Non-ferrous Extractive Metallurgy
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Lecture No. # 11
Refining of Metals – Physical Methods

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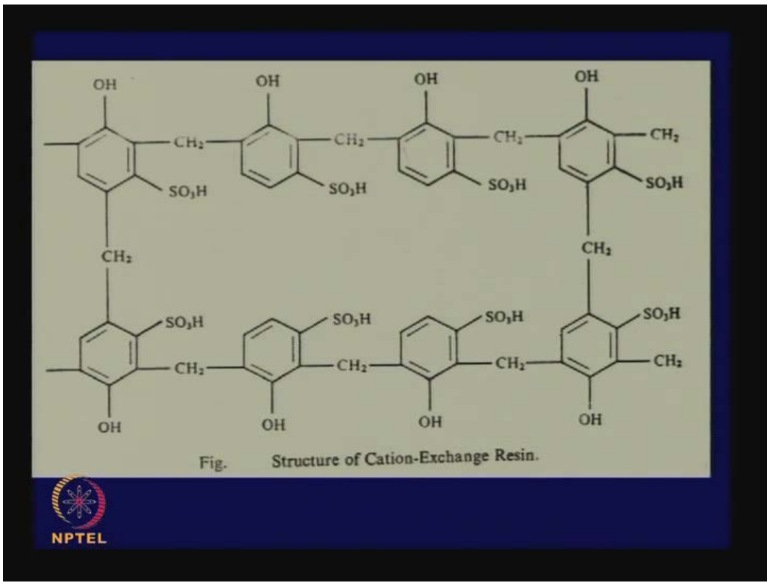

Fig. Structure of Cation-Exchange Resin.

Before I come to physical methods of refining, I have to complete what I had started discussing, that is, the purification of leach liquor using resins. This is a chemical method; it is not a physical method, and as I mentioned, resins are solids, and here is a structure of a cation exchange resin. The large molecules you can see that the inter collected and crossed linked chains are there and there are certain sites. In this case, S O 3 H where a cation exchange is possible means H would be replaced by a metallic cation when a leach liquor containing that metallic value comes in contact with this resin. So, resin is a solid through which the leach liquor will go, leach liquor with metallic values, and the metallic ions would be preferentially absorbed by the resin at that site.

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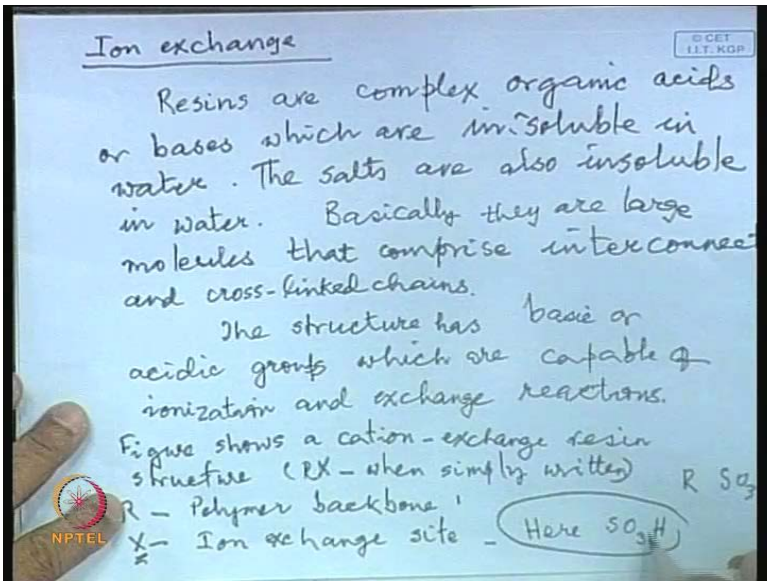

Ion exchange

Resins are complex organic acids or bases which are in-soluble in water. The salts are also insoluble in water. Basically they are large molecules that comprise interconnec
and cross-linked chains.

The structure has basic or acidic groups which are capable of ionization and exchange reactions.

Figure shows a cation-exchange resin structure (RX – when simply written) R SO_3

R – Polymer backbone

X – Ion exchange site – Here SO_3H

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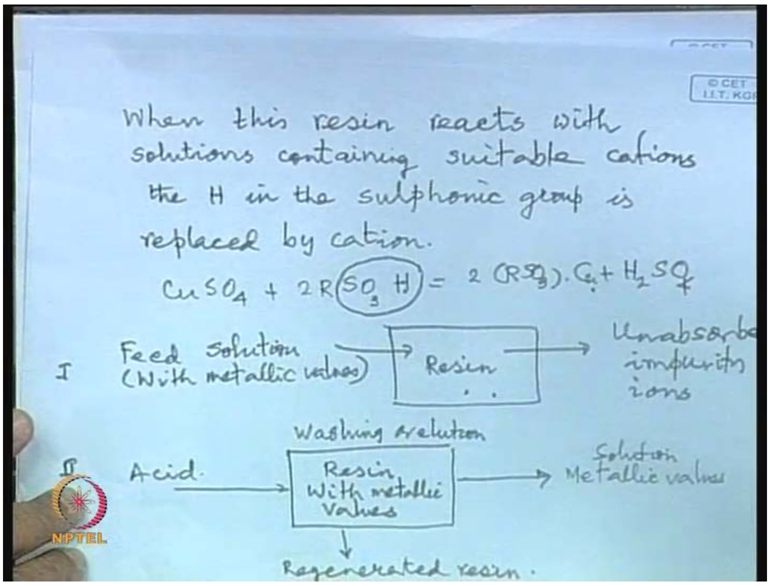

When this resin reacts with solutions containing suitable cations the H in the sulphonic group is replaced by cation.

$CuSO_4 + 2R\boxed{SO_3H} = 2(RSO_3).Cu + H_2SO_4$

I Feed solution (With metallic values) → Resin → Unabsorbe impurity ions

Washing / elution

II Acid → Resin With metallic Values → Solution Metallic values

↓

Regenerated resin.

Now, we can write such a resin as r x - where r is the polymer backbone, and x is the ion exchange site. Here, x is S O 3 H. So, the polymer can be written as S R S O 3 H because a cation will be exchanged, this is called a cation exchange resin. And I had, as I had mentioned, when this resin will react with solutions containing suitable cations, the H in the sulphonic group is replaced by cations and we represent it by writing like this. This is the resin. The sulphonic group is replaced by copper; it produces H 2 S O 4. So, when the feed solution goes through resin, this resin will absorb the copper in this area, unabsorbed impurities will go through. The reaction can be reversed and we call it washing or illusion where, we regenerate resin and only now the solution will have the metallic ions that were observed in the first place.

