Non-ferrous Extractive Metallurgy

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Lecture No. #42

Review and Summary (contd.)

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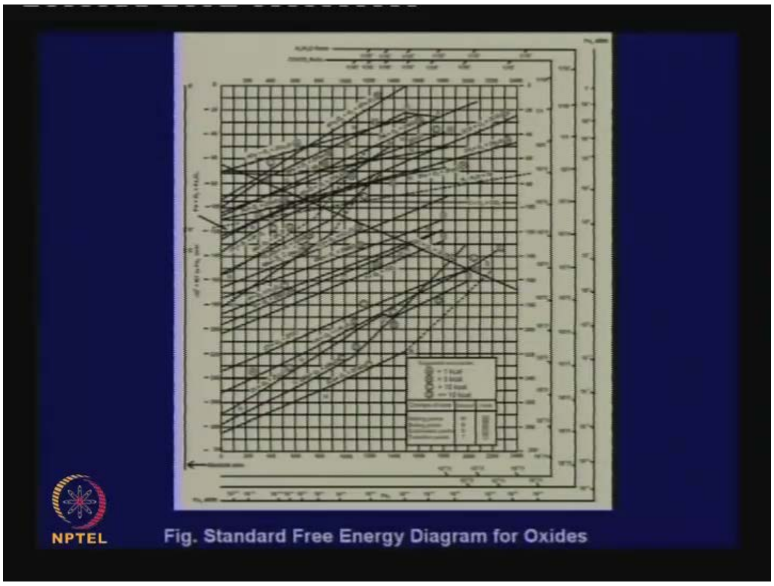

Fig. Standard Free Energy Diagram for Oxides

Friends, I am reviewing the entire course, and we just discussed Ellingham diagrams and explained why the free energy plot, free energy of formation plots for oxides go this way, and the slope is negative for C O. In case you wonder, why the slopes suddenly changes for these lines, it has something to with a phase change, something solidifies or volatilizes, this has been discussed. So, I would not discuss that again.

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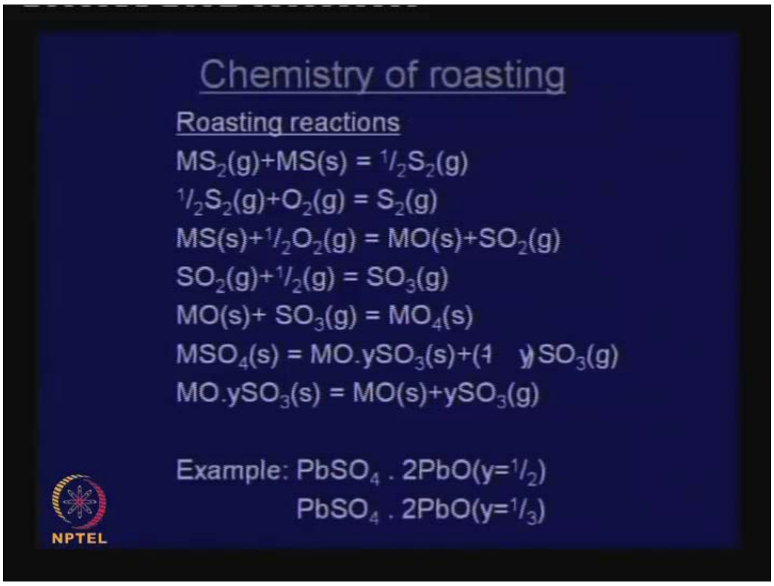

Chemistry of roasting

Roasting reactions

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

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

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

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

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

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

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

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

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

Now, regarding the various steps in pyro metallurgy, we can consider (( )) roasting, smelting, etcetera; there has been, I have discussed lot of things. I have said there can be so many kinds of roasting reactions, where we talked about converting sulphides to oxides or sulphates or lower oxides, and all these there have been many examples of this, there are also free energy diagrams for metal sulphides.

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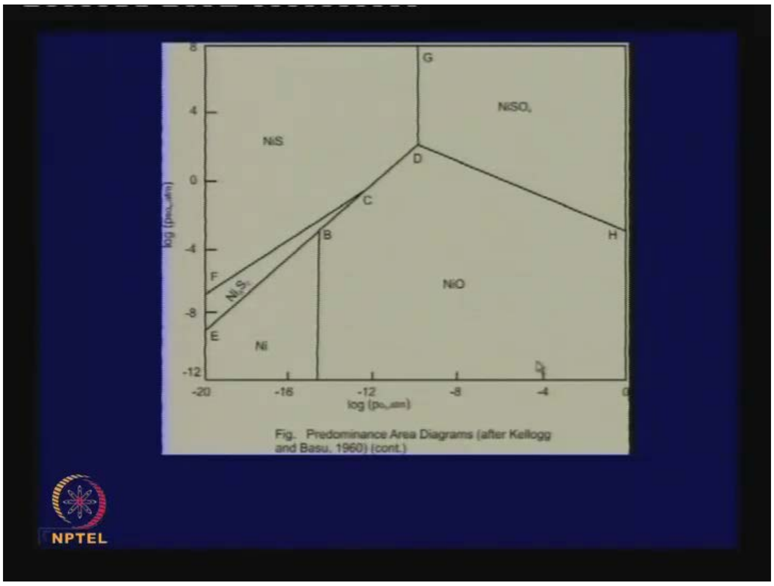

Fig. Predominance Area Diagrams (after Kellogg and Basu, 1960) (cont.)

Then I have discussed the predominance area diagrams, that show which phases will be stable under different conditions of p S O 2 and log p O 2 starting with a sulphide, we can make the sulphate, we can make the oxide, we can make a lower sulphide, we can make the metal all depend depending on the phase stabilities.

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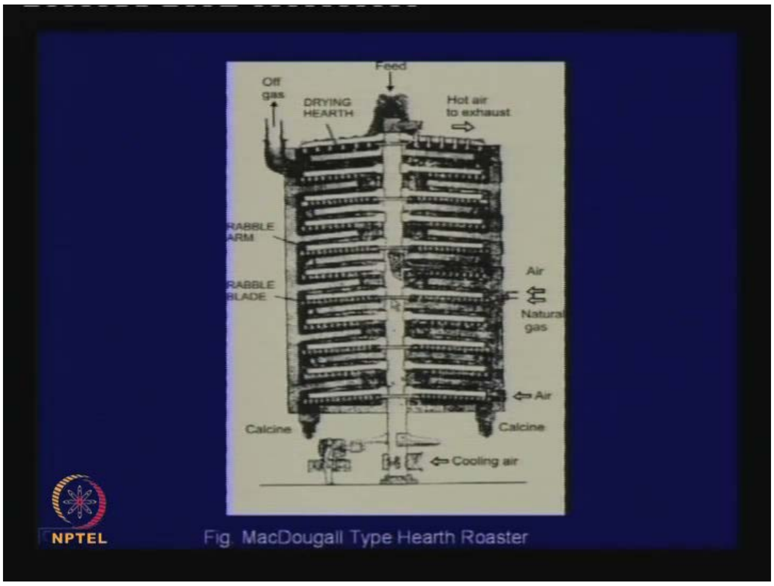

Fig. MacDougall Type Hearth Roaster

And I have also indicated how, we can draw these diagrams by taking into account in different reactions. This is the Hearth Roaster which is commonly used for roasting where the feed goes through one hearth to another and these these rotate and because of rotation, the some hearths are stationary on this, there is a rotating device and they so, them from one to the other and they are all sloped. Later, it was found, actually it is during the falling of particles that maximum oxidation took place.

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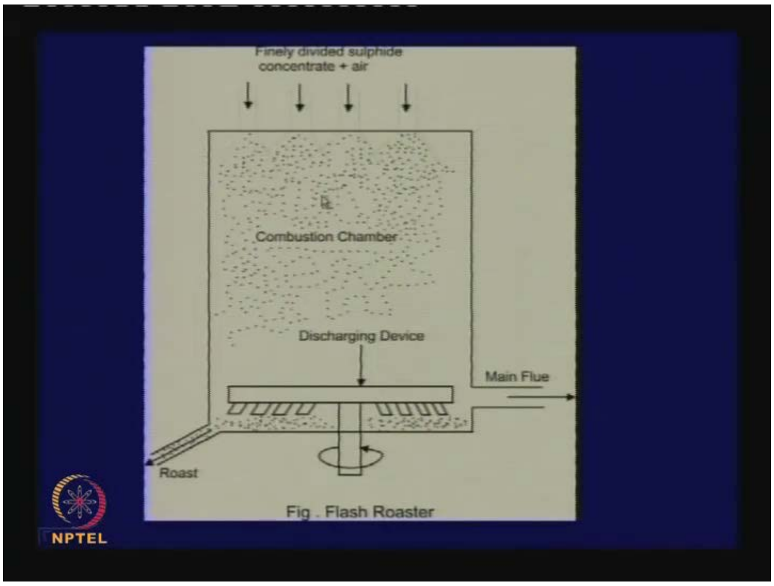

Fig . Flash Roaster

So, the idea for a Flash Roaster (( )) that instead of bothering about passing the sulphides from one hearth to another, why not just drop from the top, the concentrate and air and you get at the bottom, the calcine. It it can be done then there is a sintering machine where also roasting takes place in continues manner then we have talked about smelting blast furnace smelting as it is applied for iron making, this can be applied for lead. We have talked about Reverberatory furnace where reactions occur over a longtime, we produce it can produce matte which is a mixture sulphides and slags.

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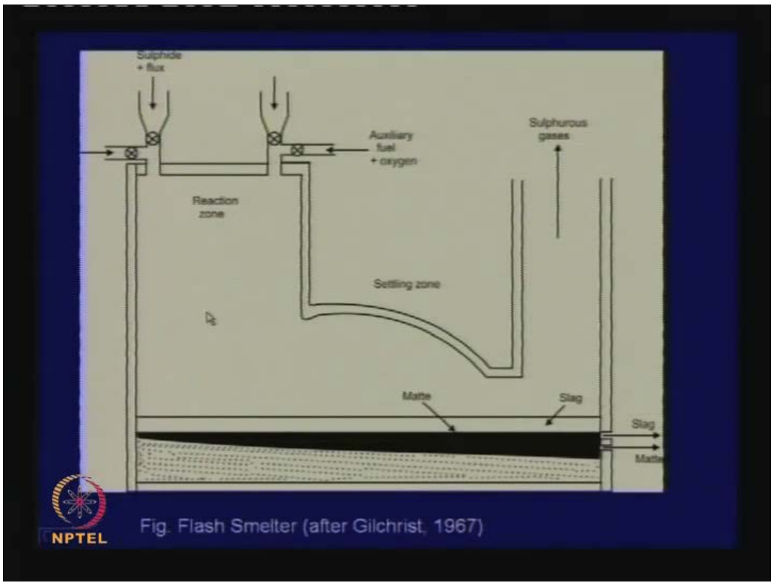

Fig. Flash Smelter (after Gilchrist, 1967)

And we have talked about the reactors where one combines roasting as well as smelting. So, initially thought of flash roasting, now here is the here is the flash smelter, after roasting, it can be, it gets smelted also and again we can directly produced matte and slag. We have discussed this in more detail with reference to some oxidation reactions, the applications of the Ellingham diagrams and how we generate the stability stability diagrams; I would not go into all this.

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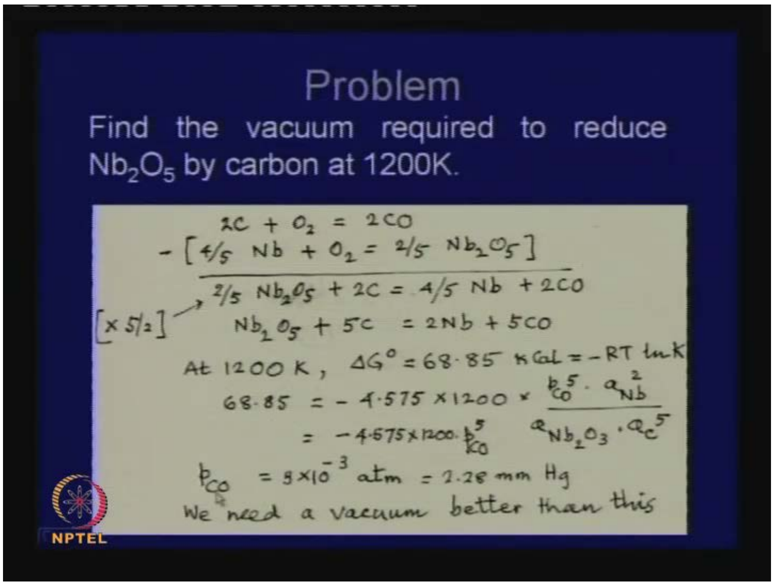

Problem

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

$$2C + O_2 = 2CO$$

$$-\left[4/5\ Nb + O_2 = 2/5\ Nb_2O_5\right]$$

$$2/5\ Nb_2O_5 + 2C = 4/5\ Nb + 2CO$$

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

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

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

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

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

We need a vacuum better than this

I have given an example of application of vacuum when vacuum is required and we can calculate, what kind of vacuum we need for a reaction to happen which normally will not happen. See normally for reduction of this free energy change is positive but, if you can remove the C O application of a vacuum then we find that equilibrium partial pressure is this, so, below that pressure of p C O the reaction can be made possible.

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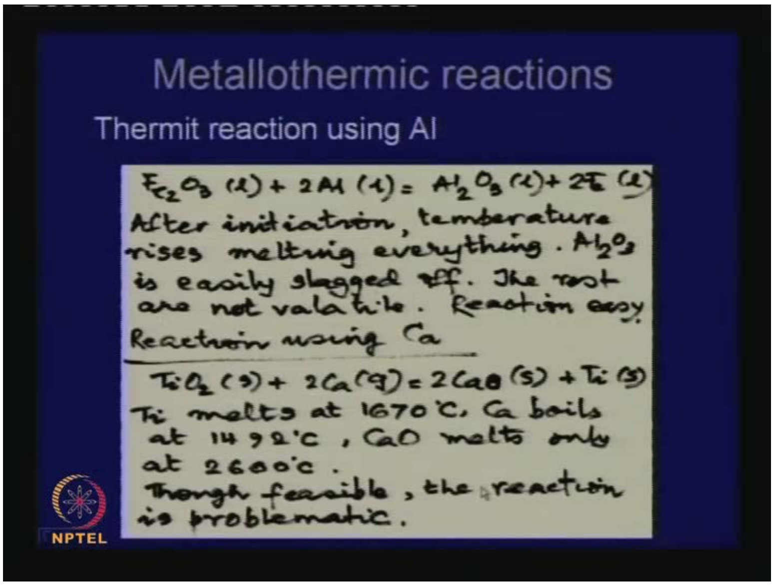

Metallothermic reactions

Thermit reaction using Al

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

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

Reaction using Ca

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

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

Though feasible, the reaction is problematic.

We have done talked about thermit analysis, Thermit reaction analyzed that, we have talked about a similar reaction which you call now metallothermic reactions of calcium reducing T i O 2 and then I mentioned that, we can write a chemical reaction like this but, sometimes in metallurgical operation, this will not be accepted because calcium as a reducing agent would become gas at the temperature where this should happen. So, it it will require a (( )) or closed chamber. Titanium melts at 1670 degrees, calcium boils at 1492, calcium oxide will melt only at 26,000 degree. So, there is a mismatch of melting points and boiling points, this sort of things will not form the basis of on metallurgical operation.

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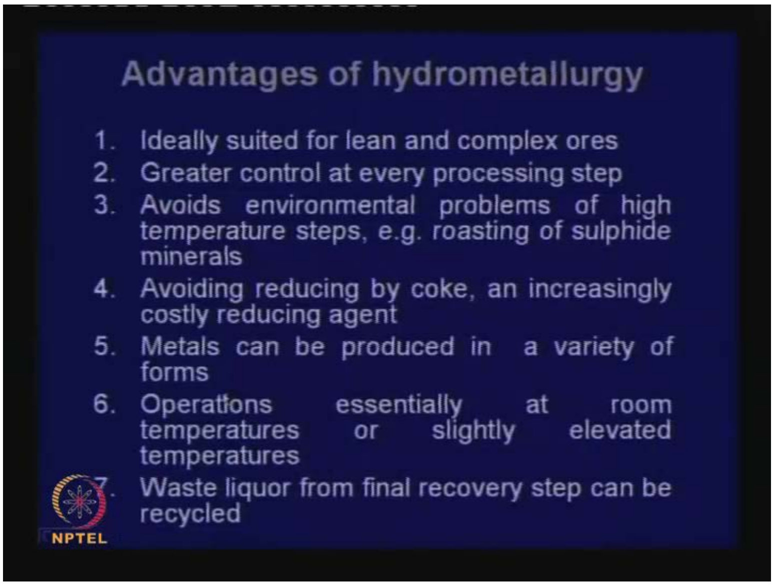

Advantages of hydrometallurgy

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
7. Waste liquor from final recovery step can be recycled

We came to hydrometallurgy (( )) saw the advantages and I mentioned it is ideally suited for lean and complex ores, there is greater control because things are happening at low temperatures, room temperatures very often or slightly elevated temperatures but, they are it is easy to control because things are not happening far too rapidly. Environmental problems coming out of gaseous emissions are not there. We do not have to depend on coke as pyrometallurgical operations very often depend on, it is becoming a costly reducing agent there is no question of C O 2 emission.

It does not mean all hydrometallurgical operations are very clean environmentally because many of the operations also rejects slimes, they reject effluents which are also not good for the environment. Metals can be produced in the variety of forms not liquids of course, but the solids can be in crystalline form in powdery forms sometime it can even produce particles of given shapes as you do in the case of nickel when you reduce the nickel ammine solutions by hydrogen.

