Materials and Energy Balance in Metallurgical Processes

Prof. S. C. Koria

Department of Materials Science and Engineering

Indian Institute of Technology, Kanpur

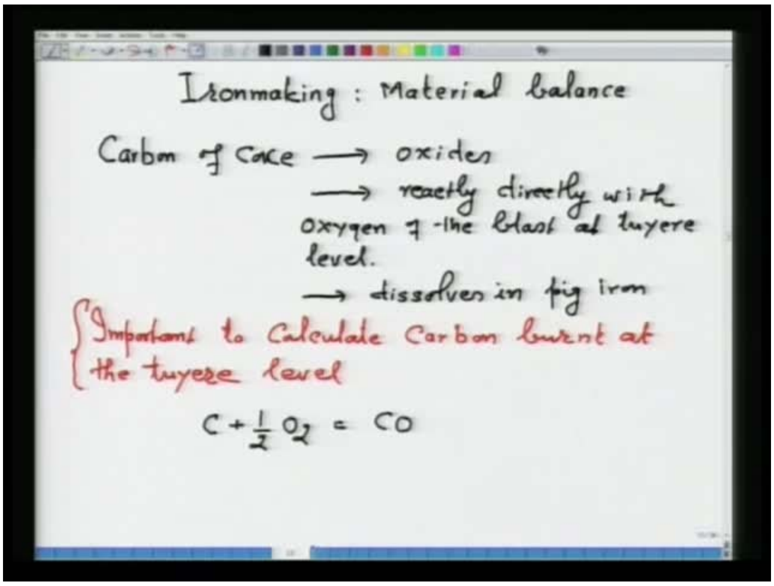
Module No. # 01

Lecture No. # 29

Material and Heat Balance in Ironmaking-I

This lecture is in continuation of the previous lecture on iron making, that is lecture 28. Now, in that lecture I have solved one problem and we did some material balance calculation.

(Refer Slide Time: 00:50)



I will show you some of the important things based on that particular problem. So, in the blast furnace iron making it is equally important how the carbon of the coke reacts with the burden. In fact, the carbon of the coke, say carbon of coke, it reacts directly with oxides like Fe 2 O 3, SiO 2, P 2 O 5 and so on. Also, carbon of the coke reacts directly with say oxygen of the blast at tuyere level or you may call the coke combust at the tuyere level, but in the coke carbon in fact combust as a combust or reaction whichever way.

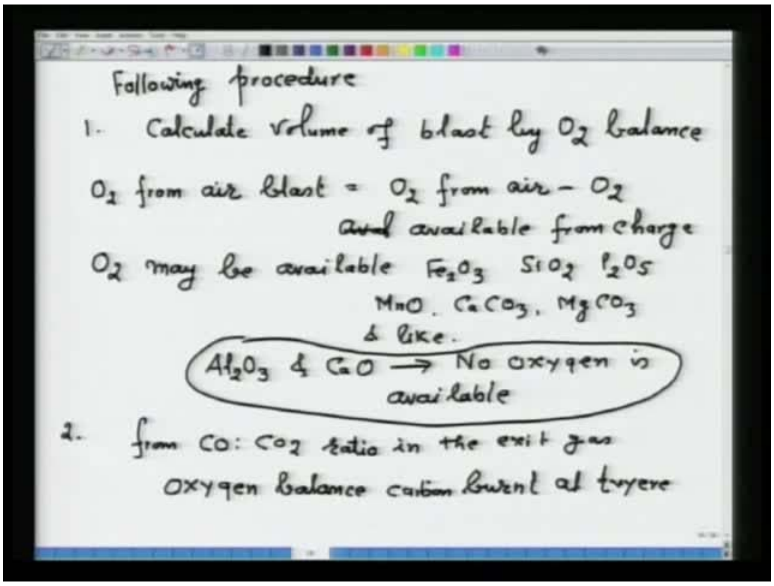
Also, the third important function of carbon is that the carbon also dissolves in pig iron or dissolves in hot metal and you get this so-called hot metal.

Now, it is also important in this connection to calculate the amount of carbon that is burnt at the tuyere level. What I am trying to say it is important to calculate carbon burnt at the tuyere level.

In order to calculate All that we can calculate is only how much amount of carbon is burnt at the tuyere level whether it is 70 percent or 80 percent or 60 percent because that particular carbon which is combusting at tuyere level will give us the so-called carbon monoxide.

The reaction of carbon with oxygen at the tuyere level that is C plus half O 2 - that is equal to carbon monoxide. We have to find out what is the fraction of the carbon that is in fact reacting or combusting at the tuyere level. For that purpose one can adopt the following procedure. The following procedure may be adopted; following procedure could be adopted.

(Refer Slide Time: 03:27)



The first thing is to calculate volume of blast, and this volume of the blast, you can calculate either from nitrogen balance or from oxygen balance. That is I write here, calculate volume of blast, for example, by oxygen balance.

If top gas volume is given then you can calculate, otherwise you have to perform the oxygen balance. If top gas analysis is given then you can do from nitrogen balance, but in case top gas amount is not known then you have to perform the oxygen balance.