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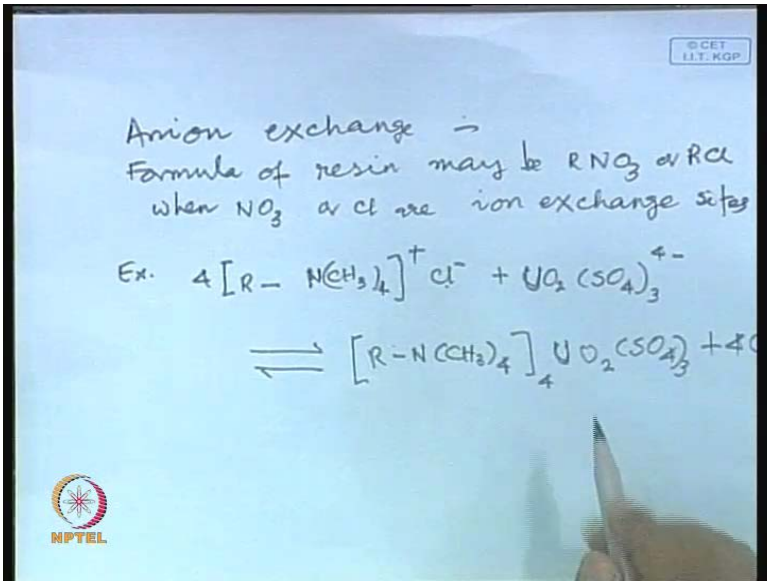

Anion exchange :-

Formula of resin may be RNO_3 or RCl

when NO_3 or Cl are ion exchange sites

Ex. $4[R-N(CH_3)_4]^+Cl^- + UO_2(SO_4)_3^{4-}$

$\rightleftharpoons [R-N(CH_3)_4]_4UO_2(SO_4)_3 + 4$

Now, this is cation exchange resin. There can be anion exchange also. It might surprise you how can metal be present in an anion, but there are complexes were anion can be, can contain a metallic value. An example is this. The formula for a resin can be R N O 3 or R R C l, and this N O 3 and C l will be ion exchange sites. Here is a an example a polymer backbone with a, with a, group like this C l here, and uranium solutions containing such anions which has uranium in them will be absorbed; chlorine will be released, chlorine ions will be released. So the chlorine ions will come out; uranium will go in an ion exchange site, and again subsequently, that uranium, this, this, uranium in that ion can be recovered and the resin generated.

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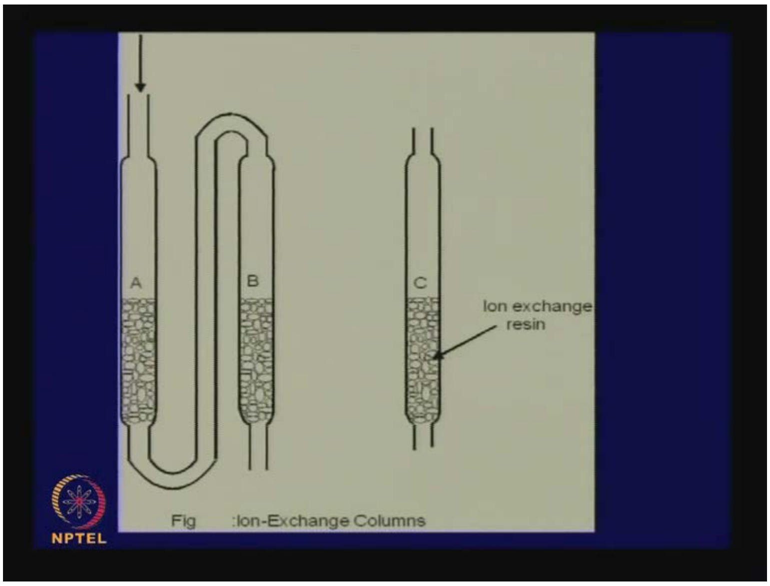

Fig :Ion-Exchange Columns

This is the simple way of representing this. We have ion exchange columns; columns containing resins, and if we pass the solution containing metallic ions through them, they will absorb and you can go through a series of them. There are many things involved in this ion exchange thing. There is a question of kinetics; there is a question of selectivity. Sometimes it is not possible to absorb all of a particular ion; may be some other metallic ions will also be absorbed. So, these things are details I need not go into, but just to show you how it will be done in practice. It is not that it will go through a series of columns. They use various arrangements.

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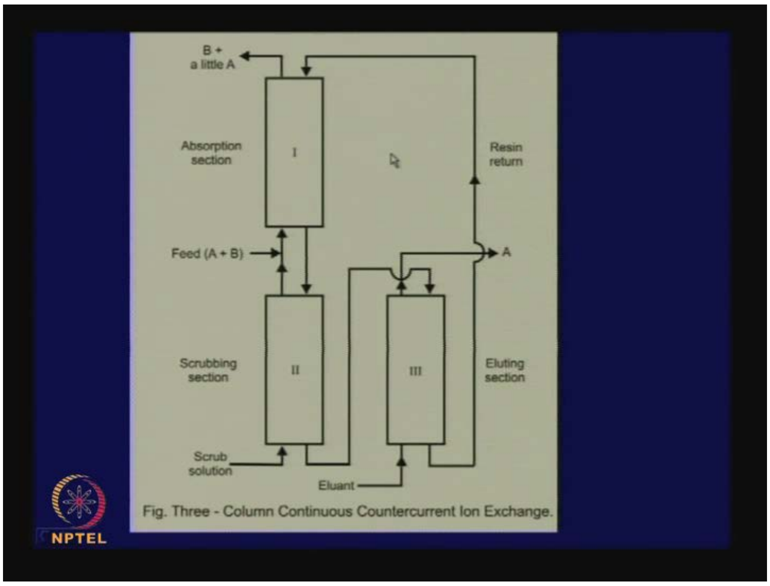

Fig. Three - Column Continuous Countercurrent Ion Exchange.

Now, here is 1, three column continuous counter current ion exchange. Continuously the feed solution will go through and the, and you will keep recovering the metallic values. Now, the weight is done here is the, suppose the feed has a and b and we have to separate a and b. We are more interested in the, in the, value b and there is little bit of a.

Now, this is the scrub solution. The solution is coming; the feed is coming here. It goes to the absorption section and it gives out b plus little a and the solution will go now to a elusion section where the eluant will regenerate the resin. It will go through and it will also give a out here. So, a will come out here continuously; resin will be continuous it will return here, and what we get here is the thing we do not want b, but some amount of a would definitely be there. Now, this is the kind of thing. We have many some more complicated that continuously we keep producing a solution containing a and continuously we return the resin.

