Steel Quality Role of Secondary Refining and Continuous Casting
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Module - 02
Lecture - 10
Degassing

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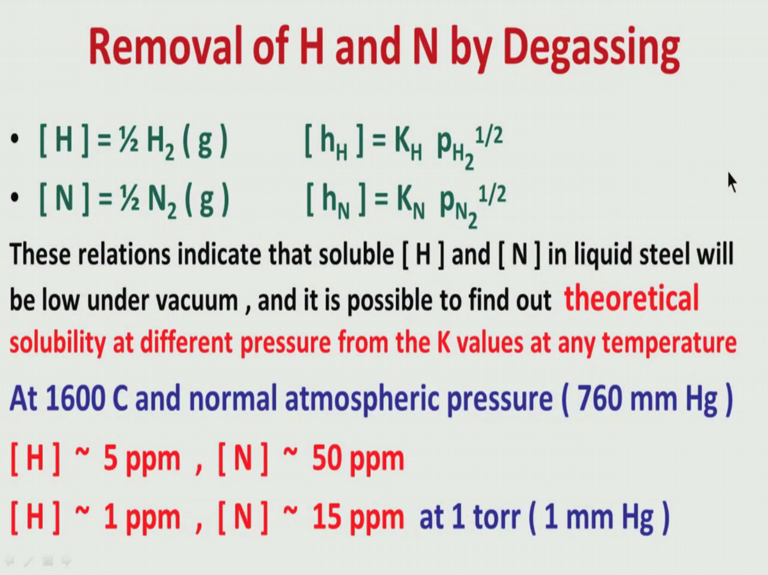

Removal of H and N by Degassing

- $[\mathrm{H}] = \frac{1}{2}\mathrm{H}_2(g)$ $\quad [h_H] = K_H\ p_{H_2}^{1/2}$
- $[\mathrm{N}] = \frac{1}{2}\mathrm{N}_2(g)$ $\quad [h_N] = K_N\ p_{N_2}^{1/2}$

These relations indicate that soluble [H] and [N] in liquid steel will be low under vacuum , and it is possible to find out theoretical solubility at different pressure from the K values at any temperature

At 1600 C and normal atmospheric pressure (760 mm Hg)

[H] ~ 5 ppm , [N] ~ 50 ppm

[H] ~ 1 ppm , [N] ~ 15 ppm at 1 torr (1 mm Hg)

I am coming to another important requirement of secondary refining. First I have talked about decarburization; that means, sorry I have talked about deoxidation rather; that means, the oxygen level in liquid steel has to be brought down. Then I have talked about the sulphured in liquid steel has to be brought down because if there is good amount of sulphur residual sulphur you have more amount of manganese sulphured in steel or may be calcium sulphured in steel. So, this will create sulphide inclusions. So, the inclusion contain is more cleanliness is affected, so first deoxidation.

Next step is desulphurization, now I talk about degassing. Why degassing is necessary because I have told you earlier that hydrogen nitrogen as gaseous elements which are present in liquid steel.

So, they have to be removed you know they have to be brought down to a tolerable level how it is done it is done by degassing. Now let us look at it what do I mean by degassing. Hydrogen nitrogen they are present in steel as soluble hydrogen and nitrogen as element, now from this hydrogen nitrogen from the solid steel it must go to the surface of the solid steel and then will get transform to the gas hydrogen and nitrogen. This is the way hydrogen is transformed; that means, hydrogen as element in dissolved in liquid steel must get transferred to the surface and then only it is possible to remove this as hydrogen gas at the liquid steel gas interface it is possible. So, first hydrogen in liquid steel must get transferred to the surface then at the surface this you know reaction takes place.

Similarly, nitrogen in liquid steel must get transferred to the from the bulk to the surface and the surface this reaction will takes place; that means, atomic nitrogen elemental nitrogen will go to the you know molecular nitrogen as gas and remove thus gas from the surface. So, you know what are the activity coefficients Hendrian activity coefficient of hydrogen is equal to the reaction constant K H in to partial pressure of hydrogen to the power half you know hydrogen is a gas here. So, what is the activity of hydrogen it is partial pressure of hydrogen because you do not have only hydrogen there may be there are other gaseous constituents like when you are taking of you know atmosphere there may be hydrogen there may be nitrogen there may be hydrogen is getting generated. So, as a partial pressure is important.

