Iron Making
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Lecture – 26
Iron Making Lecture 26

So, now the next one is about Phosphorus.

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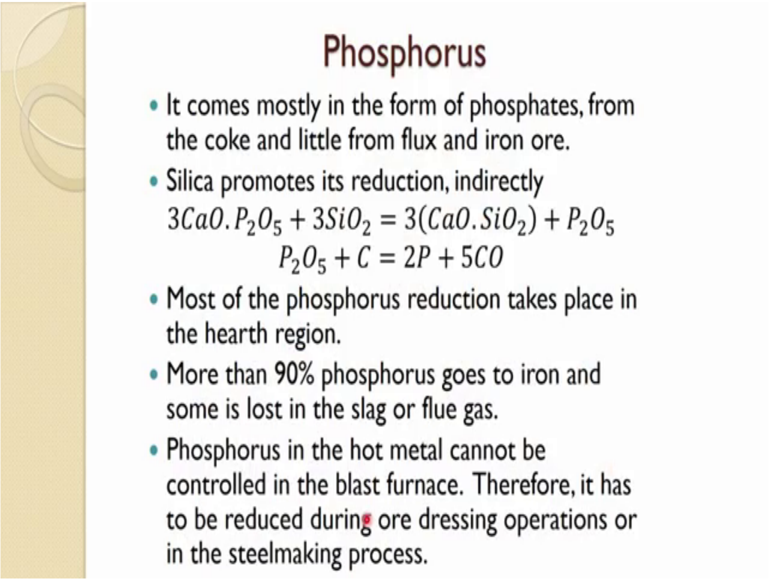

Phosphorus

- It comes mostly in the form of phosphates, from the coke and little from flux and iron ore.
- Silica promotes its reduction, indirectly

$$3CaO.P_2O_5 + 3SiO_2 = 3(CaO.SiO_2) + P_2O_5$$
$$P_2O_5 + C = 2P + 5CO$$

- Most of the phosphorus reduction takes place in the hearth region.
- More than 90% phosphorus goes to iron and some is lost in the slag or flue gas.
- Phosphorus in the hot metal cannot be controlled in the blast furnace. Therefore, it has to be reduced during ore dressing operations or in the steelmaking process.

So, it comes mostly in the form of phosphates from the coke and little from flux and iron ore. So, silica promotes it is reduction in an indirect way. So, calcium phosphate select with silica calcium silicate and P 2 O 5 and with further react with carbon which reduces the phosphorus and from the CO gas.

So, most of the phosphorus reduction takes place in the hearth region; So, more than 90 percent phosphorus goes to iron and some is lost in this slag or flue gas phosphorus in the hot metal cannot be controlled in the blast furnace therefore, it has to be reduced during ore dressing operations or in the steelmaking process; So, because it cannot be controlled in the blast furnace.

So, ore dressing that is processing of the raw material in the starting should be taken care of to reduce the phosphorus; if that is not possible or it becomes expensive in that case in the steel making operation it should be done the phosphorus are reduction.

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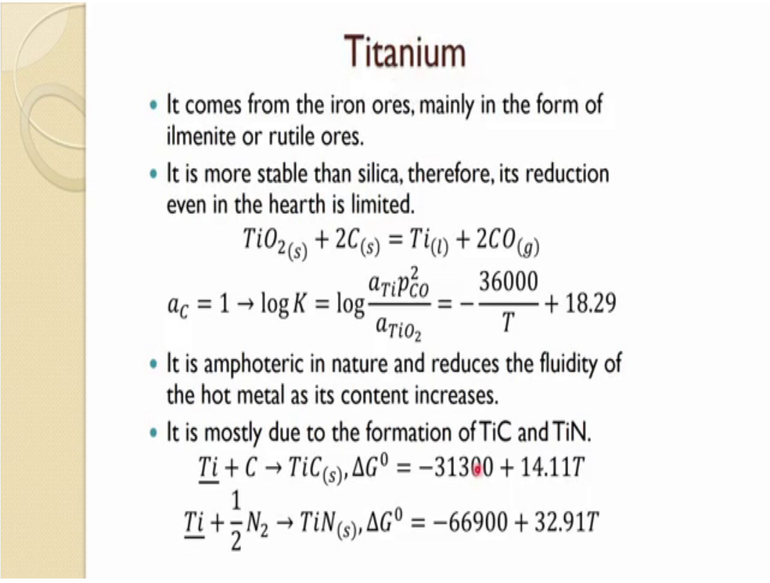

