Non-Ferrous Extractive Metallurgy

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Lecture No. #06

Principles of Carbon Reduction

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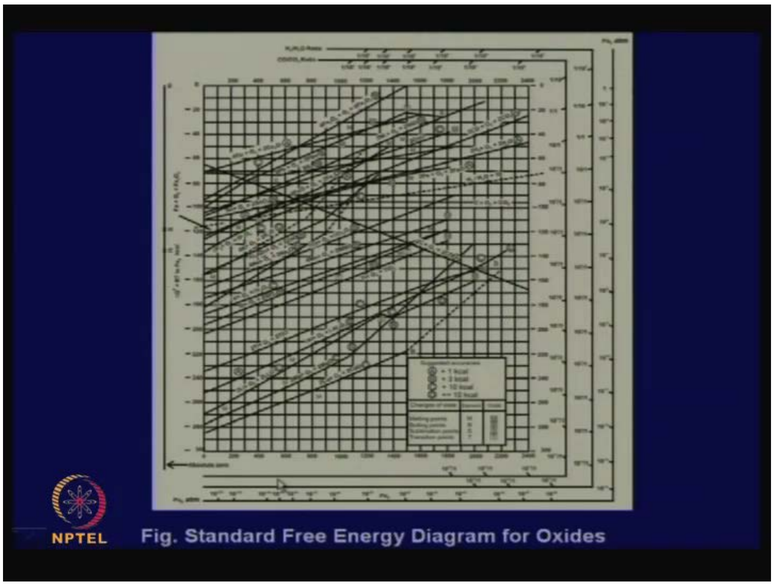

Fig. Standard Free Energy Diagram for Oxides

Now friends, during my last lecture I started discussing free energy diagram for oxides which are also known as ellingham diagrams. Let me quickly recapitulate some of the basic features of ellingham diagrams. These diagrams plot standard free energy of formation of various oxides from the metal an oxygen as a function of temperature, and the values are always with reference to one molecule of oxygen. So, all the formation reactions are so written that it is always one molecule of oxygen in the reaction, and there is a very interesting reason why we do that. We do that because then we can easily deduct values of formation of one oxide from values of formation of another oxide.

We can calculate very easily the free energy change in the reaction when one metal reduces a lesser less stable oxide to produce a more stable oxide. I will give an example of that. But first of all, let us see the relevance of this these diagrams for carbon reduction of oxides which as you know is the basic reaction in pyrometallurgy. Now, carbon forms two oxides; carbon dioxide, and carbon monoxide. The line for carbon reacting with oxygen to form CO 2 is a horizontal line because, there is no entropy change in this reaction; the same number of moles of gas are involved in the left hand side as well as, right hand side. One mole of oxygen giving you one mole of CO 2 and as I mentioned earlier, these lines represent the equation delta g naught is equal to delta h naught minus t delta s naught.

So the slope is comes from delta s naught which is the entropy change. In the case of CO reaction however, 2 C plus O 2 giving you 2 CO, we have the situation that one mole of oxygen reacts with carbon to produce two moles of CO. So the volume is increasing volume of gas; the entropy is increasing and therefore, this line has a negative slope. This implies that with increase in temperature carbon monoxide becomes increasingly stable; carbon dioxide stability does not change with increasing temperature. On the other hand all oxides which are represented by the parallel lines show that as the temperature increases, all oxides become less stable, more prone to reduction and decomposition. Now, these lines intersect carbon cuts these lines as well as formation of CO cuts this CO 2 cuts these lines as well as carbon going to carbon dioxide also cuts these lines.

Consider an intersection of this line and that line. This oxide is becoming increasingly unstable with temperature, and CO is becoming increasingly stable with temperature. Beyond this intersection, CO is comparatively more stable then the oxide. Therefore, carbon can reduce this oxide to form CO and liberate that matter. Now since the CO line has a negative slope in theory it will cut all lines of course, some intersection should be at a very high temperature; some would be at low temperatures.

So, those oxides which are not very stable will be reduced easily; oxides that are far more stable will be reduced at high temperatures in theory. It is quite possible that the temperatures require for reduction at for these metals at such high temperatures, what will be more stable? Some carbide will become more stable and not oxide because, the metal will also react with carbon in the system then we have a different kind of problem. But in theory, carbon oxygen to form carbon monoxide, this reaction can be the basis of reduction of any metal oxide at sufficiently high temperatures; how do we calculate the thermodynamic quantities free energies of formation such reactions for such reactions is very simple actually.

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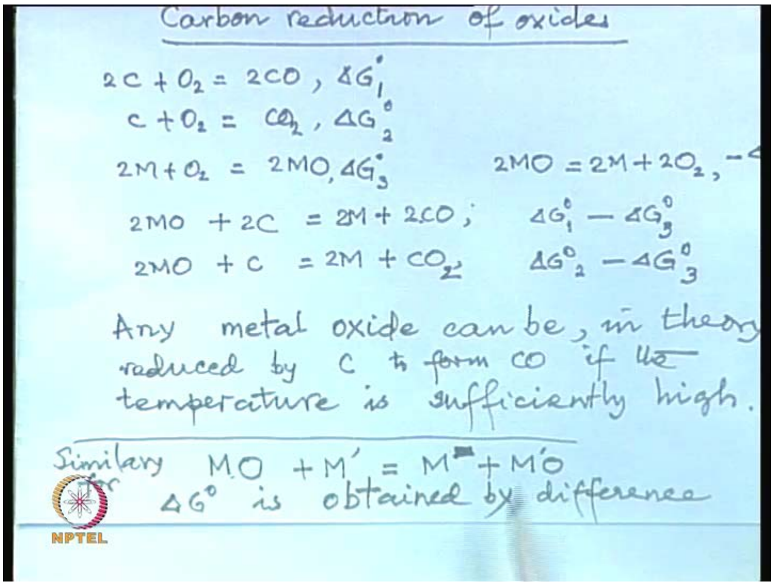

Carbon reduction of oxides

$2C + O_2 = 2CO, \Delta G^\circ_1$

$C + O_2 = CO_2, \Delta G^\circ_2$

$2M + O_2 = 2MO, \Delta G^\circ_3$ $\qquad 2MO = 2M + 2O_2, -$

$2MO + 2C = 2M + 2CO; \quad \Delta G^\circ_1 - \Delta G^\circ_3$

$2MO + C = 2M + CO_2; \quad \Delta G^\circ_2 - \Delta G^\circ_3$

Any metal oxide can be, in theory reduced by C to form CO if the temperature is sufficiently high.

Similary for $MO + M' = M + M'O$

ΔG° is obtained by difference

Consider the basic reactions here; 2C plus O 2 2CO call it delta G 1; C plus O 2 CO 2 call it delta G 2, and formation reaction from oxide the simple oxide you know we take delta G G sorry. If we write it in the reverse manner this becomes minus delta G. Now you have to add this reaction with this reaction to get the values for these like 2MO plus 2C to give you 2M plus 2CO will be obtained by delta G naught 1 minus delta G naught 3, and for 2MO plus C getting you 2M plus CO 2 will be given by delta G naught 2 minus delta G naught 3.

So, you can calculate the free energy change for the reduction of these reduction reactions by carbon to form CO and CO 2. This calculations are important in metallurgy, and there will be many examples of that. Similarly, we can calculate the free energy change when a metal M prime reduces a less stable metal oxide to produce release that metal and produce a more stable metal oxide again by taking a difference of two free energy change for two reactions.

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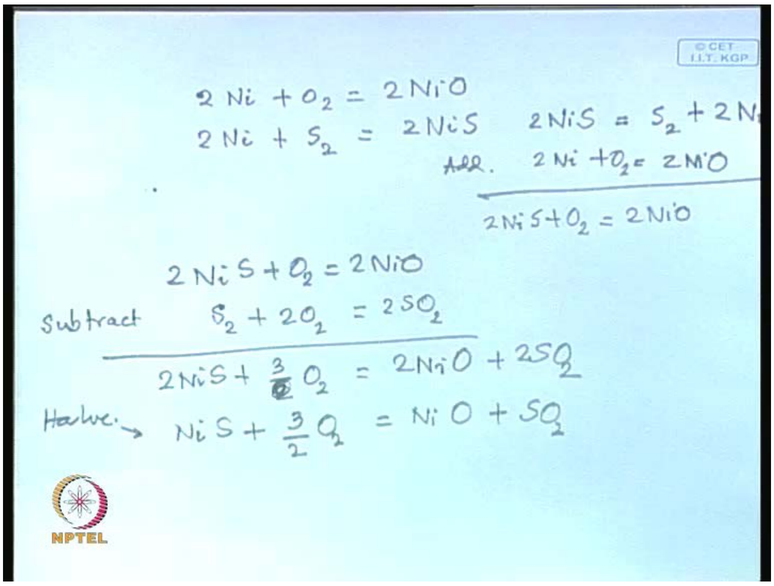

$2Ni + O_2 = 2NiO$

$2Ni + S_2 = 2NiS$ $\quad 2NiS = S_2 + 2N$

Add. $\quad 2Ni + O_2 = 2NiO$

$2NiS + O_2 = 2NiO$

$2NiS + O_2 = 2NiO$

Subtract $\quad S_2 + 2O_2 = 2SO_2$

$2NiS + \frac{3}{\cancel{2}} O_2 = 2NiO + 2SO_2$

Halve. → $NiS + \frac{3}{2} O_2 = NiO + SO_2$

Now, another thing that I had mentioned is that in this plots, the slope represent delta S naught; the change in slope is not because of change in delta S naught, but because of some melting of either metal or the metal oxide.

