Non-Ferrous Extractive Metallurgy

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Lecture No. # 07

Principles of Hydrometalling

Friends, we have discussed very briefly principles of pyrometallurgy energy in the last lecture, and it should be obvious to you that pyrometallurgy energy means metallurgical operations at high temperatures. Pyro means heat, so metallurgical operations carried out at high temperatures are called pyrometallurgical operations.

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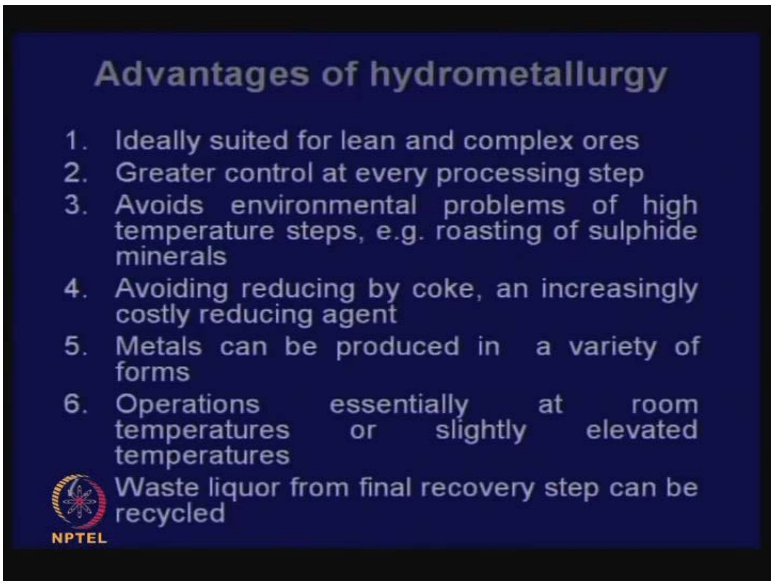

Advantages of hydrometallurgy

1. Ideally suited for lean and complex ores
2. Greater control at every processing step
3. Avoids environmental problems of high temperature steps, e.g. roasting of sulphide minerals
4. Avoiding reducing by coke, an increasingly costly reducing agent
5. Metals can be produced in a variety of forms
6. Operations essentially at room temperatures or slightly elevated temperatures

Waste liquor from final recovery step can be recycled

By the word hydro metallurgy, which we are going to discuss now; we mean exploitations of reactions in echoes media, but not exclusively; sometimes, we do make use of some organic media also, but the operations are at low temperatures, because echoes media and organic media involved they cannot be heated as water evaporate, organic media only evaporate.

But sometimes we do go beyond hundred degrees, because if you make use of auto claves, which are high pressure vessels, you can make the water boil at a temperatures higher than 100 degrees and sometimes we do that for example, in the case of leaching of alumina by sodium hydroxide. Leaching is much more effective and it is accelerated when the temperature is higher, and we get high temperatures by going beyond the normal boiling point of water by using autoclaves, but even using a high pressure will seldom go beyond temperatures of 130 degree. Most operations here hydro metallurgy would be very much near room temperatures

What are the advantages of hydrometallurgy? The advantages of hydrometallurgy have been listed here: Hydrometallurgy is ideally suited for lean and complex ores, because you are doing, you are carrying out reactions not very rapidly like in case of hydrometallurgy, you are doing it at a slower pace under controlled conditions, you can control the composition of the reagents, you can control the temperature if it is acid the p h value of the acidic media, if it is an alkali the alkalinity of the medium.

So, there is lot more control, and this is ideally suited for making, for application in the case of lean and complex ores form which we can get not one product or two product, but many products in the form of metallic ions or metallic compounds. So, number two is that there is a greater control at every processing step, it also avoids environmental problems of high temperature steps like roasting of sulphide minerals, they give out sulphurous gases which are very dangerous, also when you are letting out hot gases you are creating an environmental problem, when you use coke or coal you create c o c o 2 which cause a environmental problems. So, by avoiding or reducing coke an increasingly cost reducing agent, we also go for a process which is not dependent on coke, which often is not available.

In India today many blast furnaces are been operated on coal imported from Australia and then made it into a coke, because Indian coal is not suitable for coke making and prices of coke are going up. But this does not mean that there is no environmental problem, there are different kinds of environmental problem in hydrometallurgy which you must keep in mind, and that goes in the disadvantages to which I come later. Then advantaged hydrometallurgy is because of the control you have on reagents, and you can have additives, you can have catalysts. Metals can be produced in a variety of forms, we can produce sheets of metal, we can produce powders of metal, you can even produce powders with particular shapes of particles. These have been achieved in hydrometallurgical operations.

And since, operations essentially are at room temperature or slightly elevated temperatures things become much more convenient to handle, and the waste liquor from final recovery step can often be recycled, means you are easing some reagents which can be regenerated.

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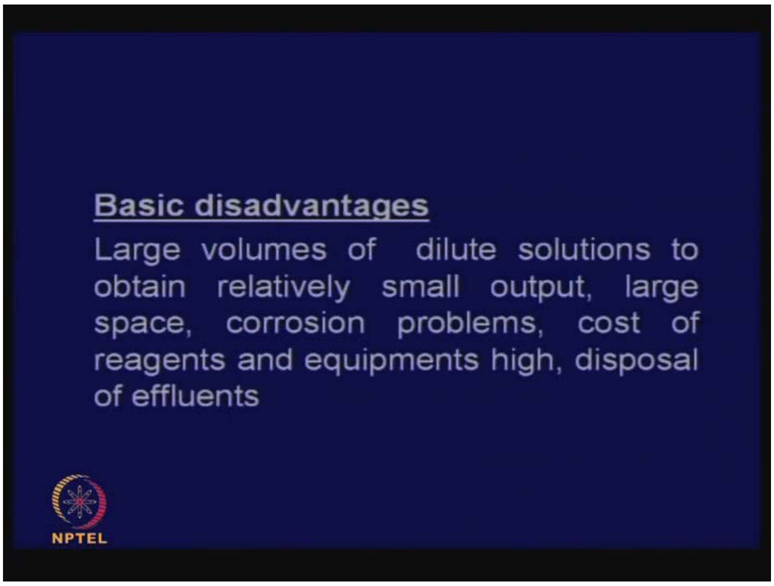

Basic disadvantages

Large volumes of dilute solutions to obtain relatively small output, large space, corrosion problems, cost of reagents and equipments high, disposal of effluents

Now, these are the advantages, but there are disadvantages also, because operations at low temperature, reaction rates are small, the concentration of reagents are moderate, we need large volumes of dilute solutions to obtain relatively small output. Now, in pyrometallurgical operations there can be a high temperature furnace in a small room, and it can produce lots of metal and slag, it is of a highly space saving unit. But in hydrometallurgy you are using large volumes of water with lot of plumbing, pipe lines, pumps, diaphragms then screens, so you need a huge floor space. And invariably hydrometallurgical plants occupies lot more space than a pyrometallurgical unit.

So, not only you have large space, because you are using reagents, you may have corrosion problems on the plumbing lines, because if liquids have to flow through pipe lines, this pipe lines might get corroded, and they also add to cost all the cost of reagents, equipments, they all add to cost, and then there are effluence is give rise to environmental problems. In pyrometallurgy, we had environmental problems from hot gases, we have sulphurous fumes c o c o 2, we have heat going out with hot gases. Here the environmental issues come up with the liquid effluence, and very often we do not know where to discharge them. Now, we cannot put them into the sea which many people have been doing, because the seas, the rivers or the ponds they have a carrying capacity, and we very often we do not know where to put it, because some of them are not very safe if you just put it on the ground. So, many special efforts may have to be made to do something about the effluence.