Titanium

- It comes from the iron ores, mainly in the form of ilmenite or rutile ores.
- It is more stable than silica, therefore, its reduction even in the hearth is limited.

$$TiO_{2(s)} + 2C_{(s)} = Ti_{(l)} + 2CO_{(g)}$$

$$a_C = 1 \rightarrow \log K = \log \frac{a_{Ti} p_{CO}^2}{a_{TiO_2}} = -\frac{36000}{T} + 18.29$$

- It is amphoteric in nature and reduces the fluidity of the hot metal as its content increases.
- It is mostly due to the formation of TiC and TiN.

$$\underline{Ti} + C \rightarrow TiC_{(s)}, \Delta G^0 = -31300 + 14.11T$$

$$\underline{Ti} + \frac{1}{2}N_2 \rightarrow TiN_{(s)}, \Delta G^0 = -66900 + 32.91T$$

Another element which is their in iron is titanium. So, it comes from the iron ore mainly in the forms of ilmenite or rutile. So, ilmenite it is a fea Ti O 3 and Ti O 2 is rutile. So, in this form titanium comes to the metal. So, it is more stable than silica therefore, it is reduction even in the hearth is limited.

So, hearth to reduce at so, this is the reaction which takes place mostly in the hearths region through carbon reacts with titanium oxide gives titanium liquid and CO gas and assuming the activity of carbon h one the equilibrium constant for this reaction can be written in this form selectivity of titanium P cos square divided by activity of Ti O 2. So, log of it and in terms of temperature the equilibrium constant is given in this.

So, it is amphoteric in nature and reduces the fluidity of the hot metal as it is content increases. So, it is not advisable to have more titanium in the ore or in the metal. So, it is mostly due to the formation of titanium car carbide in titanium nitrite. So, fluidity actually it is reduces due to the formation of these carbide and nitrite and which can be formed with a dissolve titanium react with carbon to titanium carbide and similarly titanium nitrite the free energy standard is given for this reaction this and because titanium carbide.

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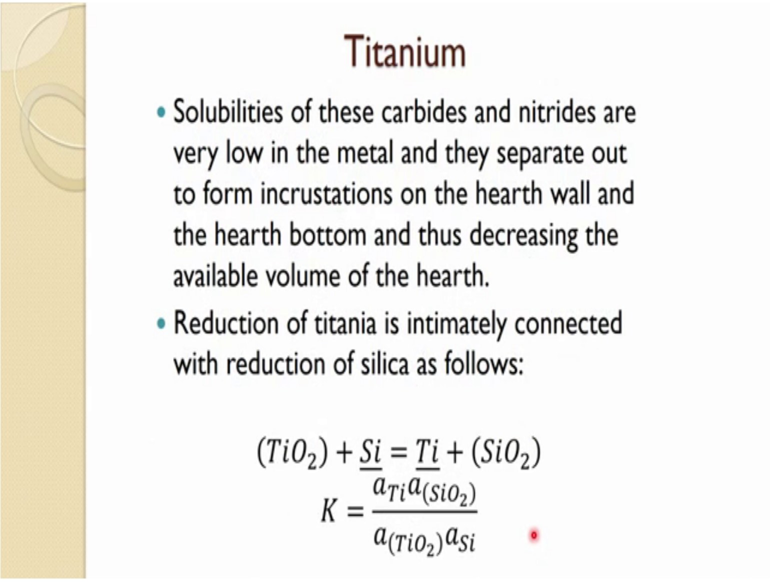

Titanium

- Solubilities of these carbides and nitrides are very low in the metal and they separate out to form incrustations on the hearth wall and the hearth bottom and thus decreasing the available volume of the hearth.
- Reduction of titania is intimately connected with reduction of silica as follows:

$$(TiO_2) + \underline{Si} = \underline{Ti} + (SiO_2)$$

$$K = \frac{a_{Ti}a_{(SiO_2)}}{a_{(TiO_2)}a_{Si}}$$

And titanium nitrite have a very low solubility in the metal they separate out to form in crustaceans on the hearth wall and the hearth bottom and thus decreasing the available volume of the hearths. So, that create hearth; so, the problem in the hearths. So, it should be removed as much as possible; however, the content of titanium in the as usually is low.

So, reduction of titanium is intimately connected with the reduction of silica also which is as well as follows. So, titanium oxide with silicon metal can be reducing to titanium and silica and equilibrium constant for the reaction is given with this. So, activity of titanium the activity of SiO 2 and activity of TiO 2 and activity silicon; So, why this equilibrium constant one can know about the partition of this metal.