Similarly for nitrogen for this reaction nitrogen as element to nitrogen and gas at the liquid steel and gas you know surface interface this reaction is taking place. So, hydrogen present as elemental hydrogen the activity of hydrogen and nitrogen in liquid steel is equal to the equilibrium constant in to partial pressure of either hydrogen or nitrogen to the power half.

So, this relations indicate that soluble hydrogen and nitrogen this are soluble hydrogen and nitrogen this are Hendrian activity and as I have told you for this amount the because it is a dilute solution; that means, hydrogen and nitrogen in liquid steel contents are very low in ppm level. So, we can assume them the Hendrian law is affective we can assume them to we almost equal to the weight percent of hydrogen and nitrogen. So, this weight percent of hydrogen nitrogen at equilibrium at any particular temperature can be found out if we know the partial pressure of hydrogen or nitrogen. Now you try to understand what this relations get this relation indicate that soluble hydrogen nitrogen in liquid steel will be low under vacuum under vacuum is partial pressure is coming down vacuum is partial pressure of all the gaseous are coming down is it not is it not. So, hydrogen also will come down partial pressure nitrogen also will come down.

So, all partial pressures will come down in the process it will help removal of hydrogen as hydrogen gas removal of nitrogen as nitrogen gas. So, from this K H and K N figures this are all equilibrium constants which are possible to get from the thermo dynamic calculations. So, we know what are the possibilities of getting you know hydrogen soluble hydrogen nitrogen at some partial pressure or at some vacuum level. So, this theoretical these are all theoretical calculations this theoretical solubility at different pressure from the K values at any particular temperature are possible.

So, let us now try to get some quantity figures I have mentioned here as sixteen hundred degree centigrade we can from the K values we know this K values are dependent on temperature. So, from thermodynamics we can get at sixteen hundred centigrade what is the K H and K N and at that particular pressures say at normal atmospheric pressure; that means, when the atmospheric pressure is one then what is the soluble hydrogen what is the soluble hydrogen this are theoretical calculations this indicate that if we use normal pressure; that means, if we do not use vacuum.

So, at normal atmospheric pressure solubility of hydrogen will be around 5 ppm solubility of nitrogen will be above 50 ppm if you have more amount of nitrogen more than 50 ppm some amount will try to come out you know from this liquid steel because the limit is this now we can bring it down. Just look at the figures when we go to vacuum; that means, you know what is called Torr; 1 Torr is one millimeter of mercury one atmospheric pressure is equivalent to seven sixty millimeter of mercury column; that means, at 1 millimeter of mercury column; that means, at 1 Torr look at the figures hydrogen can come down to one ppm nitrogen can come down to 15 ppm. So, it is very clear by using vacuum we can degas the liquid steel we can bring down the hydrogen nitrogen contents in liquid steel the process is called degassing.

So, we must create vacuum in the process. So, in whatever process there is vacuum there is a possibility of degassing there is a possibility of controlling or deducing you know soluble hydrogen and nitrogen in liquid steel which is an important requirement for getting a good quality of steel because the gaseous contents if they are present more than a critical values they can create problem during casting they can create problem during subsequent you know applications.

So, I have just try to give you an indication that how by using vacuum we can get good degassing we can get relatively good amount of degassing this dissolve hydrogen and nitrogen can be brought down by using vacuum. Now the reaction as I have told you is basically transfer of hydrogen in liquid steel to the surface and the reaction is taking place at the surface and wherever whatever gas is forming they also have to be removed from the liquid steel gas surface to the gaseous phase to the gas you know phase so that means, there are three stages. Now I will come what this figures are giving you are basically the theoretical limits theoretical you know solubility limits theoretical calculations based on thermodynamics it does not take in to account the kinetics now if you go in to the stages how this reactions are taking place; that means, if we involved kinetics then will see whatever theoretical values we are trying to get.

