Materials and Energy Balance in Metallurgical Processes

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Module No. # 01

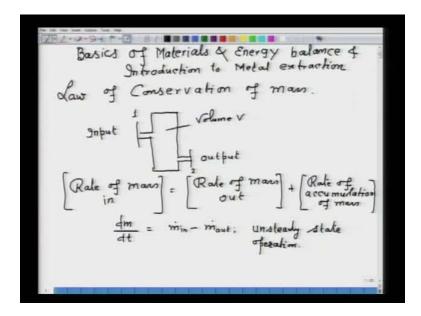
Lecture No. # 09

Basics of Materials and Energy Balance

Today's lecture will be on Basics of Materials and Energy balance. If time permits, I will introduce to Introduction to Metal Extraction, where we will be doing Material and Energy Balance in various processes. You know that materials and energy balance are the routine plant exercise. It is nothing new that I have to tell you, because every businessman or every shopkeeper or every plant owner, have to do auditing of material and energy from the point of view of the economics.

He would like to know, what the inputs are and what are the outputs of material and where are the losses. He would also like to know, what is the energy input into the system and what the energy output is; so that he can assess the energy consumption because energy consumption acts directly to the cost of the product. Probably, he would like to introduce measures like saving of energy or utilization of energy, if he happens to know how the energy is being utilized.

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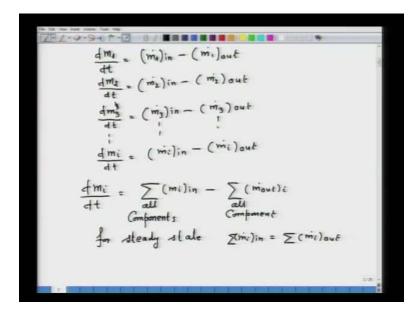


Let us see, first of all, what are the basics of materials and energy balance. I mean it is nothing very great, but it is very simple. We know that you also do a sort of balance, whenever you go to the market and do some expenditure. You are given 100 rupees. When you come back, you will like to know how you have spent 100 rupees. So, you keep an account of input and output. So, if it is possible, you can introduce the measure of. Now, similar to it; here also, you have to think in terms of inputs and output of material, energy. Now, in fact, the basic is - it is based on law of conversation of mass. Now, mass of an isolated system remains constant, irrespective of the changes occurring within the system.

Now, let us consider an open system. For example, consider an open system at this point, (Refer Slide Time: 03:01) which is point 1 and this point 2. Here, we have input and at point 2 we have output. Now, let us consider the volume as V, mass is transferred in and out of the system. Mass will accumulate, when the input and output rates are unequal. So, in this case, we can write down rate of mass in is equal to rate of mass out plus rate of rate of accumulation of mass. Now, writing down in terms of mathematical expression - m is the mass, dm by dt and that will be equal to m dot in minus m dot out. Dot represents the rate of change of mass with reference to time. So, this is in fact valid for unsteady state operation. Now, this material balance equation is written for each and every component of this system. Suppose, in a system, there are 10 different elements entering or 5 different elements entering and 5 different elements or 10 different

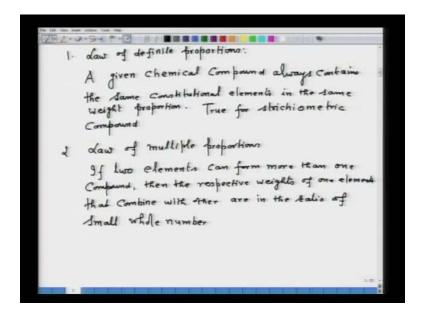
elements leaving the system. Then we have to write down the mass balance for each and every component that is entering in.

