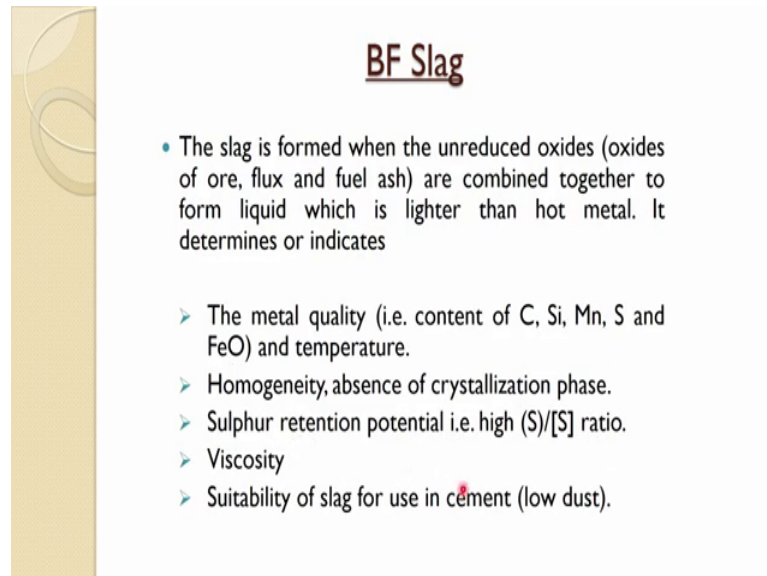


Iron Making
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Lecture – 27
Iron Making Lecture 27

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BF Slag

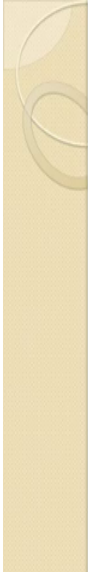
- The slag is formed when the unreduced oxides (oxides of ore, flux and fuel ash) are combined together to form liquid which is lighter than hot metal. It determines or indicates
 - The metal quality (i.e. content of C, Si, Mn, S and FeO) and temperature.
 - Homogeneity, absence of crystallization phase.
 - Sulphur retention potential i.e. high (S)/[S] ratio.
 - Viscosity
 - Suitability of slag for use in cement (low dust).

So now we would focus more on the blast furnace slag. So, what we have discussed till now are general properties of the slag and the liquid iron. So, in blast furnace the slag is formed when the unreduced oxides like oxides of ore flux and fuel ash are combined together to form liquid which is lighter than the hot metal. So, it determines or indicates the metal quality content of carbon silicon manganese sulphur and FeO and temperature.

So, slag determines what is the slag composition thing one can know what would be the metal quality in temperature homogeneity. So, absence of crystallization phase like titanium carbide in those. Sulfur retention potential; so, high ratio of the sulphide capacities of sulphur in slag and sulphur in metal. So, high ratio of it; so, this tells also about the sulphur retention capacity of the blast furnace slag. Viscosity is another important aspect of this slag whether it's a highly viscous or it has a low viscosity because that will affect the refining or transfer of the element between the metal and slag significantly.

Suitability of slag for use in cement; because finally, the slag which comes out from the blast furnace it should be usable to the cement industries. So, suitability of the slag for use in cement; so, it should have a low dust. So, these all properties should be there or it indicate these sort of things when one can see the composition of the slag of the blast furnace.

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The properties of the slag (mostly viscosity, melting point) vary widely within the BF. Slag may be classified as

- 1) Primary Slag: Partially reduced iron oxide combined with the gangue to form low temperature fusible eutectics. Slag softening and melting occurs during the descends of charge giving a shape and location to cohesive zone which is dependent on gas temperature, gas distribution and burden properties. The amount of primary slag which contains mainly SiO_2 , CaO , MgO , Al_2O_3 , FeO and small amount of MnO . MnO (up to 10%) and FeO (up to 30%) in slag contributes towards forming a low melting eutectics as shown in the next figure.

Solidus temperature is the temperature at which slag starts melting and liquidus temperature at which melting is completed.

