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

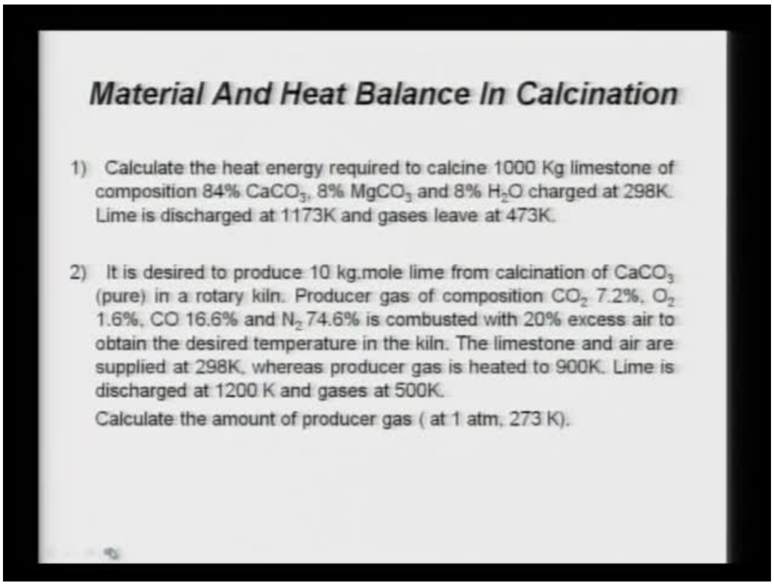
Lecture No. # 23

Reduction Smelting

Having done Mineral Processing which is the first step towards metal extraction, either from pyro metallurgy or 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 extraction. Then I will touch upon hydrometallurgical extraction unit processes. In this, calcination is the first step and that is used for several purposes. So, first of all, I am giving you the material and heat balance problem in calcination. Then, I will proceed with a little bit of concept and then straightaway I will enter into the solution of these problems.

(Refer Slide Time: 01:14)



Material And Heat Balance In Calcination

1) Calculate the heat energy required to calcine 1000 Kg limestone of composition 84% $CaCO_3$, 8% $MgCO_3$ and 8% H_2O charged at 298K. Lime is discharged at 1173K and gases leave at 473K.

2) It is desired to produce 10 kg.mole lime from calcination of $CaCO_3$ (pure) in a rotary kiln. Producer gas of composition CO_2 7.2%, O_2 1.6%, CO 16.6% and N_2 74.6% is combusted with 20% excess air to obtain the desired temperature in the kiln. The limestone and air are supplied at 298K, whereas producer gas is heated to 900K. Lime is discharged at 1200 K and gases at 500K.
Calculate the amount of producer gas (at 1 atm, 273 K).

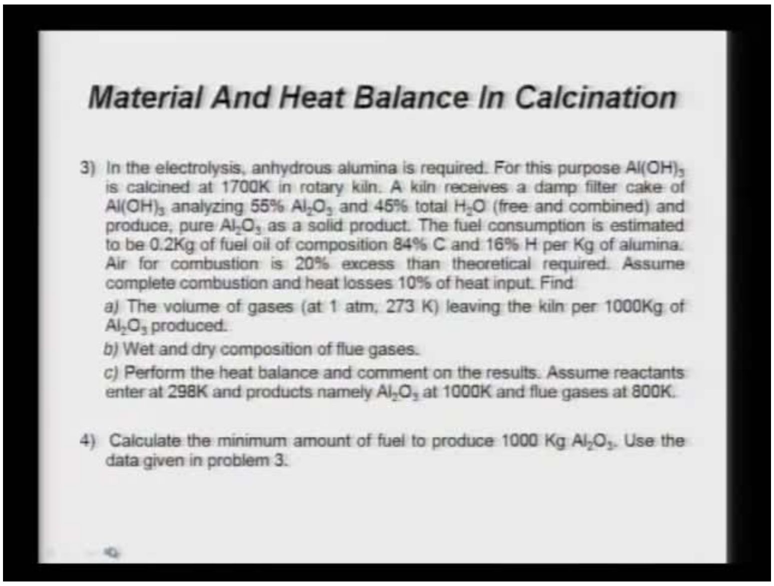
The first problem: Calculate the heat energy required to calcine 1000 kilogram limestone of composition 84 percent Calcium Carbonate, 8 percent Mg CO 3, and 8 percent H 2 O which is charged at 298 kelvin. Lime is discharged at 1173 kelvin and gases leave at 473 Kelvin.

This limestone is not used as such in various steel making processes or in non-ferrous metal extraction processes. As you will see in the solution of the problem - the decomposition of limestone is associated with a large amount of adsorption of energy; it is highly an endothermic reaction. Therefore, use of lime requires that limestone should be calcine and therefore, this problem is included in order to appreciate you, the fact that charging of lime after calcination of limestone is very important step; that is the objective of this particular problem.

Second - it is desired to produce 10 kg mole lime from calcination of Calcium Carbonate. Calcium Carbonate is pure in a rotary kiln; in the first problem - it was only having 84 percent Calcium Carbonate, and 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 they rotate 2 to 3 degree from the horizontal axis. From one side, the feed enters and from other side, the Calcine material discharges. These kilns are around 20 to 24 meter long and they are frequently heated by external source of energy and they are used - for example, oil or producer gas. So, this problem is concerned about that.

You see that producer gas of composition CO 2, O 2, CO and Nitrogen is combusted with 20 percent excess air to obtain the desired temperature in the kiln because normally, the temperature inside the kiln is very high and it may go of the order of 1400 to 1500 degree Celsius. The limestone and air are supplied at 298 Kelvin, whereas 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 lower temperature than the kiln means that there is some sort of heat transfer occurring before the product and the byproduct leave the rotary kiln. This is problem number 2.

(Refer Slide Time: 04:02)



Material And Heat Balance In Calcination

3) In the electrolysis, anhydrous alumina is required. For this purpose $Al(OH)_3$ is calcined at 1700K in rotary kiln. A kiln receives a damp filter cake of $Al(OH)_3$ analyzing 55% Al_2O_3 and 45% total H_2O (free and combined) and produce, pure Al_2O_3 as a solid product. The fuel consumption is estimated to be 0.2Kg of fuel oil of composition 84% C and 16% H per Kg of alumina. Air for combustion is 20% excess than theoretical required. Assume complete combustion and heat losses 10% of heat input. Find

a) The volume of gases (at 1 atm, 273 K) leaving the kiln per 1000Kg of Al_2O_3 produced.

b) Wet and dry composition of flue gases.

c) Perform the heat balance and comment on the results. Assume reactants enter at 298K and products namely Al_2O_3 at 1000K and flue gases at 800K.