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For example, if we have component 1 dm 1 upon dt will be equal to m dot 1 in minus m dot 1 out. Similarly, for component 2, we will write dm 2 upon dt will be equal to m 2 dot in minus m 2 dot out and so on. I can write down for third component d m 3 upon dt that will be equal to m 3 dot in minus m 3 dot out and so on say for i th component that becomes dm i upon dt is equal to m dot i in minus m dot i out. Now, for a system with multiple inputs and output streams, the material balance equation for i th component becomes dm i upon dt is equal to sigma m i in all components minus sigma m dot out of all components. This is again for all components: say, for i th component that is what it means. Now, for a steady state, as the name suggests that there is no accumulation of mass within the system and therefore sigma m dot i in will be equal to sigma m dot i out. That is the basis when the system is in steady state. Now, for a chemically reacting system, in addition to the law of conservation of mass, the following two laws must also hold.

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First law is law of definite proportions. Now, a given chemical compound always contains the same constitutional elements in the same weight proportions. This is only true for stoichiometric compounds and for non-stoichiometric compounds, this may not hold good. For example, FeO has Fe 1 and O 1 atom and it is also available as Fe 0.95O So, in that case this law of definite proportion will not be valid.

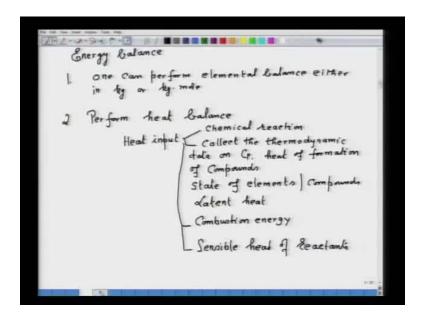
So, I will just write down a given chemical compound always contains the same constitutional elements in the same weight proportions. For example, in Fe2O3, there will be 2 atoms of iron combining with 3 atoms of oxygen. For example, in Cu2S, there are 2 atoms of copper combining with 1 atom of sulphur. However, copper and sulphur are the same constitutional elements, but CuS is also formed. So, in that case, it will not be valid and that means, it is true for stoichiometric compounds. For non-stoichiometric compound, you have to find out in what proportion the elements are combined.

Second important law is law of multiple proportions. This law states, if two elements can form more than one compound, I repeat once again, if two elements can form more than one compound, then the respective weights of one element that combines with a given weight of the other are in the ratio of a small whole number.

I think, I should write it. If two elements can form more than one, then the respective weights respective of one element combines with other in the ratio of small whole numbers. So, you will very often come across the various compounds, stoichiometric as

well non-stoichiometric in nature. In case of stoichiometric compounds, the combination of elements is clear, but in case of non-stoichiometric compound, you must know in what proportion the elements are combined. So, you can perform the material balance. Now, I mean this is basic and I think all of you are aware that input should be equal to output, when there is a steady state and this is a very simple thing.

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Now, about the energy balance; one important thing for energy balance is energy balance cannot be done without material balance; whenever, you are required to solve a problem of energy balance without performing material balance energy, balance cannot be done. So that is one important thing. Now, here are some tips. For example, one can perform elemental balance either in kg or kg mole.

Now, it is a matter of practice and matter of convince about how you perform the material balance. You can perform in kg or gram or in gram mole or in kg mole also. If you ask me, I will prefer or I will do the material balance by considering kg mole because I find it very convenient by determining the input and output of masses in terms of kg mole because later on the thermodynamic values, which I will be getting in the literature are given in per kg mole and they are also given in per kg. So, what I wanted to say is that you have to develop your own habit, whether kg is suitable for you or kg mole is suitable for you. The thermodynamic values are available in kg, kg mole, gram and as well as in gram mole and there is no problem at all. It is just a matter of convenience; the

material balance in kg mole becomes little bit easier. Say, if you write down the stoichiometric equations, then immediately, it is apparent how many moles are entering in and how many moles are entering out. So, I find it little easier, but you have to make your own style of solving these problems. Once you have done the material balance of all inputs, it is very important to know where the input of materials is going in.

Say, you have x kg or x kg mole of certain material and you have to see how much of that is going into the products. The products could be metal, it could be slag, waste product or in the gaseous form. So, to collect all such information, make a box to determine material balance and then proceed to solve the heat balance and that is very important. Another important thing for the energy balance is to make the basis of calculation. You have already made, while doing material balance. For example, 1 kg mole and then you follow that kg mole until the end of your heat balance or you can do 100 kg mole or 10 kg mole, whatever is convenient to you, but do not change the basis till the end of the problem number. Number 2: the several energy balance is done by considering a reference temperature of 298 kelvin.