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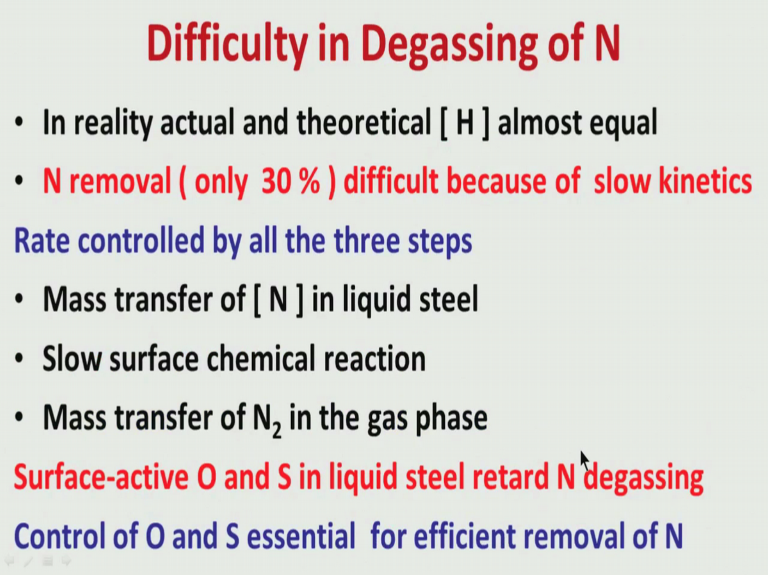

Difficulty in Degassing of N

- In reality actual and theoretical [H] almost equal
- N removal (only 30 %) difficult because of slow kinetics

Rate controlled by all the three steps

- Mass transfer of [N] in liquid steel
- Slow surface chemical reaction
- Mass transfer of N_2 in the gas phase

Surface-active O and S in liquid steel retard N degassing

Control of O and S essential for efficient removal of N

Some of them may not be possible to achieve in reality. So, if we now talk of kinetics will come to find that hydrogen. So, whatever theoretical H value theoretical hydrogen solubility you have calculated in reality the actual hydrogen is also more or less similar that is not much away problem; that means, theoretical value whatever we have calculated you know here; that means, at say 1 Torr we have calculated the theoretical hydrogen is possible to bring it down to one ppm at this level of vacuum. So, in reality it is possible to get one ppm of hydrogen at a vacuum level of one Torr almost equal; that means, it is possible in that order, but nitrogen removal you know degassing of nitrogen is not that efficient why I will come to it now and I am just mentioning here like unlike hydrogen where it is possible to get about 80-90 percent you know 80-90 percent of the theoretical level of degassing here degassing of nitrogen is only to the extent of 30 percent maximum say 40 percent.

So, this is difficult because of the slow kinetics now let us see what are the steps as I have told that nitrogen first has to be or hydrogen also first has to be there has to be a mass transfer of this atomic or nitrogen or hydrogen in liquid steel from the bulk to the surface of the steel to the interface of you know liquid steel and gas this are first step then the surface chemical reaction will happen. That means, as I was telling you this reaction will happen; that means, atomic hydrogen will give rise to gaseous hydrogen atomic nitrogen will give rise to gaseous nitrogen. So, this reaction is the next step after that; that means, whenever atomic nitrogen is forming gaseous nitrogen then this mass transfer of nitrogen in the gas phase is also another step.

If it remains at the interface then the reaction will be slower you know further reaction is difficult. So, this must get removed there has to be a mass transfer now these three steps they are rate controlled the whole reaction is rate controlled; that means, that they are controlled by these three steps which are relatively sure from nitrogen compared to hydrogen that is the basic difference between nitrogen and hydrogen; hydrogen you all of us know that very small in atomic size then they are diffusivities very fast. So, this mass transfer of hydrogen is faster mass transfer of hydrogen gas in the gas phase is also faster, but nitrogen relatively slower its diffusion. So, mass transfer of relatively slower compare to hydrogen.

