

Materials and Energy Balance in Metallurgical Processes

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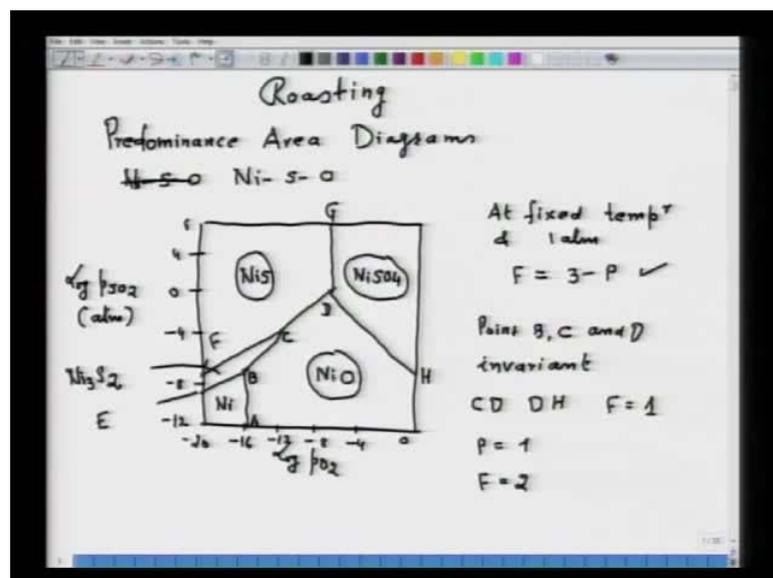
Module No. # 01

Lecture No. # 15

Predominance area Diagram

Let me give little more concept on roasting before we proceed to material and heat balance. As I said earlier, roasting is a heavy process especially implied for conversion of sulphide to oxide in behalf of the difficulties that I have already initiated.

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Now, one of the important things in case of roasting is to predict the phases or number of phases which can form at a particular temperature. So that information can be derived from the predominance area diagram; I will give little bit detail about the predominance area diagram. As the name suggest, this predominance area diagram gives the information about the stability of a phase for a given partial pressures of SO₂ and oxygen. Remember, this predominance area diagram is constructed at constant temperature and pressure.

As I have said that when we apply the phase rule to the equilibrium of the phases, when there is a condensed phase and also temperature is a constant, then the degrees of freedom it becomes equal to 3 minus p. Accordingly, we need a three dimensional diagram if we want to construct a predominance area diagram for MSO system that is metal sulfur and oxygen system, where p_{SO_2} , p_{O_2} and temperature are the variables. But now, if you take temperature also as a constant, then for a given temperature we can predict the equilibrium phases by considering the variation of p_{SO_2} and p_{O_2} .

Now, let us consider a system; for example, nickel sulfur and oxygen system. Let us consider a system, which is nickel sulfur and oxygen system. Let me draw the predominance area diagram, so these are the axis; here we have log of p_{SO_2} in atmosphere; here we have log of p_{O_2} and the skills are say minus 20, say minus 16, minus 12, minus 8, minus 4 and here it is start from minus 12, then we have minus 8, we have minus 4, then 0 and 4 and 8. These are just order of magnitude (Refer Slide Time: 02:30).

The lines that I am going to draw may not comply with the value of the axis that I have given, so that goes something like this (Refer Slide Time: 03:40). This one, this one and then as shown, these are the variations. So here, the various phases are this is nickel sulfide, this is $NiSO_4$, this is NiO , this is nickel and this one is Ni_3S_2 .

These diagrams are drawn at fixed temperature and at one atmospheric pressure. Under this condition, the degree of freedom F becomes equal to 3 minus P; so what we have to note from this figure? The stability of the phases; there are regions, I will just note down the point. Let me take this is at A, this is at B, this is C, this one is E, this one is F, D, G and H (Refer Slide Time: 05:00).

So, the diagram contains the variation of p_{SO_2} and p_{O_2} , and the variations are shown in terms of the lines; for example, D H, C D, B C and C F. Then the diagram also has the invariant point; for example, the point B, C and D are invariant points, what does that means an invariant point? That means, here the degree of freedom should be equal to 0. All the three phases will coexist at a particular value of p_{SO_2} and p_{O_2} , so you see at point D the phases NiS , $NiSO_4$ and NiO will coexist. At point C NiS , Ni_3S_2 and NiO will coexist; at point B, NiO and Ni_3S_2 will coexist. According to phase rule, number of

phase is equal to 3 then degree of freedom is equal to 0; that means, these B, C, D are the invariant point in the predominance area diagram.

Whereas, the lines say along the line C D or line D H; what we have there? If the number of phases are 2 then we have degree of freedom F is equal to 1; that means, along the line the degree of freedom is equal to 1; that means, the NiS or NiO can be present at different values p_{SO_2} for a given value of p_{O_2} or for different value of p_{O_2} for a given value of p_{SO_2} ; that is what? This means the variation of p_{SO_2} with p_{O_2} along the line C D D H.

