### **Materials and Energy Balance in Metallurgical Processes**

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Module No. # 01

#### Lecture No. # 22

# **Exercise-II Matte Smelting**

In the previous lecture, we have seen matte smelting and I have illustrated matte smelting by solving two problems; or, rather three problems. Now, I thought that let me give you two more problems and discuss the solution of these problems so that you can understand the quantification of matte smelting.

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Material Balance In Matte Smelting

4) The proximate analysis of copper concentrates (wt. %) is as follows:

Cu\_S 20%, FeS\_49%, SiO\_26%, Ai\_O<sub>3</sub> 5%. The concentrate is smeltene in a furnace in presence of iron ore and limestone. The analysis of iron ore is 81% Fe<sub>2</sub>O<sub>3</sub> and 19% SiO\_2 and that of limestone is 93% CaCO<sub>3</sub> and 7% SiO\_3. The grade of matte is 45% and the ratio of SiO\_3. FeO:CaO in slag is 45:40:15. The oil amounts to 12% of the charge and analyzes 85% C, and 15% H. The air used is 10% excess than theoretical required for smelting

Calculate (per tonne of concentrate):

a) weight of each flux
b) volume of air and % composition of gases.

Now, here is the next problem that is in continuation with my previous lecture; that is, problem number four. The proximate analysis of copper concentrates is as follows: Cu 2 S FeS 2 SiO 2 and all are given. The concentrate is smelted in a furnace in presence of iron ore and limestone. Here both are used as a fluxing agent. The analysis of iron ore is

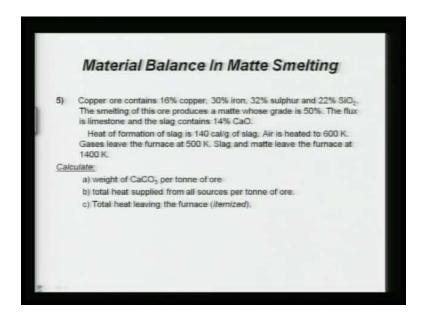
given and that of limestone is also given. The grade of matte is 45 percent and the ratio of SiO 2 is to FeO is to CaO in slag is 45 is to 40 is to 15. The ratio is also given; the slag is forming in this particular ratio of the different components of the oxides. The oil amounts to 12 percent of the charge and analyzes the composition is also given to you. Very often, most of the matte smelting operations are required to use extra source of energy; sometimes it requires. It depends on the process; it depends on the analysis of the ore and sulphur content and so on and so forth. So, it is quite possible that some of the matte smelting operation do require extra amount of fuel.

Here 12 percent of the charge that is a fuel, which is used and composition is given. Air is 10 percent excess. You must have noticed by now in various lecture say on roasting or smelting and so on. The chemical reactions accompanying the transformation of one phase to another in roasting as well as in smelting do not occur with the stoichiometric amount of air.

You always require some amount of excess air. So, what should I say at this particular point that the industrial operations always require an excess amount of air. Now, it is up to the skill of the operator that how beautifully you control the excess amount of air. Somebody may do a 10 percent; somebody may do 20 percent; somebody even do with 30 percent. So, all that is required took the control of excess air because the control of excess air is also important. The more air you use, the more nitrogen will enter, and more nitrogen will take the heat from the reactor to the atmosphere. So, that is also an important issue over here.

Now, we calculate per tonne of concentrate weight of each flux and volume of air and so on.

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The next problem is say copper ore contains 16 percent copper 30 percent iron and so on. The smelting of this ore produces a matte whose grade is given. The flux is limestone and slag contains 14 percent CaO.

Now, various data on the heat are given. You can go through these data and understand those data because whenever there is a formation of slag, it is also (()) by heat of formation. You do require to supply extra amount of heat for heat of formation. Also, here it is given at what temperature they leave. So, you must have understood from the statement of the problem that I would like you to do heat balance also and that is what is written. You have to calculate calcium carbonate, total heat supplied and total heat leaving the furnace. So, these are the two problems.