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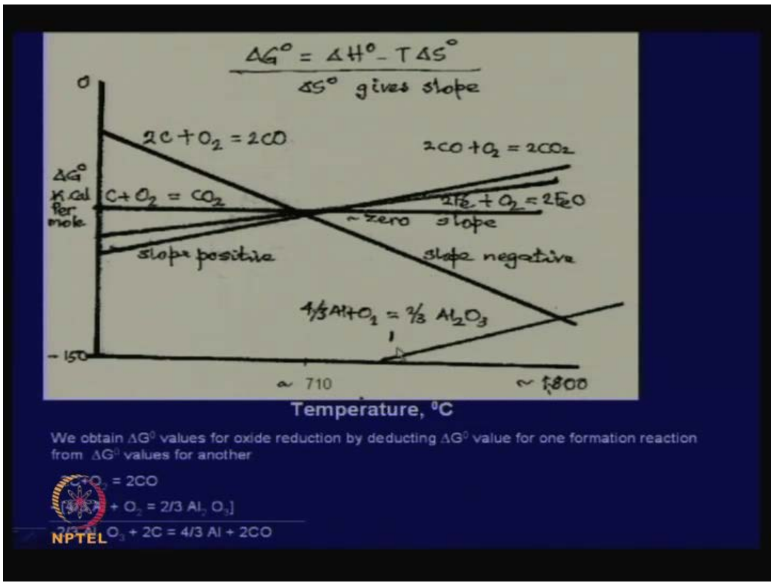

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

ΔS° gives slope

We obtain ΔG^0 values for oxide reduction by deducting ΔG^0 value for one formation reaction from ΔG^0 values for another

$2C + O_2 = 2CO$

$-[4/3 Al + O_2 = 2/3 Al_2O_3]$

$2/3 Al_2O_3 + 2C = 4/3 Al + 2CO$

Now, let us take this example of reduction of Al 2 O 3 by carbon. So, we have to combine these two reactions; 2C plus O 2 2CO and 4 by 3 aluminum plus O 2 2 by 3 Al 2 O 3, you have to deduct the free energy values for this reaction from the free energy change for the axis reaction and then, we get the desired reaction 2 by 3 Al 2 O 3 plus 2C

4 by 3 Al plus 2CO and we can calculate the free energy change for that reaction. You can see here that the carbon going CO, that line is represent approximately by this line; carbon oxygen reaction to form CO 2 is about this line. This intersection takes place at around 710 and for iron oxide the line is here. So we can say that, f e o can be reduced by both carbon to form either CO 2 or CO at around here, but the line for Al 2 O 3 can be met only by the line for CO, this line that represents carbon oxygen reaction to form CO 2 does not cut this Al 2 O 3 line.

We can say that, if we can have temperatures of around 1800 degrees even a stable oxide like Al 2 O 3 will be reduced by carbon to form CO because, beyond this point CO becomes more stable as compared to Al 2 O 3. However, as I mentioned although this is in theory, we cannot ignore another reaction that will take place that will form aluminum carbide which will not be reduced by CO. So this reaction actually it cannot be exploited in the industry. But, for lesser less stable oxides where these lines are less higher above will find many reactions many reactions are possible where the reduction is by carbon. There is another thing that happens

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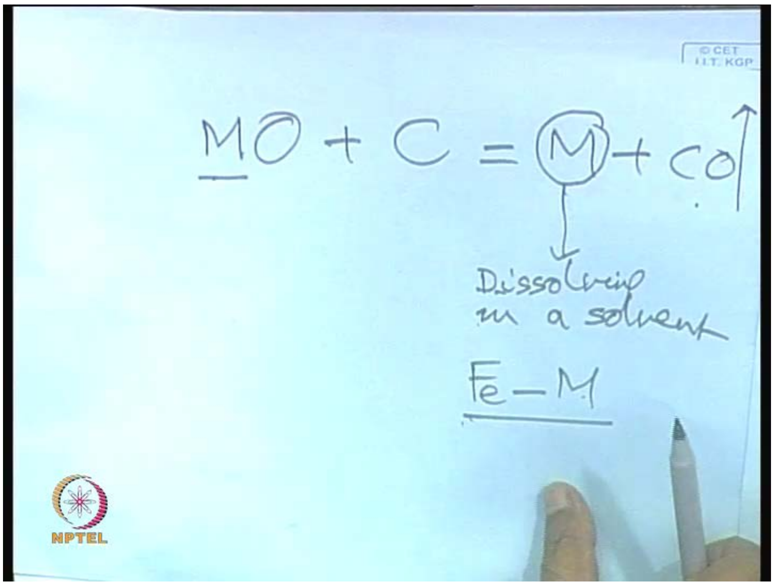

$$\underline{M}O + C = M + CO\uparrow$$

Dissolving in a solvent

$\underline{Fe - M}$

That suppose, there is a metal oxide which is reduced by carbon to form metal and carbon monoxide.

Suppose, the temperature is very high, we can help the reaction in two ways. We can apply vacuum if you can apply vacuumed and release CO from the system then, this reaction will driven to the right and it can take place at lower temperatures. The other way would be, if we can lower the activity of M by dissolving in something for example, suppose, we produce not the metal, but a ferroalloy a metal dissolved in a pool of iron then, the activity of metal will go down and the reaction will driven to the right, will be able to carry out the reaction at a lower temperatures will also eliminate, if not totally partially the tendency to form a carbide because, you can formation of a carbide will depend on activity of the metal.

So, in the case of those oxides which are very stable and which will lead very high temperatures for reduction by carbon, we can help the reduction reaction by using by producing ferroalloys. This is basis of production of ferrochromium, ferromanganese, ferrovanadium, etcetera which are possible because, the metal being produced is being dissolved in iron and you can drive the reaction to the right side. Unfortunately, we do not produce anything called ferro aluminum otherwise; if we could dissolve aluminum in iron then, this reaction would have occurred at a much lower temperatures because, aluminum activity will go down.

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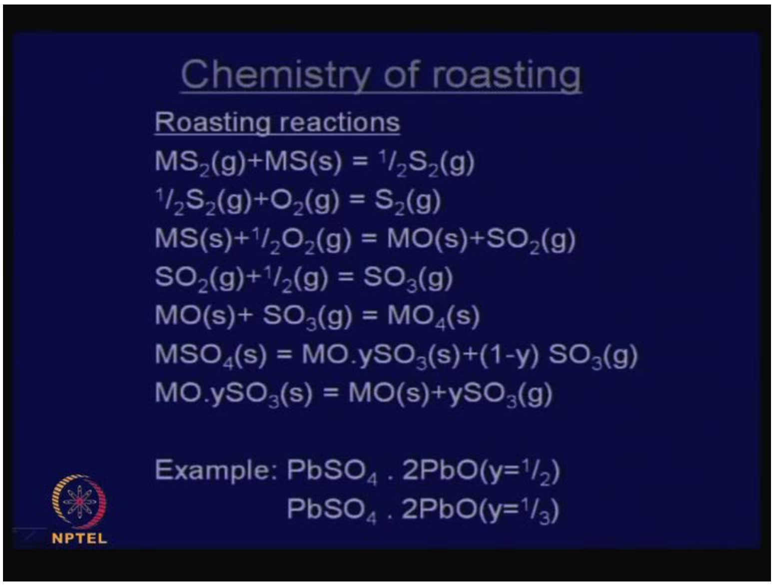

Chemistry of roasting

Roasting reactions

$MS_2(g)+MS(s) = {}^1/_2S_2(g)$

${}^1/_2S_2(g)+O_2(g) = S_2(g)$

$MS(s)+{}^1/_2O_2(g) = MO(s)+SO_2(g)$

$SO_2(g)+{}^1/_2(g) = SO_3(g)$

$MO(s)+ SO_3(g) = MO_4(s)$

$MSO_4(s) = MO.ySO_3(s)+(1-y)\ SO_3(g)$

$MO.ySO_3(s) = MO(s)+ySO_3(g)$

Example: $PbSO_4 . 2PbO(y={}^1/_2)$

$PbSO_4 . 2PbO(y={}^1/_3)$

Let us now proceed. The thermodynamics has been extensively applied in the case of roasting reactions also to understand the reactions. Now, during roasting all kinds of reactions are possible, I am writing some reactions here as we can see. Let us assume the sulphide is written as MS 2 like FES 2. It can react with other sulphides like FES, release sulphur; the sulphur oxygen reaction is possible, the metal sulphide can react with oxygen to produce a metal oxide and SO 2; the reaction between SO 2 and there should be half O 2, oxide and SO 3 can form MO 4. Then there also this sort of products are possible.