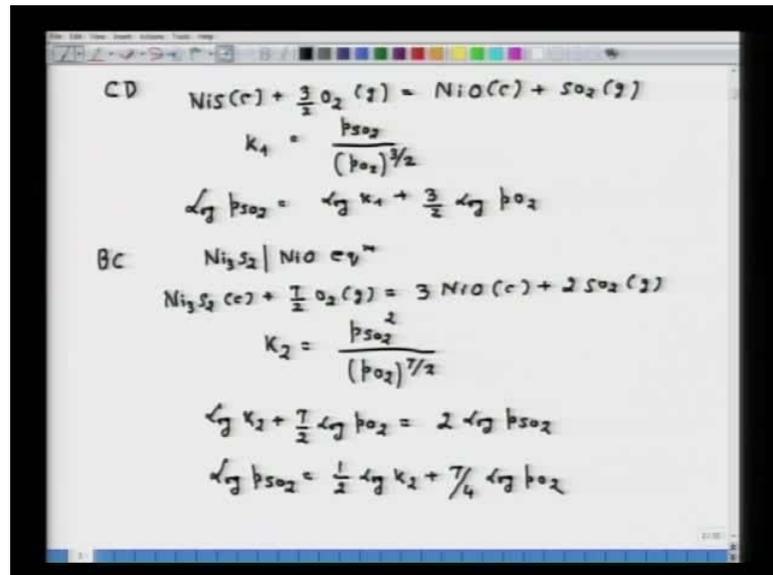
Now again, say if we put; for example, p is equal to 1 then we get f is equal to 2 that is degree of freedom is equal to 2, these regions are represented by the area. That means, the phase NiO, the phase NiS, and phase NiSO₄ can exist for a various combination of p_{SO_2} and p_{O_2} .

For example, this NiO can exist at different value of p_{SO_2} or p_{O_2} . Several values of p_{SO_2} and p_{O_2} can make phase NiO stable that is what the degree of freedom; that means, you have two degrees of freedom, you can change p_{SO_2} and p_{O_2} and get the phase; for example, NiO or NiSO₄ or NiS, so that is what the principle of construction of these diagram means.

Now these diagrams are in fact constructed by considering the equilibrium values; that means, in the system NiSO we have to consider all possible reactions which can take place. Once, you consider all possible reaction we have to know the free energy value, from the free energy we calculate the equilibrium constant and from the equilibrium constant we find out the variation of p_{SO_2} and p_{O_2} , and of course the temperature is constant.

Also, in order to avoid the complexity these diagrams are constructed by considering the activity of the condensed phase that is equal to one. However, if the activity is not less than one then a prediction about the phases which is made from this diagram has to be modified. So, what I am going to illustrate in the following is how to construct these diagrams to know the stability of the phases by considering that the activity of condensed phase is equal to one.

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So, let me write down first of all the reactions; for example, the line C D, if you see the predominance area diagram the line C D represents the equilibrium between NiS which is at condensed phase plus 3 by 2 O₂ gaseous phases that is equal to NiO condensed phase plus SO₂ gas.

The line represent the equilibrium between NiS and NiO, if I write down the value of K₁ as I said they are putting it by taking **condensed phase is equal to** the activity of condensed phase is 1 - that is the pure phase. Then, K₁ will be equal to p_{SO2} upon p_{O2} to the power 3 by 2. As such, I can write down log of p_{SO2} that will be equal to log of K₁ plus 3 by 2 log of p_{O2}.

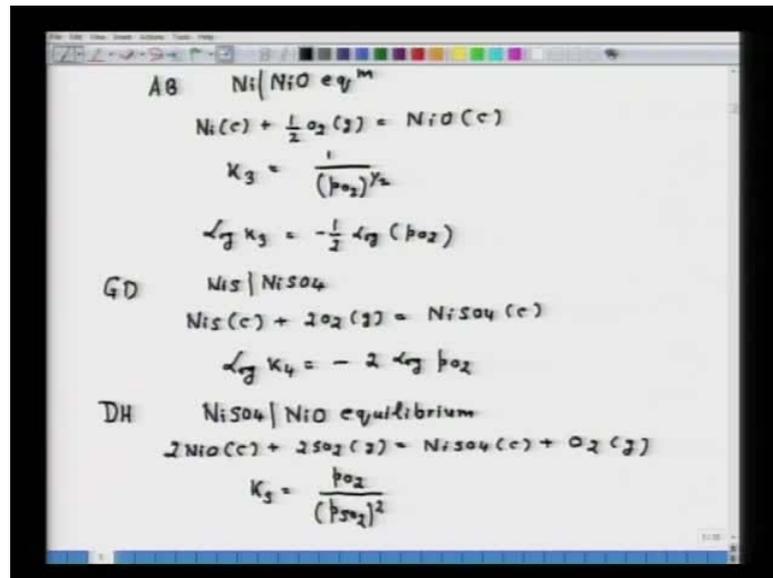
If I plot K₁, I know from the delta log values how p_{SO2} varies with log p_{O2}, I can take various values. If you plot log p_{SO2} against log p_{O2} the slope of the lead will be 1.5. So, that is how these diagrams are constructed; you place this line in the diagram.

