

Materials and Energy Balance in Metallurgical Processes

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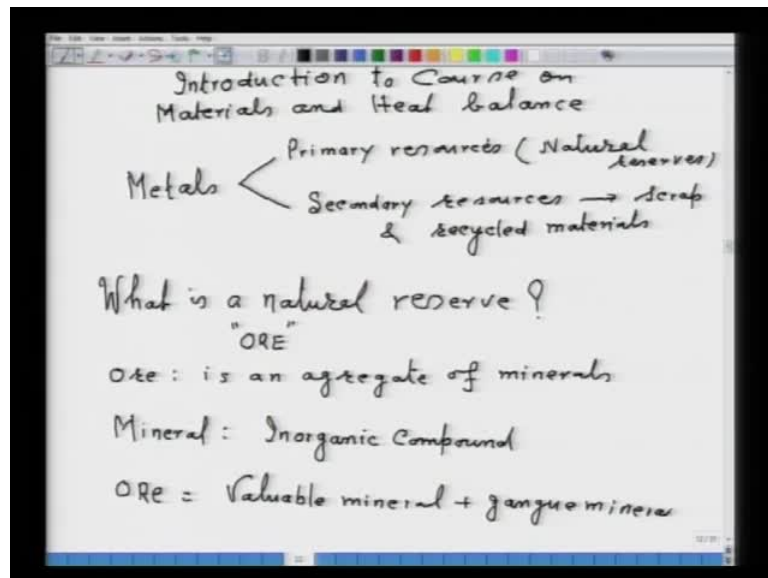
Module No. # 01

Lecture No. # 01

Introduction to Course

Let me introduce you to the course on materials and heat balance. What I have thought, the best way to introduce the course content of this lecture is to see energy and environment issues related to metal production.

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Now say, metals; they can be obtained either from primary resources; that is also called natural reserves or from secondary resources.

Secondary resources mostly are scrap and recycled material.

Metals, as all of us know, are required for the development of different industrial sectors; may be construction, may be aircraft, may be heavy industry, wherever metals are used.

So, needless to mention, there is a very large requirement of different metals for different industrial sectors, therefore the secondary resources which are from scrap or recycled material; they hardly can meet the enormous requirement of metal for the growth of the several industries.

Therefore, we are mainly concerned with the use of natural reserves for the production of metal; and that is where the course starts.

What is a natural reserve of a metal? The natural reserve of a metal, any metal, is called ore, where ore is an aggregate of minerals. That means, the ore will have, along with the metallic mineral, I mean, the mineral of a metal, in which we are interested, plus there are several other type of mineral.

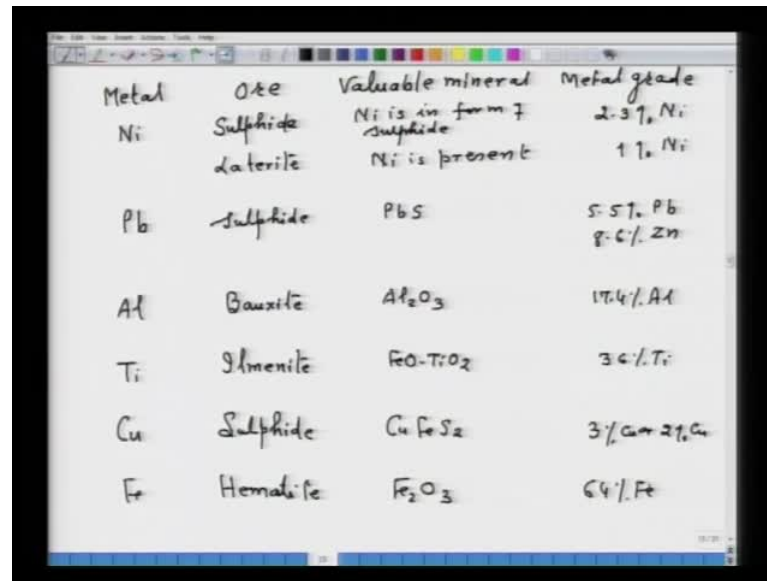
So in fact ore is an aggregate of minerals; and a mineral in general definition is an inorganic compound in which elements are combined in fixed stoichiometric proportions.

For example if I take Al_2O_3 . In Al_2O_3 , 2 atoms of aluminum are combined with 1.5 moles of oxygen.

Or, if you take Fe_2O_3 , same 2 moles of iron; they are combined with 1.5 moles of oxygen. That has to be very clear. The natural reserve of a metal is an ore, in the form of mineral; that is important.

We can say that ore consist of valuable mineral plus gangue mineral. Now, with the valuable mineral, I mean, out of all the mineral that are present in ore, valuable is the one from which we want to extract the metal.