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Material Balance In Matte Smelting
Answers

1) a) Cu = 13.9 %, Fe = 23.9%, S = 27.2% b) 82.6%
c) m=0.11, n=0.2 d) 12.7%

2) Limestone = 209.3 kg . Slag = 558.1 kg . Matte = 365 kg

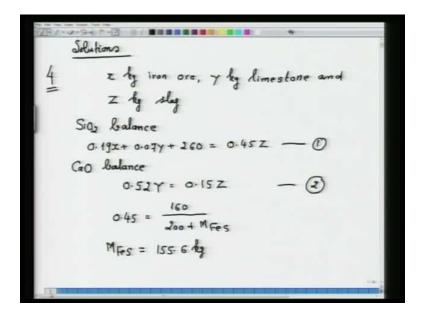
3) a) Weight of matte = 267.4 kg, grade = 37.4%
b) 845.2 kg SiO<sub>2</sub> 41.6%, Al<sub>2</sub>O<sub>2</sub> 5.5 %, CaO 20.7%, FeO 32.2%
c) Volume of gases (i)From sulphur = 1989 m³ (ii)From carbon = 1980 m³
d) 1972 m³

4) a) Limestone = 191.5 kg, Slag = 664 kg, Iron Ore = 133.6 kg
b) 3107.5 m³ CO<sub>2</sub> 8.2%, SO<sub>2</sub> 5.5%, H<sub>2</sub>O 4.4%, N<sub>2</sub> 80%, O<sub>2</sub> 1.9%

5) a) 147.5 kg b) 382651 kcal
c) Matte = 71290 kcal , Slag = 224304 kcal , Gases = 89915 kcal
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The answers for all the problems say in the previous lecture problem and this one are given over here. Now, I will proceed to discuss the problem. By now, I hope you must have rate the problem and you must have understood how to solve these particular problems.

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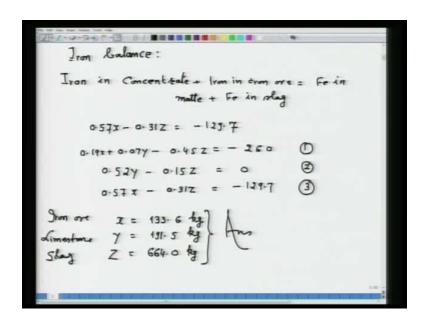
Let us discuss the solutions of these problems. Fourth: Let us consider say x kg iron ore, y kg limestone and z kg slag. Let us first of all do SiO 2 balance because the components in this slag and the proportions are given. I will make use of this. If I do SiO 2 balance,

SiO 2 balance will lead me 0.19x plus 0.07y plus 260; that is equal to 0.45z; that is, you have to take into account SiO 2 from all sources.

Now, let us do CaO balance. Let me put this equation as number 1. Then I get the CaO balance 0.52y; that is equal to 0.15z. Let us put this equation number 2. Now, because we have three variables, I need one more equation. I am looking for an iron balance. Before I do iron balance, I have to see the various sources from where iron enters and it leaves.

First of all I have to find... Grade of matte is given; that is, 0.45 that is equal to 160 upon 200 plus M FeS. So, if I solve, I get from here M FeS; that is equal to 155.6 kg. Now, I know that much of amount of iron is going to the matte. Now, I can do the iron balance and find out the amount of iron that is entering into the slag.

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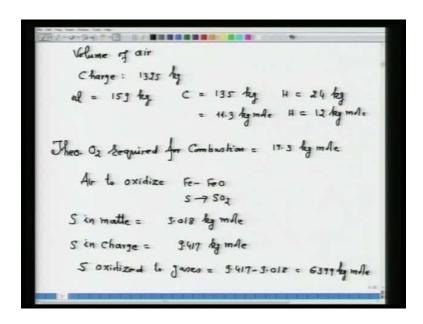


Now, I have to do iron balance. So, if I do iron balance, I write iron in concentrate; I have to see iron from all sources plus iron in iron ore. That is equal to iron in matte plus iron in slag. If I write down all the values from where the iron is entering and if I do that, then I will be getting an equation which is 0.57x minus 0.31z; that is equal to minus 129.7.