Now, this is an advantage because the values or the thermodynamic values like specific heat content, heat of reaction, heat of formation are all available at 298 kelvin. It is again a matter of practice. Now, once you have done this and then perform heat balance. Now, needless to mention heat input is equal to heat output because we are talking of a steady state. We are not performing heat balance under unsteady state, we can also perform under unsteady state in that we know what is the accumulation of energy in the system. Normally, in most of the plants, it is required that the plant is operating at a steady state for days with inputs and output of energy and so on.

So, you perform the heat balance. It is very simple; heat input is equal to heat output. Although it looks to be simple, but you have to consider all sources from which heat is entering. If I write few sources for you, for example, heat input is by chemical reaction. You have to see whether in a system, chemical reaction is occurring. Now, I have already illustrated how to calculate the heat of reaction when I was discussing thermochemistry. Here, it is important to calculate chemical the heat of reaction because of the chemical reaction. It could be exothermic or it could be endothermic. Accordingly, the sign convention must very clear negative for exothermic. If you want to do that for endothermic, it is positive. You can declare it in the beginning that this is the convention

I am going to follow, but you have to stick to the convention and that is an important thing.

Now, the temperature is also very important. You have to see whether the products, the reactants are entering at what temperature. So, accordingly heat of reaction has to be calculated as per the formula, which I have given in thermochemistry and that is the heat of reaction at 298 plus heat of reaction at the prevailing temperature. You have to do these and proper calculations are very important. The next step is - you collect the thermodynamic data and this is the most important step while performing the heat balance. You have to know from where, which data will be available while going through the problems over here. I will give you the data, I will give you the source, but in an unknown situation, if you are required to do heat balance, you must know how to collect the data. In certain cases, the data may not be available, then you should be able to derive the data from basic thermodynamic and that is important.

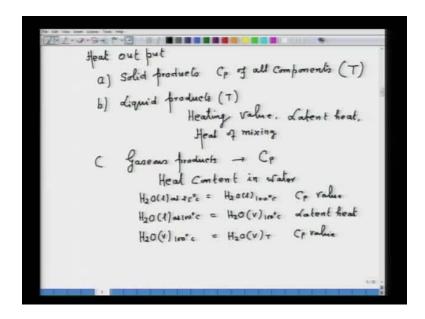
So, collect the thermodynamic data on C p and that is a specific heat. It is available in kilocalorie per kg mole per degree celsius or joule or kilo joule per kg mole per degree kelvin per degree Celsius and all these values are available. Follow a certain system of collection of the data in proper units. So, you do not end up in a problem. Collect the data on heat of formation of compounds. Normally, these heat of formation of compounds are available at 298 kelvin. Now, you should know the state of elements or compound, why I am telling this thing because if there is a transformation in the solid phase, I mean there could be transformation within the solid phase and transformation in melting and boiling. So, at all these transformations, temperature change does not occur, but you have to consider the latent heat. So, with this context, it is important to know the state of element or compound, when you attempt to make a heat balance of a particular problem.

So, if it is a solid state transformation, then you have to know at what temperature the transformation is occurring from alpha to beta and within what range. Accordingly, you have to use the C p value in that range and you should also know the melting point. The important thing over here is to know the latent heat and I have written it simply because many times, I have seen while performing heat balance, we might forget latent heat, but there is no reason for forgetting. So, latent heat can be for transformation, either in the solid state transformation or in the liquid transformation, from solid to liquid and liquid

to gas. In that stage, you have to see, what is the latent heat and also heat input could be of combustion energy.