Now because they select not only forming just at a hearth it is start forming somewhere from the cohesive zone where it is start melting up a.

So, gangue material combined and form slag. So, do have a different type of slag from cohesive zone to the hearth reason and these are the one which we would be discussing now. So, the property of the slag mostly viscosity melting point vary widely within the blast furnace. Slag may be classified as primary slag and the what is it this is partially reduced iron oxide combined with the gangue to form low temperature fusible eutectics. Slag softening and melting occurs during the descends of charge giving a shape and location to the cohesive zone which is dependent on the gas temperature gas distribution and the burden properties.

So, the things which we were talking about the cohesive zone. So, that is where actually the oxide combined with the gangue material mostly CaO , SiO_2 to form low temperature fusible eutectics. So, this is a low temperature eutectics and it starts sort of fuse softening

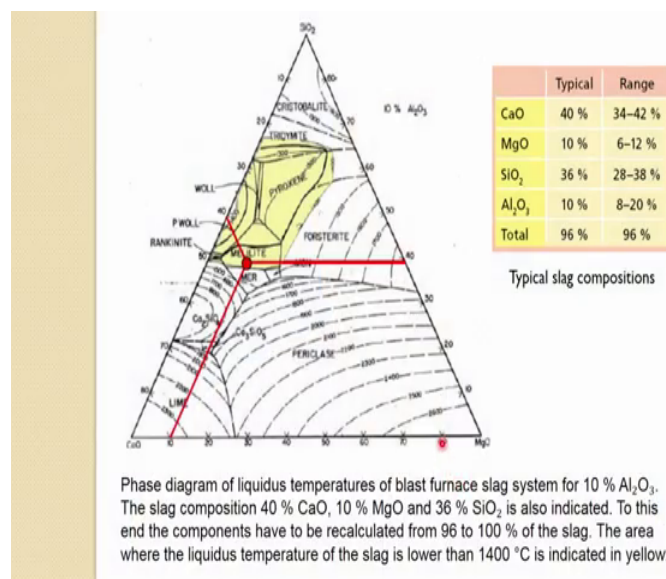
and start melting slowly. So, the amount of primary slag which contains mainly SiO_2 , CaO , MgO , Al_2O_3 , FeO and a small amount of manganese oxide.

So, in this region the main constituent of the slags are these; manganese oxide sometime it may go up to 10 percent and of course, the FeO up to thirty percent as we had mentioned before in the reduction of hematite how it progresses $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ to FeO and Fe_2O_3 its almost 100 percent utilization than 80 percent and then quite low for FeO 30 percent.

So, quite a lot wustite FeO is also known as a wustite. So, this wustite is all carried over near the cohesive zone. So, do get lots of iron oxide in the cohesive zone and it has to be reduced further. So, up to thirty percent in slag contribute towards forming a low melting eutectics as shown in the next figure. Here of course, we have to use the solidus and liquidus temperature. So, usually solidus temperature in respect to these here is the temperature at which slag starts melting and liquidus temperature at which melting is completed.

So, that is the upper boundary of cohesive zone is this solidus temperature they said which are slag is starts melting and lower boundary of the cohesive zone is the liquidus temperature. So, after that if all this one is in the liquid form which drip which is dripping down through the coke matrix. So, now, we will see how the this eutectic in this next figure.

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So, this is a phase diagram mostly SiO_2 calcium oxide magnesium oxide.

And a 10 percent Al_2O_3 ; so, Al_2O_3 is fixed how much your SiO_2 CaO MgO is changing. So, SiO_2 is 100 percent here and then it cost reducing to this axis; similarly MgO is 100 percent here reducing towards this, similarly CaO is 100 percent at this partition and reducing towards SiO_2 . So, that 80 is showing the 80 percent CaO if we take a point here 80 percent CaO , 10 percent MgO and your about 10 percent SiO_2 .