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Metal	Ore	Valuable mineral	Metal grade
Ni	Sulphide	Ni is in form of sulphide	2.3% Ni
	Laterite	Ni is present	1% Ni
Pb	Sulphide	PbS	5.5% Pb 8.6% Zn
Al	Bauxite	Al_2O_3	17.4% Al
Ti	Ilmenite	$FeO \cdot TiO_2$	36% Ti
Cu	Sulphide	Cu_2FeS_2	3% Cu + 2% Cu
Fe	Hematite	Fe_2O_3	64% Fe

Let us see the ore, valuable mineral gangue mineral and so on. If I put here metal; put here, say, name of the ore; valuable mineral; then I put here, metal grade.

Now, for example, if I take nickel as a metal, then ore is sulphide ore, in which nickel is in the form of sulphide; it could be Ni_3S_2 ; or it could be Ni_3FeS_2 or so on.

The metal grade in case of sulphide ore is 2.3 percent nickel; the oxidic ore - that is called lateritic ore, in which nickel is present and the grade of the nickel is 1 percent nickel.

Let us take lead; sulphide ore, which is called galena; it is name of the ore and here the valuable mineral is PbS. Metal grade is 5.5 percent for lead; and sometimes it contains zinc also. The grade of zinc is 8.6 percent zinc.

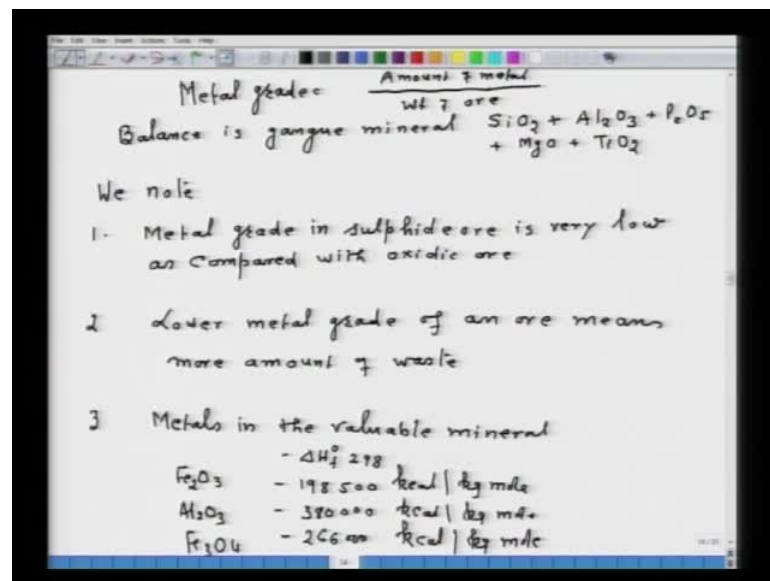
Let us take the aluminum, which is again an oxidic ore. The name of the ore is called bauxite. The valuable mineral here is Al_2O_3 and metal grade is 17.4 percent aluminum. Though I am giving an absolute value, but it may be ranging from this to this.

Similarly, for titanium, name of the ore is Ilmenite and it is form of $FeO \cdot TiO_2$, from which titanium is to be determined; and the metal grade is 36 percent titanium.

Similarly I can take copper; for this - sulphide ore. Here the valuable mineral is CuFeS_2 and the grade of the copper noticed is 3 percent copper or 2 percent copper, very low grade.

Similarly, iron; name of the ore, all of you know, is hematite is Fe_2O_3 and metal grade is the 64 percent iron.

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Before we analyze this table, I wish to define a metal grade. Metal grade is equal to amount of metal in ore upon weight of ore. Amount of metal upon weight of ore; that is how the metal grade is defined.

All the other, the balance; that is, I have written 64 percent iron or 2 percent copper and so on; the balance is gangue mineral in the table and this gangue mineral essentially consist of SiO_2 . For all types of ore that I have listed in the table, gangue mineral SiO_2 plus Al_2O_3 , P_2O_5 and MgO ; sometimes you can have TiO_2 also.

In some of the ore, for example, hematite has SiO_2 , Al_2O_3 , P_2O_5 and so on.

Similarly, for example, if you have chalcopyrite or the sulphide ore of copper, CuFeS_2 is the valuable mineral; SiO_2 , Al_2O_3 and Fe_2O_3 ; they are the gangue minerals; it depends upon which ore you are considering.

Now, we note from the table the following; first is: metal grade in sulphide ore is very low as compared with oxidic ore.

So you see, iron grade is 64 percent, whereas, copper grade is 2 percent; that is, what is meant is that means a large amount of gangue material will be produced, when sulphide ores are treated.

Second it means that lower the metal grade of an ore, it means more amount of waste will be generated, because you have to remove more in order to get the metal.