Now, this fuel is used as a heat source, if you use fuel as a heat source, then two things you must know. Number one: what is the chemical composition? Number 2: what is the heat of formation? What is the calorific value of the fuel and what is the energy that is released on combustion? So, this is the combustion energy. In many processes, you will find that the reactants are heated, for example, in various high temperature processes, sometimes air is heated and the reactants are heated. So, you must also know which is a sensible heat of reactants? Now, you have to calculate sensibly, but to calculate that you must know what is the temperature at which the reactants are entering. It is an important thing.

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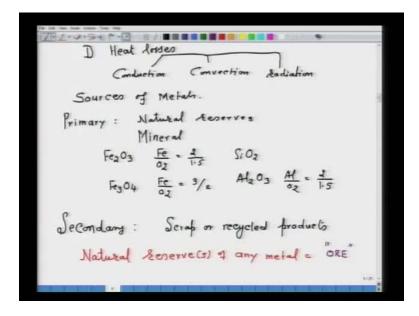
Now, some term for heat output. You have to see in what stream, heat is taken out. It may be taken out as solid products. For solid products, you must know C p of all components. If there is a phase transformation in the solid in that temperature range, then probably it is also important to know the latent heats. b) Liquid product- In solid products, you also require to know what the temperature is. In liquid products, you have to know what the temperature is and whether a liquid product that is exiting the system at the melting point or above the melting point and these are the important issues. Here, you have to see how products are forming. Temperature of each product, composition of each

product, C p value of each product and you should also know the heating value. To say, heat content at that particular temperature and if you are calculating latent heat from 298 degree at 298 kelvin, then heat of mixing... if you recall in the lecture on thermodynamics, I said various heat input and various heat output turns heat of mixing because when a liquid solution forms, for example, if silicon dissolves in iron, there is a heat of solution or there is a heat of mixing. Similarly, the two oxides that dissolve in certain cases generates heat. So that heat of mixing should be known. We should also know where heat of mixing is produced by addition of which, oxide heat of mixing will be available. So that information must be known in order to come to a exact or accurate heat balance.

Now, C) It is the gaseous product. Now, normally, in almost all metal extraction processes that we are concerned have the output as solid product, liquid product or gaseous product or combination of all the three or two. So, for the gaseous product, you are required to calculate how much heat is been taken out and we require the value of C p. Now, I would like to tell one important thing that many students I found they are doing the mistake not knowingly, but they are not cautious enough.

When you want to calculate heat content in water, So, you have to consider these steps. Probably, it will help yoy, H2O liquid at 25 degree celsius is equal to H2O liquid at 100 degree celsius. You should know the C p value of that. Then H2O liquid at 100 degree celsius is equal to H2O vapor at 100 degree celsius. Here, we should know that there is a transformation and so you must know latent heat, say, H2O vapor at 100 degree celsius to H2O vapor at that temperature and you must again know the value of C p. It is important here because the C p is also a function of temperature. Accordingly, you must collect the important values and many times a mistake occurs in calculating the heat content in water. Suppose water or the water vapor is being discharged. For example, 1400 degree celsius, if you select the state of water as liquid, then you have to calculate the heat content. First of all, you bring vapor from that temperature to 100. latent heat will be what Then from liquid to 25 degree.

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So, I mean that these are the things you must consider. Another important one is D calculation of heat losses. Now, heat losses are very important feature and they are an integral part of the high temperature extraction processes. You must be able to calculate heat losses. Now, here the mechanism is very clear- the conduction, convection and radiation. So, invoking the appropriate loss and the method of calculation, you should be able to calculate heat losses because these heat losses, if they are in very large amount, then one should think of how to minimize these heat losses to conserve the amount of energy. So, with this, say, these are slight basics of materials and energy balance. I will again say it is just a sort of a common sense. If I summarize, what I said until now. I will say it just as a common sense. Everyday, your dad must be giving 100 rupees and at night, he must be asking what is your balance? So, you must be able to tell him, you gave me 100 rupees in the morning. Now, I am left with a 5 rupee and immediately he will ask you, where did you spend? Give me the balance, the same thing here. Your plan manager has given you, for example, 100 tons of raw material and he wants to know what are the outputs. So, his objective is to minimize the losses, if at all they are occurring, this is what the whole objective of this material and heat balance exercise.