Now, I am summarizing all the three equations. That is, 0.19x plus 0.07y minus 0.45z; that is equal to minus 260. Next is 0.52y minus 0.15z; that is equal to 0, and 0.57x minus

0.31z; that is equal to minus 129.7. So, this is equation 1, equation 2 and equation 3. So, one can solve three variables and three equations. So, the value of x is equal to 133.6 kg, value of y is equal to 191.5 kg and value of z is equal to 664.0 kg. So, that is the answer about what is asked. x is in fact iron ore, this is limestone and this is slag.

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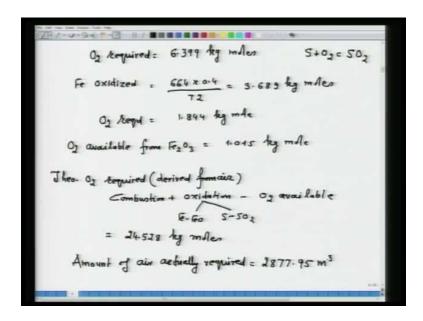
Now, let us calculate about the volume of air. First of all, we have to find out the amount of oil. So, amount of oil is 12 percent of the charge. Note that charge consists of whatever you are charging to convert the charge into matte. So, you are charging concentrate iron ore plus limestone not only concentrate. So, it is 12 percent of all. So, the charge total is 1325 kg; you have to add up all the amount.

The amount of oil that is equal to 159 kg, accordingly, carbon that is equal to 135 kg, and hydrogen that is equal to 24 kg as per the percentage, which are given. So, I am writing here 11.3 kg mole and hydrogen is 12 kg mole. So, once I know these things I can calculate theoretical oxygen or theoretical O 2 required for combustion; that will be equal to 17.3 kg mole. So, we are considering for complete combustion and that is important. Nothing is given; you can only calculate by considering complete combustion; that is, C plus O 2 is CO 2 and H 2 plus half O 2 is equal to H 2 O.

Now, you also require air to oxidize; say iron to FeO and sulphur to SO 2. So, we have to find out how much amount of oxygen would be required here. For that we have to do something; say first of all, we will do sulphur in matte because we have to find out how

much amount of sulphur is going to the gases. So, sulphur in matte; that is equal to 3.018 kg mole. You know that sulphur in matte consists of Cu 2 S and Fe S. You have to convert it and you have to get in sulphur in matte. So, sulphur in charge; that will be equal to 9.417 kg mole. You have to see a sulphur, which is entering into the furnace from the different sources. You do that and you will get this value. So, sulphur oxidized to gases – now, you can very well guess what it will be. That will be 9.417 minus 3.018 and that will be equal to 6.399 kg mole.

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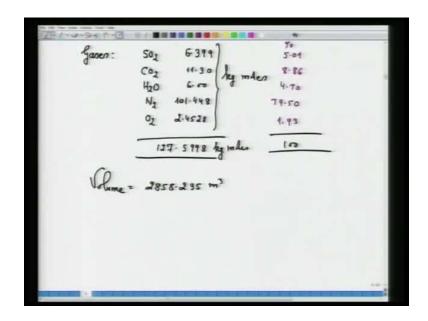
Now, I can calculate the oxygen required; O 2 required. I hope you must be remembering the reaction will be S plus O 2; that is equal to SO 2. Because the problem does not say SO 3 or anything, you have to consider formation of SO 2. So, oxygen required will be equal to 6.399 kg moles.

Now, about the iron oxidized, we can calculate the amount of FeO. From the FeO, we can calculate how much oxygen is required by Fe plus O 2; that is, equal to half O 2. That is, you can calculate iron oxidized, which will be equal to 664 into 0.4 upon 72; that is equal to 3.689 kg moles. So, oxygen required will be half of it; 1.844 kg mole.

The problem also says some oxygen is also available from charge; you know that you are charging Fe 2 O 3. So, oxygen available or available oxygen is only from Fe 2 O 3. You know the amount of Fe 2 O 3 because they calculated its amount and that oxygen will be 1.015 kg mole.