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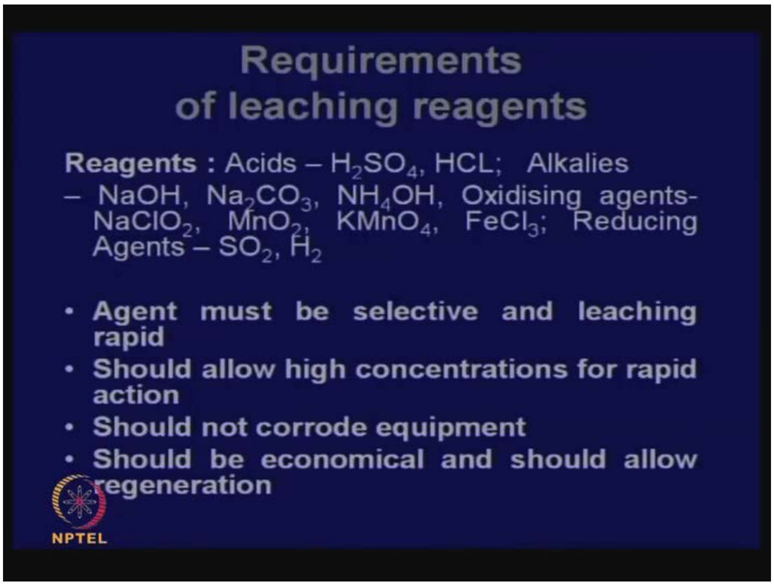

Requirements of leaching reagents

Reagents : Acids – H_2SO_4, HCL; Alkalies – NaOH, Na_2CO_3, NH_4OH, Oxidising agents- $NaClO_2$, MnO_2, $KMnO_4$, $FeCl_3$; Reducing Agents – SO_2, H_2

- **Agent must be selective and leaching rapid**
- **Should allow high concentrations for rapid action**
- **Should not corrode equipment**
- **Should be economical and should allow regeneration**

What are the reagents that we use? Reagents can be acids, they can be acids like h 2 s o 4, h c l you know that h 2 s o 4 is a stronger medium for leaching, but sometimes h c l may be preferred. There are alkalis, sodium hydroxide, sodium carbonate, ammonium hydroxide, oxidizing agents unnecessary sometimes like n a c l o 2 or m n o 2 k m n o 4 h c l 3 which oxidize some species in the echoes media. Sometimes we need reducing agents s o 2 and h 2 to reduce certain species in the echoes media. Think of the kinds of leaching reactions I have here.

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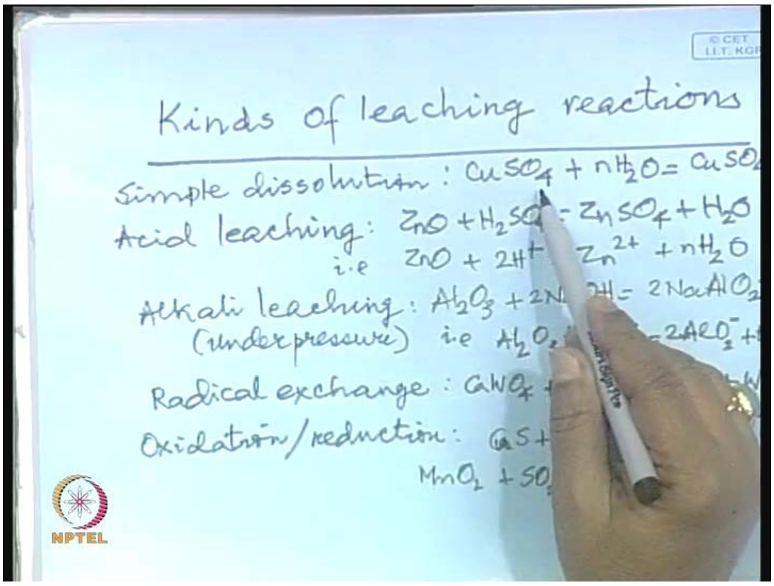

Kinds of leaching reactions

Simple dissolution : $CuSO_4 + nH_2O = CuSO_4$

Acid leaching: $ZnO + H_2SO_4 = ZnSO_4 + H_2O$

i.e $ZnO + 2H^+ = Zn^{2+} + nH_2O$

Alkali leaching: $Al_2O_3 + 2NaOH = 2NaAlO_2$

(underpressure) i.e Al_2O_3 $= 2AlO_2^- +$

Radical exchange : $CaWO_4 +$

Oxidation/reduction: $CuS +$

$MnO_2 + SO_2$

You know, you can have a leaching reaction which is a simple dissolution reaction, like if one has produced copper sulphate by some means, even you know by roasting of copper sulphide you can produce sulphate, simply water will dissolve you do not need anything else.

Acid leaching, there are many examples of acid leaching, roasted zinc sulphide will be z n o that will be by dilute sulphuric acid will leached to produce zinc sulphate in solution, in ionic terms you can write it like this Z n o plus 2 h plus to give you zinc ions and water, they can be alkali leaching and I refer to alumina, that alumina can be leached by sodium hydroxide to produce sodium aluminate in solution, this is often carried out above hundred degrees by having the reaction in an auto clave. An auto clave is a shield chamber where there is high pressure, and water has been boiled until at higher temperature, so you go up to temperature 120 or 130 and the reaction rates are high.

And sodium hydroxide dissolves alumina we write this as n a l o 2, but in ionic terms a l 2 o 3 is being dissolved by o h ions to get ions like a l o 2 minus, and there are also other kinds of ions (( )) ions that are produced. There can be radical exchange, means you have a solid c a w o 4 leached with a carbonate, the carbonate enters where w o 4 was there w o 4 comes out to give w o 4 2 minus ions, so you have replaced w o 4 by c a c o 3 and this is called a radical exchange. There can be oxidation reduction reactions, like copper sulphide being leached by ferric ion to give c u 2 plus and 2 f e 2 plus it becomes reduced to ferrous or m n o 2 plus s o 2 m n 2 plus s o 4 3 minus it is a reduction reaction. So, this sort of reactions takes place during leaching, and there are some essential requirements of leaching reagents

Firstly, agent must be selective, means you do not need a reagent which will dissolve everything. We want to take out the metallic values you want, not everything, so they must be selective, leaching must be rapid. You cannot have a reagent which will make you wait for long times, days and months, it has to be finished within reasonable time. The reagent should allow high concentrations for rapid action; any leaching regent is likely to be stronger if it is made stronger. Means, if it is sulphuric acid high concentration sulphuric acid, if it is h c l high concentration of hydrochloric acid, but using very high concentration has its problems. So, that is why I am saying that we should know whether can use high concentration for rapid action, it should not corrode the equipment. Problem is if we use high concentration of acids may corrode the plumbing of the equipment.

Lastly, it has to be economical and should allow regeneration, because otherwise the hydrometallurgical operation would become far too costly cost is of course, which guides every process.

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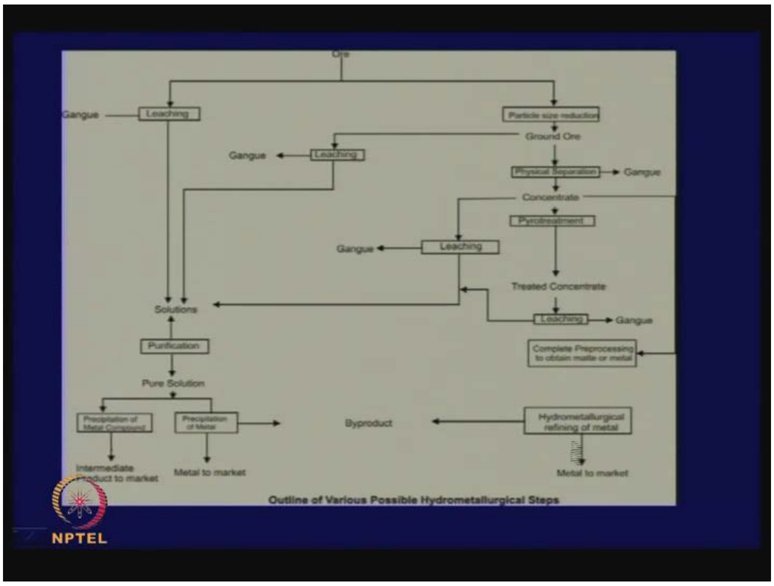

Outline of Various Possible Hydrometallurgical Steps

This is in a nutshell the outline of various possible hydrometallurgical steps, there is the over that you want to treat of course, not over from the mines it has to be processed to, which has gone through mineral beneficiation techniques. It gets leached you gets solutions, which are purified you get a pure solution, you can precipitate a pure compound from which you get an intermediate product to market, or from the precipitation, from the pure solution you can precipitate the metal that the metal goes to the market and you can get some byproducts.