4) Calculate the minimum amount of fuel to produce 1000 Kg Al_2O_3. Use the data given in problem 3.

Problem number 3: In the electrolysis, anhydrous alumina is required. Now, the concept of anhydrous alumina is that Bauxite after leaching gives you hydrous alumina that is AlOH 3.

Now, as such, electrolysis of AlOH 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, should be anhydrous; in the sense, there should be no water in the Al 2 O 3, which you are going to charge in the Hall-Héroult cell. So, in electrolysis, anhydrous alumina is required. Now, for your information, in anhydrous alumina, the water is mostly chemically combined. It is not possible to remove the water just by heating to 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.

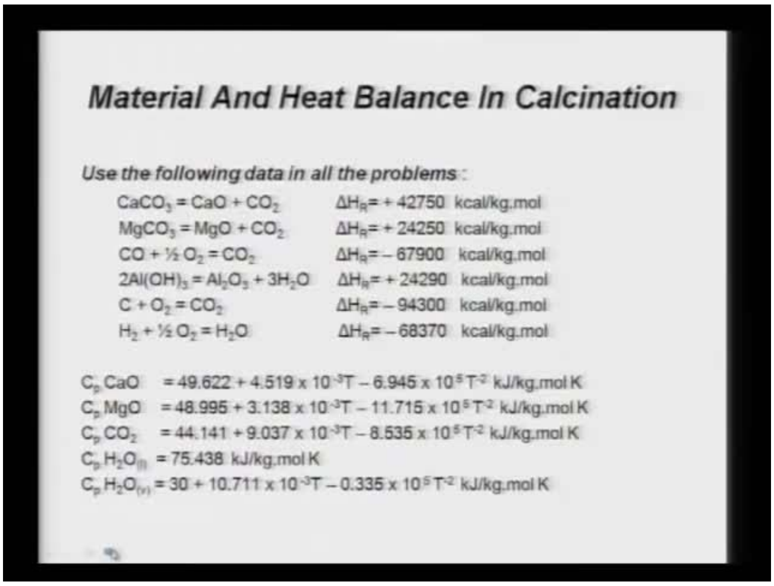
So, for this purpose, a large amount of energy is required to produce anhydrous alumina in order that alumina can be electrolyzed to produce Aluminum. For this purpose AlOH 3 is calcined at 1700 Kelvin in a rotary kiln. A kiln receives a damp filter cake of AlOH 3 analyzing 55 percent Al 2 O 3 and 45 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. See, it is also required, a source of energy and therefore, the energy calculation is a very important step in almost all pyro metallurgical extraction. So, 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 losses; 10 percent of heat input; 20 percent excess air is used for combustion. Now, you have to find out volume of gases, 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 1000 kg Al 2 O 3. Use the data given in problem 3. Here, the whole idea is to know what the minimum fuel is. The minimum fuel is that fuel at which the heat input becomes equal to heat output. So, these are the problems that I have selected.

(Refer Slide Time: 07:02)



Material And Heat Balance In Calcination

Use the following data in all the problems :

$CaCO_3 = CaO + CO_2$ $\Delta H_R = +42750$ kcal/kg.mol

$MgCO_3 = MgO + CO_2$ $\Delta H_R = +24250$ kcal/kg.mol

$CO + \frac{1}{2} O_2 = CO_2$ $\Delta H_R = -67900$ kcal/kg.mol

$2Al(OH)_3 = Al_2O_3 + 3H_2O$ $\Delta H_R = +24290$ kcal/kg.mol

$C + O_2 = CO_2$ $\Delta H_R = -94300$ kcal/kg.mol

$H_2 + \frac{1}{2} O_2 = H_2O$ $\Delta H_R = -68370$ kcal/kg.mol

$C_p\ CaO = 49.622 + 4.519 \times 10^{-3}T - 6.945 \times 10^{5}T^{-2}$ kJ/kg.mol K

$C_p\ MgO = 48.995 + 3.138 \times 10^{-3}T - 11.715 \times 10^{5}T^{-2}$ kJ/kg.mol K

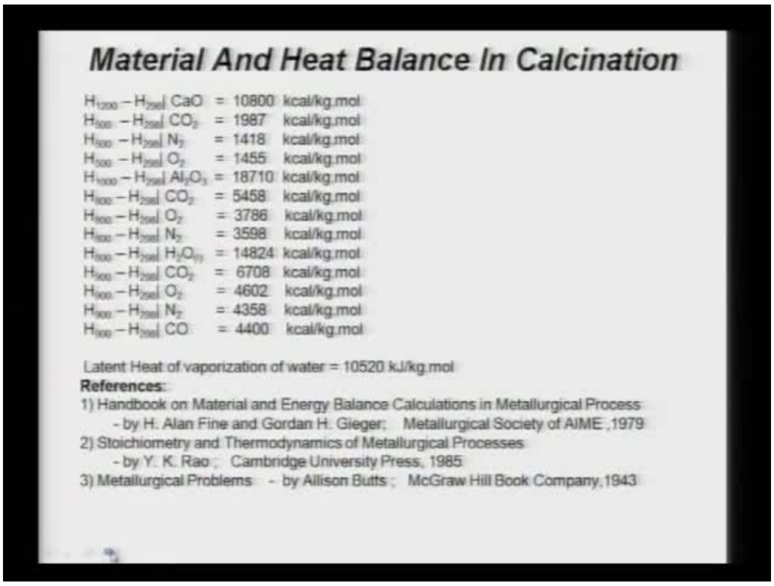
$C_p\ CO_2 = 44.141 + 9.037 \times 10^{-3}T - 8.535 \times 10^{5}T^{-2}$ kJ/kg.mol K

$C_p\ H_2O_{(l)} = 75.438$ kJ/kg.mol K

$C_p\ H_2O_{(v)} = 30 + 10.711 \times 10^{-3}T - 0.335 \times 10^{5}T^{-2}$ kJ/kg.mol K

Here, you will be requiring some of the data especially to calculate the heat balance.

