Non-ferrous Extractive Metallurgy
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Lecture No. # 43
Review and Summary (Contd.)

Young friends, this will be the last lecture in this lecture series. And in this lecture, I am going to review modules 6 to 9. The previous 5, I have quickly reviewed in the last two lectures. I have to rush through the main points in these modules, because there there was so much that I discussed. But there are certain points I like to emphasize and I would like to take that you take note of the following.

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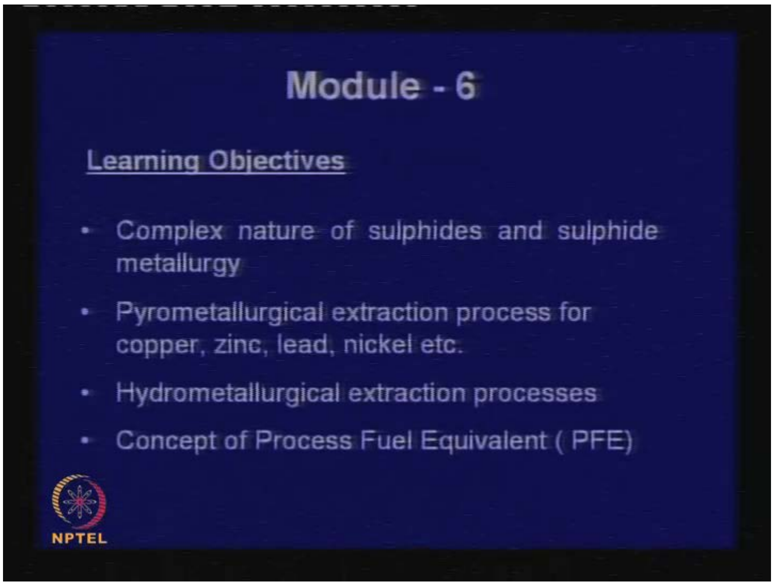

Module - 6

Learning Objectives

- Complex nature of sulphides and sulphide metallurgy
- Pyrometallurgical extraction process for copper, zinc, lead, nickel etc.
- Hydrometallurgical extraction processes
- Concept of Process Fuel Equivalent (PFE)

In module 6, our learning objectives was to know about the complex nature of the sulphides, learn about the pyrometallurgical extraction processes for a few metals, then the hydrometallurgical extraction processes. And a very important concept called process fuel equivalent.

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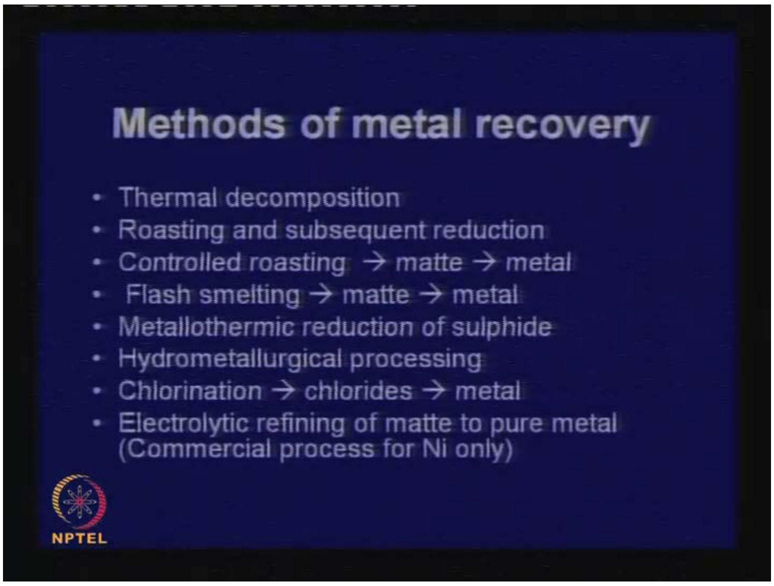

Methods of metal recovery

- Thermal decomposition
- Roasting and subsequent reduction
- Controlled roasting → matte → metal
- Flash smelting → matte → metal
- Metallothermic reduction of sulphide
- Hydrometallurgical processing
- Chlorination → chlorides → metal
- Electrolytic refining of matte to pure metal (Commercial process for Ni only)

I mentioned there are many methods of metal recovery. And these methods involve thermal decomposition, roasting, subsequent reduction, and controlled roasting. And in this, I must mention that in the case of copper metallurgy, we talk about a phase, which does not appear in other places, it is a matte; matte is a mixture of sulphides.

In copper metallurgy, we start with a sulphide concentrate from which we remove iron, most of the iron and iron oxide and finally, we are left with a mixture of copper sulphide and iron sulphide that is called matte. It does not need reduction by control oxidation, once we got remove FeS, then we start oxidizing copper sulphide, then there is a reaction between C u 2 S and and copper oxide and copper sulphide and copper comes out. That is what happens during converting.

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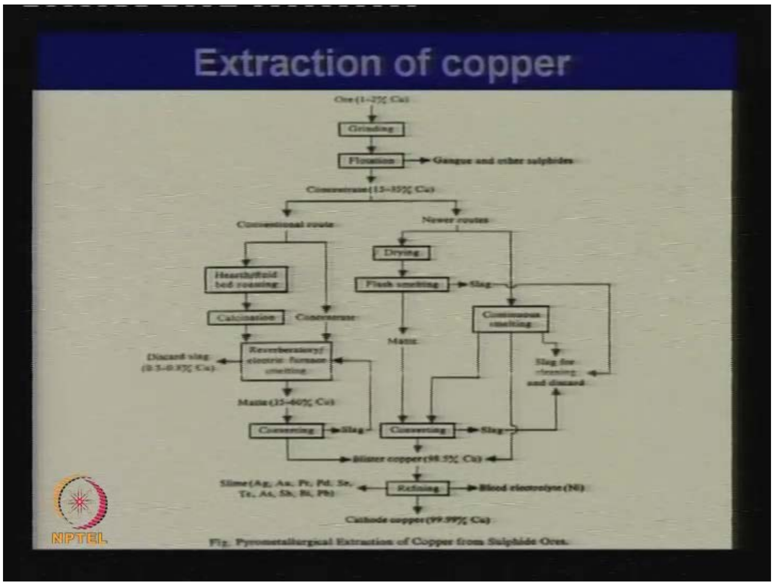

Extraction of copper

Fig. Pyrometallurgical Extraction of Copper from Sulphide Ores.

I mentioned the pyrometallurgical steps in extraction of copper. In a conventional route, there are lots of operations, we have roasting, then reverberatory smelting, converting, these are combined in the flash smelting process, roasting and smelting are combined; when you go for continuous copper, then all three steps are combined. So, once steps are combined, your energy requirements become less in the sense, the steps are exothermic. But if you have too many steps, too many reactors, then lot of heat losses, but when you combine steps from the energy point of way, it is better.

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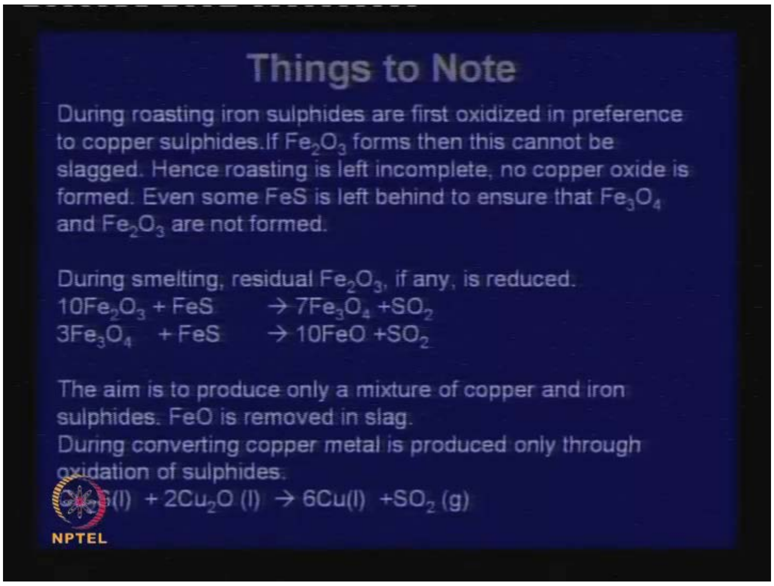

Things to Note

During roasting iron sulphides are first oxidized in preference to copper sulphides. If Fe_2O_3 forms then this cannot be slagged. Hence roasting is left incomplete, no copper oxide is formed. Even some FeS is left behind to ensure that Fe_3O_4 and Fe_2O_3 are not formed.

During smelting, residual Fe_2O_3, if any, is reduced.

$10Fe_2O_3 + FeS \rightarrow 7Fe_3O_4 + SO_2$

$3Fe_3O_4 + FeS \rightarrow 10FeO + SO_2$

The aim is to produce only a mixture of copper and iron sulphides. FeO is removed in slag.

During converting copper metal is produced only through oxidation of sulphides.

$S(l) + 2Cu_2O\ (l) \rightarrow 6Cu(l) + SO_2\ (g)$

And also the exhaust gases come out in concentrated streams, so we can we can go for acid recovery. Then, we went through what happens during copper? The problem during roasting of copper sulphide is that, if you try to roast copper sulphide, copper will not form the oxide, until iron it forms oxide, because affinity of iron towards oxygen is more than affinity of copper towards oxygen.

And here, if we allow too much of oxidation of iron, then slagging will be difficult. So, idea would be to take it only 2 F e O states which can be removed. So, we we ensure that, F e does not go into the higher oxides and that is why we leave some F e, S behind and we get a matte which goes subsequently for smelting operation and converting.

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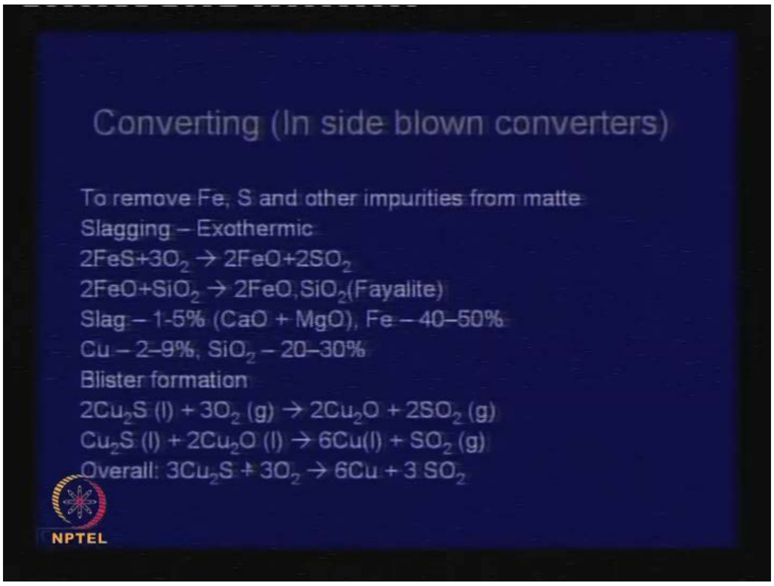

Converting (In side blown converters)

To remove Fe, S and other impurities from matte

Slagging – Exothermic

$2FeS+3O_2 \rightarrow 2FeO+2SO_2$

$2FeO+SiO_2 \rightarrow 2FeO.SiO_2$(Fayalite)

Slag – 1-5% (CaO + MgO), Fe – 40–50%

Cu – 2–9%, SiO_2 – 20–30%

Blister formation

$2Cu_2S\ (l) + 3O_2\ (g) \rightarrow 2Cu_2O + 2SO_2\ (g)$

$Cu_2S\ (l) + 2Cu_2O\ (l) \rightarrow 6Cu(l) + SO_2\ (g)$

Overall: $3Cu_2S + 3O_2 \rightarrow 6Cu + 3\ SO_2$

The final reaction is very interesting reaction when we are left we have a reactions C u 2 S plus 2 C u 2 O 6 C u S O 2. Once the matte is oxidized and we have twice as much C u 2, then C u 2 S, then there is a suddenly reaction between the two and copper comes out. So, all the reactions are actually oxidation reaction in the case of copper. We are not reducing anything anywhere.

And that is why, we can think of combing these are the conventional reverberatory smelting furnace that can be an electric smelting furnace, finally there is converting in a side blown convertor, we cannot blow from the bottom. I have discussed exactly what happens when the converting reaction takes place. I have talked about copper loss in slag and which which is related to percentage copper in reverberatory furnace matte.

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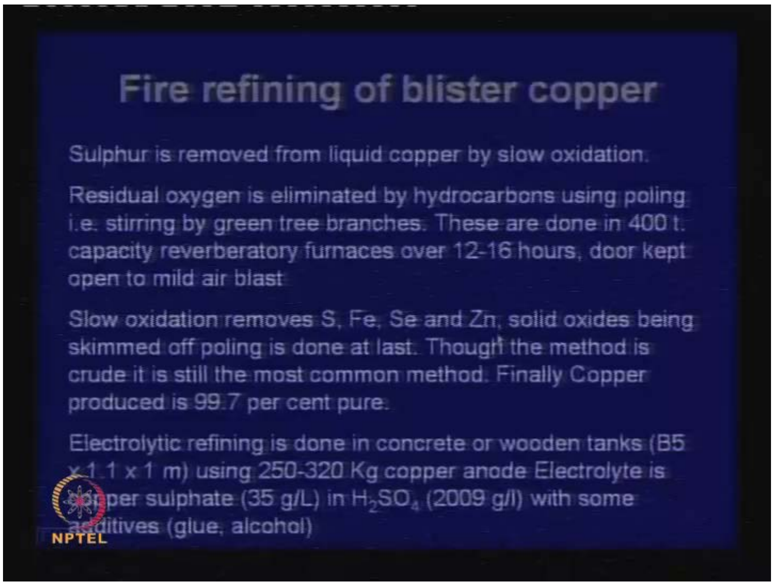

Fire refining of blister copper

Sulphur is removed from liquid copper by slow oxidation.

Residual oxygen is eliminated by hydrocarbons using poling i.e. stirring by green tree branches. These are done in 400 t. capacity reverberatory furnaces over 12-16 hours, door kept open to mild air blast.

Slow oxidation removes S, Fe, Se and Zn, solid oxides being skimmed off poling is done at last. Though the method is crude it is still the most common method. Finally Copper produced is 99.7 per cent pure.

Electrolytic refining is done in concrete or wooden tanks (B5 x 1.1 x 1 m) using 250-320 Kg copper anode Electrolyte is copper sulphate (35 g/L) in H_2SO_4 (2009 g/l) with some additives (glue, alcohol)

Then, there was a discussion on fire refining of copper, because the blister copper that comes as many impurities.

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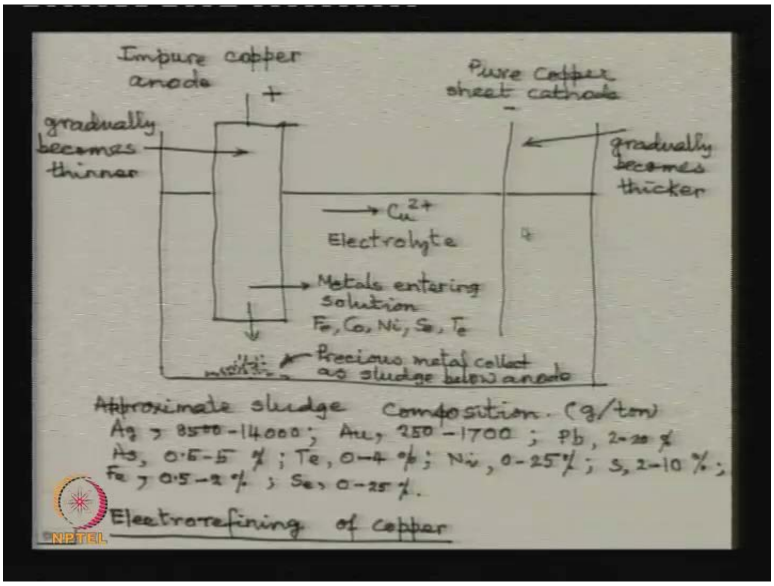

Approximate sludge Composition. (g/ton)
Ag, 8500-14000; Au, 250-1700; Pb, 2-20 %
As, 0.5-5 %; Te, 0-4 %; Ni, 0-25%; S, 2-10 %;
Fe, 0.5-2 %; Se, 0-25 %.

Electrorefining of copper

And there are many pyrometallurgical steps to finally get copper, but finally we will get an impure copper and that needs electro refining. In the process of electro refining, it releases as slimes or sludge at the bottom of the anode, a solid residue which has all the precious metals. Some impurities that dissolve in the in the electrolyte are to be rejected, essentially in electro refining copper moves from impure anode to a pure cathode.

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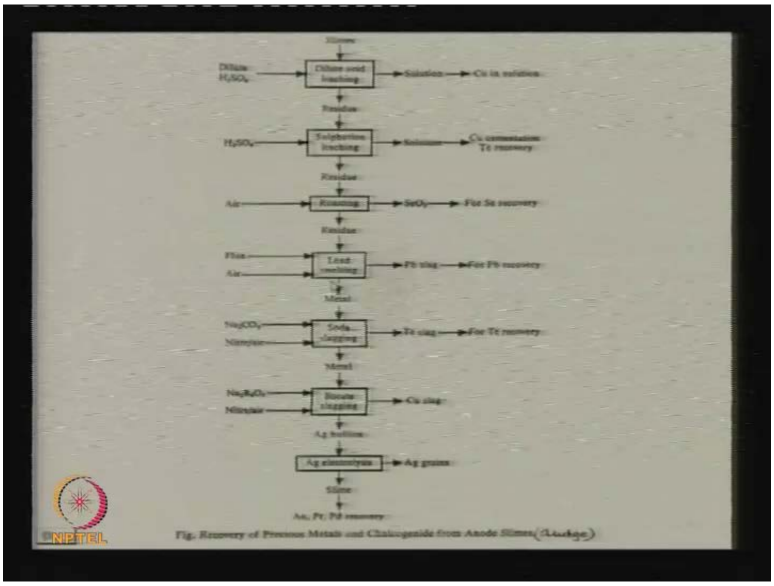

Fig. Recovery of Precious Metals and Chalcogenide from Anode Slimes (Sludge)

The slimes give a source of many many important by products. And we go through elaborate steps, chemical steps to remove them one by one, we get silver, we get tellurium recovery, we can get lead, we can get selenium. These are all very standard steps that have evolved over centuries of trial and error.