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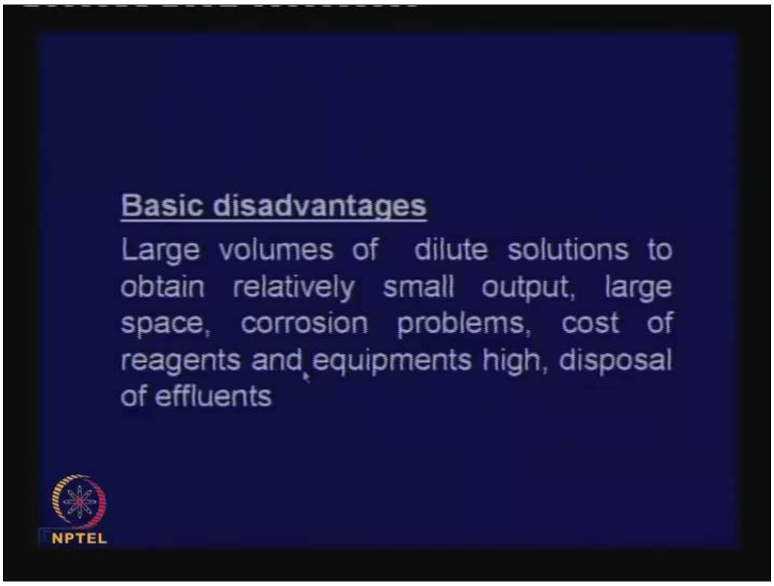

Basic disadvantages

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

There are some basic disadvantages which I have already mentioned that, we are dealing with dilute solutions we need lot of plumbing, pumping and there is tremendous amount of space is required, there are corrosion problems, reagent cost, equipment cost are high effluents can create problems.

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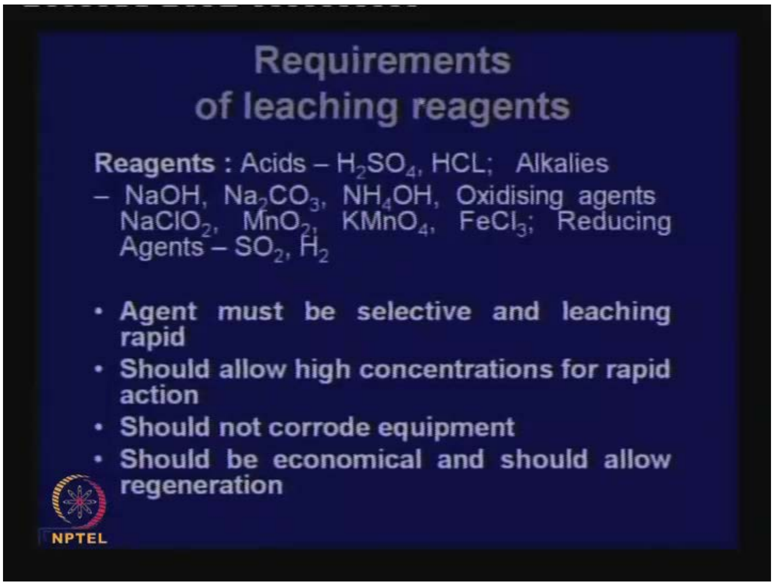

Requirements of leaching reagents

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**

Now, essentially in hydrometallurgy, we have to we need a concentrate which will be leached. During leaching generally, we take the metallic values in solution and the gang is rejected in the solids but, opposite of that is also done. We saw in the case of monazite leaching by alkaline in our country, alkalis dissolve away the undesirables, the desirable part remains in the insoluble residue. In the case of aluminum, alkali leaching takes the aluminum value into solution; the titanium ion that we do not want come in the leach liquor is separated as a solid residue.

So, leaching does not mean taking metallic value in the solution, it can take the metallic value preferentially in the residue also. So, the whole idea is the agent must be selective, leaching must be rapid; should allow high concentrations for rapid action; the leaching agent should not corrode equipment; it should be economical and should allow regeneration. Now, there are whole ranges of things used in leaching.

Sulphuric acid is very common and acids are stronger reagents, they dissolve things faster to a greater extent but, there is also danger of dissolving all kinds of things, we do not want to dissolve, whereas the alkalis are milder reagents but, they may be safer from the view of more impurities coming into solution and there are also during leaching many reducing agents are used like M n O 2, K M n O 4, F e C l 3, etcetera to increase the oxidation potential.

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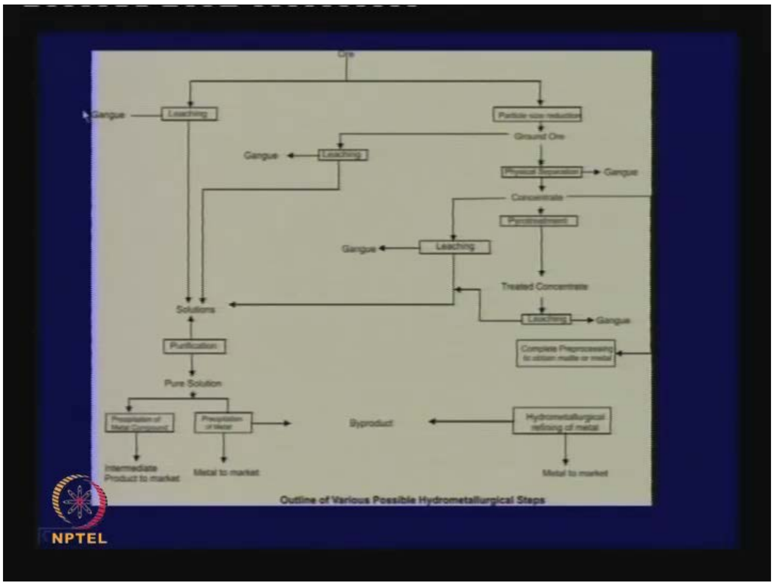

Outline of Various Possible Hydrometallurgical Steps

The various hydrometallurgical steps, I gave a flow sheet leaching then purification etcetera etcetera and then that is some other things you know that you can (( ))

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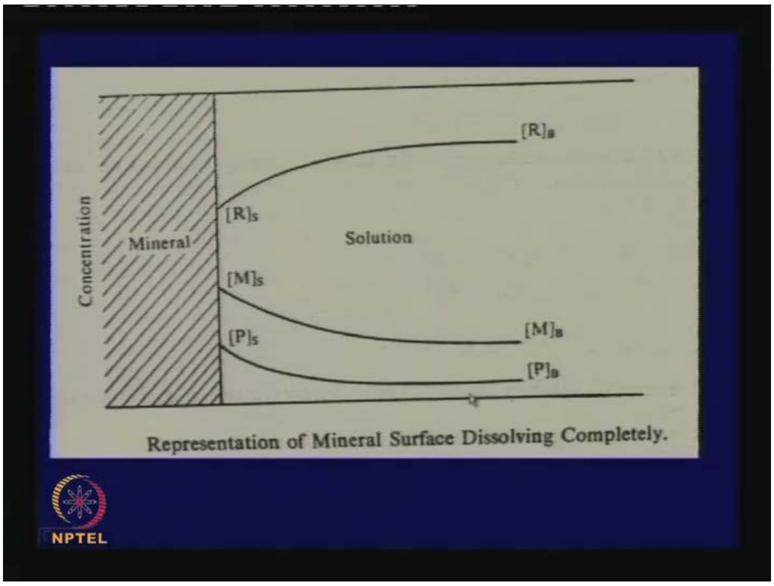

Representation of Mineral Surface Dissolving Completely.

I tried to show, how kinetics can be applied in analyzing leaching reactions like here is a solid mineral surface which is reacting with a leaching medium and we (( )) as the reagen reagent concentration from the bulk getting depleted when it comes to the surface, it is coming this way, metallic values that dissolves at the surface, diffuse out into the bulk and when it diffuse out, there must be a concentration profile going down the concentration must be increased here. If there are some other products, residues apart from metallic (( )) solution, this would also have a concentration profile.

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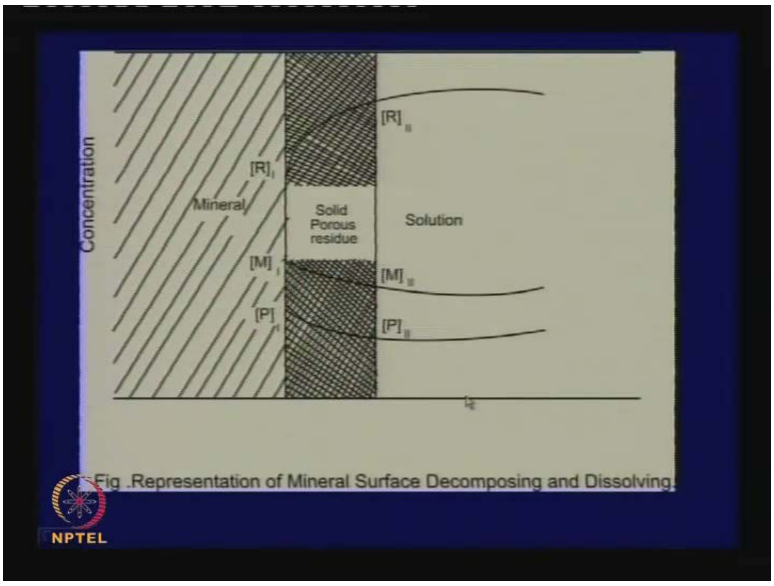

Fig .Representation of Mineral Surface Decomposing and Dissolving

If there is a solid porous residue then the diffusion processes takes place through that residue, reagent has to reagent has to sorry the reagent has to come through the layer to the surface of the mineral and the metal that is going into the solution has to diffuse through the porous the porous residue etcetera etcetera. Suppose, there is a leaching reaction where the intermediate residue layer is not porous but, it is very adherent then leaching reaction will stop. So, this possibility is also there.

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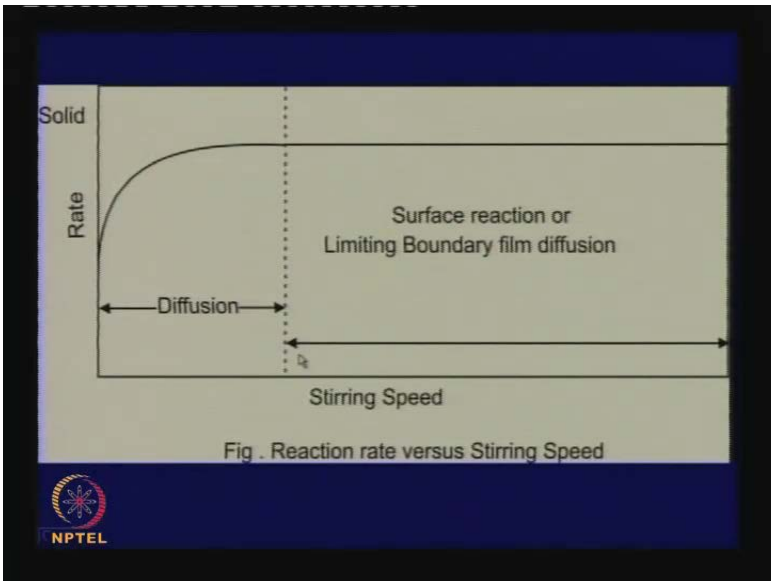

Fig . Reaction rate versus Stirring Speed

We discussed little more from kinetic point of view that any leaching reaction can be expedited by by stirring because there is a concentration profile at the surface and there is a concept of boundary layer, where say ninety nine percent of the concentration change takes place. So, if you stir the solution, the boundary profile is reduced (( )), the concentration profile is made steeper because the boundary layer becomes thinner and the stirring speed increases. But in this case, if you plot the stirring pace against rate we find that beyond a certain stirring speed, the rate of diffusion cannot increase because they they it has been reduced to the minimum the boundary layer thickness then only temperature will have to be increased.

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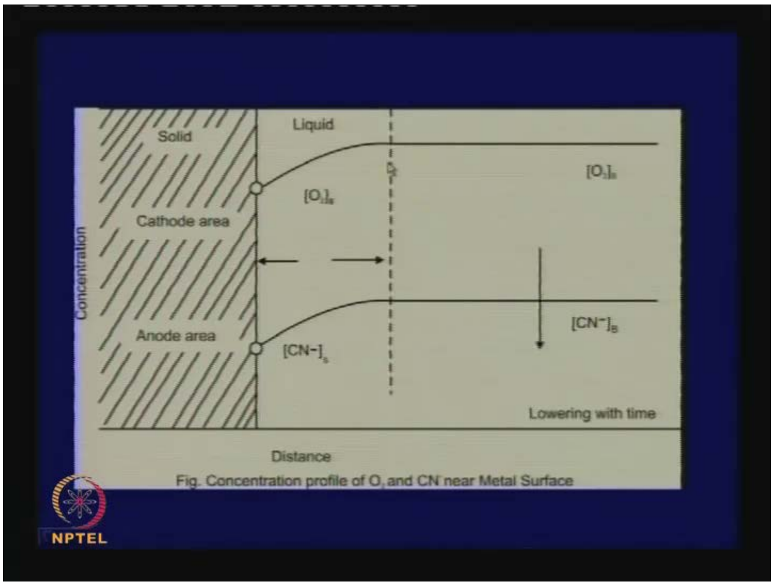

Fig. Concentration profile of O_2 and CN^- near Metal Surface

So, we have done this sort of analysis and we have done this analysis particularly in case of cyanaidation of gold, there is a surface where there are gold particles and cyanaidines are in the solution, cyanaidines have to diffuse towards the surface, the oxygen has to diffuse to the surf surface and gold cyanide that forms at the surface have to diffuse out.

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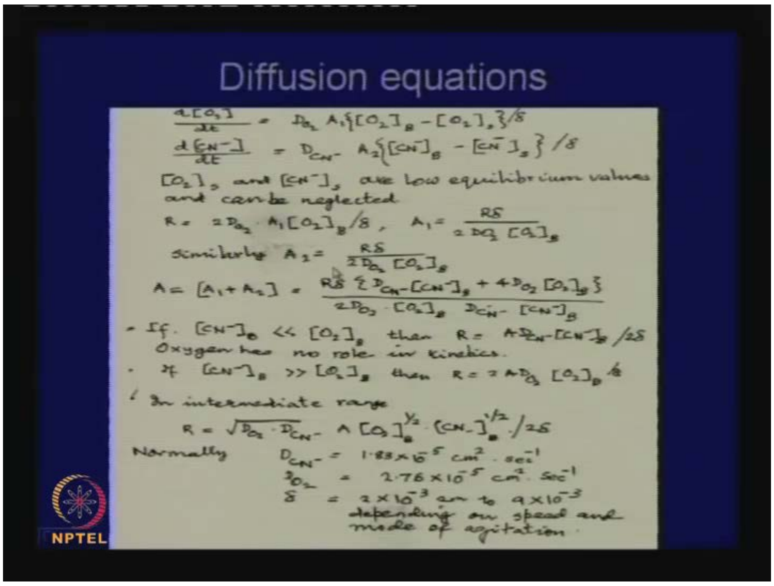

Diffusion equations

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

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

$[O_2]_s$ 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 $R = AD_{CN^-}[CN^-]_B/2\delta$
  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 $D_{CN^-} = 1.83\times10^{-5}\ cm^2 \cdot sec^{-1}$
$D_{O_2} = 2.76\times10^{-5}\ cm^2 \cdot sec^{-1}$
$\delta = 2\times10^{-3}$ cm to 9×10^{-3} depending on speed and mode of agitation.

So, this is an analysis of that to know, what will be important, when, is partial pressure of oxygen important because that is also reactant is cyanide concentration important because that is also, there as a reactor then we analysis that under different conditions, something is more important than the other.

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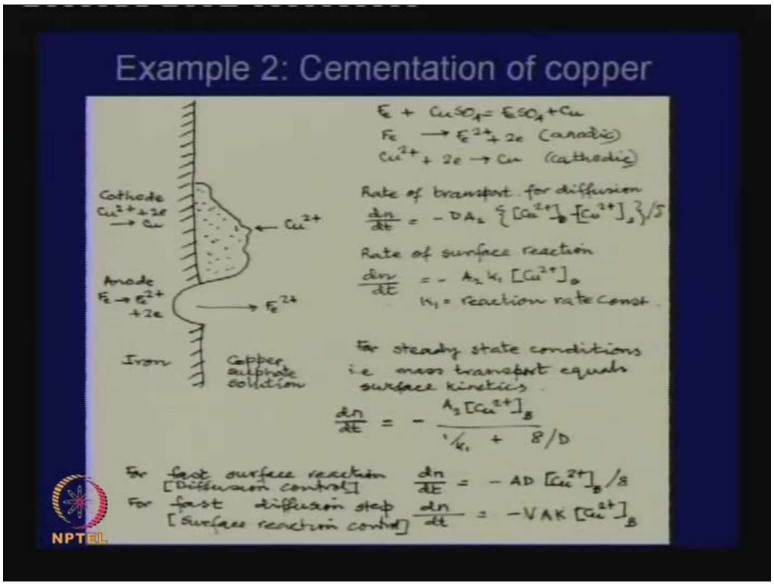

Example 2: Cementation of copper

$Fe + CuSO_4 = FeSO_4 + Cu$

$Fe \rightarrow Fe^{2+} + 2e$ (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] $\frac{dn}{dt} = -VAK[Cu^{2+}]_B$

We talked about the cementation reaction that iron fillings put into copper sulphate to produce ferrous sulphate and copper will precipitate. It is an electrochemical reaction with a cathode area and an anode area, we made an analysis to understand, what factors will govern the rate of the cementation process, it is not very difficult to understand.