Third important thing that we notice from here, and that all of you know, that metals in the valuable mineral is either in the form of sulphide or in the form of oxides; they are chemically combined.

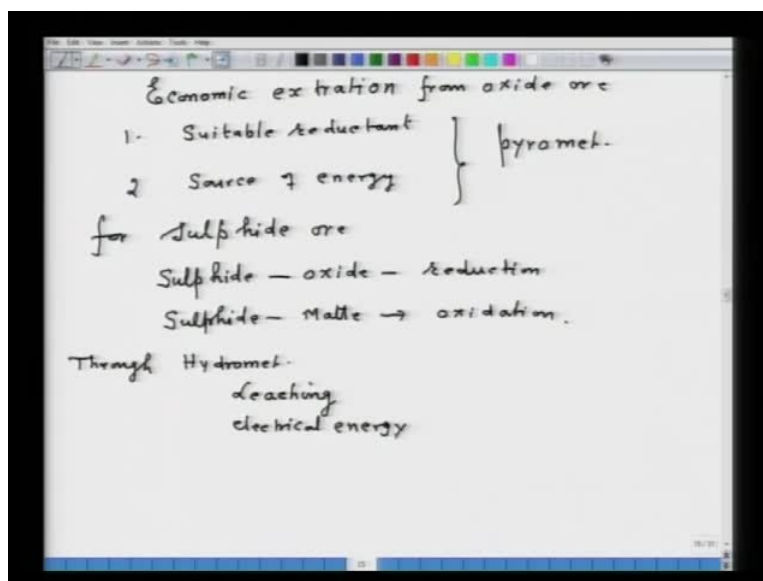
Therefore, these oxides or sulphide; if you want to separate them, a very high energy is required. I will give you some of the energy required. For example, Fe_2O_3 , the heat of formation value at 298 Kelvin, it is minus 1985000 kilo calories per kilogram mole. That much amount of heat you will be requiring, if you want to dissociate iron Fe_2O_3 into iron and oxygen.

Say, if I take Al_2O_3 , you will be requiring around minus 380000 kilo calorie; you can imagine; these are per kilogram mole.

So, imagine the amount of material that you want to produce. For example, if I take say Fe_3O_4 , you will be requiring around minus 266000 kilo calorie per kg mole of the energy.

Similarly, I mean, I can list down the heat of formation that would be required, or heat of formation that is associated with the formation of the compound or sulphide; that means, you have to provide that much of energy in order to get the metal.

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The economic extraction of metal from oxide ore: what it requires? First of all, suitable reductant, because naturally, so much amount of energy is very difficult to provide; it should be highly economical; so, we have to see a suitable reductant, which is cheaply and abundantly available.

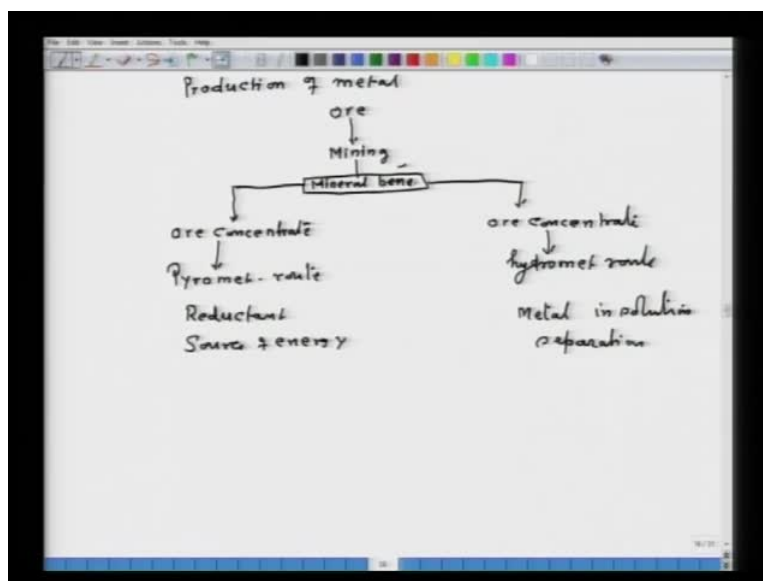
And second thing we require is source of energy. Why do we required source of energy? We have to separate the gangue from the metal and these 2 things, when we want to employ pyrometallurgical route, pyromet route.

Now similarly, for sulphide ore, the extraction of metal; though thermodynamically possible to reduce a copper sulphide or led sulphide directly into metal, but it is highly environmentally hazardous.

Therefore, what is done is the sulphide ore is first converted to oxide and then followed by reduction; again, you have to find out a suitable reducing agent, when we want to go for pyrometallurgical route. In some cases sulphide is converted to matte. Matte is a mixture of sulphide; and then followed by oxidation to get the metal. So, these are the things that you will require.