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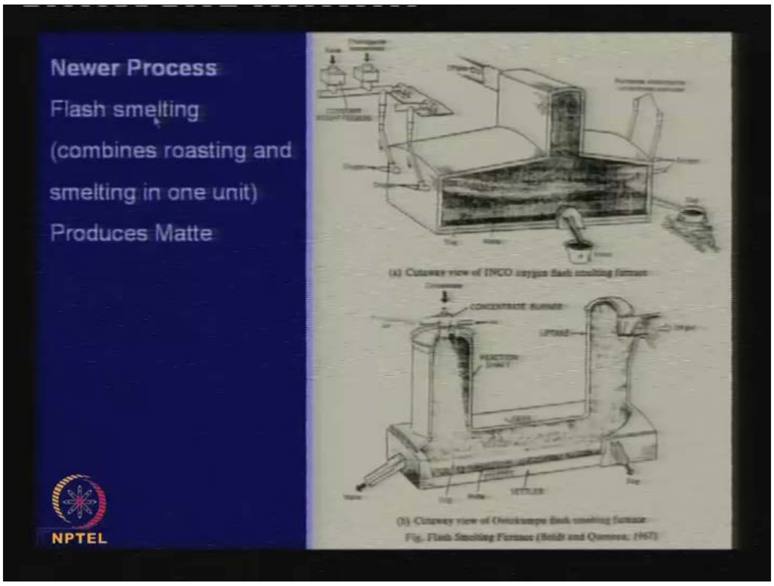

Newer Process

Flash smelting

(combines roasting and smelting in one unit)

Produces Matte

(a) Cutaway view of INCO oxygen flash smelting furnace

(b) Cutaway view of Outokumpu flash smelting furnace

Fig. Flash Smelting Furnace (Boldt and Queneau, 1967)

Our greater interest in copper metallurgies, how we are combining reverberatory, smelting, converting and before that roasting, all in one in continuous copper making processes. In processes like flash smelting, roasting and smelting are combined, converting is not done, and there are different designs of reactors.

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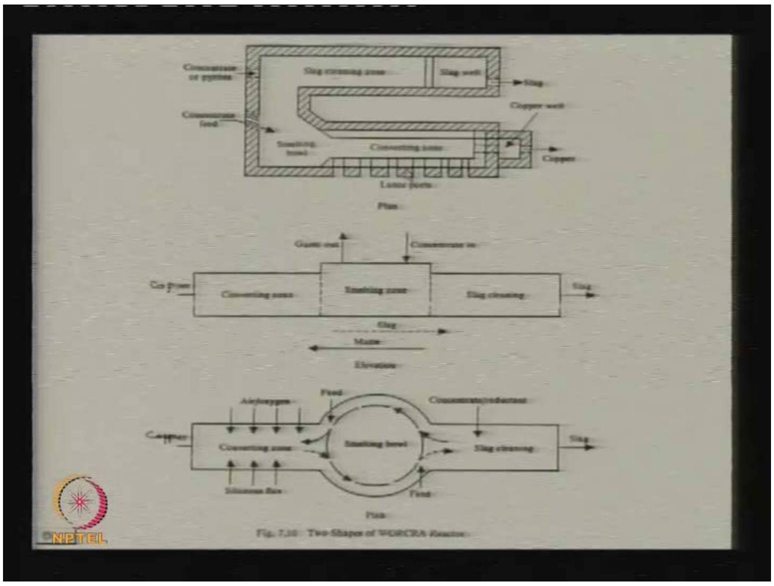

Fig. 7.10 Two Shapes of WORCRA Reactor

But then, there are also newer processes where all three are combined; that we have roasting, smelting, converting in one furnace and there are different kinds of furnaces. The main feature of this furnace will be that, since from roasting to converting, partial pressure of oxygen has to gradually increase. In the same reactor, there there would be different zones, where partial pressure of oxygen will be different. The other feature is, there is always counter current flow of matte and slag.

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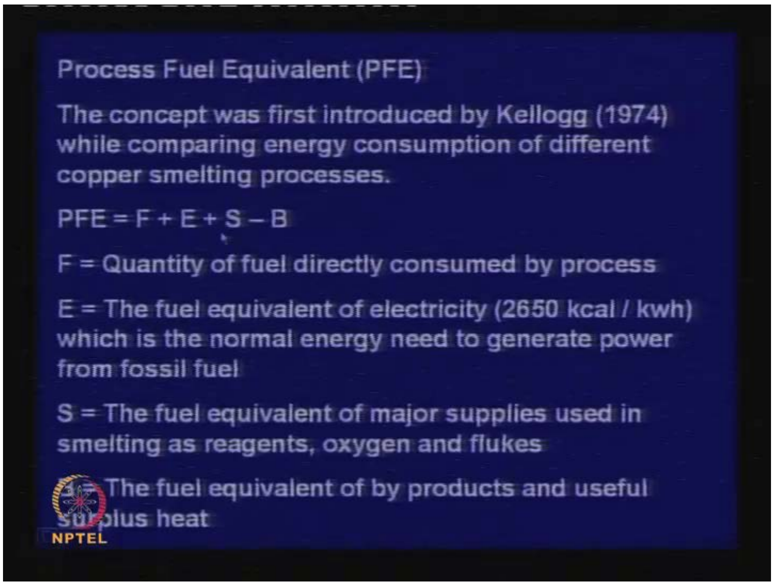

Process Fuel Equivalent (PFE)

The concept was first introduced by Kellogg (1974) while comparing energy consumption of different copper smelting processes.

PFE = F + E + S – B

F = Quantity of fuel directly consumed by process

E = The fuel equivalent of electricity (2650 kcal / kwh) which is the normal energy need to generate power from fossil fuel

S = The fuel equivalent of major supplies used in smelting as reagents, oxygen and flukes

B = The fuel equivalent of by products and useful surplus heat

So, all these designs have been discussed and I have shown (Refer Slide Time: 07:52), how these two, these counter current flow. The concept of process fuel equivalent to which I am coming quite with frequently, it is very important. It is vital for analyzing any metallurgical step. The Process Fuel Equivalent, PFE is the quantity of fuel directly consumed by process, fuel equivalent of electricity that we may be using in the process, so these are the energy inputs.

There is also another parameter S, which is the fuel equivalent of major supplies. The input materials have also required some power, energy when they were produced that has to be taken into account; from that, we take away the fuel equivalent of by products and useful surplus heat.

Very often, we tend to forget the S term that after all the raw materials that we used, also have required energy for their production. So, only using such a term can we look at the energy equivalent.

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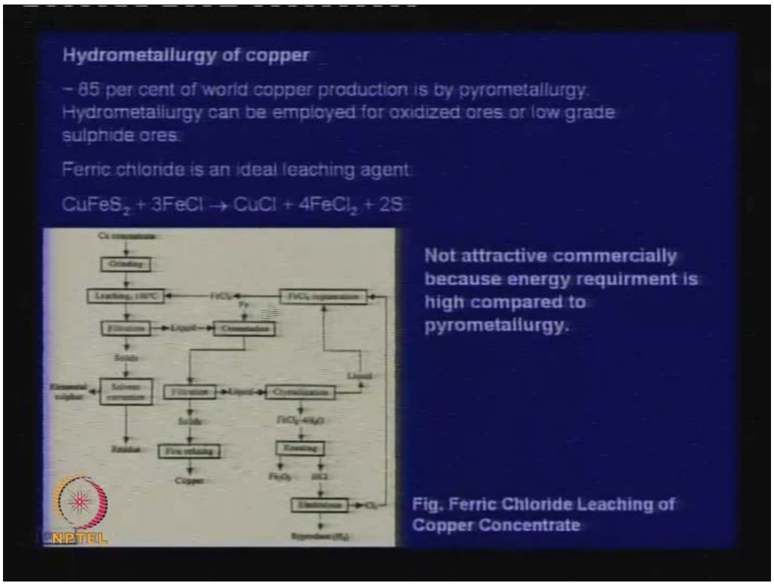

Hydrometallurgy of copper

~ 85 per cent of world copper production is by pyrometallurgy. Hydrometallurgy can be employed for oxidized ores or low grade sulphide ores.

Ferric chloride is an ideal leaching agent.

$CuFeS_2 + 3FeCl \rightarrow CuCl + 4FeCl_2 + 2S$

Not attractive commercially because energy requirment is high compared to pyrometallurgy.

Fig. Ferric Chloride Leaching of Copper Concentrate

We have talked about hydrometallurgy of copper, where the copper sulphide you roasted to copper oxide, then taken into solution. And then once we have a solution, we go for electrolysis and electro refining.

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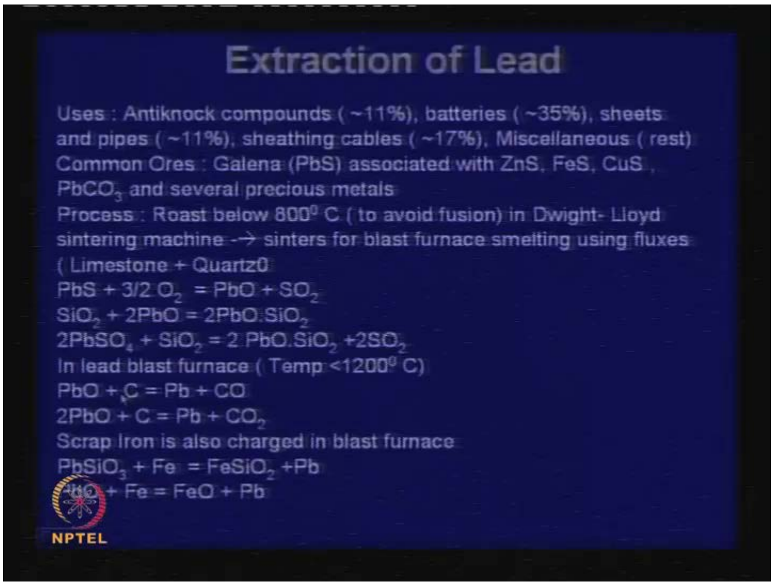

Extraction of Lead

Uses : Antiknock compounds (~11%), batteries (~35%), sheets and pipes (~11%), sheathing cables (~17%), Miscellaneous (rest)
Common Ores : Galena (PbS) associated with ZnS, FeS, CuS , $PbCO_3$ and several precious metals
Process : Roast below 800⁰ C (to avoid fusion) in Dwight- Lloyd sintering machine --> sinters for blast furnace smelting using fluxes (Limestone + Quartz0
$PbS + 3/2\ O_2 = PbO + SO_2$
$SiO_2 + 2PbO = 2PbO.SiO_2$
$2PbSO_4 + SiO_2 = 2\ PbO.SiO_2 + 2SO_2$
In lead blast furnace (Temp <1200⁰ C)
$PbO + C = Pb + CO$
$2PbO + C = Pb + CO_2$
Scrap Iron is also charged in blast furnace
$PbSiO_3 + Fe = FeSiO_2 + Pb$
$PbO + Fe = FeO + Pb$

There is also bacterial leaching in the case of copper ores, some bacteria help take copper into solution, but that takes long time is ideally suited for low grade ores. Extraction of lead is relatively simple pyrometallurgical step. Lead sulphide concentrate is oxidized or rather, which is which is done in a sintering machine to produce lead oxide sinters, and we need sinters, because they must be hard, they have to go into the blast furnace. This blast furnace is shorter in height and it operates at a maximum, the (()) temperature is not as high as that in iron blast furnace, it is around 1000 degrees.

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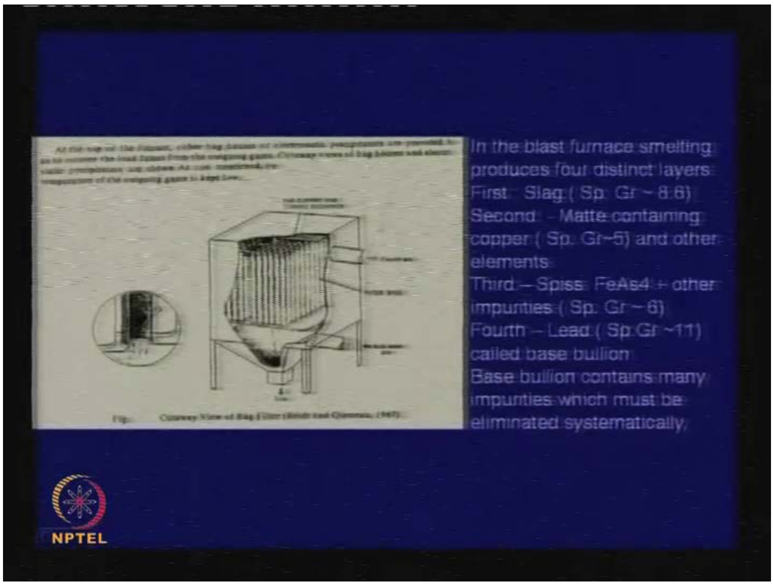

In the blast furnace smelting produces four distinct layers
First: Slag (Sp. Gr ~ 8.6)
Second: - Matte containing copper (Sp. Gr~5) and other elements
Third – Spiss: FeAs4 + other impurities (Sp. Gr ~ 6)
Fourth – Lead (Sp Gr ~11) called base bullion
Base bullion contains many impurities which must be eliminated systematically.

And it is straight simple P b O being reduced by coke to produce lead, that lead is called lead bullion, of special importance is the question of lead lead fumes coming out from the top which could be very poisonous. So, they have to be trapped in filter, special filter bags and that is why I have shown one drawing of that.

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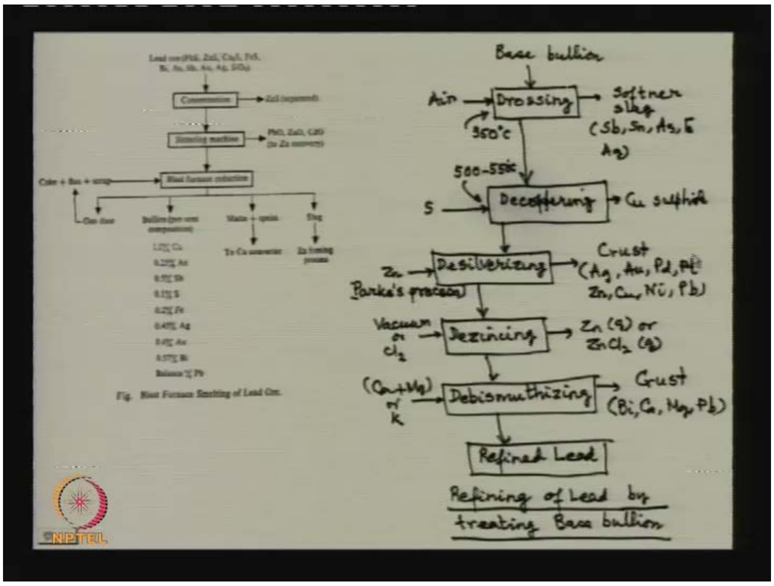

In the case of lead, there is a very elaborate process of refining of the lead bullion. Now here, the initial step is aims at producing lead in a bulk form, all recovery maximum recovery, but the impurities also come. And then, only after we have produced lead in a bulk form, bulk form called lead bullion that we take the bullion. And then go through various steps for taking out important by products. One of the very important by products is silver and for silver removal, there is a standard processing pyrometallurgy called Park's process.

When in the molten state, if you add zinc, zinc dissolves gold as well as other precious metals and that forms a crust that can be removed. And then, there are the other processes, steps for removable of other things.

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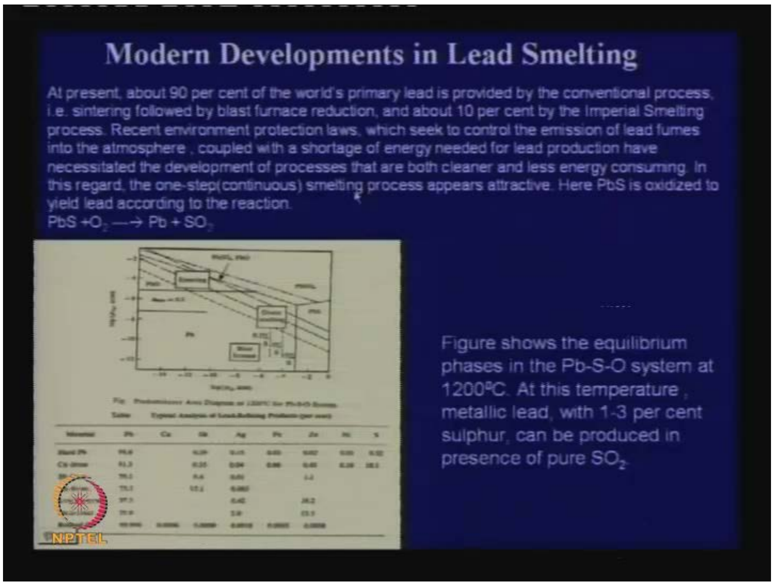

Modern Developments in Lead Smelting

At present, about 90 per cent of the world's primary lead is provided by the conventional process, i.e. sintering followed by blast furnace reduction, and about 10 per cent by the Imperial Smelting process. Recent environment protection laws, which seek to control the emission of lead fumes into the atmosphere , coupled with a shortage of energy needed for lead production have necessitated the development of processes that are both cleaner and less energy consuming. In this regard, the one-step(continuous) smelting process appears attractive. Here PbS is oxidized to yield lead according to the reaction

$PbS + O_2 \longrightarrow Pb + SO_2$

Figure shows the equilibrium phases in the Pb-S-O system at 1200ºC. At this temperature , metallic lead, with 1-3 per cent sulphur, can be produced in presence of pure SO_2.

People have tried to think of avoiding a complicated flow sheet and try I have tried to produce lead in one step continuous smelting process as we have for copper, but this has not become, so popular as yet.

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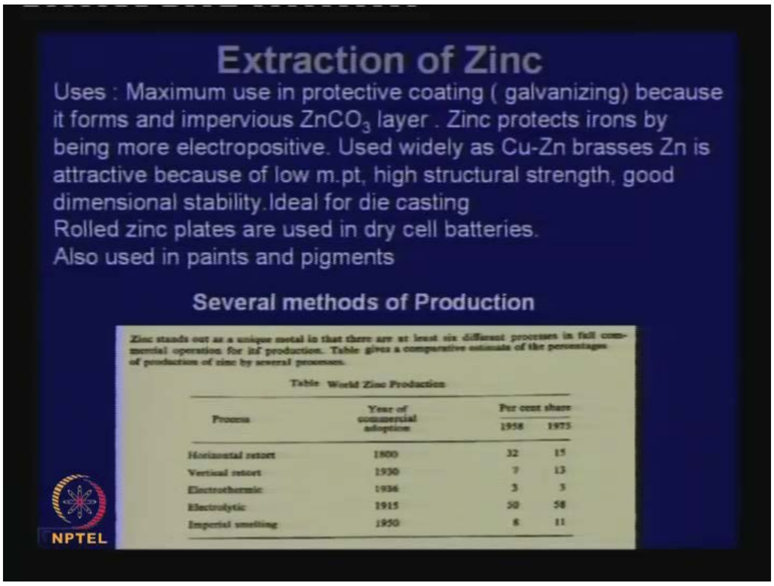

Extraction of Zinc

Uses : Maximum use in protective coating (galvanizing) because it forms and impervious $ZnCO_3$ layer . Zinc protects irons by being more electropositive. Used widely as Cu-Zn brasses Zn is attractive because of low m.pt, high structural strength, good dimensional stability. Ideal for die casting

Rolled zinc plates are used in dry cell batteries.