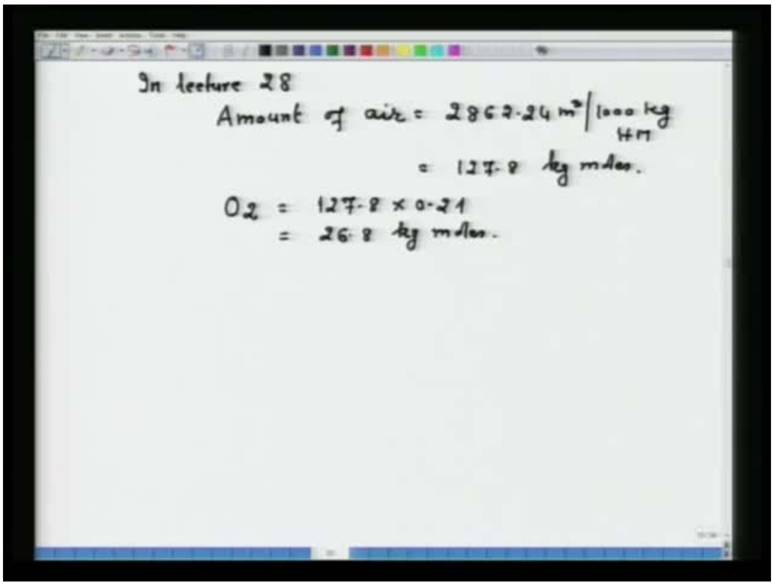
This balance is that oxygen from air blast that will be equal to oxygen from air minus oxygen available from charge. In this connection, the oxygen may be available and this proper accounting you have to keep. Oxygen may be available say through reduction of Fe 2 O 3, reduction of SiO 2 and here, you have to see how much amount of silicon is going to pig iron and the amount of SiO 2 going to slag, then P 2 O 5, MnO and then calcium carbonate.

Decomposition of calcium carbonate gives you CaO plus CO 2. If you do the oxygen balance then 1 mole of CaCO 3 gives you 1 mole of oxygen. If the charge contains magnesium carbonate also and like that

Now, remember here that from Al 2 O 3 and calcium oxide no oxygen is available. This is an important thing. No reaction Al 2 O 3 plus carbon in the blast furnace occur so that you can get oxygen of Al 2 O 3

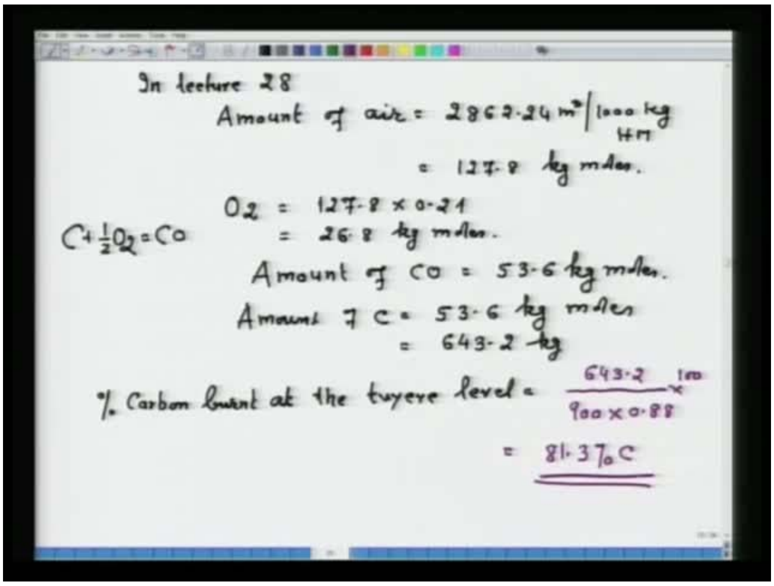
This is the first step. The second step is that one can then perform from CO to CO 2 ratio in the exit gas, from this what can do say oxygen balance will tell us the carbon burnt at the tuyere. This is because all the oxygen which is injected at the tuyere level reacts with carbon and that is why I have written that all the carbon is burnt at the tuyere level.

(Refer Slide Time: 07:35)



Now, in lecture 28 that is in the previous lecture, you recall, we have determined amount of air and this amount of air was 2862.24 meter cube per 1000 kg hot metal. This will be equal to 127.8 kg moles. From here, O 2 will be 127.8 into 0.21 that will give you 26.8 kg moles. You know that oxygen finds its partner as carbon only at tuyere level and nothing else is over there.

(Refer Slide Time: 08:48)



From the reaction C plus half O 2, that is equal to CO 2, we can find out the amount of CO and that will be equal to 53.6 kg moles. Therefore, amount of carbon will also be

53.6 kg moles. So, that will be equal to 643.2 kg. In order to find out percent carbon burnt at the tuyere level, we have all the details; that will be equal to 643.2 - that is the carbon that is burnt at the tuyere level.

You recall in that problem, we have said 900 kg per ton of hot metal coke and containing 0.88 percent fraction of carbon or 88 percent carbon into 100; then I will be getting around 81.3 percent. What this calculation means? This calculation suggests that 81.3 percent of carbon at the tuyere level is burnt and it produces carbon monoxide.

Rest, let us say around 18 or 19 percent of carbon is used up for direct reduction. That is this carbon reacts directly with the oxides say Fe 2 O 3, Fe 3 O 4, SiO 2 and P 2 O 5.