Now through hydrometallurgical route, through hydromet route, we require leaching and electrical energy.

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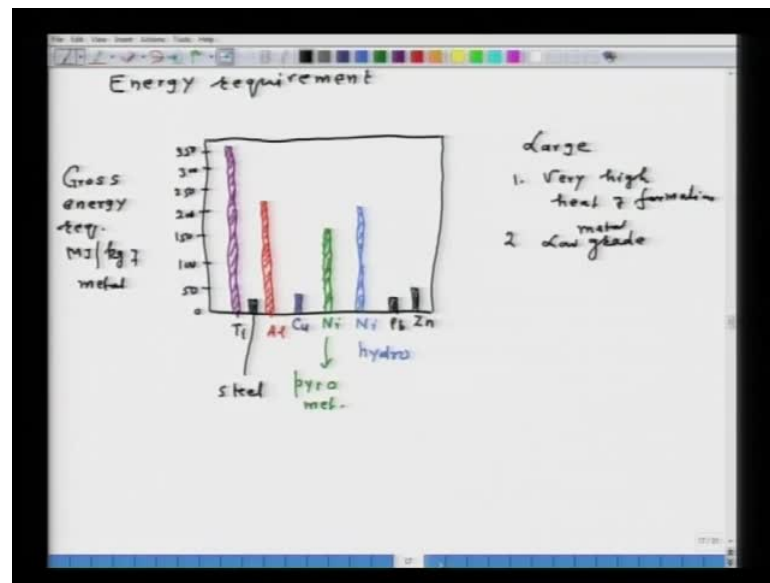
So, let us further follow it up. Let us consider a production of metal from an ore. Let us consider a general flow sheet of production of metal from an ore. For example, I take an ore; whatever the ore from the natural reserve, I have to subject it to mining operation; and this mining operation has to be followed by mineral beneficiation.

And from here, I will be getting ore concentrate. And ore concentrate for pyrometallurgical route. Or depending upon the quality of the ore concentrate, I can go for, this is again ore concentrate, I can go for hydromet route.

This will comprise of almost all production of metal from natural reserve; first step is mineral beneficiation, followed by extraction of metal either from pyromet or from hydromet.

From pyromet, it is clear you require reducing agent, a reductant and source of energy. Here, you have to bring metal in the solution. Metal is brought in solution and followed by separation. Again for large tonnage of metal production, pyro-metallurgical is most preferred route, as compare to hydro-metallurgical extraction. Because large amount of metal can be produced by pyrometallurgical method. So, what we notice from here is that in pyrometallurgical extraction, there is a large amount of energy is required.

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Let us see the energy requirement for metal production. I will just give you a plot, say this is the one. I put here 0, 50, 100, 150, then I have 200, 250, 300, and let us say 350.

And this is the gross energy requirement in megajoule per kg of metal. Let me take, first of all, titanium. Now, titanium would require around 350 megajoule per kg. See that very enormous amount of energy is required; this is for the titanium.

Now, on the other hand if I take, say aluminum; that will be requiring around approximately 200 megajoule per kg of metal.

You can imagine the amount of energy that would be required for nickel; if you talk of nickel, nickel will be somewhere around say 150; this is nickel, when we go for pyrometallurgical route, pyromet route.

Now, if you go for hydromet route, then slightly higher energy is required; this is for nickel through hydromet route.

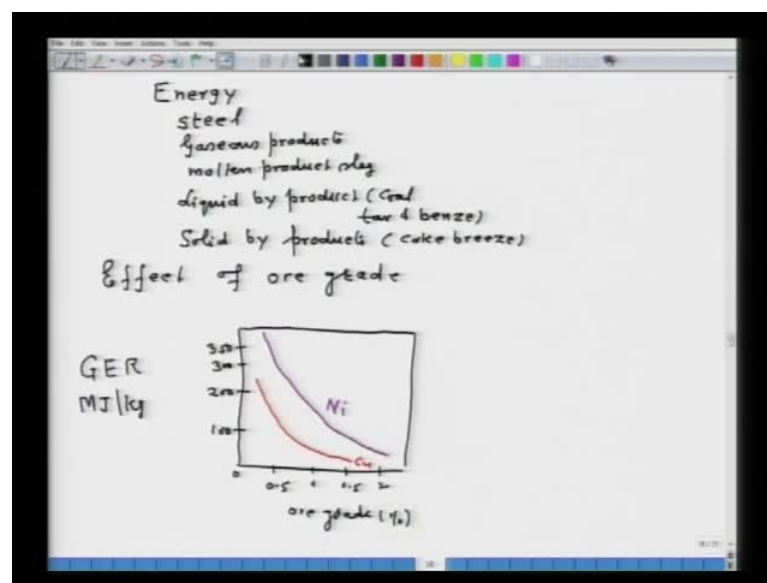
Say, for copper, somewhat less energy is required; this is for the copper; and for a steel also, we require very less amount of energy; this is for the steel. Then for lead also, very small amount of energy is required; and for zinc also, somewhat this type of energy is required; this is for the zinc; and this is for lead

So, this is just an estimate of the gross energy requirement. Now, this large amount of energy that is required is because of 2 factors.