Sometimes, one has to go through come here in little more indirect manner, because we might have to first undergo particle size reduction, ground ore will go through this process, and the ground ore may have to undergo physical separation to take out gangue. We might go through a concentration steps, then we might go through a pyro treatment, sometimes we combine pyro treatment with hydro, and the treated concentrate goes for leaching, sometimes this concentrate can directly go for leaching and so on and so forth. So, either we end up here, or we can take the concentrate and complete reprocessing to obtain metal or some metal compound.

So, these are basically the different kinds of step that are involved in hydro metallurgical operations, and sometimes as I mentioned hydro metallurgical can be combined with pyrometallurgy also.

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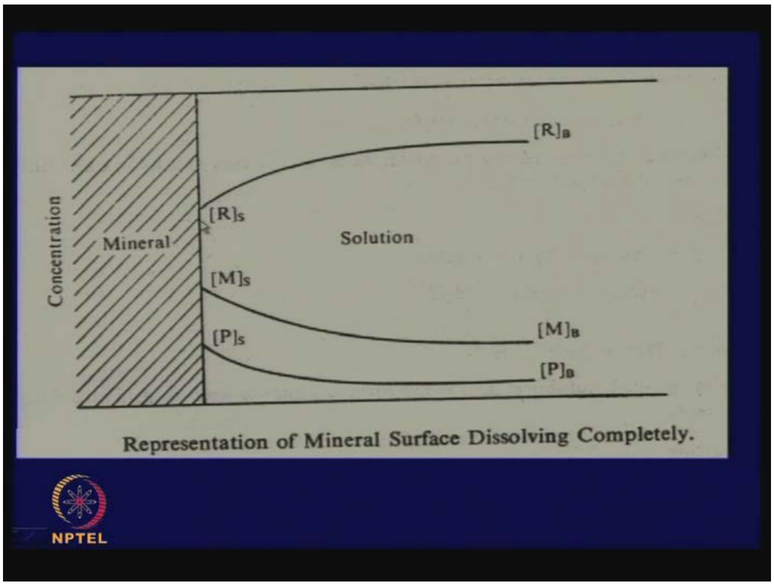

Representation of Mineral Surface Dissolving Completely.

Now, considered basically what happens in a leaching reaction, we have a mineral surface, it is not a pure mineral it may have other things also, but the idea is that a reagent has to come to the mineral surface, react, produce a metal ion or a metal ion complex which will be taken into the solution, this is the metallic value we get. And when this is reacting with the regent that has come to the mineral surface, you may produce some other products which will diffuse out entity bulk.

Now, the solution here we usually call bulk solution, and that is why we are writing the word b, the letter s means surface. Though essentially, we have a concentration gradient, because the reagent when it comes from the bulk will get consumed (( )) it comes to the surface, and when it is being consumed there has to be a concentration profile from a certain value, it will drop down to some equilibrium value at the surface. Similarly, when the metal ion or metal ion complexes are produced at the surface, when they go out into the bulk there will be diffusion and the concentration will drop, same with the products. This sort of diffusion phenomenon, phenomena is normally understood in terms of a diffusion across a boundary layer.

We say that up to the pretty close to the surface the concentration in the bulk does not change, then the concentration drops because there is a concentration drop at the surface, because it is getting consumed. Similarly, when a metal ion or metal ion complex is produced at the surface, slowly it will diffuse out it diffuses out because of a concentration gradient, or else why should it diffuse. It goes out because in the bulk it is not there it is lot of it is here, so it will gradually go out of here to there because of a concentration gradient. And again this diffusion phenomenon has to be analyzed in terms of a diffusion boundary layer, there is a boundary layer where bulk of the dropped in the concentration takes place, and then in sort of flattens out same with the product.

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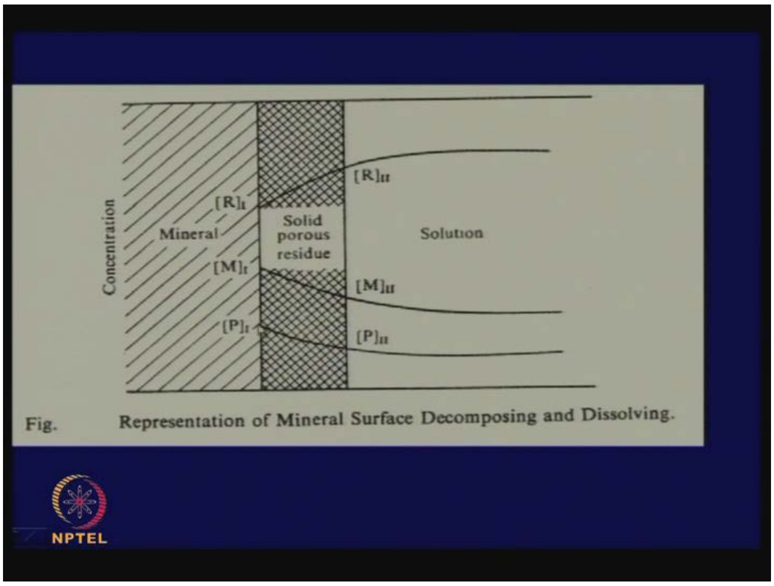

Fig. Representation of Mineral Surface Decomposing and Dissolving.

We can have a more complicated step, where when there is a reaction at the mineral surface by the leaching medium, you produce a solid porous residue also. Suppose, you create a product which is not porous, then leaching reaction will stop because the reagent will create some layer, and beyond that it cannot proceed any further the leaching stops. But, we can have a situation where the regent comes from the bulk then it goes to the mineral surface, there is a reaction. Because of that reaction a solid porous residue is formed which gradually thickens, so as the reaction proceeds the reagent has to diffuse in through the solid porous residue. And when the reaction takes place, it again forms metal ions or metal ions complexes, they must also diffuse out through a product layer then into the bulk solution.

If there are other products been found that are in solution, they will also have to diffuse out through the porous layer and then it will enter the bulk solution. So, in a situation like this there are several steps in the reaction, one is that reagent moves towards the porous layer, it diffuses through the porous layer and most of the diffusion takes place across a boundary layer, there is a reaction at the mineral surface, so produce a metal iron or metal iron complex which must diffuse out through the porous layer, and again it is because of a concentration gradient, the diffusion will be dictated by the concentration gradient, it will go out through the porous layer then into the bulk, and if there are products, other products found, which are not solids, which do not enter the solid porous residue face but soluble, they must also be go out through this porous layer.

So, many things happen one after the other. We want to analyze leaching reactions in terms of basically two phenomena, one is the diffusion phenomena, diffusion to the surface of the mineral, and another is the chemical reaction that takes place at the surface. There are situations when this diffusion process is slow, the chemical reaction here is fast, in that case the entire thing will be dictated by the rate of diffusion, because always diffusion of the reagent allows the reagent to come to the mineral surface, few more reactions can take place. On the other hand there can be situation where the diffusion process is fast, but the reaction at the boundary is slow, at the interface is slow. In that case, the slow steps becomes rate control, same thing can happen in this case also.

Let me give a simple example, suppose you consider dissolution of sugar in water. Now, the surface of sugar is dissolving in water, there is a concentration gradient near the surface, at near the surface sugar dissolves to produce a saturated layer of sugar, from there sugar has to diffuse out because the bulk solution is not saturated, concentration of sugar is low, so it will diffuse out from here. There are two steps here, one is at the surface solid sugar is dissolving to make a saturated layer at the interface, from that saturated layer the sugar is going into the bulk. You know, that when you use a stirrer the rate of dissolution increases, why does it increase? It increases because as you increase the intensity of stirring, the boundary layer thickness decreases, means the layer that showed a concentration profile becomes much narrower, so the gradient becomes faster, the concentration of the surface and concentration of the bulk and therefore, if a gradient becomes higher the rate becomes higher.