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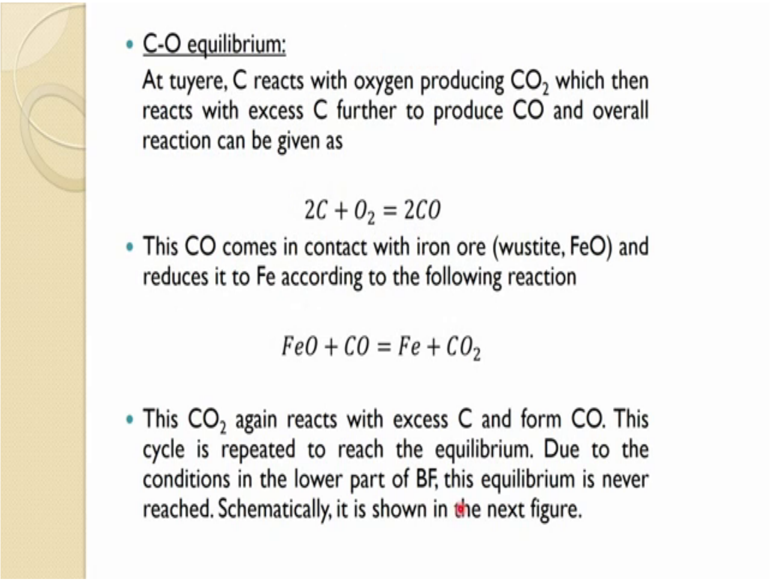

- C-O equilibrium:
  At tuyere, C reacts with oxygen producing CO_2 which then reacts with excess C further to produce CO and overall reaction can be given as

$$2C + O_2 = 2CO$$

- This CO comes in contact with iron ore (wustite, FeO) and reduces it to Fe according to the following reaction

$$FeO + CO = Fe + CO_2$$

- This CO_2 again reacts with excess C and form CO. This cycle is repeated to reach the equilibrium. Due to the conditions in the lower part of BF, this equilibrium is never reached. Schematically, it is shown in the next figure.

Another reaction in the bottom part of the hearth is a occur this is carbon reacting with oxygen in the tuyere region. So, that is the CO equilibrium of course, we have discussed about this in detailing is stake region, but now because we are talking about the lower part of the blast furnace we again are touching upon this.

So, CO equilibrium; So, at tuyere carbon reacts with oxygen producing CO 2 which, then reacts with excess carbon further to produce CO and overall reaction can be given as carbon plus oxygen equal to 2 CO if you remember when we were talking about the combustion zone in the raceway. We talked about this reaction that at in front of the tuyere oxygen is in excess amount.

So, carbon dioxide is form which is like a oxidizing atmosphere there, but as soon as it reaches near the raceway boundary where more carbon is available it is reduce at to CO and this is essentially about that reaction and now this CO goes up and it comes in contact with iron ore in the form of wustite.

As you remember we mentioned near the cohesive zone at the formation of the cohesive zone melting of the ore and gang wustites. So, it makes a low eutectic solid. So, it is start melt melting at the upper boundary of the cohesive zone and lower boundary of the cohesive zone it becomes or liquid and in that one most of the quantity of iron is in FeO form not in any other oxide and of course, the remaining some liquid iron.

So, this CO when it comes in contact and with this FeO; which is dripping down from the cohesive zone into the dropping zone it reduces iron according to this reaction. So, FeO plus CO gives you iron plus CO 2 at this um. So, in this reaction what is happening; which CO 2 is forming again.

So, the because in the lower part of the blast furnace especially in the dripping zone everything else in the liquid from except the coke. So, plenty of carbon is available in that. So, this CO 2 again comes in contact with the carbon and form CO. So, this cycle is repeated to reach the equilibrium due to the condition in the lower part of the blast furnace this equilibrium is never reached.

So, a schematically it is shown in this figure.