So, the phase diagram of liquidus temperature of blast furnace slag system for 10 percent Al_2O_3 ; the slag composition here we are assuming 40 percent calcium oxide 10 percent magnesium oxide and 36 percent SiO_2 ; this also indicated in this to this and the components have to be recalculated from 96 to 100 percent of the slag, the area where the liquidus temperature of the slag lower than 1400 degree Celsius in the indicated in yellow.

So, usually the slag typical slag composition is about 40 percent CaO , 10 percent MgO , 36 percent SiO_2 , 10 percent Al_2O_3 that is how we put it this is a typical slag composition and usually it is that sort of range which can be adjusted that is why it is said 96 to 100 percent because this comes to 96 percent.

So, other things are there which can be adjusted and this composition which is shown here that point actually belongs to this. So, which is showing about your you look at MgO is about 10 percent SiO_2 is about 36 percent and CaO is about 40 percent and 10 percent Al_2O_3 and this lines are indicating the temperature.

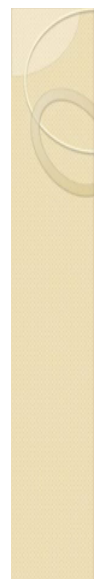
So, isotherms; so, you can see if this you have a very high content of MgO the temperature liquid temperature is quite high. So, this actually a liquidus temperature and these are the phases which are indicating various phase mullite, forsterite, tridymite, cristobalite of silica phase like that. So, you can see 1700, 1600 and then 1400 and that is where it is written and it is lower than 1400.

So, it is lying over here which is lower than 1400 when you come to over silica recite again it is showing 17 ah 16, 15, 1400 boundary here again this is a 1400, this is 1300, 1300 this boundary similarly here 1700, 1600, 1500 and that is 1400.

So, this region what you are having is a liquidus temperature of the slag less than 1400. So, if your composition of the slag you adjust within this region you will have the liquidus temperature of this of course, if you adjust properly you can have even a liquidus temperature somewhere in the range of 1300 degree Celsius in this; however, one is to see what would be the effect of this composition in terms of mass transfer of this element between the slag and the iron.

So, by studying this one can even adjust the liquidus temperature and the composition of the slag.

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2) Bosh slag: Volume of slag increases in this region and so the content of SiO_2 , Al_2O_3 and CaO in the slag while content of FeO and MnO is reduced to their reduction. Due to decrease of FeO content in the slag (by direct reduction of FeO with Carbon), the liquidus temperature of the slag increases as it flows down further into the lower part of the BF. If the rise in temperature in the lower zone of BF is not commensurate with the increase in liquidus temperature of the slag than it may re-solidify. Usually, presence of lime, magnesia and MnO keep the liquidus temperature low which can be seen from figures below. For high basicity slag with higher liquidus temperature; extra SiO_2 is added.

So, now; so, that was the primary slag which is in the cohesive zone after it becomes totally liquid and below the lower boundary of the cohesive zone bosh slag is start for me. So, bosh slag is the volume of slag increases in this region and so, the content of SiO_2 , Al_2O_3 and CaO in the slag while content of FeO and MnO is reduced to their reduction.

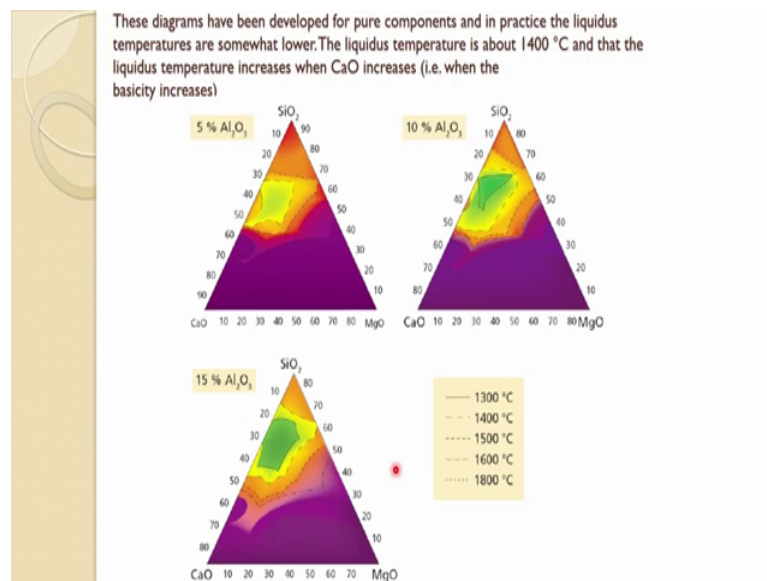
So, due to decrease of FeO content in the slag by direct reduction of FeO with carbon the liquidus temperature of the slag increases as it flows down further into the lower part of the blast furnace. If the rise in temperature in the lower zone of blast furnace is not commensurate with the increase in liquidus temperature of the slag then it may re solidify.