So, mass transfer of nitrogen in liquid steel is slower mass transfer of nitrogen in gas also slower more over this reaction of from nitrogen atom to nitrogen gas at the interface is also slow because of the presence of oxygen and sulphur we know that oxygen sulphur or surface active. That means, if oxygen and sulphur are present in liquid steel there will always be some oxygen and sulphur in liquid steel we are trying to deoxidize we are trying to desulphurize, but it is not 0 it some equilibrium values are obtains it is near to those values. So, whatever oxygen and sulphur are present in liquid steel they will compete with nitrogen atoms to go to the surface between liquid steel and gas.

So, there is a competition. So, since oxygen and sulphur are very surface actives possibility of oxygen and sulphur going more at the interface is relatively large. So, in competition oxygen sulphur they are successful nitrogen becomes a bit unsuccessful. So, that is why not only the transfer of nitrogen is slow transfer of nitrogen in liquid steel this slightly slower compare to hydrogen, but there also the reaction; that means, from nitrogen to nitrogen gas at surface also slow because many of the sides are already occupied by the oxygen and sulphur. So, therefore, more is oxygen and sulphur in liquid steel less will be the nitrogen at the surface. So, here again control of oxygen and sulphur is coming in to picture.

So, I have try to explain here why first deoxidate decarburization is necessary; that means, due deoxidation is necessary; that means, we are trying to control oxygen to very low level this helps in good desulphurization; that means, we are controlling sulphur also to some lowest level in liquid steel. Now if you have low oxygen and low sulphur in liquid steel, so the competition from these 2 elements from these 2 elements to nitrogen is relatively less. So, there is a possibility of more nitrogen going to the interface. So, more nitrogen can go there is a more probability of the you know liquid steel gas reaction from nitrogen as element to nitrogen in gas will be more. So, this rate controlling steps here you know this slow surface reaction will be slightly faster.

So, it is always necessary to control oxygen sulphur for efficient removal of nitrogen. So, this is one important requirement for getting good denitrogenation in liquid steel degassing of nitrogen in liquid steel the oxygen and sulphur soluble oxygen and sulphur must be low; that means, there has to be good deoxidation there has to be good desulphurization then only you should go for degassing that is the reason you know there is a sequence of reactions there is a sequence of processes for secondary refining first there is deoxidation then only you will get good desulphurization. As I have explained to you earlier if you have low amount of dissolved oxygen in ox in liquid steel then only it is possible to transfer sulphur; that means, transfer of sulphur from liquid steel to slag will be faster when we have no amount of soluble oxygen in liquid steel I have already discussed just few minutes back this aspect.

Now when the good amount of deoxidation is there then good amount of desulphurization will be there and both of these are complete; that means, we have very low oxygen and sulphur in liquid steel then only we should go for degassing and then we can get relatively better amount of degassing of nitrogen. So, whatever theoretical values I was discussing like you know at one talk we must get theoretically about fifteen ppm nitrogen or one ppm hydrogen for hydrogen as I have mentioned is not a problem hydrogen more or less theoretical and in realistic situation of more or less similar.

Not for nitrogen normally we do not get. So, low soluble nitrogen at 1 Torr it may be 30 it may be 40 ppm even at you know at one atmospheric pressure this nitrogen level is relatively more because you know as I have told you this difficulty in removing nitrogen because of this steps because of this kinetics steps all reaction involves several steps which is known thermo dynamically we can theoretically get to some values, but if we consider the kinetics then will get a realistic values. So, from the kinetics we know that for getting a good amount of degassing particularly for nitrogen we must control oxygen and sulphur in liquid steel.

Now I have talked about three essential requirements of secondary refining I talked about good deoxidation why it is necessary it is necessary to get good cleanliness dissolved oxygen should below total oxygen also should come down because if you allow the you know the aluminum inclusions or the deoxidant float up and get absorbed I have talked about good desulpharization why it is necessary because the sulphur dissolve sulphur soluble sulphur must come down in liquid steel. So, I have liquid steel should have less sulphite inclusions. So, you know the inclusion level should be less it is more clean steel I have talked about why hydrogen and nitrogen level must be brought down how it is brought down in secondary refining before degassing why deoxidation is necessary desulphurization is necessary. So, now, let us come to some typical examples of secondary refining how it is done in reality.