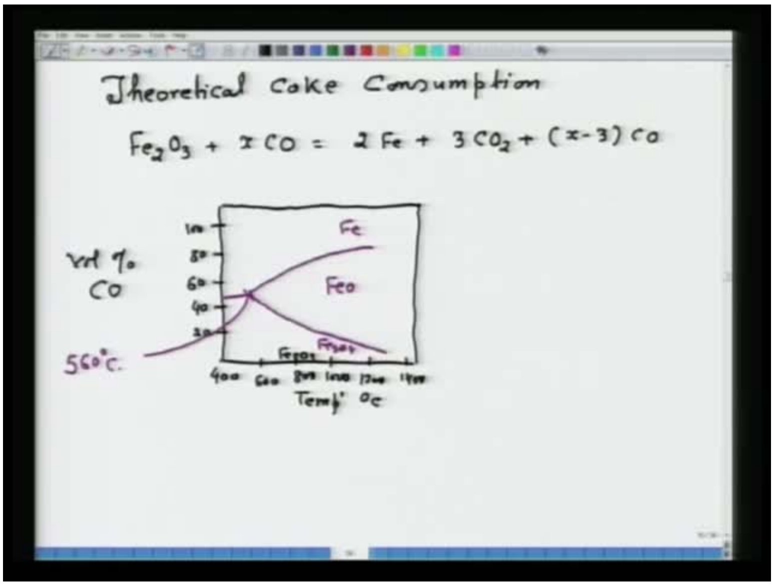
Remember this indirect reduction produces heat, whereas direct reduction is an endothermic reaction. This particular calculation gives you an idea about the percentage of indirect vis-a-vis direct reduction.

In fact, more is the amount of carbon that is burnt at the tuyere level more is the amount of carbon monoxide that will be produced. That is what this calculation means. So, in this particular problem around 81.3 percent of carbon is burnt at the tuyere.

Normally, in all such problems, if you calculate in the blast furnace iron making, somewhere 70 to 80 percent of carbon is always burnt at the tuyere level. As you recall, I have said that coke maintains permeability of the burden till it reaches the tuyere level because rest of the components of the burden. For example, iron ore and limestone fuse and change their shape, calcium carbonate decomposes to CaO and CO 2 is expelled, Fe 2 O 3 changes to Fe 3 O 4, 2 FeO and so on.

So, only coke maintains the permeability of the burden so that higher percentage of carbon burning at the tuyere level, it looks to me as a good functioning of the blast furnace.

(Refer Slide Time: 12:21)



Now, another thing I would like to say is how to determine theoretical coke consumption. When you say theoretical coke consumption then we mean determining the coke consumption based on the stoichiometric requirement.

Here, one has to think how Fe 2 O 3 is reduced to iron. In a well-accepted model, Fe 2 O 3 changes to Fe 3 O 4, then to FeO and to iron and it is a topochemical reduction. It is not that Fe 2 O 3 is first converted to Fe 3 O 4 then to FeO and then to iron. No, it is a topochemical pattern of reduction. If you want to get Fe 2 O 3 to iron then we must maintain a certain amount of carbon monoxide in the gaseous mixture. If you maintain that amount of carbon monoxide in a gaseous mixture then Fe 2 O 3 will be able to reduce to iron. What is that mixture? For example, if we write down the reaction Fe 2 O 3 and we say carbon monoxide is not known to us, we put plus x amount of carbon monoxide that will be equal to 2 moles of iron plus 3 moles of carbon dioxide plus x minus 3 moles of carbon monoxide.

Now, writing an equation is always easy, but then what should be the amount of CO? What percentage of CO should be maintained in a gaseous mixture of CO, CO 2? Well if carbon is being combusted with the air then the mixture CO, CO 2 and nitrogen.

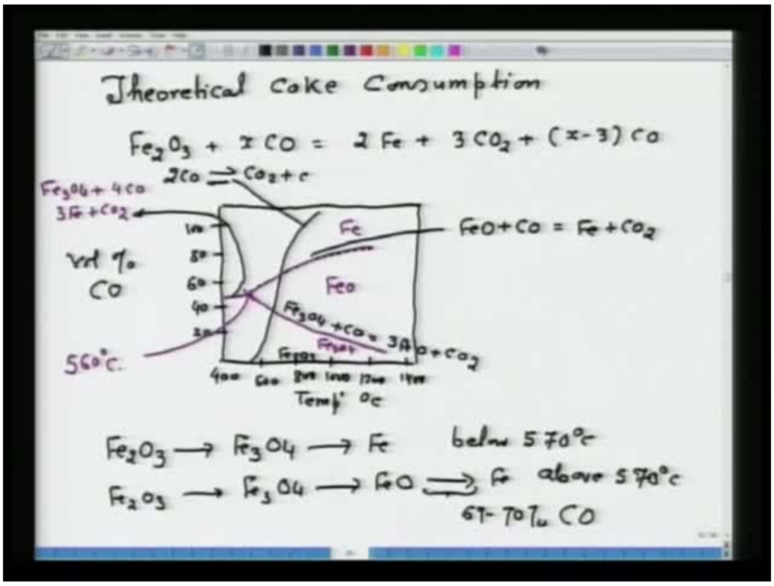
Even then, you have to find out what should be the percentage carbon monoxide in CO and CO 2 should be there so that this reaction is feasible. As you recall that this sort of information can be obtained by thermodynamic calculation. This is not the objective of the course, but what I wanted to say is there are equilibrium diagram from iron, carbon, oxygen equilibrium. One can find out what should be the optimum ratio of CO, CO 2 that should be maintained. I am not talking of the exit gas; I am talking at the point where Fe 2 O 3 should be able to reduce to Fe. In this particular sequence, though I have written equation in 1 step, but in the reduction of Fe 2 O 3 to iron, Fe 2 O 3 to iron in that sequence it is FeO to Fe - this is the most difficult step and FeO to Fe reduction require a very high percentage of carbon monoxide than Fe 2 O 3 to Fe 3 O 4 or Fe 3 O 4 to FeO.