So, see the effect of FeO because FeO is present in quite high form in the primary slag. So, liquidus temperature is low, but as it cause comes into the bosh region we have more SiO₂ S which is coming out by burning of coke and in that one you have Al₂O₃ and of course, mod dissociation of calcium carbonate occurs and more CaO is available while FeO and MnO MnO content is reduced.

So, due to decrease of this the liquidus temperature of the slag increases. So, if we do not take care of this and liquidus temperature goes quite high it means re solidify when the blast furnace that will have very adverse effect on the blast furnace operation. So, usually presence of lime magnesia and MnO keep the liquid temperature low which can be seen from figures below. So, for high basicity slag with high liquidus temperature extra SiO₂ is added for high liquidus temperature.

So, we one has to ah put more lime on magnesia to keep the liquidus temperature low.

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So, this diagram have been developed for pure component again and in practice the liquidus temperature somewhat lower because there are many other impurities which are present. So, the liquidus temperature is about 1400 degree Celsius and that the liquidus temperature increases when CaO increases and when the basicity increases. So, when you increase the CaO naturally basicity will increase which is a ratio of mostly as a CaO by SiO₂ or CaO plus Al₂O₃ or CaO plus MgO divided by SiO₂ plus Al₂O₃ that is how do you define the basicity.

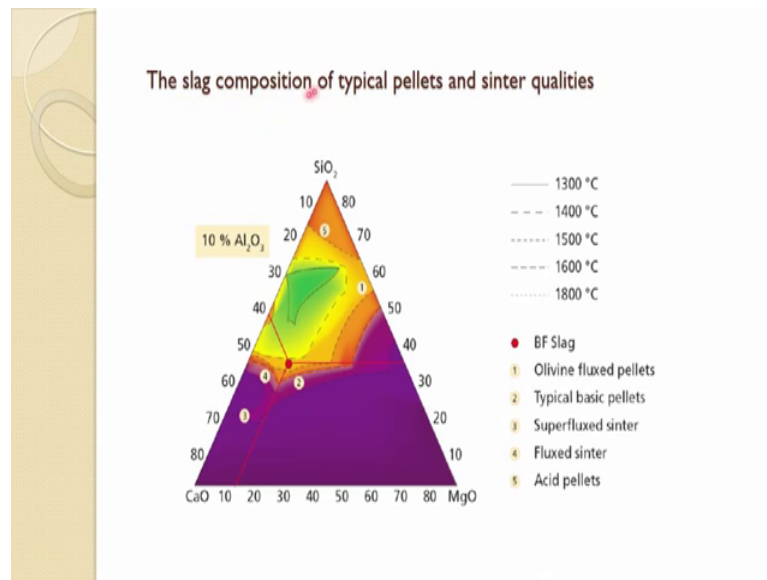
So, in this one if you have a five percent Al_2O_3 and again in the same way SiO_2 , CaO 100 percent SiO_2 100 percent decreasing this direction MgO 100 percent decreasing this direction. So, it shows the effect of Al_2O_3 addition. So, one can see SiO_2 actually ah when 5 percent Al_2O_3 is there; your SiO_2 constant actually is quite high and your solidus temperature actually a liquidus temperature has increased you can see these are 1300 degree this is 1800 is somewhere here 1600 1500 isotherm this is a 1400 isotherm and this is 1300 so in fact, 1300 sort of isotherm is quite heavy and sort of a missing.