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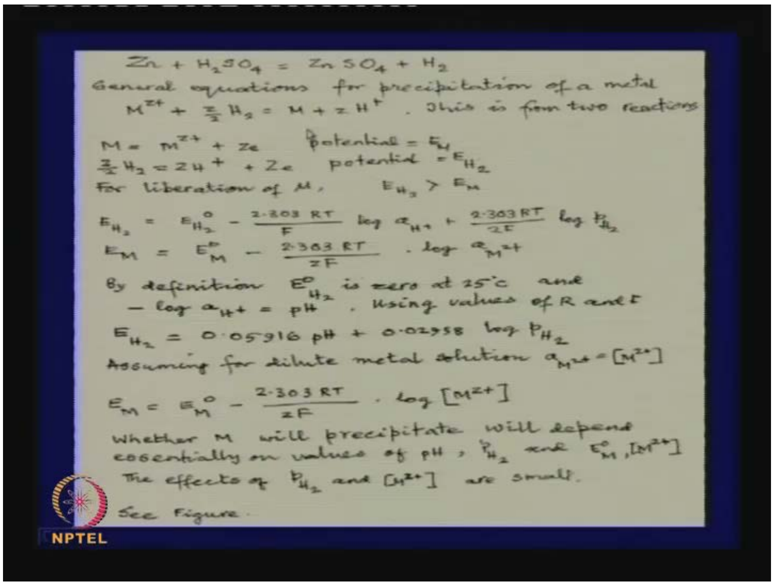

$Zn + H_2SO_4 = ZnSO_4 + H_2$

General equations for precipitation of a metal

$M^{z+} + \frac{z}{2} H_2 = M + zH^+$. 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, $E_{H_2} > E_M$

$$E_{H_2} = E^0_{H_2} - \frac{2.303\,RT}{F} \log a_{H^+} + \frac{2.303\,RT}{2F} \log p_{H_2}$$

$$E_M = E^0_M - \frac{2.303\,RT}{zF} \cdot \log a_{M^{z+}}$$

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

$$E_{H_2} = 0.05916\,pH + 0.02958 \log p_{H_2}$$

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

$$E_M = E^0_M - \frac{2.303\,RT}{zF} \cdot \log [M^{z+}]$$

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.

Then we have come to very important area and we did look at it from thermodynamic point of view, that zinc when reacts with H 2 S O 4 releases hydrogen because zinc is more electropositive. We can write a general thing that a metal ion which is more electropositive dissociates hydrogen ions. Now, suppose we have in the solution nickelines, cobaltines, can we precipitate them out as a metal by hydrogen? Now, normally, if the metal is not very reactive obviously, metal ion will not react metal ion metal ion will not react to generate hydrogen but, if it is a reactive metal, let it to react to produce hydrogen then how will hydrogen precipitate from the solution a metal which is reactive.

For that, we have to do an analysis, we have written this reaction in the other way, that we intend to convert metal ions and solutions into the metallic form by reaction with hydrogen and normally, as I said reactive metal ions cannot be converted to metal because the other this reaction will predominant but, we can make this thermodynamically feasible by increasing the pressure of hydrogen, reducing hydrogen ion concentration and try to see whether we can push it to the right.

This will never be possible for say sodium or potassium or cesium and things like that which is so reactive, it does not matter, how much of hydrogen pressure we apply or how much you lower this down which means how much acid you will make (( )). But there are cases which are marginal cases, where this will happen and this is the kind of analysis we have done. We have we have looked at we have expressed this in terms of hydrogen ion potential p H and pressure and come up with an equation in terms of metal ion concentration, which is a function of electrode potential of metal and one has to be more than the other. So, that the reaction takes place.

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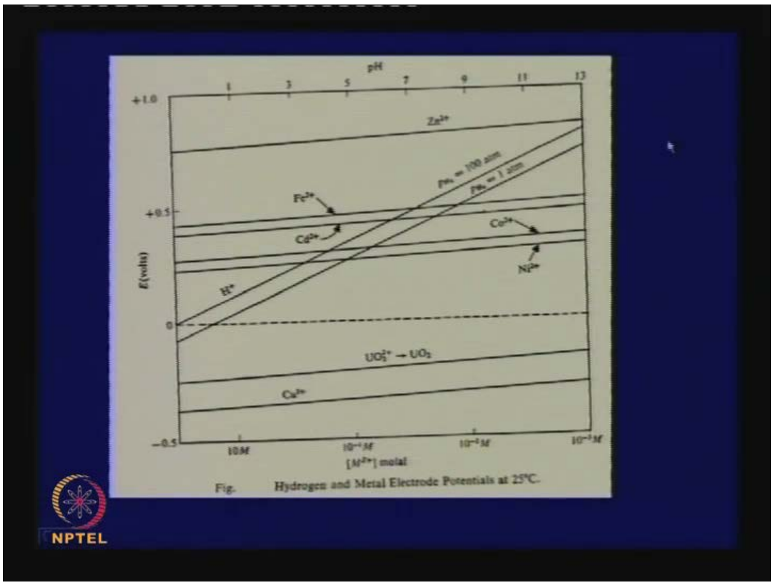

Fig. Hydrogen and Metal Electrode Potentials at 25°C.

And then finally, we have got a plot which shows the variation of potential with metal ion concentration for various values of p H 2 and various values of p H. And we have shown that while normally say nickel ion will not detect will cannot give nickel metal but, if we go to a suitable p H value or if we apply the suitable p H 2 value, the lines for hydrogen ion potential and metal ion potential, in case of nickel and cobalt will cross.

Something like zinc cannot be cannot be zinc metal cannot be produced, no matter what pressure of hydrogen you give or what is the value, no matter how alkaline it is because it is far too above in the electrochemical series. So, this analysis we have done, we have found the p H requirements for equilibrium p H values and then we shown, that if you try to make something very alkaline then also there is a danger of precipitating hydroxides.

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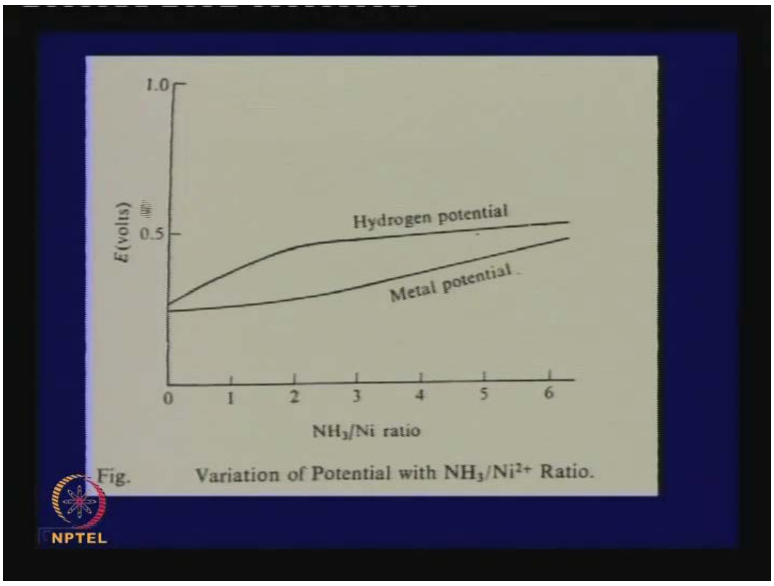

Fig. Variation of Potential with NH_3/Ni^{2+} Ratio.

So, we say there has to be precaution taken and one way would be to stabilize the metal ion as an ammine and we have discussed the, what is the optimum condition so, in the case of nickel and discuss several other things. Then an interesting thing I am also said that while nickel and cobalt can be precipitated from acid solutions with hydrogen ion pressure, hydrogen gas pressure under normal range (( )) adjusting the pH, the particle that come out can be of various shapes depending of some catalyst, that we can we put in the system and we have talked about some catalyst, that give rise to particular shapes of nickel nuclei for more details, you have to see the book.

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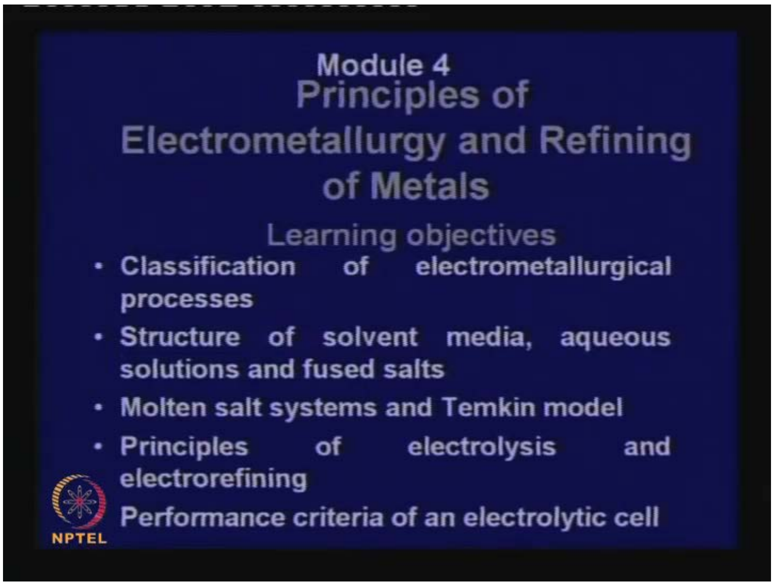

Module 4

Principles of Electrometallurgy and Refining of Metals

Learning objectives

- Classification of electrometallurgical processes
- Structure of solvent media, aqueous solutions and fused salts
- Molten salt systems and Temkin model
- Principles of electrolysis and electrorefining

Performance criteria of an electrolytic cell

In module module 4, we have talked about electrometallurgy and refining of metals. We have combined the two because electrometallurgy generally produces metals of very high purity, generally there are exceptions and refining of metals also aims at producing high purity. So, electrometallurgy in a ways is a step towards refining, that is why, I have put them together. Secondly, electrometallurgy has come in the history of metallurgy much later than pyrometallurgy and hydrometallurgy because electrometallurgy had to depend on invention of electricity otherwise; you know we would not have electrometallurgical process.

We have given a classification of electrometallurgical processes. We have talked about structure of solvent media, aqueous solution fused salts, where electrolysis takes place. Then we have gone in to some very interesting discussion of molten salts systems and Temkin model. We have talked about principles of electrolysis and principles of electrorefining. Then we have talked about performance criteria of an electrolytic cell.

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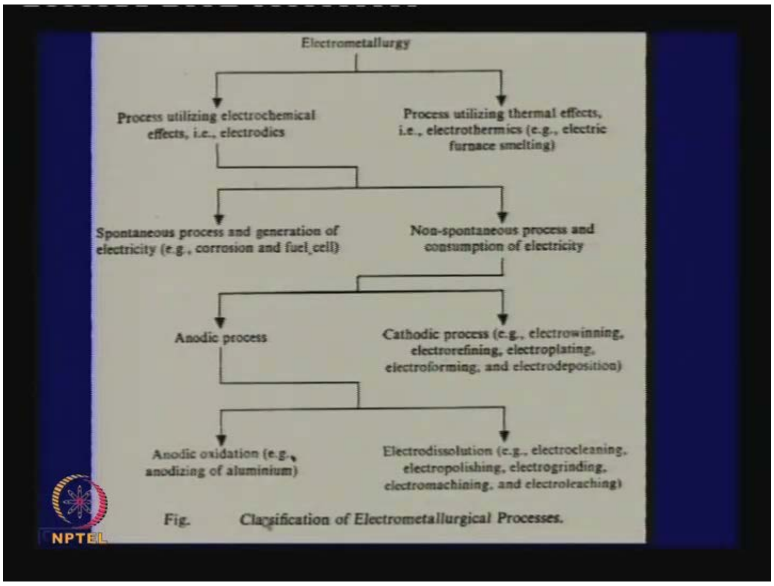

Electrometallurgy

Process utilizing electrochemical effects, i.e., electrodics

Process utilizing thermal effects, i.e., electrothermics (e.g., electric furnace smelting)

Spontaneous process and generation of electricity (e.g., corrosion and fuel cell)

Non-spontaneous process and consumption of electricity

Anodic process

Cathodic process (e.g., electrowinning, electrorefining, electroplating, electroforming, and electrodeposition)

Anodic oxidation (e.g., anodizing of aluminium)

Electrodissolution (e.g., electrocleaning, electropolishing, electrogrinding, electromachining, and electroleaching)

Fig. Classification of Electrometallurgical Processes.

Here, is a classification of electrometallurgical processes. Now, by the word electrometallurgy many things are many things are implied but, we have picked up from the entire gamut of things, only this area and that is neither this nor this nor that nor this, what they are, we have talked about electrowinning and electrorefining, only these two we have talked about. We have not talked about many other things because they are not directly related to electrolytic process electrolysis.

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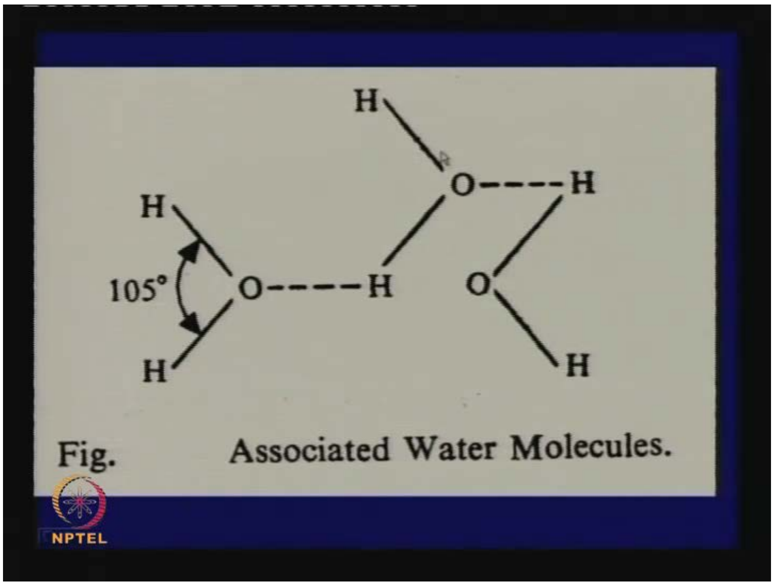

Fig. Associated Water Molecules.

This is a structure of water, water molecule you know, water is a polar molecule. So, we never have H 2 O, we have many H 2 O molecules associated because of this kind of bonding, that is how we get hydrated ions.

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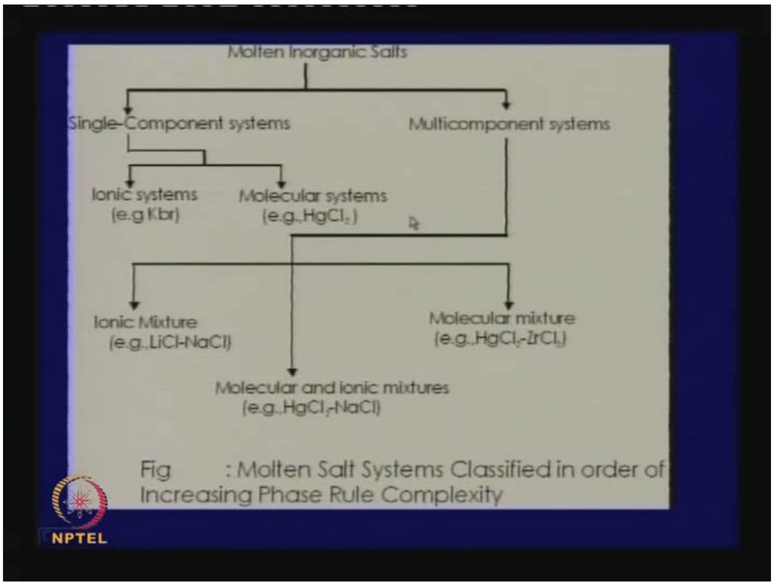

Molten Inorganic Salts

Single-Component systems

Multicomponent systems

Ionic systems
(e.g Kbr)

Molecular systems
(e.g.,$HgCl_2$)

Ionic Mixture
(e.g.,LiCl-NaCl)

Molecular mixture
(e.g.,$HgCl_2$-$ZrCl_4$)

Molecular and ionic mixtures
(e.g.,$HgCl_2$-NaCl)

Fig : Molten Salt Systems Classified in order of Increasing Phase Rule Complexity

As we (( )) molten salt systems, they can be of many kinds, single component systems, multi component systems and etcetera etcetera. You will find, when we talk about fused salt electrolysis very rarely we have a single component system, always it is multi component, there are many good reasons for that. First of all, when you mix two, three salts, the temperature, melting temperature comes down. So, you can carry out an electrolysis and electrorefining process at a lower temperature. There are also some other reasons try to remember that or or else I will remind you just now.

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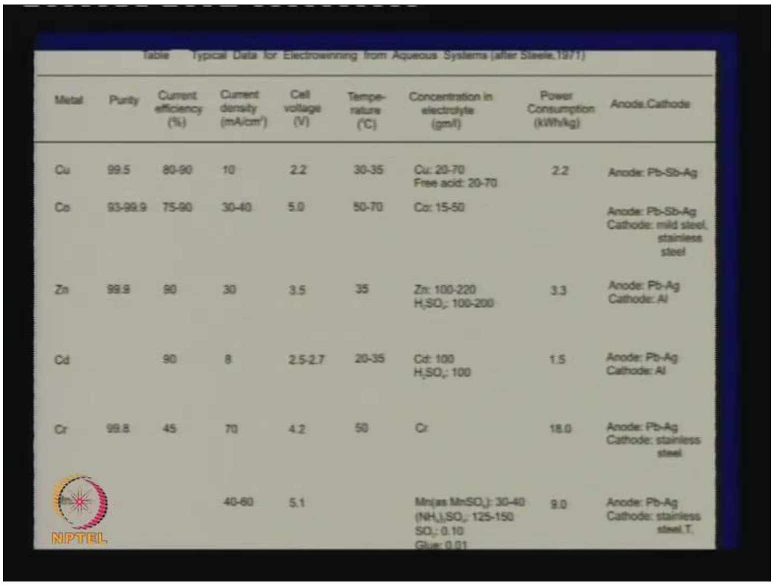

Table Typical Data for Electrowinning from Aqueous Systems (after Steele,1971)

Metal	Purity	Current efficiency (%)	Current density (mA/cm^2)	Cell voltage (V)	Tempe-rature (°C)	Concentration in electrolyte (gm/l)	Power Consumption (kWh/kg)	Anode.Cathode
Cu	99.5	80-90	10	2.2	30-35	Cu: 20-70 Free acid: 20-70	2.2	Anode: Pb-Sb-Ag
Co	93-99.9	75-90	30-40	5.0	50-70	Co: 15-50		Anode: Pb-Sb-Ag Cathode: mild steel, stainless steel
Zn	99.9	90	30	3.5	35	Zn: 100-220 H_2SO_4: 100-200	3.3	Anode: Pb-Ag Cathode: Al
Cd		90	8	2.5-2.7	20-35	Cd: 100 H_2SO_4: 100	1.5	Anode: Pb-Ag Cathode: Al
Cr	99.8	45	70	4.2	50	Cr	18.0	Anode: Pb-Ag Cathode: stainless steel
Mn			40-60	5.1		Mn(as $MnSO_4$): 30-40 $(NH_4)_2SO_4$: 125-150 SO_2: 0.10 Glue: 0.01	9.0	Anode: Pb-Ag Cathode: stainless steel,T.