First of all, very high heat of formation, as you know it; and second, is on the low grade ores, rather low metal grade of the ore.

These are the factors, probably, that determine the so called the gross energy requirement.

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Now, what energy do we supply? We supply energy that we employ to produce, say, steel in the steel industry, that results in production of products as well as byproduct.

So, what energy we supply to the steel plant, it produces, for example, steel that you require; it also produces gaseous product; it also produces molten product, say for example, slag.

Then, you also produce liquid byproduct, that is, coal tar and benzene, say, in the coking process. Then you have solid byproducts and these are, for example, coke breeze, in the coking process; the last one is dust.

Similarly, in case of nonferrous metals, the energy which is supplied to nonferrous industry whether it is zinc; whether it is copper or lead the products will be liquid metal, followed by slag, dross and **speiss**.

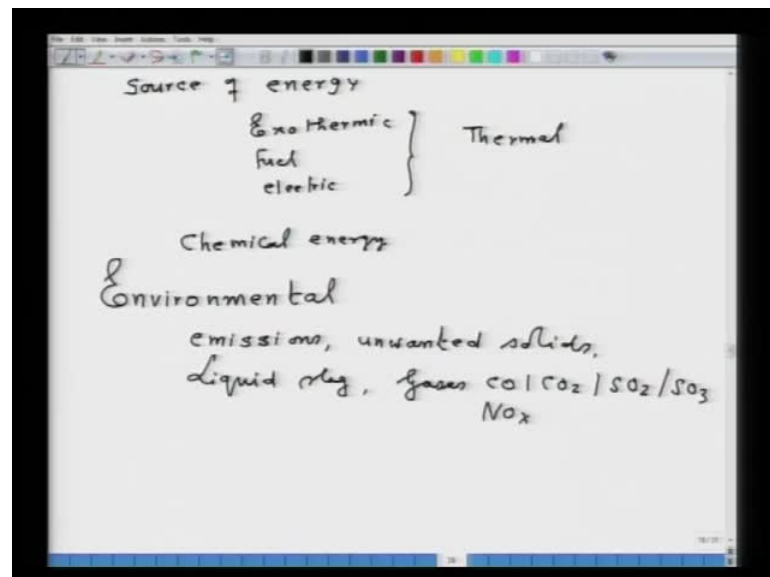
What I wish to say is that whatever energy you supply for the production of the metal, besides the product, the byproduct or the production of byproduct is a part of the production of the metal; that means, these byproduct are going to be produced.

Now, let us see now effect of ore grade on gross energy requirement. I will again try to plot, say here (Refer Slide Time: 24:40), I take for example, ore grade or metal grade.

I will take here 0, 0.5, 1, 1.5 and 2 and here I take 100, 200, 300 and somewhere 350; and that is again gross energy requirement - megajoule per kg; mind you, I am plotting as a function of the metal grade of the ore.

So, I just take 2 examples: copper and nickel. For copper, this is the case for copper whereas, above is the case is for nickel. So you see, what important message that you get from this particular plot is that lower is the metal grade in the ore, higher will be the energy consumption; higher is the metal grade of the ore, lower is the energy consumption. That point is important. That means ore grade will play very important role, because a large amount of energy will be required during mining and mineral beneficiation operation, particularly when the metal grade of the ore is very very low.

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That is the issue, in case of the energy production. Now I will give you little idea about the source of energy.

Source of energy: it could be exothermic reactions, which is not a problem at all; then fuel, that is the fossil fuel is another source of energy; and the electric energy, but the electric energy if it is derived from fuel, then we are talking again of fuel as a source of energy, but if it is derived from other than the fossil fuels, then it is an extra source of energy.

So, you require, for example thermal energy because you have to heat. So energy supply is an important issue. How you are going to supply energy; how much amount of energy is required; how much amount of the fuel is to be supplied and so on and so forth.

And second, we also require to supply chemical energy. Chemical energy means the energy that is required for reducing; for example, you have got an oxide you want to reduce; you have to search for a reductant, which is abundantly, cheaply and economically available. If you have seen an Ellingham diagram, of which you are aware, you can find a number of reductants, which can reduce a particular oxide

But remember, you are producing the metal on a tonnage scale, so you cannot afford to use a reductant, which is not economical, which is expensive; therefore, the requirement here is that it is cheaply and abundantly available.

