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. # 13

Calcination Concepts and Exercises

Having done this mineral processing, that is the first step towards metal extraction either from pyro metallurgy of hydro metallurgical route. Now, we are in a position to go ahead with the various unit processes of metal extraction. Here, first I will deal with the pyro metallurgical and then I will touch upon hydro metallurgical extraction unit processes also.

Now in this, calcination is the first step and that is use for several purposes. So here I am giving you first of all the material and heat balance problem in calcination then, I will proceed with little bit amount of concept and then straight away I will enter into the solution of these problems.

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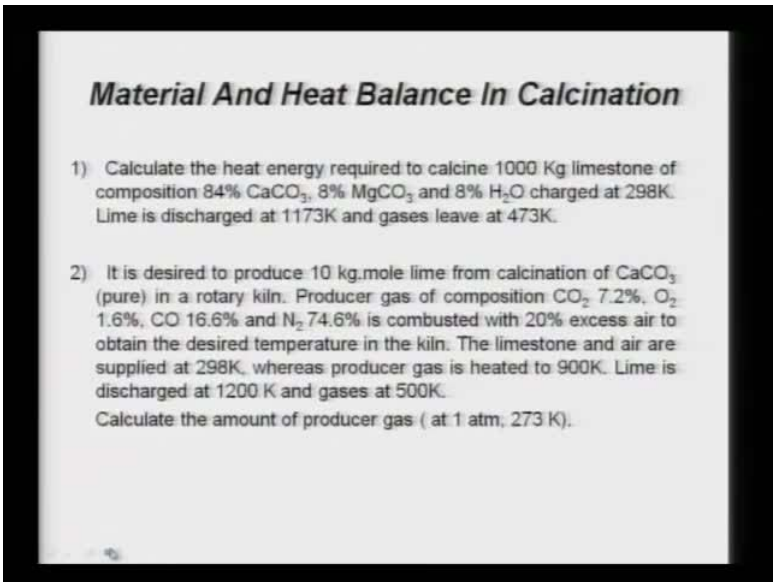

So, the first problem: calculate the heat energy required to calcine 1000 kilogram of limestone of composition, 84 percent of calcium carbonate, 8 percent Mg C O 3 and 8 percent H 2 O which is charged at 298 kelvin. Lime is discharged at 1173 kelvin and gases leave at 473 kelvin.

I mind you, this limestone is not yet used as such in various steel making processes or in non ferrous metal extraction process as you will see in the solution of the problem; that the decomposition of limestone is associated with a large amount of absorption of energy is highly endothermic reaction.

Therefore, use of lime requires that limestone should be calcine and therefore, this problem is included in order to appreciate the fact that charging of lime after calcination of lime stone is very important step that is the objective of this particular problem.

Second, it is desire to produce 10 kg mole lime from calcination of calcium carbonate, calcium carbonate is pure in a rotary kiln, while in the first problem it was only having 84 percent calcium carbonate; in the second it is 100 percent calcium carbonate.

Rotary kiln is very often used to produce lime from Calcination of limestone. Rotary kilns are very long kiln and rotate 2 to 3 degree from the axis of the horizontal axis of a one side, the feed enters and from other side, the calcine material discharges; around 24 meter long this kiln and they are frequently heated by an externals source of energy and they are use for example, oil or producer gas. So, this problem is concerned about that.

So, you see the producer gas of composition this CO_2, O_2, CO and nitrogen is combusted with 20 percent excess air to obtain the desire temperature in the kiln, because normally the temperature inside the kiln is very high and it may go of the order of 1400 or 1500 degree Celsius.

The limestone and air are supplied at 298 kelvin, where as the producer gas is heated to 900 kelvin, lime is discharged at 1200 kelvin and gases at 500 kelvin. Now, the fact that they are discharging at low temperature then, the kiln they are is occurring some sort of heat transfer before the product and the byproduct leave the rotary kiln, this is the problem number 2.

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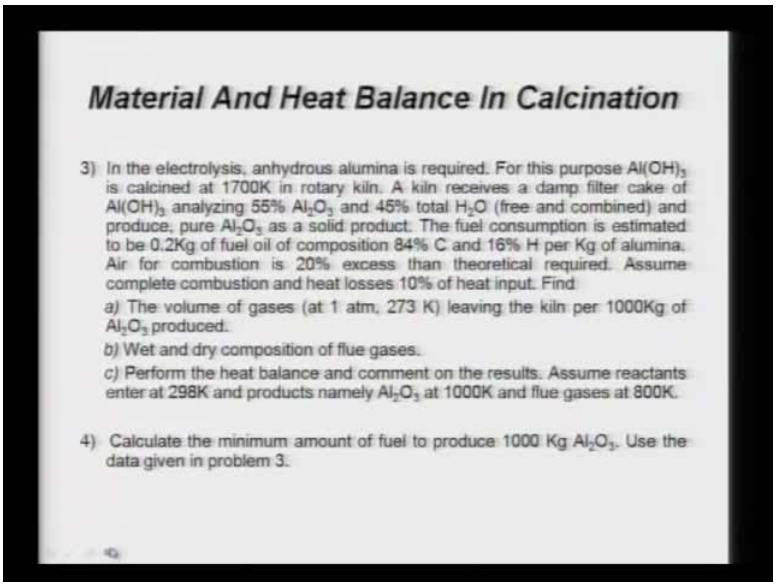

Problem number 3: In the electrolysis, anhydrous alumina is required. Now, the concept of anhydrous alumina is bauxite after leaching, it gives you it gives you hydrous alumina that is Al O H 3.

Now, as an electrolysis of Al O H 3 is not possible, because then only hydrogen will evolve. So for that, it is required that the Al 2 O 3 which is used for electrolysis to produce aluminum it should be anhydrous, since there should be no water into the Al 2 O 3 which you are going to charge in the all around cell.