Now, you have to consider next equilibrium; for example, if you notice in the diagram the line B C represents the equilibrium between Ni₃S₂ and NiO, this equilibrium, this lines means, now I put it the equation Ni₃S₂ condensed phase plus 7 by 2 O₂ gaseous phase, that is equal to 3 NiO condensed phase plus 2 SO₂ gaseous phase.

Again, I have to know the delta g naught values and then I can calculate K₂ that will be equal to p_{SO2} raise to the power 2 upon p_{O2} raise to the power 7 by 2. If I put log of K₂

plus 7 by 2 log of p_{O_2} that will be equal to 2 log p_{SO_2} , so I have to find out relation between p_{SO_2} and p_{O_2} , in this case log of p_{SO_2} that will be equal to 1 by 2 log of K_2 plus 7 by 4 log of p_{O_2} . So again, if you plot for this equilibrium, Ni_3S_2 NiO equilibrium, in a log p_{SO_2} against log p_{O_2} plot then this slope will be 7 by 4.

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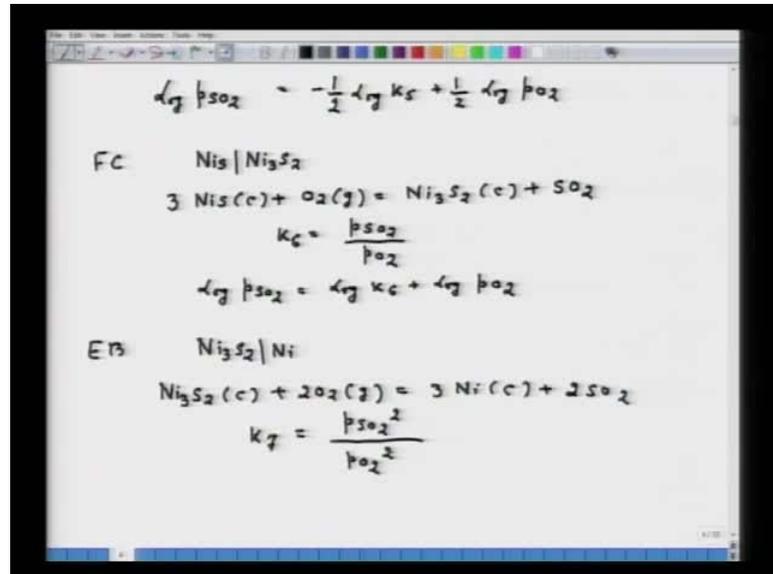
If I consider; for example, AB - the line AB represents Ni NiO equilibrium, so I will write down nickel condensed phase plus half O₂ gaseous phase that is equal to NiO condensed phase. So, K_3 that will be equal to 1 upon p_{O_2} to the power half, from here log K_3 that will be equal to minus half log of p_{O_2} .

So, you see Ni NiO equilibrium is independent of p_{SO_2} and hence a vertical line in the predominance area diagram for nickel sulphur oxygen system. Now, if you consider line GD, line GD in fact is the equilibrium between NiS and NiSO₄. So, this is equilibrium between NiS and NiSO₄, again I write down the equation say NiS condensed phase plus 2 O₂ gaseous phase that is equal to NiSO₄ condensed phase.

If I write down log of K_4 that is equal to minus 2 log p_{O_2} , you see NiS NiSO₄ equilibrium is also independent of p_{SO_2} . Therefore, we will also get a vertical line on log p_{SO_2} verses log p_{O_2} plot. Line D H, now D H represents NiSO₄ NiO equilibrium, so I will write down 2 NiO condensed phase plus 2 SO₂ gaseous phase that will be equal to NiSO₄ condensed phase plus O₂ gaseous phase. These reactions which I have written,

remember these are the stoichiometric reaction; that is an important thing that they are the stoichiometric reactions.

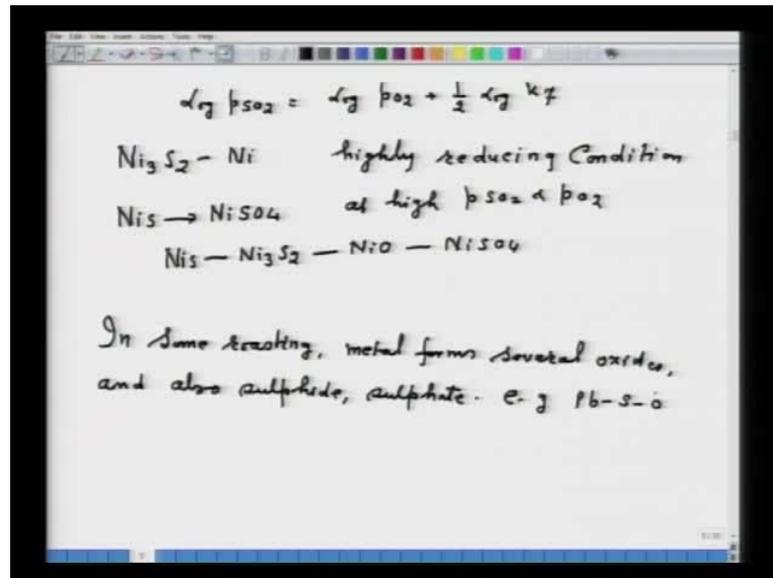
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We can write down K5 that is equal to pso2 upon po2, so simply that become log of pso2 that will be equal to minus half log K5 plus half log po2, so that is how it look basically. Now again, we look at the line FC, line F C represents equilibrium between NiS and Ni3S2. So, we have to write down the stoichiometric reaction, 3 NiS condensed phase plus O2 gases phase that is equal to Ni3S2 condensed phase plus SO2.