(Refer Slide Time: 07:05)



Material And Heat Balance In Calcination

$H_{1200} - H_{298}| CaO = 10800$ kcal/kg.mol
$H_{500} - H_{298}| CO_2 = 1987$ kcal/kg.mol
$H_{500} - H_{298}| N_2 = 1418$ kcal/kg.mol
$H_{500} - H_{298}| O_2 = 1455$ kcal/kg.mol
$H_{1000} - H_{298}| Al_2O_3 = 18710$ kcal/kg.mol
$H_{800} - H_{298}| CO_2 = 5458$ kcal/kg.mol
$H_{800} - H_{298}| O_2 = 3786$ kcal/kg.mol
$H_{800} - H_{298}| N_2 = 3598$ kcal/kg.mol
$H_{800} - H_{298}| H_2O_{(l)} = 14824$ kcal/kg.mol
$H_{900} - H_{298}| CO_2 = 6708$ kcal/kg.mol
$H_{900} - H_{298}| O_2 = 4602$ kcal/kg.mol
$H_{900} - H_{298}| N_2 = 4358$ kcal/kg.mol
$H_{900} - H_{298}| CO = 4400$ kcal/kg.mol

Latent Heat of vaporization of water = 10520 kJ/kg.mol

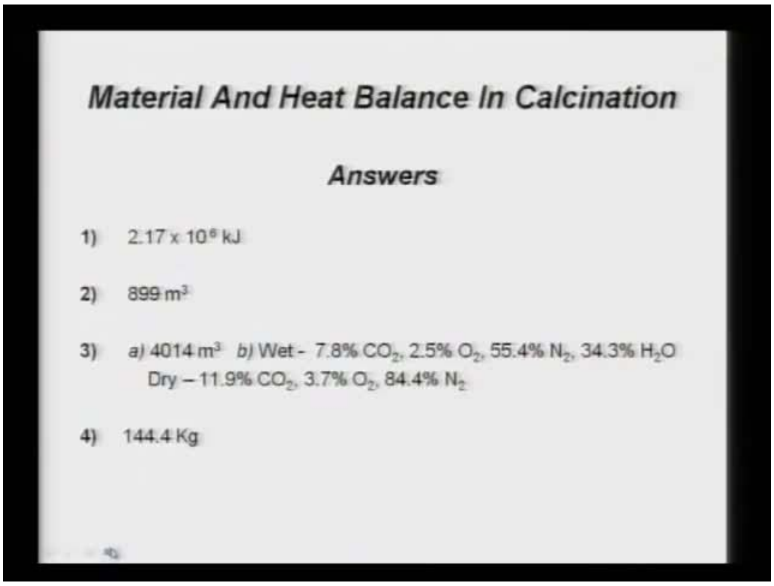
References:

1) Handbook on Material and Energy Balance Calculations in Metallurgical Process
   - by H. Alan Fine and Gordan H. Gieger; Metallurgical Society of AIME ,1979
2) Stoichiometry and Thermodynamics of Metallurgical Processes
   - by Y. K. Rao ; Cambridge University Press, 1985
3) Metallurgical Problems - by Allison Butts ; McGraw Hill Book Company,1943

So, these are the data and these are the further data. Now, here, what I have done is - 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 to please try to calculate by using the CP value of respective Calcium Oxide, CO 2, N 2, O 2 or whatever the product which are being discharged - that will give you an additional practice.

Whether you can calculate the heat content from CP value or not, it requires patience to see that you can do integration properly. However, these make your life easy, but see that you do also by using the CP calculation. Latent heat is also given, and here I have given some of the references.

(Refer Slide Time: 07:56)



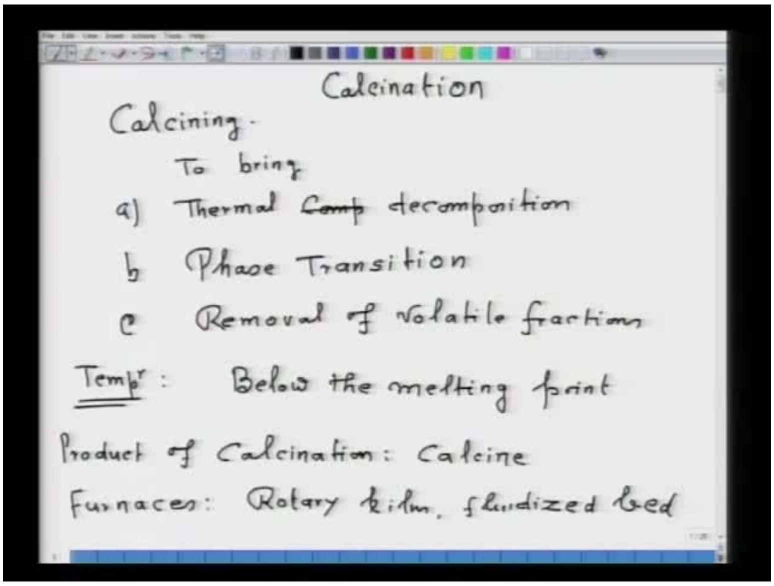
Material And Heat Balance In Calcination

Answers

1) 2.17×10^6 kJ
2) 899 m^3
3) *a)* 4014 m^3 *b)* Wet - 7.8% CO_2, 2.5% O_2, 55.4% N_2, 34.3% H_2O
   Dry – 11.9% CO_2, 3.7% O_2, 84.4% N_2
4) 144.4 Kg

As usual, here, I have given the solutions for these problems.

(Refer Slide Time: 08:05)



Calcination

Calcining.

To bring

a) Thermal ~~Comp~~ decomposition

b Phase Transition

c Removal of volatile fractions

Tempr : Below the melting point

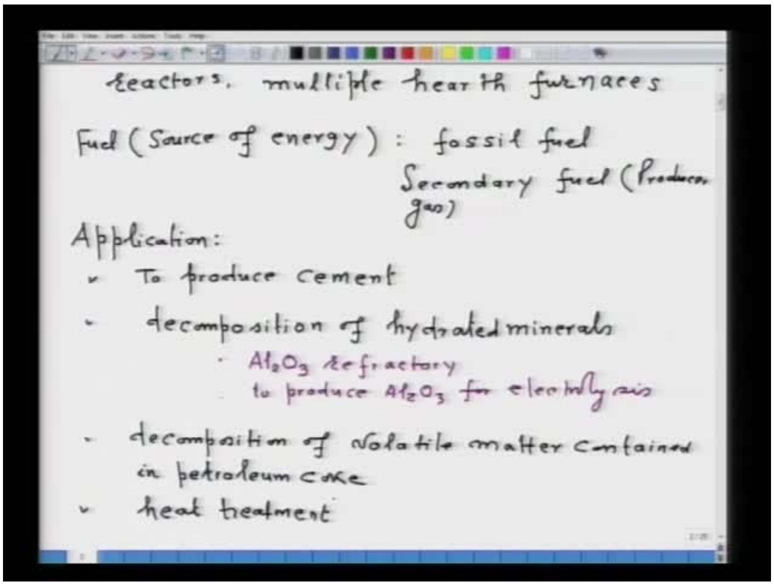
Product of Calcination : Calcine

Furnaces: Rotary kiln, fluidized bed

Now, let us go for the solution of these problems. First of all, let me tell you what calcination is. In fact, calcination is also referred as a calcining. It is a thermal treatment process applied to ores and other solid materials. Why? In order to bring thermal composition, or the other thermal decomposition because you want to decompose; for example, Calcium Carbonate to Calcium Oxide and CO 2 or Mg CO 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 can include more.