So, in the electrolysis anhydrous alumina is required. Now, for your information in this anhydrous alumina, the water is most if chemically combined. So, it is not possible to remove the water just by heating by 100 or 200 degree centigrade; you have to go to 1200 or 1300 or even 1400 degree Celsius to remove the chemically combined water from the product which you obtain after the Bayer's process.

It is for this purpose, a large amount of energy is required to produce an anhydrous alumina, in order that alumina can be electrolyze to produce aluminum. For this purpose, Al O H 3 is calcine at 1700 kelvin in a rotary kiln. A kiln receives a damp filter cake of Al O H 3 analyzing this 55 percent Al 2 O 3 and 45 percent total H 2 O, free and combined of which the proportion of combined water is very high and produce pure Al 2 O 3 as a solid product.

The fuel consumption is estimated to be 0.2 kg of fuel oil of composition, 84 percent carbon and 16 percent hydrogen per kg of aluminum you see. There is also required a source of energy and therefore, the energy calculation is a very important step in all most all pyro metallurgical extraction.

Say, you are using around 0.2 kg, per kg alumina; that is around 200 kg for 1 ton of alumina, in order to have that anhydrous alumina. Assume complete combustion and heat loses, 10 percent of heat input, 20 percent excess air is use for combustion or you have to find out, volume of gasses wet and dry composition and perform the heat balance. Now, this is a very important step.

Fourth, calculate the minimum amount of fuel to produce thousand kg Al 2 O 3 use a data given in problem 3. Now, here the whole idea is to know, what is the minimum fuel? The minimum fuel is that fuel at which, the heat input becomes equal to heat output.

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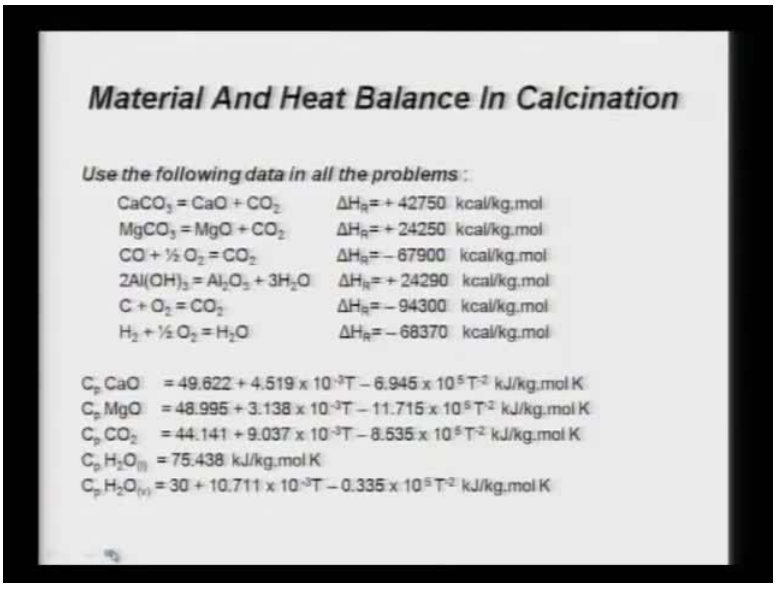

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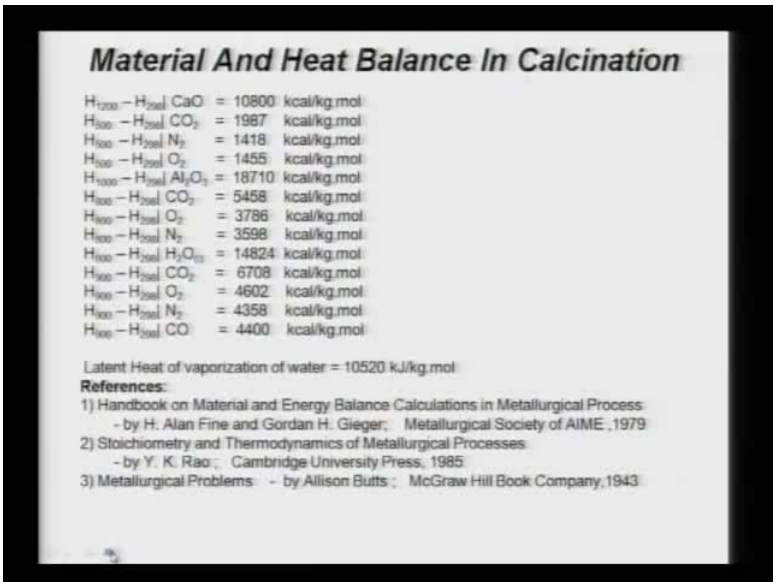

So, these are the problems that I have selected. Now, here some of the data you will be requiring to calculate the material heat; especially to calculate the heat balance. These are the data and these are the further data (Refer Slide Time: 07:18). Now here, what I have done? I have given you the heat content at the temperature at which the problem is there.

That means for example, calcium oxide is leaving at 1200 kelvin, so data are given according to that. However, I will request you that, please try to calculate by using the c p value of respective of calcium oxide of C O 2, N 2, O 2 or whatever the product which are being discharge, that will give you an additional practice. Whether you can calculate the heat content from c p value or not, this all requires a patience to see that you can do integration properly. However, this makes your life easier but, see that also with the by using the c p calculation.

Latent heat is also given and here I have given some of the references. As usual here I have given the solutions for these problems (Refer Slide Time: 08:13).