I will just illustrate by way of an equilibrium diagram. I will just plot it here say for example, on the x axis I am putting as temperature in degree celsius. Somewhere here is 400, I am trying to be on the scale 800, this is 1000, this is 1200 and somewhere here 1400 degree celsius.

Here, let us say we have 20, we have 40, we have 60, we have 80 and here it is 100. This is the volume percent CO. This diagram it goes For example, this is how this diagram goes and this particular temperature is 560 degree celsius. now let me put All these lines represent the equilibrium between the oxides.

Say this area is FeO, this area is Fe and below is Fe 3 O 4 and much below it is Fe 2 O 3. All that it means that Fe 2 O 3 to Fe 3 O 4 requires very low amount of carbon monoxide, Fe 3 O 4 to FeO requires little higher amount of carbon monoxide whereas, FeO 2 to Fe requires a larger amount of carbon monoxide. This particular line on this side, it says this is FeO plus CO that is equal to Fe plus CO 2.

(Refer Slide Time: 17:24)



This particular line, if I write here, Fe 3 O 4 plus CO that is equal to 3 FeO plus CO 2 and below this Fe 2 O 3 to Fe 3 O 4 that requires a very low amount of carbon monoxide.

We are not much interested in this. What we are interested is this region above iron. If I want to get Fe 2 O 3 to iron my CO, CO 2 ratio must be above this particular line; otherwise Fe 2 O 3 to iron will not be obtained. That is what is an important thing. On this particular curve one can also super impose, the so called (18:25) woodward reaction and this goes something like this.

This particular reaction is 2 CO, CO 2 plus C - that means as you go to high temperature CO forms and so on. Now, utilizing this diagram for our purpose, what this diagram says is it is possible to reduce Fe 2 O 3 to Fe 3 O 4 to iron that is below 570 degree celsius and this particular equation is this particular line. This particular line denotes the so called Fe 3 O 4 plus 4 CO that is equal to 3 Fe plus CO 2.

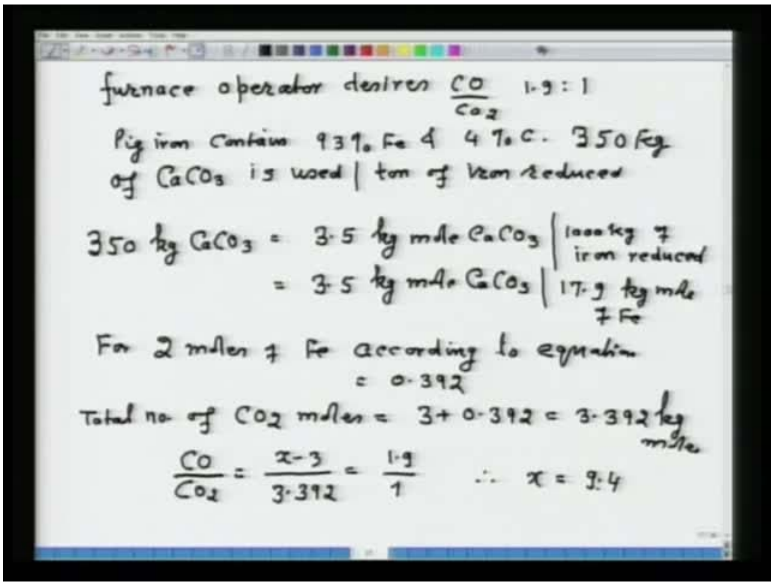
However, here no liquid iron will form because you know the melting point of iron; I need not tell you. Above 570 degree celsius, we have Fe 2 O 3 going to Fe 3 O 4 and it goes to FeO and then it goes to iron; this is above 570 degree celsius.

Now, this particular step is the most sluggish step in the reduction of iron oxide to iron and this FeO to Fe for example, if you take 900 or 1000 degree celsius approximately 69 to 70 percent of CO is required in order to reduce FeO to Fe. That is an important thing.

That means, if the volume percent of CO is more than 69 percent then iron formation will take place and this also explains why iron forms in the blast furnace just above the tuyere level because just above the tuyere level where the carbon combust with oxygen it forms CO and very high percentage of CO is available.

As the CO ascends and the burden descends, the temperature of the gases drops and the CO decomposes to CO 2 plus C. So, CO by CO 2 ratio or the volume percent of CO decreases and you come into a regime where Fe 2 O 3 can be reduced only up to FeO. This also explains that particular point.

(Refer Slide Time: 21:17)



Now, deriving say this particular information from this diagram, one can see what should be the theoretical coke consumption now. Let me take an example for it.