Also used in paints and pigments

Several methods of Production

Zinc stands out as a unique metal in that there are at least six different processes in full commercial operation for its production. Table gives a comparative estimate of the percentage of production of zinc by several processes.

Table World Zinc Production

Process	Year of commercial adoption	Per cent share	
		1958	1975
Horizontal retort	1800	32	15
Vertical retort	1930	7	13
Electrothermic	1936	3	3
Electrolytic	1915	50	58
Imperial smelting	1950	8	11

Zinc is a particular interest to us, because it was produced for the first time in India. The problem in reducing zinc oxide by carbon is that, zinc comes out as a vapour, so we need to have condensers. In India, in ancient times we had the vertical condensers as well as horizontal condensers that is a pyrometallurgical extraction. But today, hydrometallurgical extraction has become much more important, where we take zinc into solution after roasting and calcinations.

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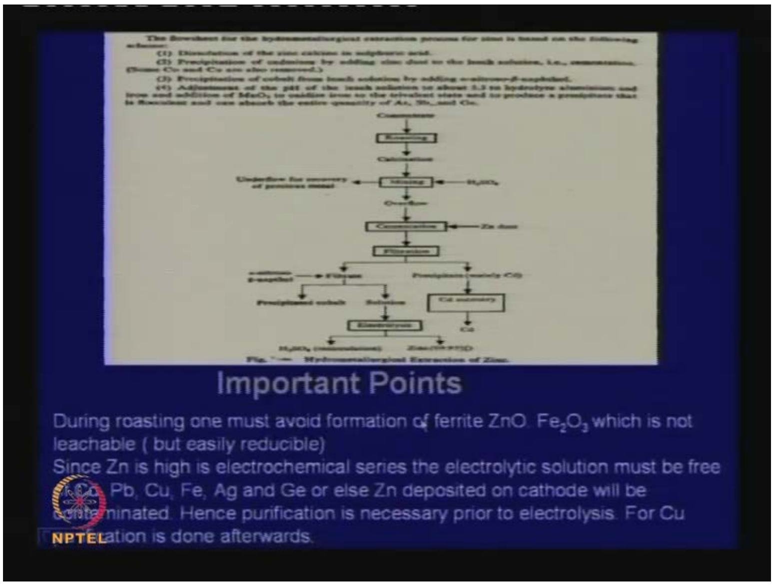

Important Points

During roasting one must avoid formation of ferrite ZnO. Fe_2O_3 which is not leachable (but easily reducible)

Since Zn is high is electrochemical series the electrolytic solution must be free Co, Pb, Cu, Fe, Ag and Ge or else Zn deposited on cathode will be contaminated. Hence purification is necessary prior to electrolysis. For Cu ation is done afterwards.

The solution goes through very elaborate purification process, because unless the solution is very very very pure, it will not be possible to electrolyze zinc. Because, we have to depend on activation over potential to ensure that, hydrogen potential becomes more than the zinc potential, that is why zinc can be displaced.

Normally, you know zinc will displaced hydrogen from acid solutions, but because of activation over potential, which would be created when a current is being passed, zinc can taken out of zinc solution. There is another important point that, when we are roasting zinc sulphide concentrate, one has to avoid formation of zinc ferrite, which cannot be leached. So, in extractive metallurgy of zinc, the formation of zinc ferrite is a very important subject.

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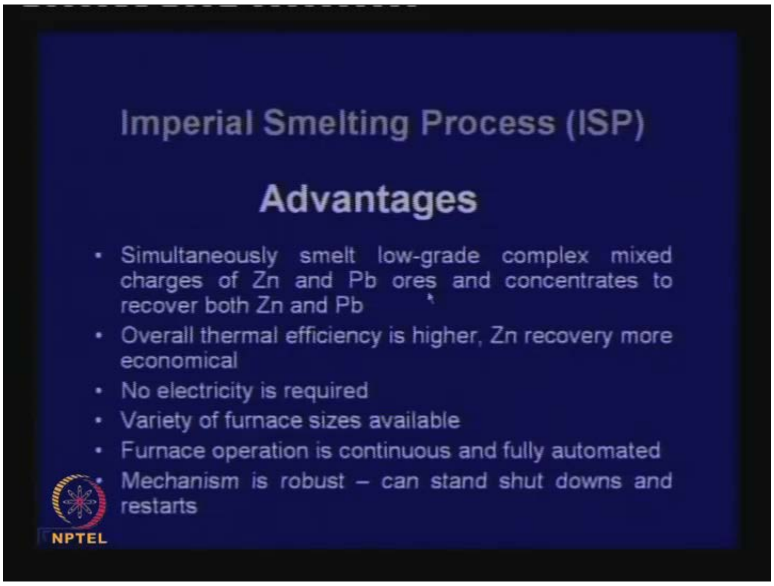

Imperial Smelting Process (ISP)

Advantages

- Simultaneously smelt low-grade complex mixed charges of Zn and Pb ores and concentrates to recover both Zn and Pb
- Overall thermal efficiency is higher, Zn recovery more economical
- No electricity is required
- Variety of furnace sizes available
- Furnace operation is continuous and fully automated
- Mechanism is robust – can stand shut downs and restarts

Then, there is the modern process where we again go back to pyrometallurgy and the process called imperial smelting process can simultaneously produced by a pyrometallurgical reduction in the blast furnace, both lead and zinc. Lead will come out from the bottom as it is, zinc will come out at the top as a vapour.

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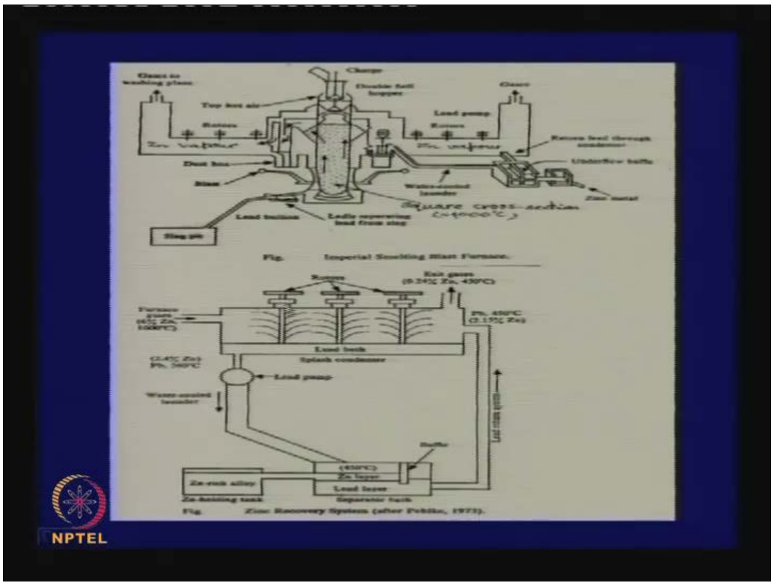

Then in imperial smelting process, they have the method of dissolving the zinc vapours in a spray of molten lead to form a z zinc lead alloy; and when that alloy is cooled, zinc separates out according the phase diagram. And that lead will be re-circulated, it is a very tricky process, but that is the basis.

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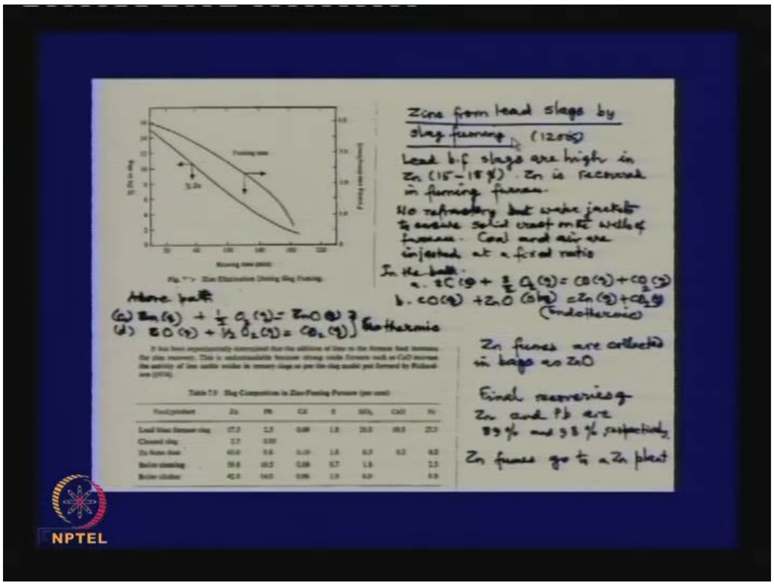

Zinc from lead slags by slag fuming (1200)

Lead b.f slags are high in Zn (15–18%). Zn is recovered in fuming furnace.

No refractory but water jackets to ensure solid crust on the walls of furnace. Coal and air are injected at a fixed ratio

In the bath:

a. $2C(s) + \frac{3}{2} O_2(g) = CO(g) + CO_2(g)$

b. $CO(g) + ZnO\,(slag) = Zn(g) + CO_2(g)$ (Endothermic)

Above bath

$$\left.\begin{array}{l}(c)\ Zn(g) + \frac{1}{2} O_2(g) = ZnO(s) \\ (d)\ CO(g) + \frac{1}{2} O_2(g) = CO_2(g)\end{array}\right\} \text{Exothermic}$$

Zn fumes are collected in bags as ZnO

Final recoveries

Zn and Pb are 89% and 98% respectively

Zn fumes go to a Zn plant

And another interesting subject is recovery of zinc by zinc slag fuming. In many lead slags, zinc will be there, there is a process called the fuming process for recovery of zinc.

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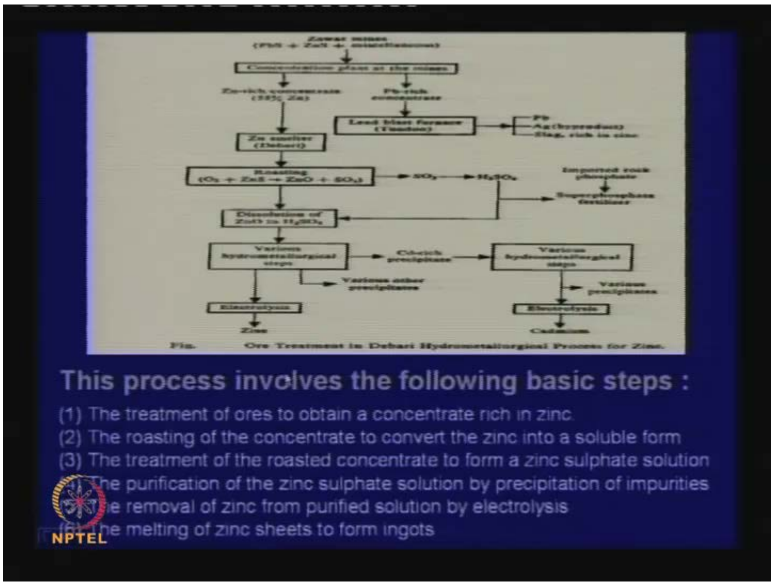

Fig. Ore Treatment in Debari Hydrometallurgical Process for Zinc.

This process involves the following basic steps :

(1) The treatment of ores to obtain a concentrate rich in zinc
(2) The roasting of the concentrate to convert the zinc into a soluble form
(3) The treatment of the roasted concentrate to form a zinc sulphate solution
he purification of the zinc sulphate solution by precipitation of impurities
e removal of zinc from purified solution by electrolysis
he melting of zinc sheets to form ingots

We I have discussed how, what are the steps in the process we follow in production of zinc in Udaipur, initially the company were Udaipur zinc limited. Now, it has been privatized and the company which is producing zinc is called sterlite. The ores first produce a concentrate rich in zinc.

Then, there is a roasting of the concentrate to convert zinc to soluble form. Then there is a zinc sulphate solution, which is purified and that from that zinc is obtained by electrolysis. This zinc is very very pure, better than 99.99 percent, more than what we required for galvanizing, but we have to have pure solution, that is why we get very pure zinc, whether we like it or not. The concentrates also go to another place near Chittor in Rajasthan, where the imperial smelting process operates.

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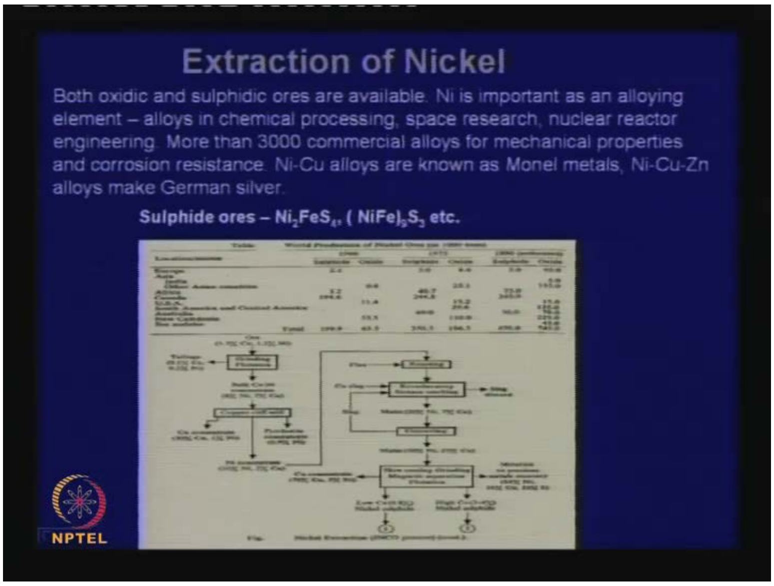

Extraction of Nickel

Both oxidic and sulphidic ores are available. Ni is important as an alloying element – alloys in chemical processing, space research, nuclear reactor engineering. More than 3000 commercial alloys for mechanical properties and corrosion resistance. Ni-Cu alloys are known as Monel metals, Ni-Cu-Zn alloys make German silver.

Sulphide ores – Ni_2FeS_4, $(NiFe)_9S_8$ etc.

I have talked about extraction of nickel we are not extracting nickel in India. But we have chromite mines, which produce an over burden that is accumulating that has 0.6 to 0.8 percent nickel. And although, we have had lot of R and D work and we have even run pilot plants for recovery of nickel from that over burden, till today we do not have a commercial process.

Nickel comes from both oxidic sources the chromite over burden is an oxidic source. But in some countries, Nickel also is found along with some sulphide ores that contain copper also, there a matte route would be followed, I would avoid the going into the details of this.

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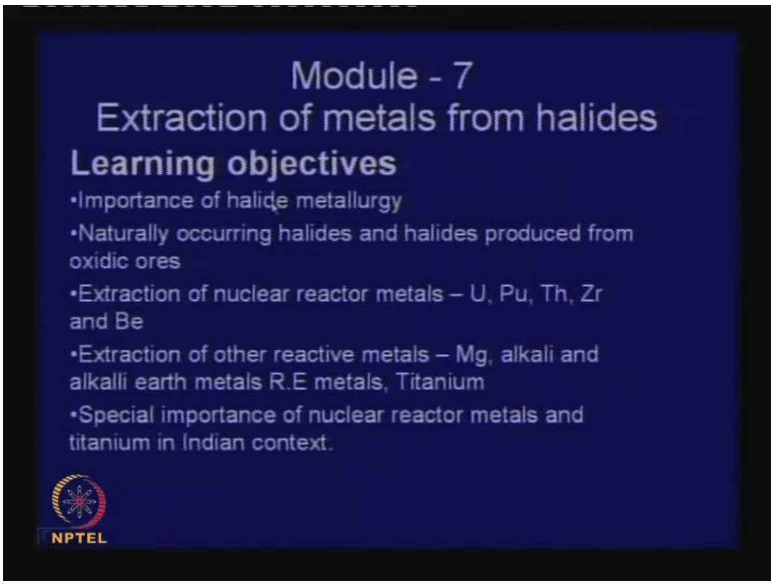

Module - 7

Extraction of metals from halides

Learning objectives

- Importance of halide metallurgy
- Naturally occurring halides and halides produced from oxidic ores
- Extraction of nuclear reactor metals – U, Pu, Th, Zr and Be
- Extraction of other reactive metals – Mg, alkali and alkalli earth metals R.E metals, Titanium
- Special importance of nuclear reactor metals and titanium in Indian context.

In module 7, we discussed extraction of metals from halides. And I made a distinction between halides that are in nature like magnesium chloride, sodium chloride in sea water or magnesium chloride in some deposits, which are found in sea beaches exposed sea beds. These are natural halides, but I have also talked about extracting metals from halides that are produced from oxides.

I have put them in this module, because even though we have oxides of titanium or uranium or thorium, we do not directly go from there to the metal; we have to first convert the oxides to pure halides and from there, we will obtain the metal. So, that is why we we have put it in this category.

We talked about the importance of halide metallurgy, made the distinction between naturally occurring halides and halides produced from oxidic ores. And then, we have gone into discussing nuclear metals and non nuclear metals from halides. Uranium, plutonium, thorium are nuclear metals, which produce energy through fission reaction. Zirconium and beryllium are not fissionable metals, but they are vitally important in nuclear reactors. Then, I have ended by discussing production of magnesium and sodium.

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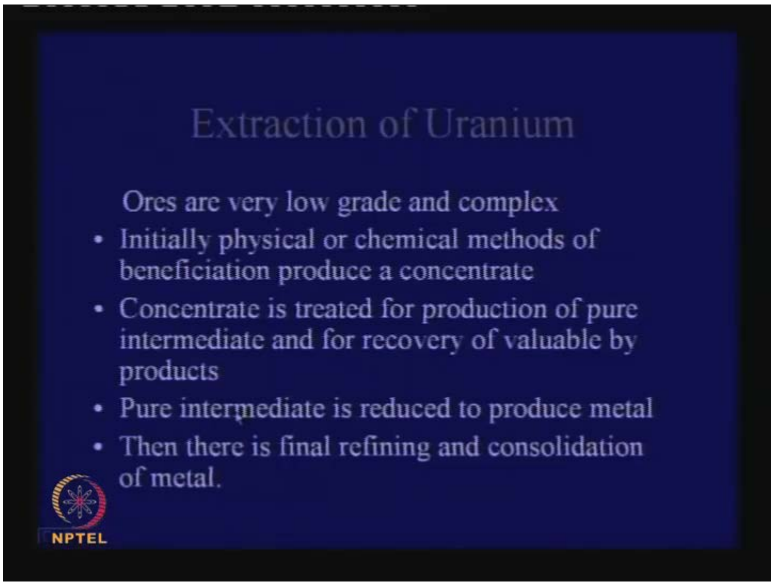

Extraction of Uranium

Ores are very low grade and complex

- Initially physical or chemical methods of beneficiation produce a concentrate
- Concentrate is treated for production of pure intermediate and for recovery of valuable by products
- Pure intermediate is reduced to produce metal
- Then there is final refining and consolidation of metal.