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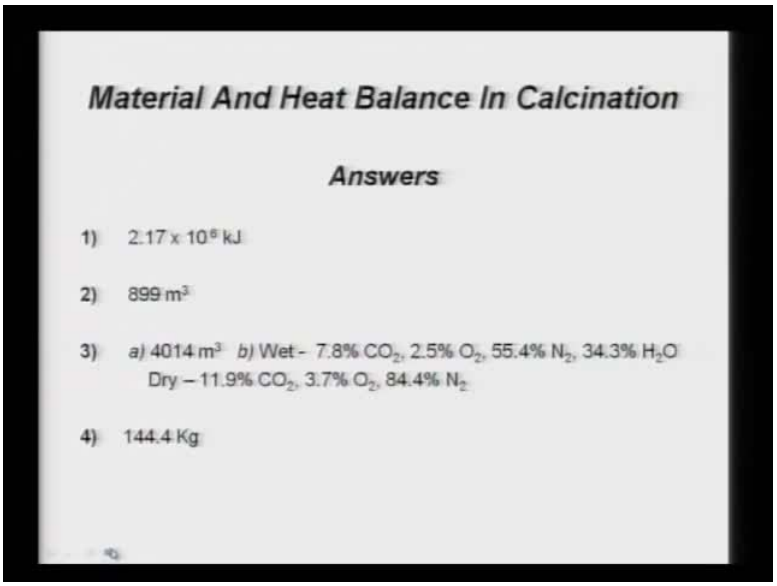

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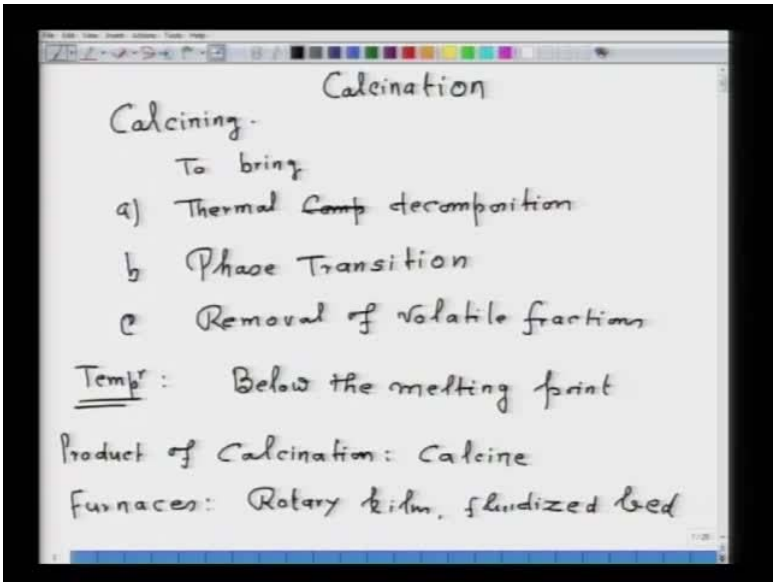

Now, let us go for the solution of these problems. First of all, let me tell you, what is calcination? In fact calcination, this also referred as a calcining, it is a thermal treatment process apply to ores and other solid materials; why, in order to bring thermal composition or thermal decomposition, because you want to decompose. For example, calcium carbonate to calcium oxide or C O 2 or Mg O C O 3 and so on. Second possibility could be phase transition, third removal of volatile fractions; these are some of the objectives of calcination however, you include more.

Now, the temperature involved say, below the melting point of the components of the raw material. That means you treat them in the solid state; so product is also solid. However, if the volatile components like C O 2 or H 2 O they will be leaving the system.

Product of calcination is sometimes called calcine, now the furnaces which are used they are called rotary kiln. Very commonly rotary kiln is employed for production of cement.

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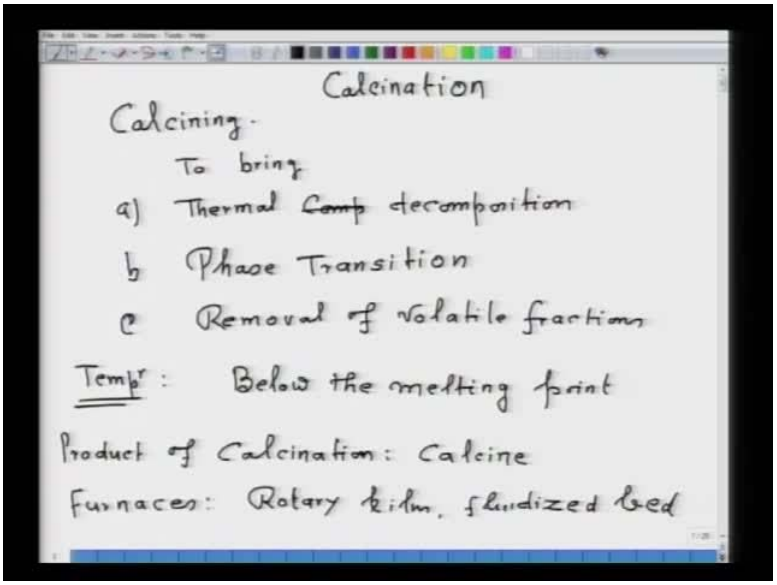

Cement industry rotary kiln is a very big application, also calcination of limestone, also the removal of water from alumina and so on. Then fluidized bed reactors, multiple hearth furnaces and the fuel or fuel, let another you can put source of energy.

Source of energy, in some case it is the fossil fuel that is could be oil natural gas or there could be secondary fuel which are derived from fossil fuel and normally sometimes producer gas is used, as you have seen in the problem.

Oil, natural gas all are the sources of energy; so it is also energy consuming unit process. Some of the applications of calcination: one particular application is to produce cement - now here the calcination is one of the important steps, where you get calcium oxide and that is further mix to produce cement. So, in cement industry the decomposition of limestone is a very important in your process.

Second application is decomposition of hydrated minerals. Now, this decomposition is done for one purpose could be we want to make say Al 2 O 3 refractory.

Here, bauxite is the material to produce Al 2 O 3 refractory. Now, bauxite also contains the water which is chemically combined, so straight away you have to calcinate in order to produce an alumina, which is free from water and mind you, alumina is very important effective material in all pyro metallurgical extraction industries.