Now, suppose a furnace operator desires CO upon CO 2 ratio as 1.9 is to 1, pig iron it contains as 93 percent iron and 4 percent carbon. Also, 350 kg of calcium carbonate is used per ton of iron reduced; mind you it is not per ton of pig iron it is per ton of product iron.

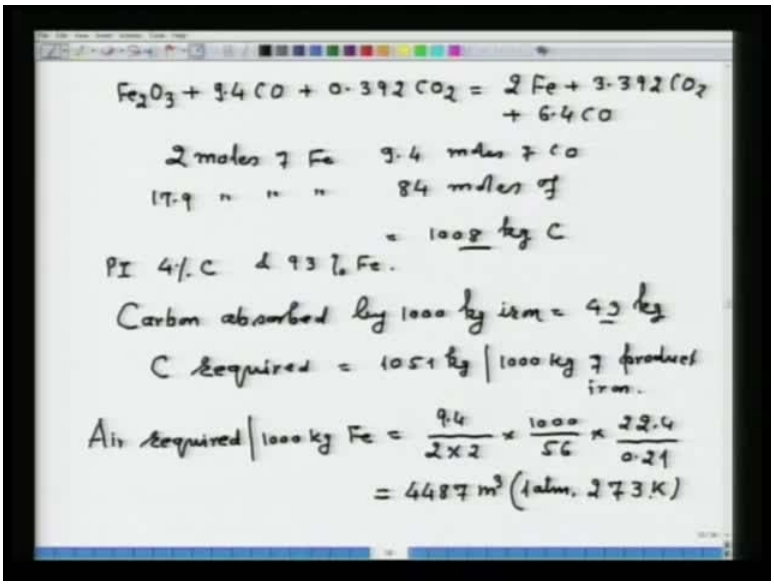
We have to calculate the theoretical coke consumption. 350 kg calcium carbonate that is equal to 3.5 kg mole of calcium carbonate. This 3.5 kg mole calcium carbonate is per 1000 kg of iron reduced - that is per 1000 kg of product iron. That means, I can also write down now 3.5 kg mole calcium carbonate per 17.9 kg mole of iron; in that I divide 1000 by 56.

Then I can find out for 2 moles of iron - that is my equation which I have written earlier. For 2 moles of iron according to equation which I have written or according to stoichiometric equation written in terms of CO, CO 2, that will be equal to 0.392. What does it mean? That means this extra amount of CO 2 is coming into the picture which will not be available by the combustion of carbon; that is an important thing. Whereas, the reaction which we have written we have not taken this into account. Now say total number of CO 2 moles that will be how much? 3 moles, I have already written according to this equation. So, total moles will be 3 plus 0.392 and that will be 3.392 kg moles.

That point is important to remember because when you want to find out how much amount of theoretical coke that is combust or theoretical amount of coke that is required then the sources from where CO 2 is coming into the reaction - extra CO 2 must be deducted; that is the only thing.

Now, our ratio becomes CO upon CO 2 that is equal to x minus 3. It is very easy 3.392 and that is equal to 1.9 upon 1. From here, we can find out x that is equal to 9.4.

(Refer Slide Time: 25:29)



I can write down the reaction that is Fe 2 O 3 plus 9.4 CO plus 0.392 CO 2 that is equal to 2 iron plus 3.392 CO 2 plus 6.4 carbon monoxide.

Now it is straight forward. What do we see? 2 moles of iron because we have to calculate per 1000 kg product iron, but in the pig iron the iron is 930; remember that difference. I am calculating per 1000 kg of product iron. So, 2 moles of iron requires 9.4 moles of carbon monoxide and therefore, 17.9 moles of iron will be requiring 84 moles of say carbon. CO and C carbon are one and the same thing.

This 84 moles of carbon will be equal to 1008 kg carbon. You have to find out the total amount of coke that will be required. The problem says pig iron contains 4 percent carbon and 93 percent iron.

Carbon which is absorbed, remember by not 930 kg of iron, but 1000 kg of iron because our basis of calculation is 1000 kg of iron reduced. So, carbon absorbed by 1000 kg iron will be equal to 43 kg. We can calculate this. It is very simple. Carbon required will be sum total of 1008 plus 43 that will be equal to 1051 kg per 1000 kg of let us put it product iron or iron reduced. They are one and the same thing. That is how the theoretical amount of carbon can be calculated. About the coke, if you know the percentage of carbon in the coke accordingly one can find out the amount of coke that is required.

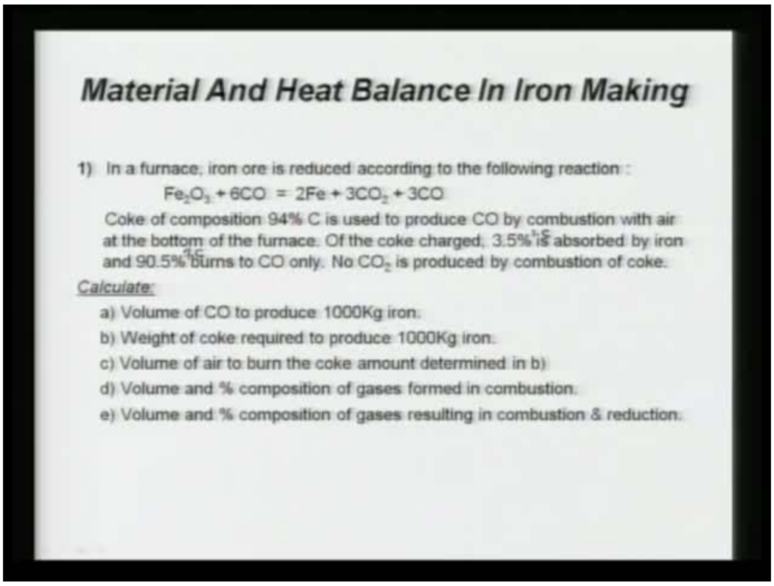
We can also find out from here air required per 1000 kg of product iron. that will be equal to 9.4 moles are required to produce 2 moles of iron and 9.4 moles of CO.