All these ores of uranium or thorium, they are kind of low grade. So, always we have a low grade and complex ore that needs up gradation through various techniques. And the idea will be to first finally, produce a pure intermediate an halide or an oxide from which you will get the metal.

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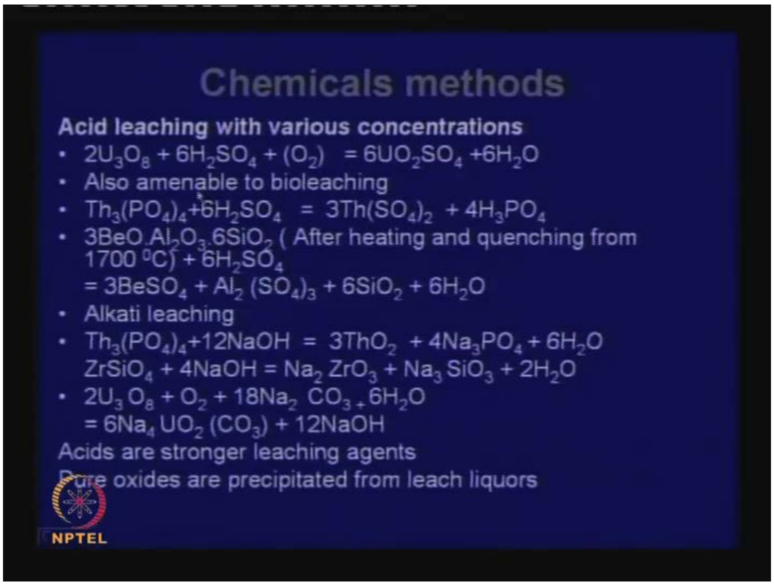

Chemicals methods

Acid leaching with various concentrations

- $2U_3O_8 + 6H_2SO_4 + (O_2) = 6UO_2SO_4 + 6H_2O$
- Also amenable to bioleaching
- $Th_3(PO_4)_4 + 6H_2SO_4 = 3Th(SO_4)_2 + 4H_3PO_4$
- $3BeO.Al_2O_3.6SiO_2$ (After heating and quenching from 1700 ^0C) + $6H_2SO_4$ $= 3BeSO_4 + Al_2(SO_4)_3 + 6SiO_2 + 6H_2O$
- Alkati leaching
- $Th_3(PO_4)_4 + 12NaOH = 3ThO_2 + 4Na_3PO_4 + 6H_2O$
  $ZrSiO_4 + 4NaOH = Na_2ZrO_3 + Na_3SiO_3 + 2H_2O$
- $2U_3O_8 + O_2 + 18Na_2CO_3 + 6H_2O$ $= 6Na_4UO_2(CO_3) + 12NaOH$

Acids are stronger leaching agents

Pure oxides are precipitated from leach liquors

I have not gone into the details of how to produce the concentrates and produce the oxide. I have talked about leaching of the oxides and concentrates, either by acids or by alkali.

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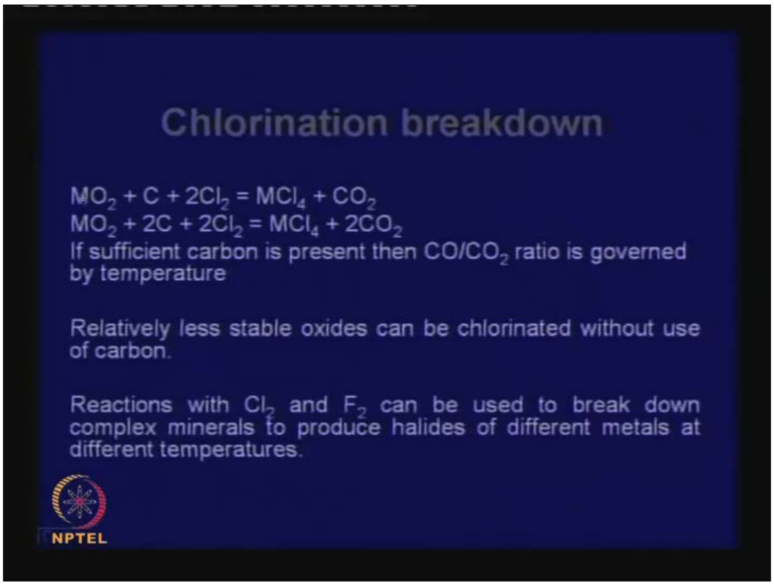

Chlorination breakdown

$MO_2 + C + 2Cl_2 = MCl_4 + CO_2$
$MO_2 + 2C + 2Cl_2 = MCl_4 + 2CO_2$
If sufficient carbon is present then CO/CO_2 ratio is governed by temperature

Relatively less stable oxides can be chlorinated without use of carbon.

Reactions with Cl_2 and F_2 can be used to break down complex minerals to produce halides of different metals at different temperatures.

And then, from the purified starting material, we can chlorinate to produce a chloride from which we will get the metal or we can also fluorinate. In the case of very stable oxides I have mentioned that, you need presence of carbon for chlorination without carbon, they cannot be chlorinated. Carbon is a kind of reducing agent, which we can we can visualize, the carbon first reduces the metal oxide and then, the metal reacts with chlorine to produce the vapour.

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Reduction of metal halides

- Metallothermic reduction of halides allows oxygen free operation and, therefore, superior metallic product.

Choice of reduction method will depend on

- Thermodynamic feasibility and kinetics
- The heat balance
- Melting and boiling points of constituents
- Densities of metal and slag

We have talked in detail about various metallothermic reactions. We can use metals, which produce very stable halides or oxides generally calcium or magnesium. We go for this route metallothermic reduction for some advantages which are listed that, if we are going for metallothermic reduction of halides, then we have an oxygen free reaction. So, the metal produced does not get re-oxidized, we get a superior product.

But the choice of metallothermic reduction depends on number of factors. First of all, the feasibility in terms of free energy change in the reaction, in terms of enthalpy change, so that we can tell whether the reaction itself is making available sufficiently. If not, we have to have a booster reaction, we have to put in another reaction that gives us supply heat; we have to worry about the melting points and boiling points of reactants and products to see, whether it allows easy handling or it is possible to do things under normal conditions. We also have to worry about separation of metal and slag big for cleaner recovery.

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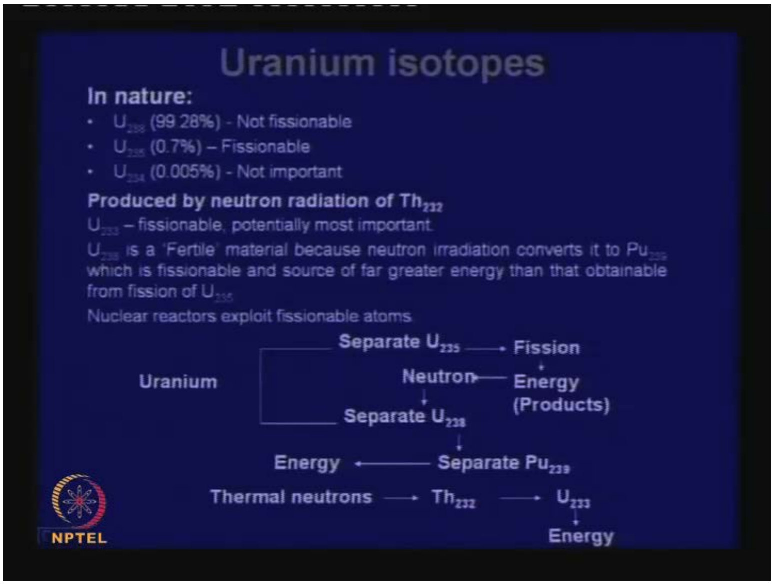

Uranium isotopes

In nature:

- U_{238} (99.28%) - Not fissionable
- U_{235} (0.7%) – Fissionable
- U_{234} (0.005%) - Not important

Produced by neutron radiation of Th_{232}

U_{233} – fissionable, potentially most important

U_{238} is a 'Fertile' material because neutron irradiation converts it to Pu_{239} which is fissionable and source of far greater energy than that obtainable from fission of U_{235}

Nuclear reactors exploit fissionable atoms

I went into a good bit of discussion on how we get nuclear energy. The vital element is uranium, without uranium we cannot have a nuclear energy program. Uranium has three isotopes of which only U 255 is fissionable, this (( )) which is so small in percentage you can ignore, U 238 is not fissionable, but you call it a fertile material, because it can be converted to a fissionable element plutonium 239.

So, from uranium we are getting a fissionable isotope and a and a fertile isotope which gives plutonium 239. Another isotope of uranium can be produced by neutron neutron irradiation of thorium, thorium 232 which will give uranium 233. That would be the most promising starting material for nuclear energy, why? Because, per neutron absorbed, uranium 233 produces more neutrons as compared to the fission of plutonium or uranium 235.

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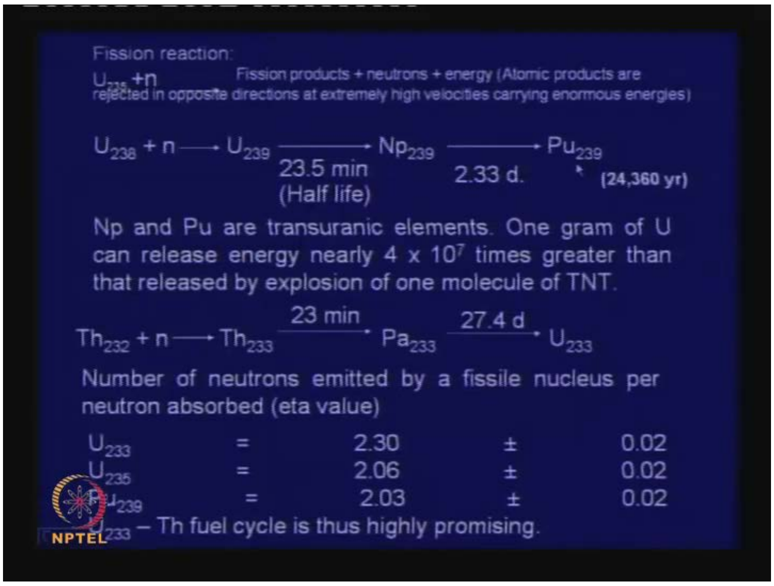

Fission reaction:

U_{235} +n Fission products + neutrons + energy (Atomic products are rejected in opposite directions at extremely high velocities carrying enormous energies)

$$U_{238} + n \longrightarrow U_{239} \xrightarrow[\substack{23.5\text{ min}\\(\text{Half life})}]{} Np_{239} \xrightarrow[2.33\text{ d.}]{} Pu_{239}\ (24{,}360\text{ yr})$$

Np and Pu are transuranic elements. One gram of U can release energy nearly 4 x 10^7 times greater than that released by explosion of one molecule of TNT.

$$Th_{232} + n \longrightarrow Th_{233} \xrightarrow{23\text{ min}} Pa_{233} \xrightarrow{27.4\text{ d}} U_{233}$$

Number of neutrons emitted by a fissile nucleus per neutron absorbed (eta value)

U_{233} = 2.30 ± 0.02

U_{235} = 2.06 ± 0.02

Pu_{239} = 2.03 ± 0.02

U_{233} – Th fuel cycle is thus highly promising.

This is called eta value that number of neutrons emitted by a fissile nucleus per neutron absorbed, for U 233 is 2.3, for U 235 is 2.06, U 239 is 2.06. Now, the point to notice, all the uranium 235 239 sorry plutonium 239 comes from uranium 238 by this reaction (Refer Slide Time: 23:59), it does not mean that all of uranium 238 will be will give rise to plutonium, as a matter of it only tiny fraction of uranium 235 will give uranium 239.

And there has to be elaborate chemicals steps and chemical engineering steps for recovering it from a complete, a huge evaluated mass, but we now have methods of those.

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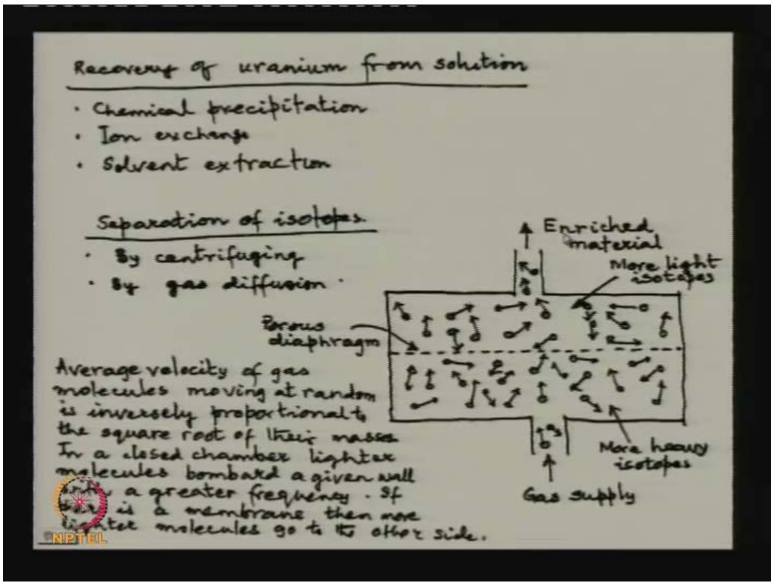

Recovery of uranium from solution

- Chemical precipitation
- Ion exchange
- Solvent extraction

Separation of isotopes.

- By centrifuging
- By gas diffusion.

Average velocity of gas molecules moving at random is inversely proportional to the square root of their masses. In a closed chamber lighter molecules bombard a given wall with a greater frequency. If there is a membrane then more lighter molecules go to the other side.

A very key thing is separation of the isotopes. And I have talked about centrifuging and gas diffusion, these two will separate uranium 235 for uranium 238, because their atomic weights are different. In gas diffusion, the idea is to have a gas supply which has both the isotopes in some in the form of volatile compound.

All the molecules are moving all over the place, but the lighter the lighter isotopes are lightly to (()) on a membrane more frequently and therefore, escape. So, from the other side of the membrane, we get an enriched material, which has more U 235 as compared to U U 2 239, this is one way.

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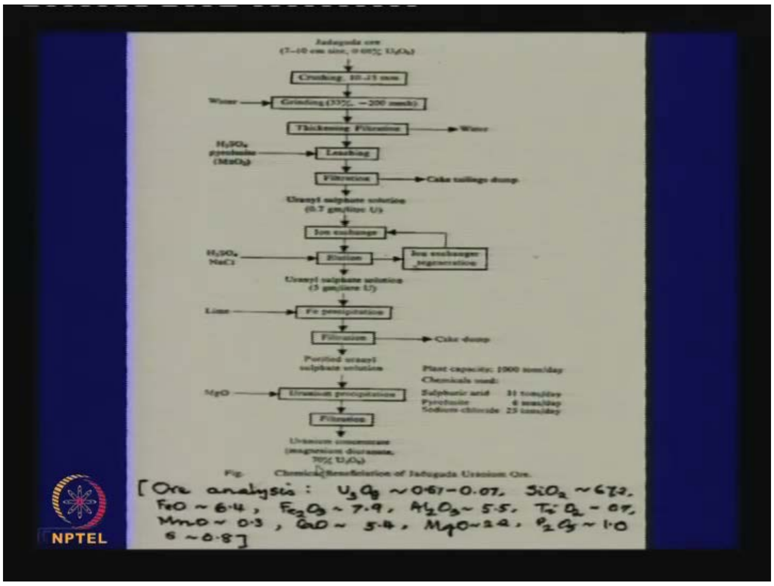

Fig. Chemical Beneficiation of Jaduguda Uranium Ore.

[Ore analysis: U_3O_8 ~0.67–0.07, SiO_2 ~67.2, FeO ~6.4, Fe_2O_3 ~7.9, Al_2O_3 ~5.5, TiO_2 ~0.7, MnO ~0.3, CaO ~5.4, MgO ~2.4, P_2O_5 ~1.0, S ~0.8]

Then, I have talked about the way we are treating uranium ore in Jaduguda mines, we are starting from something which is 0.08 percent U 3 O into C, how lean the ore is. But, yet from that we go through various steps to produce a concentrate, which is 70 percent U 3 O 2.

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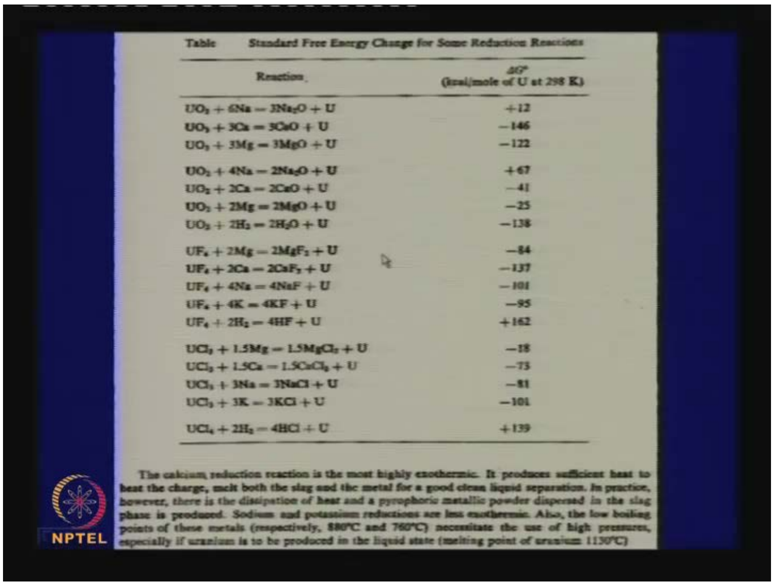

Table Standard Free Energy Change for Some Reduction Reactions

Reaction	ΔG° (kcal/mole of U at 298 K)
$UO_3 + 6Na = 3Na_2O + U$	+12
$UO_3 + 3Ca = 3CaO + U$	−146
$UO_3 + 3Mg = 3MgO + U$	−122
$UO_2 + 4Na = 2Na_2O + U$	+67
$UO_2 + 2Ca = 2CaO + U$	−41
$UO_2 + 2Mg = 2MgO + U$	−25
$UO_3 + 2H_2 = 2H_2O + U$	−138
$UF_4 + 2Mg = 2MgF_2 + U$	−84
$UF_4 + 2Ca = 2CaF_2 + U$	−137
$UF_4 + 4Na = 4NaF + U$	−101
$UF_4 + 4K = 4KF + U$	−95
$UF_4 + 2H_2 = 4HF + U$	+162
$UCl_3 + 1.5Mg = 1.5MgCl_2 + U$	−18
$UCl_3 + 1.5Ca = 1.5CaCl_2 + U$	−73
$UCl_3 + 3Na = 3NaCl + U$	−81
$UCl_3 + 3K = 3KCl + U$	−101
$UCl_4 + 2H_2 = 4HCl + U$	+139

The calcium reduction reaction is the most highly exothermic. It produces sufficient heat to heat the charge, melt both the slag and the metal for a good clean liquid separation. In practice, however, there is the dissipation of heat and a pyrophoric metallic powder dispersed in the slag phase is produced. Sodium and potassium reductions are less exothermic. Also, the low boiling points of these metals (respectively, 880°C and 760°C) necessitate the use of high pressures, especially if uranium is to be produced in the liquid state (melting point of uranium 1130°C)

And only when you have that that, again further purification will produce a pure oxide; from that, we can produce a fluoride or chloride. And then, we can think of reducing by some metal by the oxide or the fluoride. There we have to take in to account, where free energy change is more, where the enthalpy, the exothermic heat available is more and of course, the physical conditions of the reducing reductant product, etcetera.