We can write down log of K6 that will be equal to pso2 upon po2; we can write down log of pso2 that will be equal to log of K6 plus Log of po2 that is how the equilibrium between NiS and Ni3S2 goes. The last line EB represents the equilibrium between Ni3S2 and Ni. We can put the equation Ni3S2 condensed phase plus 2 O2 gaseous phase that will be equal to 3 nickel condensed phase plus 2 SO2.

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If I write down K7, it will be equal to p_{SO_2} power 2 upon p_{O_2} to the power 2. So, if I simplify and rearrange, I get \log of p_{SO_2} that will be equal to \log of p_{O_2} plus half \log K7. What I mean to say here is these are the various equilibrium values on which the construction of the diagram is based.

That means, now from the literature one has to obtain the value of ΔG_{naught} for a respective reaction, if it is not available then we have to determine the values and from the value of ΔG_{naught} . One can find out the value of K, then one can plot this diagram and then one can know that these are the stable phases at a particular temperature which will depend upon the variation of p_{SO_2} and p_{O_2} .

Now here, a caution is needed, because these diagrams at the present what I have illustrated there I have taken the activity of the condensed phases is equal to 1. In case, when the activity is not equal to 1, then the pressure variation will shift according to the magnitude of the activity coefficient that is represented by the deviation from the ideal behavior.

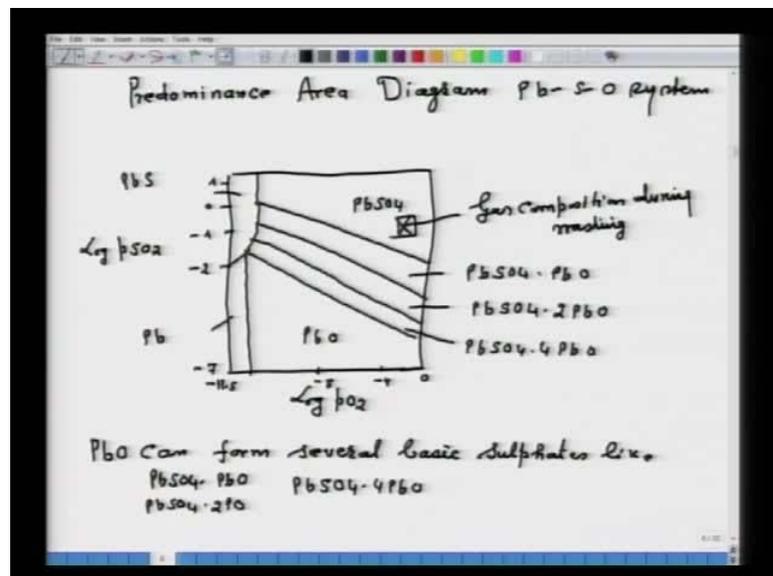
What we have seen from here is that the phase $NiSO_4$; if you look to the predominance area diagram it is possible under highly oxidizing condition, whereas the reduction of NiS or Ni_3S_2 nickel is also possible under highly reducing condition. So, like this these information can be obtained from these diagram that means, I just note down two or three information; that means, Ni_3S_2 to nickel based on the predominance area diagram

is possible under highly reducing condition, whereas if we want to convert nickel sulphide to nickel sulphate NiSO_4 then it is possible at high p_{SO_2} and p_{O_2} . You see this diagram, it is on the extreme right side the NiSO_4 exist, but in practice the nickel sulphide is converted to nickel sulphate through the following route. Nickel sulphide first converted to Ni_3S_2 , then converted to NiO and then converted to NiSO_4 .

One prediction that is made by the diagram is possibility of NiS to NiSO_4 , it is possible under highly reducing condition. But then, again it comes to the economic feasibility, so economically it is done NiS Ni_3S_2 NiO and then to nickel sulphate. That means, this information they are to be modified by the practical considerations.

Now, in roasting operation the metal form several oxides and sulphides - basic sulphate and sulphate. For example, in some roasting the metal forms several oxides and also sulphides, sulphate. For example, the system lead sulphur and oxygen; let us see the predominance area diagram of lead sulphur oxygen, because lead is also an important metal and the lead also occurs in the sulphide form.