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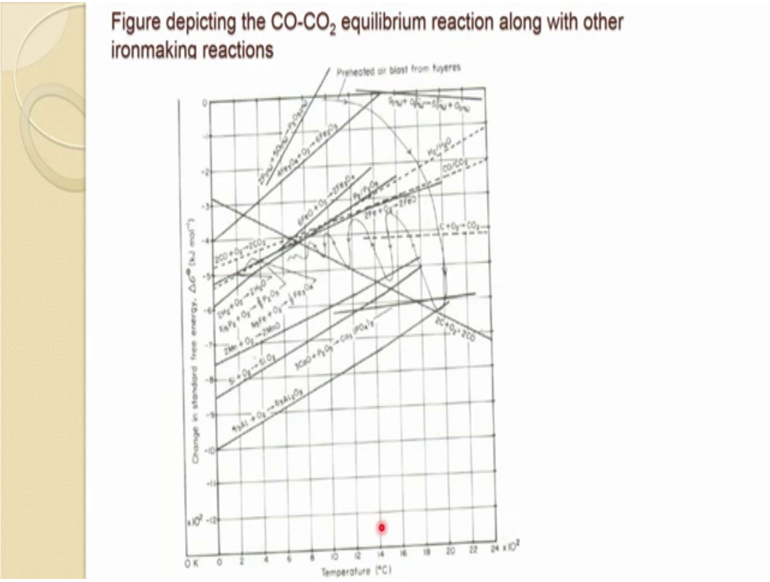

Figure depicting the CO-CO_2 equilibrium reaction along with other ironmaking reactions

So, this is showing about the CO, CO 2 equilibrium in the lower part of the blast furnace; So, if you look at is y axis is the change in standard free energy say standard Ellingham diagram for the oxide in temperature on the x axis. So, free heated air blast from this tuyere is entered somewhere at this temperature and keeps on increasing with the reaction.

So, CO, CO 2 form and the CO 2 goes a becomes high, but as soon as it comes in contact with the excess carbon CO is formed and CO is forming this is a CO line and then now

CO is formed, but this CO comes in contact with the wustite fu. So, it reduces the iron. So, CO 2 content increases further and this line is showing CO CO 2 ratio.

But again this comes in contact with us carbon CO is formed. So, the this cycle keeps on repeating itself and never as you can see it is never reached equilibrium especially in the dropping zone or lower part of the blast furnace. So, this is about CO CO 2 equilibrium which we did not touch upon previously. So, we thought we will just talk a little bit about this one.

Now, the we will switch on to some other part. So, which is about the liquid slag and melt, but before go going to that we would like to have some physico chemical.

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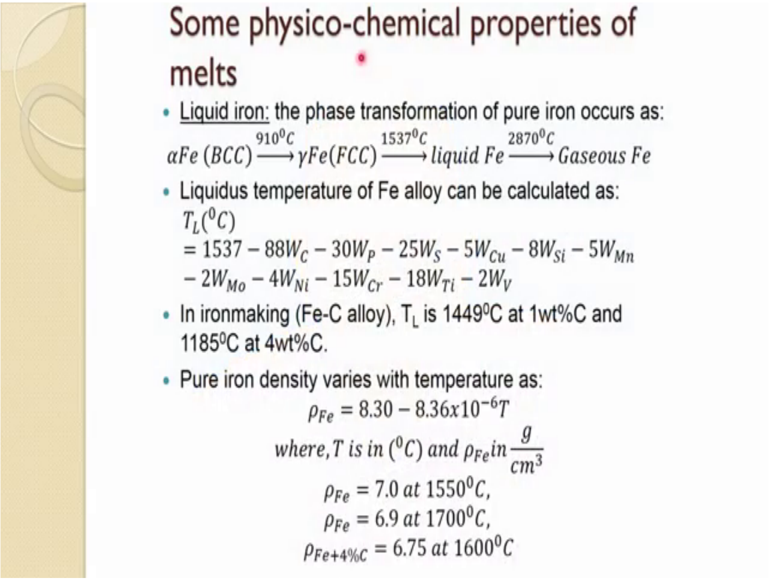

Some physico-chemical properties of melts

- Liquid iron: the phase transformation of pure iron occurs as:

$$\alpha Fe\ (BCC) \xrightarrow{910^0C} \gamma Fe(FCC) \xrightarrow{1537^0C} liquid\ Fe \xrightarrow{2870^0C} Gaseous\ Fe$$

- Liquidus temperature of Fe alloy can be calculated as:

$$T_L(^0C) = 1537 - 88W_C - 30W_P - 25W_S - 5W_{Cu} - 8W_{Si} - 5W_{Mn} - 2W_{Mo} - 4W_{Ni} - 15W_{Cr} - 18W_{Ti} - 2W_V$$

- In ironmaking (Fe-C alloy), T_L is 1449⁰C at 1wt%C and 1185⁰C at 4wt%C.
- Pure iron density varies with temperature as:

$$\rho_{Fe} = 8.30 - 8.36x10^{-6}T$$

$$where, T\ is\ in\ (^0C)\ and\ \rho_{Fe} in \frac{g}{cm^3}$$

$$\rho_{Fe} = 7.0\ at\ 1550^0C,$$

$$\rho_{Fe} = 6.9\ at\ 1700^0C,$$

$$\rho_{Fe+4\%C} = 6.75\ at\ 1600^0C$$

Properties of melt; so, we have a liquid iron. So, the phase transformation of pure iron occurs as alpha iron you must be aware of that. So, body centers cubic center. So, body center cubic at 900 degree Celsius when temperature reach reaches is converted into gamma iron and at 1537 degree Celsius it is it is keep on heating it converts into liquid iron. So, this is the melting point of the iron and if you heat it further then at 2870 degree Celsius it becomes into vapor form of gaseous iron.

