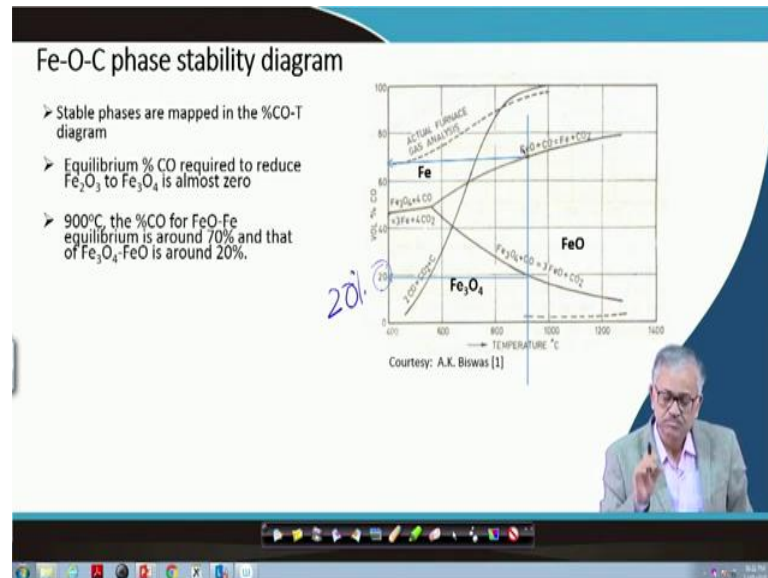
And now let us see that equilibrium percentage of CO required to reduce Fe_2O_3 to Fe_3O_4. It may be seen that this reaction is almost irreversible without requiring any equilibrium requirement for CO. In contrast, if we see the Fe_3O_4 to FeO equilibrium, say at 900°C, the equilibrium volume percentage of CO required is around 20% and that for FeO to Fe is as high as 70%!. It is to be noted these volume percentage of CO represent the percentage in the CO, CO_2 mixture, excluding nitrogen in blast furnace gas.

So, at 900°C, 70 volume percentage of CO will remain in equilibrium with Fe-FeO system. That means only 30% of the CO in CO, CO2 mixture will be utilized for reduction reaction at 900°C. At further higher temperature the CO utilization percentage for this reaction further decreases. Similarly, you can see that for Fe3O4 to FeO reaction the CO utilization percentage is 20% and it further decreases with increase in temperature.

Since CO utilization is only 30%, moles of CO required to convert one mole of FeO to Fe, will be 100/30 = 3.3.

So the revised equation for FeO-Fe, considering the equilibrium at 900°C may be given as:

FeO + 3.3 CO = Fe + 2.3CO + CO₂

Similarly, the revised equation for Fe₃O₄ to FeO at 900°C, will be given as:

Fe₃O₄ + 1.25 CO = 3FeO + CO₂

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And another that you must note is the actual blast furnace gas composition, shown by dotted line in the upper part of the figure. Please note that volume percentage of CO in BF gas is much higher than equilibrium composition as indicated by buodouard line. Even in upper part of the furnace the the CO percentage is more than 60%, indicating inferior CO utilization due to limited indirect reduction in the shaft. Therefore, better bed permeability, better gas-solid interaction in the shaft is a must to promote indirect reduction and enhance CO utilization, reduce coke rate and enhance productivity. Obviously, the data representing the blast furnace that is poorly operated.

Thank you.