So oxygen would be half of 9.4 and also half of that because 2 moles of iron are involved. Think it over. That will be 9.4 2 into 2 into 1000 by 56, total moles of iron into 22.4, it is 1 kg mole of iron is 22.4 meter cube at 1 atmosphere and 273 Kelvin and divide by 0.21, that is the fraction of oxygen in the air.

So, that is equal to 4487 meter cube at 1 atmosphere and 273 Kelvin. This is how you will be calculating the theoretical coke requirement. In a given problem, one can also calculate when CO, CO 2 ratio is given. What I wanted to specify here is that once CO upon CO 2 ratio is specified then one can calculate how much amount of coke would be required and once we can calculate the amount of carbon then we can calculate the amount of blast also.

Now, let solve some of the problems. As I said, let us now solve some material and heat balance in iron making problems and let us see, whether you have understood the theoretical part or not.

(Refer Slide Time: 30:29)

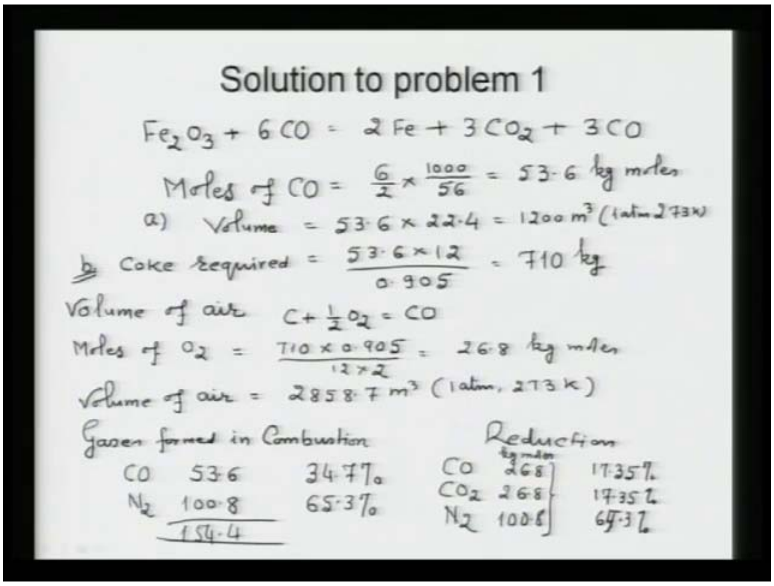


As such let us take the problem number 1. The problem number says the furnace iron ore is reduced according to the following reaction. Reaction is given to you Fe 2 O 3 plus 6 CO that is equal to 2 Fe plus 3 CO 2 plus 3 CO.

Coke of composition for 94 percent carbon is used to produce carbon monoxide by combustion with air at the bottom of the furnace. Of the coke charged 3.5 percent is absorbed by iron and 90.5 percent burns to carbon only.

Here, say of the coke charged, 3.5 percent of carbon is absorbed by iron and 90.5 percent of carbon burns to CO only; coke that means carbon burns. No CO 2 is produced by combustion of coke that means carbon combust to CO. One has to find out volume of CO to produce 1000 kg iron, weight of coke required to produce 1000 kg iron, volume of air to burn the coke amount determined in b, volume and percentage composition of gases form in combustion and volume and percentage composition of gases resulting in combustion and reduction. That means here combustion is also taking place as well as reduction of iron oxide is also taking place. So, let us find out both.

(Refer Slide Time: 31:57)



If we try to attempt this particular problem, I write down the reaction say Fe 2 O 3 plus 6 carbonmonoxide that is equal to 2 Fe plus 3 CO 2 plus 3 CO - that is the reaction is given to us.

Now we can straightaway calculate, say moles of carbon monoxide is equal to 6 by 2 into 1000 upon 56 that is equal to 53.6 kg moles.

The volume is equal to 53.6 into 22.4 and that is equal to 1200, this is meter cube mind you and this is at 1 atm and 273 Kelvin.

This is the answer for part a. Now part b, straightaway coke required would be 53.6 into 12 because C plus half O 2 is CO, divide by 0.905 and that is equal to 710 kg. That is the answer for b. We have to find out volume of air to burn the coke. The reaction which we will be choosing, because The problem says no CO 2 is forming. So, the reaction is C plus half O 2 that is equal to CO; that is the reaction which is there.

From here, we can calculate moles of oxygen; moles of O 2 required will be equal to 710 into 0.905 upon 12 - that will be equal to 26.8 kg moles.