Now, theoretical oxygen required; let me put derived from air because you have to subtract what Fe 2 O 3 is supplying. So, that will be whatever oxygen required for combustion plus oxidation minus oxygen available. Oxidation - Fe to FeO as we have calculated earlier and sulphur to SO 2. So, if I do all that, then theoretical oxygen required would be 24.528 kg moles. Once I know the theoretical oxygen required, then there is no problem; 10 percent excess. So, actual oxygen will be 1.1 times this and I can calculate the amount of air. So, the amount of air actually required will be equal to 2877.95. So, that is the answer and this is the meter cube (Refer Slide Time: 17:09). All that you have to do is - divide theoretical oxygen by 0.1, multiply by 22.4, and take 10 percent excess of that. So, you will get this amount of air.

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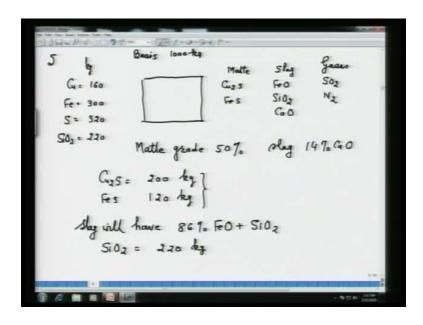
Next is the gases, which are forming – you have SO 2, CO 2, H 2 O, nitrogen and oxygen. Mind you: Since you are using excess here, there will be oxygen also in the flue gases. I will put here that is SO 2 is 6.399, CO 2 is 11.30, H 2 O is 6.00 and nitrogen is 101.448. Note that the very large amount of nitrogen that is obtained in the flue gas because nitrogen is inherit and whatever you supply will go out with the flue gas. Not only this, it will also carry a large amount of heat. Oxygen is 2.4528. These values are all in kg moles. So, I can write down the percentage. Percentage will be in percent - 5.01, 8.86, 4.70; note that amount of nitrogen is very high (Refer Slide Time: 18:53). Therefore, one has to be very cautious in using the excess amount of air because it does not matter. If you have a large amount of heat that is more than required, then there is no

problem. However, whenever there is a heat deficit, then this control of excess air is important – one.

Second - this nitrogen will also carry large amount heat. The quality of heat will be very high because the temperature of the flue gases is very high; at least the temperature will be that of the smelter; 1000 or 1100 degree celsius. So, higher is the temperature, higher is the quality of heat. So, when the quality of heat is very high, then it takes a very large amount of heat with it. Appropriate waste heat recovery devices must also be thought of to recover the heat. So, that is what is important. Oxygen is 1.93 percent. So, the total flue gas is equal to 127.5998; in kg moles. This becomes 100; it should become 100.

The volume of the gases will be 2858.235 meter cube at 1 atmosphere and 273 kelvin. Again you are noting here the ratio between volume of air and volume of flue gas is approximately 1 is to 1. So, that also says that the solution to your problem is rather ok.

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Now, let us take problem number 5. Problem number 5 says you are charging; I am putting in kg. Charge is say - copper is 160 kg, iron is 300 kg, sulphur is 320 kg, and SiO 2 is equal to 220 kg. Say - basis of calculation is 1000 kg concentrate. Based on that, I converted this amount.

Here you get matte. Matte contains Cu 2 S as per the statement of the problem and contains Fe S. It contains slag; that contains FeO, SiO 2 and calcium oxide. Then, you have gases; you have SO 2 and N 2.

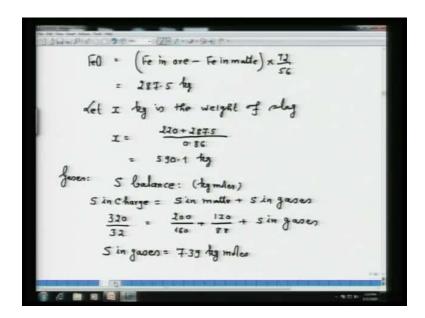
Now, here you have to do heat balance also. As I have said that before you enter into the venture of heat balance or into the doing of heat balance, you must be very clear about the material balance. All the values should be ok for heat balance because otherwise, the mistake will be carried over till the end of the heat balance. So, be careful while doing the material balance first. Matte grade given is 50 percent and it is also said that the slag contains 14 percent CaO, which is found by the addition of limestone.