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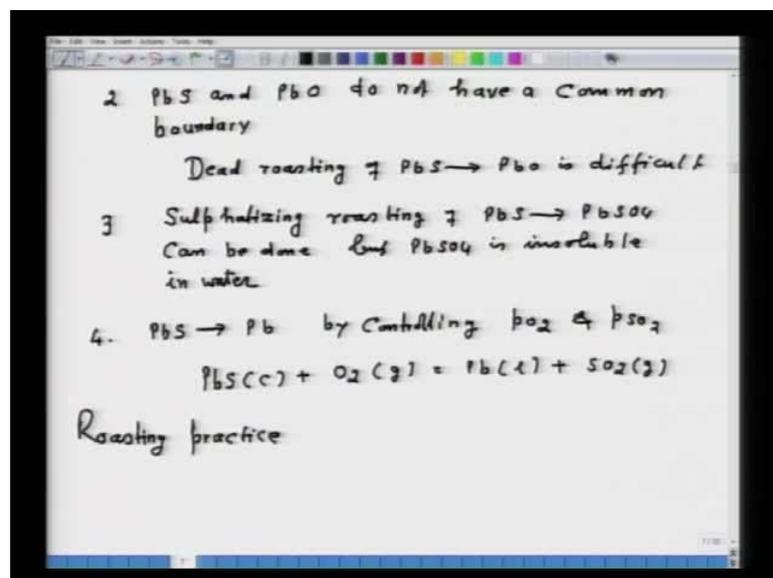
Let us see the roasting in PbS and O system; I again just put the predominance area diagram for PbS O system. So, this diagram it looks as shown (Refer Slide Time: 23:00). Again, I am plotting here; for example, log of p_{SO_2} against log of p_{O_2} , left side is highlighted you see and right side is gradually proceeding towards oxidizing condition.

So, the some of the phases that goes well, I will note down the time say some of the magnitudes say minus 11.5, where here is minus 8, minus 4 and 0. Here I put; for example, minus 7, let me put somewhere hear as minus 2, then minus 1, 0 and 1. This will be minus 1, this is what closed. The various oxides that can form; these are the various oxides, this portion is for lead, this is for lead oxide, this is for PbSO₄ and this region is for PbS (Refer Slide Time: 24:15).

So, this one is PbSO₄ into 4 PbO, this one PbSO₄ into 2 PbO and this one is PbSO₄ into PbO. Normally, in roasting of the lead sulphite ore the gas composition lies somewhere in this particular region, this is the gas composition during roasting operation.

Some important information we can derive from here. First of all, this PbO can form several basic sulphates like as you note from here PbSO₄ PbO, then PbSO₄ 2PbO and PbSO₄ 4PbO. That means, if our objective is to convert PbO to PbSO₄ then it goes to PbSO₄ 4PbO, then 2PbO, then 1PbO and then ultimately to lead sulphide.

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Second important thing is that PbS and PbO do not have a common boundary, if you note the diagram they do not have a common boundary. That means, roasting of PbS will always form PbO and PbSO₄. When PbS in PbO does not take the common boundary and if you carry out the roasting then there will be always the formation of PbO and PbSO₄. So that means dead roasting of PbS is difficult; that means, dead roasting of PbS to PbO is difficult.

Now, this you can easily explain from the predominance area diagram, if it would have been a common boundary then it would have been possible, but since there is no common boundary it suggests that PbS to PbO will always have the formation of PbSo₄ and that is what in practices also there.

Third important that you note from here is the sulphatizing roasting of PbS to PbSo₄ can be done, but PbSo₄ is insoluble in water. Now, this is with reference to hydrometallurgical extraction because in hydrometallurgical extraction you want to dissolve the metallic part in the solution. Once, if the PbS convert to PbSo₄ then PbS is difficult to dissolve, so that information is important from that point of view.

Now fourth important thing is that PbS to lead is possible by controlling p_{O_2} and p_{SO_2} ; that means, this reaction PbS condensed phase plus O₂ gaseous phase that is equal to Pb liquid plus SO₂ gaseous phase, so this reaction is also possible. What I have illustrated from the predominance area diagram is the process of roasting; under what condition, what phase it can form will be dictated by p_{SO_2} and p_{O_2} ratios for a given temperature. So, this information can be very easily derived from this diagram.

