Materials and Energy Balance in Metallurgical Processes

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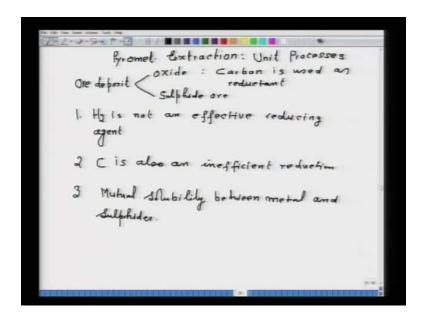
Module No. # 01

Lecture No. # 14

Pyromet Extraction Unit Processes

Let us now consider pyrometallurgical extraction of metals and the unit processes that are required to extract metal from the respective ores. Now, what will I do? I will first of all, give the general introduction and then I will consider one by one unit processes required for extraction of metal through pyrometallurgical root.

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Now, all of you know that ore deposits in the nature; they are either oxide ores or you have sulphide ores. Now, with this I mean that most of the metal ore deposits, they are either in the form of oxides or in the form of sulphides - majority of the metal occurs in these two particular forms.

As you recall that the production of metal involves removal of oxygen from the valuable mineral that is for example, oxygen from Fe 2 O 3 and then followed by separation of metal from the gangue mineral; whereas in the oxide ore, it is easy to reduce the oxide by carbons. I have also mentioned that the reductant should be easily, economically and cheaply available.

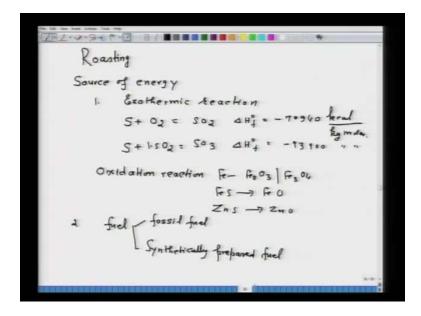
You can look at the Ellingham diagram, which is a plot of RT In PO 2 against temperature. You can find out which element can reduce the oxide, so you will note that the several elements can reduce for example, Fe 2 O 3 but one element which is abundantly, cheaply and economically available that should be used. So in this connection, for oxide ore in most of the cases, carbon is used as a reductant. Carbon can easily reduce Fe 2 O 3 or if we have zinc oxide then it can also easily reduce and we can get the metal.

Now, as regards sulphide ore, there are certain issues. So, as regards sulphide ore, there are problems that it is very difficult to reduce sulphide directly into the metal. First say, hydrogen is not an effective reducing agent to produce metal from sulphide. Second, carbon is also an inefficient reductant. This information you can get from Ellingham diagram of sulphides.

Third issue in case of reduction of metal sulphides, that there exist a mutual solubility between metal and sulphides. This mutual solubility between the metal which is produced with the sulphide, it makes extraction very difficult. Therefore, the production of metal from sulphides cannot be done by directly reducing sulphide into metal; so the only route is that for sulphide to be converted to oxide.

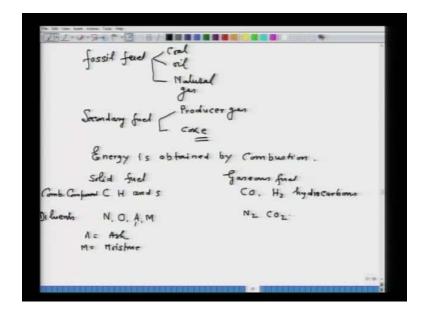
Therefore, in all pyrometallurgical extraction of metal from sulphide ore, one of the important unit process is called the roasting. This is the most important unit process for production of metal from sulphide ore and the process is called the roasting. Now, before I go in detail about the roasting, it is also important to note that all pyrometallurgical extraction they require source of energy. I give a brief account of source of energy which is then followed by roasting.