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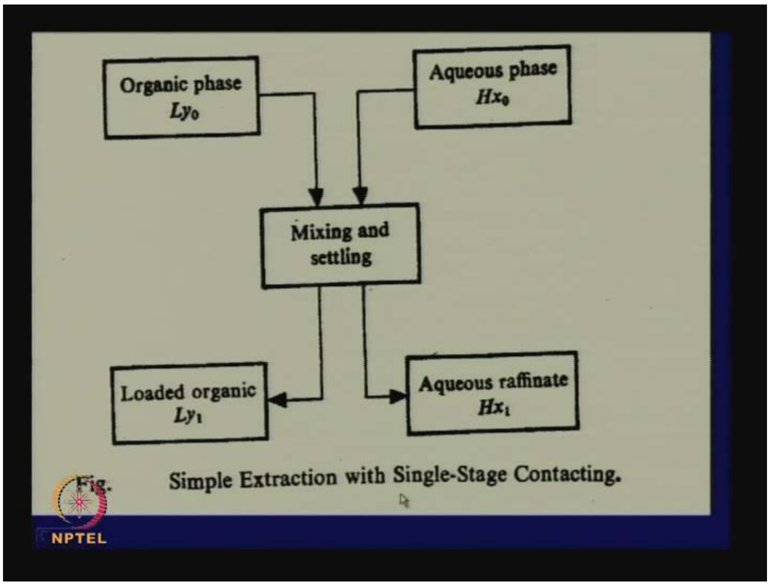

Organic phase Ly_0

Aqueous phase Hx_0

Mixing and settling

Loaded organic Ly_1

Aqueous raffinate Hx_1

Fig. Simple Extraction with Single-Stage Contacting.

Something similar happens in or in solvent exchanging. Now, in ion exchange, we are absorbing metallic values in the form of the metallic ions or metallic ion complexes in a solid iron matrix, ion, the solid resin matrix by exchange reaction at some sites. In solvent extraction, the metallic values are selectively absorbed in an organic medium. We call it organic solvent. Here is a schematic representation. We have an aqueous phase that contains the metallic values.

We have the organic phase which will selectively dissolve the metallic values you are interested in. There is mixing and there are allowed to settle. The organic phase and the aqueous phase do not mix, but when they come in contact and they, the organic phase will dissolve the metallic values. So, after we have allowed them to settle, the organic phase is called loaded organic because it loaded means it is now loaded with a metallic values, and the aqueous raffinate means the aqueous phase from which the particular metal that you are aiming at has been taken out. This is a simple extraction with single stage contacting. It has just come in contact for once and then you separate it to 2 and it is called single stage contacting.

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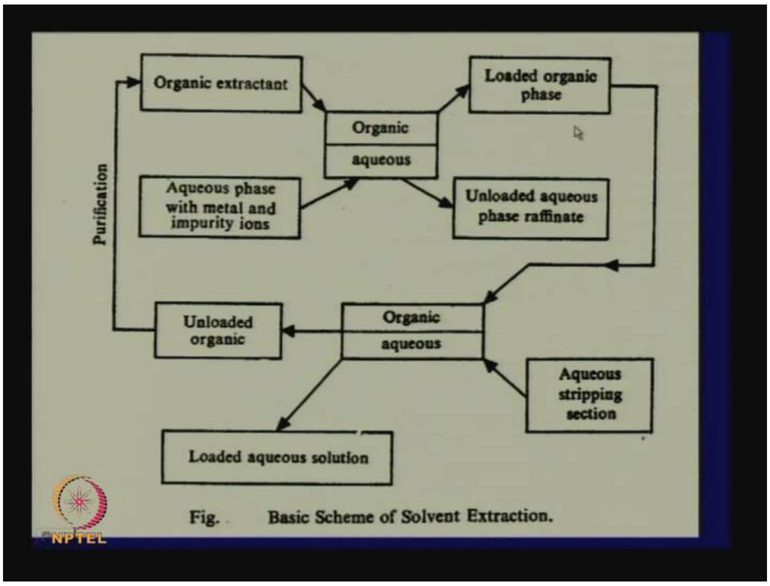

Fig. Basic Scheme of Solvent Extraction.

This is the basic scheme of solvent extraction that will be done in, in, practice. That the organic phase and the aqueous phase are brought in contact with each other. We are showing organic phase on top because it is lighter aqueous phase at the bottom; it has the metallic value. This organic phase will get loaded by what it has absorbed from the aqueous phase. Then at another stage, this organic phase would be brought in contact with an aqueous stripping section means fresh clear water, which will take out from the organic part.

The metallic ions that were absorbed and produce loaded aqueous solution, which means this reaction is reversed. Some metallic values have been taken in. Later on, there are stripped out of that. So, we have a loaded organic phase; we have now an aqueous stripping section which will take out from the aqueous phase the metallic values that had gone. Now, this organic phase will become unloaded, unloaded organic extract into (( )) there, and aqueous phase with metal and impurity ions are coming here, and this how it is a basic scheme, but it will be done in a very complicated manner in the industry; this is continuous counter current solvent exchange.

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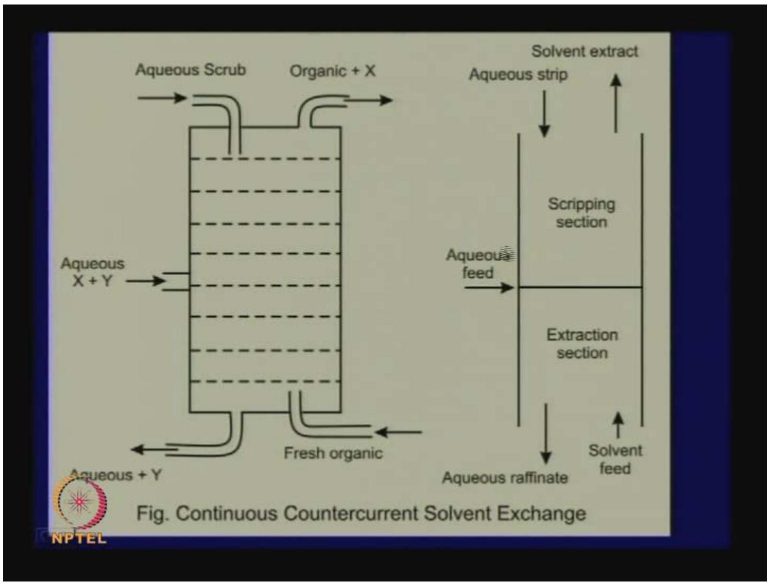

Fig. Continuous Countercurrent Solvent Exchange

In this, the, the, fresh organic is going into the system aqueous with x plus y goes in. Organic will absorb the x part that need will go come out, and the scrubbing aqueous layer will take out aqueous plus y. So, there will be separation of x and y, and what we can show is that, we have an aqueous stripping section. This is a stripping section; this is an extraction section. This part extraction is taking space because solvent feed is going and aqueous raffinate is coming this way. Raffinate means from which you have taken out the metal part, and the solvent is going here with loaded, and here, the aqueous strip solution is coming out. So, these are the kind of schemes that will take place here.