I have mentioned that, when a reaction is not feasible, we can drive it to the right by either dissolving the metal in the form of an alloy or taking out the salt that is being produced in solution in a flux.

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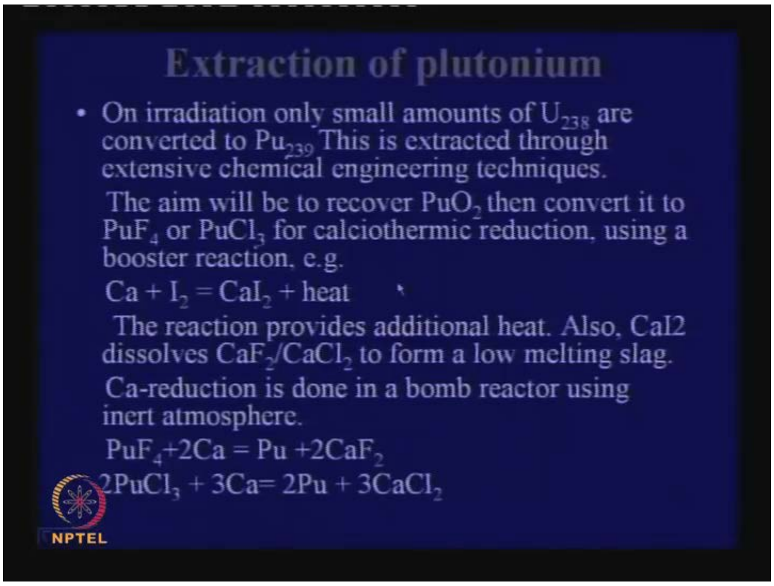

Extraction of plutonium

- On irradiation only small amounts of U_{238} are converted to Pu_{239} This is extracted through extensive chemical engineering techniques.

The aim will be to recover PuO_2 then convert it to PuF_4 or $PuCl_3$ for calciothermic reduction, using a booster reaction, e.g.

$Ca + I_2 = CaI_2 + heat$

The reaction provides additional heat. Also, CaI2 dissolves $CaF_2/CaCl_2$ to form a low melting slag.

Ca-reduction is done in a bomb reactor using inert atmosphere.

$PuF_4 + 2Ca = Pu + 2CaF_2$

$2PuCl_3 + 3Ca = 2Pu + 3CaCl_2$

There are applications of this in different cases, I will come to that. And when there is not enough heat available, we will produce (( )) something called a booster reaction. There are many many many reactions possible, the one booster reaction is add calcium and iodine, it will produce calcium iodide; give heat and this calcium iodide would also would act as a flux to dissolve the salt, that comes out of metallothermic reduction.

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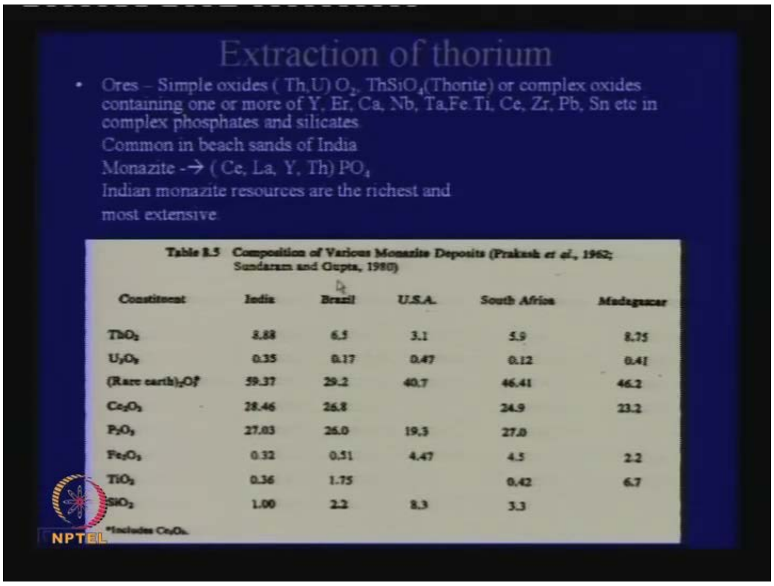

Extraction of thorium

- Ores – Simple oxides (Th,U) O_2, $ThSiO_4$(Thorite) or complex oxides containing one or more of Y, Er, Ca, Nb, Ta,Fe Ti, Ce, Zr, Pb, Sn etc in complex phosphates and silicates

  Common in beach sands of India

  Monazite -→ (Ce, La, Y, Th) PO_4

  Indian monazite resources are the richest and most extensive

Table 8.5 Composition of Various Monazite Deposits (Prakash *et al.*, 1962; Sundaram and Gupta, 1980)

Constituent	India	Brazil	U.S.A.	South Africa	Madagascar
ThO_2	8.88	6.5	3.1	5.9	8.75
U_3O_8	0.35	0.17	0.47	0.12	0.41
$(Rare\ earth)_2O_3^*$	59.37	29.2	40.7	46.41	46.2
Ce_2O_3	28.46	26.8		24.9	23.2
P_2O_5	27.03	26.0	19.3	27.0	
Fe_2O_3	0.32	0.51	4.47	4.5	2.2
TiO_2	0.36	1.75		0.42	6.7
SiO_2	1.00	2.2	8.3	3.3	

*Includes Ce_2O_3.

We have given a flow sheet for recovery of plutonium from (()) fuel. Then, we had talked about started talking about thorium, which comes from beach sands. The beach sands, which are available all along the coastal line of India or the certain areas in the western coast and eastern coast very important deposits, are found in Kerala. And our thorium deposits are very very big, they are in the beach sands and in the beach sands, there are many many constituents.

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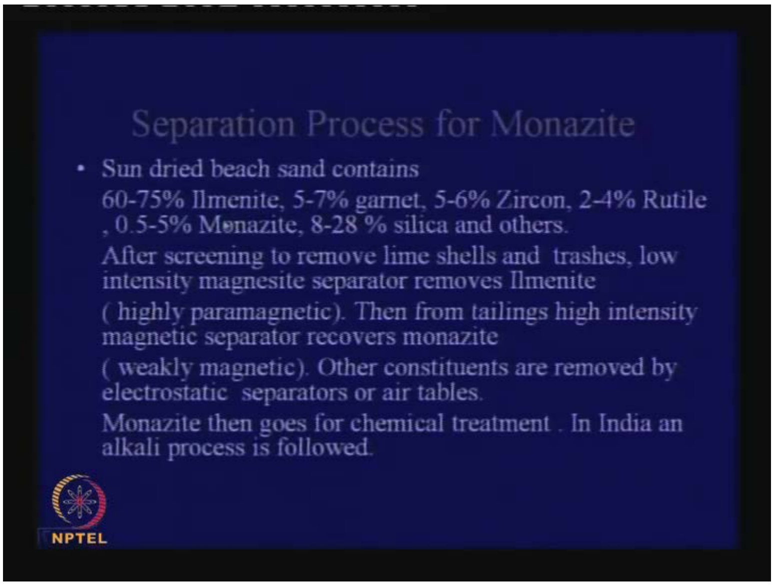

Separation Process for Monazite

- Sun dried beach sand contains

  60-75% Ilmenite, 5-7% garnet, 5-6% Zircon, 2-4% Rutile , 0.5-5% Monazite, 8-28 % silica and others.

  After screening to remove lime shells and trashes, low intensity magnesite separator removes Ilmenite (highly paramagnetic). Then from tailings high intensity magnetic separator recovers monazite (weakly magnetic). Other constituents are removed by electrostatic separators or air tables.

  Monazite then goes for chemical treatment . In India an alkali process is followed.

The constituents are mainly first ilmenite, then there is garnite, zircon, rutile, monazite, it is this monazite which has the thorium. We have industries trying to extract TiO 2 call synthetic rutile from ilmenite and we also are taking out the monazite fraction for extraction of thorium. We are not working on extraction of titanium as yet, but the beach sands provide us an important source for TiO 2 production and thorium production.

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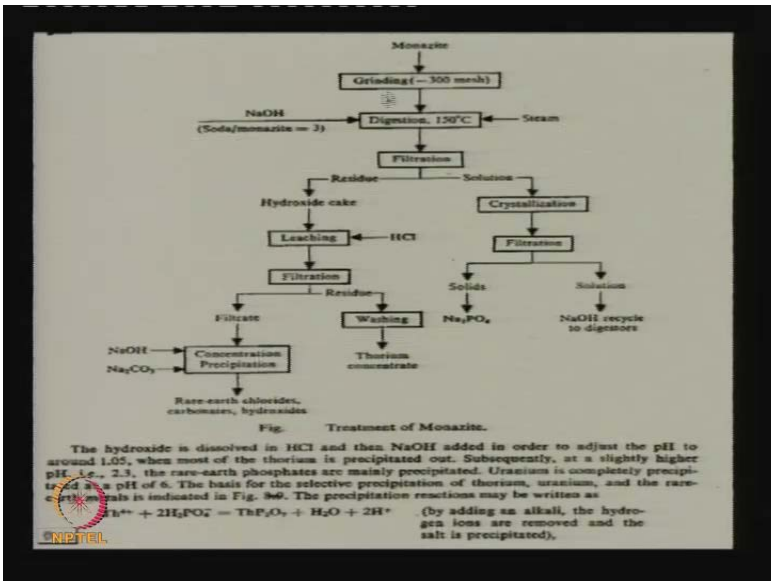

Fig. Treatment of Monazite.

The hydroxide is dissolved in HCl and then NaOH added in order to adjust the pH to around 1.05, when most of the thorium is precipitated out. Subsequently, at a slightly higher pH, i.e., 2.3, the rare-earth phosphates are mainly precipitated. Uranium is completely precipitated at a pH of 6. The basis for the selective precipitation of thorium, uranium, and the rare-earth metals is indicated in Fig. 9.9. The precipitation reactions may be written as

$Th^{4+} + 2H_2PO_4^- = ThP_2O_7 + H_2O + 2H^+$ (by adding an alkali, the hydrogen ions are removed and the salt is precipitated),

About treatment of monazite a flow sheet has been given. The thing that we need to note is in India, we do not follow an acid leaching process; we follow an alkali leaching process. The peculiarity of which is that, during leaching the metallic values will go into the insoluble, not in the soluble.

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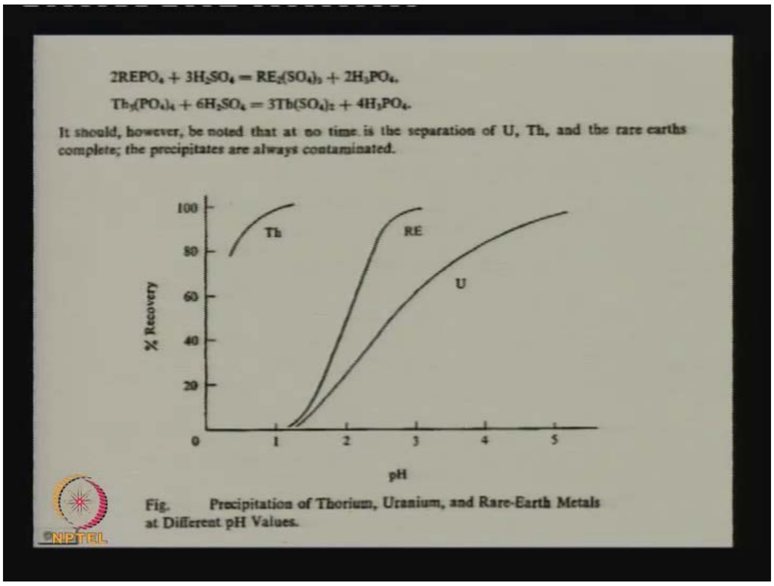

$2REPO_4 + 3H_2SO_4 = RE_2(SO_4)_3 + 2H_3PO_4.$

$Th_3(PO_4)_4 + 6H_2SO_4 = 3Th(SO_4)_2 + 4H_3PO_4.$

It should, however, be noted that at no time is the separation of U, Th, and the rare earths complete; the precipitates are always contaminated.

Fig. Precipitation of Thorium, Uranium, and Rare-Earth Metals at Different pH Values.

Then again if you produce pure T h O 2 we talk about reduction by various reductants and normally we will find this calcium reductant, reduction that is most favorable. Now here, T h O 2 being reduced by calcium can produce thorium; but if you produce introduce some calcium chloride in it, then the C a O produce by the reaction of calcium and T h O 2 will dissolve in calcium chloride. So, the activity of C a O will go down, the reaction will be driven to the right made more feasible.

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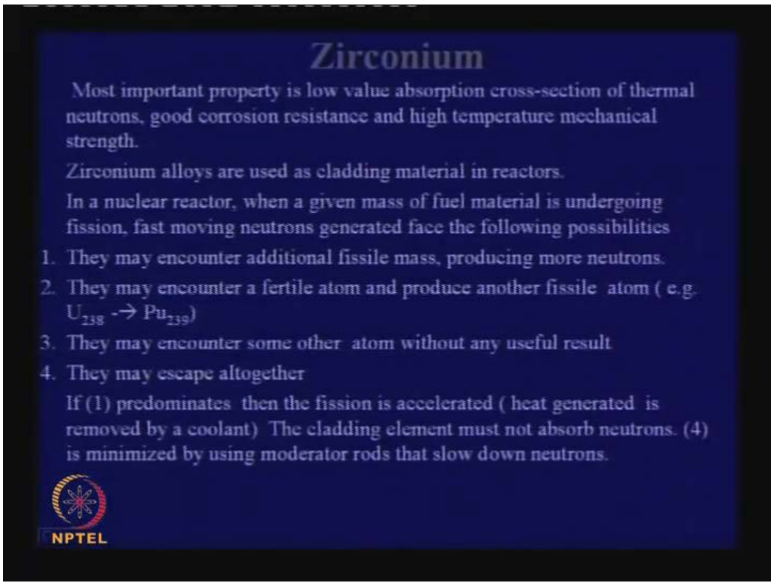

Zirconium

Most important property is low value absorption cross-section of thermal neutrons, good corrosion resistance and high temperature mechanical strength.

Zirconium alloys are used as cladding material in reactors.

In a nuclear reactor, when a given mass of fuel material is undergoing fission, fast moving neutrons generated face the following possibilities

1. They may encounter additional fissile mass, producing more neutrons.
2. They may encounter a fertile atom and produce another fissile atom (e.g. $U_{238} \rightarrow Pu_{239}$)
3. They may encounter some other atom without any useful result
4. They may escape altogether

If (1) predominates then the fission is accelerated (heat generated is removed by a coolant) The cladding element must not absorb neutrons. (4) is minimized by using moderator rods that slow down neutrons.

I have talked about the importance of zirconium. Zirconium is used as a cladding material in the reactors. A cladding material is, where the the fissionable material is kept and when during fission, neutrons are emitted; this cladding material will allow them to pass from one tube to another tube. So, in the pile, they can they can go from one place to another without being absorbed and being lost.

That's and also, zirconium is ideal, because it it it retains strength at high, not zirconium pure zirconium alloys, it will have high temperature resistance it will not the it will be able to withstand irradiation, it will not be corroded. And so there are many many advantages.

Now, during a nuclear fission reaction, what happens is, a mass splits into two nearly equal half which go in two directions with high velocities; small amount of mass is converted into energy, high velocity neutrons are emitted. And if this neutron can have phase four possibilities, they may escape additional fissile mass.

Now, they may encounter additional fissile mass producing more neutrons, they may encounter fertile atom produce a fissionable atom like from U 238 to U 239. They may encounter some other atom without any useful result or they may escape all together. Now, sometimes we need moderators to slow down the velocity of these neutrons, so that, they do not escape all together.

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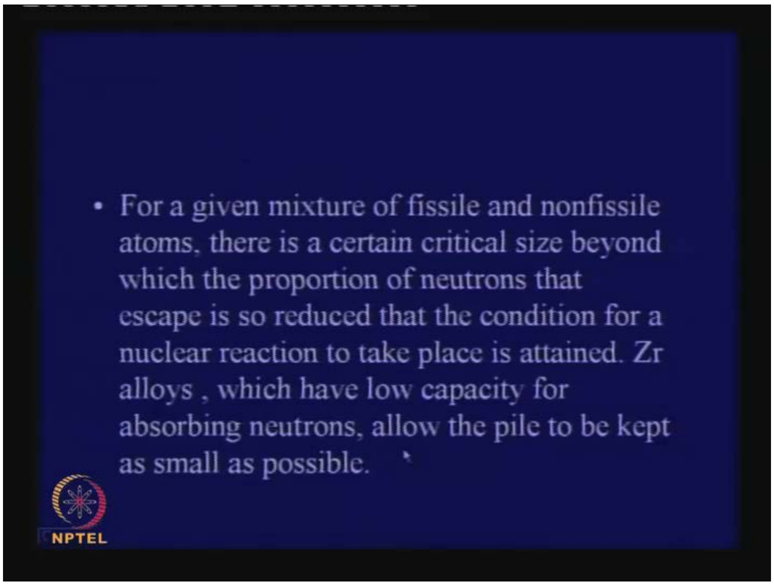

- For a given mixture of fissile and nonfissile atoms, there is a certain critical size beyond which the proportion of neutrons that escape is so reduced that the condition for a nuclear reaction to take place is attained. Zr alloys , which have low capacity for absorbing neutrons, allow the pile to be kept as small as possible.

And for a given mixture of fissile and non-fissile atoms, there is a certain critical size beyond which the proportional of neutrons that escape is so reduced that condition for a nuclear reaction to take place is attained. Zirconium alloys, which have low capacity for absorbing neutrons, allow the pile to be kept as small as possible.