Another important case here is: how energy is obtained from the fuel? By combustion. How, by combustion? The elements of the fuel that are converted into products of combustion and these products of combustion are again discharged into the atmosphere.

That means larger the energy requirement, larger is the fuel consumption and larger amount of products of combustion will be discharged into the atmosphere, meaning thereby, you are creating an environmental issue over there.

In selection of the fuel, temperature is also an important issue; you have to create a particular temperature; so for that, the selection of the fuel is again an important issue.

You have to provide an oxidizing medium. Oxygen is the issue. From air you will get the oxygen. In air, did all of you know that 1 mole of oxygen is derived from 4.76 moles of air; that means 3.76 moles of nitrogen.

If you are supplying, say one mole of oxygen, for a particular reaction, from air, then you are also having 3.76 moles of nitrogen; and these nitrogen will take away a large amount of heat.

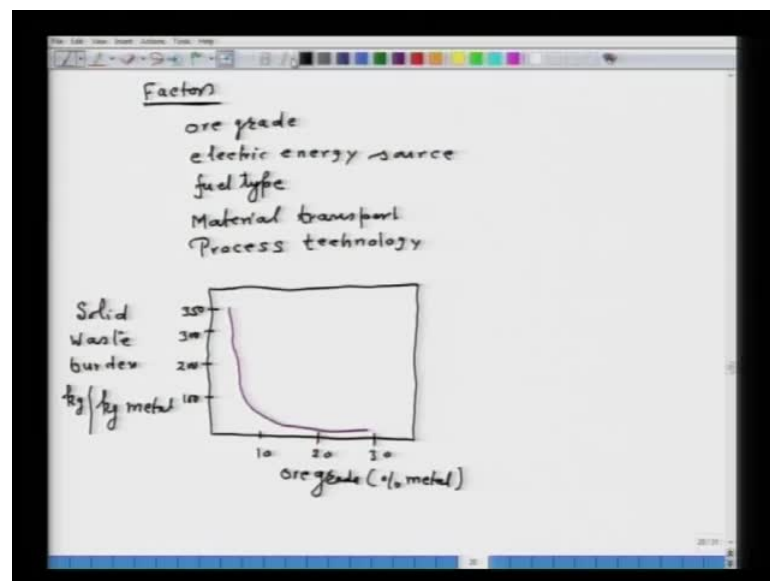
So what I mean to say is in pyrometallurgical extraction, you have to optimize, you have to economize the source of energy; you have to see that the combustion which occur by way of air, it has to be optimized, otherwise you will have a large amount of energy consumption. This is an energy consumption issue related to metal production.

Let us see what the environmental issues are. Let me address a little bit of environmental issues. Now you have already noted that by use of energy, the products of combustion are discharge into the atmosphere.

When you produce the metal, except metal which is a product, rest are all byproduct; you have to see what you are going to do. Either reuse it, recycle it or recirculate it. If not, then you will be dumping it into the atmosphere; you will be dumping on the earth. That means, again, there are environmental issues.

The production of metal from the ores result in the formation of emissions; unwanted solids; liquid, say liquid slag - slag is a mixture of oxide; then gases like CO, CO₂, SO₂, SO₃, NO_x and so on. These things, you are producing during mining and during processing operations; directly you are producing.

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And indirectly you are producing by consumption of raw materials, because when raw materials are processed, again these things will be produced.

The factors which affect the environmental impact:

One is the ore grade; second is the electrical energy source; third is the fuel type.

fourth material transport, because when you produce large tons of metal, say for example, steel, you are producing 7000 tons or 5000 tons per day, you can imagine the amount of raw material that will require to transport.

Then the process technology.

These are some of the factors that will affect the so called environmental impact. Out of which, the ore grade is the most important thing because if you notice, higher is the metal grade in the ore, less will be the byproduct that will be produced.

Now, once after beneficiation and mining, you have produced a concentrate of a required quality or of a required grade; then emissions from downstream processing are not very significantly affected. So what I am going to draw for you is, I am going to give you a picture. I plot here; say, if I put here, solid waste burden in kg per kg metal; as I said, once you can concentrate of a particular grade, then this figure can be thought of in general terms.

And if I put here, ore grade, in percent metal, say, here I put 100, 200, 300 and say 350; here I put 10, 20 and 30.