One of the purposes could be produce alumina refractory and another purpose could be to produce alumina for electrolysis. As all of you know, because that Al 2 O 3 should be anhydrous in the sense of anhydrous otherwise, there is evolution of hydrogen and you will be consuming a large amount of electrical energy to produce aluminum if you do not remove water from alumina.

Third application could be decomposition of volatile matter, which is contained in petroleum ore. Another application could be heat treatment to effect phase transformation; however in a strict sense, you do not call it to be calcination but, since you are applying the heat below the melting point of the material.

You may class each under as a calcination heat treatment and you may not class, it does not matter but, all that you require a solid state transformation from room temperature to another temperature. These are the certain applications of the calcination. Now, having given those things, let us straight away go to the problem to the solution of problem number 1.

Now problem number 1, we have to calculate the heat energy to calculate 1000 kg limestone and composition everything is given to us.

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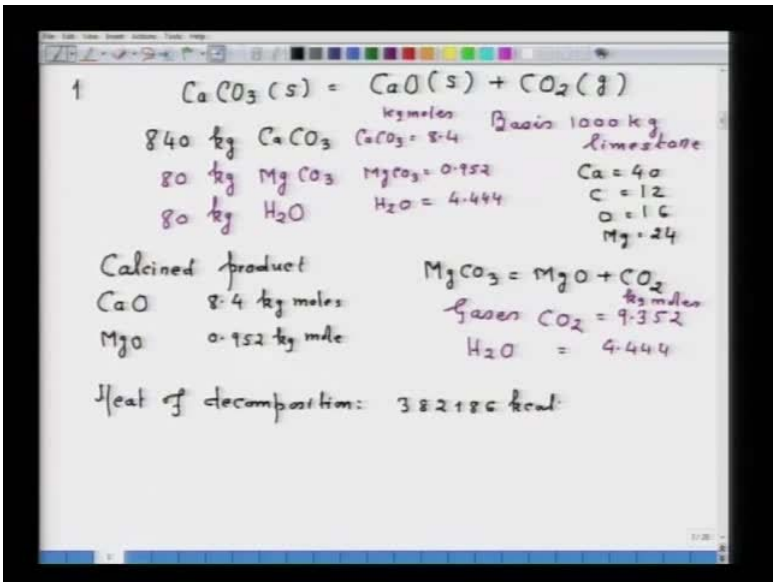

So, the reaction that takes place is C a C O 3 - solid that is equal to C a O - solid plus C O 2 - gas, this is the reaction or this is the decomposition reaction. Now, we have 840 kg C a C O 3, we are taking say 1000 kg limestone as the basis. The basis is as already being given in the problem 1000 kg limestone, 840 kg C a C O 3, 80 kg Mg C O 3 and 80 kg water, so this are given to us.

We can straight away calculate the calcined product. Now before that, what I have used? I have use atomic weight of calcium as 40, carbon as 12, oxygen as 16 and magnesium as 24. So, from here I will be getting say, kg moles of calcium carbonate that will be equal to straight away 8.4, kg moles of Mg C O 3 that will be equal to 0.952, and kg moles of water that will be equal to 4.444.

Once you know this, now the calcine product immediately we can write down, say calcium oxide and magnesium oxide. So calcium oxide straightaway 1 kg mole 1 kg mole and 1 kg mole C a O will be 8.4 kg moles, Mg O will be 0.952 kg moles. Similarly the reaction for Mg C O 3 will be Mg O plus C O 2, solve. We have the calcine product, now the gases that will form because the gases will also form, so we have to know the gases.

Gases that will be forming the C O 2, C O 2 is coming because of the decomposition and the sources of C O 2 is C a C O 3 and Mg C O 3, so you have to add both of them and H 2 O these are the two forces.

H 2 O is coming from the limestone composition of gases, C O 2 that will be equal to 9. 352 kg moles and H 2 O that will be equal to 4.444 they are in kg moles. Now, we have to calculate heat energy, so we have to calculate now heat of decomposition. The values I have given, I will straight away write down the heat of decomposition that will be equal to 382186 kilo Calorie; that is the heat of the composition.

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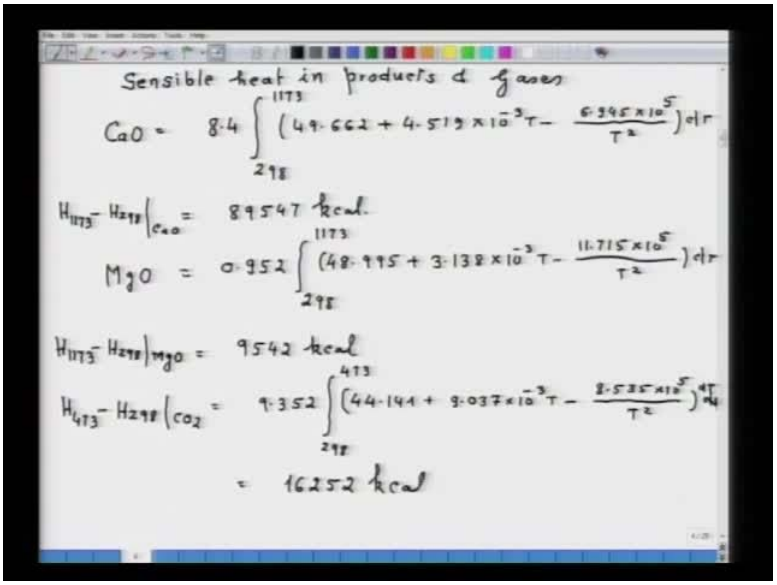

Then I have to find out now, sensible heat in products and gases that is all, that is what I have to find out and for that and if I sum total of all these, that is what the energy I require, if I want to decompose calcium carbonate.

So sensible heat for example, in C O that will be equal to 8.4 kg moles, integrate it from 298 to 1173 kelvin, 49.662 plus 4.519 into 10 to the power minus 3, T minus 6.945 into 10 to the power 5, for T square this I have to integrate to dt.