So, naturally high silica actually increased the solidus temperature. So, melting is quite difficult; so, if you have more ah this less silica and more SiO_2 you can see this is 1300 degree Celsius region where one can have a molten slag liquidus temperature of that at 10 percent Al_2O_3 and some reduction in SiO_2 . And in this one of course, when 15 percent you are really covering a wide range of slag composition at 1300 degree Celsius liquidus temperature.

. So, you can adjust your composition within this. So, it is goes to somewhere sixty five SiO_2 you take or maybe just 55 somewhere here and you can have 15 percent and about 45 or 35 percent or CaO . So, that sort of composition over here will if the 15 percent Al_2O_3 will give a the liquidus temperature of 1300 degree Celsius which probably desired in iron making operation.

So, by a studying this ternary and quaternary diagram one can actually adjust the composition of slag to get the proper liquidus temperature of the slag and of course, in that way the fluidity and viscosity of the slag.

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The slag composition of typical pellets and sinter qualities; so, how does it from where the composition of sinter and pellets lie in the ternary or quaternary diagram one can see in that way. So, we already discussed where the typical blast furnace slag lie is lies in this ternary diagram with 10 percent Al_2O_3 fix. So, this is the typical composition of the blast furnace slag which is in around 1400 degree Celsius liquidus temperature the melting point of that.

And now if we look at the olivine fluxed pellet that is we talked during the pelletization. So, where more SiO_2 is there; so, that composition lie somewhere here which is lying there liquidus temperature somewhere between 1500 to 1400 degree Celsius. So, quite high and that may narrow down the cohesive zone region, but not only that it will also comes closer to the tuyere region.

So, one has to see the advantage and disadvantage of it how, but typical typically you have more actually basic pellets to form a good slag. So, typical basic pellet actually lie somewhere here between 1600 and 1800 this also gives a quite high liquidus temperature. And where you have about 35 20 and almost like 50 or 45 percent Si CaO super flux super naturally in super flux ones you have a higher amount of lime and that is how this is indicated in the figure over here number 3.

So, which is having almost 60 plus percentage of CaO and then the SiO_2 is of course, a quietly about 25 percent or 30 MgO is also low about 5 to 10 percent um. So, this is a

typical composition of the super flux pellet and which has sort of a solidus temperature the range of about 1800 degree Celsius between 18 and 1700 I would say that is the solidus temperature for the super flux sinter.

And then you have a fluxed sinter which of course, has the less called a lime and if you remember this sintering operation we discussed during the sintering. And where we talked about how do you produce sinter you puts lots of lime and other during granulation process and that is where you control this lime content and that is how you make super flux and flux pellet.

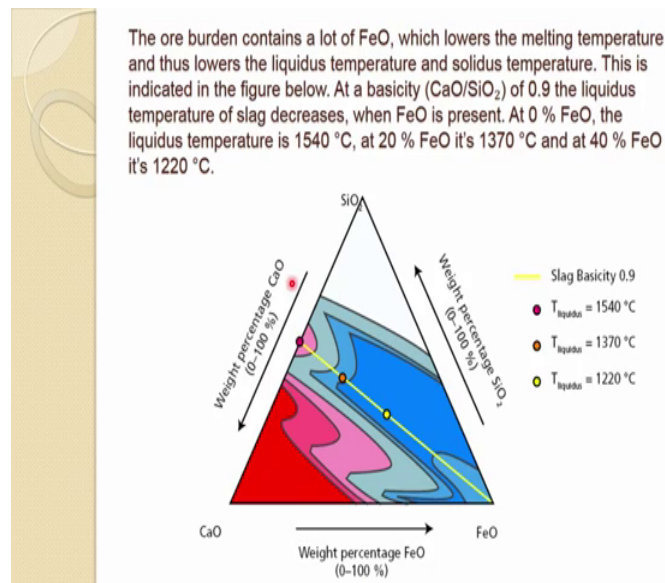
So, in flux pellet there is a less lime. So, this is the number fourth composition where flux sinter is lime. So, you have a about 50 percent or less lime in that and again MgO is not that much 5 percent plus MgOs Si O 2 is about 35 percent or so, and this temperature is about in the range of 17 to 1600 the liquidus temperature for this flux sinter.