I have given you some data to show, what kind of purities are obtained you see during electrowinning from aqueous solution, we get purities of 99, 99.9, 99.8. Very often we have to have such purities because unless the solution is pure, you cannot do zinc electrolysis because zinc is normally above hydrogen. It is only in a pure solution that you can have activation over potential where, the hydrogen potential exceeds that of zinc in the (( )).

So, we need extreme purification of the zinc leach liquor, yet the metal we produce really is not required at that purity for most application, most important application is galvanizing which we will do with the lower purity but, (( )) we have to pure, put pure zinc. In some cases like copper, we settle for a slightly lower thing but, it has to go for electrorefining later on because we want recover from there precious metals. We have also given some ideas about the kind of, what kind of salt mixtures we take, what kind of current densities we have cell voltage etcetera etcetera etcetera.

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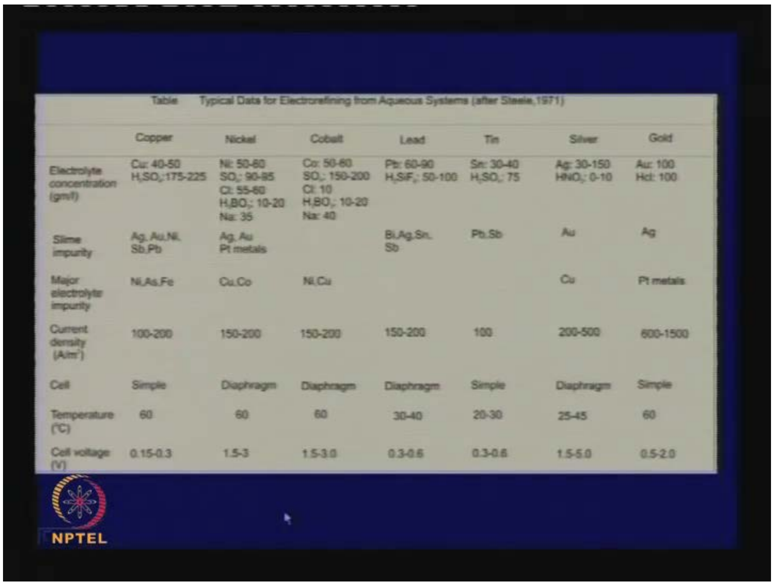

Table Typical Data for Electrorefining from Aqueous Systems (after Steele,1971)

	Copper	Nickel	Cobalt	Lead	Tin	Silver	Gold
Electrolyte concentration (gm/l)	Cu: 40-50 H_2SO_4:175-225	Ni: 50-60 SO_4: 90-95 Cl: 55-60 H_3BO_3: 10-20 Na: 35	Co: 50-60 SO_4: 150-200 Cl: 10 H_3BO_3: 10-20 Na: 40	Pb: 60-90 H_2SiF_6: 50-100	Sn: 30-40 H_2SO_4: 75	Ag: 30-150 HNO_3: 0-10	Au: 100 Hcl: 100
Slime impurity	Ag, Au,Ni, Sb,Pb	Ag, Au Pt metals		Bi,Ag,Sn, Sb	Pb,Sb	Au	Ag
Major electrolyte impurity	Ni,As,Fe	Cu,Co	Ni,Cu			Cu	Pt metals
Current density (A/m²)	100-200	150-200	150-200	150-200	100	200-500	600-1500
Cell	Simple	Diaphragm	Diaphragm	Diaphragm	Simple	Diaphragm	Simple
Temperature (°C)	60	60	60	30-40	20-30	25-45	60
Cell voltage (V)	0.15-0.3	1.5-3	1.5-3.0	0.3-0.6	0.3-0.6	1.5-5.0	0.5-2.0

We have given you some typical data for aqueous more data for electro electro aqueous system so, electrorefining which is one step beyond electrolysis and that is to produce purer copper and get some by products out.

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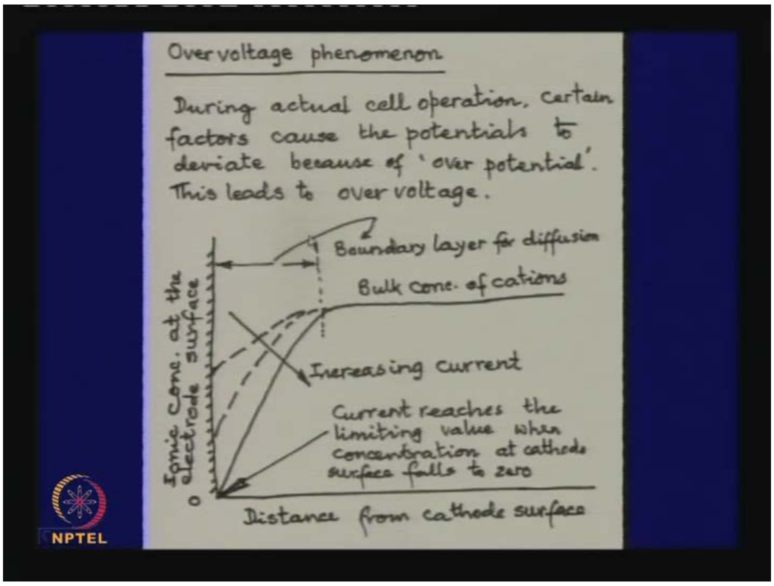

Over voltage phenomenon

During actual cell operation, certain factors cause the potentials to deviate because of 'over potential'. This leads to over voltage.

I have talked about this over voltage phenomenon, which changes the voltage at the electrode either because of a concentration over potential because during when the current flows, the bulk cations are flowing towards the cathode, the flow has to be because of a concentration gradient. This gradient becomes steeper, when the current increases because there is more flow of the cations and which means, you have a steeper gradient that is why, a greater flow, but there is limit beyond which we cannot push it further and that is becomes rate controlling.

So, there is because of this concentration gradient, a concentration over potential and then a limiting current for a or a given area of the electrode, a limiting current density which limits the amount of metal you can deposit on a cathode in a given cell because of concentration over potential, my analysis shows that the potential of the electrode does not changes so much, but then it sets a limit to production.

Now, in some cases, the limiting step is not concentration over potential but, activation over potential which makes it possibility to have zinc in zinc electrolysis, but then this concept of limiting current density is very important, why it is important because then in a given cell we are fixed, how do we increase the productivity for that couple of methods are available, we can rearrange the electrodes in various manners or you can use a fluidized bed cathode, where the effective surface area of the cathode becomes much larger.

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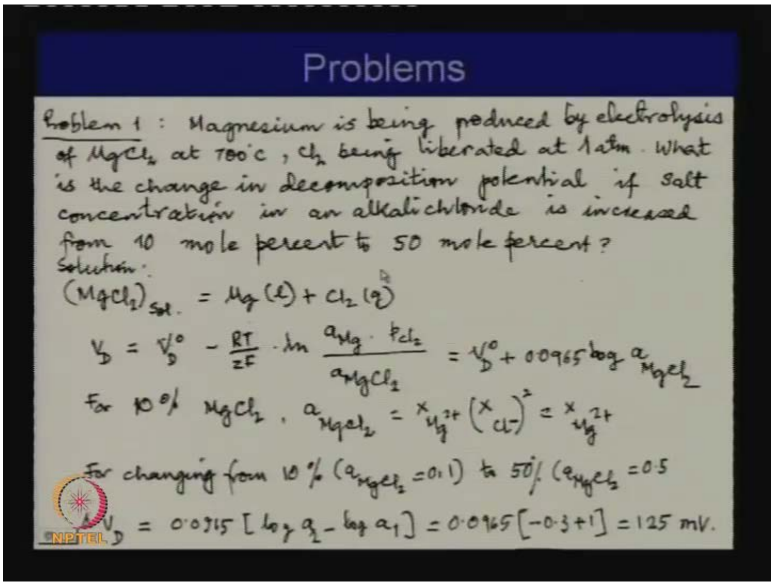

Problems

Problem 1 : Magnesium is being produced by electrolysis of $MgCl_2$ at 700°C, Cl_2 being liberated at 1 atm. What is the change in decomposition potential if salt concentration in an alkali chloride is increased from 10 mole percent to 50 mole percent?

Solution:

$$(MgCl_2)_{sol.} = Mg(l) + Cl_2(g)$$

$$V_D = V_D^0 - \frac{RT}{zF} \cdot \ln \frac{a_{Mg} \cdot p_{Cl_2}}{a_{MgCl_2}} = V_D^0 + 0.0965 \log a_{MgCl_2}$$

For 10% $MgCl_2$, $a_{MgCl_2} = x_{Mg^{2+}} (x_{Cl^-})^2 = x_{Mg^{2+}}$

For changing from 10% ($a_{MgCl_2} = 0.1$) to 50% ($a_{MgCl_2} = 0.5$

$$\Delta V_D = 0.0915 [\log a_2 - \log a_1] = 0.0965 [-0.3 + 1] = 125 \text{ mV}.$$

I have shown a figure of that, before that I have given one or two solutions, one or two problems, simple problems of one for fused salt electrolysis one for aqueous electrolysis.

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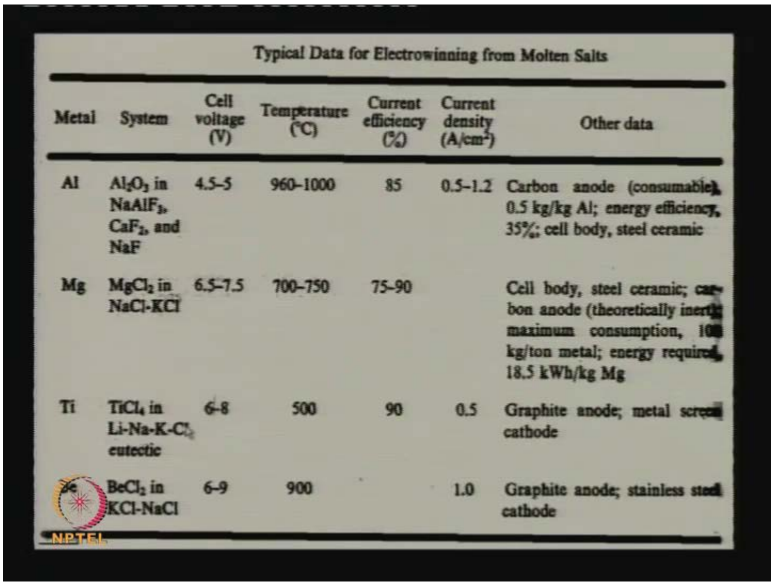

Typical Data for Electrowinning from Molten Salts

Metal	System	Cell voltage (V)	Temperature (°C)	Current efficiency (%)	Current density (A/cm^2)	Other data
Al	Al_2O_3 in $NaAlF_3$, CaF_2, and NaF	4.5–5	960–1000	85	0.5–1.2	Carbon anode (consumable), 0.5 kg/kg Al; energy efficiency, 35%; cell body, steel ceramic
Mg	$MgCl_2$ in NaCl-KCl	6.5–7.5	700–750	75–90		Cell body, steel ceramic; carbon anode (theoretically inert); maximum consumption, 100 kg/ton metal; energy required, 18.5 kWh/kg Mg
Ti	$TiCl_4$ in Li-Na-K-Cl eutectic	6–8	500	90	0.5	Graphite anode; metal screen cathode
Be	$BeCl_2$ in KCl-NaCl	6–9	900		1.0	Graphite anode; stainless steel cathode

I have giving some data for electrowinning from molten salts, what kind of cell voltages in this case would be slightly higher because you are dealing with more stable salts at higher temperatures, your current efficiency suffer because other kinds of reactions can take place, your energy efficiency will be lower, many other data we have given, but you will you will see in all cases, the supporting electrolyte which dissolves the solute is never a single salt, mostly it is a salt mixture, incidentally the supporting electrolyte, the salt mixture has to be more stable than the solute otherwise, something else will get electrolyzed from that supporting electrolyte.

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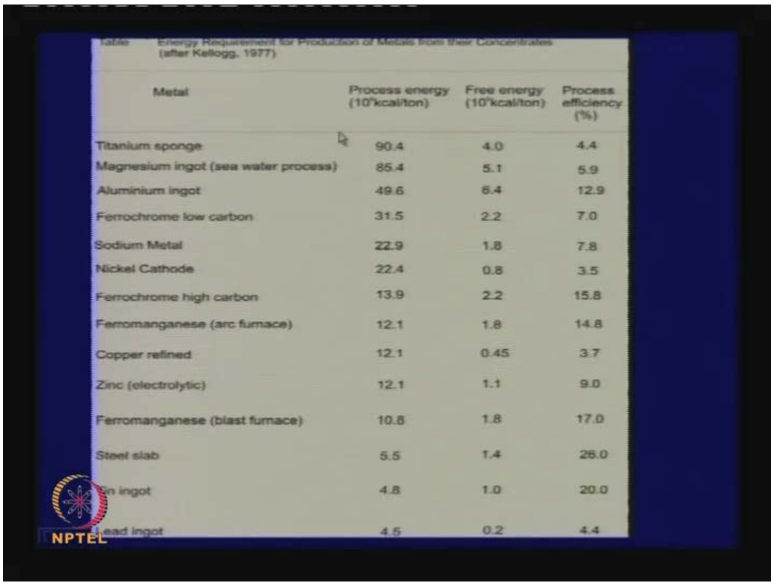

Table Energy Requirement for Production of Metals from their Concentrates (after Kellogg, 1977)

Metal	Process energy (10^6kcal/ton)	Free energy (10^6kcal/ton)	Process efficiency (%)
Titanium sponge	90.4	4.0	4.4
Magnesium ingot (sea water process)	85.4	5.1	5.9
Aluminium ingot	49.6	6.4	12.9
Ferrochrome low carbon	31.5	2.2	7.0
Sodium Metal	22.9	1.8	7.8
Nickel Cathode	22.4	0.8	3.5
Ferrochrome high carbon	13.9	2.2	15.8
Ferromanganese (arc furnace)	12.1	1.8	14.8
Copper refined	12.1	0.45	3.7
Zinc (electrolytic)	12.1	1.1	9.0
Ferromanganese (blast furnace)	10.8	1.8	17.0
Steel slab	5.5	1.4	26.0
in ingot	4.8	1.0	20.0
Lead ingot	4.5	0.2	4.4

Then we have come to talk about the energy requirement and we have seen that energy requirement in electrometallurgical processes will be more, in pyrometallurgical process it will be low.

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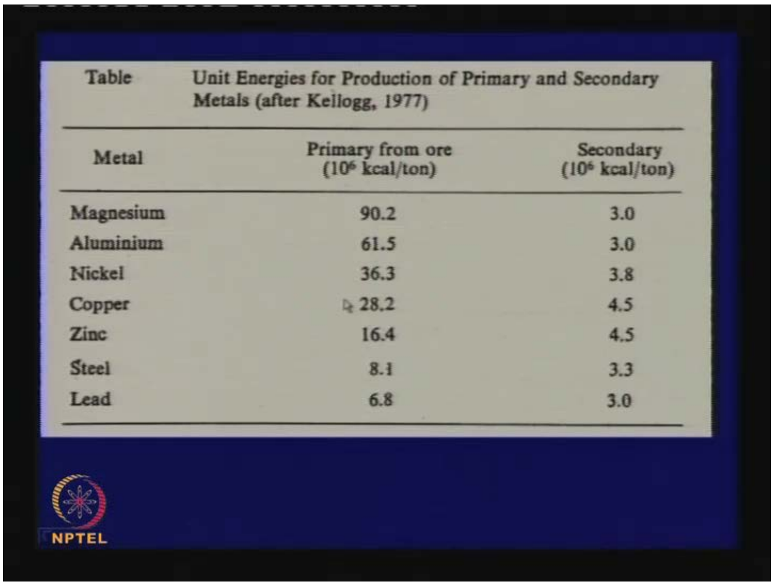

Table Unit Energies for Production of Primary and Secondary Metals (after Kellogg, 1977)

Metal	Primary from ore (10^6 kcal/ton)	Secondary (10^6 kcal/ton)
Magnesium	90.2	3.0
Aluminium	61.5	3.0
Nickel	36.3	3.8
Copper	28.2	4.5
Zinc	16.4	4.5
Steel	8.1	3.3
Lead	6.8	3.0

We have also discussed the unit energies for production of primary secondary metals. Again to show, how things are different when there is a electrometallurgical operation because of the use of electricity, your energy consumption is very high. Steel, lead where your concentrates are of high grade and the operation does not need too much of energy, your energy consumption is better.