In other words, when you have a in a system you have metal, sulphur and oxygen, you can produce oxide; you can produce different sulphides; you can produce sulphates; you can produce compounds, which can be written as a combination of oxide and sulphate. What will exist at a particular temperature will depend on the partial pressures of sulphur and oxygen or if you fixed a pressures of sulphur and oxygen then, what will exist? What phases will be present will depend on the temperature. This information is vital in necessary because, if you want to control roasting reactions, we would like to aim at certain products, we must know what should be the value of partial pressure of oxygen, partial pressure of sulphur and what should be the temperature.

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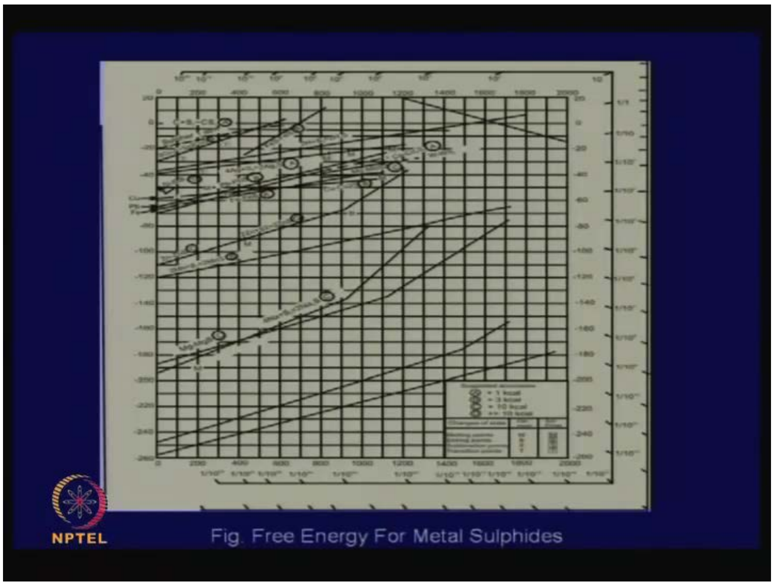

Fig. Free Energy For Metal Sulphides

So let us see, how will be that. There are Ellingham diagrams for sulphides also, where all the reactions are shown for formation of the sulphides for reactions between the metal and sulphur always between S 2 sulphur vapor. So all the reactions as in the case of oxides it was a O 2; it is written in terms of H 2 and whatever we did with sulphides or oxides, we can do the same thing here. But, we do not consider these diagrams for reduction by carbon or not even so much for metallothermic reaction, but there are other uses of this diagrams and I will I will I will try to show you one or two uses.

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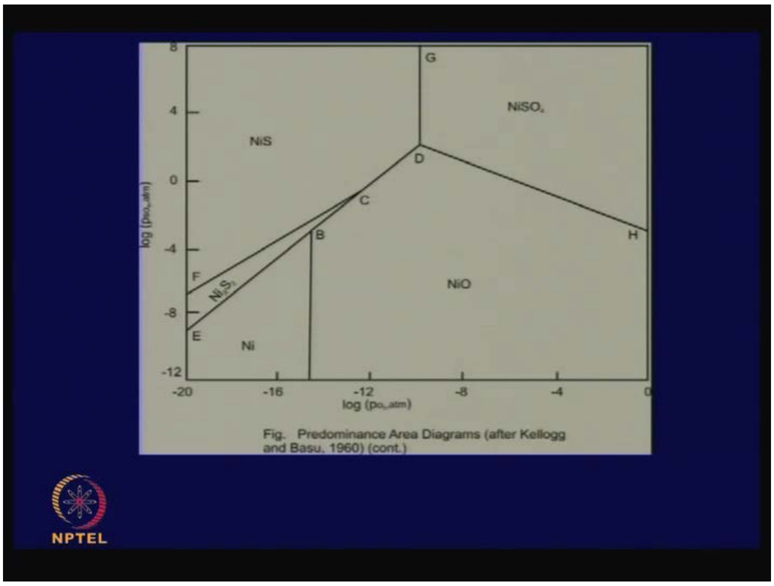

Fig. Predominance Area Diagrams (after Kellogg and Basu, 1960) (cont.)

People have been able to draw using thermodynamic data diagrams called predominance area diagrams. Now, predominance area diagram show us that at a particular temperature for different values of TO 2 and PSO 2, what are the phases that represent. This will be for a particular temperature which means that, we can have this phase for a variety of combinations of partial pressure of oxygen and partial pressure of SO 2 there are limits. But, if you have the partial pressure of oxygen at this, and if it exceed the value of PSO 2 beyond this then, you will end up with this NiSO 4. So, how do we draw such diagrams? I will give you an example of a simple example.

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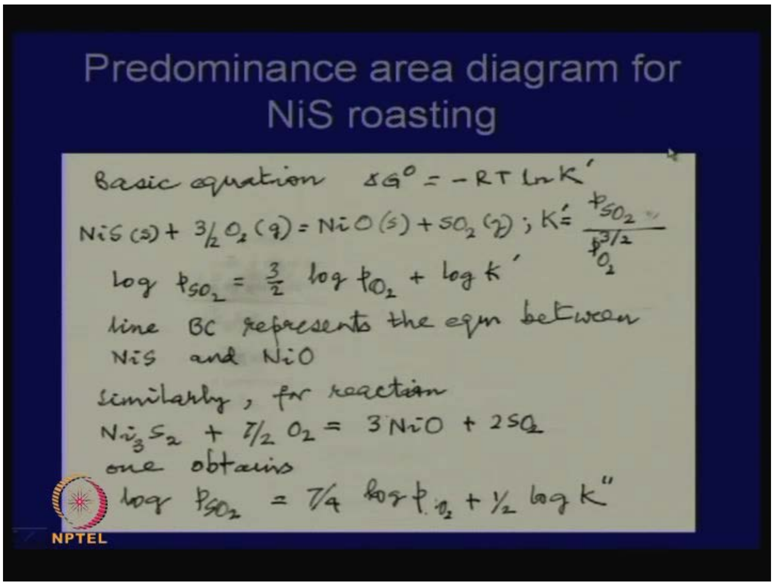

Predominance area diagram for NiS roasting

Basic equation $\Delta G^0 = -RT \ln K'$

$NiS(s) + 3/2\, O_2(g) = NiO(s) + SO_2(g)$; $K' = \dfrac{p_{SO_2}}{p_{O_2}^{3/2}}$

$\log p_{SO_2} = \frac{3}{2} \log p_{O_2} + \log K'$

line BC represents the eqm between NiS and NiO

similarly, for reaction

$Ni_3S_2 + 7/2\, O_2 = 3NiO + 2SO_2$

one obtains

$\log p_{SO_2} = 7/4 \log p_{O_2} + 1/2 \log K''$

That suppose we want to study the NiS; this diagram of roasting of NiS with there are many many reactions possible. Let us consider one particular reaction that is nickel sulphide giving you NiO and SO 2. Now, we know that the basic reaction for this would be delta G naught minus RTlnK prime, where k prime with equilibrium constant which is written like this. Now from this, if you take log, we can write log PSO 2 3 by 2 log PO 2 plus log K prime. We are considering an equilibrium between NiS and NiO and that is the line BC NiS and Ni. Now similarly, for reaction Ni 3 S 2 7 by 2 O 2 3NiO 2 SO 2, we will obtain another equation.