So, then if we go on increasing the stirring rate, the rate of dissolution will increase, it does not mean this will go on indefinitely. Beyond a certain stirring speed the diffusion rate has become as fast as it could, and it cannot be accelerated anymore. In that case, if we have to increase the rate of dissolution, we have to increase the temperature of the system so that the reaction at the surface is accelerated, because in the limiting case where you have come to a situation, where you cannot increase the gradient anymore. The diffusion at the boundary layer has become faster compared to the reaction at the interface, where from the lattice of the solid sugar particles are coming into create the interface layer. So, if we increase the temperature the surface concentration of sugar will go up, and that reaction will be speeded up but not by stirring anymore.

So, whenever we have the situation like this, we have a concentration gradient, this concentration gradient can be changed by stirring of the system, but there are always practical limits of stirring, we cannot go beyond a certain stirring speed. So, all leaching reactions are analyzed in terms of some concentration profiles that you can draw in our mind.

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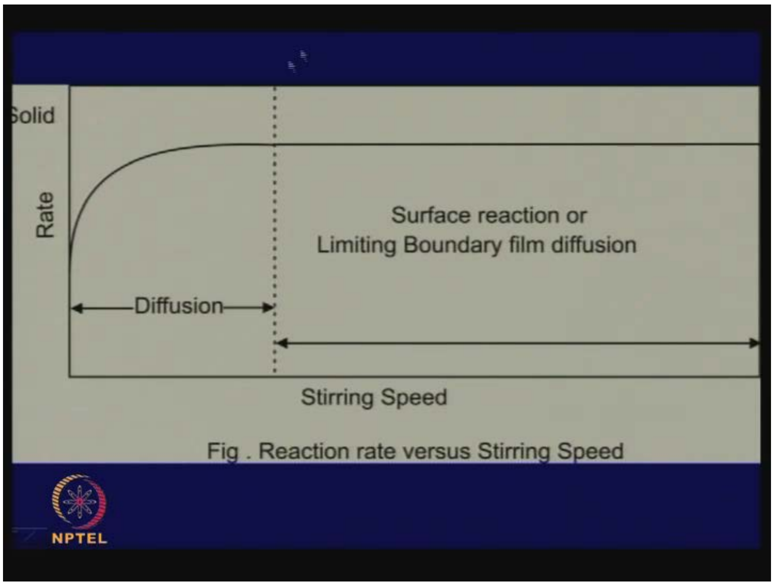

Fig . Reaction rate versus Stirring Speed

Now, here is a situation where a reagent is going from the bulk to the surface, now this is where actually the diffusion is taking place, diffusion in the boundary layer is taking place, because it is been eaten up here the species has to move toward this, and then from here to here it goes because there is a concentration gradient, this minus this divided by a boundary layer, diffusion layer and that defines a boundary layer.

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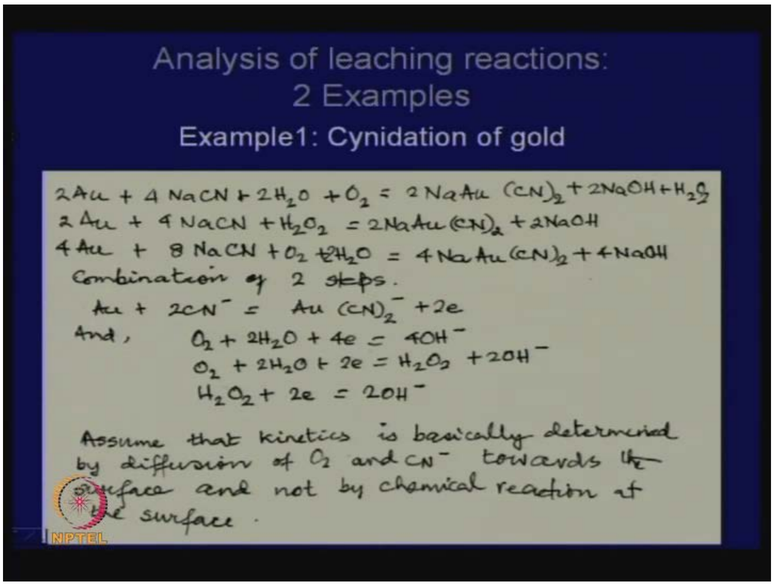

Analysis of leaching reactions: 2 Examples

Example1: Cynidation of gold

$2Au + 4NaCN + 2H_2O + O_2 = 2NaAu(CN)_2 + 2NaOH + H_2O_2$

$2Au + 4NaCN + H_2O_2 = 2NaAu(CN)_2 + 2NaOH$

$4Au + 8NaCN + O_2 + 2H_2O = 4NaAu(CN)_2 + 4NaOH$

Combination of 2 steps.

$Au + 2CN^- = Au(CN)_2^- + 2e$

And, $O_2 + 2H_2O + 4e = 4OH^-$

$O_2 + 2H_2O + 2e = H_2O_2 + 2OH^-$

$H_2O_2 + 2e = 2OH^-$

Assume that kinetics is basically determined by diffusion of O_2 and CN^- towards the surface and not by chemical reaction at the surface.

Now, let us consider a very practical example, where this kind of analysis helps us to understand the reaction. Consider the cyanidation of gold, there are… it can be written in two ways. The first reaction is 2 a u 4 n a c n plus 2 h 2 o plus o 2 to produce 2 n a a u c n twice plus 2 n o s plus h 2 o 2. The other reaction is written, which is which follows that, so over all reaction is this 4 a u plus a 8 n a c n plus oxygen plus h 2 o giving you n a a u c n 2 plus 2 n a o h. So, here what is happening is the cyanide, sodium cyanide in solution is reacting with gold, not to take out gold ions from the surface of gold, which is it is taking a complex a u c n 2 minus. Now, try to understand why we are doing cyanidation? You may say gold is gold, it is always in free state and all that, but that is not so.

Gold is found after mining embedded in rock surfaces, it not in free, it is in free state, but locked with all kinds of things, so the entire crushed ground rock is treated by cyanide solution, and gold is taken out of the whole thing into a solution, not as gold ions but as gold cyanide ions. So, what is the reaction? We can understand the reaction as a combination of two steps; the gold is attacked by cyanide ions, which mean cyanide ions have moved from the bulk to the gold surface taken out gold, and the other is this, that we have another reaction that is producing (( )).

So, oxygen is also moving towards the surface, because without oxygen this reaction cannot take place. Cyanide ions are moving towards the gold surface, and what is coming out is a u c n 2 minus ions and 2 h o ions from the gold surface. This is what we are schematically showing here that oxygen is moving towards the surface of gold particle, and c n minus ions is also going towards the surface and from there is a u c n 2 minus is coming in. We have the same situation, we have a boundary layer across which diffusion is taking place, and there is one area we call Cathodic area, one area we call anodic area. Let us analyze this little further.

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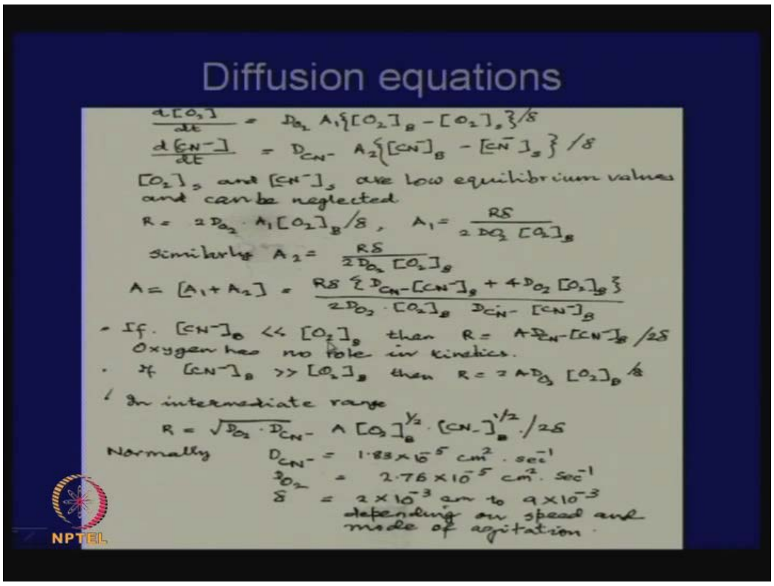