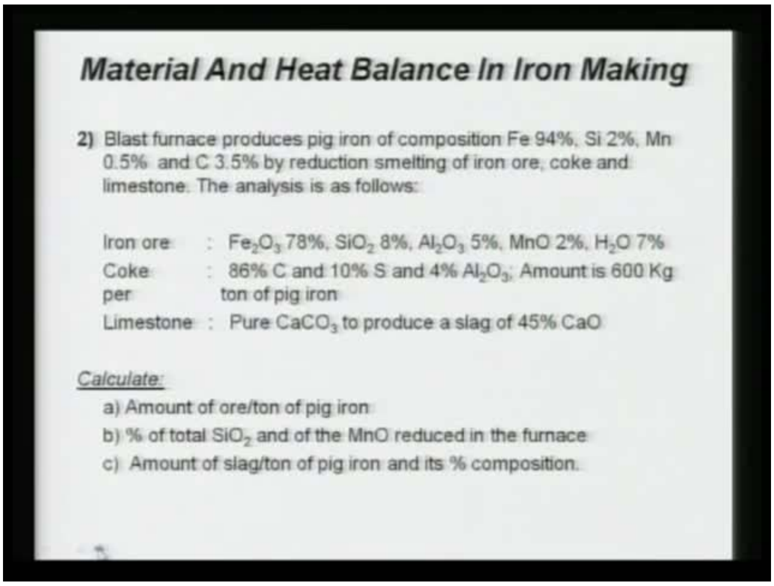
Of course, the moles of oxygen because if you follow this reaction C plus half O 2, CO then naturally you should divide by 2 also; that becomes 26.8 kg moles. Volume of air, I do not think I have to perform any calculation 26.8 divided by 0.21 into 22.4. Volume of air straightaway will be 2858.7 meter cube; here I have to mention 1 atmosphere and 273 Kelvin because I am using 1 kg mole is 22.4 meter cube.

Now the gases formed in combustion. This is in combustion. So, gases formed in combustion one can write carbon monoxide and another gas is nitrogen. Why nitrogen is coming? It is because air contains O 2 and N 2. So, CO is 53.56 kg moles and nitrogen is 100.8 and this total is 154.4 kg moles.

So, percentage we can calculate that will be 34.7 percent and it will be 65.3percent. Now during reduction, the gases formed that will be CO, CO 2 and nitrogen.

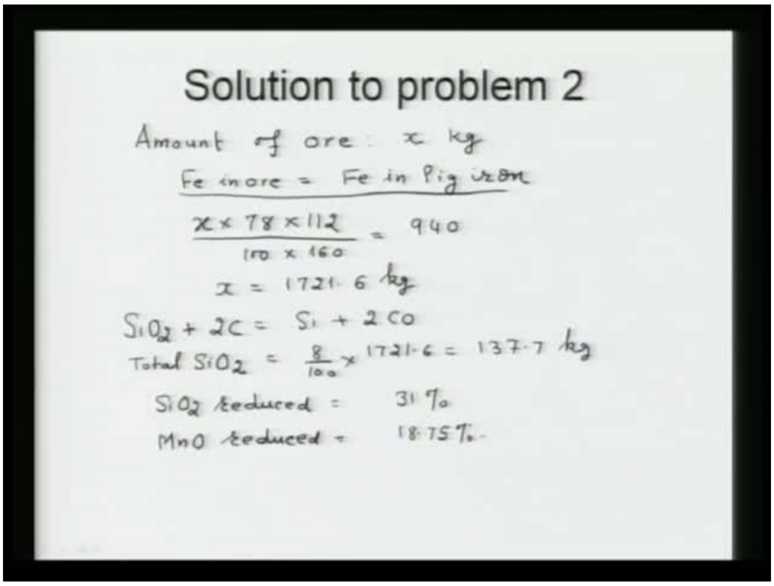
So, CO is 26.8 kg moles, CO 2 26.8 and nitrogen 100.8 because nitrogen is inert it does not take part in any reaction; so it does not matter. The percentage would be 17.35, 17.35 and this will remain 65.3 percent. They are all in percentage and these are all in kg moles. So, that is how the problem number 1 will be solved.

(Refer Slide Time: 37:57)



Let us see the problem number 2. The problem number 2 says that the blast furnace produces pig iron of composition iron 94, silicon this, manganese this, carbon this by reduction smelting of iron ore, coke and limestone. The analysis is as follows: iron ore analysis given as Fe 2 O 3, SiO 2, Al 2 O 3, MnO, H 2 O, coke 86 percent carbon, 10 percent sulphur and 4 percent Al 2 O 3. It is a baked quality coke because it contains very high amount of sulphur. However, it is a problem; so, we should not bother about it, but it is not a good quality coke. Amount is 600 kg per ton of pig iron. Limestone, pure calcium carbonate is used and it produces slag of 45 percent calcium oxide. Calculate amount of ore per ton of pig iron, percentage of total SiO 2 and of the MnO reduced in the furnace and amount of slag per ton of pig iron and its percentage composition. Let us go to the solution to problem number 2. What it says, first of all you have to find out amount of ore.