Now, how do you analyze these? Look at this, look at these two equations 2Ni plus O 2 2NiO from Ellingham diagrams, you can get the free energy change values of this 2Ni plus S 2 2NiS, we can get the free energy change for this from the Ellingham diagram from sulphides. Now, you write it in the reverse this reaction so that you can add these two equations to get a equation that represents oxidation of NiS to NiO. So, we can get the delta G naught value for this reaction 2NiS plus O 2 plus 2NiO considering the free energies of formation of the oxide and sulphur.

From this, the delta G naught value for this has some value; this will have another value; this values are also available so if you subtract this value from that value, we will get the delta G naught for this reaction 2NiS plus 3 by O 2 2NiO plus 2SiO 2 and finally, if you have it you will get the delta G naught value for this. Now, if you have the delta G naught value for this then, we can do the, we can get the value of K because, delta G naught is equal to minus RTlnK prime and once we have that value of K prime if you substitute there then, you get an equation that relates PSO 2 with log PO 2 for a particular temperature. For different values of T, we will get different relationships and in using that, we can draw the boundaries between NiS and NiO. Similarly, we have to consider the various equilibrium and we can draw these lines. Now obviously, if you consider the equilibrium between nickel and nickel oxide, it will depend only on PO 2 it has nothing to do with SO 2 at all; that is why this is a vertical line.

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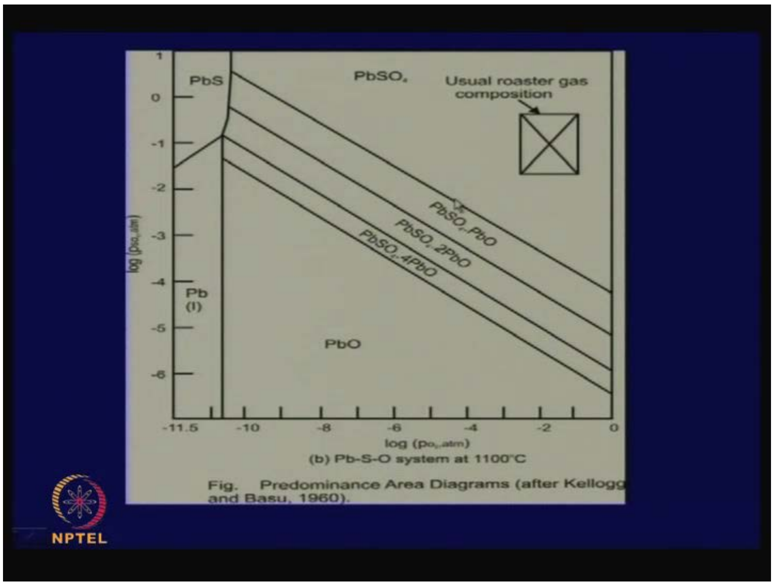

(b) Pb-S-O system at 1100°C

Fig. Predominance Area Diagrams (after Kellogg and Basu, 1960).

Similarly, NiS and NiSO 4 would also the boundary also would be a vertical line. We have also this sort of phase stability diagrams or predominance area diagrams for other oxides, sulphates and sulphides. This is a very very important diagram because, we need to know that when we take lead sulphide, and we roast it to get PbO where should furnace operate. Normally this is the range where the usual roaster gas composition is usually here. Now, you know this sort of calculations gives us the limiting value; so this is the equilibrium value. Obviously, if suppose you get a equilibrium temperature T, the actual operation in the industry would be higher temperatures for various reasons. Firstly, to accelerate the rates or sometimes to melt different phases, but we still want to know the limiting values that will tell us exactly where the operation should be carried out.

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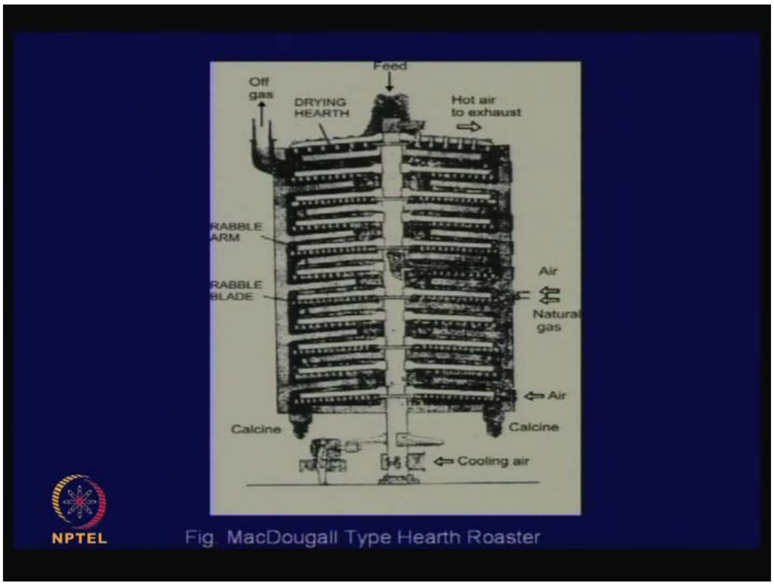

Fig. MacDougall Type Hearth Roaster

Now, let us go back to some things I mentioned earlier; I had talked about roasting. Roasting means you take a sulphide and you convert it into an oxide or a sulphate or whatever it is; there are so many reactions. This is a roaster which is very commonly used to very commonly used in industry called Hearth Roaster. Here, there are many many hearths and the there is a central shaft on which this hearths are circular hearths and the whole thing rotates.

The the the hearths rotate and the feed from the top actually goes from one hearth to another in this fashion, and see these are the teeth which sort of go through the charge. So the charge flows from one to the other one to the other. One is stationary; this part is stationary; these are the attached to the centre shaft which are rotating and these are the teeth the teeth kind of make the charge flow from one to the other. So the by the time the sulphide has come from here to the bottom you get a calcine you got the oxide. Now, lot of experiments on this showed that actual roasting reactions took place when the particles are falling from one hearth to the other; immediate by people have taken samples not so much as when they were on the hearth and there been stirred or they were there going from one place to another.

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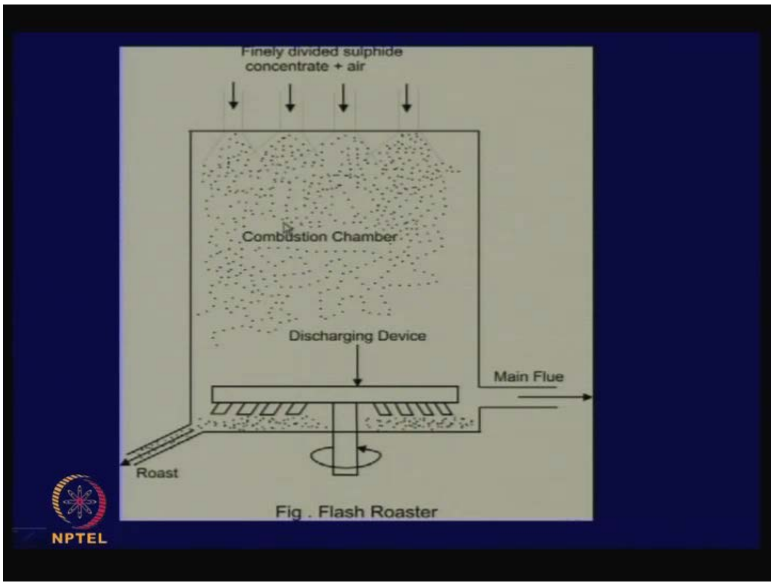

Fig . Flash Roaster

So, that give an idea of this flash roaster which is what is used in the industry now. There the idea is that finely divided sulphide concentrate and air is allowed to drop through a combustion chamber maintained at the certain temperature, and this is discharging device you get the roaster straight away. What will be the nature of the product? Will depend on of course, the partial pressure of oxygen and on temperature etcetera, but this is a very rapid process that the multiple hearth roaster will take very long time because, a central shaft is rotating and the charge is coming very slowly from top to the bottom. But here, it is practically almost instantaneous of course, this is a height of the camber. They simply drop through a hot chamber and immediately roast it and they are taken away.