Diffusion equations

$$\frac{d[O_2]}{dt} = D_{O_2} A_1 \{[O_2]_B - [O_2]_s\}/\delta$$

$$\frac{d[CN^-]}{dt} = D_{CN^-} A_2 \{[CN^-]_B - [CN^-]_s\}/\delta$$

$[O_2]_s$ and $[CN^-]_s$ are low equilibrium values and can be neglected

$R = 2D_{O_2} \cdot A_1 [O_2]_B/\delta$, $A_1 = \frac{R\delta}{2D_{O_2}[O_2]_B}$

Similarly $A_2 = \frac{R\delta}{2D_{O_2}[O_2]_B}$

$$A = [A_1 + A_2] = \frac{R\delta \{D_{CN^-}[CN^-]_B + 4D_{O_2}[O_2]_B\}}{2D_{O_2} \cdot [O_2]_B \; D_{CN^-} \; [CN^-]_B}$$

- If. $[CN^-]_B \ll [O_2]_B$ then $R = A D_{CN^-}[CN^-]_B/2\delta$ Oxygen has no role in kinetics.
- If $[CN^-]_B \gg [O_2]_B$ then $R = 2AD_{O_2}[O_2]_B/\delta$
- In intermediate range

$$R = \sqrt{D_{O_2} \cdot D_{CN^-}} \; A [O_2]_B^{1/2} \cdot [CN^-]_B^{1/2} / 2\delta$$

Normally $D_{CN^-} = 1.83 \times 10^{-5}$ cm^2. sec^{-1}

$D_{O_2} = 2.76 \times 10^{-5}$ cm^2. sec^{-1}

$\delta = 2 \times 10^{-3}$ cm to 9×10^{-3} depending on speed and mode of agitation.

We can write the diffusion of oxygen towards the gold surface in terms of a diffusion equation, the diffusion coefficient of oxygen. This is a gradient of oxygen, dissolve oxygen in the bulk, dissolve oxygen in the surface, divided by delta which is the boundary layer thickness, and a one is the area at the site where this reaction is taking place. Similarly, for c n minus ion diffusion which is going towards the surface, diffusion coefficient of c n minus, cyanide ion in the bulk minus cyanide ions at the surface of gold. Now, we can assume that at equilibrium these two will be very low values, means all oxygen that has gone to the surface of gold for dissolution of gold has been consumed, cyanide ions are consumed so these two terms will go out, and you can write for the rate of reaction, a reaction like this that two d o two a one only this term will be there from which you can get the value of a one.

This reaction is taking place at another site, and so we can get the value of a two. If you add a one and a two we get the total area surface on which everything or taking place, and we get an expression like that. Now, we can look at this expression, and come up with many conclusions that if the dissolved oxygen is much larger compared to the cyanide concentration, then will end up with an expression in which there is no oxygen in the expression, so oxygen will have no role in kinetics, which means there can be situations where one does not have to ensure high concentration values at all. If cyanide concentration is very large compared to the oxygen in solution, then we get another expression, where the cyanide concentration term is not there so cyanide concentration becomes immaterial, it is governed only by the oxygen dissolve oxygen.

In the intermediate range will have an expression, and we know, one knows there is such values of diffusion coefficients of c n minus, diffusion coefficients of dissolved oxygen and normal value of boundary layer thickness, like it is 2 into 10 to the power minus 3 centimeter to 9 into 10 to the power minus 3 centimeters. So, we can actually estimate the rate of dissolution of gold in cyanide media assuming different conditions, and we can compare them with the actual situation. If we find that it is matching one where the cyanide concentration does not matter, the rate, then we do not bother about the cyanide concentration. If you find that there it is actually following a mechanism, where cyanide concentration matters dissolved oxygen does not matter, so the process has to be designed accordingly.

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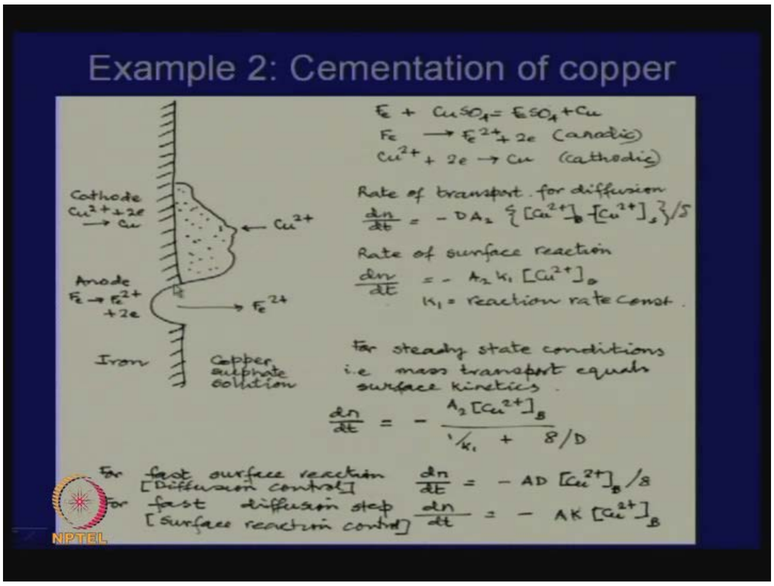

Example 2: Cementation of copper

$Fe + CuSO_4 = FeSO_4 + Cu$

$Fe \longrightarrow Fe^{2+} + 2e$ (anodic)

$Cu^{2+} + 2e \rightarrow Cu$ (cathodic)

Rate of transport for diffusion

$\frac{dn}{dt} = -DA_2 \{[Cu^{2+}]_B - [Cu^{2+}]_s\}/\delta$

Rate of surface reaction

$\frac{dn}{dt} = -A_2 k_1 [Cu^{2+}]_s$

k_1 = reaction rate const.

For steady state conditions i.e mass transport equals surface kinetics.

$$\frac{dn}{dt} = -\frac{A_2 [Cu^{2+}]_B}{1/k_1 + \delta/D}$$

For fast surface reaction [Diffusion control] $\frac{dn}{dt} = -AD[Cu^{2+}]_B/\delta$

For fast diffusion step [Surface reaction control] $\frac{dn}{dt} = -AK[Cu^{2+}]_B$

So, these are the sort of things that are actually done to understand these reactions. I will give you another example of a hydro metallurgical reaction which can be analyzed in terms of this electro chemical theories. It pertains to cementation of copper from copper sulphate. Copper is less reactive as compared to iron, if you look at the order of reactivity in terms of electro potentials or free energies of formations of compounds, so the copper compounds are not as stable as compounds of iron therefore, if we put iron filings into copper sulphate, iron will dissolve and copper will be precipitated. This actually, ancient metallurgists and chemists found out long ago.

Now, we have the similar situations here, that this is the surface of iron, you put metal filings, iron filings, but assume a particle with the surface like this, in that surface there are some cathode areas where the copper ions in the solution are moving towards that, this reaction is taking place c u 2 plus 2 e producing copper, and this copper is building up. In another area we have the anodic reaction that iron surface gives rise to f e 2 plus and consuming electrons, so that in some areas copper ions are coming, depositing copper metal, in some other areas iron is being consumed and f e 2 plus is going into this solution. Actually, in an actual situation you cannot tell which would be a cathodic area, which would be a anodic area, there are some reasons why it becomes.

But this is a very simplistic representation. Essentially, what it means that when you put copper iron filings much of it will get consumed and you will deposit powders of copper metal. And we can analyze this using diffusion equation, there will be a diffusion equations for the diffusion of copper ions, there will be a diffusion equation for if we neglect the surface concentration, this will be diffusion equation to give the rate of transport of copper ions. Similarly, there will be diffusion equation for a iron, so analyzing these sort of things we understand the process much better.