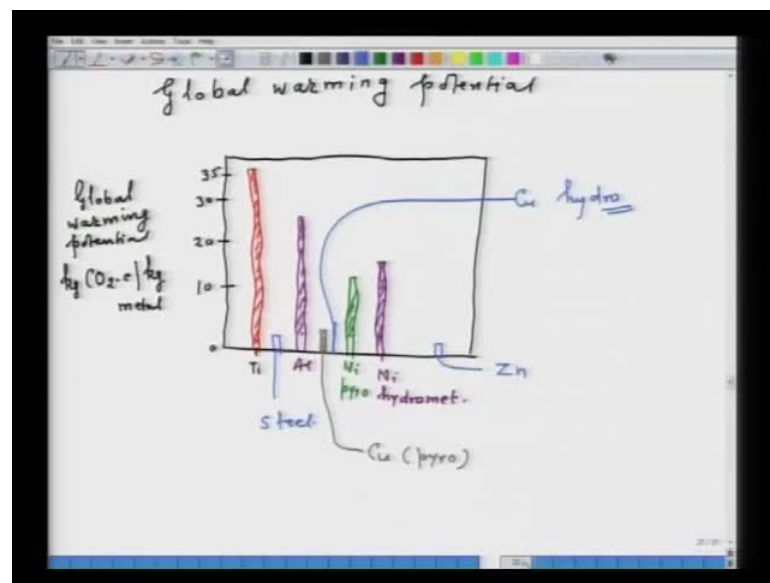
So this curves something like this; so you note from here that lower is the grade, for example, less than 10 percent, a large amount of waste burden will be produced. This is quite natural because if the metal grade is 10 percent, we are producing 90 percent waste. So ore grade plays a very important role. Now, as the metal demand grows, you will expect or you will use more natural reserve to produce the metal.

Now, the question is what about the quality of the natural reserves? You must have heard that the high quality ore reserves of particular metals, they are depleting. That means you will be employing lower grade ore in order to sustain the economic needs of the country; or in order to sustain the diversified needs of the industrial sector.

In the future, if the proper technologies are not developed, then more amount of waste is likely to be produced when the low grade or low metal grade ores are processed. It is quite natural, when high grade ores are depleting, you have to see that you supply the metal which is required for the industrial growth.

How will you do it? The only way is that you exploit low grade reserves. So what I wanted to say is that the ore grade will become a very important issue in the near future, particularly when you treat low grade metal ores.

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Let us see, also the global warming potential. You must have heard that global warming is becoming very important.

All of a sudden, the last few years people are talking that because of the discharge of the gases, a large-scale global warming is coming into the picture; and there are problems over there; energy used in fact is directly associated with the discharge of the carbon dioxide gases; and it is considered to be one of the causes of global warming.

Why I put this particular thing to your attention is that because you require large amount of energy derived from the combustion of fossil fuel; and the combustion of fossil fuel will generate, if it is perfect combustion, the product is carbon dioxide.

So it is in that perspective, you have to look into the consumptions of energy, in terms of the global warming potential. I will just try to again have a plot; this one, so this let us

take 0, 10, 20, 30; and let me take somewhere here, 35; and this is global warming potential, evaluated in tons of kilogram CO₂ equivalent, per kg metal.

Again if you take, say titanium, it has a very high environmental impact; this is for the titanium. Now if you take again for aluminum, this is for the aluminum. The quantification which are shown on the ordinate, it is more or less approximate.

I will give the reference from where I have taken the value; so, if you are interested, you can go to the original reference and update yourself. For nickel-pyromet route; and this is for the nickel-hydromet route. For zinc, it is quite a small bit; similarly, for a steel it is also very small; this is for zinc; this is production of steel; and somewhere here, we have copper; this one is copper from pyro means; and this is for copper-hydromet, by hydromet route.

My whole objective to show these things is to give a feel that production of metal requires energy; and as you require energy, there are issues on the environment. What I wanted to illustrate from here is that energy and environmental issues are part of the metal extraction from the natural reserves.

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Process efficiency PE-

$$PE = \frac{\text{free energy kcal/ton x 10}^6}{\text{Process energy required to produce metal; (kcal/ton)}}$$

Two issues are considered

- Energy Requirement
- Waste generation.
- Materials and heat balance

Now, let us see another feature. If I define for example, the process efficiency - PE; that is equal to theoretical energy that you require to produce a metal; mind you, the theoretical energy is the free energy change.

That will be free energy in kilo calorie per ton; divide by process energy required to produce metal, the units again in kilo calorie per ton; when we are defining efficiency, if I multiply by hundred, then this is the process efficiency.

Now, for your information or you may be surprised that the process efficiency for most of the pyrometallurgical extraction lay between... How much, can you guess? Its value lies between 4 to 8 percent for titanium sponge, magnesium ingot, fluorochrome low carbon, sodium metal, nickel cathode, refined copper and lead ingot.

That means these metal production; they have a very low, of the order of 4 to 8 percent; that is the process efficiency; that means a significant amount of energy is required for production of these metals. You require a very large amount, then theoretically what would have been required. However, there are definitely scientific and technological reasons for the low process efficiencies.