Now, please do this exercise, however if you try you can get those values also in the reference which I have given but, then they are intermediate temperature where you will not find the value, so it is better to develop the practice of integration.

So if you do that, then the calcium oxide will be equal to, the content in calcium oxide 89547 that is kilo calorie; this is the heat content or I might have written H 1173 minus H 298 in calcium oxide that is what well.

Similarly, I can find out for Mg O that will be equal to now 0.952, again I have to integrate from 298 to 1173, 48.995 plus 3.138 into 10 to the power minus 3, T minus 11.715 into 10 to the power 5, T square integrated d t. So I get now, H 1173 minus H 298 for Mg O that will be equal to 9542 kilo calorie.

Then I have to calculate, now the gases are discharging at 473 kelvin; so I write H 473 minus H 298, for C O 2 - the moles C O 2 are 9.352, I have to write it c p value 298 to 473, 44.141 plus 9.037 into 10 to the power minus 3 T, minus 8.535 into 10 to the power 5 upon T square, integrate to dt. So that will be dt here, this value is coming 16252 kilo calorie.

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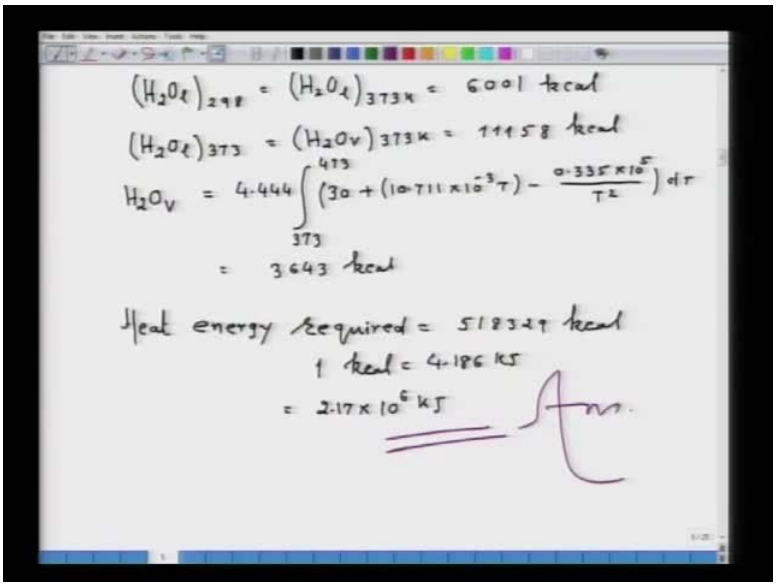

Be careful while calculating the heat content in water vapor, so we are starting 298 is our basis. First, we will calculate H 2 O - liquid 298 that is equal to H 2 O - liquid 373 kelvin and this value is 6001 kilo calorie. Do not forget to it; let us in theta by operation. So, another state is H 2 O - liquid 373 kelvin that will be equal to H 2 O vapor at 373 kelvin, all of you know at the latent heat temperature change does not occur; so this value is 11158 kilo calorie.

Now, I have to heat the H 2 O - vapor 4.444 that will go from 373 because 100 kelvin already has been taken into account to 473, 30 plus 10.711 into 10 to the power minus 3, T minus 0.335 into 10 to the power 5 upon T squared dt and this value is 3643 kilo calorie.

The heat energy required as asked in the problem, I think by now all of you can guess you have to sum total all the energies, because the heat of decomposition that is also endothermic reaction. So, there will be large amount heat absorption plus all the heat carried out. All that heat if you do not supply, the decomposition of calcium carbonate will not occur.

So all that you have to add and the addition brings 518329 kilo calorie, now I have used 1 kilo calorie, that is equal to 4.186 kilo joule and that gives me the 2.17 into 10 to the power 6 kilo joule and that is the answer for problem number one.

That is the way, you will be proceeding to solve. My appeal to you again that, please solve these problems on your own without seeing the solution, because if you look to the solution you will be carried away by my way in which I have done. I would like you to develop your own ways and see that you come off with the innovative ways. I am sure that there will be definitely alternative way to solve the problem and who knows that your way or your way of solution may be much better than what I have done, so please do yourself that is an important thing.

Now, second problem: in a second problem, you have to produce 10 kg mole of lime and so on. So, what we have to do? We have to calculate the amount of producer gas. First thing, how will you calculate the amount of producer gas? Because producer gas amount is being asked, so the only way to calculate the amount of producer gas is do the heat balance.

If you do the heat balance because all the energies coming from the combustion of producer gas; so if you do heat input and make it equal to heat output, now only variable in your equation would be the amount of producer gas and you can solve that way.

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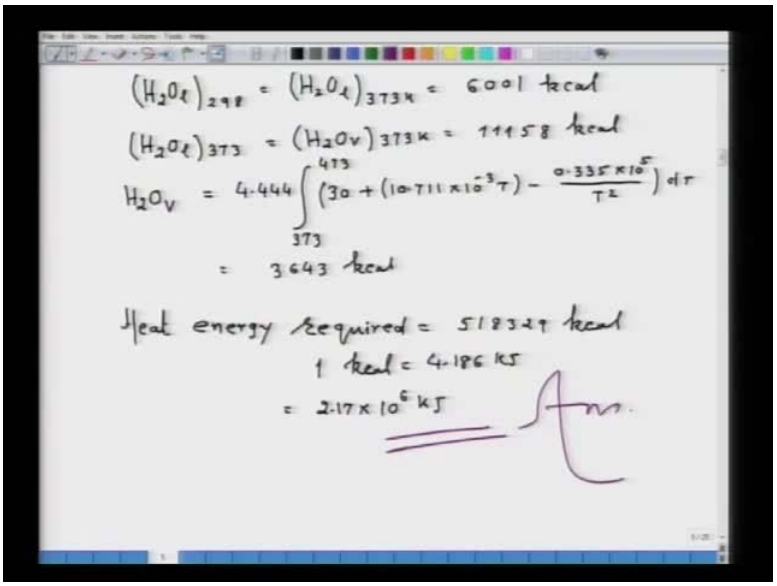

So, heat balance is the key to solve problem number 2 and now I will just make a box for you so that I mean, I will find it very convenient when I make a box and try to put all the values over here. It is not necessary that you also do in the same way. So what I will do, what we are doing? Say 10 kg mole of calcium carbonate they are entering at 298 kelvin right.