And also sometime we have acid pellets which are use for a special purpose when we need it. So, acid pellets means more SiO₂ should be present in there and that composition is lying that is why toward the SiO₂ feticide. So, this is you know 5 and which indicates again 1800 the like 1800 plus sort of a liquidus temperature. So, very high SiO₂ content more than 70 percent SiO₂ contents usually in this one and lime is very low about 10 and similarly the MgO is also quite low about 5 and 10 percent Al₂O₃.

So, why add adjusting this raw material composition because nowadays in the modern blast furnace they are mostly 80 to 90 percent material raw material of iron ore is fed in the form of either pellets or sinters; hardly 10 percent is in the form of iron ore. So, one can adjust the composition of these raw material especially the pellet in sinter according to this ternary or for quaternary diagram. And can adjust the liquidus temperature of the slag and can work out in which reason it should come.

So, the operation of the blast furnace would be smooth um. So, the this ternary and quaternary diagram I quite helpful in adjusting the composition of the pellets sinter in thus about this slag properties.

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Now, the ore burden contains a lot of FeO. So, till now we did not discuss about the iron oxide of course, this is more in the cohesive region which lowers the melting temperature and thus lowers the liquidus temperature and solidus temperature this is indicated in the figure below.

At a basicity CaO ratio of CaO to SiO₂ of 0.9; the liquidus temperature of slag decreases. When FeO is present at 0 when FeO is present at 0 percent FeO the liquidus temperature is 1540 at 20 percent FeO 1370 at 40 percent FeO is 1220.

So, this again determine ternary diagram is showing mostly it is taking the composition of SiO₂, CaO, FeO which no in the actual blast make this is not the case you have many other component you of course, you have MgO you have Al₂O₃ you can have a small amount of manganese and so, forth. So, and these all will contribute also in lowering the temperature, but at the moment we are just talking the effect of CaO sorry FeO on this solidus temperature the and liquidus temperature.

So, SiO₂; so, well as I said SiO₂ percent decreases in this direction similarly FeO percentage decreases in this and CaO decreases in these direction. So, 100 percent CaO 100 percent FeO 100 percent SiO₂ at the three vertices of the triangle. And the slag basicity which we have said a 0.9 which is a typical one in the blast furnace per things have we take it.

So, this is the line which is showing about the slag basis constant slag bases 0.9. So, you can and this is the solidus temperature at 1540 degree Celsius that is when 0 percent FeO. So, essentially it is having 0 percent FeO, but about if would say 40 50 percent joules CaO and about 55 percent SiO₂ and of course, FeO is 0. So, that is anyway 45 or 55 around point nine it keeps and that is the point which it is showing 0 percent FeO the liquidus temperature is about 1500 40 degrees Celsius.

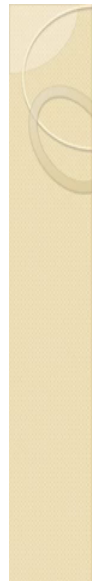
And as the FeO content increases the liquidus temperature reduces. So, when we go to 20 percent of FeO it reduce a to 1370. So, these are of course, the temperature isotherm of that; so, when temperature is 13 FeO content in this slag is 20 percent. So, which comes here and this would be somewhere. In fact, there and these would be here.

So, that composition gives you lower liquidus temperature 1370 and if bosh type content increase is increased further to 40 percent then which it comes to here this point and liquidus temperature reduce as to 1220 degree Celsius this is where as you have a cohesive zone composition between 20 to 40 percent and of course, you have MgO and MnO.

So, that also reduces the liquidus temperature in this. So, it further reduce at to and that is why melting a start somewhere around 1100 to 1150 degree Celsius in the cohesive zone; in the upper zone of the cohesive and it becomes totally liquid at the lower boundary of the cohesive zone.