So, this is for the pure iron. So, as you can see melting point of pure iron is very high. So, it is really you cannot it is very difficult to achieve that sort of temperature throughout the furna in the blast furnace through out of it, but; however, for impure iron liquidus temperature of this it decreases it decreased. So, this we will see the effect of impurities on the liquidus temperature.

So, liquidus temperature that is the temperature at which it completely made. So, completely in liquid form; so, liquidus temperature of the iron alloy can be calculated as. So, 1537 that is the actual melting point of iron and if there is no impurities that would be the liquidus temperature.

However; if you have a carbon or phosphorus, sulfur, copper, silicon, manganese, molybdenum, nickel, chromium, titanium or vanadium all of these contribute with contribute in reducing the temperature. So, as you can see if we have a one weight percent carbon the liquidus temperature reduces to 1449 degree Celsius and if it is 4 weight percent carbon as you know in the blast furnace mostly especially in lower part of the blast furnace in the hearth lots of carbon. So, it is a carbon saturated melt it is reduces almost 1185 degrees Celsius at 4 weight percent of carbon the liquidus temperature iron.

So, the this is the effect of alloying elements on the melting point of liquid iron and one can calculate the liquidus temperature using this equation. Similarly density of the iron varies with temperature and this empirical correlation can be used with respect to temperature for density variation and. So, where T is in degree Celsius and iron density is given in gram per centimeter cube. So, at 1550 degree Celsius iron density is 7 at 1700 degree Celsius the 6.9. So, at a temperature goes up start decreasing.

And in the blast furnace if you look at and we consider 4 percent carbon in iron then the density of iron is about 6.75 at 1600 degree Celsius. So, the, but roughly one can calculate the density of iron is using this empirical correlation with respect to temperature.

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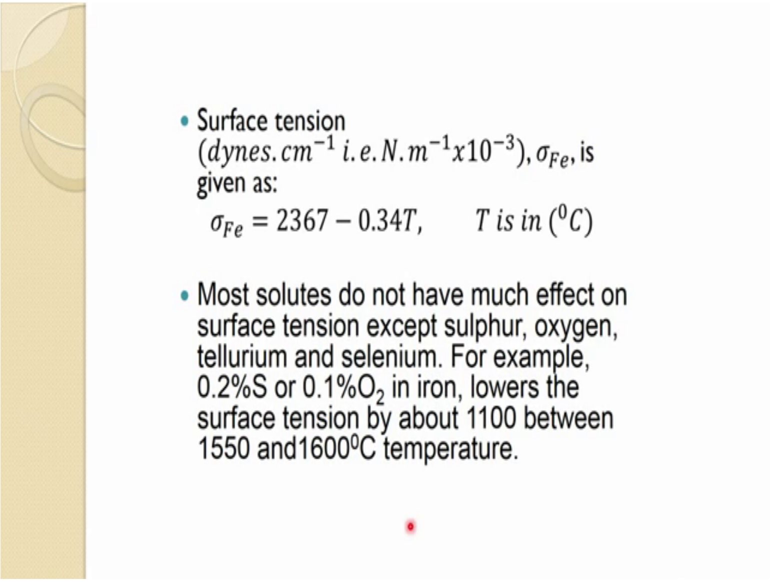

- Surface tension $(dynes.cm^{-1}\ i.e.N.m^{-1}x10^{-3}), \sigma_{Fe}$, is given as:

$$\sigma_{Fe} = 2367 - 0.34T, \qquad T\ is\ in\ (^{0}C)$$

- Most solutes do not have much effect on surface tension except sulphur, oxygen, tellurium and selenium. For example, 0.2%S or 0.1%O_2 in iron, lowers the surface tension by about 1100 between 1550 and1600^{0}C temperature.

Similarly, the surface tension of the iron is of course, surface tension varies with temperature. So, it is a function of temperature. So, it is given by this empirical correlation. So, surface tension of iron sigma Fe equal to 2367 minus 0.34 T the T is the temperature in degree Kelvin and the surface tension is given in this equation in dynes per centimeter which can be converted into in case your si unit Newton per meter into 10 to power minus 3.