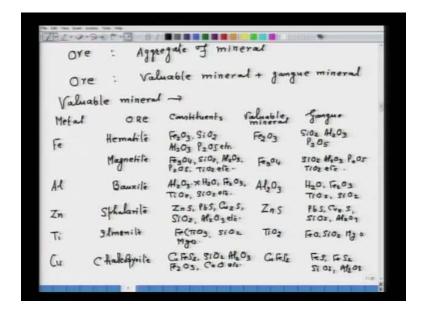
Now, let us apply these concept to actual metal extraction processes. Now, before we go to that a brief account of the metal extraction process is very much desirable because without this you may not be able to understand how to apply these balances. So, with this I will give you a brief introduction to metal extraction. Now, first thing, I would like to

say, what are the sources of metals? Sources of metals occur in the nature as minerals. Metal in nature does not occur as metal and that is a very important thing you must know. So, there are two sources: one is the primary source. Primary sources are te natural reserves. Natural reserves, as I said, metals are in form of minerals oxides or sulphides. It is important to know what is a mineral because, when a question is asked as what is the difference between mineral and ore. I found many students sometimes get confuse. So, I be should very clear that a mineral is an inorganic compound in which elements are combined in stoichiometric proportion. You should be very clear in this. I repeat again, a mineral is an inorganic compound in which elements are combined in stoichiometric proportion and so the natural occurrence of metal is mineral and as I said it is an inorganic compound.

For example, I take a Fe2O3, 2 molecules of iron are combined with 1.5 molecules of oxygen. The ratio of Fe upon O2 is equal to 2 upon 1.5. Take SiO2, 1 molecule of silicon is combined with 1 molecule of oxygen. Similarly, we take Fe2O4 and the ratio for example, if I write Fe upon O2 will be 3 by 2. Let us take Al2O3, the ratio of aluminum upon O2 will be equal to 2 upon 1.5 and that is the meaning of mineral is. The elements are combined in mixed proportions.

Another source is secondary. The secondary resource is a scrap or recycled products. The amount of metal or the amount of consumption of metal with which we are concerned is enormous. It is in million tons and hardly the secondary resources can meet a very large requirement of the human beings. Therefore, the main resource or source of metal is the primary reserves. So, I will write in red ink- natural reserve or reserves of any metal is called , I will write with a different ink ore. So, remember, there is a difference between ore and a mineral. A mineral is an inorganic compound in which elements are combined in a stoichiometric proportion. Whereas, an ore is an aggregate of minerals.

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Remember, ore in fact is an aggregate of minerals. It means ore of a metal will consist of valuable mineral plus all other minerals is called as gangue minerals. What does a valuable mineral mean? A valuable mineral is a one that we are interested in the production of metal. For example, I consider a metal, name of the ore, constituent of the ore, valuable mineral and gangue mineral.

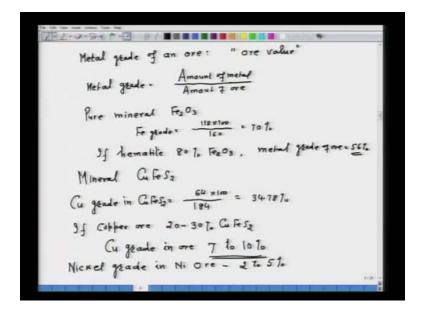
Now, gangue mineral is a waste. Now, remember, when I say it as a waste, it is vest with reference to the metal in which I am interested in production. Otherwise, gangue is also a mineral. So, remember, when I say it is a gangue is waste, for production of that particular metal, rest all is a waste with reference to that particular metal. So, for example, I take the metal as iron and the name of the ore is hematite. Now, hematite contains Fe2O2, SiO2, Al2O2, P2O5 etc. Now, we are interested in iron and so valuable mineral is Fe2O3 and all other. For example, SiO2, Al2O3, P2O5 are considered to be gangue, but they are also mineral because SiO2, 1 molecule of silicon and 2 atoms of oxygen. Silicon is also a metal, which is very important. Al2O3, aluminum is also a metal. Similarly, another example, I have constituents as Fe3O4, SiO2, Al2O3, P2O5 and TiO2 etc. The valuable mineral is Fe3O4 and rest are all, say, SiO2, Al2O3, P2O5 and TiO2 etc are the gangue minerals.