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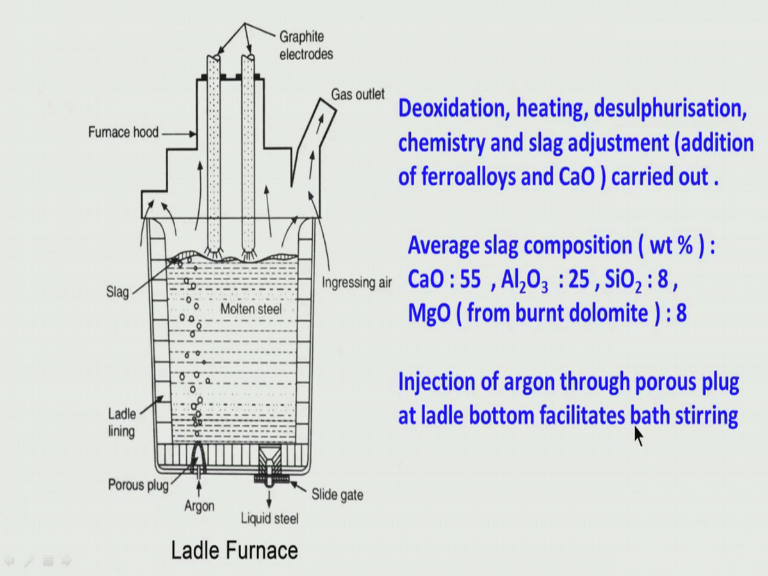

Deoxidation, heating, desulphurisation, chemistry and slag adjustment (addition of ferroalloys and CaO) carried out .

Average slag composition (wt %) : CaO : 55 , Al_2O_3 : 25 , SiO_2 : 8 , MgO (from burnt dolomite) : 8

Injection of argon through porous plug at ladle bottom facilitates bath stirring

Actually how it is done I have talked about to you ladle furnace is a very common you know secondary refining process. Now let us see what is happening ladle furnace we know thus we have to tap the liquid steel from BOFA; that means, in the primary stage we are tapping liquid steel in a ladle we are taking care that slag from the primary you know stage should not come should be restricted predicable should not come it has to be control within very small amount in the slag because it has FeO it has m N o it has P2O5 all these oxides are undesirable in the ladle. So, there should be cut off the primary slag should be cut off there should be no carry about of this slag in the ladle now when you have got a ladle now you can do secondary refining in a ladle I have mentioned this secondary defining processes are done in ladle.

So, now, this ladle first gets into this ladle furnace chamber in this chamber the whole chamber can be it can be ladle can be put in the side this we just see what are the facilities are there you see there are you know electrodes graphite electrodes which can be inserted in the ladle so that means, the possibility of heating up is that you can do lot of additions in the ladle why additions unnecessary because you know you have to form a good amount good basic slag basic slag in the ladle how do you form. So, you have to add some calcium oxide may be some small amount of calcium fluoride if necessary. So, for slag formation some addition is necessary for getting a good you know the desired chemistry some addition of ferroalloys may be necessary may be at to adjust manganese may be at to adjust silicon may be at to adjust other alloying elements.

Whatever or the requirement is in the particular rate. So, some addition for of ferroalloys for getting you know the desired chemistry is necessary may be you have to adjust the carbon and small amount of some condition may be necessary for adjusting for getting the desired carbon level. So, all these additions are possible in re furnace. So, what else is possible then you have to add some aluminum you know for getting good deoxidation. So, deoxidation heating desulphurization chemistry and slag adjustment you are adding ferroalloys and CaO all these are carried out in ladle furnace everything is possible in ladle furnace except degassing; degassing is not possible because it is not under vacuum. So, except degassing deoxidation is possible heating is possible desulphurization is possible chemistry adjustment is possible.