Now, the temperatures involved are 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 there are volatile components like CO 2 or H 2 O, they will be leaving the system. Product of calcination is sometimes called Calcine. The furnaces which are used are called rotary kiln. Very commonly, rotary kiln is employed for production of cement. In cement industry rotary kiln is a very big application; also calcination of limestone; also the removal of water from alumina and so on.

(Refer Slide Time: 11:14)



reactors, multiple hearth furnaces

Fuel (Source of energy) : fossil fuel
Secondary fuel (Producer gas)

Application:

- To produce cement
- decomposition of hydrated minerals
    - Al_2O_3 refractory
    - to produce Al_2O_3 for electrolysis
- decomposition of volatile matter contained in petroleum coke
- heat treatment

Then, fluidized bed reactors, multiple hearth furnaces and the fuel, or you can put source of energy. Source of energy - in some case, it is the fossil fuel; that could be oil, natural gas, or there could be secondary fuel which are derived from fossil fuel. Normally, sometimes producer gas is used, as you have seen in the problem. Oil, then natural gas - all these are the sources of energy. So, it is also an energy consuming unit process.

Applications: Some of the applications of calcination - one particular application is to produce cement. Here, the calcination is one of the important steps where you get Calcium Oxide and that is further mixed to produce cement. So, in cement industry, the decomposition of limestone is very important process.

Second application is decomposition of hydrated minerals. This decomposition is done for one purpose which could be we want to make, say Al 2 O 3 refractory. Now, here Bauxite is the material to produce Al 2 O 3 refractory. Bauxite also contains the water which is chemically combined; so, you have to straightaway calcinate in order to produce an alumina which is free from water; mind you, alumina is a very important refractive material in all pyro metallurgical extraction industries.

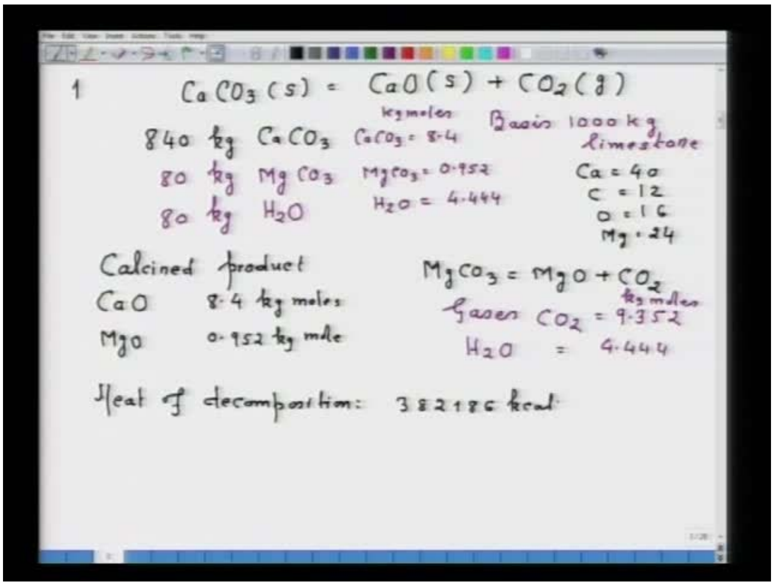
So, one of the purposes could be to produce alumina refractory, and another purpose could be to produce alumina for electrolysis in Hall Heroult cell, as all of you know, because that Al 2 O 3 should be anhydrous; otherwise, there is evolution of Hydrogen and you will be consuming a large amount of electrical 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 coke; 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 it as a calcination heat treatment and you may not class it- it does not matter. But for all that, you require a solid state transformation from room temperature to another temperature.

So, these are the certain applications of the calcination. Having given those things, let us go to the solution of problem number 1.

Now problem number 1: you have to calculate the heat energy to calculate thousand kg limestone and composition. Everything is given to us.

(Refer Slide Time: 16:22)



1 $CaCO_3(s) = CaO(s) + CO_2(g)$

840 kg $CaCO_3$ kg moles $CaCO_3 = 8.4$ Basis 1000 kg limestone

80 kg $MgCO_3$ $MgCO_3 = 0.952$

80 kg H_2O $H_2O = 4.444$

$Ca = 40$
$C = 12$
$O = 16$
$Mg = 24$

Calcined product
CaO 8.4 kg moles
MgO 0.952 kg mole

$MgCO_3 = MgO + CO_2$

Gases kg moles
$CO_2 = 9.352$
$H_2O = 4.444$

Heat of decomposition: 382186 kcal

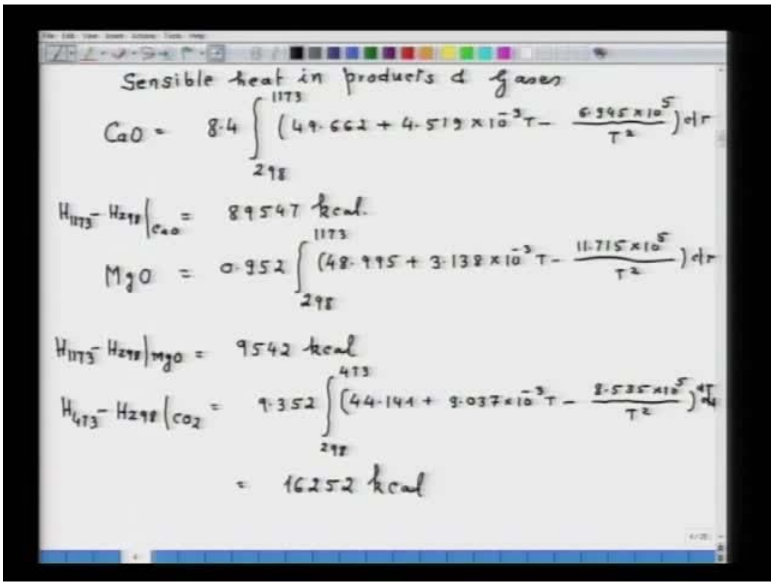
So, the reaction that takes place is Ca CO 3 solid; that is equal to CaO solid plus CO 2 gas. This is the reaction or this is the decomposition reaction. Now, we have 840 kg Ca CO 3; we are taking say 1000 kg limestone as the basis; now, the basis is already being given in the problem - 1000 kg limestone. So, 840 kg Ca CO 3, 80 kg Mg CO 3 and 80 kg water; this is what is given to us.