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Let us talk little bit about source of energy. Source of energy: 1 it could be exothermic reaction. For example, S plus O 2 that will give you S O 2 and delta H naught f at 298 that is equal to minus 70940 kilo calorie per kg mole, highly exothermic reaction or it is also possible formation of sulphur trioxide and where delta H naught f that is equal to minus 93900 kilo calorie per kg mole or certain other oxidation reactions for example, iron to Fe 2 O 3 or Fe 3 O 4 it may also release heat then Fe S to Fe O or Zn S to Zn O and so on. They are also the source of production of energy is required for almost all pyrometallurgical extraction. Another source is the fuel and here one has fossil fuel and synthetically prepared fuel.

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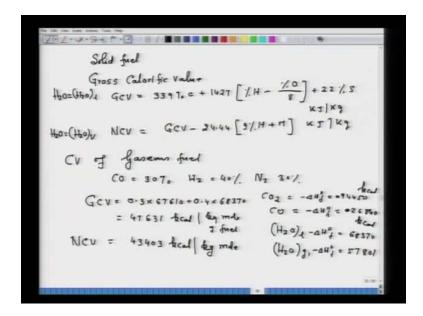


Under fossil fuel, one can use coal, oil or natural gas All these fuels are used for generation of thermal energy and the secondary fuel that could be derived from the fossil fuel, one is the producer gas and another is the coke. You know coke; it is used for reduction smelting in blast furnace of production of iron; it is not a naturally occurring material.

In all these fuels, that is whether fossil fuel or secondary fuel, the energy is obtained by combustion. Now, in all fuels, we have combustible component and we have diluents for example, in solid fuel the combustible component of carbon, hydrogen and sulphur, they are the combustible component. That means, they will combust and release the amount of energy contained in the fuel in the form of products of combustion. Whereas, diluents or sometimes they may also be called incombustible components, they are nitrogen, oxygen, ash and moisture; A - stands for ash and M - stands for moisture.

Whereas, in case of gaseous fuel, the combustible components are carbon monoxide; then hydrogen, then hydro carbons. Hydro carbons and diluents are nitrogen or carbon-di-oxide because they do not take part in the combustion. So of the fuel, the most important in case of pyrometallurgical extraction is the amount of energy released.

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In case of solid fuel, the amount of energy released by combustion of 1 kg of fuel and the products of combustion, are considered in the reference state that energy is called the calorific value. We define 1 as the gross calorific value; so we can calculate gross calorific value. Now, in calculation of gross calorific value, the standard state of product of combustion H 2 O, is H 2 O liquid.

This can be calculated by a formula GCV that is equal to 339 percent carbon plus 1427 percent H minus percent O upon 8 plus 22 percent sulphur, we get the value in kilo joule per kg carbon. Whereas, in NCV the state of H2O is vapor, so in NCV the state of H2O, that is equal to H2O vapor- where in GCV the state of H2O that is equal to H2O liquid. NCV that is equal to GCV minus 24.44 9 percent H plus moisture, again kilo joule per kg.

Now, I am not going into the details because my emphasis is on the unit process. So just, we may be requiring these energy values while performing the heat balance in the various unit processes. However, those who are interested in these things I have detailed in my video lecture course on fuel furnace in refractory, very detailed accounts on this calorific value and analysis all are given. So, you are requested to refer to those particular lectures.

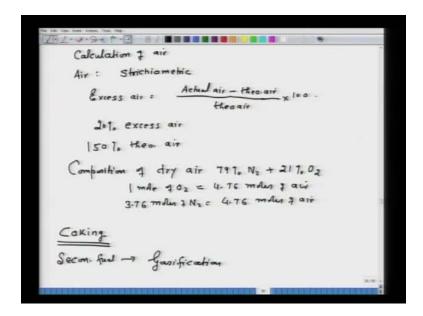
Similarly, we can determine calorific value of gaseous fuel from various heat of formation or heat of combustion value of the products of combustion. Now, for example, let us take a fuel, which has say C O that is equal to 30 percent, H 2 that is equal to 40 percent and nitrogen that is equal to 30 percent. Now, by knowing the heat of formation value of the C O and hydrogen because, here C O and hydrogen are the combustible component, you know that for C O 2 minus delta H naught f that is equal to minus 94450 kilo calorie per kg mole.