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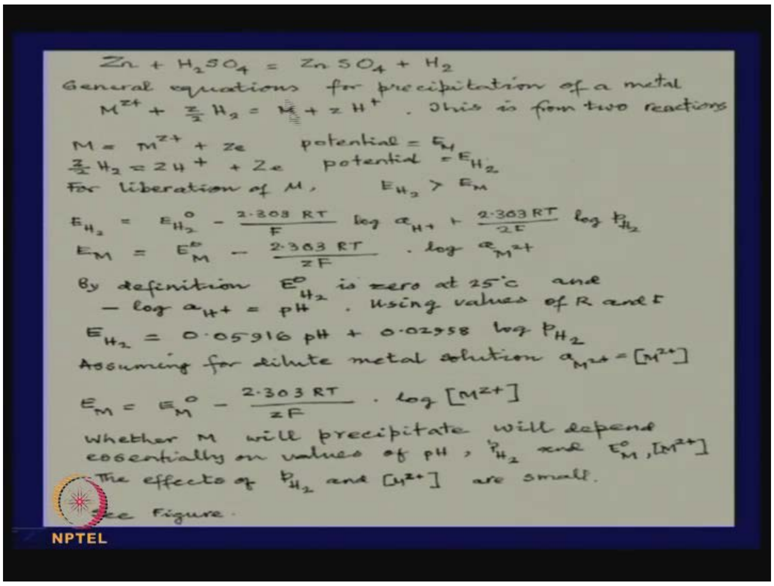

$Zn + H_2SO_4 = ZnSO_4 + H_2$

General equations for precipitation of a metal

$M^{z+} + \frac{z}{2} H_2 = M + z H^+$. This is from two reactions

$M = M^{z+} + ze$ potential $= E_M$

$\frac{z}{2} H_2 = zH^+ + ze$ potential $= E_{H_2}$

For liberation of M, $E_{H_2} > E_M$

$$E_{H_2} = E^0_{H_2} - \frac{2{\cdot}303\,RT}{F} \log a_{H^+} + \frac{2{\cdot}303\,RT}{2F} \log p_{H_2}$$

$$E_M = E^0_M - \frac{2{\cdot}303\,RT}{zF} . \log a_{M^{z+}}$$

By definition $E^0_{H_2}$ is zero at 25°C and $-\log a_{H^+} = pH$. Using values of R and F

$$E_{H_2} = 0{\cdot}05916\,pH + 0{\cdot}02958 \log p_{H_2}$$

Assuming for dilute metal solution $a_{M^{z+}} = [M^{z+}]$

$$E_M = E^0_M - \frac{2{\cdot}303\,RT}{zF} . \log [M^{z+}]$$

Whether M will precipitate will depend essentially on values of pH, p_{H_2} and E^0_M, $[M^{z+}]$

The effects of p_{H_2} and $[M^{z+}]$ are small.

See Figure.

Now, I come to a very interesting topic which has been analyzed using the concept of electrode potentials, and that is hydrogen reduction to obtain metals from solutions. Now, when zinc is put into sulphuric acid zinc dissolves and hydrogen evolves, this is because zinc is placed above hydrogen in the electro chemical series. We can write for precipitation of metals, we have to write the reverse reaction that metal ions will be precipitated by hydrogen gas to produce metal and hydrogen ions. Now, in this case tell me when can we reverse the reaction? We can reverse the reaction by increasing very high pressures of hydrogen, or by doing something so that the acid concentration becomes so low, it becomes so highly alkaline media that this reaction will be to the left. So, this reaction can go this way or that way depending on p h of the solution; pressure of hydrogen and of course, the basic nature of the metal.

Like if it is zinc or metals above zinc, it will be relatively more difficult to precipitate by using hydrogen, but metals that are placed below hydrogen in the electro chemicals series will not so difficult from the point of electro precipitation. Let us look at it little more systematically, the precipitation of metal ion, metal from a solution containing metal ion by hydrogen is in general, this is the expression you can write z is the value c m z plus plus x by 2 h 2 is equal to m plus z h plus 2 is z by 2. This actually, is a combination of two reactions; one is m metal going into solution as m z plus, and the other hydrogen ion going into solution as hydrogen ion. What we want is that, this reaction should predominate rather than this reaction. If there is a stronger tendency for hydrogen to form hydrogen ions, then metal to metal ions then this reaction will go this way, that reaction will go that way

Now, let us see when we can do this? For liberation of m we say that the potential for hydrogen should be more for the potential for the metal. Now, e h 2 is written as e h 2 standard addition potential minus 2.303 r t by f log a h. This is a standard thing, according from this reaction we can write this, now you know that minus log a h is actually p h and this is 0, so this e h 2 can be written simply as point 0.05916, this is the expression that comes from here and plus a p h term. A p h term plus log p h 2 whereas, for metal will have expression, the potential of the metal standard electro potential minus this term log concentration of n z plus. Whether m will precipitate will depend essentially on values of p h pressure of hydrogen, and standard electro potential of metal, metal ion concentration. Generally, the effects of p h 2 and n 2 plus are small, because n z plus it is in a log term, it involves a log term. So, most important parameters will be the p h terms and the essential nature of the metal.

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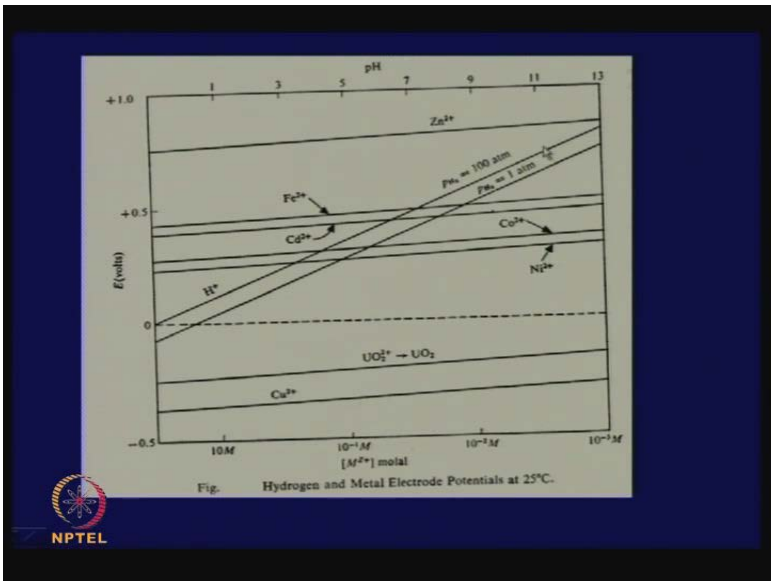

Fig. Hydrogen and Metal Electrode Potentials at 25°C.

So, here is a simple diagram to explain this, we are plotting here the electrode potentials of copper, iron, cadmium, zinc, nickel, cobalt. In this axis we are putting metal ion concentration in molal. Here there is a p h axis for hydrogen, this is the potential. The plot gives us… these are the plots for hydrogen, by increasing the pressure from 1to 100 atmospheres there is only change this much of change. Whereas, these are the lines for different metals as a concentration of the metal ion in concentration, you see the effect is not very much, but the differences are coming from their nature, basic nature of electro potentials. These are highly electro positive metals are placed very high, these are less reactive metals placed low.

This diagram tells us that no matter what is the p h value, hydrogen will always precipitate copper from copper sulphate solution or any solution containing copper ions, this is very easily known, because you have a copper, an echoes media with copper ions just pass hydrogen copper will get precipitated. This we know even from the electro potential series, copper is placed where hydrogen. More important are those who are just around that. So, we find that if we come to a metal like say nickel, nickel will precipitate only if the p h value is more than this, then the hydrogen potential will become more than nickel potential, and I am taking only the one atmospheric pressure value. Similarly, for cobalt we have a situation, if the p h value is below this, means it is acidic it will not be precipitated as a metal, if it is on this side if the p h is more alkaline, we will then precipitate the metal.

Now, in the case of zinc, even if we go to almost purely alkaline thing p h value is 13, still the zinc potential is greater than hydrogen potential even if it is hundred, so the metal will not be precipitated. So, we control the precipitation of metal from echo solutions by controlling the p h value mostly, because the ionic concentration is not a strong parameter, and pressure of hydrogen is also does not change the situation very much. These are the guiding equations from which we find that e h 2 is equal to a p h term, and here you have the standard electro potential of the metal.