Now, we can straightaway calculate the calcined product. Before that, what I have used? I have used atomic weight of Calcium as 40, Carbon as 12, Oxygen as 16, and magnesium as 24. So, from here, I will be getting Calcium Carbonate, the kg moles of Calcium Carbonate - that will be equal to 8.4; kg moles of Mg CO 3 - that will be equal to 0.952, and kg moles of water - that will be equal to 4.444.

Once you know this, immediately we can write down the calcine product - Calcium Oxide and magnesium oxide. So, Calcium Oxide is 1 kg mole, 1 kg mole and 1 kg mole; so, Ca O will be 8.4 kg moles and MgO will be 0.952 kg moles. Similarly, the reaction for Mg CO 3 will be MgO plus CO 2, solved. So, we have the calcined product. Now, the gases will form. We have to know the gases that will be forming, that are CO 2; CO 2 is coming because of the decomposition. The sources of CO 2 are Ca CO 3 and Mg CO 3. So, you have to add both of them and H 2 O. These are the 2 sources. H 2 O is coming from the limestone composition. So, CO 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 heat of decomposition. The values I have given. I will write down the heat of decomposition and that will be equal to 382186 kilo calorie - that is the heat of decomposition.

(Refer Slide Time: 20:37)



Sensible heat in products & gases

$$CaO = 8.4\int_{298}^{1173}\left(49.662 + 4.519\times10^{-3}T - \frac{6.945\times10^{5}}{T^2}\right)dT$$

$$H_{1173} - H_{298}\Big|_{CaO} = 89547 \text{ kcal.}$$

$$MgO = 0.952\int_{298}^{1173}\left(48.995 + 3.138\times10^{-3}T - \frac{11.715\times10^{5}}{T^2}\right)dT$$

$$H_{1173} - H_{298}\Big|_{MgO} = 9542 \text{ kcal}$$

$$H_{473} - H_{298}\Big|_{CO_2} = 9.352\int_{298}^{473}\left(44.141 + 9.037\times10^{-3}T - \frac{8.535\times10^{5}}{T^2}\right)dT$$

$$= 16252 \text{ kcal}$$

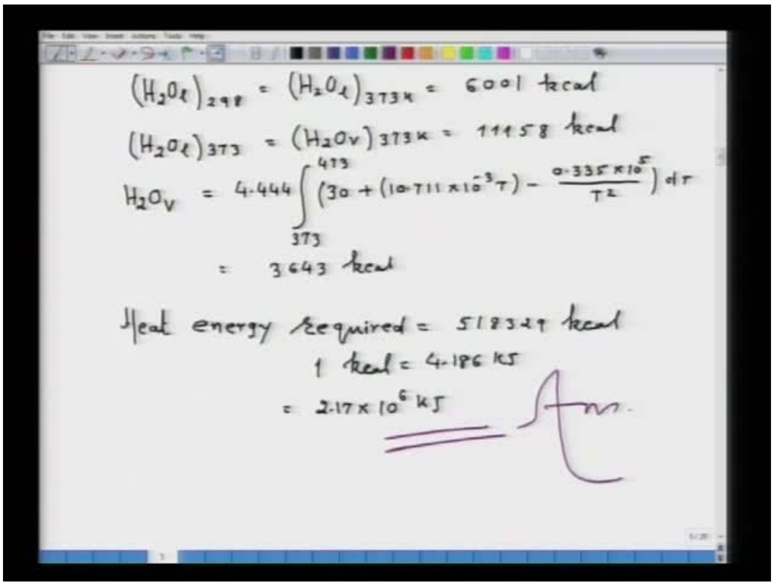
Then, I have to find out sensible heat in products and gases. For that, if I sum total all these - that is the energy I require if I want to decompose Calcium Carbonate. So, sensible heat, for example, in C a O will be equal to 8.4 kg moles. Integrate it from 298 to 1173 Kelvin; 49.662 plus 4.519 into 10 to the power minus 3 T minus 6.945 into 10 to the power 5 upon T square; this I have to integrate to dt.

Please do this exercise. However, if you try, you can get those values also in the reference which I have given. But then, there are intermediate temperatures where you will not find the values. So, it is better to develop the practice of integration. So, if you do that, then the Calcium Oxide will be equal to, heat contained in Calcium Oxide is equal to 89547 kilo calorie - this is the heat content, or we can write - H 1173 minus H 298 in Calcium Oxide.

Similarly, I can find out for MgO - that will be equal to 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 upon T square. Integrate it to d t. So, I get H 1173 minus H 298 for MgO that will be equal to 9542 kilo calorie.

Then I have to calculate, let us say HCO. Now, the gases are discharging at 473 Kelvin. So, I have to write H 473 minus H 298 for CO 2; the moles of CO 2 are 9.352. I have to write its CP 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 it with dt. So, that will be dt here; so, this value is coming 16252 kilo calorie.

(Refer Slide Time: 25:10)



$(H_2O_l)_{298} = (H_2O_l)_{373K} = 6001$ kcal

$(H_2O_l)_{373} = (H_2Ov)_{373K} = 11158$ kcal

$$H_2O_v = 4.444 \int_{373}^{473} \left(30 + (10.711 \times 10^{-3} T) - \frac{0.335 \times 10^{5}}{T^2}\right) dT$$

$= 3643$ kcal

Heat energy required $= 518329$ kcal

1 kcal $= 4.186$ kJ

$= 2.17 \times 10^{6}$ kJ

Ans.

Be careful while calculating the heat content in water vapor. So, when 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 (( )) let in theta (( ). 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 that, at the latent heat temperature change does not occur. So, this value is 11158 kilo calorie.