(Refer Slide Time: 39:00)

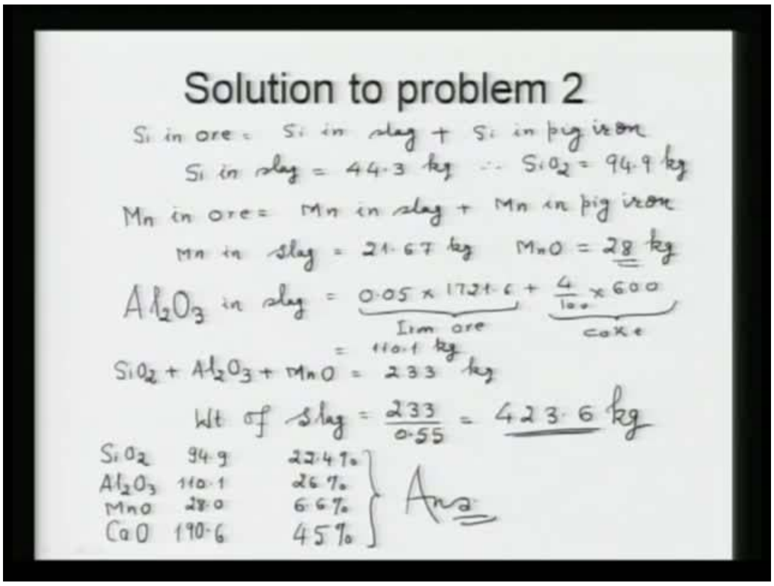


In order to find out amount of ore, you have to do iron balance because iron in this particular problem from the ore it goes to pig iron. We can make it iron in ore that is equal to iron in pig iron. This is a qualitative thing; you have to plug in the values.

If you plug the values and we will get, Suppose, if we take the amount of ore if you take let us take x kg then we have x into 78 into 112 upon 100 into 160 that is equal to 940 kg pig iron for 1 ton basis. So, amount of ore is straightaway x it comes to be equal to 1721.6 kg. What is important in order to find out amount of ore? You have to do iron balance.

In order to find out SiO 2 and MnO reduced, we have to take the reaction say SiO 2 plus 2 C that is equal to Si plus 2 CO. Total SiO 2 that is equal to 8 upon 100 into 1721.6 that is equal to 137.7 kg. We can find out SiO 2 reduced - that is whatever amount of silicon in the pig iron and silicon that you have charged. Whichever way you want to do it, convert to SiO 2. So, SiO 2reduced will be 31 percent. This calculation is easy and I think you can perform. Similarly, MnO reduced, again here you have to take into account manganese in pig iron that is what is reduced and total MnO that you are charging. It is again a simple calculation. If you do that, that will come to be equal to 18.75 percent. Then we have to calculate the amount of slag. For that what we do? We do, say silicon balance.

(Refer Slide Time: 41:51)



Silicon in ore is equal to silicon in slag plus silicon in pig iron. Again we have to plug in the values; from these values we will be getting silicon in slag that will be equal to 44.3 kg.

You can plug in the values, percentage everything is given. From here, the SiO 2 in slag will be 60 by 28 of 44.3 that will be 94.9 kg. Now, manganese in ore that is equal to manganese in slag plus manganese in pig iron.

Since we are given the composition of iron ore and we are given the composition of slag, we know how much amount of Mn we have charged and how much amount of Mn is entering into pig iron; the rest is entering into slag.

There are no other losses; everything is there. If we perform this particular calculation then we will be getting Mn in slag. You can simply plug in the values and you will get manganese in slag will be equal to 21.67 kg and from here, MnO will be equal to 28 kg.

This MnO, 28 kg will be in the slag. What do you think about Al 2 O 3? As I said, all Al 2 O 3 which you have charged will go to the slag; it is not reduced in the blast furnace. Please note, no reduction of Al 2 O 3 occurs. All Al 2 O 3 from all sources which is charged into the blast furnace, all of it enters into the slag. So, Al 2 O 3 in slag should be equal to 0.05 into 1721.6 plus 4 upon 100 into 600; this Al 2 O 3 is from iron ore and this Al 2 O 3 is from coke. If we sum total then this value is equal to 110.1 kg.

Now, we have SiO 2 plus Al 2 O 3 plus MnO, the total that is equal to 233 kg. That is what we have calculated - that is 110.1 plus 28 plus 94.9 that makes 233 kg comprising of SiO 2, Al 2 O 3 and MnO.

Now, the problem says that we are charging calcium carbonate to make a slag of 45 percent CaO. That means 55 percent of the slag consists of SiO 2, Al 2 O 3 and MnO because there is no iron losses given. If you read the problem very carefully in between the lines, you will find that the slag contains SiO 2, Al 2 O 3, MnO and CO and nothing else. So, 55 percent comprise of SiO 2, Al 2 O 3 and MnO.

Immediately, we can find out the weight of slag and that will be equal to 233 divide by 0.55 and that will be equal to 423.6 kg.

That is the amount of slag. We have to find out the composition of slag say SiO 2, Al 2 O 3, MnO and calcium oxide. So, SiO 2 is 94.9 kg, Al 2 O 3 110.1 kg, MnO is 28.0 kg and calcium oxide is 190.6 kg. So, the total is 423.6 kg. Percentage wise that will be 22.4 percent, Al 2 O 3 will be 26 percent, MnO will be 6.6 percent and calcium oxide as it is given 45 percent.

That is how we will be calculating the amount and percentage composition of the slag. Now, rest other problems we will take up in the next lecture.