It is fired with producer gas and producer gas is entering at 900 kelvin. Mind you, the producer gas bring sensible heat into the furnace remember, so the composition of producer gas is given; C O 2, it has oxygen, it has carbon monoxide, it has nitrogen. Now C O 2 is 7.2 percent, oxygen 1.6 percent, carbon monoxide 16.6 percent, and nitrogen is 74.6 percent.

Now problem say further, that air is 20 percent excess; that means you have use 120 percent theoretical air and the supply temperature of air is 298 kelvin, that is what is given. On the output side, here lime which is 10 kg mole and say lime is discharge at a temperature of 1200 kelvin and the gases, they discharge at 500 kelvin. The gases would contain, as you can see in the problem it will contain, C O 2; now since excess air is used, it will also contain excess oxygen and since air is used, it will also contain nitrogen.

In this situation, you have to find out the amount of producer gas; all that you have to do the heat balance. Here I like to tell you that, this is again, first of all you have to make the material balance of this combustion.

For your information, I have also made one video course on fuel furnace and refractory and there, very detail calculations from combustion in different lectures are given. The problems are also given to illustrate, how to calculate. So, if you find any difficulty in calculating the amount of air which is required for the combustion, I will request you to see those video lectures on fuel furnace and technology they are also available. So, please for the details you can see those lectures on combustion and you may get feel how to calculate. I have also solved several problems over there. So coming back to this problem, let us see that Y kg mole is required for the required producer gas.

Now, first of all we have to calculate the calorific value of producer gas. The illustration of calorific value also, I have given in the earlier ports on fuel furnace and refractory. So in fact, in case of combustion the gaseous fuel, combustion the C O, hydrogen and hydro carbon they are the combustible component. C O 2, N 2 they are the diluents and they do not take part in the combustion, so mind you that is an important thing.

So, the calorific value of producer gas that will consists of only when C O is completely combusted to C O 2. So, the definition of calorific value is the amount of heat energy released when 1 kg or 1 meter cube of gas or solid fuel is burnt completely, the products of combustion is complete that is an important thing for the detail you can see I already referred the video lecture on fuel furnace and refractory.

So, the calorific value of producer gas would be equal to 11271 kilo calorie into Y because, Y is the amount of kg mole of the producer gas; that you have taken for combustion purposes.

Now straightaway, I can take the material balance. Now, if I do the material balance then amount of C O 2 that will be equal to 10 plus 0.238 Y. 10 is coming from 10 kg mole calcium carbonate will also give you 10 kg mole of carbon dioxide. Nitrogen: all the nitrogen of producer gas will be available in the gases or the output that plus the amount of air or nitrogen, of the air. So that will be equal to 0.746 Y plus 0.302 Y.

Then the excess oxygen- Now remember here, producer gas also contains oxygen. So while calculating amount of oxygen that is coming from air you have to separate the amount of oxygen that is already available in the system. So, that will be equal to 0.0134 Y.

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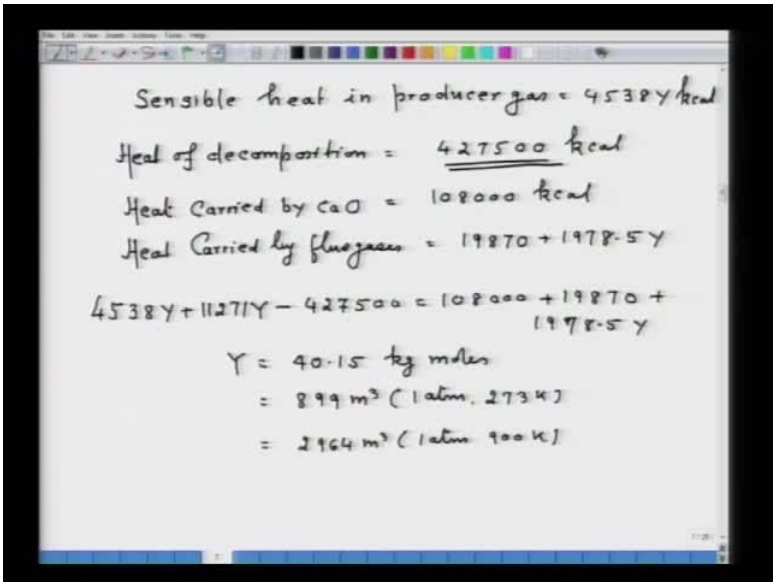

So, once you have done material balance. Now you have to do the heat input and heat output; heat input one is the sensible heat. Heat of decomposition though it is in endothermic but, it is also as a heat input. So, I will straightaway write down the values, so sensible heat in producer gas that is equal to 4538 Y kilo calorie, sensible heat in air is 0 because, air is supplied at 298 kelvin, so I am not writing.

Now, heat of decomposition of calcium carbonate, you have to calculate from the value C a C O 3, C a O plus C O 2 product minus reaction and so on that already I have illustrated in my thermo chemistry lecture. So, that will be equal to 427500 kilo calorie, mind you this is an endothermic reaction, this not exothermic.

Heat carried or taken by calcium oxide, because it is discharge at 1200 kelvin that is equal to 108000 kilo calorie. Now, heat carried by flue gases that will be equal to 19870 plus 1978.5 Y.

Now, all that you have to do the heat balance. Now, the heat balance would be say 4538 Y plus 11271 Y minus 427500 that is equal to 108000 plus 19870 plus 1978.5 Y.