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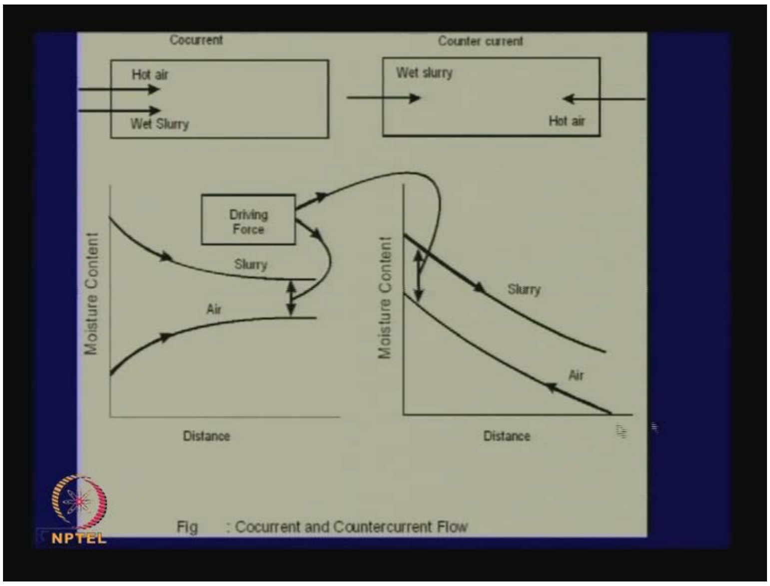

Fig : Cocurrent and Countercurrent Flow

Now, in all such things, we, we, can think of counter current or co-current flow means we can have the organic and the aqueous phase going together over a long distance or we can have them go past each other and each as its own merit. I will give a simple example. Suppose you have wet slurry and you want to dry it by hot air. You can send them through a chamber and they can run parallel to each other. Wet slurry is flowing; hot air is also going on top of through that or you can have a counter current system that, you have wet slurry going this way; hot air is coming on top of that in the other direction.

Now, the moisture content drop can be schematically shown like this. That in this case, when the wet slurry comes in contact with the hot air, there is a very big tendency to take out the moisture from the wet slurry. So, the air will begin to take in moisture; slurry will begin to loose the water content, but gradually you come to situation where the difference becomes so small that the driving forces become so small. So, on the other hand, in the counter current flow, slurry begins to lose moisture; air begins to take the moisture. The driving flow does not change. So, you can continue the process of removal of moisture over a long distance very very effectively.

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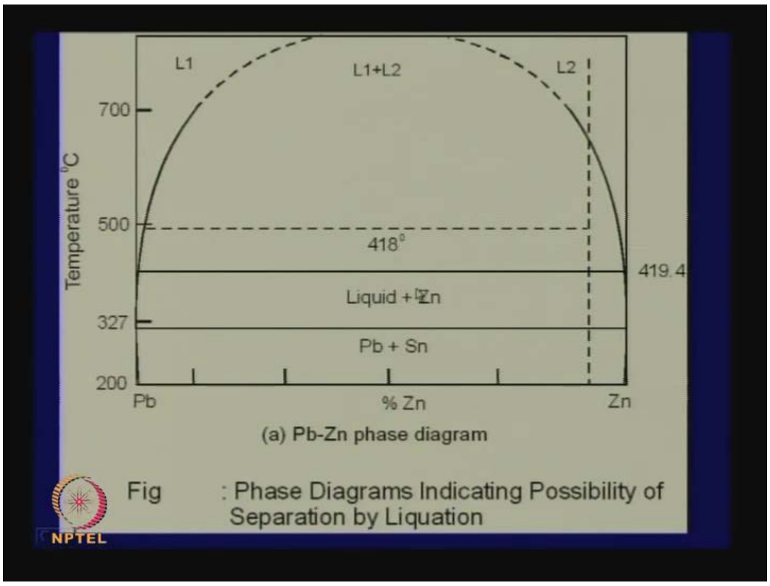

(a) Pb-Zn phase diagram

Fig : Phase Diagrams Indicating Possibility of Separation by Liquation

So, the counter current exchange processes are very very meaningful in the industry. Not only in, in, the case of solvent extraction but in many places, you will find that counter current flow concept is made use of. Now, that, with that, I will complete discussions of chemical methods of purification. I would like to take a few minutes to talk about physical methods of separation of impurities from metals. There are many many ways of doing that and I do not think. We need to discuss everything here because essentially we are discussing only the general principles. When you come to individual metals, we might have to repeat some of the things we have mentioned here and look at them little more critically.

Here is a phase diagram between lead and zinc. This will be of great importance in understanding what is done in lead zinc blast furnace where we would find a way to recover zinc vapors. Now, in lead zinc blast furnace, in a blast furnace, lead is produced at the bottom by smelting operations. Now, if lead ore's also have zinc, zinc vapors will go out; they are dissolved in lead at a higher temperature, and then that lead is cooled, so that zinc comes out of the lead in the liquid state.

It is a very interesting device that captures the zinc vapors in molten lead by spraying molten lead on the zinc vapors and you got the zinc lead alloy. Then that thing is cool down; so, the zinc precipitates out, and the lead is still molten; it is re-circulated for spraying. So, that lead zinc system is very very important.

Now, this is the phase diagram of the lead zinc system. You know the melting point of zinc is here. The melting point is led only 327. So, if you go slightly above it, we have liquid lead, so, liquid lead and zinc together. So, if you want to separate lead from zinc or zinc from lead, all we have to do is to take the alloy to above 327 and zinc solid will come out. What would be have left behind is liquid and zinc will float on top of liquid because zinc is lighter than that. It is very simple method of separating zinc from led.

Now, in imperial smelting process, we will deliberate; this is Z n. We will deliberately produce that lead zinc alloy by spraying lead on zinc vapors, but there can be situations where you have the zinc impurity in lead that can be very easily taken out just by heating the alloy to above the melting point of lead.

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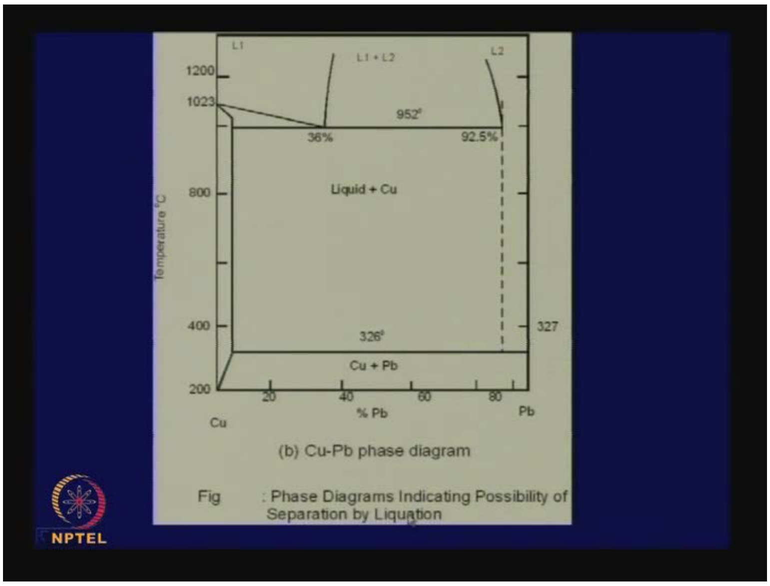

(b) Cu-Pb phase diagram

Fig : Phase Diagrams Indicating Possibility of Separation by Liquation

This kind of principle is evident in many many phase diagrams. Here is a phase diagram between copper and lead. Again melting point of lead is very low, whereas melting point of copper is very high 10, 83. So, there is a large region, region, where we will have copper plus a liquid layer. That liquid layer will be mostly lead. You may have some small amount of copper, but we can effectively separate copper and lead simply by using the simple process. Such process, is called, are called liquation. The word liquation means you take out part of the alloy by liquefying; so, it is called liquation.