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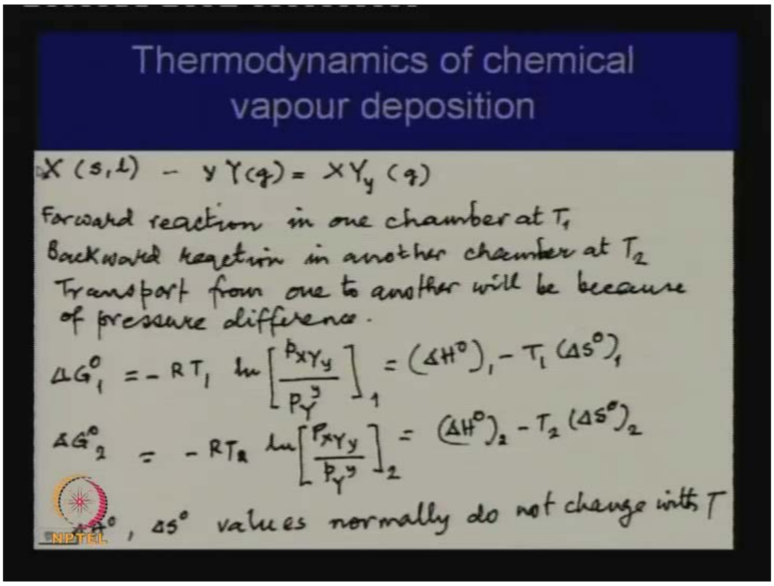

Thermodynamics of chemical vapour deposition

$X(s,l) - yY(g) = XY_y(g)$

Forward reaction in one chamber at T_1

Backward reaction in another chamber at T_2

Transport from one to another will be because of pressure difference.

$$\Delta G^0_1 = -RT_1 \ln\left[\frac{p_{XY_y}}{p_Y^y}\right]_1 = (\Delta H^0)_1 - T_1(\Delta S^0)_1$$

$$\Delta G^0_2 = -RT_2 \ln\left[\frac{p_{XY_y}}{p_Y^y}\right]_2 = (\Delta H^0)_2 - T_2(\Delta S^0)_2$$

ΔH^0, ΔS^0 values normally do not change with T

Then I discussed just to show, how thing are analyzed a very interesting reaction goes in the name of van Arkel process or we can also call it the a vapour transport process, that we can take an impure metal make it react with a gas phase to produce a second gas phase as one temperature then decompose that gas phase at another temperature to produce pure metal. So, take impure metal, this should be plus react with a gas phase produce an intermediate gas take it out then sometimes at a higher temperature will decompose to produce this, sometimes at a lower temperature it will produce a purer metal.

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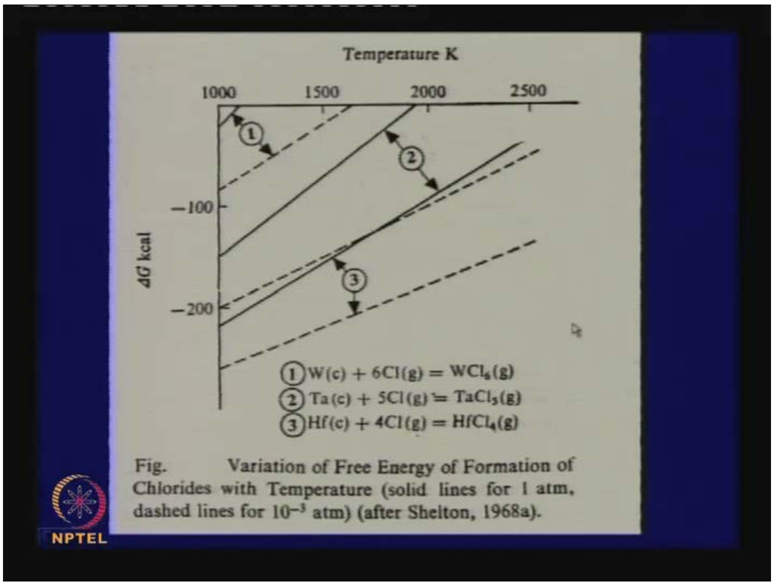

① $W(c) + 6Cl(g) = WCl_6(g)$
② $Ta(c) + 5Cl(g) = TaCl_5(g)$
③ $Hf(c) + 4Cl(g) = HfCl_4(g)$

Fig. Variation of Free Energy of Formation of Chlorides with Temperature (solid lines for 1 atm, dashed lines for 10^{-3} atm) (after Shelton, 1968a).

And I have given an analysis as to how this is to be done and what are the factors that govern it and take for particular reference we have taken reaction in case of Tungsten, Tantalum, Hafnium. You form an intermittent chloride which will be decomposed to produce pure tungsten in another chamber.

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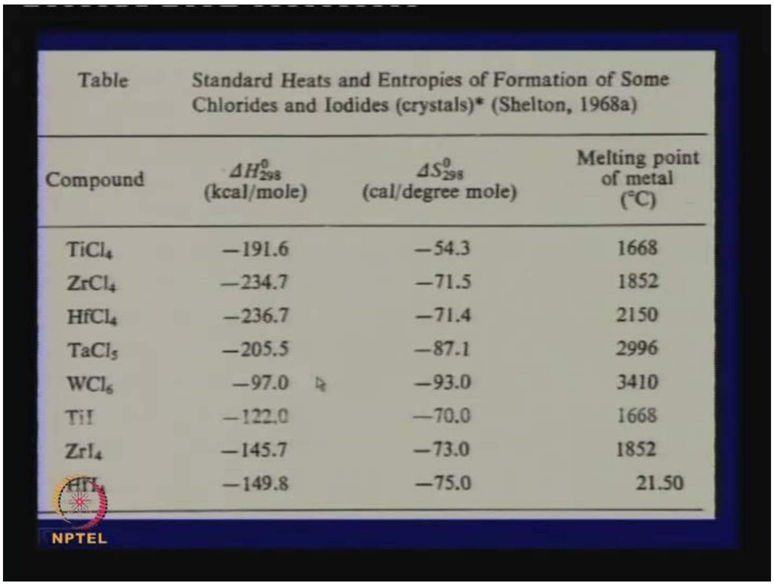

Table Standard Heats and Entropies of Formation of Some Chlorides and Iodides (crystals)* (Shelton, 1968a)

Compound	ΔH^0_{298} (kcal/mole)	ΔS^0_{298} (cal/degree mole)	Melting point of metal (°C)
$TiCl_4$	−191.6	−54.3	1668
$ZrCl_4$	−234.7	−71.5	1852
$HfCl_4$	−236.7	−71.4	2150
$TaCl_5$	−205.5	−87.1	2996
WCl_6	−97.0	−93.0	3410
TiI	−122.0	−70.0	1668
ZrI_4	−145.7	−73.0	1852
HfI_4	−149.8	−75.0	21.50

And we have shown that we have to understand the reaction in terms of enthalpy change, entropy change and melting point.

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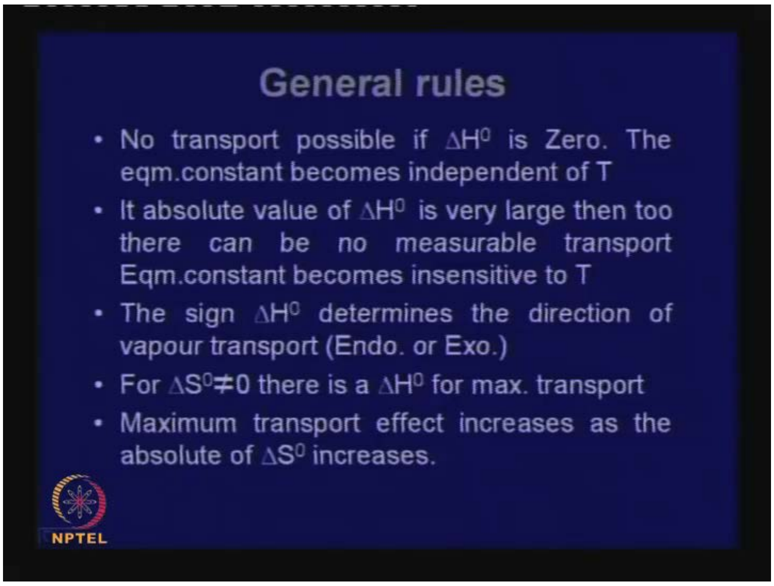

General rules

- No transport possible if ΔH^0 is Zero. The eqm.constant becomes independent of T
- It absolute value of ΔH^0 is very large then too there can be no measurable transport Eqm.constant becomes insensitive to T
- The sign ΔH^0 determines the direction of vapour transport (Endo. or Exo.)
- For $\Delta S^0 \neq 0$ there is a ΔH^0 for max. transport
- Maximum transport effect increases as the absolute of ΔS^0 increases.

Then we came to some general conclusions, that no transport of this kind is possible, if the delta H value is 0, if the actual temperature of delta H naught is very large then too there can be (( )) measurable transport and it is delta H naught sign, that depends the direction of vapour transport. Then there is also this element that delta S naught, if it not equal to 0 is a delta (( )) some condition regarding entropy change also, this you have to cannot be done (( )).

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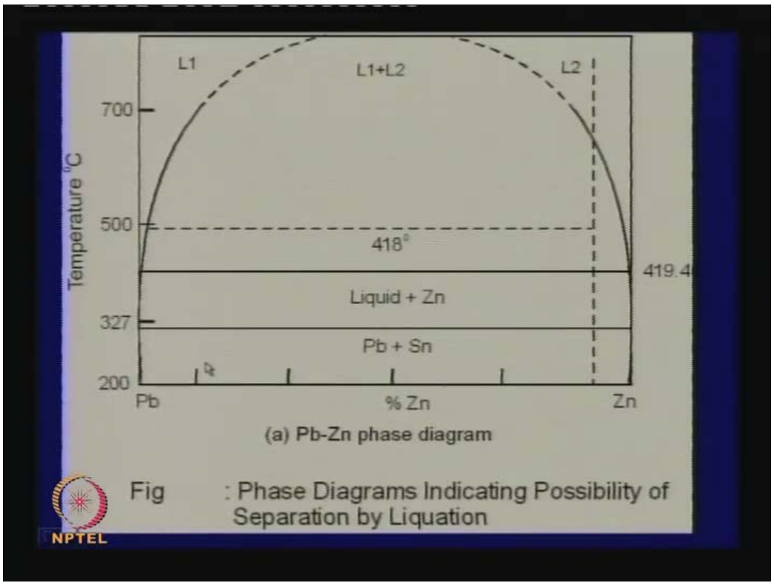

(a) Pb-Zn phase diagram

Fig : Phase Diagrams Indicating Possibility of Separation by Liquation

I have also talked about purification using ion exchange resin and solvent extraction how things are done, I would not go into those, talked different methods of refining, separation by Liquation and this there have been examples of that later on. If we have impurities like lead, if you consider lead-zinc diagram, you see what happens when you go to higher temperatures, we can create two liquids, one very rich in zinc, 1 very leach in lead.

So, if you have an alloy of this composition, it will go to that temperature will produce a liquid lead percentage so much, zinc percentage so much and their relative proportions will depend on the lever rule. So, this is one way from a alloy, we can separate out the component simply by heating. Similar equation possibility of separation by liquation another system another system

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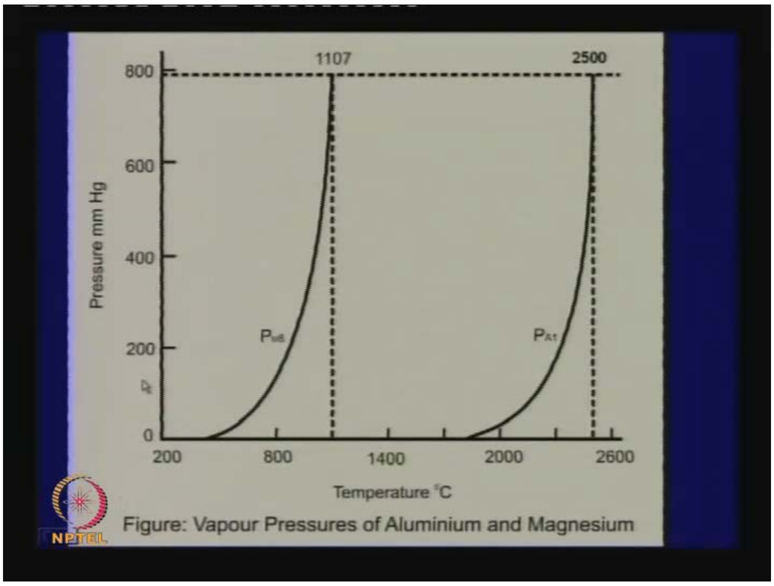

Figure: Vapour Pressures of Aluminium and Magnesium

We can separate constituents from an alloy by differential distillation like, if you have aluminum and magnesium, if we reheat the alloy magnesium will evaporate first because this is the vapor pressure of magnesium, it reaches one atmosphere at low temperatures aluminum will will volatilize at much higher temperatures

(No audio from 32:04 to 32:22).

We have talked about vapor liquid equilibrium, we have talked about zone refining, we have, I have talked about these things in a very cursory manner because they have given in books, you know arc melting, electron beam melting, electro slag refining these things one has to read out. Now, up to this we discussed the principles then we came into the extraction processes for specific metals and these were done in three different models, metals from oxide sources, metals from sulphide deposits and metals from halides, not all naturally occurring halides, but naturally occurring halides and also halides which were the starting point of some metals and this halides may have to be prepared from oxide deposits talking about metals which come from oxides.

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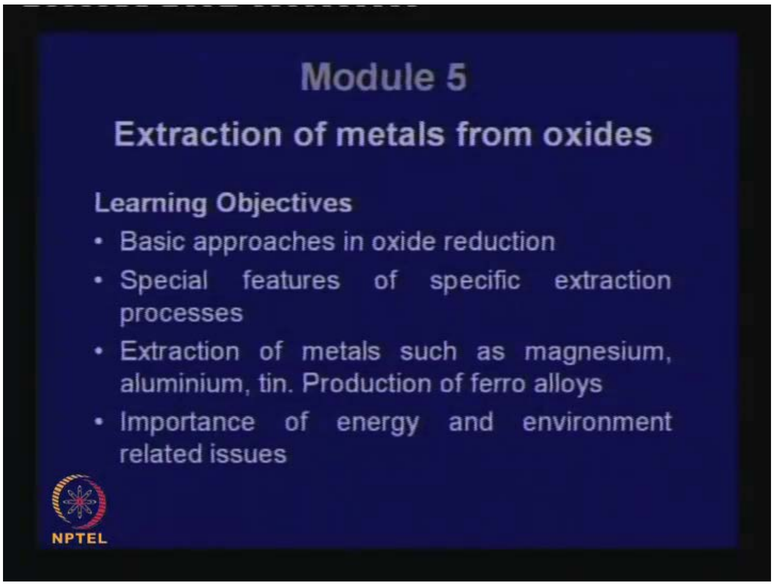

Module 5

Extraction of metals from oxides

Learning Objectives

- Basic approaches in oxide reduction
- Special features of specific extraction processes
- Extraction of metals such as magnesium, aluminium, tin. Production of ferro alloys
- Importance of energy and environment related issues

And the learning objectives was basic approaches in oxide reductions; special features of specific extraction processes and extraction of metals such as magnesium, aluminum, tin, ferroalloys also I included in this because they also come from oxide sources and I have given some discussion on energy and environment related issues which I will discuss in more detail towards the end. Magnesium, we have talked about its uses.

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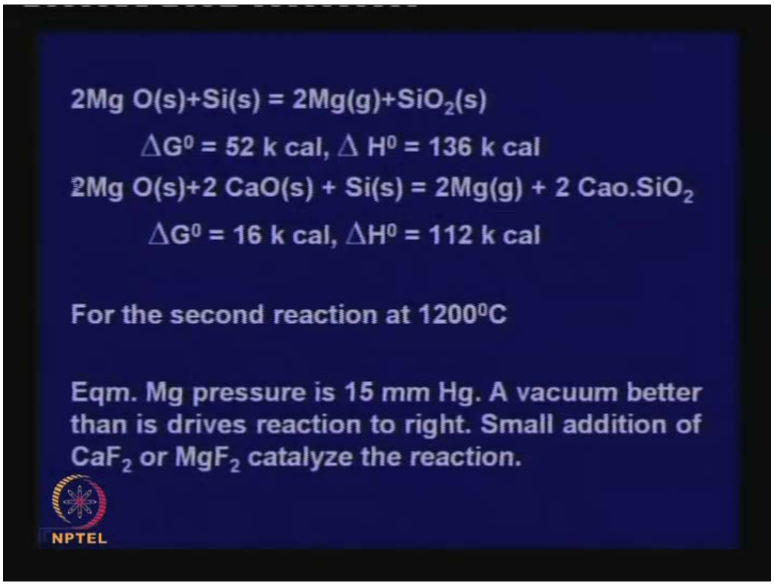

$2MgO(s)+Si(s) = 2Mg(g)+SiO_2(s)$

$\Delta G^0 = 52$ k cal, $\Delta H^0 = 136$ k cal

$2MgO(s)+2CaO(s) + Si(s) = 2Mg(g) + 2 Cao.SiO_2$

$\Delta G^0 = 16$ k cal, $\Delta H^0 = 112$ k cal

For the second reaction at 1200^0C

Eqm. Mg pressure is 15 mm Hg. A vacuum better than is drives reaction to right. Small addition of CaF_2 or MgF_2 catalyze the reaction.

And then we have seen, the essentially the process depends on dolomite decomposed to produce M g O and C a O reduced by ferrosilicon or silicon, magnesium comes out as a vapour and the reaction is made possible by taking out the vapour continuously by a vacuum. That is why, the reaction becomes possible and this was first introduced in Second World War by doctor pidgeon and that is why, it goes in the name of pidgeon’s process. Reducing agent is ferrosilicon, we also produce a slag but, the trick is that the metal comes out as a vapour with a pressure at a pressure lower than 15 millimeter and that is what makes the reactions possible.

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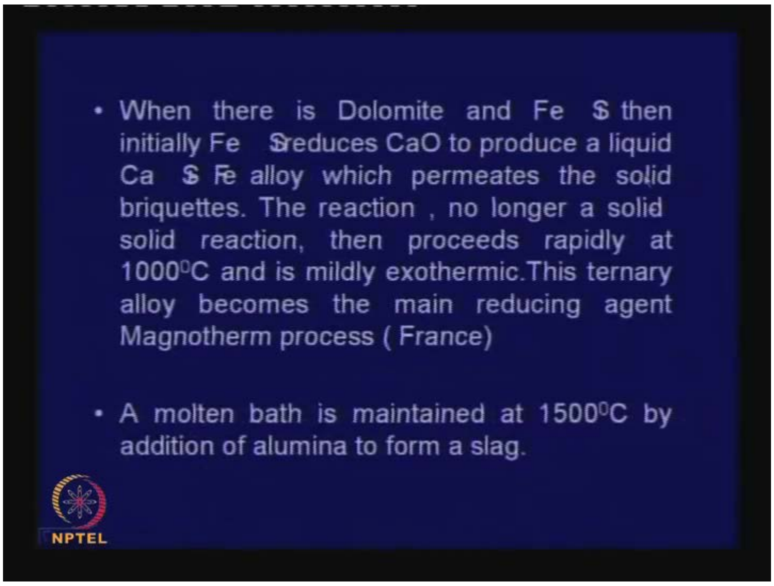

- When there is Dolomite and Fe Si then initially Fe Si reduces CaO to produce a liquid Ca Si Fe alloy which permeates the solid briquettes. The reaction , no longer a solid solid reaction, then proceeds rapidly at 1000^{0}C and is mildly exothermic.This ternary alloy becomes the main reducing agent Magnotherm process (France)
- A molten bath is maintained at 1500^{0}C by addition of alumina to form a slag.