But, it is possible to effect substantial energy savings by use of correct science and technology. So what I have illustrated now is that there is a relation, or there are environmental and energy issues related to production.

The aim of this course, which is on materials and heat balance, is to develop so called quantitative feel about the energy requirement and waste production to extract metal from the ore. While developing the course, 2 issues, I have considered:

One is the energy requirement - that means you take iron, copper, lead or zinc; for 1 kg how much amount of energy you require? That will be the motive behind development of the course; and second is the production of waste that will be generated. Keeping these 2 issues in mind and seeing the strong relationship between the energy and environment, I thought that in a course on material and heat balance, it will be very important to appreciate, quantitatively, the amounts involved in energy as well as in the generation of the waste.

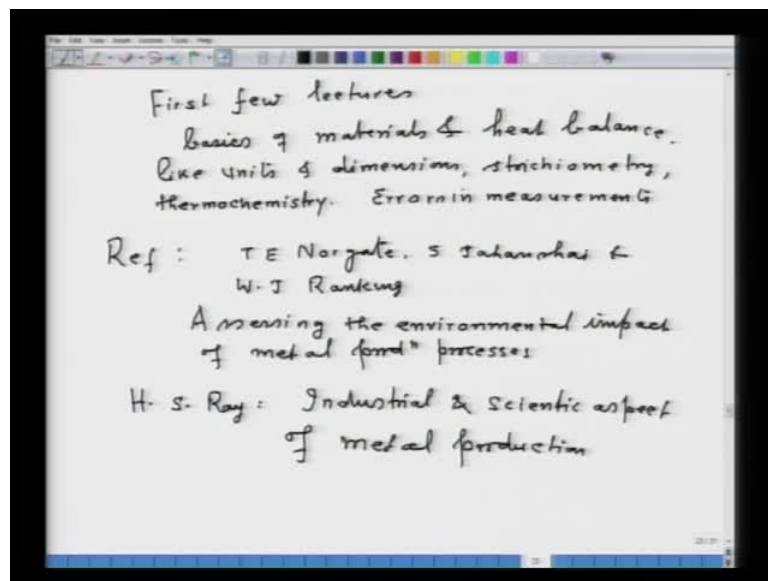
Now, in order to meet these objectives, there is emphasis I have given on material and heat balance.

Now, let me say very frankly that it is not the intension of this course to give you the detailed process flow sheets or the detailed description of the processes. The objective of

this course is to do material and heat balance; and to this effect, the conceptual part, as required to solve the material and heat balance, for a particular process or for a particular extraction of metal are given to the extent it is required for solving the material and heat balance problem.

By that, I mean that if the details are required, if you want to learn more, you have to see the proper references, which I will give from time to time, as I will go into the lecture part of it. Regarding the organization of the course, what I have done is that I will be devoting first few lectures on basics of materials and heat balance, like illustrating units and dimensions, stoichiometry and thermochemistry. I will also be making several attempts to solve the problems; that is as much that could be solved, I will be doing in the development of this course.

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Also one of the important things that I have also included is the errors in measurement. Because many a times, by material and heat balance, we can calculate, for example, the amount of mass that is required; so, we know the mass flow rate of the material.

We know that is the temperature; we can calculate the temperature, but then we have to make sure that that is actually the temperature; and for that measuring techniques are required; and the measuring techniques, they are associated with errors; therefore, it is important to see what errors in measurement can do.

And how to consider those errors in measurement, while comparing the calculated value of, say temperature, or flow rates, or weight of the material and so on with actually measured values. For that, I have also included the so called errors in measurement. Now in the remaining lectures what I will do is I am going to cover the materials and heat balance in several metal extraction processes.

The typical examples I will be including are ferrous as well as nonferrous metals, both.

In the metallurgical industry or in the material processing industry, also cement industry or any high temperature industry, large amount of fossil fuel is used in the furnaces.

So I am also going to consider the material and heat balance in the furnaces, which are used for solid metal processing in metallurgical industry. Similarly, one can use these concepts in the cement industry also, where also very high temperatures are required to produce the cement from the raw material.

So this is what I will be covering in this particular course. More emphasis, I will be giving on problem solving. After giving the concept, wherever it is required, then immediately I will proceed to solve the problems. I have given solved problems as well as unsolved problems; both I have given.

I will give some references from where I have taken these lectures - One is the article by T E Norgate, S Jahan Shai and W J Ranking. This is an online article on assessing the environmental impact of metal production processes. Now, this lecture is available online and one can use it if you look it up in Google; and second lecture is by H S Ray, which is on industrial and scientific aspect and of metal production; this lecture of H S Ray is also available online; look it up in Google.