For carbon monoxide that is equal to minus 26840 kilo calorie, so you can determine those. Though we can get the gross calorific value that will be 0.3 into 67610 plus 0.4 into 68370, whereas the H 2 O liquid, the minus delta H naught f that will be equal to 68370. Now, since I have written minus delta H naught f here, so there is no need to write here minus or minus that implies this one (Refer Slide Time: 14:32).

Whereas H 2 O gaseous minus delta H naught f that is equal to 57801. So, if I calculate GCV that will come 47631 kilo calorie per kg of per kg mole of fuel because, we have selected 1 kg mole of fuel. Similarly, I can calculate NCV, only I have to substitute here for H 2 O vapor then I will be getting 43403 kilo calorie per kg mole. So these calculations will need, while performing heat balance in the unit processes that will be taking.

Now, another important thing, in case of this combustion is the calculation of air. Here also you will find detailed description in my video lecture course on fuel furnace in refractory, I am giving a very brief account.

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Calculation of air, you may use stoichiometric amount; stoichiometric amount is that amount which is required for complete combustion C to C O 2, H 2 to H 2 O. Also by observing the stoichiometric of the reaction, whatever amount of oxygen and from there, you calculate the amount of air that is called the stoichiometric amount of air. That means, the stoichiometric amount of air is calculated by following the stoichiometric of the reaction - any chemical reaction. If you follow the stoichiometric then you are calculating the stoichiometric amount of air.

Now, in several calculations, you require to calculate excess air. Now, this excess air that is equal to actual air minus theoretical air. Now, this theoretical air is also called stoichiometric air and is also called air for perfect combustion all these names they mean, that you have calculated the amount of air by observing the stoichiometry of the reaction divide by theoretical air into 100.

We can express for example, if you say 20 percent excess air then in fact, we are using 120 percent theoretical air. You may say, we are using 150 percent theoretical air then, we can say, we are using 50 percent excess air. So, these are the different name that you will find while solving the problems on the unit processes.

Also, we will take composition of dry air, will take 79 percent nitrogen plus 21 percent oxygen. So, with this 1 mole of oxygen - 1 mole of O 2 - that is equal to 4.76 moles of

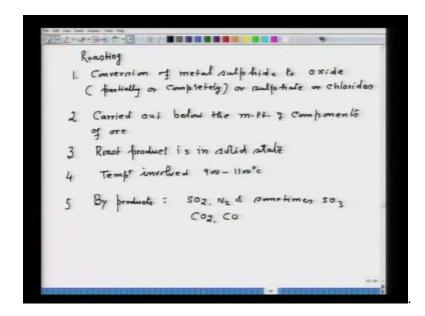
air or 3.76 moles of nitrogen that is equal to 4.76 moles of air, whichever we want to understand.

Now, also, the temperature raised by the products of combustion is called adiabatic flame temperature. This temperature can be easily calculated, if required for the heat balancing operation in unit processes by doing the heat balance; heat input is equal to heat output. Now, all these illustrations is very detailed given in my video lecture course on fuel furnace and refractory. Here, I have just given brief account as required for calculation on the material and heat balance in case of unit processes.

Now, here, I will also like to give a brief account on as I said that pyrometallurgical extraction also uses the so called coke. The process of manufacturing of the coke is called coking. In coking, coal is heated out of contact of air and the product which is obtained after heating is called the coke. Remember, coke is not a natural reserve of fuel; it is prepared by distractive distillation of coal that is, heating the coal out of contact of air.

Another term that I have use is secondary fuel and this secondary fuel is prepared by gasification process. That is here, the coal is converted to a gaseous fuel by using air plus steam, so the product of gasification will be C O and hydrogen. So, this is just a brief account of the source of energy for carrying out the high temperature pyrometallurgical extraction processes. s with these brief accounts, I will now say to proceed to the roasting - that is what the first unit process.