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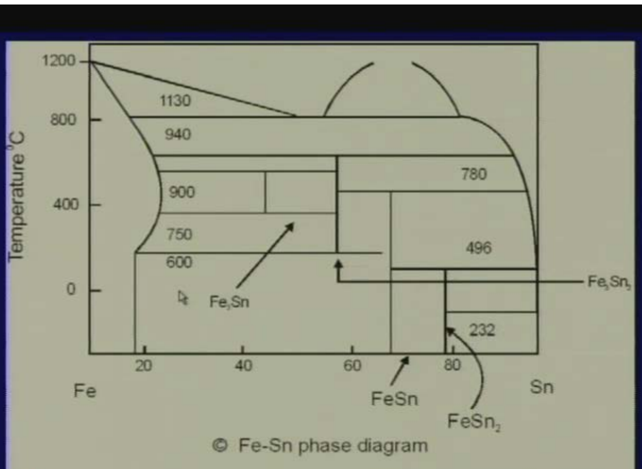

© Fe-Sn phase diagram

Fig : Phase Diagrams Indicating Possibility of Separation by Liquation

The other phase diagrams, I phase diagram between iron and tin. There are regions where simply by adjusting the temperature, we can separate tin from lead. In this case, tin is very low melting, whereas iron is very high melting; so, it should not be difficult.

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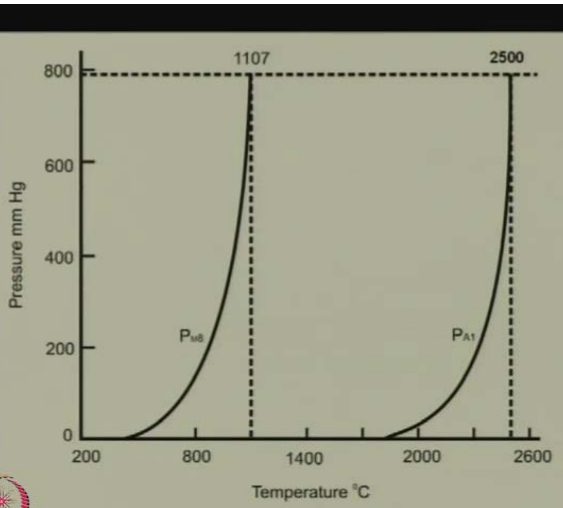

Figure: Vapour Pressures of Aluminium and Magnesium

If the volatility of the components in an alloy are different, then of course we can separate them by, by, heating at different temperatures. You may be aware that the ancient Egyptians first invented a process of gold recovery from rocks which had grains of gold.

Nobody knows how they did it, but that process continued for many hundreds of years. What was done is that, crushed rock containing gold particles were treated with liquid with mercury and the way to do that was to make a slurry, mixture of rock and in a gold pool of mercury and the slurry was allowed to flow down a slope. Lot of disturbances was created. So, that there was good contact within rock particles and mercury, and mercury dissolved gold, pure gold to form an amalgam.

Now, so, you have an amalgam which contains mercury and gold. From that, gold can be recovered very easily by heating the amalgam and mercury will volatilize away. They also had a very interesting of ensuring that all mercury has been separated. You know the ancient in Egyptians had invented beam balances and some of them were so accurate. They will measure with a hundredth of a gram and these balances are found in Egyptian Cairo museum also.

So, they employed these balances to find out whether mercury has been completely eliminate, and the way to do that was make an amalgam, heat it, weigh the whole thing periodically. So, every time they will weigh; they will find that weight has gone down and they knew that mercury has volatilized; gold is still there. When they found the weight was not going down any further on heating, they knew all gold has gone out. So, this is a very simple example of separating a volatile metal from an alloy simply by heating.

We can also separate magnesium and aluminum. This should be magnesium by the same principle. Here are the vapor pressures of magnesium as a function of temperature, vapour pressure of aluminum as a function of temperature. You find that magnesium acquires a very high vapor pressures at relatively low temperatures compared to the aluminum, which need higher temperatures to come to the same values of vapor pressure.

So, a pressure millimeter mercury is 800. We reach that in 1100 110 degrees for mercury and 25 (( )). So, we can, if we heat it somewhere here, the entire magnesium will be separated from aluminum. So, this is we can call that fractional distillation. Now only fractional distillation we use for liquids but this in case of fractional distillation.

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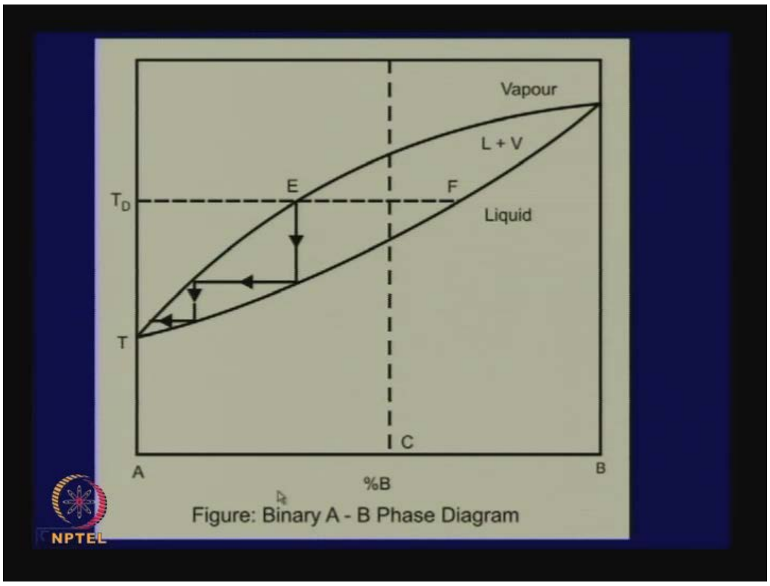

Figure: Binary A - B Phase Diagram

Actually if you look at a binary phase diagram, like this is what is happening that, in this case fortunately the, they are very separated, but in many phase diagrams, what happens is - if you go to a situation, you will have a vapor phase in contact with the liquid phase, and of course, the relative amounts are given by the lever rule. So, we get a vapor of one composition, liquid of one composition. This liquid is richer in b; this vapor is richer, richer, in A. So, if you separate this vapor from that liquid and this process can be continued so that you can separate A from B.