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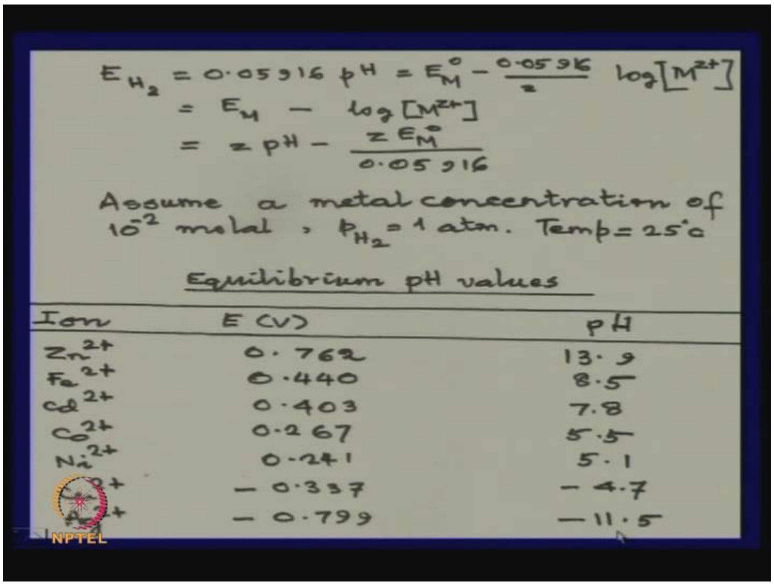

$$E_{H_2} = 0{\cdot}05916\ pH = E_M^\circ - \frac{0{\cdot}05916}{z}\log[M^{2+}]$$
$$= E_M - \log[M^{2+}]$$
$$= z\,pH - \frac{zE_M^\circ}{0{\cdot}05916}$$

Assume a metal concentration of 10^{-2} molal, $p_{H_2} = 1$ atm. Temp = 25°c

Equilibrium pH values

Ion	E (v)	pH
Zn^{2+}	0·762	13·9
Fe^{2+}	0·440	8·5
Cd^{2+}	0·403	7·8
Co^{2+}	0·267	5·5
Ni^{2+}	0·241	5·1
[illegible]$^{2+}$	− 0·337	− 4·7
[illegible]$^{+}$	− 0·799	− 11·5

These are the two most parameters, and we can calculate the equilibrium p h values for some standard conditions of one atmosphere of hydrogen, pressure of hydrogen temperature is 25 degrees, and a metal concentration of 10 to the power of minus 2 molal, which is a normal concentration in hydro metallurgy and these are the conditions. Zinc precipitation in theory requires 13.9 which is barely achievable; you can never precipitate zinc from echo solutions. Iron 8.5 p h, cadmium 7.8, cobalt 5.5, nickel 5.1, copper and silver no problem at all, I mean it will be precipitate no whatever, it is very easy to precipitate even in acid solutions you can precipitate copper and silver, there is a problem however.

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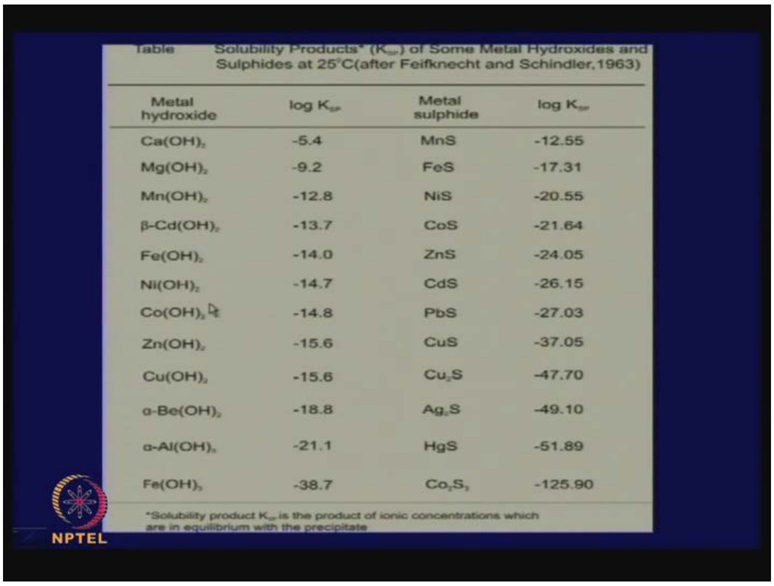

Table Solubility Products* (K_{sp}) of Some Metal Hydroxides and Sulphides at 25°C(after Feifknecht and Schindler,1963)

Metal hydroxide	log K_{sp}	Metal sulphide	log K_{sp}
$Ca(OH)_2$	-5.4	MnS	-12.55
$Mg(OH)_2$	-9.2	FeS	-17.31
$Mn(OH)_2$	-12.8	NiS	-20.55
β-$Cd(OH)_2$	-13.7	CoS	-21.64
$Fe(OH)_2$	-14.0	ZnS	-24.05
$Ni(OH)_2$	-14.7	CdS	-26.15
$Co(OH)_2$	-14.8	PbS	-27.03
$Zn(OH)_2$	-15.6	CuS	-37.05
$Cu(OH)_2$	-15.6	Cu_2S	-47.70
α-$Be(OH)_2$	-18.8	Ag_2S	-49.10
α-$Al(OH)_3$	-21.1	HgS	-51.89
$Fe(OH)_3$	-38.7	Co_2S_3	-125.90

*Solubility product K_{sp} is the product of ionic concentrations which are in equilibrium with the precipitate

The problem is many of these metals like iron, nickel, cobalt tend to precipitate oxides at high the alkaline solutions. Let us concentrate mostly on nickel and cobalt, because these are two metals for which hydrogen reduction has become very important, and large quantities of nickel and cobalt are precipitated from echoes media by hydrogen reduction. The problem is things become easier if you are going to a higher p h value, means more alkaline solution, but if you have more alkaline solution then you have a danger of precipitation of the oxide, what do you do then? There is a very interesting solution to this, and the solution is nickel ions will precipitate as an hydroxide by reacting with o h ions, we can reduce the activity of nickel ions by forming some complexes, nickel amines for example, by adding ammonia. But if you do that the nickel has been more stabilized, it will not react with hydroxide, it will not give you the precipitate, but then reduction of nickel ion to nickel metal will become more difficult.

So, on one it is not a win-win situation, you are doing something which is good from the point of view of eliminating hydroxide precipitation, but by making it more stable you are making precipitation on nickel metal from nickel ion little more difficult than what it was. Now, lot of work has been done to find out how do you find an optimum condition?

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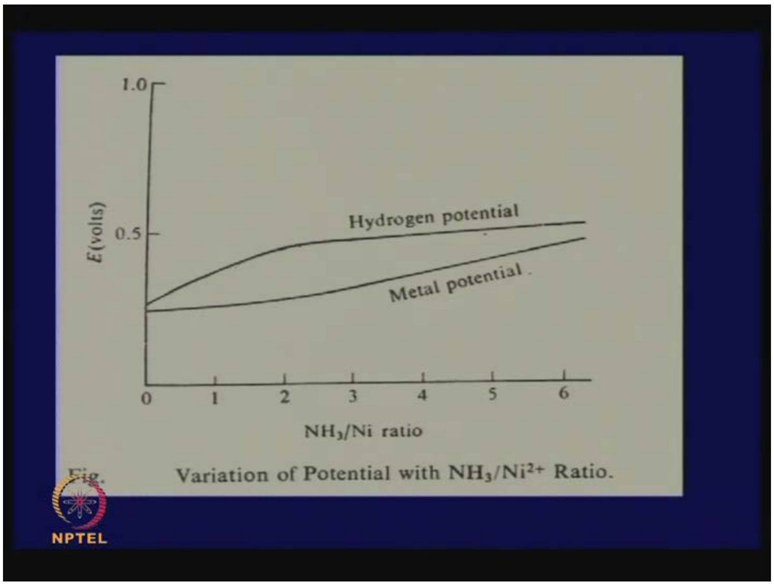

Fig. Variation of Potential with NH_3/Ni^{2+} Ratio.

People have found that there is an optimum condition. Incidentally what do I mean by nickel amines?