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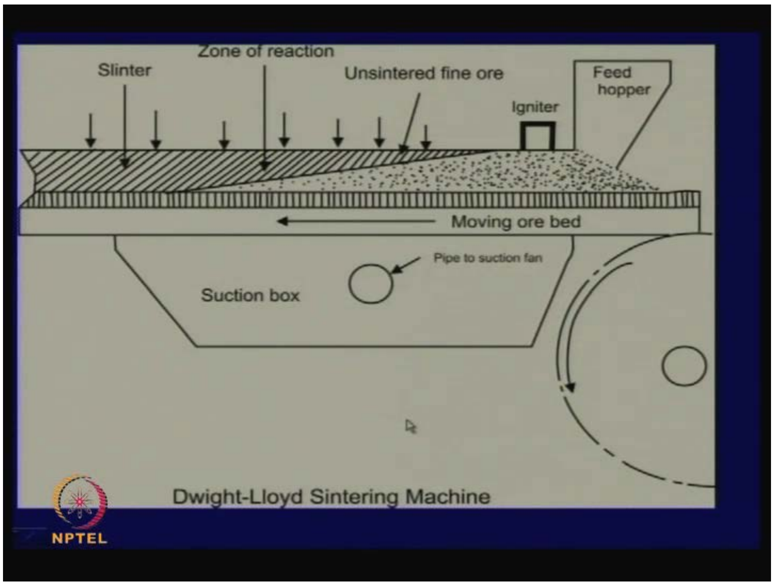

Dwight-Lloyd Sintering Machine

Now, this give rise to another idea to which I would come

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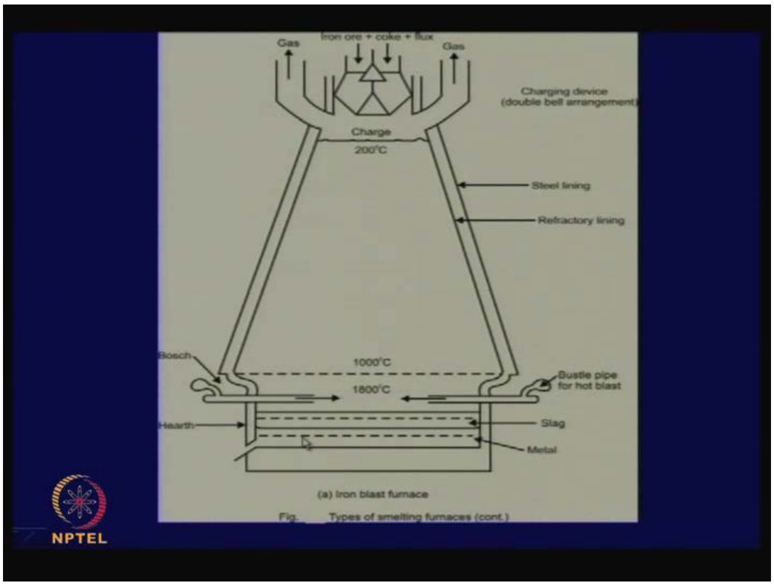

(a) Iron blast furnace

Fig. Types of smelting furnaces (cont.)

that for that I have to come to the concept of smelting. Now I had mentioned in roasting, there is no melting you are charging, you are heating a solid charge sulphide and it becomes a solid oxide. But, in the system, if you bring in a reducing agent like carbon and some fluxing agents like calcium oxide and quartz, you create a slag phase that operation is called melting, where you create like in blast furnace; you create slag and you create metal and there is separation between one and the other.

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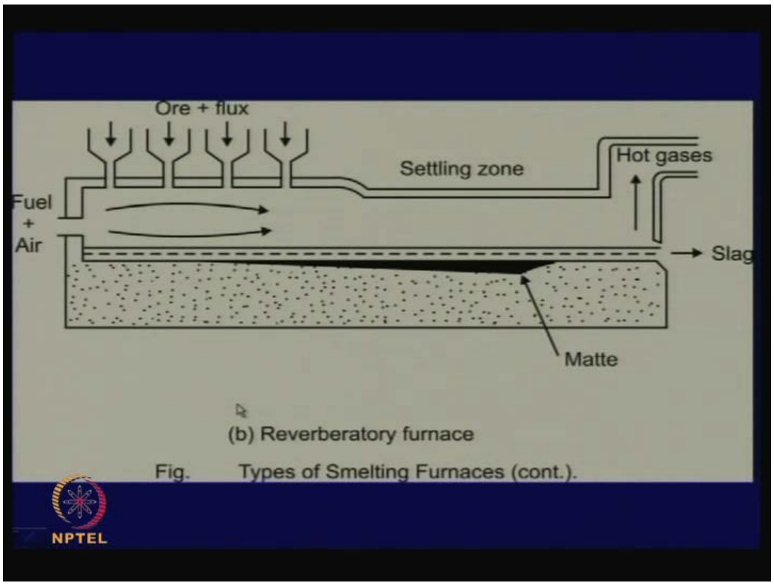

(b) Reverberatory furnace

Fig. Types of Smelting Furnaces (cont.).

We have smelting in case of sulphide ores also, but sulphides do not give metal straight away; what they do is a phase called matte, and we have an operation called smelting where the sulphides are first partly roasted and then, the whole charge reduce there is a slag phase, and we do have a separation of slag from the metallic values by the metallic values stay basically as a mixture of sulphides. In the case of copper, iron sulphide and copper sulphide we call that matte. So, there is matte slag separation; so smelting can be of two kinds; metal slag separation or matte slag separation. This I will discuss in detail in when we come to extraction of copper.

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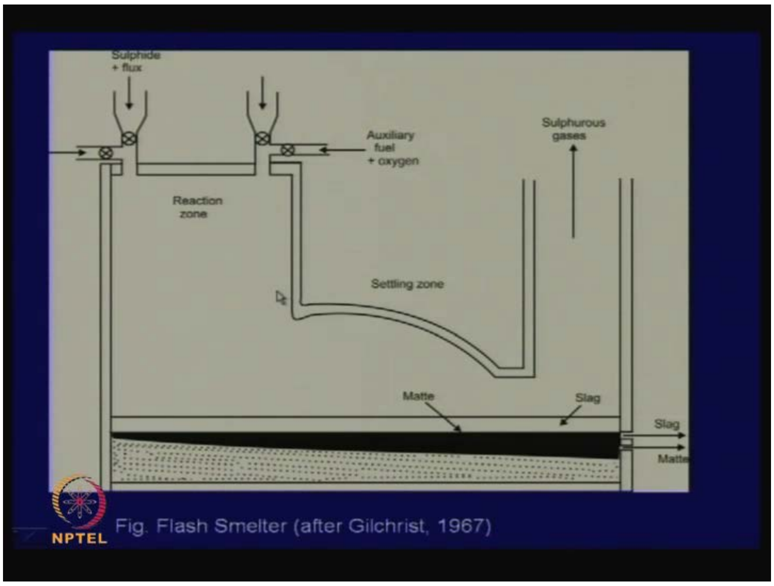

Fig. Flash Smelter (after Gilchrist, 1967)

Now, this idea of flash smelting has come flash roasting has come into flash smelting also. There the idea is the sulphide is particles are dropped into a chamber, hot chamber on controlled oxygen partial pressure along with the fluxing material, and there is auxiliary fuel and oxygen to maintain temperature. So, while in flight and then later on it not only produces the calcine, but calcine also reacts with reducing agents, and you end up with a slag and matte. So, this is also a very rapid process; flash melt, flash roasting is where there is no reducing agent, we are simply calcining it very quickly and flash smelting is, where in a flash you are calcining then, you are also fluxing out and again you are producing a slag and a matte to separate phases.

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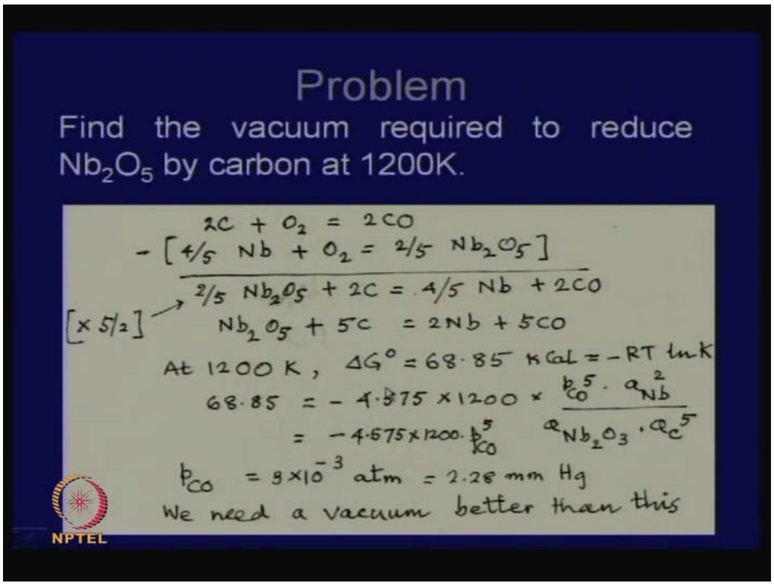