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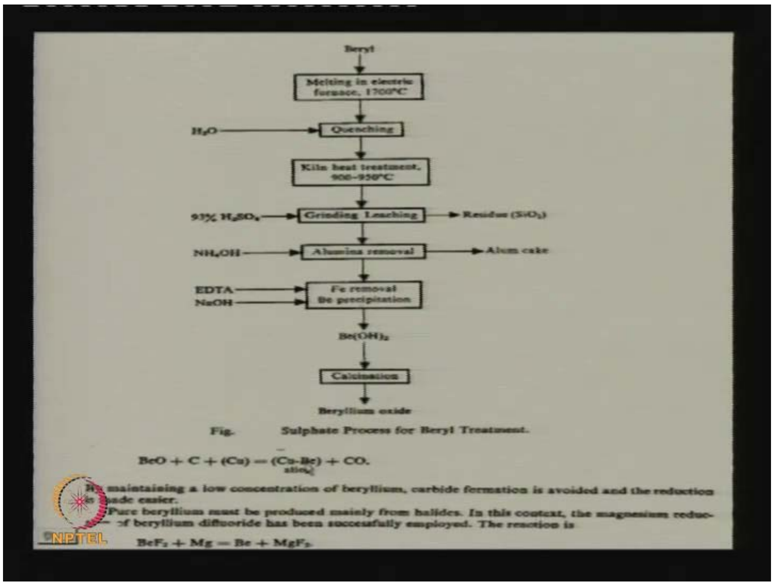

Fig. Sulphate Process for Beryl Treatment.

$$BeO + C + (Cu) = \underset{\text{alloy}}{(Cu\text{-}Be)} + CO.$$

By maintaining a low concentration of beryllium, carbide formation is avoided and the reduction is made easier.

Pure beryllium must be produced mainly from halides. In this context, the magnesium reduc-
of beryllium difluoride has been successfully employed. The reaction is

$$BeF_2 + Mg = Be + MgF_2.$$

I have given flow sheets for production of zirconium oxide, from zircon production of zirconium sponge and reduction of powder. And then, we have discussed beryllium, which is also a highly reactive metal. Beryllium oxide, if reduced by carbon as sufficiently high temperature will produce beryllium, but that will have carbon in it, because beryllium carbide also forms.

Now to avoid that, if we introduce copper in the system then instead of beryllium we produce copper beryllium alloy and because the beryllium activity is low, this reaction will go to the right will take place more favorably. And the advantages copper beryllium alloy finds application in industry. So, we have many advantages, through the presence of copper.

Free energy change for the reaction is made more negative, reaction moves to the right. The beryllium activity beings much low, beryllium carbide does not form and copper beryllium that we produce finds the application in industry readily. Here, the beryllium percentage actually is very small, it is mostly copper.

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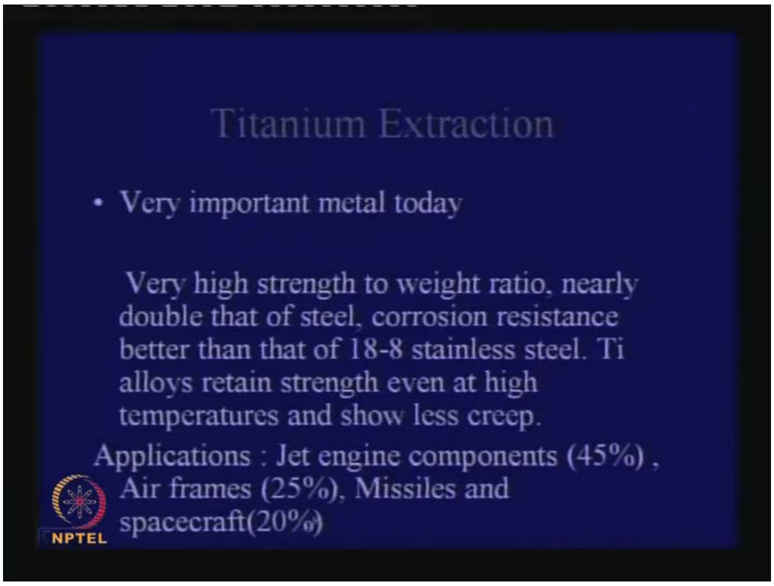

Titanium Extraction

- Very important metal today

Very high strength to weight ratio, nearly double that of steel, corrosion resistance better than that of 18-8 stainless steel. Ti alloys retain strength even at high temperatures and show less creep.

Applications : Jet engine components (45%), Air frames (25%), Missiles and spacecraft(20%)

Titanium needs special importance emphasis, because it is a very important metal. It has many properties that attract all metallurgist very high strength to weight ratio nearly double that of steel, then corrosion resistance better than 18-8 stainless steel. They retain strength even at high temperature and show less creep.

So, titanium aluminum alloys have become must in aerospace application. They are used in jet engine components, air frames, missiles and spacecrafts. But, we are not producing titanium, because the technology is not that easy.

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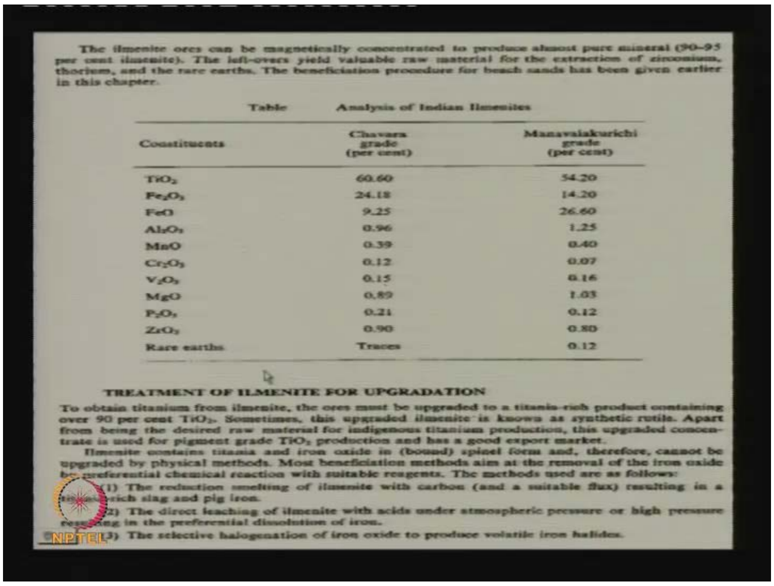

The ilmenite ores can be magnetically concentrated to produce almost pure mineral (90–95 per cent ilmenite). The left-overs yield valuable raw material for the extraction of zirconium, thorium, and the rare earths. The beneficiation procedure for beach sands has been given earlier in this chapter.

Table Analysis of Indian Ilmenites

Constituents	Chavara grade (per cent)	Manavalakurichi grade (per cent)
TiO_2	60.60	54.20
Fe_2O_3	24.18	14.20
FeO	9.25	26.60
Al_2O_3	0.96	1.25
MnO	0.39	0.40
Cr_2O_3	0.12	0.07
V_2O_5	0.15	0.16
MgO	0.89	1.03
P_2O_5	0.21	0.12
ZrO_2	0.90	0.80
Rare earths	Traces	0.12

TREATMENT OF ILMENITE FOR UPGRADATION

To obtain titanium from ilmenite, the ores must be upgraded to a titania-rich product containing over 90 per cent TiO_2. Sometimes, this upgraded ilmenite is known as synthetic rutile. Apart from being the desired raw material for indigenous titanium production, this upgraded concentrate is used for pigment grade TiO_2 production and has a good export market.

Ilmenite contains titania and iron oxide in (bound) spinel form and, therefore, cannot be upgraded by physical methods. Most beneficiation methods aim at the removal of the iron oxide by preferential chemical reaction with suitable reagents. The methods used are as follows:

(1) The reduction smelting of ilmenite with carbon (and a suitable flux) resulting in a titania-rich slag and pig iron.

(2) The direct leaching of ilmenite with acids under atmospheric pressure or high pressure resulting in the preferential dissolution of iron.

(3) The selective halogenation of iron oxide to produce volatile iron halides.

Now, I mention that India has ilmenite and given the analysis of two sources from which we can get ilmenite, these are beach sands. They can be very easily upgraded, because ilmenite is easily attracted by magnets. So, using low intensity magnetic separation we can make a concentrate.

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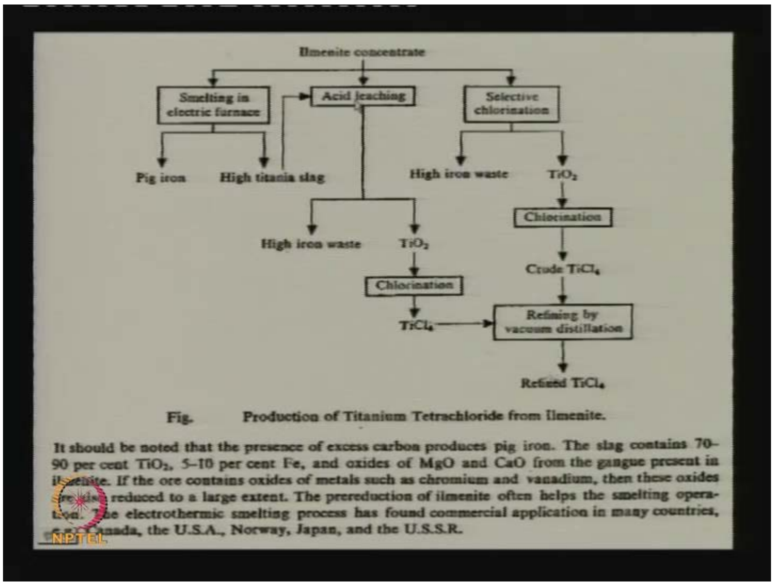

Fig. Production of Titanium Tetrachloride from Ilmenite.

It should be noted that the presence of excess carbon produces pig iron. The slag contains 70–90 per cent TiO_2, 5–10 per cent Fe, and oxides of MgO and CaO from the gangue present in ilmenite. If the ore contains oxides of metals such as chromium and vanadium, then these oxides are reduced to a large extent. The prereduction of ilmenite often helps the smelting operation. The electrothermic smelting process has found commercial application in many countries, [illegible] Canada, the U.S.A., Norway, Japan, and the U.S.S.R.

And then, there are three basic approaches to get titanium from TiO2 we are not following any of them that (( )) one can go straight for smelting in an electric furnace to produce pig iron, because it has Fe O, there the iron values recovered. Titania goes into slag titanium, so from which we have to produce a halide by chlorination.

By acid leaching, one can take out TiO 2 in solution, but then the iron part is wasted. If we go for selective chlorination, remove Fe O as a volatile chloride then, also the iron value is wasted. But, ultimately these two routes, the idea would be to produce a chloride titanium tetra chloride vapour. And then from that TiCl 2 vapour produce titanium either by magnesium reduction or sodium reduction.

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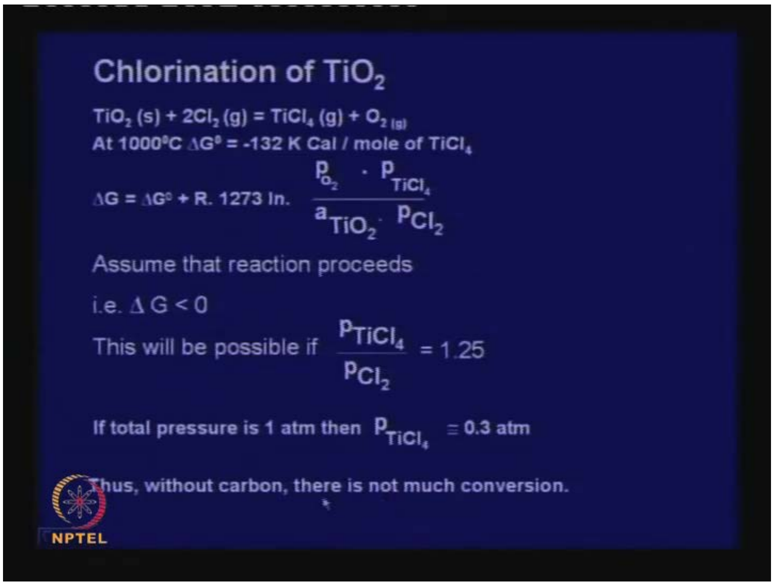

Chlorination of TiO_2

$TiO_2(s) + 2Cl_2(g) = TiCl_4(g) + O_{2(g)}$

At 1000°C $\Delta G^0 = -132$ K Cal / mole of $TiCl_4$

$$\Delta G = \Delta G^0 + R.\ 1273\ \ln.\ \frac{p_{O_2} \cdot p_{TiCl_4}}{a_{TiO_2} \cdot p_{Cl_2}}$$

Assume that reaction proceeds

i.e. $\Delta G < 0$

This will be possible if $\frac{p_{TiCl_4}}{p_{Cl_2}} = 1.25$

If total pressure is 1 atm then $p_{TiCl_4} \equiv 0.3$ atm

Thus, without carbon, there is not much conversion.

Now, I have given a simple example have to (( )) show that, if you consider TiO 2, 2 Cl 2 reaction and analyze it thermodynamically we will find that without carbon, there is not much conversion, but you will bring in carbon in the system then, this reaction goes far more to the right and there is lot more conversion.

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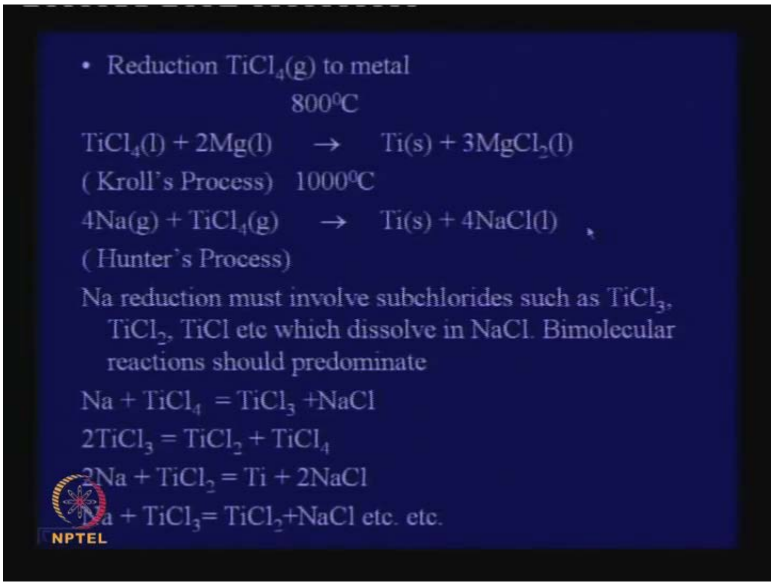

- Reduction $TiCl_4(g)$ to metal

$$TiCl_4(l) + 2Mg(l) \xrightarrow{800^0C} Ti(s) + 3MgCl_2(l)$$

(Kroll's Process)

$$4Na(g) + TiCl_4(g) \xrightarrow{1000^0C} Ti(s) + 4NaCl(l)$$

(Hunter's Process)

Na reduction must involve subchlorides such as $TiCl_3$, $TiCl_2$, TiCl etc which dissolve in NaCl. Bimolecular reactions should predominate

$Na + TiCl_4 = TiCl_3 + NaCl$

$2TiCl_3 = TiCl_2 + TiCl_4$

$2Na + TiCl_2 = Ti + 2NaCl$

$Na + TiCl_3 = TiCl_2 + NaCl$ etc. etc.

Reduction by magnesium is molecular in nature, but it is easier it takes place at a lower temperature. The product will be powdery it needs subsequent vacuum melting and for consolidation, sodium reduction is as a very interesting feature that it is essentially electrochemical in nature and that is why we get a good product. But, in the industry sodium reduction is not very popular.

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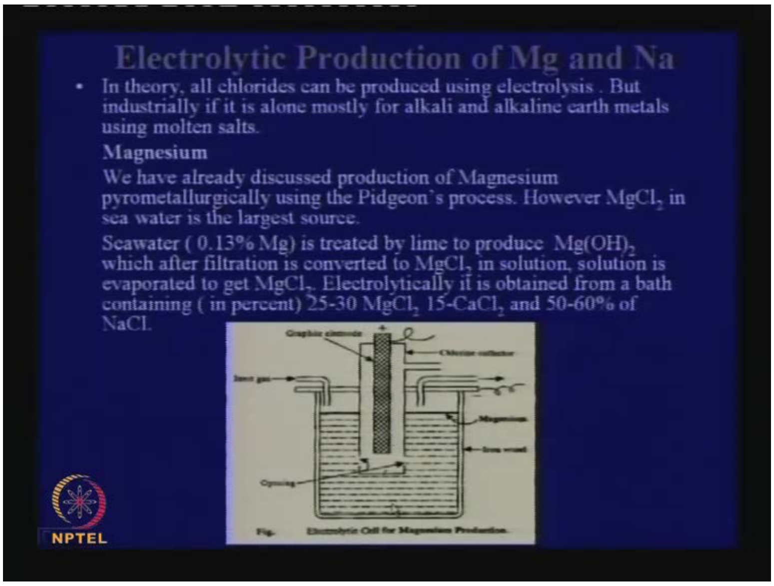

Electrolytic Production of Mg and Na

- In theory, all chlorides can be produced using electrolysis . But industrially if it is alone mostly for alkali and alkaline earth metals using molten salts.

Magnesium

We have already discussed production of Magnesium pyrometallurgically using the Pidgeon's process. However $MgCl_2$ in sea water is the largest source.

Seawater (0.13% Mg) is treated by lime to produce $Mg(OH)_2$ which after filtration is converted to $MgCl_2$ in solution, solution is evaporated to get $MgCl_2$. Electrolytically it is obtained from a bath containing (in percent) 25-30 $MgCl_2$ 15-$CaCl_2$ and 50-60% of NaCl.

Fig. Electrolytic Cell for Magnesium Production.

Essentially magnesium reduction is what is used and then whatever we get the thing would have to be consolidated. I ended that module by talking about magnesium electrolysis and sodium electrolysis; there I mention the special features of the electrolytic cells, which ensure that the metal released does not react with chlorine. In the case of magnesium, chlorine is released here it escapes, magnesium floats up it never comes and contact with chlorine.