Another example, I take aluminum and the name of the ore is bauxite. Now, bauxite has Al2O3 into x H2O, Fe2O3, TiO2, SiO2 etc. Now, in this aggregate of mineral, which is

called an ore? The valuable one is only Al2O3 and rest all, say, H2O, Fe2O3, TiO2 and SiO2 are gangue minerals. Another example, I take zinc and sphalarite is the name of the ore. Sphalarite may contain zinc sulphide, lead sulphide, Cu2S, SiO2, Al2O3 etc. You do not know what the nature has stored for you. Here, I want to get only zinc as it is the valuable material. So, zinc sulphide and with reference to this PbS, Cu2S, SiO2, Al2O3 are gangue mineral. Although Pb is also a metal, It can also be recovered from the gangue depending upon its concentration Similarly, if I take an example, I can take titanium and Ilmenite is the ore. In ilmenite composition, you have Fe, TiO3, SiO2, MgO etc. Now, the valuable mineral is titanium dioxide and rest, say, FeO, SiO2, MgO are all gangue minerals.

Now, another important metal is copper. Ore name is chalcopyrite and chalcopyrite constituents CuFeS2, SiO2, Al2O3, Fe2O3, calcium oxide etc. Now, here the valuable mineral is only CuFeS2 and all other for example, FeS, FeS2, SiO2, Al2O3 are all considered to be the gangue minerals. So, what we note from here is that ore being an aggregate of minerals, we must know what is the quantity of metal that an ore has and so that quantity is quantified by defining metal grade.

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Metal grade of an ore indicates ore value. Now, as I said, if the metal grade is high, then the gangue mineral is low. Accordingly, less effort has to be taken to remove the gangue.

So, metal grade is a very important issue. Now, how to define metal grade? Metal grade is equal to amount of metal upon amount of ore, if I want to define metal grade in an ore.

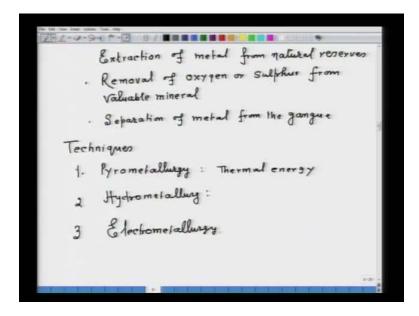
Now, for example, I can also define metal grade of a pure mineral. In that case, I have to take the amount of metal in the mineral upon amount of mineral. Now, for example, I take a pure mineral, Fe2O3, then iron grade in pure Fe2O3 will be equal to 112 into 100 upon 160 and that makes 70 percent. What does it mean? 30 percent is a waste and that has to be removed, if you want to get iron. Now, for example, hematite, which is an ore contains 80 percent of Fe2O3 and then the metal grade of ore or iron grade of ore is equal to 56 percent. What does it mean? 44 percent is the gangue and that has to be removed, if you are possessing the natural reserve, which is hematite and that is important.

Now, let me give another example. Let us consider a mineral for copper, which is say CuFeS2. Now, let us find out the copper grade. Copper grade in CuFeS2 pure mineral will be equal to 64 upon 184 into 100 is equal to 34.78 percent. Now, see the copper grade in pure CuFeS2 is 34.78 percent. Now, imagine if copper ore has 20 to 30 percent CuFeS2, which is normally the case or it could be even less than that. Thus the content of CuFeS2 could be 20 to 30 percent or could be even less than that. In that case, the copper grade in ore will be 7 to 10 percent. What does this mean? It means out of every 100 kilo gram of ore, you have only 7 to 10 kilo gram of copper and rest is gangue or you can call it as a waste with reference to the copper and they have to be removed. That is an important thing you must understand from here. Now, similarly, say nickel grade, which is again an important strategic metal. Nickel grade in nickel ore also varies and it is for your information. Although it depends on location to location, it varies between 2 to 5 percent. So, accordingly, the amount of waste that we are producing from synthesize or from the processing of the natural reserves of these metal is an ore.