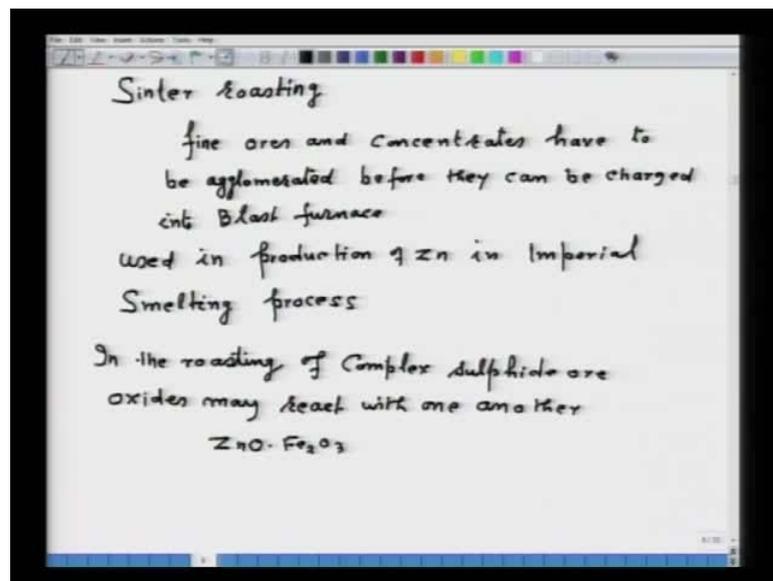
If you see, the roasting practice depends upon the metal to be recovered from sulphide ore. It is not always that you convert all sulphide into oxide, no. The technological feature will also decide whether it is required to convert all sulphide to oxide or not. For example, in the production of copper, it is not desirable that all sulphur of the ore should be converted to oxide in the roasting stage, because the technology is like that. Because, the technology demands that copper sulphide should be retained till it is present to the copper production stage. Whereas, if you consider the production of zinc, the production of zinc it demands that zinc sulphide should be completely converted to zinc oxide that is called the dead roasting.

So, what I wanted to illustrate from here is that it is not always necessary that you convert all sulphide into oxide during the roasting stage; it depends on the technology for a particular extraction of metal. Now in the sense, all nonferrous ore contain iron in it, so one of the important objective of roasting is to convert FeS to FeO, so that it can be removed during the metal production stage.

Now, in that process, for example in copper extraction, when you want to oxidize FeS to FeO then **in that process some of the copper** some of the sulphide of the copper also gets

oxidize to Cu, although the objective is not to convert sulphide to oxide. Whereas, in case of zinc sulphide you want dead roasting, so iron is easily converted to oxide. So, these are some of the things that the technology demands **how much to be converted** how much sulphur is to be converted in to oxide?

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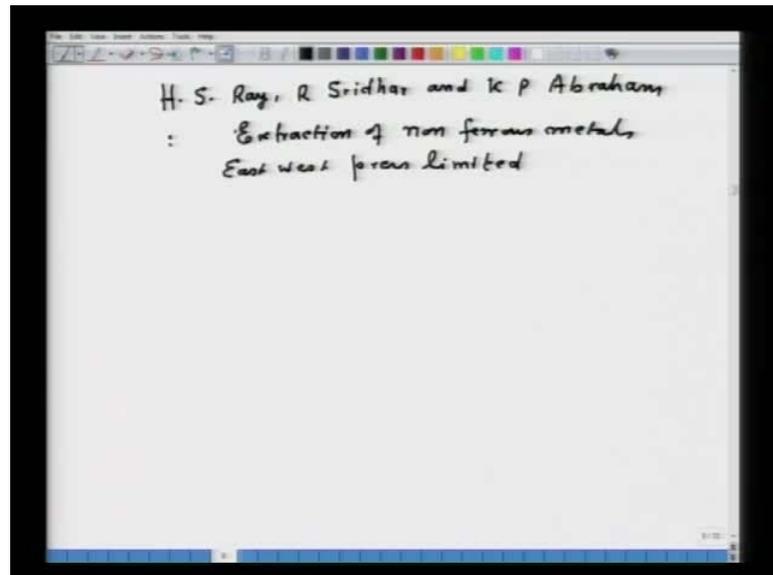


Another important technology of roasting that is called sinter roasting. Now, the sinter roasting is in fact a combination of sintering and roasting. In certain extraction processes of metal particularly from sulphide ore where blast furnace is used, their physically straight of the roast product is also important.

In the sintering roasting, the ore concentrate is sintered as well as simultaneously roasted. This sinter roasting is required when fine ores and concentrates have to be agglomerated before they can be charge into a blast furnace, otherwise what will happen? Will result in lot of dust, this particular sinter roasting is typically used in production of zinc in imperial smelting process, which uses blast furnace to produce zinc from ore concentrate, so this is about the sinter roasting. Sometimes what happens, Say in the roasting of complex sulphide ores the oxides may react with one another and typical example, in the roasting of zinc the oxide formation like ZnO , Fe_2O_3 .