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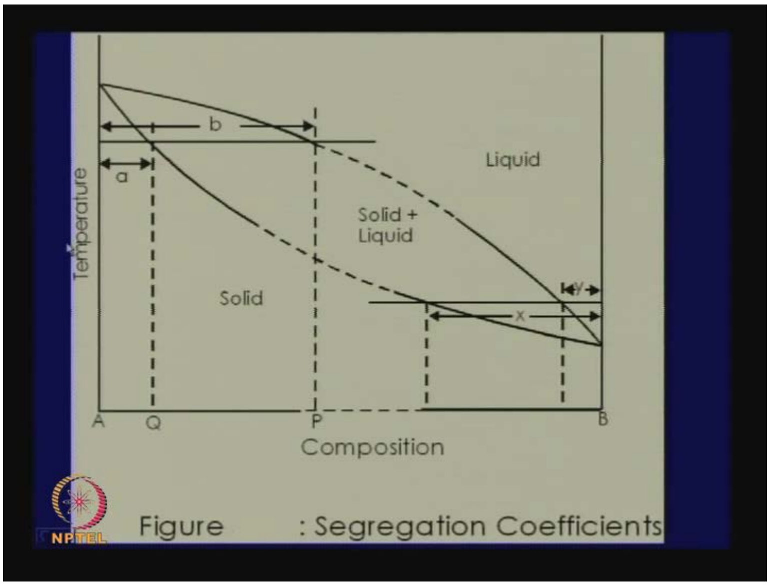

Figure : Segregation Coefficients

Now, if a similar principle based on the solid liquid equilibrium is made use of in a very intersecting technique called zone refining. Now, suppose we have a and b in a system and we heat it up to this temperature. What does this temperature show this? This temperature shows there will be a equilibrium between a liquid of this composition and a solid of this composition. Of course, there will be very little bit of this liquid because there is a lever rule; it is inversely propositional to a lever.

If you are here, yes, suppose your starting composition is this, then if you go here, you will have a liquid of this composition, solid of this composition; which means if you create a liquid phase inside a solid, the composition of the liquid is different from the composition of the solid.

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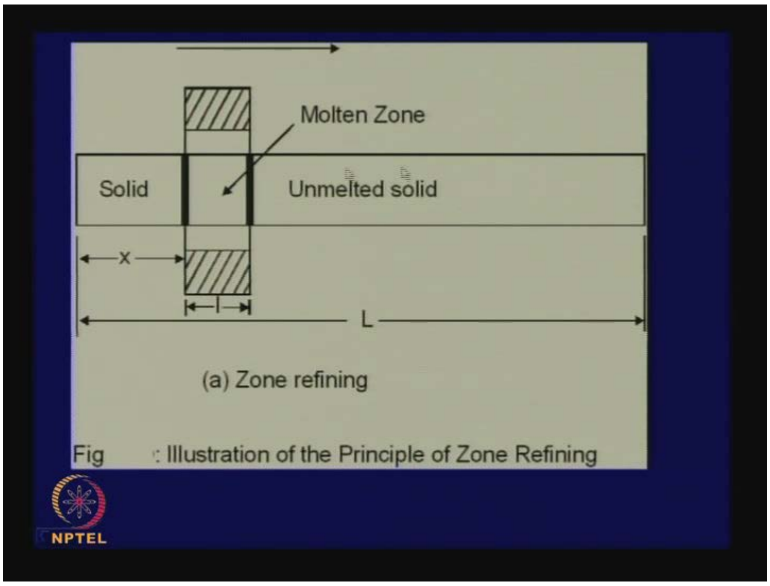

(a) Zone refining

Fig : Illustration of the Principle of Zone Refining

This basic principle is made use of in zone refining. Suppose we have a rod of metal, impure metal and we have a furnace which can move all, all, this furnace. Inside the furnace, there is a heating chamber the, it is horizontally it is placed and a furnace moves along the length access or it can be other way the furnace is fixed, but the, the, metal rod is goes through the furnace, and suppose in this furnace, we melt a very small zone. We have to melt a small zone; otherwise, the zone will fall off. See, if you melt a small zone, then in this zone where it is melted. We will have a difference in composition between the liquid here and the solid in contact with it.

And if we keep on moving this zone of molten metal melt, molten layer all along the axis, then we keep precipitating something preferentially on this side and the liquid preferentially keeps on absorbing something else, so that eventually by many many passes we can purify the solid and impurities can be taken to one side or impurities can be left behind on one side.

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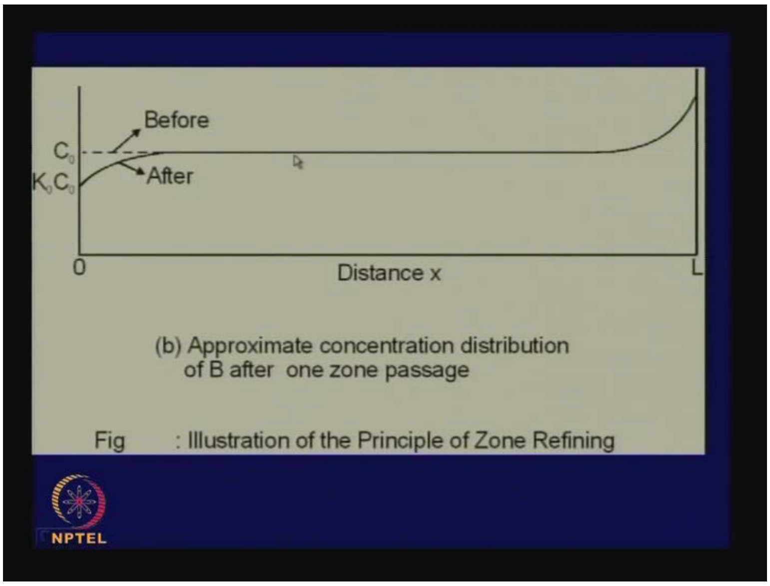

(b) Approximate concentration distribution of B after one zone passage

Fig : Illustration of the Principle of Zone Refining

Well, this is a principle which, it is an illustration of the principle that approximate concentration distribution of b after one pass will be like this. After one pass, we would have taken a concentration of impurities to one side and it would have been lowered here, because we have taken out impurities from this side by dissolving into the liquid layer and liquid layer keeps on moving goes there. If you keep on doing that, then eventually this will become, there will be more like this and this layer will increase. So, slowly will get one kind of composition on this side and all the impurities go to other side.