Now, we have to calculate all that amount. So, if I calculate now, you know the definition of matte grade that amount of copper upon amount of matte. So, if I do that, then I will be getting amount of Cu 2 S and amount of Fe S. So, Cu 2 S will be 200 kg and Fe S will be 120 kg. This is how we know the amount of matte.

Now, we have to calculate the amount of slag. Since 14 percent CaO is in the slag, which means... Here we also know that little bit chemistry of matte smelting is also known to you. In this particular problem, the slag will contain FeO, SiO 2 and CaO and that is all. There is no other source of any other component in the slag except the three, which I have mentioned. What are they? FeO, CaO and SiO 2.

We are given 14 percent CaO. So, balance is FeO and SiO 2. That means the slag will have 86 percent FeO plus SiO 2. Now, we know say SiO 2 is equal to 220 kg. Because whatever SiO 2 in the charge, it enters in this slag (Refer Slide Time: 24:16). That is what the chemistry of matte smelting says.

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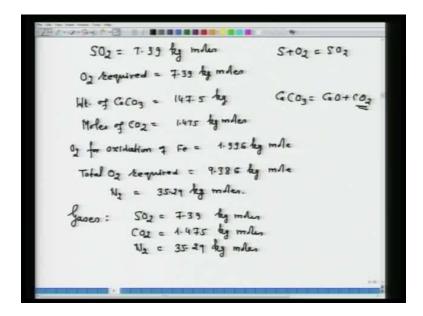


Now, we have to find out FeO in slag. FeO in slag will be equal to iron in ore minus iron in matte. That iron will go into slag. If I want to find out FeO, that will be into 72 upon 56. So, that will be equal to 287.5 kg, which is the amount of FeO that is entering into the slag.

Let x kg is the weight of slag. Then I can easily find out x and that will be equal to 220 plus 287.5 divide by 0.86. So, now I get x that is equal to 590.1 kg. That is the amount of slag. Now, the whole idea of knowing the amount of slag is to determine SiO 2, FeO and calcium oxide.

Now, we have to know the amount of gases. For the gases, we have to do sulphur balance. What does this sulphur balance says? Sulphur in charge is equal to sulphur in matte plus sulphur in gases; that is what the sulphur balance is. I am doing sulphur balance in kg moles, however you can do in kg also. As long as you are consistent with the units there is no problem at all. Now, I will write down sulphur in charge; that is 320 upon 32; sulphur in matte is 200 upon 160 plus 120 upon 88 plus sulphur in gases. By simple mathematics, I can find out sulphur in gases and that will be equal to 7.39 kg moles.

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Therefore, SO 2 would also be equal to 7.39 kg moles because you know that S plus O 2 is equal to SO 2. O 2 required will also be equal to 7.39 kg moles. Now, say weight of calcium carbonate; since you know the amount of slag, we know percentage calcium oxide. From there we can find out the weight of calcium carbonate; that will be 147.5 kg.

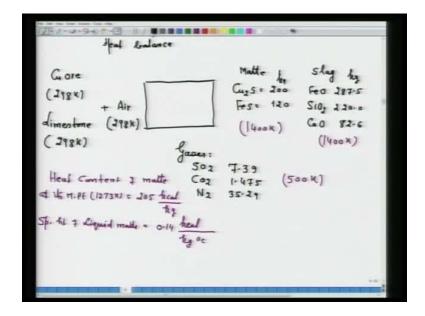
Easily you can find out say - calcium oxide is 14 percent and weight of slag is 590.1 kg. So, 14 percent of that 590.1 is calcium oxide. From there you convert to kg mole and find out the calcium carbonate and so on. So, that is how you find the weight of calcium carbide.

Now, weight of calcium carbonate is known to you. So, we know the moles of CO 2 because calcium carbonate on dissociation gives to you calcium oxide plus CO 2 and this CO 2 will be in the exit gases. So, moles of CO 2 will be equal to 1.475 kg moles.