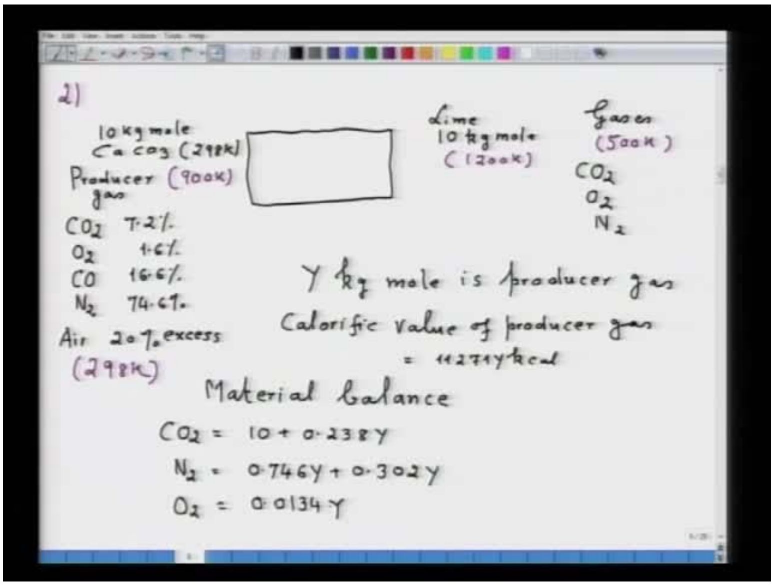
Now, I have to heat the H 2 O vapor. H 2 O vapor is equal to 4.444 - that will go from 373 because 100 Kelvin already has been taken into account to 473, 30 plus 10 .711 into 10 to the power minus 3 T minus 0.335 into 10 to the power 5 upon T square dt; this value is 3643 kilo calorie.

The heat energy required as asked in the problem - what would be the heat energy required? I think, by now, all of you can guess. You have to sum total all the energies because the heat of decomposition is also endothermic reaction.

So, there will be large amount of heat absorption plus all the heat carried out. So, if you do not supply all that heat, the decomposition of Calcium Carbonate will not occur. So, all that you have to add and the addition brings 518329 kilo calorie. I have used 1 kilo calorie - that is equal to 4.186 kilo joule; that gives me the 2.17 into 10 to the power 6 kilo joule. That is the answer for problem number 1. That is the way you will be proceeding to solve.

My appeal to you again is that please solve the problem on your own without seeing the solution because if you look to the solution, you will be carried away by the 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 your way of solution may be much better than what I have done. So, please do yourself; that is an important thing.

(Refer Slide Time: 28:40)



2)

10 kg mole
$CaCO_3$ (298K)
Producer gas (900K)
CO_2 7.2%
O_2 1.6%
CO 16.6%
N_2 74.6%
Air 20% excess
(298K)

Lime
10 kg mole
(1200K)

Gases
(500K)
CO_2
O_2
N_2

Y kg mole is producer gas
Calorific value of producer gas
= 11271Y kcal

Material balance

CO_2 = 10 + 0.238Y
N_2 = 0.746Y + 0.302Y
O_2 = 0.0134Y

Now, second problem: In the 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, the only way to calculate the amount of producer gas is to do the heat balance.

You do the heat balance because all the energies are coming from the combustion of producer gas. If you do heat input and make it equal to heat output, then only variable in your equation would be the amount of producer gas and you can solve that way. So, heat balance is the key to solve problem number 2.

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 we are doing is, say 10 kg mole of Calcium Carbonate are entering at 298 Kelvin. It is fired with producer gas and producer gas is entering at 900 Kelvin; mind you, the producer gas brings sensible heat into the furnace. So, the composition of producer gas is given: CO 2; it has oxygen; it has Carbon monoxide; it has Nitrogen.

Now, CO 2 is 7.2 percent, oxygen 1.6 percent, carbon monoxide 16.6 percent and Nitrogen is 74.6 percent. The problem further says that air is 20 percent excess. That means you have use 120 percent theoretical air and the supplied temperature of air is 298 Kelvin; that is what is given.

On the output side, your lime which is 10 kg mole and say lime discharge at a temperature of 1200 Kelvin, and the gases discharge at 500 Kelvin. The gases would contain, as you can see in the problem, it will contain CO 2. Since excess air is used, it will also contain excess oxygen; since air is used, it will also contain Nitrogen. So, in this situation, you have to find out the amount of producer gas. Now, you have to do the heat balance. Here, I would like to tell you that 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 very detail calculations on combustion in different lectures are given there. 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. For the details, you can see those lectures on combustion and you may get a 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 the required for producer gas. 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 portions on fuel furnace and refractory's. In fact, in case of combustion, the gaseous fuel combustion, the CO, Hydrogen and hydro Carbon - they are the combustible component. C, O 2, N 2 - they are the diluents; they do not take part in the combustion. So, mind you, that is an important thing.

So, the calorific value of producer gas will consist of only when CO is completely combusted to CO 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 are complete; that is an important thing. For the details, you can see, I already referred the video lectures on fuel furnace and refractory's. So, the calorific value of producer gas (Refer Slide Time: 28:40) that 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.

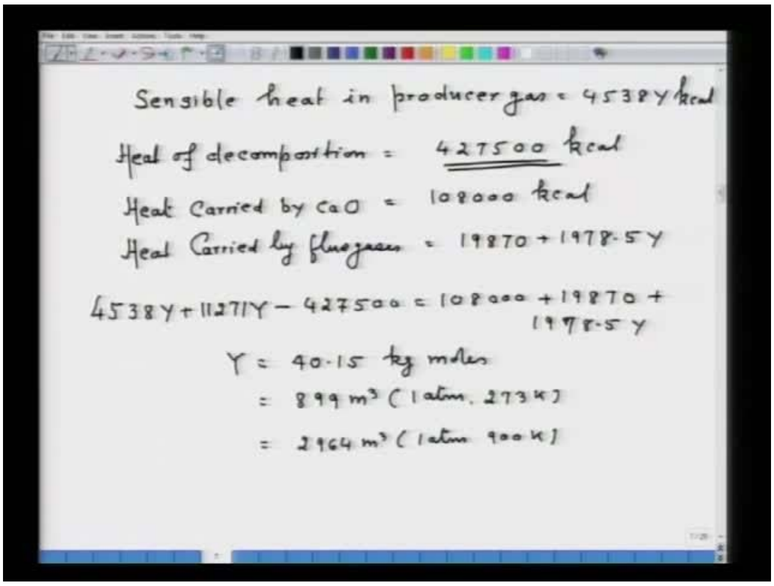
Now, I can take the material balance. If I do the material balance, the amount of CO 2 - that will be equal to 10 plus 0.238 Y. 10 is coming from 10 kg mole Calcium Carbonate; it will also give you 10 kg mole of Carbon dioxide.