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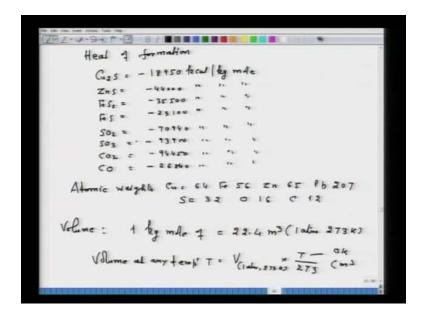


Now, roasting in fact is a first step to extract metal from sulphide ores. As I said, sulphide ores cannot be used to produce metal directly by reduction either by carbon or hydrogen. First step roasting is performed and roasting is conversion of metal sulphide to oxide - partially or completely oxide - that will depend on type of metal, partially or completely or sulphate or chlorides because oxide can easily reduced; sulphate can be easily dissolved and that is why roasting is a first step to extract metal from sulphate ore.

Second: it is carried out - that is an important; carried out below the melting point of the components of the ore that means, you do not go above the melting point. By virtue of this, the roast product is in solid state. You have ore concentrate in the solid state, so roast product is also in the solid state. The temperature involved during roasting is of the order of 900 to 1100 degree Celsius however, it depends upon the various factors.

Another important manifestation of roasting is that say, byproduct of roasting - product is roasted ore or roast product whatever you want in the byproducts of roasting - they are S O 2; rich S O 2 because sulphide ore has 20 percent sulphur or even 30 percent of the sulphur depending on the deposit, so a large amount of a S O 2 will be produced; Nitrogen and sometimes S O 3. All these sulphurious gases S O 2, S O 3 can be used to manufacture H 2 S O 4 and if fuel is also used then you may have carbon dioxide and C O is also possible here.

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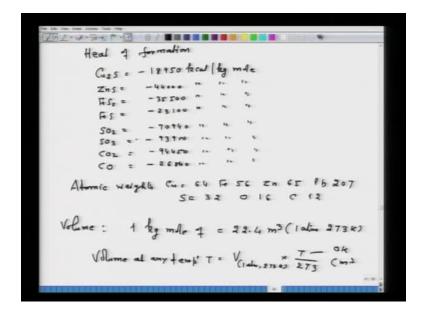


Now, certain heating value, I would like to give you certain heat of formation value, so that you can see large amount of heat is generated during roasting. For example Cu 2 S, it as heat of formation minus 18950 kilo calorie per kg mole; Zn S minus 44000 kilo calorie per kg mole; Fe S 2 minus 35500 kilo calorie per kg mole; Fe S minus 23100 kilo calorie per kg mole and then you have S O 2, S O 3, C O 2 and C O. S O 2 is minus 70940; S O 3 is minus 93900; C O 2 that is minus 94450 and C O minus 26840 (Refer Slide Time: 25:29).

However these values, we will be using when we do the heat balance of the roasting process. Now, various atomic weights that we will use for calculation: atomic weights copper I will be using 64, iron 56, zinc 65, lead 207, sulphur 32, oxygen 16, carbon 12, I will not be using any fraction, so these are the things that I am using (Refer Slide Time: 26:15).

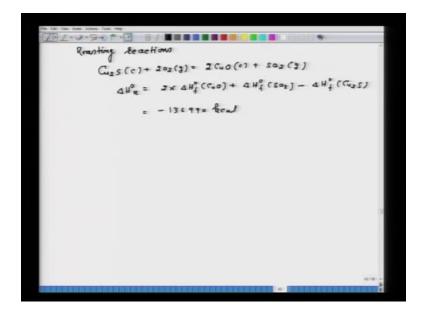
Also, volume of gas I will be expressing say1 kg mole of any gas that is equal to 22.4 meter cube at 1 atmosphere and 273 kelvin. So, volume of gas at any temperature T that will equal to V at 1 atmosphere and 273 kelvin into T upon 273, where T is in degree kelvin that will be meter cube at 1 atmosphere and the refer temperature.