We have talked about the mechanism, how it takes place. You might think, it is a reaction between a solid and a solid which is not true because solid solid reactions cannot be very efficient. How often do solid particles come in contact with each other, the surface of contact will be very small but, essentially which is a reaction of a solid with a liquid. Initially, the iron reduces C a O to produce a liquid calcium and it permeates the solid a liquid calcium iron alloys permeates the solid briquettes and that is, where the reaction takes place it is not a solid solid reaction. And advancement of this process is where we make everything molten by having a bath at 1500 degree centigrade by additional alumina to form a slag is called electro thermal process.

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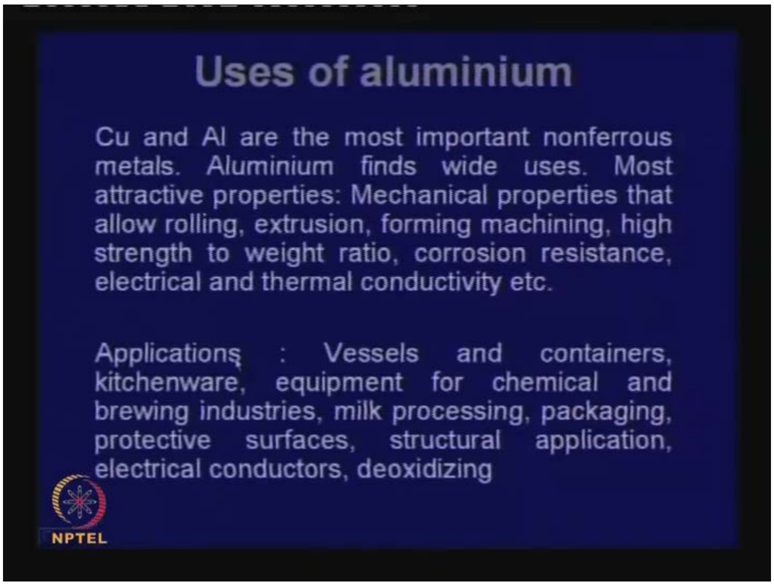

Uses of aluminium

Cu and Al are the most important nonferrous metals. Aluminium finds wide uses. Most attractive properties: Mechanical properties that allow rolling, extrusion, forming machining, high strength to weight ratio, corrosion resistance, electrical and thermal conductivity etc.

Applications : Vessels and containers, kitchenware, equipment for chemical and brewing industries, milk processing, packaging, protective surfaces, structural application, electrical conductors, deoxidizing

Then we came to aluminum, there are many uses of aluminum and today after steel, the most two important metals are aluminum and copper.

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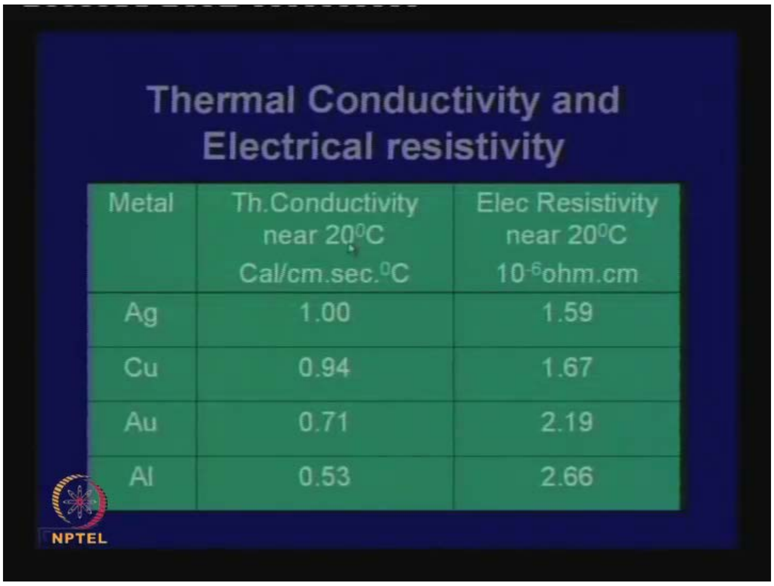

Thermal Conductivity and Electrical resistivity

Metal	Th.Conductivity near 20°C Cal/cm.sec.°C	Elec Resistivity near 20°C 10^{-6}ohm.cm
Ag	1.00	1.59
Cu	0.94	1.67
Au	0.71	2.19
Al	0.53	2.66

Aluminum of course, has good thermal conductivity and electrical resistivity. It comes forth in the category, silver, copper, gold are better than that.

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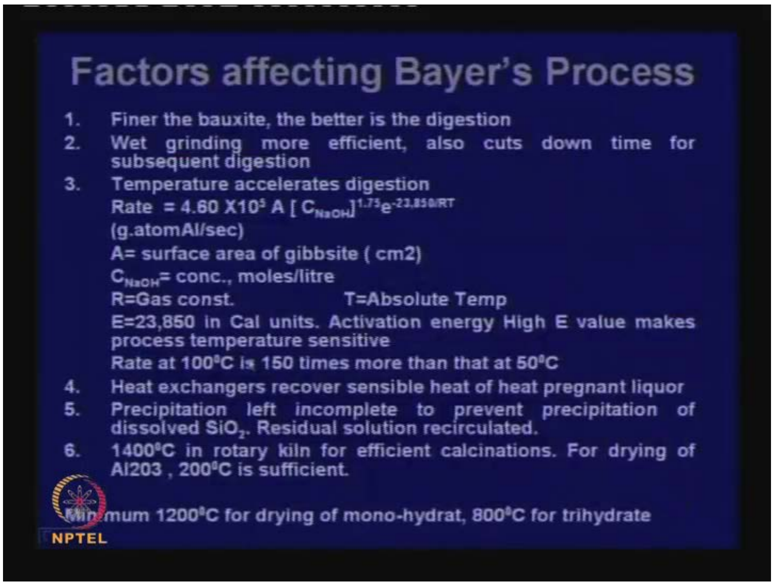

Factors affecting Bayer's Process

1. Finer the bauxite, the better is the digestion
2. Wet grinding more efficient, also cuts down time for subsequent digestion
3. Temperature accelerates digestion
   Rate $= 4.60 \times 10^5 A [C_{NaOH}]^{1.75} e^{-23,850/RT}$
   (g.atomAl/sec)
   A= surface area of gibbsite (cm2)
   C_{NaOH}= conc., moles/litre
   R=Gas const. T=Absolute Temp
   E=23,850 in Cal units. Activation energy High E value makes process temperature sensitive
   Rate at 100°C is 150 times more than that at 50°C
4. Heat exchangers recover sensible heat of heat pregnant liquor
5. Precipitation left incomplete to prevent precipitation of dissolved SiO_2. Residual solution recirculated.
6. 1400°C in rotary kiln for efficient calcinations. For drying of Al203 , 200°C is sufficient.

Minimum 1200°C for drying of mono-hydrat, 800°C for trihydrate

And the key to aluminum extraction is Bayer's process which produces pure alumina. It depends on many many factors, some of them have been considered particle size concentration of leach liquor, people have come out with a equation for the rate of leaching. Temperature should be high, but the make the temperature high and sometimes it operates at two twenty degrees leaching, you need lot of pressure in an autoclave. Some people would rather settle for lower temperatures because autoclave operation at higher temperatures means, more expensive equipment, more energy. So, the different companies have different ways of doing, no two companies act in the same manner eventually everybody tries to produce pure A l 2 O 3 from and from which will go into an aluminum cell.

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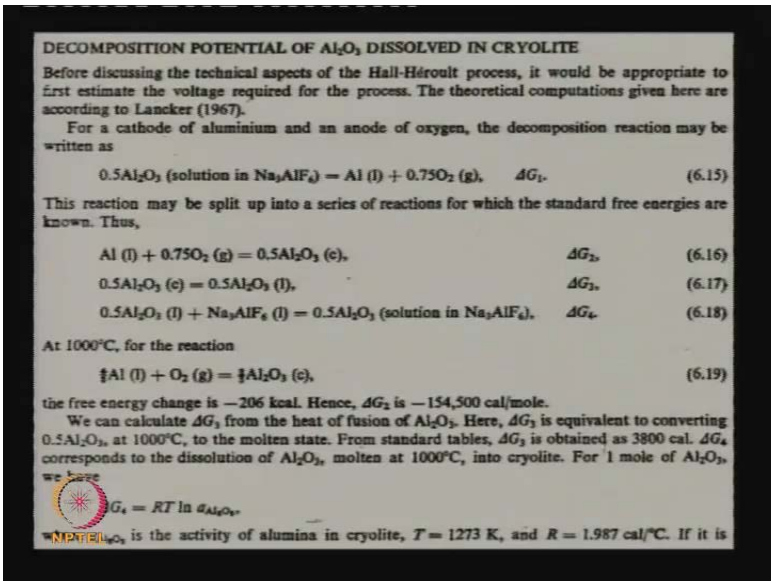

DECOMPOSITION POTENTIAL OF Al_2O_3 DISSOLVED IN CRYOLITE

Before discussing the technical aspects of the Hall-Héroult process, it would be appropriate to first estimate the voltage required for the process. The theoretical computations given here are according to Lancker (1967).

For a cathode of aluminium and an anode of oxygen, the decomposition reaction may be written as

$$0.5Al_2O_3 \text{ (solution in } Na_3AlF_6) = Al\ (l) + 0.75O_2\ (g), \qquad \Delta G_1. \qquad (6.15)$$

This reaction may be split up into a series of reactions for which the standard free energies are known. Thus,

$$Al\ (l) + 0.75O_2\ (g) = 0.5Al_2O_3\ (c), \qquad \Delta G_2, \qquad (6.16)$$

$$0.5Al_2O_3\ (c) = 0.5Al_2O_3\ (l), \qquad \Delta G_3, \qquad (6.17)$$

$$0.5Al_2O_3\ (l) + Na_3AlF_6\ (l) = 0.5Al_2O_3 \text{ (solution in } Na_3AlF_6), \qquad \Delta G_4. \qquad (6.18)$$

At 1000°C, for the reaction

$$\tfrac{4}{3}Al\ (l) + O_2\ (g) = \tfrac{2}{3}Al_2O_3\ (c), \qquad (6.19)$$

the free energy change is −206 kcal. Hence, ΔG_2 is −154,500 cal/mole.

We can calculate ΔG_3 from the heat of fusion of Al_2O_3. Here, ΔG_3 is equivalent to converting $0.5Al_2O_3$, at 1000°C, to the molten state. From standard tables, ΔG_3 is obtained as 3800 cal. ΔG_4 corresponds to the dissolution of Al_2O_3, molten at 1000°C, into cryolite. For 1 mole of Al_2O_3, we have

$$G_4 = RT \ln a_{Al_2O_3},$$

w $_2O_3$ is the activity of alumina in cryolite, $T = 1273$ K, and $R = 1.987$ cal/°C. If it is

Now, what is the reaction when alumina dissolves in cryolite ideally, we should try to get aluminum metal from aluminum ions and oxygen from A l 2 O 3 is oxygen part, unfortunately to take out oxygen as a gas, you need a platinum electrode, you cannot think of platinum electrode for the surface. People are thinking of inert electrodes which will have T i O 2 on its surface, it has not come in the industry yet. We use a consumable electrode, which is graphite, the oxygen will go to the anode which is graphite and there it reacts to form C O, C O 2 which is good news as well as bad news.

The good news is because carbon is taking part in the reaction, taking away oxygen, it makes decomposition of A l 2 O 3 easier and decomposition voltage comes down. So, the energy (( )) energy requirement comes down as compared to, if oxygen was released as oxygen. The bad news is by consuming the oxygen, removing the oxygen which reacts with carbon will generates C O or C O 2 the proportion depending on the temperature operation because it is a thousand degrees, there is more of C O than C O 2 which is something we do not want.

Now, many people have thought, what to do about it, can we inject a reducing agent at the anode say hydrogen or or methane, we have given some analysis to show, there may be marginal advantage but, there is no technology for doing such things. Ideally, we should go for a inactive electrode, where there will be no carbon consumed, no C O, C O 2, but then you have to have higher decomposition voltage, which means more energy, which means somewhere else you are producing, you are consuming more electricity. So, you have to balance this, the amount of C O, C O 2 you are sharing here, is it more than amount of C O, C O 2, you are releasing at the power plant from which you are drawing power for electrolytic solution.

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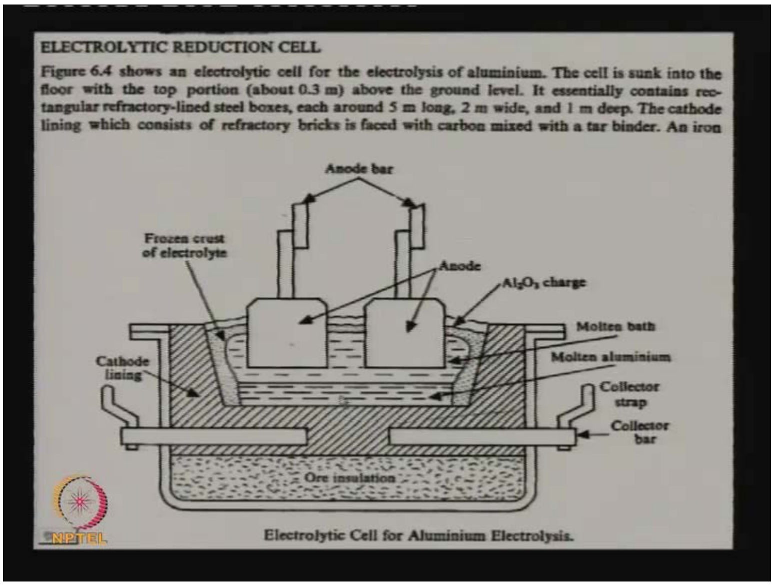

ELECTROLYTIC REDUCTION CELL

Figure 6.4 shows an electrolytic cell for the electrolysis of aluminium. The cell is sunk into the floor with the top portion (about 0.3 m) above the ground level. It essentially contains rectangular refractory-lined steel boxes, each around 5 m long, 2 m wide, and 1 m deep. The cathode lining which consists of refractory bricks is faced with carbon mixed with a tar binder. An iron

Electrolytic Cell for Aluminium Electrolysis.

I have given you a sketch of the aluminum electrolysis cell, aluminum anodes and this is the (no audio from 40:06 to 40:11) this is the cathode, this cathode eventually gets poisoned and when this cathode is thrown out, nobody knows what to do with that waste cathode because it is full of fluorides and as of now it is only dumped.

This electrode, carbon electrode gets consumed. So, it has to be changed from time to time, a fresh one is brought and screwed on or there are today soderberg electrodes where a carbon paste is continuously sent down through a pipe and the paste gradually solidifies and it is come to high temperatures and it becomes the anode, but it is consumable. The trick here is, we have aluminum at the bottom protected by the electrolyte and there is a crust of A l 2 O 3, that is how the process occurs.

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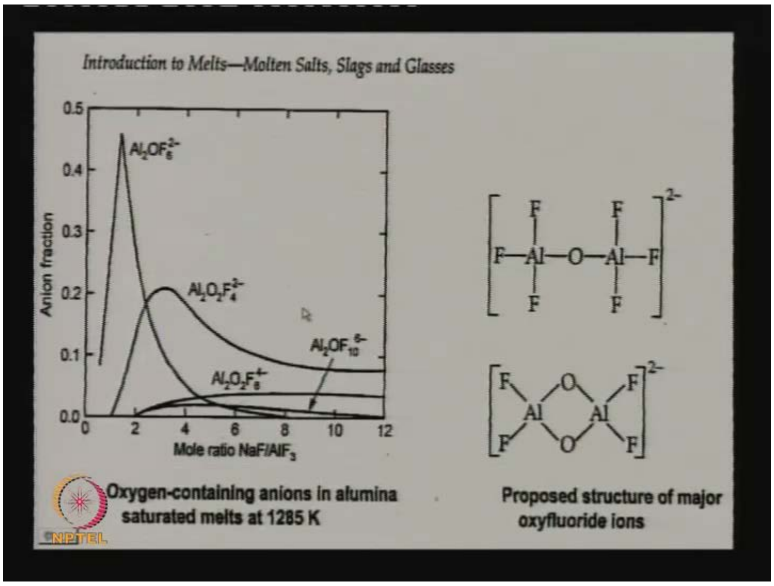

Introduction to Melts—Molten Salts, Slags and Glasses

Oxygen-containing anions in alumina saturated melts at 1285 K

Proposed structure of major oxyfluoride ions

There are equations as to, what all things affect current efficiency then we have said, it is not so simple and reaction in during electrolysis, that A l 2 O 3 decomposes to aluminum and oxygen goes and reacts with the carbon anode (( )) not so. All kinds of things takes place, there are all kinds of anions existing there and because of that existence, there is evolution of fluorine gas, their evolution of other gases that you do not want, not only they cause contaminants in the environments, they also bring down the current efficiency through undesirable reactions.