Now what is the average slag composition this is again roughly I am telling you there may be variation; variation of three four percent. So, calcium oxide is our 55 percent I have told you that for getting good desulphurization we must have good basicity. So, calcium oxide is about 50 to 55 percent alumina is about 25 percent where from alumina is coming because we are adding aluminum for deoxidation. So, alumina is the deoxidation product. So, there is good amount of alumina in the slag.

We have some amount of silica in the slag we may have where from silica is coming if there is some silicon some you know as deoxidant; that means, some amount of silica may form as deoxidation product is roughly about eight percent it may vary from maybe 6 to 10 percent then some amount of MgO is the in the slag where from it is come it is in to esteem this is coming from the burnt dolomite which is the ladle lining it is the you know there is a refractive lining this called the ladle lining here this portion ladle lining it is made up burnt dolomite. So, some amount of MgO might come and may might it actually comes from you know from this refractory erosion. So, some amount of MgO will be there in a slag.

Now this interesting look at here; I have told you there is a possibility of argon purging injection argon in the ladle. So, we call it argon purging you know there is a possibility that argon will be injected through the porous plug this is the porous plug at the bottom. So, through this porous; porous plug argon can be purged you know you see this argon bubbles arising. So, how much argon you purge also there is a theoretical you know calculations I will try to talk about it separately later on, but please try to understand this argon purging facility is there in all ladles. So, there is a you know presence of porous plug at the bottom of the ladle through that you can push argon you can inject argon and this helps in circulation in the bath you know this helps in homogenization of the bath this helps to float facilitates to float the aluminum inclusions which are forming by deoxidation reaction.

To go and to float go up and get absorbed at the slag level. So, this is very important this helps in bath stirring temperature homogenization is possible. So, in ladle furnace I am trying to talk about what are the possibilities are there deoxidation is possible heating is possible because you know this graphite electrodes are there they are used for heating. So, whenever there is a temperature drop we can use argon electrodes we can create an arc we can increase the temperature of the liquid steel we can do desulphurization because if the slag is good slag is you know is useful this is. So, much of calcium oxide is required for good desulphurization. So, it is possible. So, chemistry adjustment is possible you can add ferroalloys slag adjustment is possible as I have told you know calcium addition calcium oxide addition has been there. So, all these facilities are there in ladle furnace except degassing many things are possible to be done.

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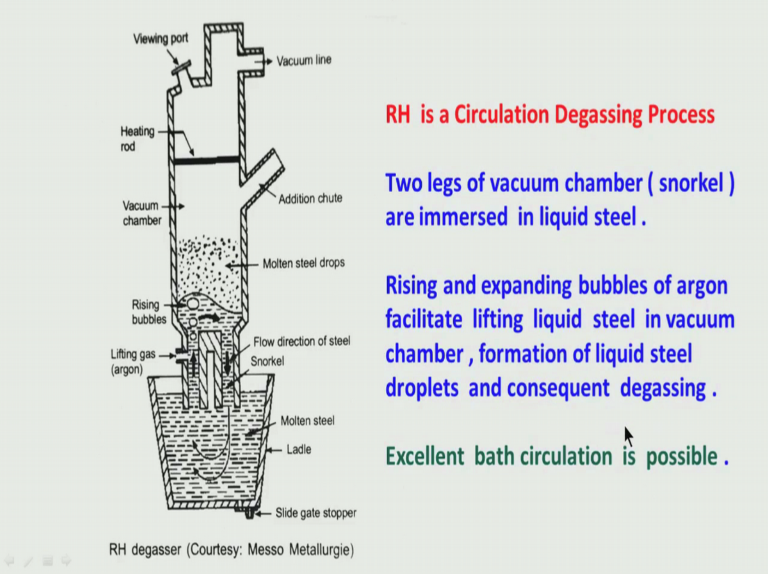

RH degasser (Courtesy: Messo Metallurgie)

RH is a Circulation Degassing Process

Two legs of vacuum chamber (snorkel) are immersed in liquid steel .

Rising and expanding bubbles of argon facilitate lifting liquid steel in vacuum chamber , formation of liquid steel droplets and consequent degassing .

Excellent bath circulation is possible .