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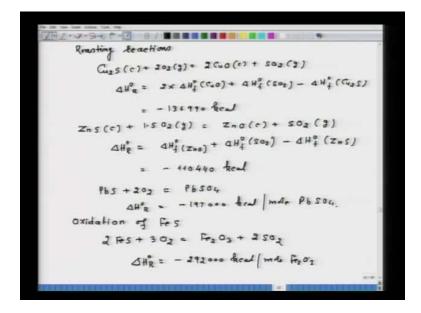
Now, let us see, the amount of heat that is generated by certain roasting reaction. Now, as I said, the roasting converts sulphide into oxide. Some roasting reactions for example, Cu 2 S in condense phase plus 2O 2 gaseous that is equal to 2Cu O condense phase plus S O 2 gaseous phase. Now, I can calculate the heat of reaction that will be delta H naught R that will be equal to 2 into delta H naught f Cu O plus delta H naught f S O 2 minus delta H naught f Cu 2 S. If you substitute the value, you will be getting that will be equal to minus 136990 kilocalorie. You see that the roasting very large amount of heat is generated and if the caution is not exercise then there is a chance that the material of the container, it may attain a very high temperature - you can see now.

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Let us take another reaction, say roasting of zinc sulphide; zinc sulphide in the condense phase plus 1.5 O 2 in the gaseous phase. You will get Zn O condense phase plus S O 2 again in the gaseous phase. Now, here again, you have to write delta H naught R heat of reaction that will be equal to delta H naught f Zn O plus delta H naught f S O 2 minus delta H naught f Zn S. Now, here I have not write delta H naught f for oxygen, because the element that is equal to 0, so there is no need to write.

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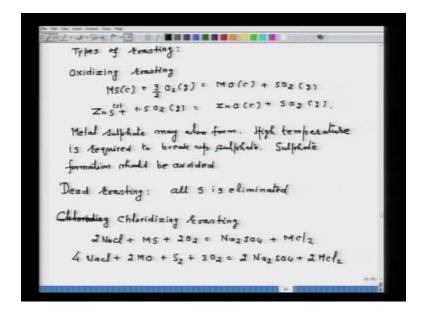


So, if I calculate this and substitute the value, you will be getting minus 110440 kilo calorie. You note form here that roasting it can be an autogenous process. An autogenous process is one which does not require any heat from outside. The heat which is generated because of the chemical reaction is so high that sometimes, you have to do or you have to cool it so that the temperature does not over shoot.

Similarly, another product you can have in the roasting of Pb S plus oxygen that may form Pb S O 4 and its delta H naught reaction that is equal to minus 197000 kilo calorie per mole of Pb S O 4. Similarly, another very important reaction in case of roasting of sulphide ore is the oxidation of iron sulphide. Now, for your information, all sulphide ore they occur along with the iron, that means for example, an ore of copper it has Cu Fe S 2. Iron is a part of the sulphide ore. In almost all sulphide ore you will find iron is also there. So many time the oxidation of Fe S or Fe S 2 that generates a very large amount of heat.

Let us see now, oxidation of Fe S. We can write down 2Fe S plus 3O 2 that is equal to Fe 2 O 3 plus 2S O 2. We can write down here delta H naught R that is equal to minus 292000 kilo calorie, this is per mole of Fe 2 O 3 (Refer Slide Time: 32:07).

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You note these are the order of magnitude of the heating value that will be generated during roasting. Now, let us see, the types of roasting. The different types of roasting:

one is oxidizing roasting. What I have written is the heat of formation value, say you have oxidizing roasting.

Now, oxidizing roasting, you have sulphide plus 3 by 2 O 2 in gaseous state that is equal to oxide in the condense phase plus S O 2. Now, for example, I have Zn S plus 1.5 O 2 in gaseous state here it is the condense state that is equal to Zn O condense plus S O 2 this is gas and this is gas. Now, in carrying out- The essentially oxidizing roasting means take a sulphide ore and pass air, provided in an oxidizing atmosphere. You have to control the amount of oxidation so that the formation of metal sulphate, it does not form if it is not required.

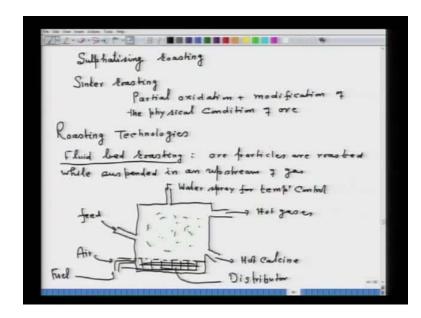
In this oxidizing roasting many times metal sulphate may also form. Now, when metal sulphate form then high temperature is required to break up the sulphate. Now, suppose, you have supplied large amount oxygen then Pb S is converted to Pb S O 4 in addition to PbO. Now, what an amount of lead that is gone to Pb S O 4 or zinc to Zn S O 4 that is lost.