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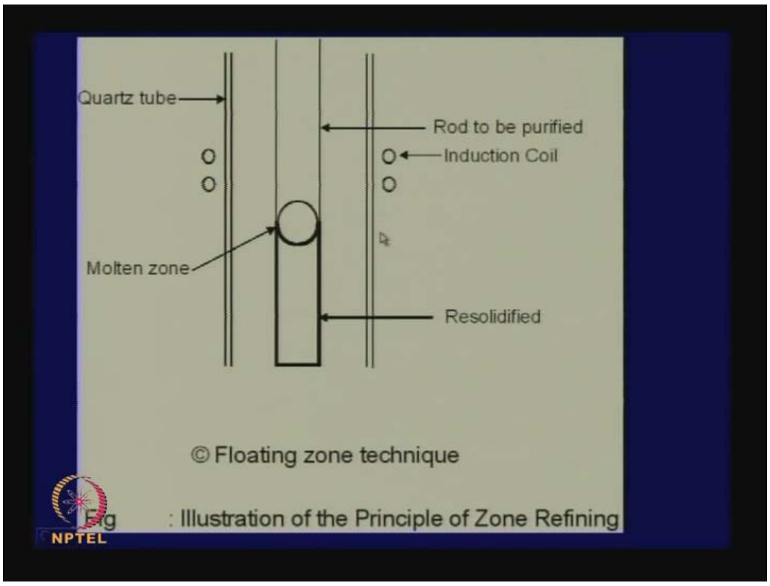

© Floating zone technique

Fig : Illustration of the Principle of Zone Refining

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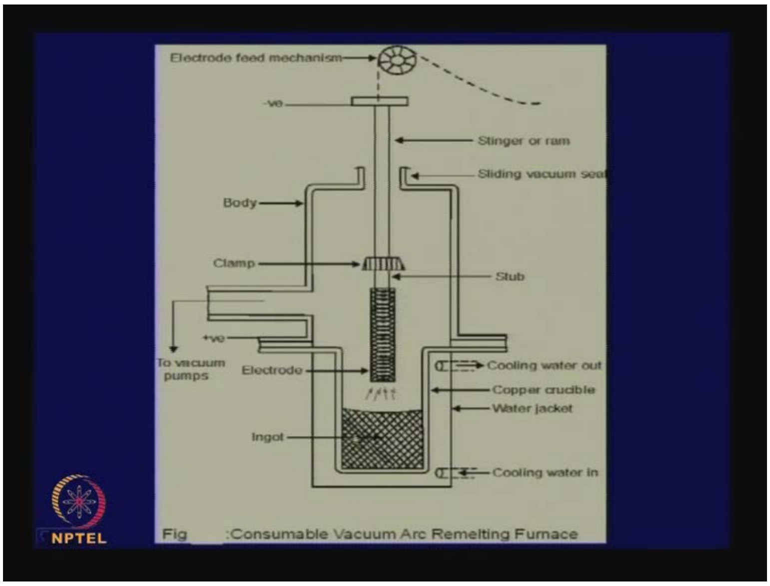

Fig :Consumable Vacuum Arc Remelting Furnace

There are also principles of zone refining done in a vertical manner. The principle is basically the same. Now, let me come to some special furnaces that are used for re-melting metals which are not in the right form and also which contain impurities. I had mentioned once that you can produce titanium in a crude form which in is, which is in spongy titanium to which needs melting for consolidation.

We can also have, during melting also we can volatilize some impurities. So, here is a device called consumable vacuum arc re-melting furnace. We have an arc electrode. We, this is the ingot and we create an arc, and by vacuum, we can remove many things at high temperatures that are here as impurities. So, the solid mass remains impurities are taken out at very high temperatures by vacuum arc melting.

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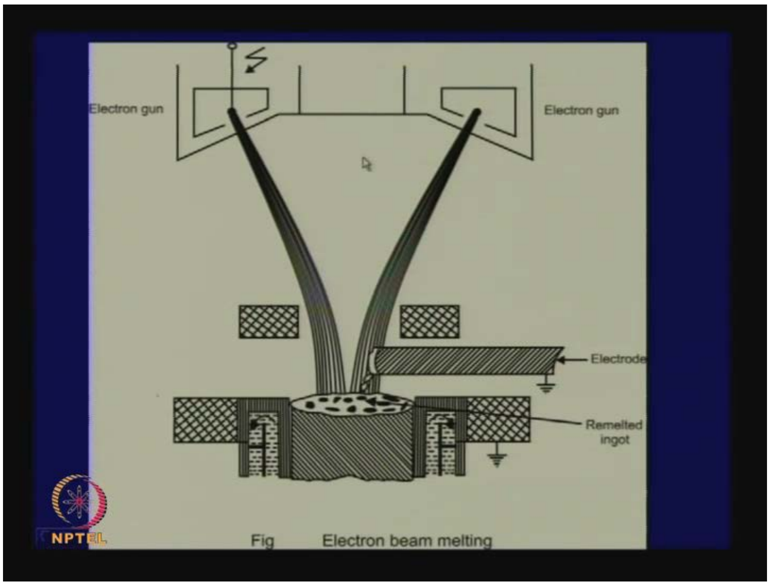

Fig Electron beam melting

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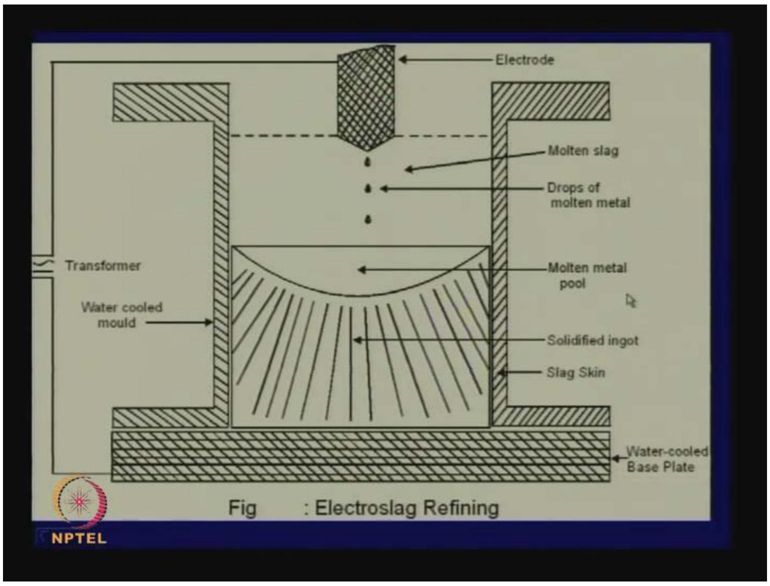

Fig : Electroslag Refining

The electron beam melting device is for consolidation of metal. Electro slag melting is also a very interesting device removing impurities from ingots. Now, the way this work here is the following that, the impure or crude metal is made into an electrode here and an arc is struck between this and a, and a, pure ingot here, and as it melts, the droplets of this goes through a molten slag layer, and during the passage through the molten slag, the impurities in the crude metal are dissolved into the slag place, only the pure metal gets deposited here.

So, slowly you get more and more of a pure metal as a, as an ingot, whereas this is consumed impurities going to the slag layer. So, this is called electro slag refining which is of course finds applications in several metals and I will discuss that when you come to that. I think with this, I come to the discussions on refining and I would now conclude my lecture so far in a few sentences.