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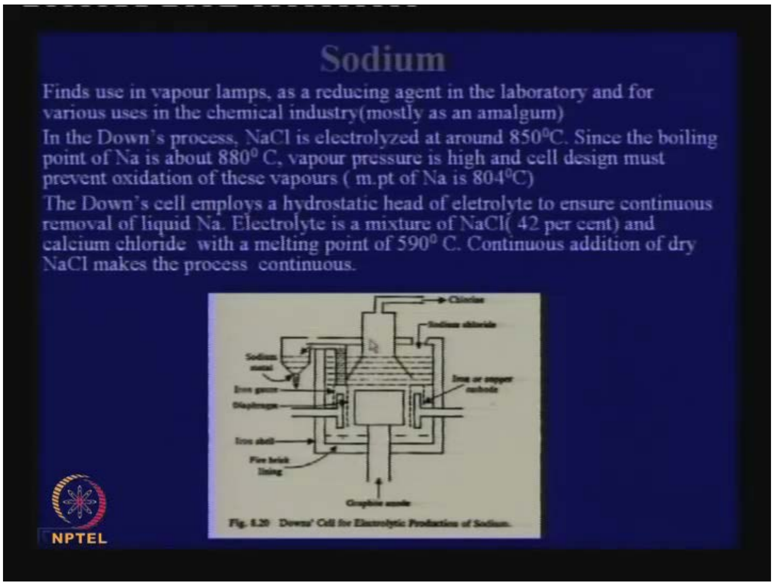

Sodium

Finds use in vapour lamps, as a reducing agent in the laboratory and for various uses in the chemical industry(mostly as an amalgum)

In the Down's process, NaCl is electrolyzed at around 850⁰C. Since the boiling point of Na is about 880⁰ C, vapour pressure is high and cell design must prevent oxidation of these vapours (m.pt of Na is 804⁰C)

The Down's cell employs a hydrostatic head of eletrolyte to ensure continuous removal of liquid Na. Electrolyte is a mixture of NaCl(42 per cent) and calcium chloride with a melting point of 590⁰ C. Continuous addition of dry NaCl makes the process continuous.

Fig. 8.20 Downs' Cell for Electrolytic Production of Sodium.

In the case of sodium, chlorine is released in the central graphite anode, if it escapes from there, magnesium goes out goes into an annular chamber where because its light it rises and hydrostatically it is taken out separated out, these are for sodium. So, actually the sodium never gets to react with chlorine.

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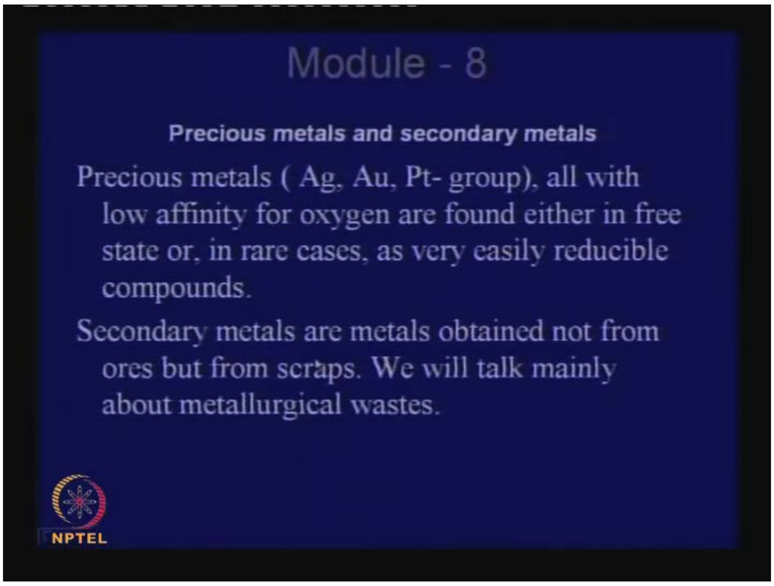

Module - 8

Precious metals and secondary metals

Precious metals (Ag, Au, Pt- group), all with low affinity for oxygen are found either in free state or, in rare cases, as very easily reducible compounds.

Secondary metals are metals obtained not from ores but from scraps. We will talk mainly about metallurgical wastes.

(( )) precious metals the point to note is, that here they are valued, because of many factors, there is of course some utility value, but more important is they have ornamental value prestige value and (( )). Gold has become a standard for financial conditions of all countries this has the highest extend value not so much as utility value, but because it shines forever it is attractive it has ornamental value it has prestige value.

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Precious Metals

- Gold is most attractive, worth being judged not in terms of rarity or usefulness
- Gold has ornamental value, prestige value and an exchange value. A symbol of wealth and power this metal is the basis of international monetary transactions.

Now, we have talked about the interesting properties of gold which makes it possible to make fine foils and plates. It goes for jewellery making to some extend that is true for silver also, platinum also.

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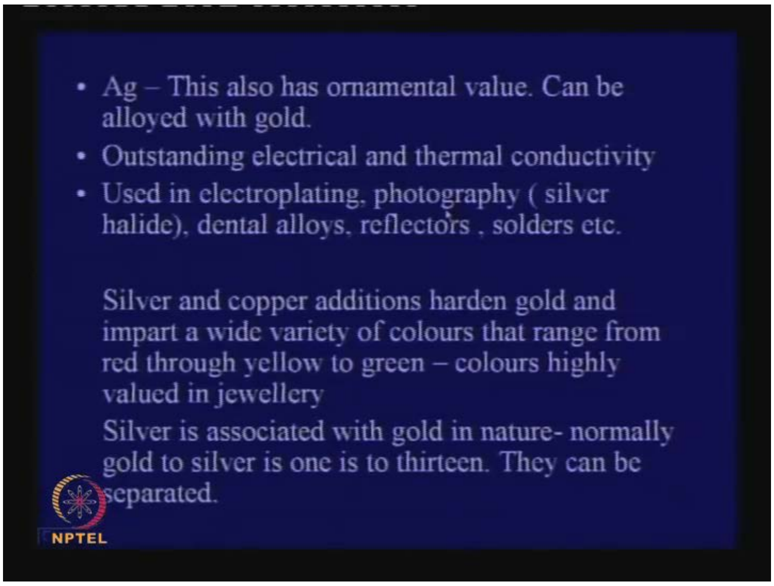

- Ag – This also has ornamental value. Can be alloyed with gold.
- Outstanding electrical and thermal conductivity
- Used in electroplating, photography (silver halide), dental alloys, reflectors , solders etc.

Silver and copper additions harden gold and impart a wide variety of colours that range from red through yellow to green – colours highly valued in jewellery

Silver is associated with gold in nature- normally gold to silver is one is to thirteen. They can be separated.

Silver has perhaps more utility value, because of its very electrical and thermal conductivity. It finds application in electricplating, photography, reflectors, dental alloys all kinds of things. And silver has to be there in gold to harden it and silver and copper can produce a range of colours from yellow to green in gold.

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Platinum Group

- High temperature melting point, resistance to corrosion and oxidation make the metals suitable for special applications (e.g. melting of salts and slags)

Other attractive properties – High ductility, low vapour pressure, low co-efficient of thermal expansion, high temperature coefficient of electrical resistivity.

As regards platinum group metals, we have they have the advantage of very high melting point, resistance to corrosion and oxidation. And in some special applications we need them without them it is not possible to melts salts and slags, which have high melting points and which have very corrosion.

There are other attractive properties also, which finds make them (( )) special applications in making thermo couples in containers that need high temperatures etcetera etcetera.

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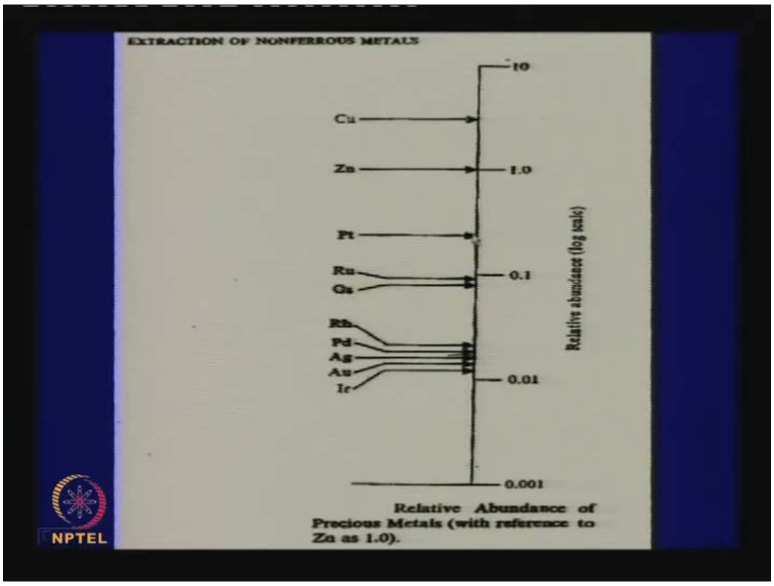

EXTRACTION OF NONFERROUS METALS

Relative Abundance of Precious Metals (with reference to Zn as 1.0).

I have shown a relative abundance of the precious metals and I indicated that platinum actually is relatively quite abundant as compared to say gold and silver, yet its prices is more, there are many reasons for it, but extracting platinum is not easy.

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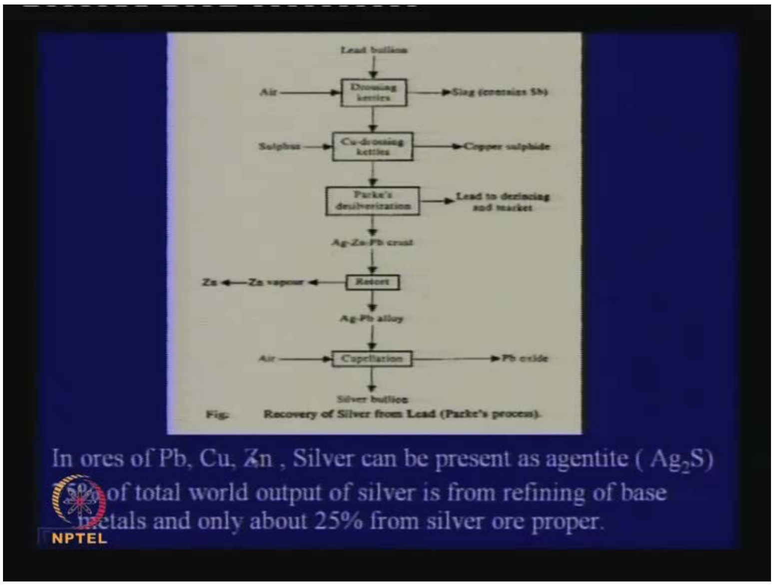

Fig. Recovery of Silver from Lead (Parke's process).

In ores of Pb, Cu, Zn , Silver can be present as agentite (Ag_2S) 50% of total world output of silver is from refining of base metals and only about 25% from silver ore proper.

I have talked about the cyanidation of gold earlier I would not do that again, we we are following gold extraction in Kolar gold fields through the cyanidation route. Silver can come from some ores, which have its which have mineral called (( )) 2 S Ag 2 S or some other thing which are not very stable, but it also is obtained from ores of lead copper and zinc it comes in the slimes during copper electro refining. It enters lead bullion and that lead bullion is the most important source for recovery of silver using Park's process which needs addition of zinc to molten lead.

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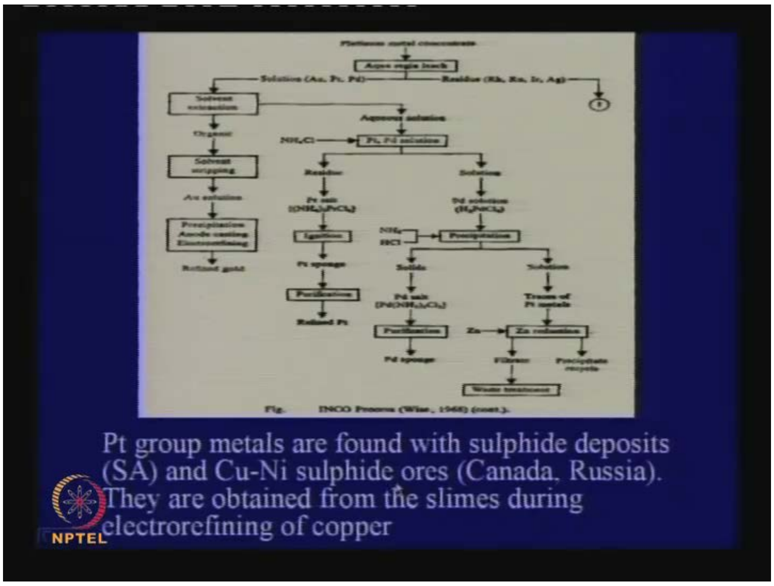

Fig. INCO Process (Wise, 1968) (cont.).

Pt group metals are found with sulphide deposits (SA) and Cu-Ni sulphide ores (Canada, Russia). They are obtained from the slimes during electrorefining of copper

I have talked about extraction of platinum group of metals from sulphide deposits of South African copper and nickel deposits in Canada and Russia I would not go through that now.

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Secondary Metals

Importance arises from the following

If scrap is recycled then environment is cleaned

Producing metals from scrap requires less energy

Does not cause depletion of primary resources

I have talked about the importance of secondary metals, that metals recovered from scrap and once you recovered that, we not only we clean the environment we get an access to metallic value, where there is lot more metal, then we have in ores and minerals. And if we can recycle more and more scrap, then we do not have the depletion of primary resources.

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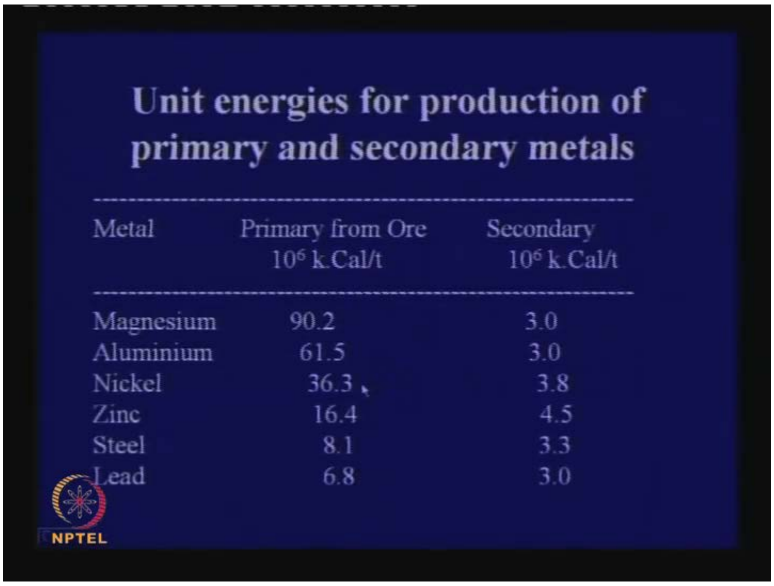

Unit energies for production of primary and secondary metals

Metal	Primary from Ore 10^6 k.Cal/t	Secondary 10^6 k.Cal/t
Magnesium	90.2	3.0
Aluminium	61.5	3.0
Nickel	36.3	3.8
Zinc	16.4	4.5
Steel	8.1	3.3
Lead	6.8	3.0

And obviously, producing the secondary metals required less energy than producing it from the primary sources.

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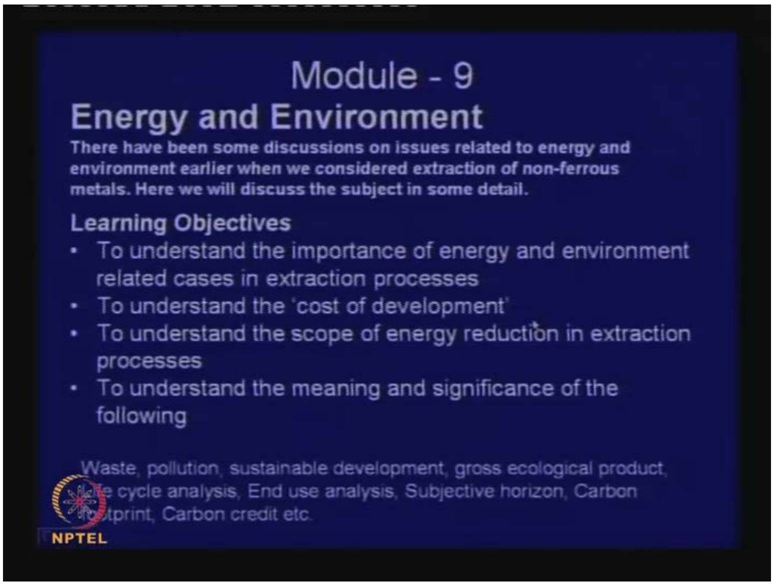

Module - 9

Energy and Environment

There have been some discussions on issues related to energy and environment earlier when we considered extraction of non-ferrous metals. Here we will discuss the subject in some detail.

Learning Objectives

- To understand the importance of energy and environment related cases in extraction processes
- To understand the 'cost of development'
- To understand the scope of energy reduction in extraction processes
- To understand the meaning and significance of the following

Waste, pollution, sustainable development, gross ecological product, life cycle analysis, End use analysis, Subjective horizon, Carbon footprint, Carbon credit etc.

Having discussed all that, I also talked little bit about extracting some metals from metallurgical wastes and treatment of metallurgical wastes that is a subject which can be discussed in this module also on energy and environment. I have delivered a number of lectures for this module, because I taught the subject is very important today.

And I have also said many things not directly related to non ferrous metals extraction. I believe the things have said that important; and anybody who is in a manufacturing industry or special if in a metal extraction industry should be aware of those issues. So, we our learning objectives were fairly wide in scope, importance of energy in environment. Then I have talked about cost of development that when we manufacture things when you have an industry operating, we want to develop the society by making available goods and services, we have to pay in some other way for that, that is the cost of development.

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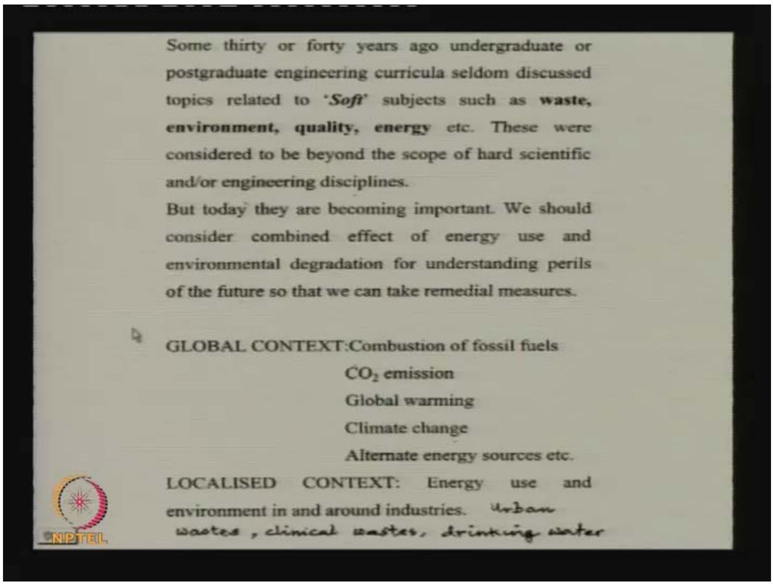

Some thirty or forty years ago undergraduate or postgraduate engineering curricula seldom discussed topics related to *'Soft'* subjects such as **waste, environment, quality, energy** etc. These were considered to be beyond the scope of hard scientific and/or engineering disciplines.