Normally, you require high temperature to break up the sulphate. Therefore, sulphate formation should be avoided when? The extraction of metal is done by pyrometallurgical means. However, if the extraction of metal is done through hydrometallurgical means then, sulphate formation is required because sulphates are easily soluble in the solvent that you are going to use. Now, another important roasting is called dead roasting. Now, the term dead roasting means, when all sulphur is eliminated and entire sulphide is converted to oxide this is called dead roasting. In dead roasting all sulphur is eliminated that is called the dead roasting.

Now, another type of roasting is Chloridizing roasting. As the name suggests, the objective of chloridizing roasting is to convert a sulphide into chlorides. So, the reaction could be a 2 Na cl; Na cl is normally used plus Ms that is a sulphide plus 2O 2 that is equal to Na 2 S O 4 plus M cl 2, you can all this is a direct chlorination.

Another is an indirect chlorination, where you use a reducing agent 4Na cl plus 2M O plus S 2 plus 3 O 2 that is equal to 2 Na 2 S O 4 plus 2 M cl 2. So chloridizing roasting is done to converts sulphide into chloride or oxide also into chloride that is what the chloridizing roasting.

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Now another roasting is also called Sulphatising roasting. As the name suggests, in the sulphatising roasting, the objective is to convert sulphide into sulphate and this is particularly required when you extract metal from hydrometallurgical means because, in the hydrometallurgical means you want that the metal should be dissolved and sulphates are easily soluble as compared to sulphites.

Another important method is Sinter roasting. Now, in sinter roasting, what is done the partial oxidation - I mean yes roasting is what partial or full oxidation- plus modification of the physical condition of the ore that is called sinter roasting. It has come from two word, sinter as well as roasting; roasting means oxidation and sintering means, you want to decrease of porosity of the sinter product. For that you again heat up and that process is called sintering. So, that is called the sinter roasting in fact both the sinter roasting oxidation plus sintering.

Now, let us see some of the roasting technologies. Now, what you require? All that you require an ore concentrate that is, a mechanism of feeding of ore concentrate. Then mechanism of supply of air because you want an oxidizing medium of course, you require a container and then a mechanism of output of the roast product. Sometimes roast product is also called Calcin and mechanism for the discharge of the gases that will in short be comprised of the so called roasting reactor.

So, for that now here one can think of, you create a bed of ore concentrate allow the air to flow and let the roasting carried out in fixed bed or you allow the particles to react with air, so there could be several ways in which the ore concentrate is supplied to an oxidizing medium.

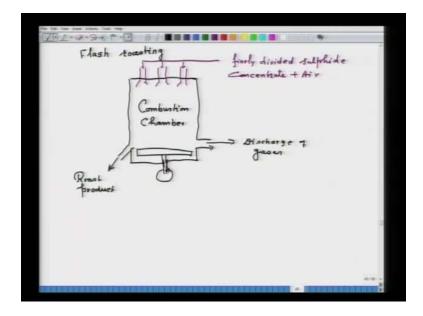
Now, say for example, in fluid bed roasting ore particles are roasted while suspended in an upward stream of gas. Now, mind you, this mechanism will have very high reaction rate because particles will be suspended directly in the air and very high surface area is exposed, so a very high reaction rate can be observed.

In the fluid bed roasting for example, something like this it can go (Refer Slide Time: 42:08). This one is for discharge of hot gases. Somewhere here, the discharge of hot Calcin you called hot Calcin or roast product they all have. Then they have form here, if some fuel is required for some purpose then there is a provision of supply of auxiliary fuel and here, you have the feed and somewhere here, this one and you supply air (Refer Slide Time: 43:21).

So, the particles are roasted while they are in suspension and this one is called a distributer, because when air is supplied, it distributes the air. So that the particles get sufficient amount of air and here sometimes what is being done? The temperature goes very high; so here, water spray for temperature control.