Problem

Find the vacuum required to reduce Nb_2O_5 by carbon at 1200K.

$$2C + O_2 = 2CO$$

$$-\left[\tfrac{4}{5}\,Nb + O_2 = \tfrac{2}{5}\,Nb_2O_5\right]$$

$$\tfrac{2}{5}\,Nb_2O_5 + 2C = \tfrac{4}{5}\,Nb + 2CO$$

$$[\times 5/2] \rightarrow \quad Nb_2O_5 + 5C = 2Nb + 5CO$$

At 1200 K, $\Delta G^\circ = 68.85$ KCal $= -RT \ln K$

$$68.85 = -4.575 \times 1200 \times \frac{p_{CO}^5 \cdot a_{Nb}^2}{a_{Nb_2O_3} \cdot a_C^5}$$

$$= -4.575 \times 1200 \cdot p_{CO}^5$$

$p_{CO} = 3 \times 10^{-3}$ atm $= 2.28$ mm Hg

We need a vacuum better than this

Now, I have been talking about this word slag quite frequently; so I would like to say a few words about, what is slag and how a slag made? But before that, let me give you one or two small examples of how thermodynamic calculations are applied in the case of reduction reaction. Now here is a small problem; find the vacuum required to reduce Nb 2 O 5 by carbon at 1200 degree K. Now, if you look at the Ellingham diagrams, this reaction reduction of Nb 2 O 5 by carbon will need very high temperatures because, if you write in this reaction Nb 2 O 5 2 c this.

Normally, if you look at the Ellingham diagrams where we have we have plotting standard free energies, it is for a given values partial pressure of CO, it will give high temperature. But, this reaction obviously can be sent forward if you find ways to reduce this carbon monoxide by a prime vacuum. So the problem is this can we reduce Nb 2 O 3 2 O 5 by carbon at a relatively low temperature of 1200 degree K, which is 900 degree centigrade. Normally it will not happen, but suppose we apply vacuum, what kind of vacuum would we lead? It is very easy.

We have the free energy change values for this reaction standard free energy change. We have the standard free energy change for formation of Nb 2 O 5. By difference, we get the standard free energy change for the reaction that you are studying which reduction of Nb 2 O 5 by carbon to form metal and CO. At 1200 degrees K, we get the value of delta G naught a 68.85 kilo calories which is minus RTlnK; K is the equilibrium constant. The equilibrium constant, we can obtain by putting the right values 68.85 RT value and taking 2.303 log K if you write. It comes to 4.575 into 1200; K is represented by this expression and so, we end up with an expression from which we can calculate that the equilibrium partial pressure of carbon monoxide would be 3 into 10 to the power minus 3 atmosphere for this reaction.

Now obviously, which is equal to 2.28 millimeter Hg; this is the equilibrium partial pressure of CO for this reduction reaction. So, if you can maintain a vacuum better than 2.28 millimeter mercury then, we can make this reaction happen at temperatures as low as 900 degrees.

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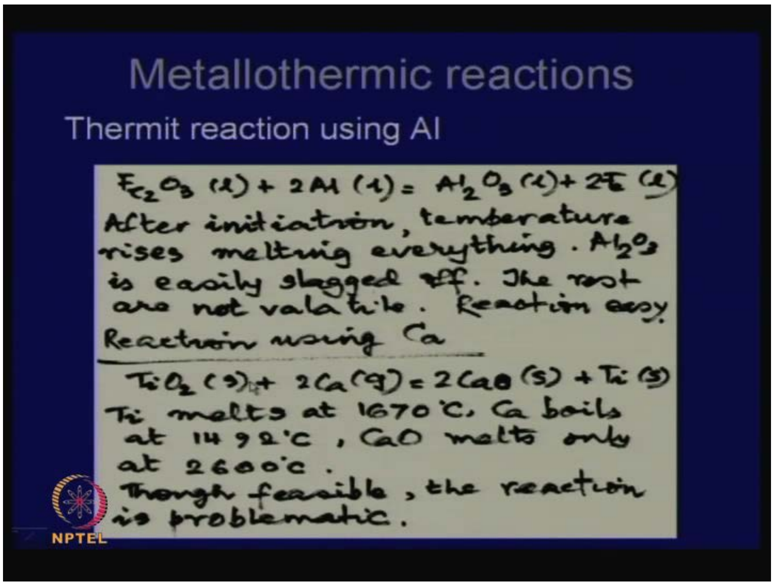

Metallothermic reactions

Thermit reaction using Al

$Fe_2O_3 (l) + 2Al (l) = Al_2O_3 (l) + 2Fe (l)$

After initiation, temperature rises melting everything. Al_2O_3 is easily slagged off. The rest are not volatile. Reaction easy.

Reaction using Ca

$TiO_2 (s) + 2Ca (g) = 2CaO (s) + Ti (s)$

Ti melts at 1670 °C, Ca boils at 1492 °C, CaO melts only at 2600 °C.

Though feasible, the reaction is problematic.

We use thermodynamic data for analysis of thermit reactions which refer to reduction of an oxide by another metal. Like right in the beginning I had said, there is a process called thermit process where Fe 2 O 3 is reduced by aluminum exothermically to produce liquid iron. All it needs is you take Fe 2 O 3 powder and aluminum power and ignite. Immediately the reaction starts the temperature is so high that everything becomes molten even Al 2 O 3 becomes molten, and the molten iron will go into the cracks in rails if we want to repair those rails. Now in this cases, as I have shown here after initiation temperature rises enormously to melt everything. Al 2 O 3 can be easily slagged off means, if you put some flux, it will it will go out very easily and the rest are not volatile so reaction is easy.

But, sometimes even such reaction are in theory there are lot of problems in practice. For example, suppose you want to reduce TiO 2 solid by calcium; this reduction needs high temperatures where calcium becomes a gas. So the reaction has to be written like; this it has to be in a closed chamber; titanium dioxide being reduced by calcium vapors to produce CaO which is solid which can be slagged off and titanium which is solid. Now, titanium melts at 1670 degrees; calcium boils at 1492 centigrade; calcium melts only at 2600. So, it is a very complicated reaction because, we are not able to get liquid phases very easily. So, thermodynamics gives us guidance about what should be the temperature etcetera. But then in practice, we need to do lot more things. This we would can discuss only when we come to extraction of individual metals.

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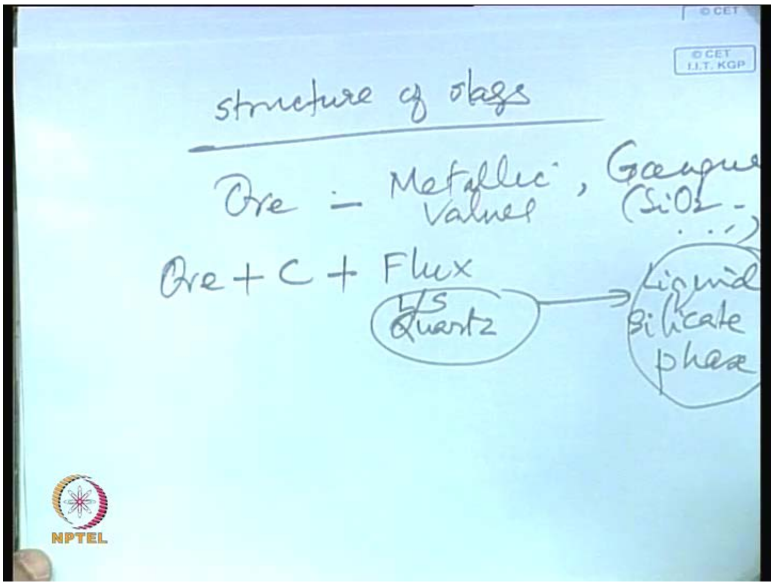

structure of slags

Ore – Metallic Values, Gangue (SiO_2 - . . .)

Ore + C + Flux (L/S Quartz) → Liquid Silicate phase

Now before we before I end this lecture, I want to say something about structure of slags. Generally in an ore, we have metallic values means minerals and we have gang; gang means things we do not want like silica, aluminum silicates many other things. Now, when we do smelting by say by reducing agent, and we add a flux; the flux is lime stone, quartz etcetera. The whole idea is to produce a liquid silicate phase which takes out many impurities, which separates out from the metal, and so that we have a clean separation between slag and metal. How do we create a fluid slag? To that, we have to go into bit of discussion of silicate structures.