Now, let us go to another you know secondary refining furnace or secondary refining possibility or the process which is known as RH I have told you R H degasser is also a common secondary refining process now what does it do the name suggest R H degasser;

that means, degassing is possible; that means, there has to be vacuum possibility of creating vacuum then only degassing is possible. So, what it does this is very interesting.

This is somewhat different from the other degassing processes I have told you there may be v d; that means, vacuum degassing there may be a VAD process; that means, vacuum arc degassing where along with degassing you can create arcing; that means, you can increase the temperature here we call it R H degasser; that means, degassing is possible. So, how degassing are we are doing this is interesting this is called circulation degassing process unless VD and VAD where you know there is a vacuum chamber we are putting the what is that called the ladle we are taking the ladle you have the liquid steel is there inside the vacuum chamber and we are evacuating using a pump. So, the vacuum is created and degassing is the in the process degassing will be there, but here just look at what is happening there is a vacuum chamber.

So, from the ladle liquid steel there are 2 legs of the vacuum chamber you call snorkel this is one leg this is another leg. So, this leg the left leg in the figure what is happening there the both are immersed in the liquid steel in the ladle the rising and expanding bubbles of argon. So, we are pushing argon from this you know opening in this slag in this snorkel left snorkel of the vacuum chamber. So, how does argon help this bubbles of expanding rising and expanding bubbles of argon they facilitate liftingly there is a pumping action they will pump the liquid steel in this chamber you see they will pump up. So, the liquid steel will be lifted in vacuum chamber this is the vacuum chamber. So, liquid steel is lifted in the vacuum chamber formation of liquid steel droplets; that means, the liquid steel will there will be droplets of liquid steel will be created by this action.

And consequent degassing as I told you how degassing takes place degassing is taking place from at the interface of the liquid steel and the gas gaseous surface. So, if you can create droplets of liquid steel this degassing reaction is enhanced because small droplets. So, the you know transportation of hydrogen nitrogen from the bulk to the interface will be enhanced because you have a small droplet you know the distance of transport or the distance; distance of travel for hydrogen and nitrogen will be less because of small droplets there be going to the surface and the droplets are present in the vacuum chamber. That means, at the surface of the droplets of liquid steel there be reaction from nitrogen in liquid steel to the gas of nitrogen or hydrogen going to the vacuum chamber vacuum phase and since the vacuum is there the this reaction; that means, from atomic nitrogen to liquid nitrogen or atomic hydrogen oh, sorry, not liquid nitrogen to gaseous hydrogen the gas the reaction of atomic nitrogen to gaseous nitrogen atomic hydrogen to gaseous hydrogen they are enhanced in vacuum.

So, we are creating first we are using the argon gas argon bubbles we are creating droplets of liquid steel where pumping of droplets or liquid steel sending it to the vacuum chamber. So, this small droplets at the interface of the small droplets this reaction you know solid gas reaction of nitrogen atom to nitrogen gas hydrogen atom to hydrogen gas will take place and the vacuum will enhance this reaction.

So, there is an excellent bath circulation is possible because the whole bath is getting circulated because of this process liquid steel is going up and finally, coming down here through this the other snorkel the other portion of the vacuum chamber. So, it is going up as you know argon gas is send through this you know channel send through this or if this. So, it is going up through this snorkel after the reaction it is coming down through this snorkel that is there is a continuous circulation of liquid steel in the ladle to the vacuum chamber in the process the extent of degassing is very good it is quite helpful in this way.