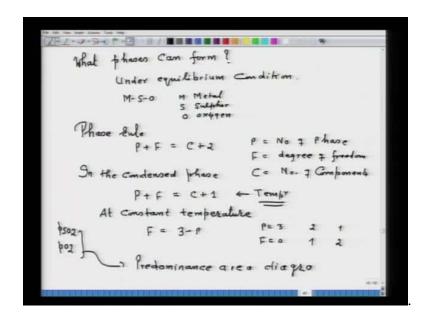
This is one of the methods of fluid bed roasting. Now, in fluid bed roasting, the heat losses are relatively small but, the temperature can rise to a very high value. There are two ways, either you have a water spray or the excessive temperature is controlled by controlling the excess amount of air, because when we use excess amount of air the nitrogen will take away the necessary heat and so you control the temperature, this is one of the methods. Another method is flash roasting. Now, in flash roasting, the finally divided sulphide concentrate plus air that is a mixture of both is passed in a reactor and there occurrs the roasting.

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That is for example, here this is the reactor (Refer Slide Time: 45:14). Here the roast product; this is the discharge of the gases and here, this is a mechanism which rotates and here the feed which consist of concentrate and air. So here, here and here, you have the finally divided sulphide concentrate plus air (Refer Slide Time: 46:31). Here roast product is out and this is in fact the combustion chamber. This rotates to make the easy discharge of the roast product. This is again another type of method, there is still other method multiple hearths roasting and so on. The details can be seen, I will give the reference towards the end. So that you are aware the methods because the whole my objective of this presentation is only to make you feel, what is a roasting, so that when we do material and heat balance you are aware what roasting consist of.

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Now, after having seen these various aspects of roasting, what is important in case of roasting is to know, what phases can form? We have metal sulphide to start with and we supply the oxidizing air there are several phases can form depending upon the partial pressure of oxygen in air and partial pressure of SO2.

Phases like sulphate, oxide, metal and intermediate oxide or sulphide anything can form. The question comes what phases can form? Suppose, if you want to control the process of roasting, you want a particular phase for a particular method, so that pyrometallurgical extraction become easier how to control these phases? The control of the phase or the prediction which phase can form, it can be done under equilibrium condition, with that I mean, if we consider a system for example, M S and O; M stands for metal, S for sulphur and O for oxygen.

If you consider M S O; this is system metal, sulphur and oxide then, prediction of phases can be made by doing certain thermodynamic calculation for formation of different product. That means what we should control? What parameter should be controlled, so that a particular phase is formed and this information can be obtained from phase rule.

I hope all of you must be aware by phase rule that is, which parameter can be controlled so that a particular phase forms this information can be obtained by phase rule. Phase

rule, we have P plus F that is equal to C plus 2, where P is number of phases, F degree of freedom and C number of components.

Now, this 2 is coming because here temperature and pressure are the factors or the thermodynamic parameter that will control the roasting process. Now, in the condense phase, the pressure has no effect. We can consider the modified form of phase rule P plus F that is equal to C plus 1.

Now, here, the temperature has remained a controlling factor. Suppose, we consider a constant temperature because, normally roasting is carried out at constant temperature. At constant temperature what will happen? We will have F that is equal to 3 minus P; 3 is coming because number of component are 3 M, S and O. Now, F the number of degrees of freedom that is equal to 3 minus P, if we have P is equal to 3 then degree of freedom that is equal to 0.

If we have P is equal to 2 then, degree of freedom is equal to 1 and if we have P is equal to 1 then, degree of freedom is equal to 2. That means, in this particular representation when we have taken a constant temperature then P S O 2 and P O 2 these are the two variables that will control the formation of which phase at a given temperature.

Mind you in deriving this, we have considered temperature to be constant. So, when we want to get the information of which phase you will form, then it is a P S O 2 and P O 2, both these parameter will decide. Based on this, if you perform the thermodynamic calculations of the various equilibrium reaction that can occur between sulphide and oxygen then, we get a diagram which is called predominance area diagram. From the predominance area diagram, one can get the information what should be a combination of P S O 2 and P O 2 at a given temperature. If we want a particular phase that will be a subject matter of next lecture.