So, most solutions do not have much effect on surfa most solutes it is takes upon. So, most solutes do not have much effect on surface tension except sulphur oxygen tellurium and selenium. So, for example, 0.2 percent sulphur or 0.1 percent oxygen in iron lower is the surface tension by about 1100 between 1550 and 1600 degree Celsius temperature. So, that is a big drop in the surface tension. So, these elements sulphur, oxygen, tellurium, and selenium they affect surface tension significantly.

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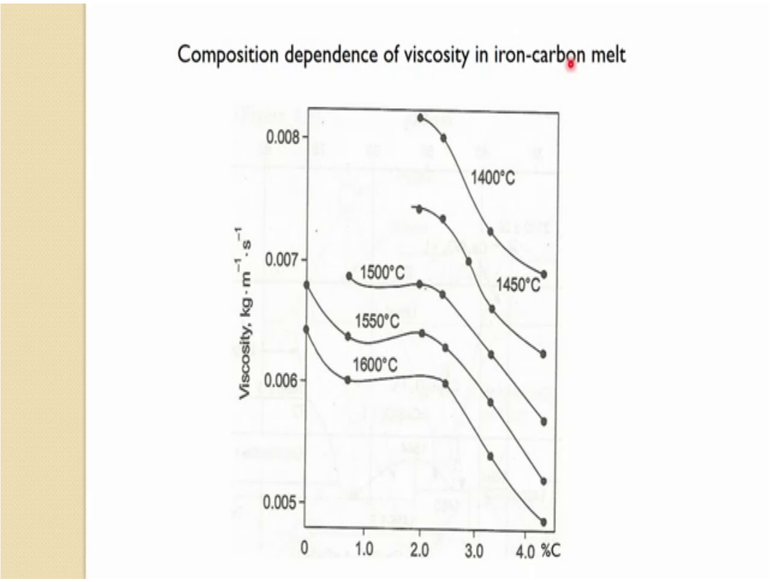

Composition dependence of viscosity in iron-carbon melt

Another property of liquid iron is viscosity. So, viscosity again it is dependent on the composition and mostly because carbon is more soluble in iron. So, this figure shows more about dependence of viscosity in iron carbon melts with respect to temperature at various temperatures; So, viscosity in kg per meters second and tempera temperature composition in terms of carbon percentage.

So, you can see as the temperatures increases or. In fact, the in increases the viscosity is decreasing and also with the percentage of percentage of carbon in present in the melt is usually reduces the viscosity which you can see in all these curve the viscosity usually reduces after tuyere as the carbon percentage in the melt increases.

But mostly between 1 and 2 percent it is similar, but as such from it is starting to and it keep on reducing. So, one can get viscosity tem density surface tension and melting temperature of the liquid iron from these correlation or figures.

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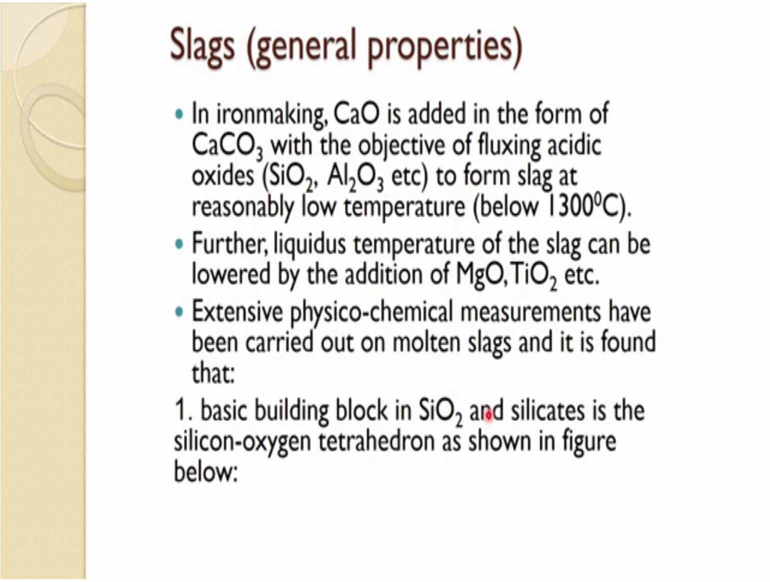

Slags (general properties)

- In ironmaking, CaO is added in the form of $CaCO_3$ with the objective of fluxing acidic oxides (SiO_2, Al_2O_3 etc) to form slag at reasonably low temperature (below 1300°C).
- Further, liquidus temperature of the slag can be lowered by the addition of MgO, TiO_2 etc.
- Extensive physico-chemical measurements have been carried out on molten slags and it is found that:

1. basic building block in SiO_2 and silicates is the silicon-oxygen tetrahedron as shown in figure below:

Similarly, now little bit about the selects general properties of the slag. So, in iron making calcium oxide or lime is added in the form of calcium carbonate. So, that is in this starting which we said and this really dissociates near the cohesive zone where temperature is about close to 1000 degree Celsius.