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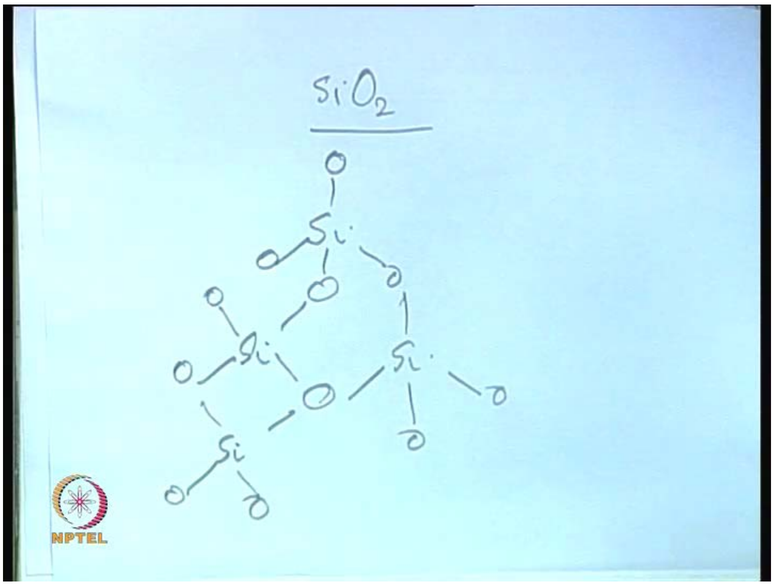

Pure silica SiO 2 already it is written like this; it is not made up of molecules of SiO 2. Silicon actually is bonded to four oxygen atoms. This is the basic unit and many such units attach themselves to one another like this. So in SiO 2, there are this tetrahedral things attached to each other so that the entire mass is actually one molecule in theory, and that is why smolten silica is very viscous because, it is the flow unit is very large. Of course, if one raises the temperature too high then, many of these bonds will break thermally. So, we make smaller and smaller flow units, but there is a very clever way we can make silica less viscous.

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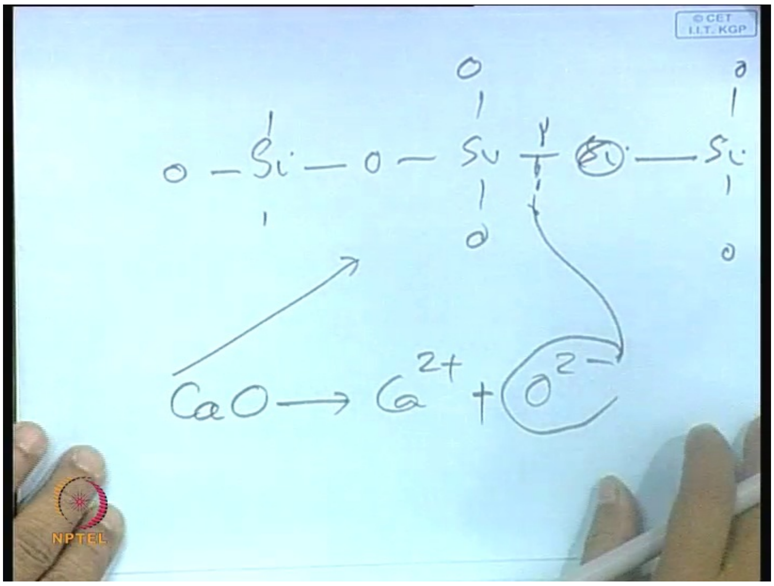

And this is, if let us represent the basic silica structure by two dimension in two dimension; these are oxygen atoms. If we add to this silica which is an acid oxide a basic oxide like calcium oxide which gives calcium, this oxygen goes and breaks a silicon oxygen bond so it splits, we from a big flow unit, we create two smaller flow units and then, it becomes less viscous.

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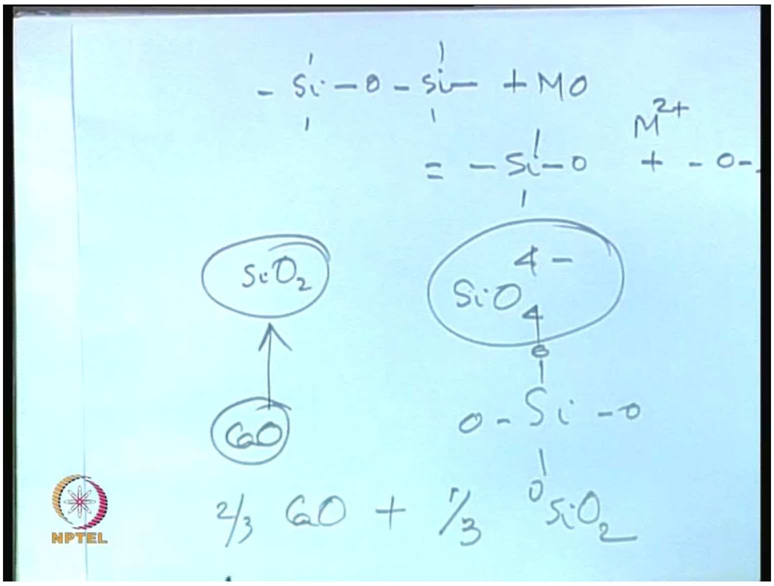

So, we can represent the reaction in a in a thing like this. This will happen with metal oxide you have added; we have broken it into and the metal ion is hanging around. Now in silica, the more calcium oxide you add, the more fluid it becomes because, the more bonds are broken; the flow units becomes smaller and smaller and smaller, but there is a limit to that. This once you have broken it down to the smallest unit which is S i, you cannot break it any further.

So, we have a long chain or a complicated thing you keep on breaking and finally, this is the smallest unit and this happen when two-thirds calcium oxide and there is one-third SiO 2 is very easy to understand why this is so because, some stoichiometric reasons if you have added sufficient amount of oxygen, SiO 2 has to go down to the smallest unit. Now then lot of work has been done on structure of silicates, and it is a very vast subject I do not want to go into that, but

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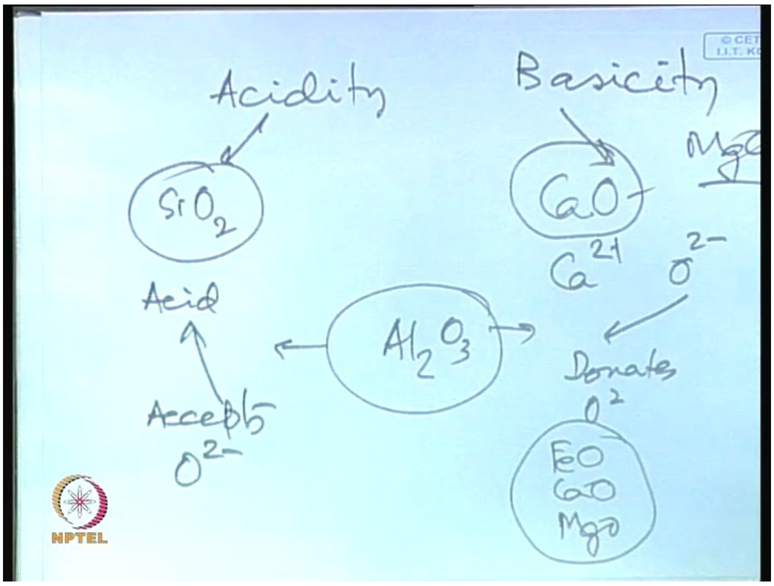

you should understand that, there is a concept of acidity and basicity in slags. Acid slags are were silica is on the higher side; basic slags are were calcium oxide is on higher side. Why this is a base? This is called the base because, it denotes oxygen ion it denotes oxygen ion. It is called an acid oxide because, it accepts oxygen ion for breaking into smaller and smaller element; do not think only calcium oxide is the basic oxide FeO, CaO, MgO there all basic oxides. Al 2 O 3 we call it is an amphoteric oxide; it sometimes it acts as a base that it denotes oxygen ions; some times its acts as an acid it adds oxygen depending on the composition.

It will be enough for you to know that, if the slag is viscous, its flow units are large because, there are polymeric silicon oxygen units in that; it can be made fluid by adding basic oxide like calcium oxide; this is the most common. Magnesium oxide also will make it fluid, but not all basic oxides are equally effective in reducing the the the viscosity of a SiO 2. In other words, the basicity of different oxides are different; so we actually have a basicity scale of different oxides; calcium oxide is high Pg MgO is not so strong a base; weaker bases are FeO. There are even other oxides which are even weaker.