Now, slag contains FeO also. Oxidation of iron will also require oxygen and that we have to find out. So, O 2 for oxidation of iron you can calculate and it will be 1.996 kg mole. So, total oxygen required or total O 2 required will be equal to 9.386 kg mole; that is, you have to add one for sulphur, to SO 2 and iron, to FeO. This is where you require the oxygen. Accordingly, nitrogen would be 35.29 kg moles. So, now I can calculate the amount of gases say - SO 2 will be 7.39 kg moles, CO 2 will be 1.475 kg moles and nitrogen is equal to 35.29 kg moles.

With this, we have done the so called material balance. Now, we are ready to perform heat balance as asked in the problem.

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Now, let us perform the heat balance. Remember: In heat balance, the basis of calculations is always 298 kelvin; unless otherwise, it is specified. I mean 298 kelvin because the heat contained and Cp values are all given at 298 heat of formation of compound and so on; they are all available at 298 kelvin. So, it is desired that you choose the reference of calculation is 298 kelvin. However, you can choose any temperature, but then you have to convert the available value into that temperature. So, that is what I thought (())

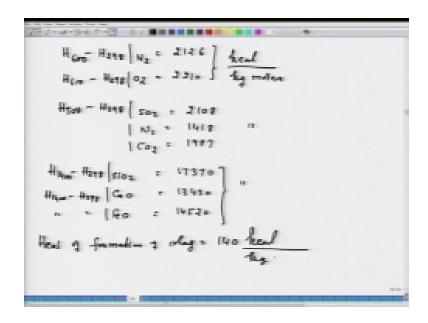
What heat balance says? I will again make a diagram so that I write down all the values over here what I have here. Here I have copper ore, which is charged at 298 kelvin. Then, we charge limestone and that is also charged at 298 kelvin. Then, charge air, which is also charged at 298 kelvin.

Now, we have matte. I mean matte Cu 2 S Fe S. So, matte; we have Cu 2 S equal to 200 kg, Fe S equal to 120 kg and it is temperature is 1400 kelvin; that is important. Then, we have to write down the slag amount; we have FeO, SiO 2 and calcium oxide. So, FeO is 287.5; I mean they are all in kg. SiO 2 is 220.0 kg and CaO is 82.6 kg and it is being discharge at 1400 kelvin.

Next, we take the gases. We have SO 2, CO 2 and nitrogen. SO 2 is 7.39, CO 2 is 1.475 and N 2 is 35.29. The gases are discharged at 500 kelvin. This is what the material balance output is. I have written here so that I can do heat balance effectively.

Let me give other thermodynamic values that are required for the calculation. It is also given - heat content of matte at it is melting point. Let us take melting point as 1273 kelvin; that is equal to 205 kilocalorie. Remember that it is per kg not kg mole. Specific heat of liquid matte is also given as 0.14 kilocalorie per kg. Remember that degree Celsius is also given.

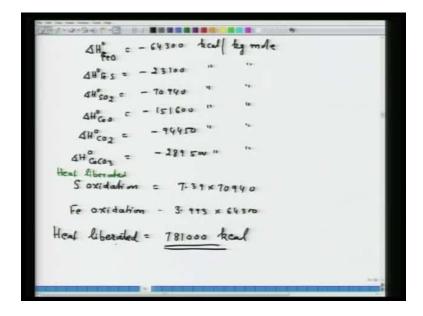
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Some values on the heat content is also given. So, H 600 minus H 298 for N 2 is equal to 2126, H 600 minus H 298 for oxygen is equal to 2210; that are given in kilocalorie per kg mole. Here onwards what I will be giving you are all in kilocalorie per kg mole. H 500 minus H 298 for SO 2, N 2 and CO 2; SO 2 is equal to 2108, nitrogen is 1418 and CO 2 is1987; values are in kilocalorie per kg mole.

Similarly, H 1400 minus H 298 for SiO 2, CaO and FeO; For this also you can write down here as H 1400 minus H 298 and similarly you can put it here. So, the values are 17370, 13430 and 14520; again all that are in kilocalorie per kg mole. It is also given that the heat of formation of slag is 140 kilocalorie per kg of slag.