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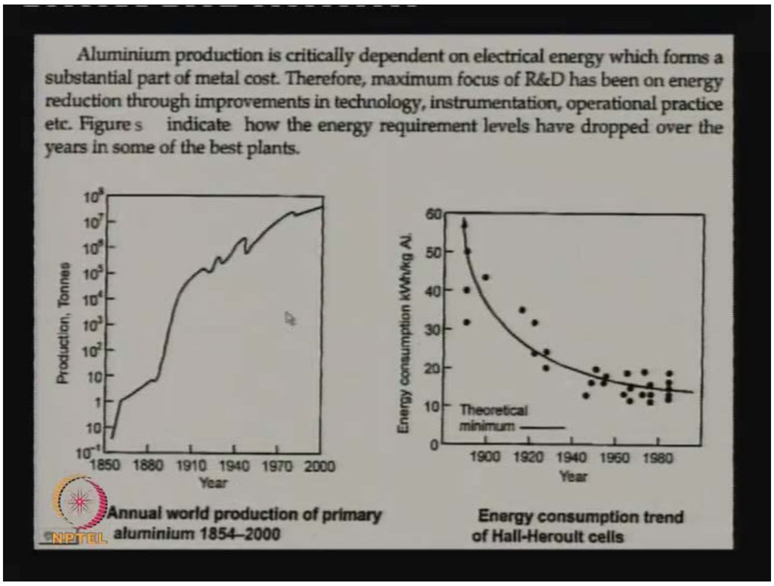

Aluminium production is critically dependent on electrical energy which forms a substantial part of metal cost. Therefore, maximum focus of R&D has been on energy reduction through improvements in technology, instrumentation, operational practice etc. Figure s indicate how the energy requirement levels have dropped over the years in some of the best plants.

Annual world production of primary aluminium 1854–2000

Energy consumption trend of Hall-Heroult cells

Now, lot of attempt has been made over the years to bring down the energy consumption and it the energy consumption has come down, it is difficult to go to the theoretical energy required for dissociate A l 2 O 3 because you need some energy to keep the bath in hot condition. The bath resistance gets heating therefore, you need in theory, some energy to decompose A l 2 O 3 and then you need some extra energy for heating up the path. That is why, it is coming down to the minimum, which is which must be about the theoretical minimum, that comes from looking at the free energy of formation.

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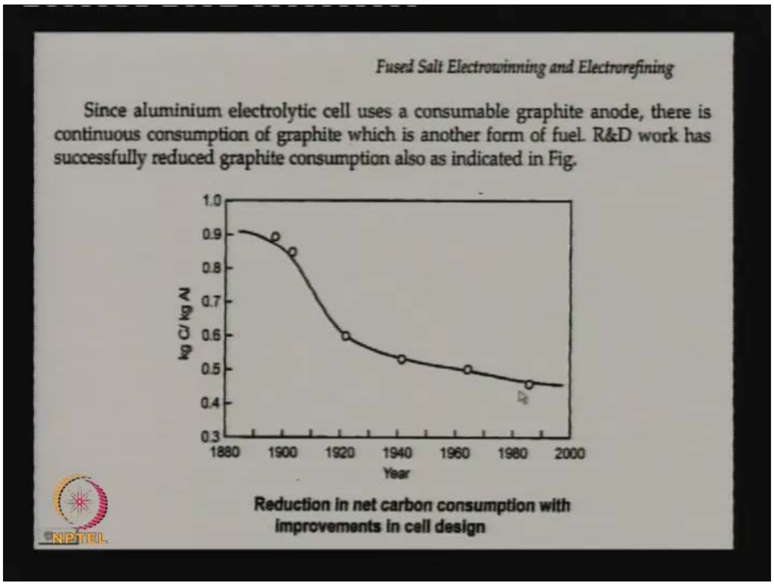

Fused Salt Electrowinning and Electrorefining

Since aluminium electrolytic cell uses a consumable graphite anode, there is continuous consumption of graphite which is another form of fuel. R&D work has successfully reduced graphite consumption also as indicated in Fig.

Reduction in net carbon consumption with improvements in cell design

Reduction in net carbon consumption with improvements in cell design, in cell design, the carbon consumption is also going down, that also would mean less generation of C O, C O 2.

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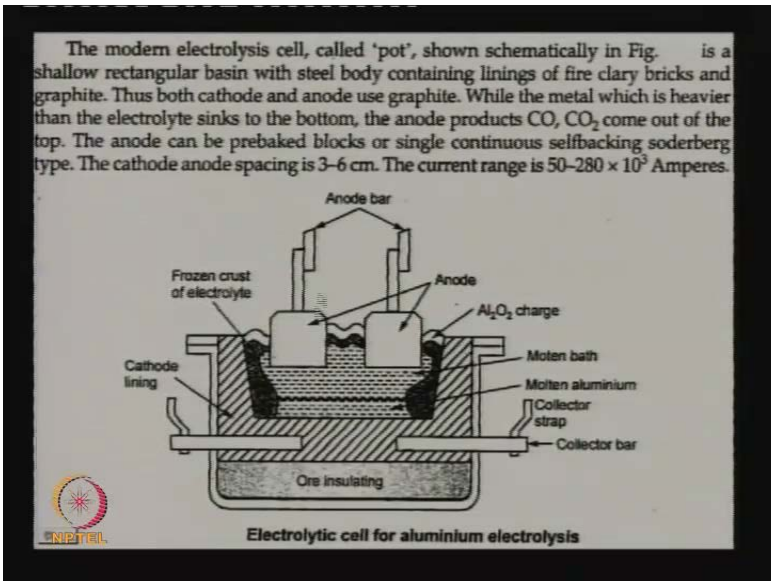

The modern electrolysis cell, called 'pot', shown schematically in Fig. is a shallow rectangular basin with steel body containing linings of fire clary bricks and graphite. Thus both cathode and anode use graphite. While the metal which is heavier than the electrolyte sinks to the bottom, the anode products CO, CO_2 come out of the top. The anode can be prebaked blocks or single continuous selfbacking soderberg type. The cathode anode spacing is 3–6 cm. The current range is 50–280 × 10^3 Amperes.

Electrolytic cell for aluminium electrolysis

This is another design of electrolytic cell which I have shown, in connection with some discussions. The cathode anode spacing, this spacing is very critical 3 to 6 centimeters, the current range is critical; all these are very critical parameters (no audio from 43:14 to 43:25).

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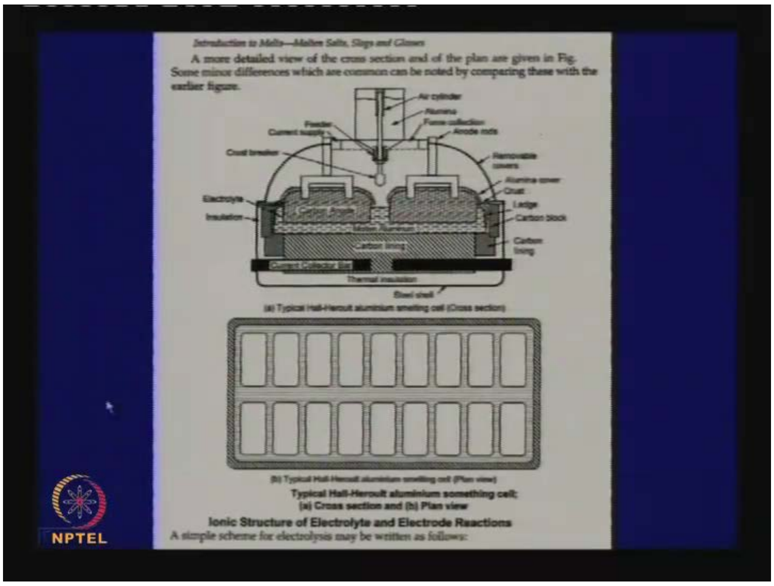

Introduction to Melts—Molten Salts, Slags and Glasses

A more detailed view of the cross section and of the plan are given in Fig. Some minor differences which are common can be noted by comparing these with the earlier figure.

(a) Typical Hall-Herault aluminium smelting cell (Cross section)

(b) Typical Hall-Herault aluminium smelting cell (Plan view)

Typical Hall-Herault aluminium something cell;
(a) Cross section and (b) Plan view

Ionic Structure of Electrolyte and Electrode Reactions

A simple scheme for electrolysis may be written as follows:

In in in reality, we have many many cells in series. This is the look from the top, this is the plan view, this is another view of the cell to show that everything is enclosed because you do not want the gases that come out, it has to go helter skelter, they all have to taken out very carefully through certain chambers, you see the carbon lining, molten aluminum on top of that, there is the there is the electrolyte layer. I have given some equations to show, that not only is aluminum and oxygen, released oxygen becomes C O, C O 2, there is also other species that come out and that is why.

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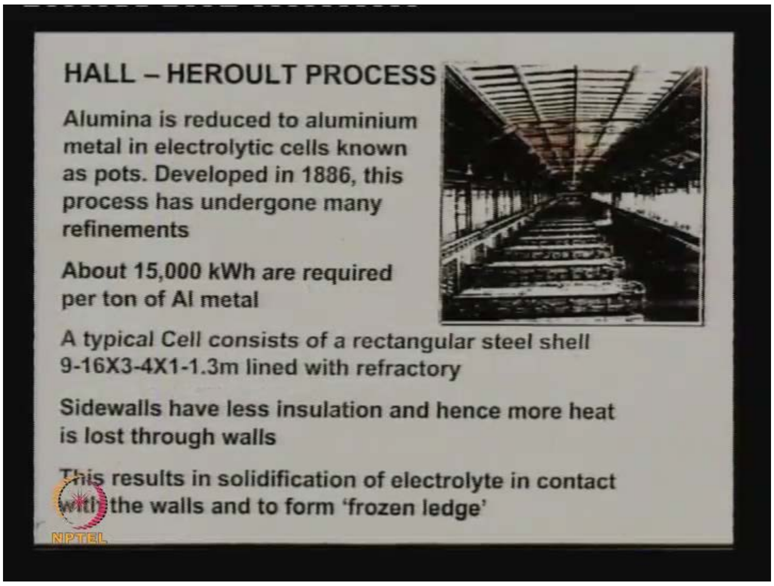

HALL – HEROULT PROCESS

Alumina is reduced to aluminium metal in electrolytic cells known as pots. Developed in 1886, this process has undergone many refinements

About 15,000 kWh are required per ton of Al metal

A typical Cell consists of a rectangular steel shell 9-16X3-4X1-1.3m lined with refractory

Sidewalls have less insulation and hence more heat is lost through walls

This results in solidification of electrolyte in contact with the walls and to form 'frozen ledge'

Then there is a very interesting discussion, I put in a paper by man from the industry because I wanted to show you, what that man finds you important in the industry, there is a picture of the aluminum electrolytic cells in a long long series that is, how your actual plant looks like.

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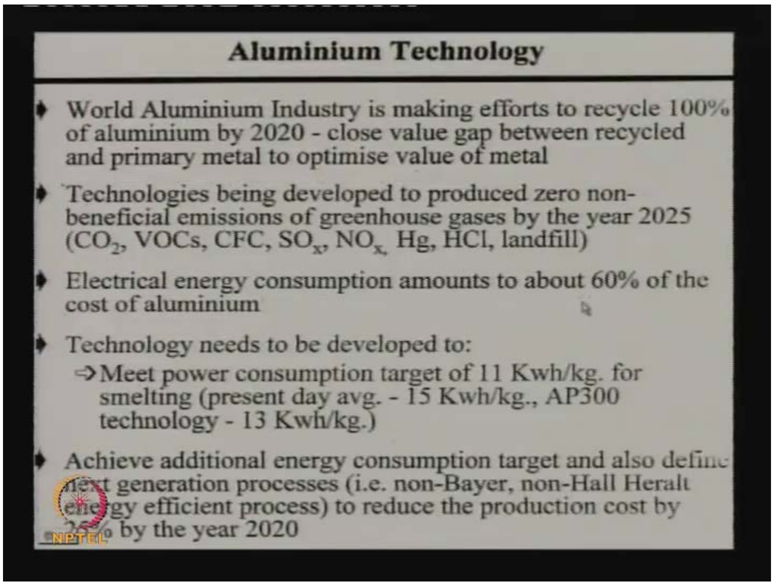

Aluminium Technology

- World Aluminium Industry is making efforts to recycle 100% of aluminium by 2020 - close value gap between recycled and primary metal to optimise value of metal
- Technologies being developed to produced zero non-beneficial emissions of greenhouse gases by the year 2025 (CO_2, VOCs, CFC, SO_x, NO_x, Hg, HCl, landfill)
- Electrical energy consumption amounts to about 60% of the cost of aluminium
- Technology needs to be developed to:
  - ⇨ Meet power consumption target of 11 Kwh/kg. for smelting (present day avg. - 15 Kwh/kg., AP300 technology - 13 Kwh/kg.)
- Achieve additional energy consumption target and also define next generation processes (i.e. non-Bayer, non-Hall Herault energy efficient process) to reduce the production cost by 25% by the year 2020

They have given some data, talks about what are the important issues that there are actually plans to recycle 100 percent of aluminum by 2020. In that case, you do not have to produce aluminum to (( )) this may not be possible. It is not a very utopian (( )) because aluminum does not get spoiled. So, when a consumer has used aluminum discarded, it is not going to get corroded. So, it can be in theory recycled, but you know in countries like in India, where we have not reached a certain level of development.

We have to keep on producing more aluminum just to satisfy the needs of the classes, who are coming up in development. So, we will not be able to recycle the entire aluminum by 2020. Advanced countries should do that. We need technologies to produce non-zero emission from cells. Electrical energy consumption has to be brought down then there are some other goals. Mostly, we are connected with energy consumption, current efficiency, gas emission, carbon consumption and the industry is, it trying to improve on all counts.

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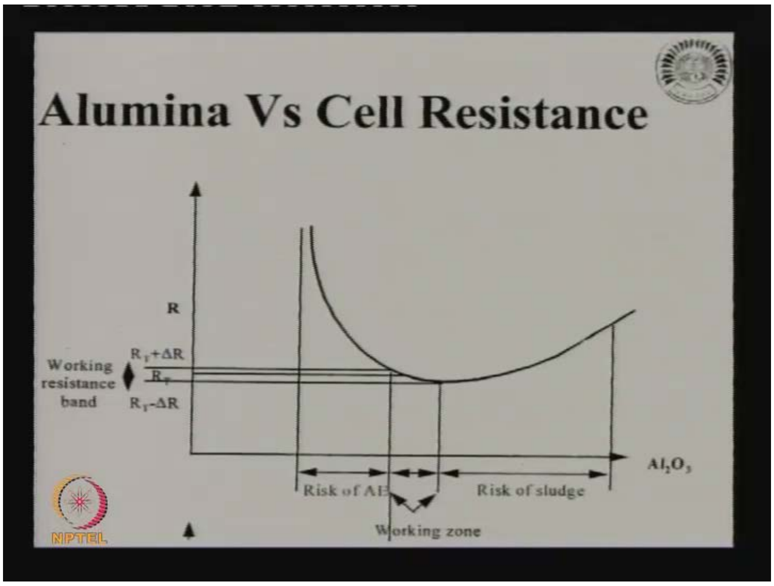

Alumina Vs Cell Resistance

There is a there was a list of R and D thrust, that I discussed, all related to what I just mentioned and then discuss the trick, a very trick of operation in aluminum cells. There is a very small window, you have there is a working zone is very small. You cannot increase the bath resistance too much, you cannot decrease it too much, if you decrease the bath resistance too much by bringing the electrodes too close then there will not be sufficient heating of the electrolyte, if you increase the resistance too much, you will get into a lot of problem because you might get into operational difficulties.

Similarly, alumina you see the alumina versus cell resistance, if the alumina falls too far below a limit, you will have what we call, anode effect, some gases covered the anode and aluminum cannot be deposited then sparks go from one cathode to anode without causing electrolysis only causes heating. If the alumina concentration is too high then it will not, it will exceed the solubility limit, it will precipitate out as a sludge, there are all kinds of problems. So, it has to be a very narrow window of 6 to 8 percent or something like that.

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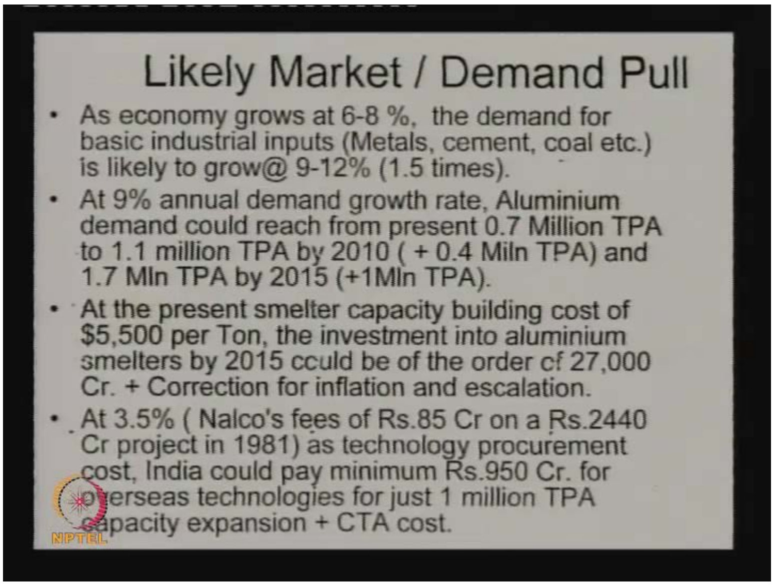

Likely Market / Demand Pull

- As economy grows at 6-8 %, the demand for basic industrial inputs (Metals, cement, coal etc.) is likely to grow@ 9-12% (1.5 times).
- At 9% annual demand growth rate, Aluminium demand could reach from present 0.7 Million TPA to 1.1 million TPA by 2010 (+ 0.4 Mln TPA) and 1.7 Mln TPA by 2015 (+1Mln TPA).
- At the present smelter capacity building cost of $5,500 per Ton, the investment into aluminium smelters by 2015 could be of the order of 27,000 Cr. + Correction for inflation and escalation.
- At 3.5% (Nalco's fees of Rs.85 Cr on a Rs.2440 Cr project in 1981) as technology procurement cost, India could pay minimum Rs.950 Cr. for overseas technologies for just 1 million TPA capacity expansion + CTA cost.