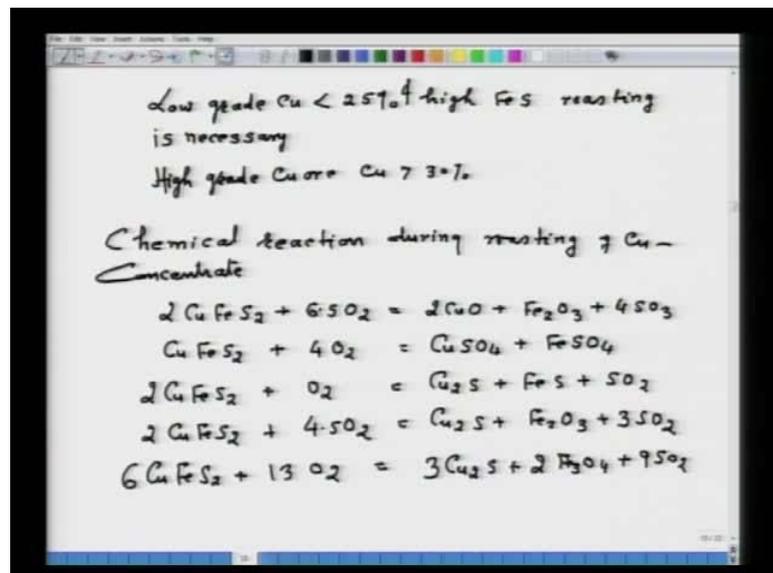
So, it is also required that what conversion is required in the roasting of sulphide concentrate? That will depend upon the condition of the production of metal or the type of ore that is required for the production of metal.

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That is all I thought for this. Now, I will give the reference that you may consult for the dominance area diagram; you can consult the book H S Ray, R Sridhar and K P Abraham from extraction of nonferrous metals. This is east west press limited. So that is what for now. If you have some questions I think I can answer those questions.

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Yes I have sir; is roasting necessary for all grades of copper concentrate? Well, mostly depends on the practice, but practically it is found for low grade copper. Say, if you have low grade copper; low grade copper means, if you have copper less than 25 percent and

high FeS then roasting is necessary, because the whole idea of roasting is to convert FeS to FeO, so that FeO can be removed in the subsequent stages.

But, even for high grade ores where copper is say somewhat greater than around 30 percent some practice does not do roasting they directly proceed to its melting operation. So, it is not always that you carry out the roasting; it depends upon the grade of the concentrate. In case of copper, definitely if the grade is high then you can eliminate the roasting stage, but in case the grade is low then you have no option except to carry out the roasting.

Sir, what are the chemical reactions occurring during roasting of copper concentrate? During roasting of copper concentrate several reactions are occurring, so we want to know the chemical reactions occurring during roasting of copper concentrate. Now there are several reactions that can occur during roasting that depends upon the partial pressure of oxygen, depending on that several phases can form CuO, Fe₂O₃, CuSO₄, SO₃, SO₂ and so on. Some of the reaction that I can give you; say for example, if you take main mineral in case of copper ore is chalcopyrite, if I take 2CuFeS₂ plus 6.5 O₂ that is equal to 2CuO plus Fe₂O₃ plus 4SO₃ (Refer Slide Time: 40:11).

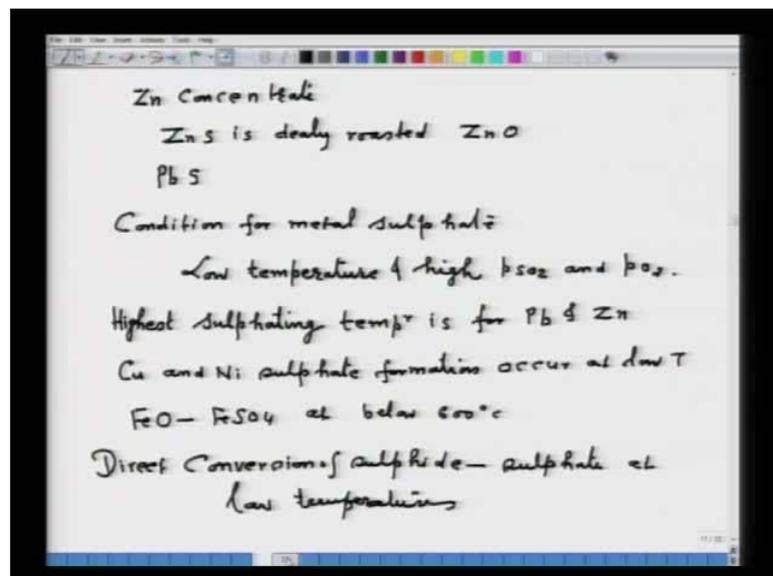
One should see during the roasting that the higher oxides of iron should not form to the extent, because ultimately if you want to produce copper you have to eliminate all- all oxides, all gangue everything as to be removed. Normally, it has been found that at higher oxides of iron are difficult to remove as compare to lower oxides. For example, you can easily remove by fluxing with SiO₂, whereas Fe₂ O₃ in Fe₃ O₄ is very difficult to remove, so that point also to be kept in mind.

Another equation that reaction is possible, say CuFeS₂ plus 4O₂ that is equal to Cu SO₄ plus FeSO₄ (Refer Slide Time: 41:00). The possibility of their formation can predicted by writing the delta g naught and K value, you can find out what should be the p_{o2}, so that this reaction possible. Another possible reaction could be 2Cu Fe S₂ that can react with O₂, it forms Cu₂S plus FeS plus SO₂, a still another reaction could be 2CuFeS₂, if I increase the amount of oxygen a 4.5 O₂ it can form Cu₂S plus Fe₂O₃ plus 3SO₂. Then again another possibility is that 6CuF₂ plus 13O₂ that can form 3Cu₂S plus 2Fe₃O₄ plus 9SO₂.