So far, up to module 4, we have discussed general principles without referring to any metal extraction process specifically. That will start from next time onwards. We will get to know how we get metals from oxides, how we get metals from sulphide sources from alloys, but so far, specifically we have not discussed an extraction process. This was sometimes a bit difficult because really to understand a principle, we want to know the details of the process also, and on the other hand, we know the processes better if you know the principles.

I thought it be better to first discuss in general some principles, which if not clear now, may become clear when we discuss the specific extraction processes. You recall that we started with the history of metals and you should now appreciate that many things we are doing today actually started four thousand years ago. The ancient man started through accidents, through trial and error, how to reduce oxides using carbon in the form of charcoal. Using a flux to produce a crude metal and produced a slag which took out the impurities.

So, all these melting processes started way back there and they produced many many things. They produced copper, tin, lead, iron. The ancient’s could not produce zinc because although you could roast zinc ore and reducing oxide by carbon, that metal volatilized and it, it, escaped, it always escapes unless may be a bit of that got absorbed. If there were other metals in the system like you know, they used this process. First, brass was made by cementation process, (( )) filings of copper heated with roasted zinc ore.

So, zinc before it is escaped, got absorbed by copper filings to produce low quality zinc. By this, at the most nine percent zinc copper brass can be produced, but the Indians found by fourth or fifth century AD, a way to condense the zinc because they understood some metal was going away. So, the retort process started in India and it really took off around ninth or tenth century AD when large scale production of zinc had started in India, and they had vertical retorts; they also had horizontal retorts and those sites are still existing in, in, the Zawar mines area in Rajasthan. One can go to hill sides where there are dozens if not hundreds of such things retorts still there. Some arrange vertically; some arrange horizontally. There are many retorts still with the charges in intact as though they somehow they were abundant all of a sudden.

But till about eighteen century, only 8 metals are known – gold, silver, iron, then we had copper, zinc, lead, mercury. Zinc its only from the eighteen, seventeenth eighteenth century that many other metals began to be discovered aluminum such an important metal was discovered only in the ninth, not discovered produced only in the nineteenth century. The chemist had of course produced it earlier, and one had to wait for the invention of electricity to be able to produce aluminum in large scale through (( )) process.

Now, today we have many metallurgical processes which come under the categories of pyrometallurgy, which is the most ancient. Then, hydrometallurgy, which was the basis of alchemy, and then electrometallurgy, which started only after the invention of electricity. We have also see that in nature, metals do not exist uniformly all over. There are pockets here and pockets there, and why these pockets are formed can be explained in terms of geochemical processes.

Now, normally we say that when we are talking about land resources, we are only talking about a, the, a crust on earth surface a few kilometers long a (( )), may be ten kilometers because you cannot do mining beyond that. So, from when you talk about land mass, land resources, we are talking about ore deposits on the, on the, surface of the earth. We can get ores from the surface of earth. The other resource of metal is also sea water because sea water contains all kinds of metals.

In the sea, there are sea organisms which are preferentially absorbs some elements. So, they become sources of those elements and there are in the sea manganese nodules or polymetallic nodules in the sea floor, which are very rich in manganese. That is why they are called manganese, but they also contain nickel, cobalt, zinc, etcetera. And the total reserves, reserves, of these nodules are very large and there are some metals which could be produced from these nodules in large quantities only if we could have them mined. It is not easy to extract manganese nodules from the ocean floor.

But there are shallow, shallow, sea beaches where not beaches shallow regions of sea, where manganese nodules if they are present should be extracted economically. We have in India processes for extraction of metallic values from manganese nodules, but we do not have a process for economical collection of manganese nodules from the sea floor. Even then, India is in this business - in international treaties etcetera. India is a partner because India has been spending a lot of money in certain sea floors, because according to international treaties unless you invest, you do not have rights. So, India has mining rights in certain areas.

So, if we in future, we might be able to get metals from these sources also. Then we have another source, very important source - that is the scrap; that is the consumer items which have been discarded. From there, we produced metals. We call them secondary metals. And you understand it is very easy, easy, to guess that the energy and effort require to produce secondary metal would be much less than the energy required to produce the primary metals which comes from the ore, because to produce from the ore, you need mining, then you, ore needs processing through mineral beneficiation techniques which are all energy intensive, cost expensive. Then you have a process store which has to go through pyrometallurgical or hydrometallurgical or electro metallurgical steps to finally give you the metal.

Now, there are some metals which form very stable compounds. They would be more difficult to produce. There are some metals which are very easily obtained because their compounds are not very stable. Some metals are there in nature, in a native state. It does not mean you can go and collect them at one time people perhaps did that, but you do not have to think about the kind of processing that you need for say uranium, zirconium and thorium. In the case of gold, gold particles are embedded in rock surfaces amongst the rocks.

Unfortunately, there is no easy way getting those gold grains. We still have to go through a hydrometallurgical process where you dissolve them in cyanide solution, and from there, we precipitate gold. Now, of all the pyrometallurgical, hydrometallurgical, electrometallurgical processes, there are special features for special metals in, in, all categories. You cannot say that this is one standard pyrometallurgical process for this group of metal, but there can be basic similarities.

Similarly, for certain metals in one group, there are (( )) sulfite, there are some basic approaches we can adopted. So, from next module onwards, we will try to discuss the, the, extractive metallurgical processes for different groups of metals, and I will group them into metals from oxide sources, metals from sulphide sources, metals from halites.

Now, there will be two kinds of metals - there are metals which are in nature in halites and many of them in sea water, because you know sea water is mostly chloride like you may say sodium, magnesium, potassium, lithium, many of them are there as chlorides, but there are also sources, oxidic sources like magnesium is also found as dolomite. We have many reactive metals which are there as oxides, but our starting material for process metallurgy will be from the halite, that we have to take the oxides, make them into halite's and the produce the metal.

So, I will not discuss them in the oxide part. I will discuss them; treat the sources as halite's. In the oxide category, we will have things like aluminum, magnesium. We would also put in Ferro alloys; we will have reactive metals, etcetera, etcetera. In the sulphides, you will have common metals copper, zinc, lead, and then, in halite's as I mentioned, there will be several metals. I will also discuss at the end production of silver, iron, platinum, all the noble metals. Finally, I will discuss the extraction metals from secondary sources.

Having done all that, I would like to devote some lectures towards the end on energy and environmental resources for the entire field of extraction metallurgy, because extraction processes are beginning to have a serious effect on the environment. You perhaps do not know that at one time, the advanced countries produced a lot of iron and steel. They are very active in non ferrous metal production, but they have now gone away from those fields because of environmental reasons, and now, they have left it to developing countries like China, India to produce iron and steel and different metals.

Whatever the reason, non ferrous metallurgy is become very important in India because we are beginning to produce increase amounts of non ferrous metals and it is opening up job opportunities; it is, it is, becoming very vital for the economy. So, I will discuss now the extraction processes for various metals from lecture, next lecture onwards. Thank you very much.