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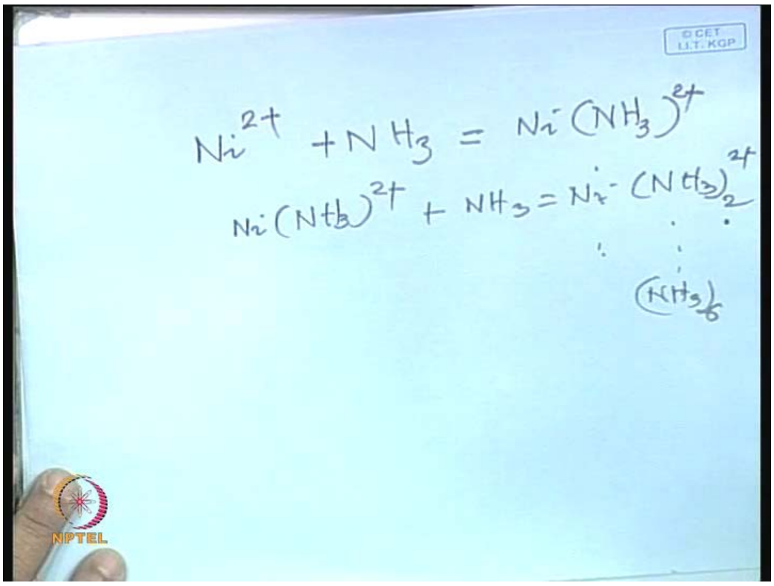

$$Ni^{2+} + NH_3 = Ni(NH_3)^{2+}$$

$$Ni(NH_3)^{2+} + NH_3 = Ni(NH_3)_2^{2+}$$

$$\vdots \qquad \vdots$$

$$(NH_3)_6$$

N i 2 plus in echo solution can react with ammonia to produce what we call an amines, and there can be higher amines also n i n h 3 2 plus plus n h 3 n i n h 3 2 2 plus it can go up to n h 3 6.

So, different and the more higher amines you have, the more stable nickel is becoming. So, when you found these amines they do not precipitate as hydroxide, but then it will become bit difficult for reduction. So, these two conflicting things are represented here with as you increase the n h 3 by n i ratio and the maximum is 6, you see the metal potential line goes like this, hydrogen potential moves like this. And they say this is where you have the best situation, where you have the maximum difference between the two, and that is where the industry operates with about 2.5 kind a function situations.

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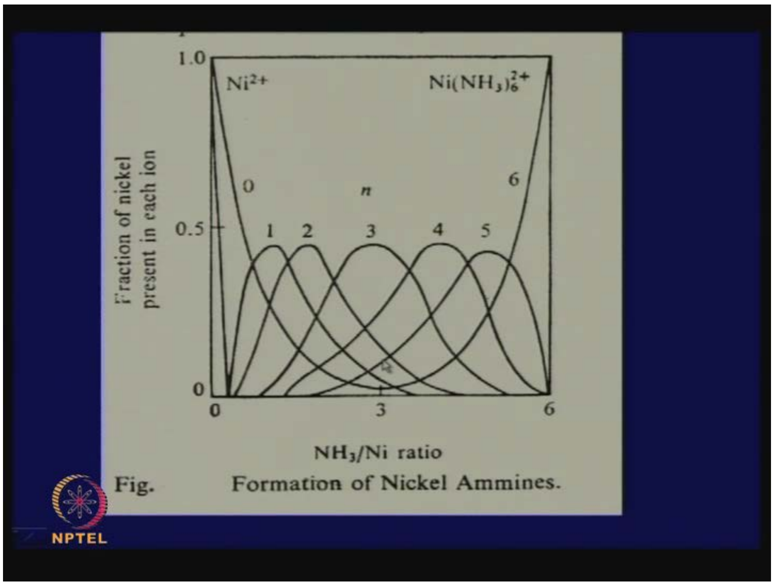

Fig. Formation of Nickel Ammines.

Now, this is the situation when we have ammonia in echo solutions with nickel. Actually, there are a series of amines formed, and depending on what is the n s t by n i ratio, you form different… all the amines are there but in different proportions like suppose, it is n h 3 by n i is 3 then this complex with 6 n h 3 is this much, this is with 5, this is the 1 with 4, this is one with 3. So, it is never one amine, you always have a combination of different amines, in different proportions depending on by n h t by n i ratio. We need nickel amines otherwise; we cannot precipitate nickel by hydrogen reduction, all though theoretical it is possible, because there is also theoretical possibility of creation of an oxide phase. So, the industry spread around with all these things, and come out with the situation where they will not precipitate the oxide, but they make it possible for precipitation of nickel from the solution.

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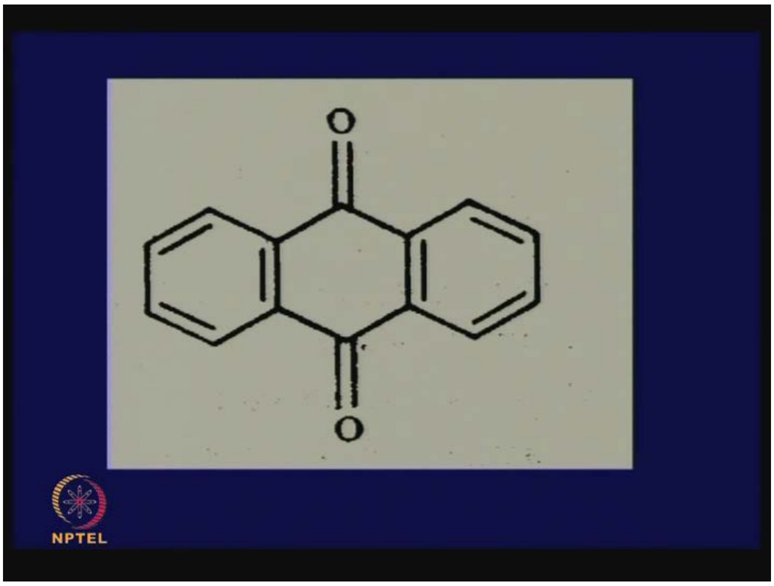

Now, there is something more interesting. They can now precipitate nickel in various forms as powders, as flat tablets, or as long small cylinders, using a additive called antara que no.

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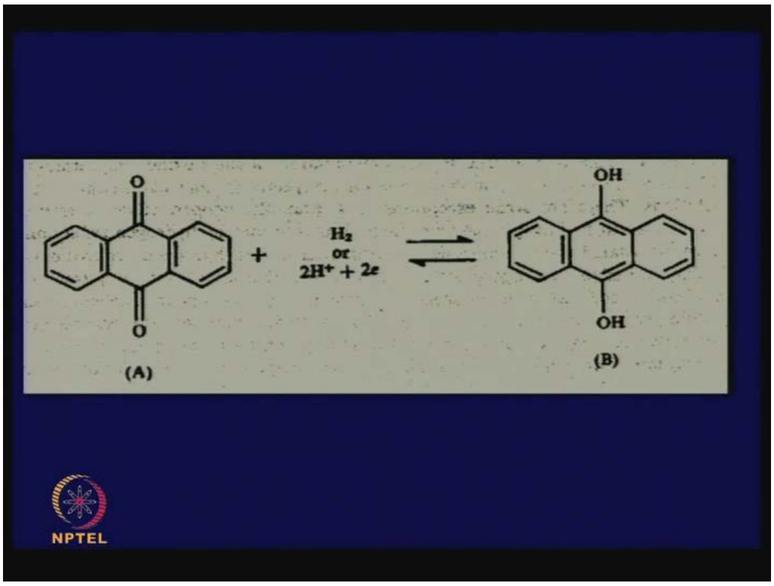

Antara que no is a catalyst, which plays around with the surface of the metal and does all kinds of things, this is its structure. The hydrogen ion comes here gets itself attached then it can come out also, and all kinds of catalytic activities takes place. And using the right kind of antara que no the quality of deposit is improved; one can control the particle size, particle shape etcetera. So, I think the time is come to close this lecture, I have very briefly discussed the principles of hydro metallurgy, staring with leaching and leaching is always… leaching involves diffusion steps of reagents toward the surface, and the products coming out of the surface, the products can be a metal ion or a metal ion complex or some products.

There can be a layer of insoluble residues through which things must go in, and things must go out. By understanding the diffusion phenomenon, you can estimate the rates of leaching reactions. And I have also discussed one very interesting example as to how we can analyze in terms of electro chemical steps, not only leaching reactions, but a precipitation reaction like, precipitation nickel and cobalt from amine complexes. Thank you very much.