Now, what I wanted to say is I want to say that several possibilities of reactions are there, but in the practice one can control the p_{O_2} and p_{SO_2} , so that the most of the FeS gets converted into FeO only. Some FeS might be converted to Fe₃O₄ or Fe₂O₃, but the roasting is carried out such that the FeS is converted to lower oxide and less copper sulphide is converted to oxide, because that will be a loss. So, in case of roasting, particularly for copper, the objective is to convert FeS to FeO rather than CuSO to CuO.

Sir, what are the applications of dead roasting? Now, as I mentioned in the lecture dead roasting is in fact conversion of entire sulphide into oxide. It is not necessary that in all metal extraction from ore you convert all sulphide into oxide. For example, in copper extraction this is not done.

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Whereas, for example in case of zinc concentrate, zinc sulphide is dead roasted and converted to zinc oxide, so any unroasted zinc sulphide, if it is of 1 percent zinc sulphide or 2 percent zinc sulphide, if it is left in the rows product then it is a loss of zinc. Now the dead roasting of a particular sulphide to oxide more or less it will depend upon the reducibility of that oxide with the easily available reduction of carbon. For example, the extraction of zinc from sulphide ore is done by dead roasting of zinc sulphide, then the zinc oxide which is formed is mixed with the coal or coke and then the zinc is produced.

Similarly, in case of lead sulphide, as I said the dead roasting of lead sulphide is difficult, because there is no common boundary between PbS in PbO if you see the predominance

area diagram. But however, another important thing in case of lead sulphide is the lead sulphide fuses at around 800 degree celsius and therefore the control of temperature is also very important.

The dead roasting in case of lead sulphide is rather difficult to achieve because of there is no common boundary, it may achieve PbS to PbSo₄ intend to PbO. However, certain amount of PbO and PbSo₄ will remain in roasting of lead sulphide, so it is not aimed at the dead roasting for lead sulphide, only zinc sulphide is deadly roasted for production of zinc via blast furnace route.

Sir, what are the conditions for metal sulphate formation? In fact, the objective of roasting for hydrometallurgical extraction is you have to convert sulphide into sulphate, because some of the sulphates are easily soluble in the leaching that you are going to employ. In general, the condition for metal sulphate formation is low temperature and high p_{so2} and p_{o2}.

Now, the sulphate formation also differs from one metal to other; for example, the highest sulphating temperature is for lead and zinc; copper and nickel sulphate formation occurs at relatively low temperatures, so it depends from metal to metal; also, FeO to FeSO₄ occurs at bellow 600 degree celsius. Now, direct conversion of sulphide to sulphate is also possible at relatively low temperatures.

Sir, can you explain phase rule and application to roasting? I have already illustrated the phase rule, now phase rule is a very important rule, it gives the number of phases or it relates the number of phases and degree of freedom with number of components.

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The image shows a whiteboard with handwritten notes. At the top left, the general phase rule is written as $-P + F = C + 2$. Below it, two specific cases are shown: $P + F = 3 + 2$ and $P + F = 3 + 1$. The equation $F = 3 - P$ is boxed. To the right, it says "M-S-O 3 Components". Below that, it says "At constant temperature" with an arrow pointing to p_{SO_2} and p_{O_2} . At the bottom left, the values $P = 3 = 2$ and $F = 0 = 1$ are written.

Now in general, the phase rule illustrates P plus F that is equal to C plus 2. This is a very important rule which determines how many degree of freedom exist for the coexistence of phases for any component system. For example, if our system has metal sulphur and oxygen, they are just three component system. Here, P is number of phase, F is the degree of freedom, C is a number of component, then P plus F that is equal to 3 plus 2.

Now, two they are coming because of the constant temperature and pressure. In roasting, normally the phases are condensed so there is no effect of pressure, so accordingly we have P plus F that is equal to 3 plus 1. Normally, roasting is carried out at constant temperature, so in that case the phase rule becomes F that is equal to 3 minus P ; that means, this is at constant temperature.

From this relation it helps to construct the predominance area diagram, because from here if P is equal to 3 then degree of freedom is equal to 0. When you have taken the temperature as constant then the variable remains p_{SO_2} and p_{O_2} . So, if P is equal to 3, F is equal 0 means, in a diagram which is constructed by plotting p_{SO_2} and p_{O_2} you will get an invariant point. Where you have to get an invariant point means at that particular point all three phases can coexist.

Now P is equal to 2, F is equal to 1 that means 2 phases can coexist for degree of freedom is equal to 1, this representation will follow a line in a diagram. For P is equal to 1, degree of freedom is equal to 2, so this particular situation will correspond in a

diagram in terms of the area; that means, you have 2 degrees of freedom, you can vary here p_{SO_2} and p_{O_2} to get that particular phase. Along the line, you can vary either this p_{SO_2} or p_{O_2} . At a fixed point, you cannot do anything; at that point all three phases will coexist, so that is what the phase rule means.