Nitrogen: All the Nitrogen of producer gas will be available in the gases or the output; that plus the amount of air or the Nitrogen of the air. So, that will be equal to 0.746 Y plus 0.302 2 Y.

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

Once you have done material balance, you have to do the heat input and heat output. Heat input one is the sensible heat; heat of decomposition , though it is endothermic, it is also a heat input .So, I will straightaway write down the values.

(Refer Slide Time: 36:29)



Sensible heat in producer gas = 4538 Y kcal

Heat of decomposition = 427500 kcal

Heat Carried by CaO = 108000 kcal

Heat Carried by fluegases = 19870 + 1978.5 Y

$$4538Y + 11271Y - 427500 = 108000 + 19870 + 1978.5\,Y$$

$$Y = 40.15 \text{ kg moles}$$

$$= 899 \text{ m}^3 \text{ (1 atm, 273 K)}$$

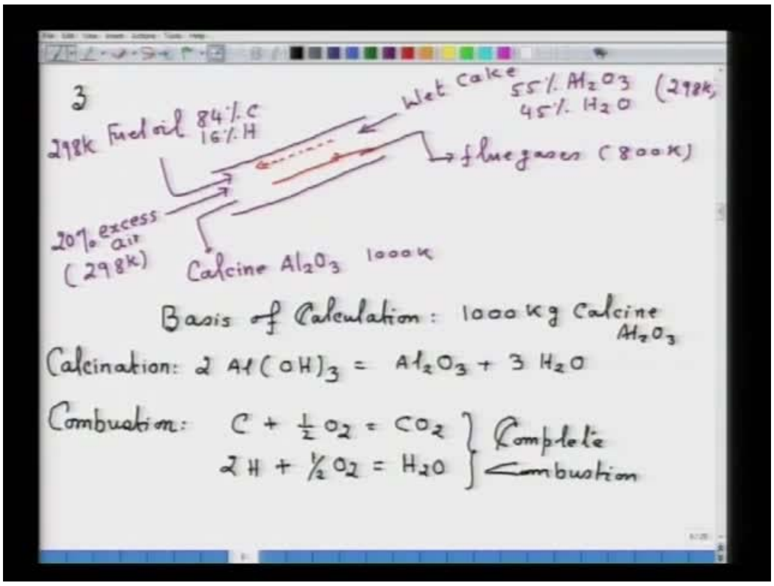
$$= 2964 \text{ m}^3 \text{ (1 atm 900 K)}$$

So, sensible heat in producer gas 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. Heat of decomposition of Calcium Carbonate - you have to calculate from the value CaCO 3, CaO plus CO 2 product minus reactant 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 and this not exothermic.

Heat carried or taken by Calcium Oxide because it is discharged at 1200 Kelvin, that is equal to 108000 kilo calorie. Heat carried by flue gases - that will be equal to 19870 plus 1978.5Y.

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 108 plus 19870 plus 19678.5 Y. So, I can calculate: Y - that will be equal to 40.15 kg moles and that will be equal to 899 meter cube expressed at 1 atmosphere and 273 Kelvin; so, that is equal to 2964 meter cube at 1 atmosphere and 900 Kelvin. This is all about problem number 2.

(Refer Slide Time: 39:42)



Basis of Calculation: 1000 kg Calcine Al_2O_3

Calcination: $2\,Al(OH)_3 = Al_2O_3 + 3\,H_2O$

Combustion:

$$\left.\begin{array}{l} C + \frac{1}{2}O_2 = CO_2 \\ 2H + \frac{1}{2}O_2 = H_2O \end{array}\right\}$$ Complete combustion

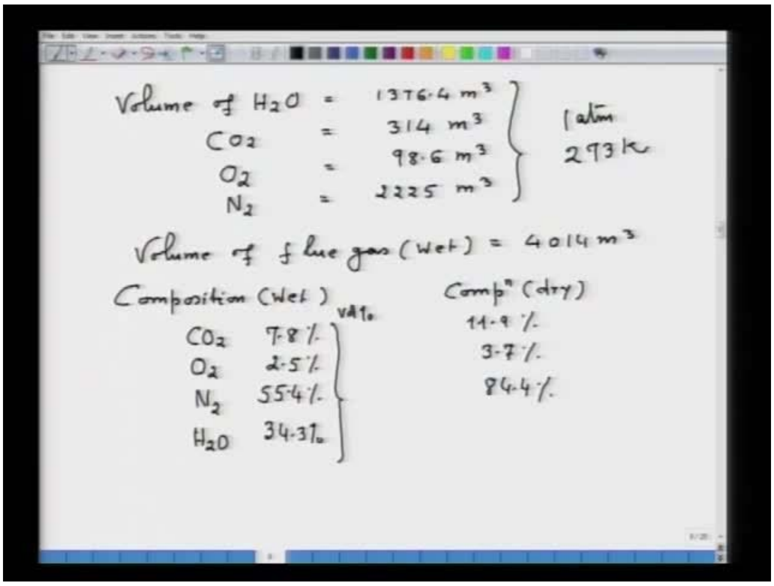
Now, let us quickly go through problem number 3. In problem number 3, we have a rotary kiln. This is a rotary kiln; in the rotary kiln, the flow is counter current. So, here, wet cake which contains 55 percent Al 2 O 3, 45 percent H 2 O. This H 2 O is chemically combined and it enters at 298 Kelvin.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

Now the flue gases are leaving at 800 Kelvin. Here, the fuel oil is supplied for combustion. So, fuel oil contains 84 percent Carbon and 16 percent Hydrogen is supplied at 298 Kelvin. Then supply 20 percent 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. As usual, we have to perform the heat balance. Well first of all, we have to do the material balance; without that we can do nothing. So, I will just proceed to solution.

Here, let me tell another thing: the wet cake 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: 42:03). 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 200 kg is already given. The various calcination reactions is 2Al OH 3; that is equal to Al 2 O 3 plus 3H 2 O - this is the calcination reaction. Then, we have combustion reaction. Combustion reaction is C plus half O 2; that is equal to CO 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 CO 2; H is H 2 O. 2H plus half O 2 that is equal to H 2 O. So, we have assumed complete combustion; it is the complete combustion.

(Refer Slide Time: 43:59)



Volume of H_2O = $1376.4\ m^3$
CO_2 = $314\ m^3$
O_2 = $98.6\ m^3$
N_2 = $2225\ m^3$
1 atm
293 K

Volume of flue gas (wet) = $4014\ m^3$

Composition (Wet) vol%		Comp^n (dry)
CO_2	7.8%	11.9%
O_2	2.5%	3.7%
N_2	55.4%	84.4%
H_2O	34.3%	

Let us now calculate the 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.