So I can calculate now Y that will be equal to 40.15 kg moles and that will be equal to 899 meter cube express at 1 atmosphere and 273 kelvin. So that is equal to 2964 meter cube at 1 atmosphere and 900 kelvin, so this is all about problem number 2.

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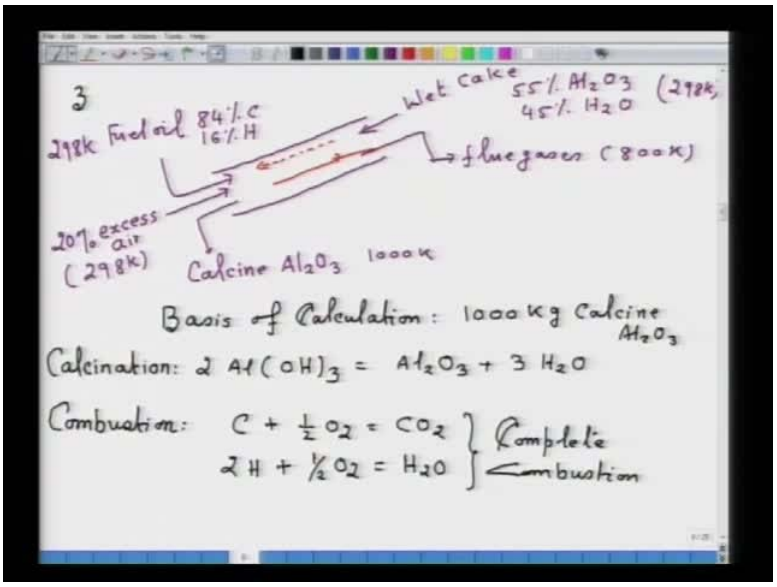

Now, let us quickly go through problem number 3. In problem number 3, we have a rotary kiln; this is a rotary kiln. Now in the rotary kiln, the flow is counter current. So here, wet cake which contains 55 percent Al 2 O 3, 45 percent H 2 O. Now, this H 2 O is mind you is chemically combined and it enters a 298 kelvin, I always prefer to write all the details of the problem on this material balance figure.

Now the flue gases, they leave at 800 kelvin. Now here, the fuel oil is supplied for combustion. So, fuel oil which contains 84 percent carbon and 16 percent hydrogen is supplied a 298 kelvin.

Here, then supply 20 excess air or you can also call 120 percent theoretical air this is also supplied at 298 kelvin, when? You have calcine alumina which is at 1000 kelvin, so that is what is given to us.

Now as usual, we have to perform the heat balance. Well first off all, you have to do the material balance without that you can do nothing. So, I will just proceed to solution. Now here well. Let me tell another thing here; the wet cake, it goes in this direction

which is the direction of flow of wet cake and this is the direction of flow of flue gases that is how the flue gases are leaving (Refer Slide Time: 42:34).

So, they are in the counter current mode. So, the basis of calculation is 1000 kg calcine Al 2 O 3. Now, amount of fuel oil is 200 kg is already given. The various calcination reactions is 2 Al O H 3 that is equal to Al 2 O 3 plus 3 H 2 O, this is the calcination reaction. Then, we have combustion reaction is C plus half O 2 that is equal to C O 2.

Now remember, if nothing is given then always assume there is a complete combustion and the product of complete combustion are very clear carbon is C O 2, H is H 2 O. 2 H plus half O 2 that is equal to H 2 O. So, we have assumed complete combustion.

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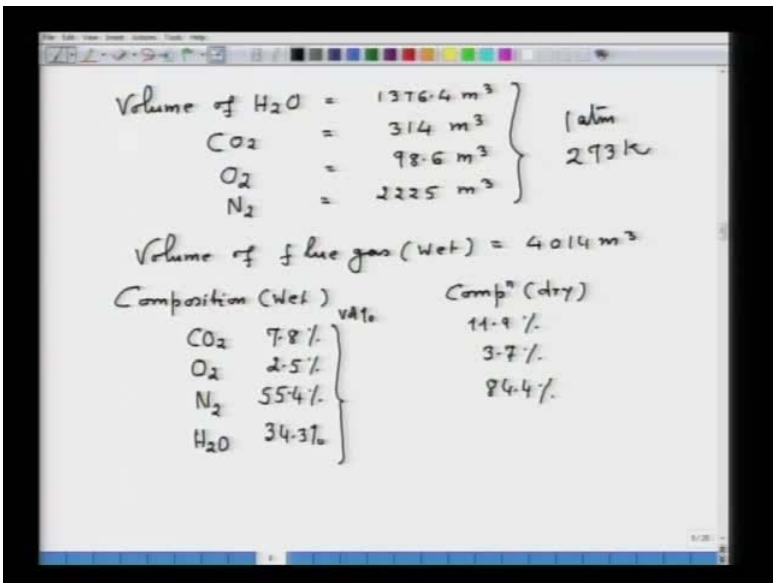

So, let us now calculate volume of H 2 O in flue gas that will comprise of volume of hydrogen that is combustible to H 2 O plus the water which is removed from the cake, so that will be equal to 1376.4 meter cube.

Similarly, we have C O 2 in the flue gas that will be 314 meter cube. Then, since we are using 20 percent excess oxygen, so there will also be excess oxygen; so excess oxygen in the flue gas that will be equal to 98.6 meter cube, Nitrogen in the flue gas that will be equal to 2225 meter cube.

Now, I tell you once again over here that it is at most important, that you should be very thorough in doing material balance because, without material balance we cannot heat

balance at all. If you have any problem you have done while doing the material balance that this problem will be carried over till the end of the heat balance because, you have to multiply all the values of the amount with the heat that has been produce. So, if you do a mistake in material balance and if you get the solution say after having ten fourteen steps then all steps will be wrong. So it is a transferred error, so you have to very careful while doing material balance problem that is very important.