So, in the form of CaCO 3 with the objective of fluxing acidic oxide acidic oxide like SiO 2 Al 2 O 3 etcetera to form select at reasonably low temperature that is below 1300 degree Celsius. So, this is still high further if you remember that now we discussed a 4 percent carbon is present in pure iron then this tem pure iron liquidus temperature reaches almost to 1200 degree Celsius.

Now, further liquidus temperature of the slag can be lowered by the addition of MgO and TiO 2 and some other oxide. So, expensive physico chemical measurement have been carried out on molten slags and it is found that basic building block in SiO 2 and silicates is this silicon oxygen tetrahedron as shown in the figure.

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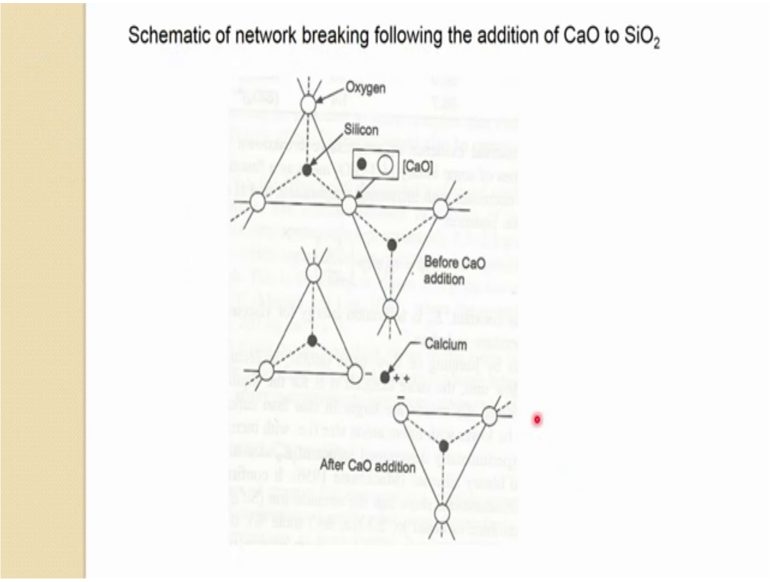

Schematic of network breaking following the addition of CaO to SiO_2

In this form; so, you can see this a sort of a tetra hedron basic block for silicates. So, 3 oxygen atom in silicon atom in the in the middle and. So, this is the basic block of slags; however, this can be break down not.

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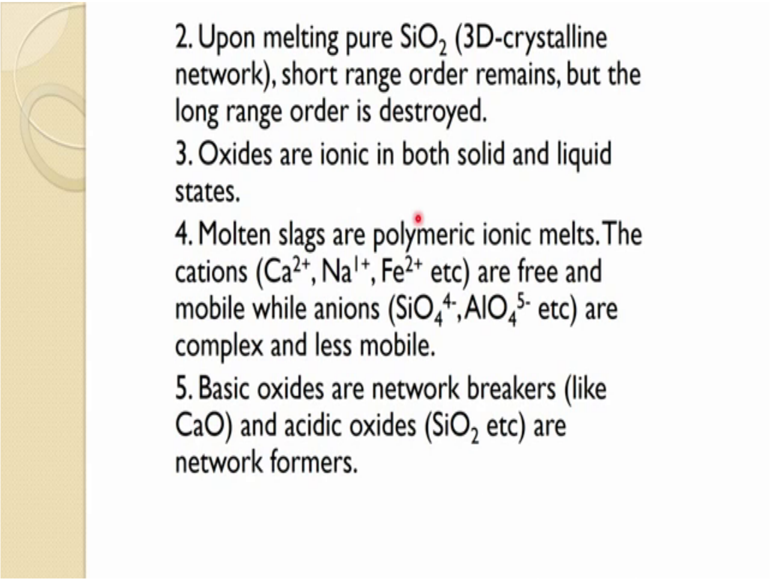

2. Upon melting pure SiO_2 (3D-crystalline network), short range order remains, but the long range order is destroyed.
3. Oxides are ionic in both solid and liquid states.
4. Molten slags are polymeric ionic melts. The cations (Ca^{2+}, Na^{1+}, Fe^{2+} etc) are free and mobile while anions (SiO_4^{4-}, AlO_4^{5-} etc) are complex and less mobile.
5. Basic oxides are network breakers (like CaO) and acidic oxides (SiO_2 etc) are network formers.