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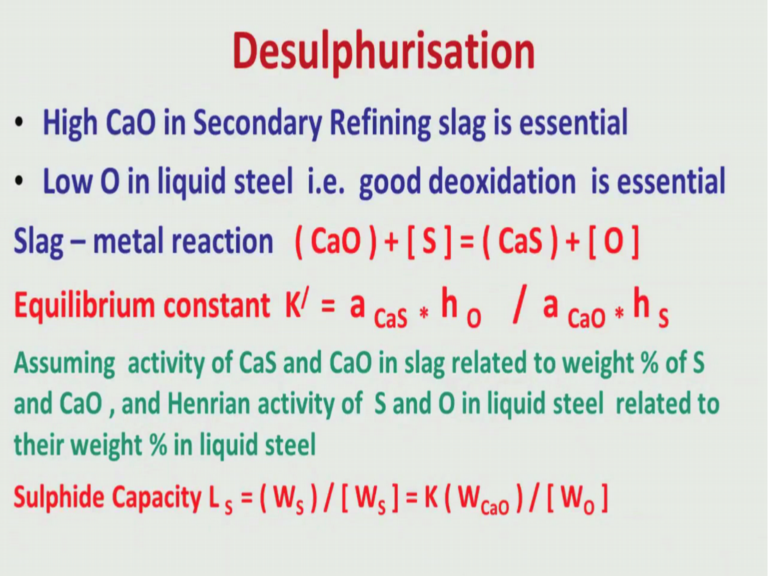

Desulphurisation

- High CaO in Secondary Refining slag is essential
- Low O in liquid steel i.e. good deoxidation is essential

Slag – metal reaction $(CaO) + [S] = (CaS) + [O]$

Equilibrium constant $K' = a_{CaS} * h_O \; / \; a_{CaO} * h_S$

Assuming activity of CaS and CaO in slag related to weight % of S and CaO , and Henrian activity of S and O in liquid steel related to their weight % in liquid steel

Sulphide Capacity $L_S = (W_S) / [W_S] = K(W_{CaO}) / [W_O]$

So, I have talked about today desulphurization how desulphurization takes place it is I have told you this basically a slag metal reaction. So, the sulphur which is present in the liquid steel will react with calcium oxide present in slag to generate calcium sulphide;

that means, the sulphur is going from the liquid steel to the slag as calcium sulphide and oxygen is also getting generated and coming in to the liquid steel. So, calcium this reaction indicates that calcium oxide in slag has to be high oxygen in liquid steel has to be low then only desulphurization is very successful I have talked about what is known as sulphide capacity it is a weight fraction of sulphur in the slag in the form of calcium sulphide divided by the weight fraction of sulphur present as elements sulphur in the liquid steel.

So, the ratio of this gives an indication of the desulphurization possibility and also or the you know the how effective is the desulphurization this is known as LS known as the sulphide capacity at equilibrium level and as I have told you this is since this is proportional to weight fraction of CaO. So, more is the c a o more is the desulphurization and it is inversely proportional to weight of weight percent of oxygen in liquid steel. So, less is the weight percent of oxygen better will be the desulphurization. So, deoxidation is the must before desulphurization to bring out to bring down the amount of oxygen in liquid steel then I have talked about degassing how hydrogen and nitrogen can be removed using vacuum you know this reaction takes place this is a reaction at the interface of liquid and gas hydrogen and nitrogen as element present in the liquid steel goes to the gaseous hydrogen and nitrogen as molecule and removed in the gas phase.

So, this reaction is depends on the partial pressure of hydrogen and nitrogen which is lowered by using vacuum. So, vacuum can vacuum level less is better is the vacuum; that means, low is the partial pressure better is the degassing, but these are I have talked about the theoretical solubility limits and I have given you some values from the theory what should be the level. But then I have also talked about that for hydrogen not of more or less the theoretical limits that can be achieved, but for nitrogen the amount of degassing is not good is only to the extent of 30 to 40 percent because of the kinetics because this mass transfer of nitrogen in liquid steel is slow you know the reaction at the surface interface between liquid steel and gas is slow in the mass transfer of nitrogen and gas is also slow.

So, to enhance this denitrogenation; that means, enhance removal of nitrogen this control of oxygen and sulphur is essential because oxygen and sulphur is very surface active. So, if they are present in liquid steel in large amount they will preferentially go to the surface and at the cost of nitrogen. So, they removal of nitrogen gets slow, this is the requirement; that means, oxygen and sulphur first deoxidation and then good desulphurization are essential for getting good amount of nitrogen then I talked about you know in ladle furnace how what are the possibilities. Then I talked about in R H which is circulation degassing process how very good bath circulation is possible and good degassing is possible.

Thank you very much.