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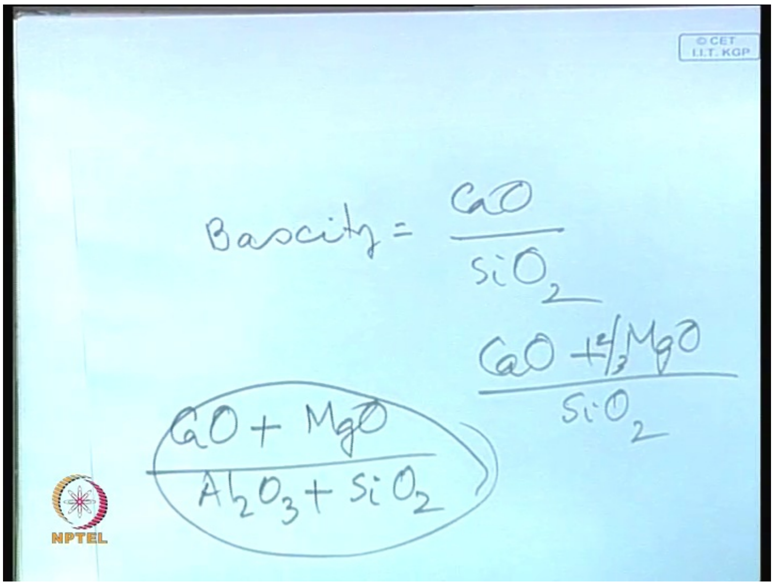

$$\text{Basicity} = \frac{CaO}{SiO_2}$$

$$\frac{CaO + \frac{2}{3}MgO}{SiO_2}$$

$$\frac{CaO + MgO}{Al_2O_3 + SiO_2}$$

There are many definitions of basicity. The commonest definition of basicity is CaO by SiO 2 and very often, you will see in pyrometallurgy operation, they will say the slag is maintained with a basicity of so and so. There are modifications required of this if there are other oxides CaO plus MgO by SiO 2 is another definition commonly used in industry. Some people say, since MgO is not as effective as CaO, this should be written as two-thirds. Some people say, under certain conditions the basicity index is base written as Al 2 O 3 plus SiO 2 etcetera. So in all pyrometallurgical operations, the operator wants to what is the basicity of the slag or is of an advised about the basicity of slag because, proper basicity defines proper viscosity of slag.

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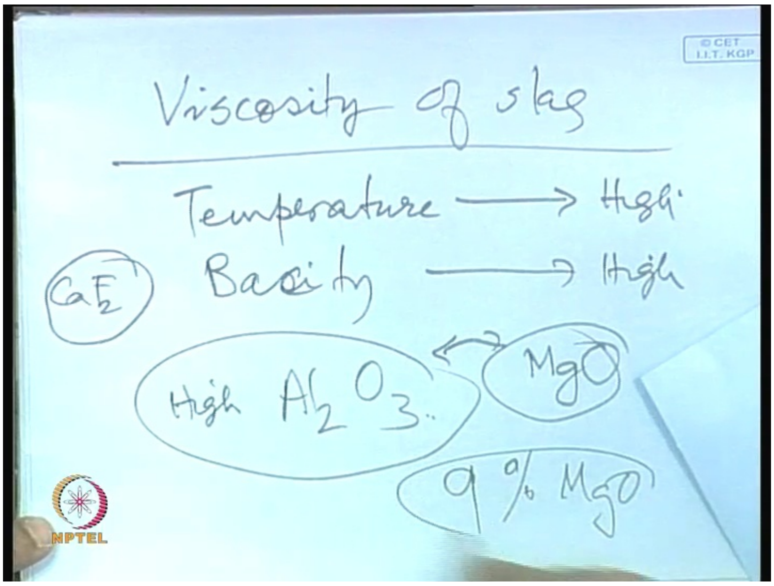

Viscosity of slag

Temperature → High

Basicity → High

CaF_2

High Al_2O_3 ↔ MgO

9 % MgO

So the viscosity of slag which is a crucial parameter in pyrometallurgical operations depends on temperature because, the higher the temperature lower will be the viscosity no matter what slag is it because, at higher temperatures bond strength to break and the other will be basicity. So temperature should be high basicity; should be high to lower viscosity or increase fluidity. There also some fluidizing agents like calcium fluoride which when added increases fluidity of slag.

Now slag basicity control is very important in the industry, and there is a common saying that any many pyrometallurgical operations, the aim is to look at the slag if the slag is right, the metal will be right. This was particularly so for blast furnace operation. In blast furnace, you have a slag layer covering the metal layer, and the slag layer is has many functions. First of all it is covering the metal layer. There is whatever gaseous atmosphere is there on top of the slag is away from the metal between slag and metal all kinds of slag metal reactions are taking place depending on the chemistry of the slag.

So the slag chemistry and slag properties are a vital importance. A simple example I have to go for that to iron and steel. Perhaps, you know that one of the problems of slags in blast furnace was because of alumina high alumina that came from iron ores Indian ores are very good. But, alumina comes from ore as well as some from coke, and Indian slags is to be very highly viscous because of Al 2 O 3 content. Many efforts have been made to remove Al 2 O 3 from iron ore, but it is very difficult.

So, it will end up with slag with lower alumina high viscosity. Many efforts were there to find out, how to bring down this Al 2 O 3 content. You cannot simply go and adding a lot of calcium oxide, increase the basicity that will increase the volume of slag and increasing the basicity will also have effect on slag metal reaction. Finally, the adverse effect of Al 2 O 3 was met by adding MgO and many blast furnace operations were found to be optimum with addition of 9 percent MgO that took care of high alumina in the slag was going to increase the basicity, the viscosity was brought down by MgO.

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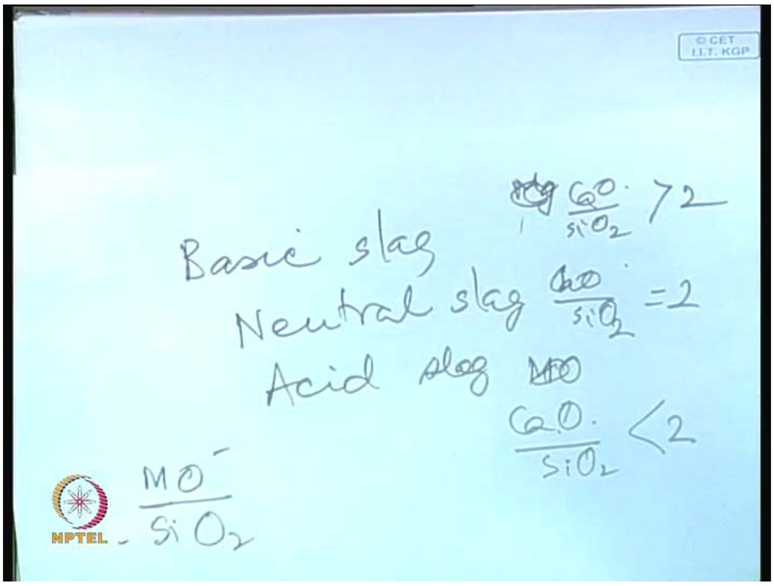

Now, why I am saying these things is that, you often come across terms like basic slag, neutral slag, acid slag. Generally by basic slag it will mean CaO by SiO 2 more than 2. MO in this case CaO by SiO 2 neutral slag will be 2; acid slag will CaO by SiO 2 less than 2. I am writing CaO in the in case there is MgO that has to come here again. So you can say MO by SiO 2 basic oxides and acid oxide their ratio governs the basicity neutrality or acidity of slag. I think with that, it is time to wind up this lecture. I have mainly discussed here, the use of Ellingham diagrams to understand reduction of oxides by carbon and reduction of oxides by metals which form more stable oxides.

I have talked about calcinations, roasting, smelting and when we talked about smelting I mentioned that in smelting you have to have a slag phase in contact with either a metal phase or a matte phase. A matte phase is not a metal phase, it is a mixture of sulphides, but when you have a slag, the first criterion for the slag must be that it should be fluid.

That it should be easily taken out; it should be easily tapped out; it should separate out very easily from the metal phase. So, we have liquid liquid separation. Sometimes, it is also important to control the chemistry of the slag, just making fluid is not enough, it should have such a chemical composition that is some reactions that are favorable to produce a purer metal are possible. Like may be the composition will be such that, it will the slag phase will observe sulphur or phosphorus another thing that you do not want in the metal phase.

So, not only fluidity is important, but chemistry is also important. But, slag phase is a vital phase, and slag chemistry physical properties of the slag, they form a very important part of pyrometallurgical operations. I think I will end the lecture on pyrometallurgical reactions right now. In the next lecture, I will move into hydrometallurgy and try to discuss some of the basic principles of hydrometallurgy. Thank you.