We will see how. So, upon melting pure SiO 2 see 3D-crystalline network, short range order remains, what the long range order is destroyed.

So, this you will see the chain it just keep on extending and make a very long chain in that so, that in silicon oxygen tetrahedron. So, that is the building block. So, which is the long chain in this form, but when you heat it up it break down and form the short range order chain. So, long range order is destroy oxide are ionic in both solid and liquid state because this is oxide. So, this is in liquid state in ionic form when you say ionic certainly the iron irons are there in the slag.

So, molten slags are polymeric ionic melt the cation like calcium sodium iron etcetera are free and mobile while anions silicate AlO 4 etcetera are complex and less mobile. So, these are freely mobile, but these are less mobile and basic oxides are network breaker. So, like CaO CaO MgO these are basic oxides. So, there these are network breaker when we say network breaker we are talking about the orders.

So, you can see this is a long chain of silica oxygen tetrahedron and if you add basic oxide like CaO. So, before addition it is combining when you add that it breaks it that chain. So, after radiation of CaO separated out and it leaves the cation in ionic charges on that and; that is how it becomes ionic ha melt insulate. So, these are network breaker that is why it is known as basic oxide are network breakers and acidic oxide like SiO 2 are network formers.

So, in the select we have quites good amount of line. So, it is breaking the network and which also then promoting the polymeric ionic melt and if you remember this correctly; when we were talking about the sulfide capacity we had written down the equation in form of in the ionic form which is mostly due to this region.

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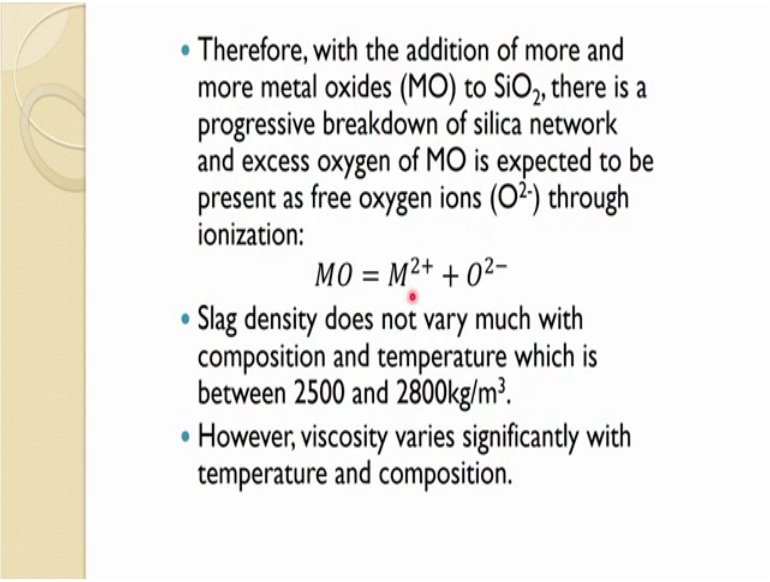

- Therefore, with the addition of more and more metal oxides (MO) to SiO_2, there is a progressive breakdown of silica network and excess oxygen of MO is expected to be present as free oxygen ions (O^{2-}) through ionization:

$$MO = M^{2+} + O^{2-}$$

- Slag density does not vary much with composition and temperature which is between 2500 and 2800kg/m^3.
- However, viscosity varies significantly with temperature and composition.

So, therefore, with the addition of more and more metal oxides like MO to SiO 2 there is a progressive breakdown of silica network and excess oxygen of metal oxide is expected to be present as free oxygen ion so, through the ionization. So, MO equal to M plus 2 plus O minus 2 so, this is the ionic form and this is the equation which we used in defining the sulfide capacity. In fact, in steelmaking also similar ways you can write the equation for the phosphate capacity.

Another one which we have not discussed here, because that dephosphorization takes place more in the steelmaking operation; So, you again present in ionic form. So, slag density does not very much with composition and temperature which is between 2500 and 2800 kg per meter cube.

However, viscosity varies significantly with temperature and composition. So, as such it does not very much the density, but the viscosity varies significantly and which can be seen from all right there is no figure, but viscosity very significantly with temperature and composition.