So, this shows the importance of ternary and quaternary diagram because using that one can really select the proper composition of the slag to operate the blast furnace in a much a smoother way and can take the corrective action at various stages. So, as you have seen the primary slag composition is quite different bosh slag composition is again very different and when we reach to hearth slag then that composition is also quite different.

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- **Final Slag:** Some of the SiO_2 comes from the ash of the coke which is burnt at the tuyere level and some goes to bosh slag. This goes to slag and sulphur content is increased. Lime is dissolved in this slag. The formation of this slag is almost completed in combustion zone. Usually bosh slag basicity is higher if the ore is rich in iron content and lower would be the slag volume. Numerical examples, in the next slide, illustrate the effect of iron content and coke ash content on the slag basicity.
- Slag forms a pool in the hearth region where it floats at the top of the metal pool. During the passage of metal droplets/rivulets through the slag layer, transfer of Mn, S, Si etc species takes place trying to reach to an equilibrium state. Therefore, it plays an important role in controlling the final chemistry of the metal before it is tapped.

So, the hearth region slag what we called also as a final slag and this is this has some of the SiO_2 comes from the ash of the coke which is burnt at the tuyere level and some goes to bosh slag. So, in this one what we are trying what it is saying that the ash which is coming out from the tuyere region by burning and ash contains the SiO_2 and have put some amount of Al_2O_3 or other thing. So,; so, some amount of SiO_2 of that ash goes to the bosh slag and remaining amount goes to the final slag.

So, other amount goes to slag and sulphur content is increased because the basicity creates a sulphur content is increased. So, you need a high basicity is slag to remove the sulphur. So, that is why the sulphur content is increased; lime is dissolved in this slag the formation of this slag is almost completed in combustion zone. So, in combustion zone it is almost get completed this final slag.

So, usually bosh slag basicity is higher if the ore is rich in iron content and lower would be the slag volume. So, usually ore is rich in iron content and less SiO_2 in that when coming from the cohesive zone region. So, your basicity usually in bosh region is high, but bosh SiO_2 zone later from the ash and then that increases decreases the basicity.

So, but because basicity is high the slag volume is low and which is a good thing in the lower part of the blast furnace. We will see now one numerical example in the next slide which will illustrate the effect of iron content and coke ash content on the slag basicity. So, this thing probably will become more clearer to you once I think we go through this

numerical example where you can compare the basicity of the bosh slag and the final slag.

So, slag forms a pool in the hearth region when it get completed somewhere in the combustion zone it comes down and forms a pool in the hearth region; where it floats at the top of the metal pool due to the lower density of the slag almost two and half times lower than iron density metal pool density I should say because the iron is not a pure iron it is a mixture of some impurities like sulphur carbon, phosphorus, manganese like that.

So, during the passage of metal droplets and rivulets through this slag layer transfer of manganese sulphurs silicon etcetera species takes place trying to reach to an equilibrium state. So, this is very important now because the density of this slag is low, but volume is high. So, it makes a big pool on top of the metal and automatically the metal has to pass through this slag layer which is quite having a good height through which it has to pass and during that passage most of the mass transfer occur in the slag region.

And of course, it now the reason you study it they do not reach to the equilibrium state because do not have that sort of time most of the reaction as we had discussed before in terms of like silicon manganese and ah sulphur and other, but its reaches quite a bit into equilibrium state, but slag acts as a refining agent in one way for metal.

So, therefore, it plays an important role in controlling the final chemistry of the metal before it is tapped. So, this is very important that it controls the final chemistry of the metal before it is tapped. So, and because it is passage in the form of droplet and it will a that also we have seen in a video that is because the flow is non wetting.

So, liquid iron is slag is coming more in the form of droplet and rivulet. And in one way this is actually a good thing because it gives the more surface area and which promotes more mass transfer. And that is why the it is its plays an important role in controlling the final chemistry of the metal before it is tapped.