Then the man from the industry has talked about market and demand pool, all the economies growing is likely to grow even faster in future. The aluminum demand, we think can reach from present 0.7 million tons to 1.1 million next year, 1.7 million tons by 2 2 2015, I am sure mister pugazhenthy has addressed these issues also. Then we have the smelter capacity of some kind, we might have bigger smelters and we do not design our own smelters. We import designs from abroad get consultants from abroad, we do not have engineers and metallurgist doing the job for us.

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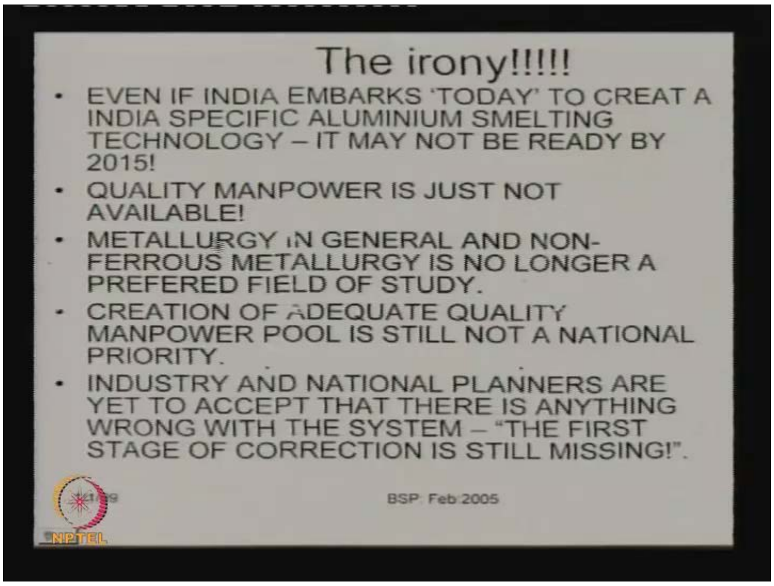

The irony!!!!!

- EVEN IF INDIA EMBARKS 'TODAY' TO CREAT A INDIA SPECIFIC ALUMINIUM SMELTING TECHNOLOGY – IT MAY NOT BE READY BY 2015!
- QUALITY MANPOWER IS JUST NOT AVAILABLE!
- METALLURGY IN GENERAL AND NON-FERROUS METALLURGY IS NO LONGER A PREFERED FIELD OF STUDY.
- CREATION OF ADEQUATE QUALITY MANPOWER POOL IS STILL NOT A NATIONAL PRIORITY.
- INDUSTRY AND NATIONAL PLANNERS ARE YET TO ACCEPT THAT THERE IS ANYTHING WRONG WITH THE SYSTEM – "THE FIRST STAGE OF CORRECTION IS STILL MISSING!".

BSP Feb 2005

So, lot of money is going out of the country, simply for this and that is why, he has listed some ironies that even, if India embarks today to create a Indian specific aluminum smelting technology, it may not be ready by 20 15, we do not have our (( )) technology. All technologies are supplied by leading companies of abroad quality man power is not available may be some of you will go incidentally until recently these companies never paid very well, but now things have changed.

The young metallurgist, who are joining these companies are being paid very heavily and I have seen some very (( )) young bright boys and girls even willing to go to very remote areas, where these alumina smelters are there or leaching leaching, the Bayer process plants are there because the pay is good, the company treats them well. So, it is a very good option for you. But essentially, the emphasis has to be creation of adequate quality man power and industry and national planners have to accept that there is something wrong with the present system of giving enough incentives, attracting young people to this industry.

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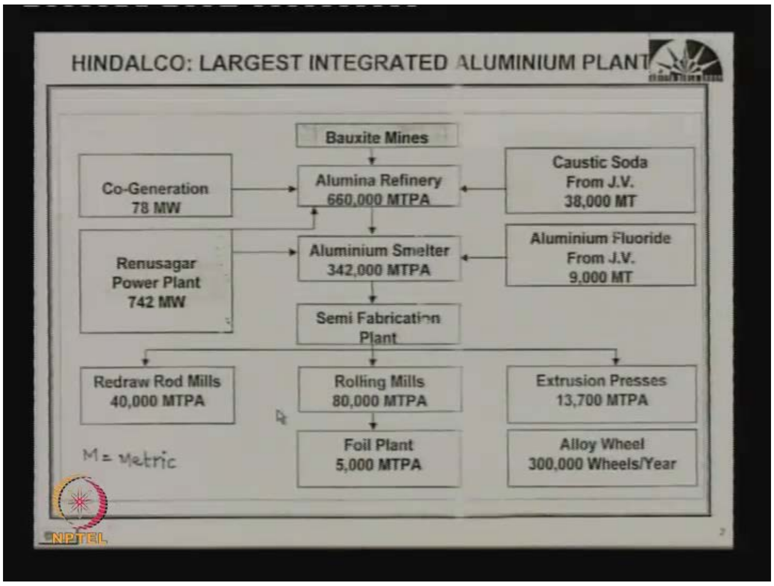

HINDALCO: LARGEST INTEGRATED ALUMINIUM PLANT

Bauxite Mines

Co-Generation
78 MW

Alumina Refinery
660,000 MTPA

Caustic Soda
From J.V.
38,000 MT

Renusagar
Power Plant
742 MW

Aluminium Smelter
342,000 MTPA

Aluminium Fluoride
From J.V.
9,000 MT

Semi Fabrication
Plant

Redraw Rod Mills
40,000 MTPA

Rolling Mills
80,000 MTPA

Extrusion Presses
13,700 MTPA

Foil Plant
5,000 MTPA

Alloy Wheel
300,000 Wheels/Year

M = Metric

I have given in details something about HINDALCO, the largest integrated aluminum plant, what they have, what they need; they have an aluminum refinery where power is coming through co-Generation. Co-Generation means simultaneous generation of electricity and steam, you need electricity, you also need steam which will go for Bayer's process, you need a caustic soda plant, you produce caustic soda which will go for leaching. In the smelter also you need power, you need aluminum fluoride then fabricated rolling mills all these things they have. You see, how this smelting capacity is gradually increasing in our country.

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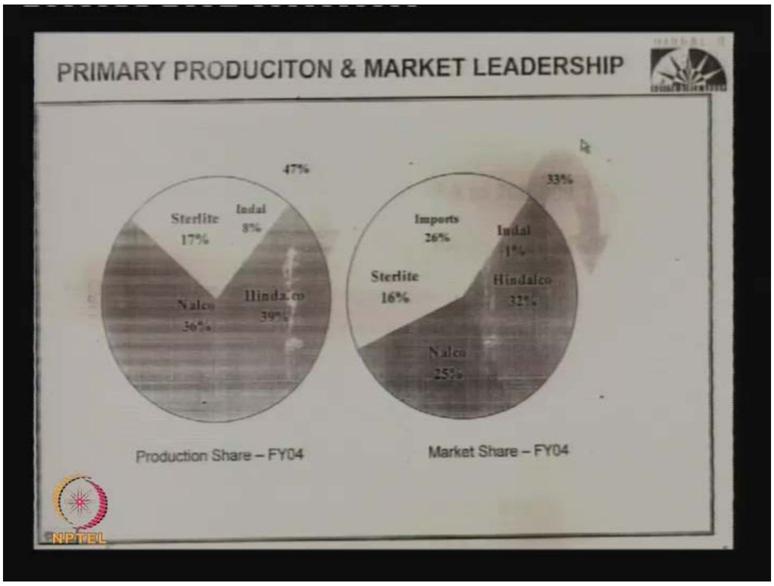

PRIMARY PRODUCITON & MARKET LEADERSHIP

Production Share – FY04

Market Share – FY04

We have shown here, which all companies are producing aluminum in India, and what is their share Sterlite, Nalco, Hindalco, Indal; this is their production share, this is their market share.

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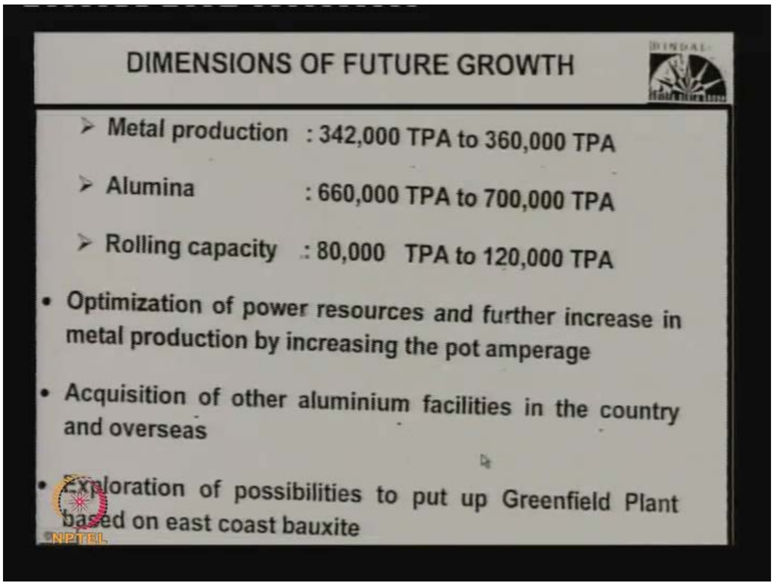

DIMENSIONS OF FUTURE GROWTH

- Metal production : 342,000 TPA to 360,000 TPA
- Alumina : 660,000 TPA to 700,000 TPA
- Rolling capacity : 80,000 TPA to 120,000 TPA

- Optimization of power resources and further increase in metal production by increasing the pot amperage
- Acquisition of other aluminium facilities in the country and overseas
- Exploration of possibilities to put up Greenfield Plant based on east coast bauxite

Then I ended the discussion by talking about dimensions of future growth. Metal production has to has to go up, aluminum production slowing up, rolling capacity has to go up and some other goals that we have.

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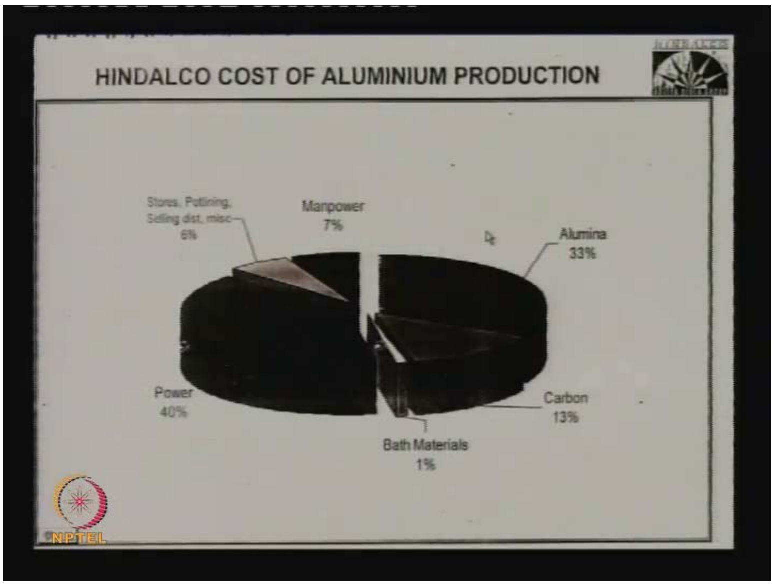

HINDALCO COST OF ALUMINIUM PRODUCTION

They about, we gave a cost cost break up. The most important thing is to show, that according to the figures given in aluminum production at HINDALCO, power is forty percent of the total cost and that you see, why aluminum is so very sensitive from the energy point of view.

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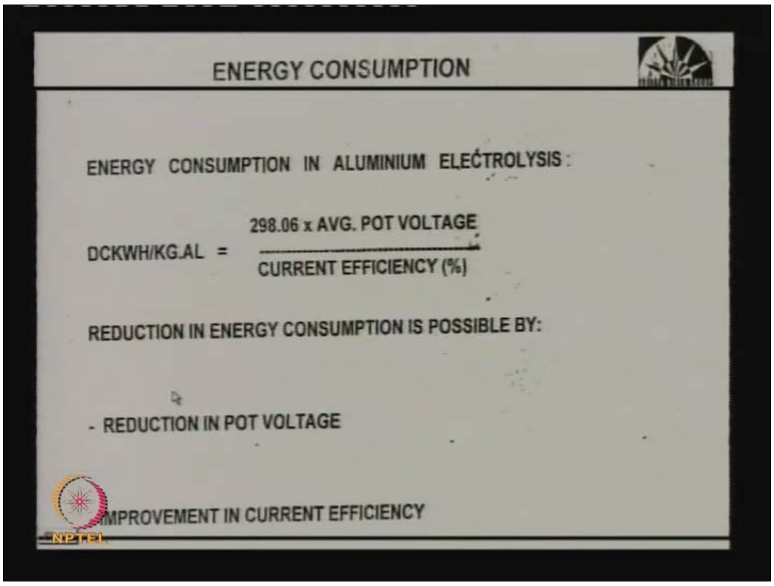

ENERGY CONSUMPTION

ENERGY CONSUMPTION IN ALUMINIUM ELECTROLYSIS :

$$\text{DCKWH/KG.AL} = \frac{298.06 \times \text{AVG. POT VOLTAGE}}{\text{CURRENT EFFICIENCY (\%)}}$$

REDUCTION IN ENERGY CONSUMPTION IS POSSIBLE BY:

- REDUCTION IN POT VOLTAGE

IMPROVEMENT IN CURRENT EFFICIENCY

Then there was an analysis of energy consumption, what we can do to bring it down, but companies definitely are trying. That is why, the the energy consumption is slowly going down, mostly because of the ave average pot voltage is going down, there is lot of computer control and other things to make the operations very smooth and standardize the quality of alumina, quality of bauxite all the operating parameters, when things are very smooth and standardized and things are controlled the process control by computers and automation then you can minimize your energy consumption.

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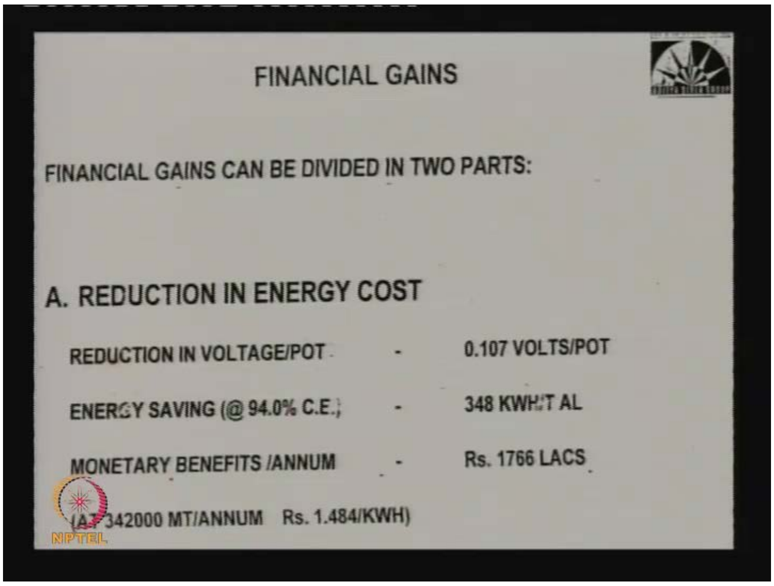

FINANCIAL GAINS

FINANCIAL GAINS CAN BE DIVIDED IN TWO PARTS:

A. REDUCTION IN ENERGY COST

REDUCTION IN VOLTAGE/POT - 0.107 VOLTS/POT
ENERGY SAVING (@ 94.0% C.E.) - 348 KWH/T AL
MONETARY BENEFITS /ANNUM - Rs. 1766 LACS
(AT 342000 MT/ANNUM Rs. 1.484/KWH)

And there was some data given as to, what are the financial implications of slight reduction in voltage and that phenomenon over the long time even small small changes in power means lot of advantage in financial terms, these are some data potline details.

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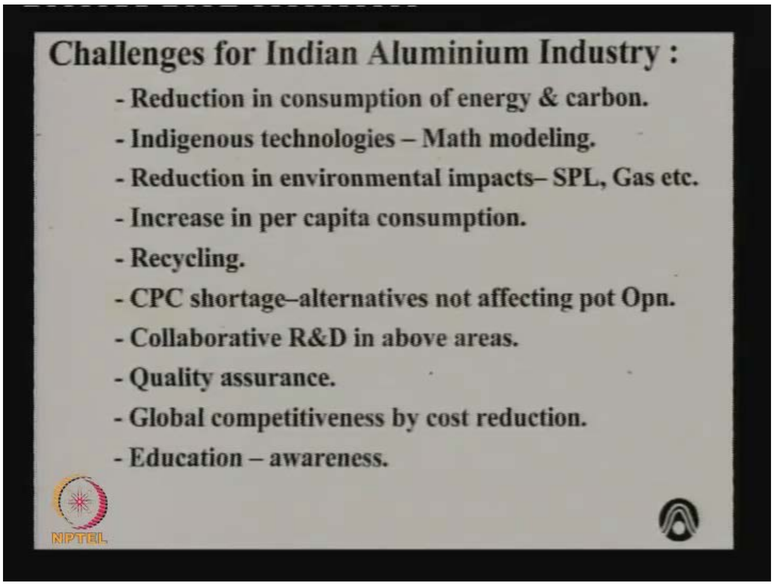

Challenges for Indian Aluminium Industry :

- Reduction in consumption of energy & carbon.
- Indigenous technologies – Math modeling.
- Reduction in environmental impacts– SPL, Gas etc.
- Increase in per capita consumption.
- Recycling.
- CPC shortage–alternatives not affecting pot Opn.
- Collaborative R&D in above areas.
- Quality assurance.
- Global competitiveness by cost reduction.
- Education – awareness.

Then there was some challenges for the Indian aluminum industry listed. What are the goals, reduction in consumption of energy and carbon, indigenous technology and mathematical model, reduction in environmental impacts, increase in per capita consumption, recycling, etcetera, etcetera. All these can be done, if bright young people come into the aluminum industry. I hope some of you will, then I have given some discussions on ferroalloys which I will not discuss now. I will end the discussion here today. Thank you. I will there are four more modules left 6, 7, 8, 9. I will quickly review them in my last lecture. Thank you very much.