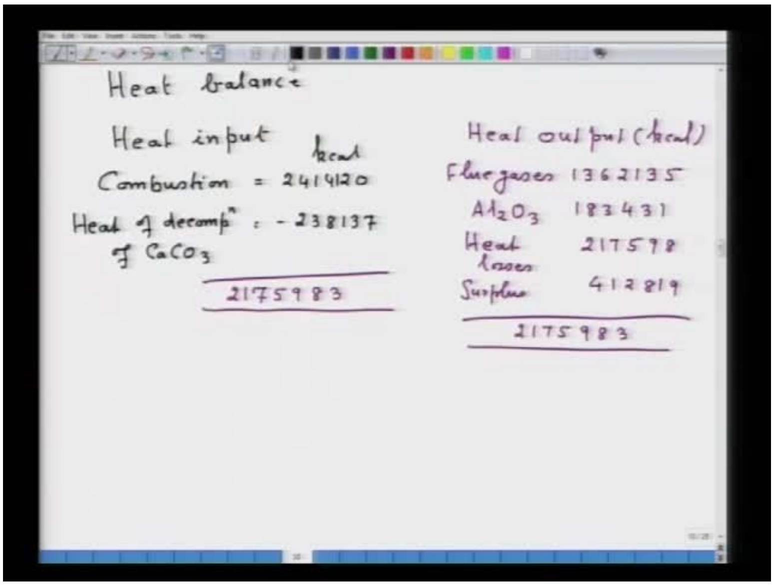
Similarly we have CO 2 in the flue gas - that will be 314 meter cube. Then, since we are using 20 percent excess oxygen, there will also be excess oxygen. So, excess oxygen in the flue gas - that will be equal to 98.6 meter cube and Nitrogen in the flue gas - that will be equal to 2225 meter cube.

Now, I may tell you once again that it is utmost important that you should be very thorough in doing material balance because without material balance, you cannot do heat balance at all. If you have any problem in what you have done while doing the material balance, that 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 produced. So, if you do a mistake in material balance and if you get the solution say after having 10 or 14 steps, then all steps will be wrong. It is a transferred error. So, you have to be very careful while doing material balance problem; that is very important.

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. Wet volume is 4014 meter cube. Then, you have to calculate composition on wet basis and you have to also calculate composition on dry basis. So, we have CO 2; we have O 2; we have Nitrogen and we have H 2 O. If you do this calculation, I have already given in the answer 7.8 percent, 2.5 percent, 55.4 percent and 34.3 percent - 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 are also expressed at 1 atmosphere and 273 Kelvin because I have taken 1 kg mole as 22.4 meter cube; so, that is what this calculation of the composition.

(Refer Slide Time: 47:34)



Heat balance

Heat input	kcal
Combustion	= 2414120
Heat of decompⁿ of $CaCO_3$	: - 238137
	2175983

Heat output (kcal)	
Flue gases	1362135
Al_2O_3	183431
Heat losses	217598
Surplus	412819
	2175983

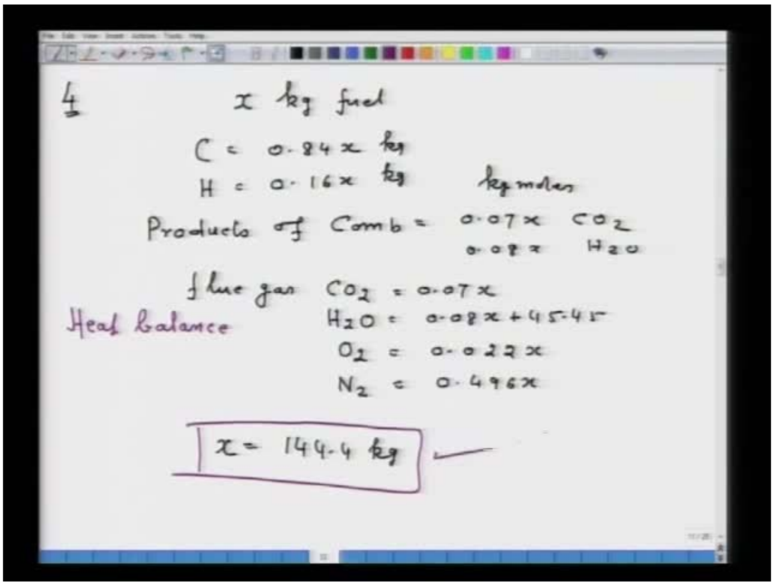
So, you have to do heat balance - all that we have to do is heat input; it will be by combustion. So, you have to calculate C plus O, 2CO 2 and H 2 plus half O 2, H 2 O. This heat input by combustion will be equal to 2414120 kilo calorie.

Then, heat of decomposition of Calcium Carbonate: Because this is 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 has been discharged at 1000 Kelvin; it will be 183431; then heat losses are given as 10 percent of the input. 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. That is how you will be doing the heat balance for the problem number 3.

Now, quickly illustrating the problem number 4; in problem number 4, you have to find out the minimum amount of fuel for calcination. As you noted in problem number 3, 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 is that fuel, at which the heat input becomes equal to heat output, and that value will be your amount of fuel that is required.

(Refer Slide Time: 50:40)



4

x kg fuel

$C = 0.84x$ kg

$H = 0.16x$ kg

kg moles

Products of Comb = $0.07x$ CO_2

$0.08x$ H_2O

flue gas $CO_2 = 0.07x$

Heat balance

$H_2O = 0.08x + 45.45$

$O_2 = 0.022x$

$N_2 = 0.496x$

$$\boxed{x = 144.4 \text{ kg}}$$

Again you have to do the heat balance. Thus, if you have x kg fuel, from here you have to start, that is unknown, your Carbon will be 0.84 x and Hydrogen will be 0.16 x. So, the products of combustion will be equal to 0.07 x - that is CO 2, and 0.08 x- that is H 2 O; mind you, they are in kg moles and this is in kg.

Once you know the products of combustion, then you have to calculate the amount of flue gas. The flue gas composition: flue gas CO 2 that is equal to 0.07x; 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 heat balance, heat input, heat output. 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 terms like heat of decomposition and heat taken by flue gas. Now, heat taken by flue gas will be in terms of x, and then, heat taken by Al 2 O 3 - if you do all that and do the balancing, then the answer will be 144.4 kg. That is what is about the calcination.