A nickel having only 5 percent nickel and 95 percent is a waste. Remember, these things are not physically separable and it is chemically combined. For example, the hematite ore has Fe2O3, chalcopyrite has CuFeS2. So, copper and sulphur are not physically combined, but they are chemically combined. Similarly, in Fe2O3, iron and oxygen are chemically combined. You cannot just do by breaking and removing sulphur from copper or removing oxygen from iron is not possible. So, what I mean is that they are

also chemically combined. So, what we can say, if you are looking from extraction of metal from natural reserves, what has to be done? What are the basics?

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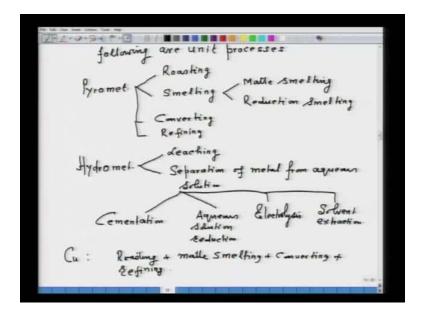
The extraction of metal from natural reserves is going to use ore. What we have to do? First step is that you have to remove oxygen or sulphur from valuable mineral because in ore of iron, we are interested in iron and nothing else. From valuable mineral, this is the first step that you have to do. Removal of oxygen or sulphur from the valuable mineral is the first step in processing the natural reserves in order to get the metal.

Second important step is separation of metal from the gangue minerals. Remember, separation might convey it to you as a physical, no not that physical. I mean it may require certain reaction that is all. The separation I mean is that once you have got the oxygen or sulphur removed from the valuable mineral, then you have an aggregate metal plus gangue. Now, you have to separate it and you cannot separate it chemically. You cannot separate it physically and so these are the two steps that are required to extract metal from natural reserves.

What are the techniques? Whatever technique you adopt, these two are the important steps. First technique is pyrometallurgy. Pyrometallurgy - the term 'pyro' means high temperature. Here, it is the temperature or thermal energy. This pyrometallurgical root is thermal energy dependent and that is where energy balance is an important issue. Second is hydrometallurgy. Root of hydrometallurgy is not thermal energy dependent, but it

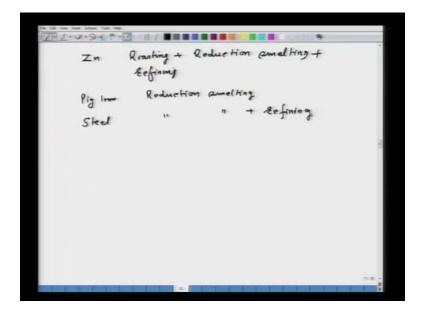
requires an enormous amount of liquids, mostly water. Third is not an independent root, but, it is combined with hydrometallurgy and that is the electrometallurgy. These are the three techniques, which can be used to extract metal from the natural reserves.

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So, the following unit processes are used. In the case of pyrometallurgical extractions; pyromet, I am writing in the short form. First step is roasting, second step is smelting or reduction smelting, third step is converting and fourth step is refining. We will take these in our subsequent lectures along with the material and energy balance. For hydrometallurgy, various unit processes are - one is the leaching and second is the separation of metal from an aqueous solution. Separation of metal from aqueous solution is done because in hydrometallurgy, you have the metal in the solution. Now, various techniques are used: One is the cementation, aqueous solution reduction, electrolysis and solvent extraction technique. Now, for example, copper by pyrometallurgical root uses roasting plus matte smelting plus converting plus refining. It combines all of them.

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I will give one or two examples. I take zinc and it combines roasting, reduction smelting plus refining. If you take, pig iron, it has reduction smelting. These are the combinations of unique process to produce the metal, say, steel by reduction smelting plus refining. So, in short, these are the various processes that are used.