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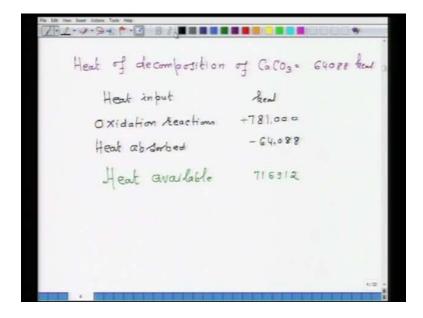


Now, some heat of formation values are also given say - delta H naught FeO; naught means 298. delta H naught FeO is minus 64300 kilocalorie per kg mole. Then, delta H naught Fe S is minus 23100 kilocalorie per kg mole, delta H naught SO 2 is minus 70940 kilocalorie per kg mole, delta H naught calcium oxide is equal to minus 151600 kilocalorie per kg mole, delta H naught CO 2 is equal to minus 94450 kilocalorie per kg mole and delta H naught calcium carbonate when it is form from its element is minus 289500 kilocalorie per kg mole.

Now, since all these data are given to you, I think one can find out the various terms concerning the heat input and heat output. Since the reactance are supplied at 298 kelvin, no sensible heat will be entering into the reactor because they are at 298 kelvin.

The heat supplied term: first will be sulphur oxidation and second is iron oxidation. That will constitute the heat input term. You know that sulphur oxidation is 7.39 into 70940. Now, let me put here that they are heat liberated. Because I am not putting minus sign here, that means I know that they are exothermic reaction. That is why I put this term heat liberated. For iron oxidation or FeO, it will be 3.993 into 64300. So, if you sum total, then the heat liberated will be equal to 781000 kilocalorie. Now, why I have to use heat liberated? Because the composition of limestone is an endothermic reaction.

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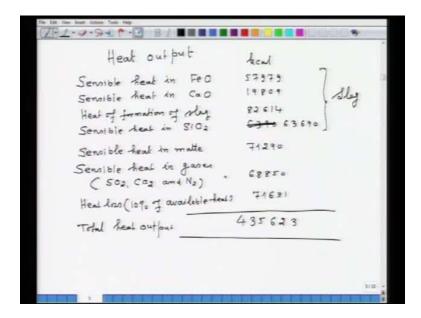


Heat of decomposition of calcium carbonate is equal to 64088 kilocalorie. Mind you: this is a highly endothermic reaction and you will see that much amount of heat will be absorbed.

I had already given the thermochemical data in order to calculate the heat output. Using those thermochemical data, which has been given to you in the problem, heat output by various outputs can be easily calculated. So, I will make the calculation for you. So, first of all, heat input consists of oxidation reaction and the amount of heat input can be easily calculated by using the heat of a formation data and that is equal to 781000 kilocalorie.

Heat absorbed is equal to 64088 kilocalorie. We have to subtract it and that is heat absorbed. For convention, I put this as minus (Refer Slide Time: 42:15) and this is exothermic reaction. I will put it plus so that there is no confusion. So, heat available would be 716912 kilocalories.

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Now, we can write down the heat output. Heat output consists of several items, for example, FeO, CaO, heat of formation and so on and so forth. I will write down all the things for you.

For sensible heat in FeO; I will put here in kilocalorie; that is equal to 57979 kilocalorie. Sensible heat in CaO is 19809. Heat of formation of slag that is 82614 kilocalorie. Sensible heat in SiO 2 is equal to 63690. All these 4 correspond to be taken out by slag. Then, sensible heat in matte is equal to 71290 kilocalorie. Sensible heat in gases; you know that the gases comprise of SO 2, CO 2 and nitrogen; that is equal to 68850.

As said in the beginning, then heat loss... Now, if not mentioned, for solving the problem, normally people take 10 percent of the heat available. If it is given, then you have to take the actual.

Let us say heat loss is 10 percent of the available heat. So, this makes 71691 kilocalories. So, total heat output is 435623. You see that heat input is much greater than heat output. So, the process is autogenous in nature.