So here, we have to calculate volume of flue gas. So, immediately we can calculate volume of flue gas, you have to calculate wet and dry; so wet volume is 4014 meter cube. Now, you have to calculate composition - the composition wet basis and you have to also calculate composition on dry basis, so we have C O 2; we have O 2; we have nitrogen and we have H 2 O.

So, if you do this calculation is I have already given in the answer 7.8 percent, 2.5 percent 55.4 percent and 34.3 percent. Now these volumes are all on volume percent. Dry that will be 11.9 percent, 3.7 percent and 84.4 percent. Mind you, all these volumes they are express at 1 atmosphere and 273 kelvin because I have taken 1 kg mole is 22.4 meter cube, so that is what this calculation of the composition.

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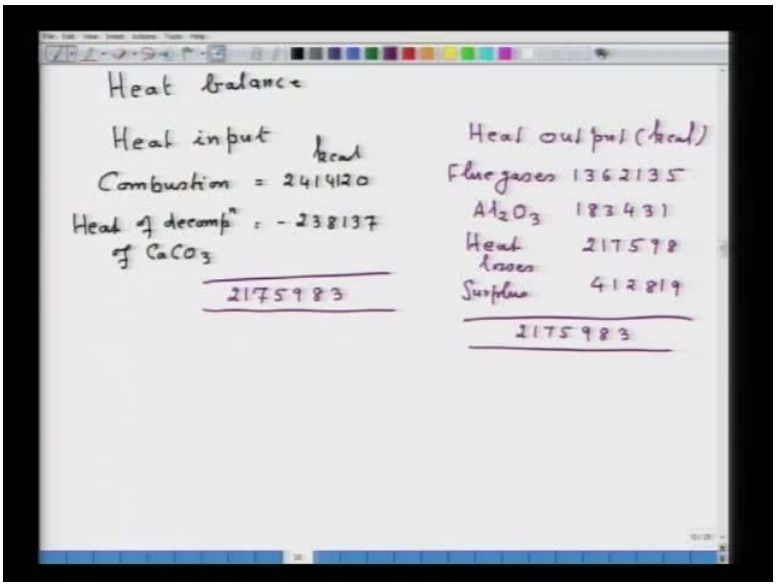

So heat balance you have to do it; heat input one will be by combustion. So you have to calculate C plus O 2 C O 2 and H 2 plus half O 2 H 2 O. So, this heat input by combustion that will be equal to 2414120 kilo calorie.

Then, heat of decomposition of calcium carbonate because this is an endothermic. If I do combustion as positive then, this will be equal to negative 238137, this is the heat input.

Now, heat output will also be in kilo calorie. Flue gases that will be equal to 1362135 then Al 2 O 3 it is being discharged at 1000 kelvin it will be 183431 then heat losses are given as 10 percent of the input. So here, the input will be 2175983, so heat losses will be 10 percent of that 217598. Then, we will be having surplus that will be 412819, so if the sum total all, it will again be equal to 2175983.

So, that is how you will be doing the heat balance for the problem number 3. Now, quickly illustrate the problem number 4. Now in problem number 4, all that you have to find out the minimum amount of fuel for calcination in problem number 3.

As I noted in problem number 3, that there is an excess amount of heat and all the amount of heat is coming from combustion of fuel. So that means, the minimum amount of fuel will that fuel at which the heat input becomes equal to heat output and that value will be your amount of fuel that is required. So, again you have to do the heat balance.

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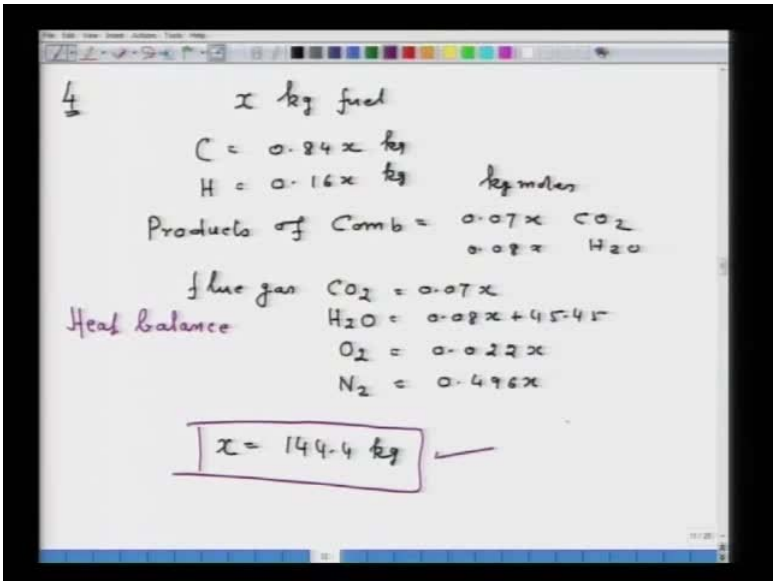

If I say, if you have x kg fuel, from here you have start that is unknown, so x kg fuel your carbon will be 0.84 x hydrogen will 0.16 x. So, the products of combustion that will be equal to 0.07 x that is C O 2 and 0.08 x H 2 O mind you, they are in kg moles. This is in kg (Refer Slide Time: 52:05).

So, once you know the products of combustion, then you have to calculate the amount of flue gas; so flue gas composition C O 2 that is equal to 0.07 x H 2 O 0.08 x plus 45.45. Oxygen 0.022 x and nitrogen that is equal to 0.496 x. Now, one have to do the again heat balance; heat input heat output, so this heat input and heat output I have already done in problem number 3. So, if you balance both then, the only unknown will be x and this x will come out to be equal 144.4 kg. Now prior to that, you have to perform heat balance and in heat balance you will be including the term like heat of decomposition, heat taken by flue gas; now heat taken by flue gas will be in terms of x.

Then heat taken by Al 2 O 3 if you do all that and you do the balancing then the answer will be 144.4 kg and that is what about the calcinaion.