But today they are becoming important. We should consider combined effect of energy use and environmental degradation for understanding perils of the future so that we can take remedial measures.

GLOBAL CONTEXT:Combustion of fossil fuels
CO_2 emission
Global warming
Climate change
Alternate energy sources etc.

LOCALISED CONTEXT: Energy use and environment in and around industries. Urban wastes, clinical wastes, drinking water

And to understand that, we first have to think, what exactly is meant by pollution, contamination.

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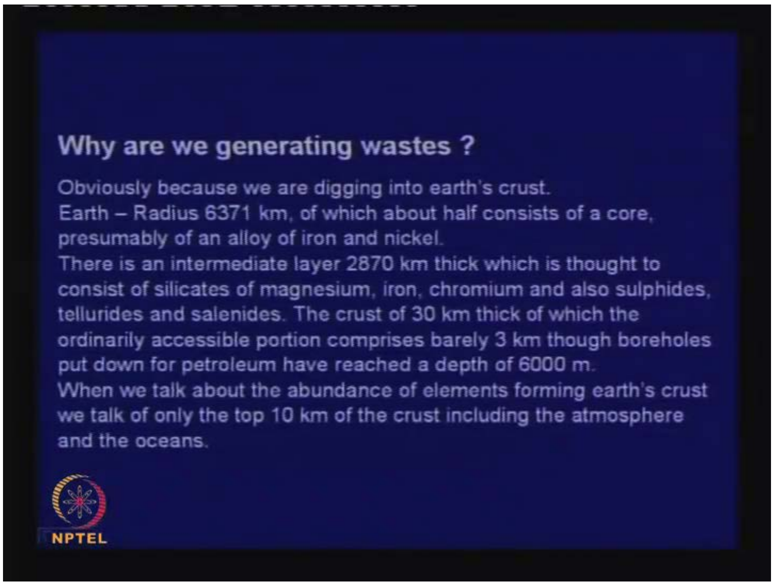

Why are we generating wastes ?

Obviously because we are digging into earth's crust.

Earth – Radius 6371 km, of which about half consists of a core, presumably of an alloy of iron and nickel.

There is an intermediate layer 2870 km thick which is thought to consist of silicates of magnesium, iron, chromium and also sulphides, tellurides and salenides. The crust of 30 km thick of which the ordinarily accessible portion comprises barely 3 km though boreholes put down for petroleum have reached a depth of 6000 m.

When we talk about the abundance of elements forming earth's crust we talk of only the top 10 km of the crust including the atmosphere and the oceans.

So, I have defined a number of terms starting with waste, then industrial waste I have discussed, why we are generating wastes? Because as our population grows as there is demand for development, there is demand for production to increase. When production increased necessarily, there will be environmental pollution unless you take extraordinary precautions.

And all that we are doing is coming by exploitation of resources of material that are available on the crust of earth, which is a few kilometers thick below that as of now we really cannot go.

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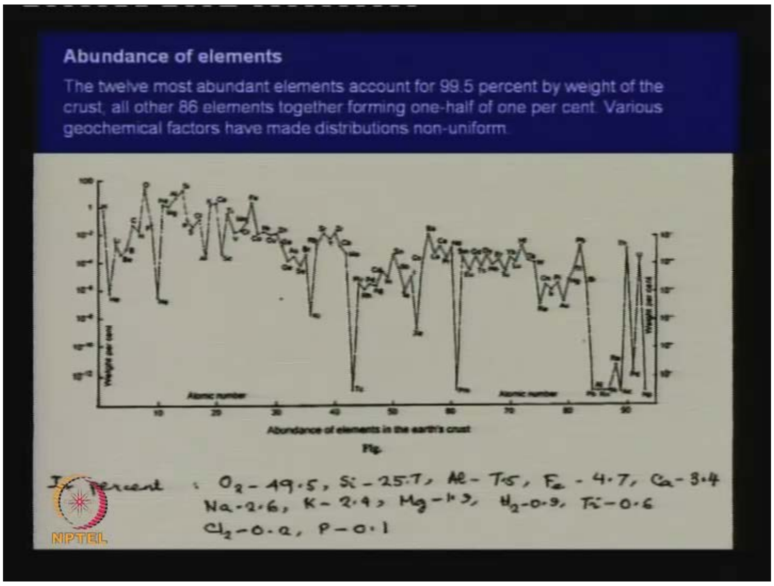

Abundance of elements

The twelve most abundant elements account for 99.5 percent by weight of the crust, all other 86 elements together forming one-half of one per cent. Various geochemical factors have made distributions non-uniform.

Abundance of elements in the earth's crust

Fig.

In percent : O_2 - 49.5, Si - 25.7, Al - 7.5, Fe - 4.7, Ca - 3.4
Na - 2.6, K - 2.4, Mg - 1.9, H_2 - 0.9, Ti - 0.6
Cl_2 - 0.2, P - 0.1

So, I went back to the relative abundance of metals to show which all metals are abundant and we found some 8 metals account for more than 90, 95 percent. And yet metals which on an average are not so abundant we get them, why? Because, they are they are concentrated in certain certain pockets had they had they not been concentrated, if all elements were uniformly distributed on the crust of the earth, it will very difficult to produce certain metals.

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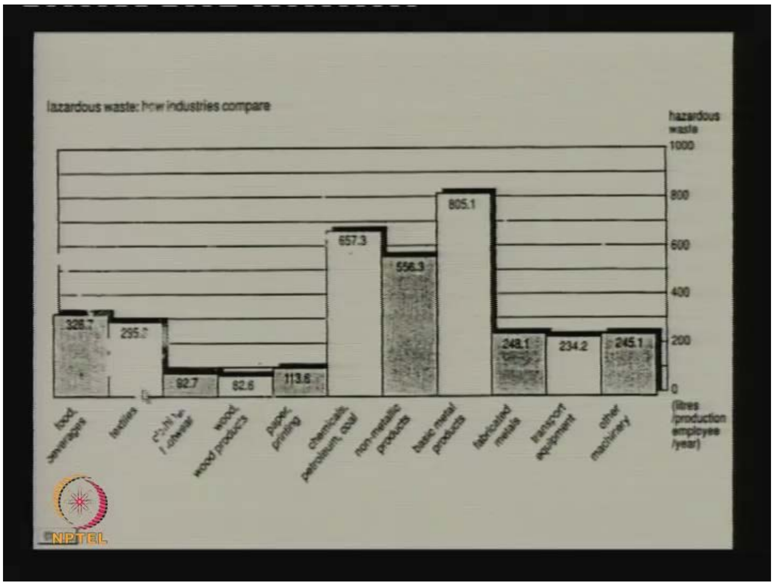

Now, the important thing to remember is, if we talk about production of hazardous wastes in various industries, industries connected with metal production or metallic products, generate the highest amounts of hazardous waste as compare to other industries like food and beverages, textiles or wooden products, paper, transport other machinery. So, the metal industries have to take special precautions.

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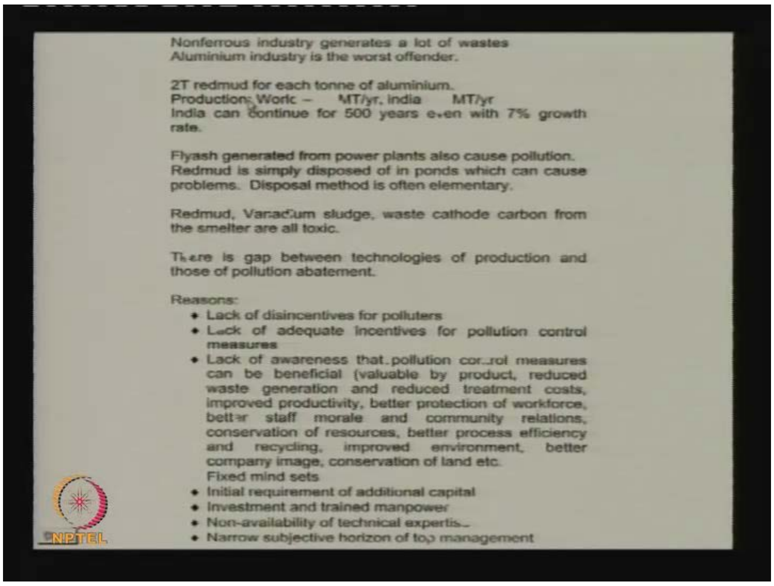

Nonferrous industry generates a lot of wastes
Aluminium industry is the worst offender.

2T redmud for each tonne of aluminium.
Production: Work – MT/yr, india MT/yr
India can continue for 500 years even with 7% growth rate.

Flyash generated from power plants also cause pollution.
Redmud is simply disposed of in ponds which can cause problems. Disposal method is often elementary.

Redmud, Vanadium sludge, waste cathode carbon from the smelter are all toxic.

There is gap between technologies of production and those of pollution abatement.

Reasons:

- Lack of disincentives for polluters
- Lack of adequate incentives for pollution control measures
- Lack of awareness that pollution control measures can be beneficial (valuable by product, reduced waste generation and reduced treatment costs, improved productivity, better protection of workforce, better staff morale and community relations, conservation of resources, better process efficiency and recycling, improved environment, better company image, conservation of land etc.
  Fixed mind sets
- Initial requirement of additional capital
- Investment and trained manpower
- Non-availability of technical expertise
- Narrow subjective horizon of top management

Just to give an example, the biggest culprit in non ferrous sector is the aluminum industry, which sometimes produces two tones of red mud for each ton of aluminum. This red mud as of now is really a waste, which is dumped in ponds that occupy large areas, we are we are not getting the land then for other uses; and red mud can also because, it has alkali have adverse consequences in the surrounding areas.

There I have given some figures about approximate wastes generated by selected non ferrous metal industries, I have shown how just the one or two industries is discharging, so many pollutants in the land and rivers all around.

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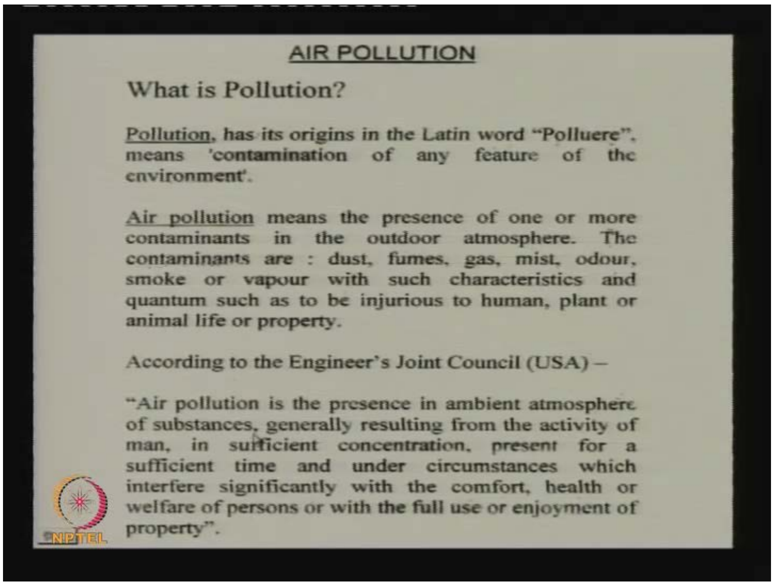

AIR POLLUTION

What is Pollution?

Pollution, has its origins in the Latin word "Polluere", means 'contamination of any feature of the environment'.

Air pollution means the presence of one or more contaminants in the outdoor atmosphere. The contaminants are : dust, fumes, gas, mist, odour, smoke or vapour with such characteristics and quantum such as to be injurious to human, plant or animal life or property.

According to the Engineer's Joint Council (USA) –

"Air pollution is the presence in ambient atmosphere of substances, generally resulting from the activity of man, in sufficient concentration, present for a sufficient time and under circumstances which interfere significantly with the comfort, health or welfare of persons or with the full use or enjoyment of property".

I went on to define the word pollution, air pollution. I given a very very good definition given by Engineer's Joint Council of U S A, where they said air pollution is the presence in ambient atmosphere of substances, generally resulting from activity of man, in sufficient concentration, present for sufficient time and under circumstances which interfere significantly with comfort, health or welfare of persons. So, comfort is also included or with the full use of enjoyment of property.

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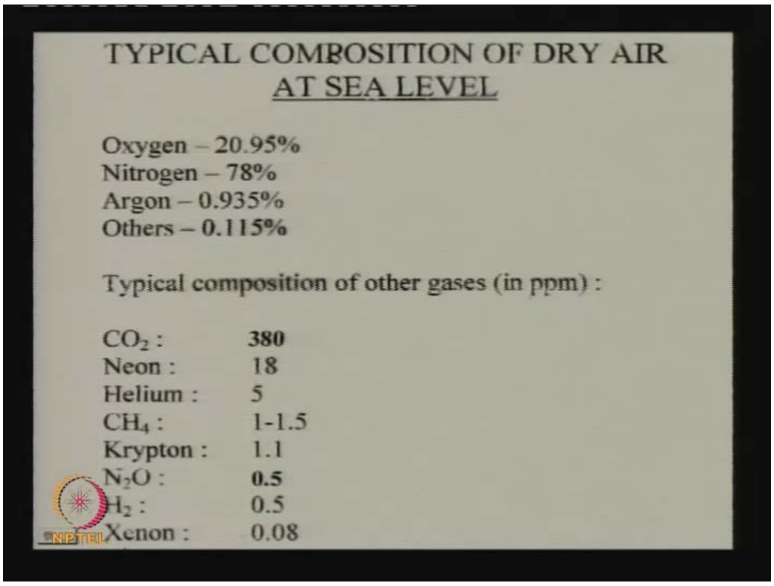

TYPICAL COMPOSITION OF DRY AIR AT SEA LEVEL

Oxygen – 20.95%
Nitrogen – 78%
Argon – 0.935%
Others – 0.115%

Typical composition of other gases (in ppm) :

CO_2 :	380
Neon :	18
Helium :	5
CH_4 :	1-1.5
Krypton :	1.1
N_2O :	0.5
H_2 :	0.5
Xenon :	0.08

So, when you talk about adverse effect we are not talking about adverse effect only on humans, animal’s plant kingdom property everything is included. We also talk about comfort and enjoyment. I have talked about the general adverse effects on health, because of pollution problems.

Then, this is important I have shown in the all activities in metal extraction processes starting from raw materials to secondary material processing; we are generating all kinds of wastes, some of which are toxic, some are not toxic, but the total volume is very very large.

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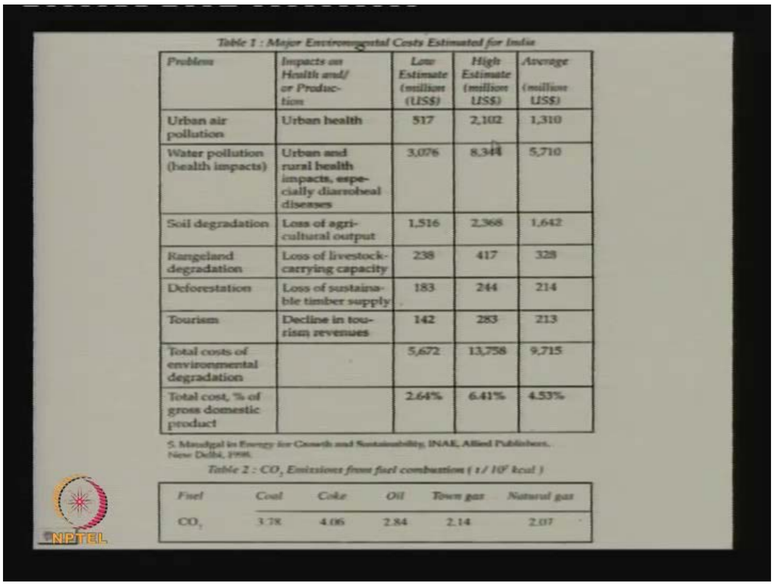

Table 1 : Major Environmental Costs Estimated for India

Problem	*Impacts on Health and/ or Production*	*Low Estimate (million (US$)*	*High Estimate (million US$)*	*Average (million US$)*
Urban air pollution	Urban health	517	2,102	1,310
Water pollution (health impacts)	Urban and rural health impacts, especially diarrhoeal diseases	3,076	8,344	5,710
Soil degradation	Loss of agricultural output	1,516	2,368	1,642
Rangeland degradation	Loss of livestock-carrying capacity	238	417	328
Deforestation	Loss of sustainable timber supply	183	244	214
Tourism	Decline in tourism revenues	142	283	213
Total costs of environmental degradation		5,672	13,758	9,715
Total cost, % of gross domestic product		2.64%	6.41%	4.53%

S. Maudgal in Energy for Growth and Sustainability, INAE, Allied Publishers, New Delhi, 1998.

Table 2 : CO_2 Emissions from fuel combustion (t / 10^6 kcal)

Fuel	*Coal*	*Coke*	*Oil*	*Town gas*	*Natural gas*
CO_2	3.78	4.06	2.84	2.14	2.07

And when we are generating all these we are creating an adverse impact on the society, and these impacts if we analyze properly we will find what is the financial implication of those impacts, impact on health impact, because of loss of agricultural output, loss of (( )) livestock carrying capacity etcetera etcetera.

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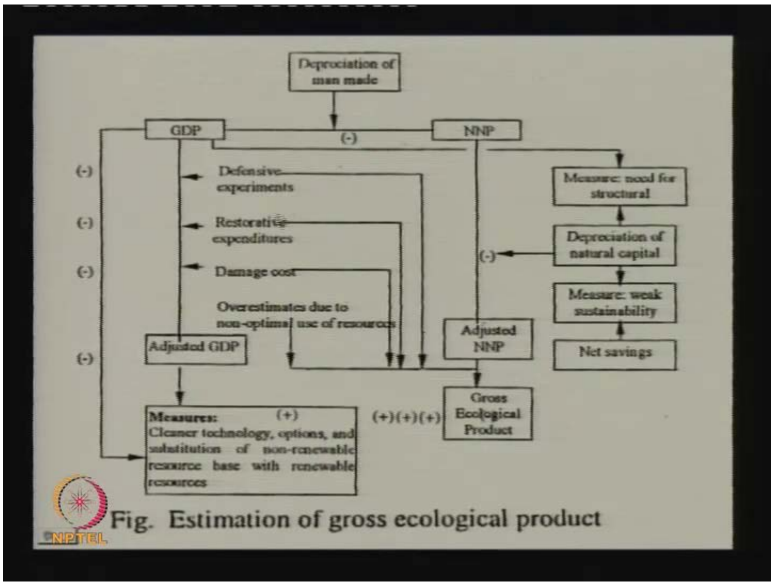

Fig. Estimation of gross ecological product

And then we I invoke the concept of that if we are talking about a GDP you have to take it out from that many many things defensive, expenditure on defensive steps, expenditure on restorative steps, damage to capital etcetera etcetera. And then you should calculate the gross ecological product.

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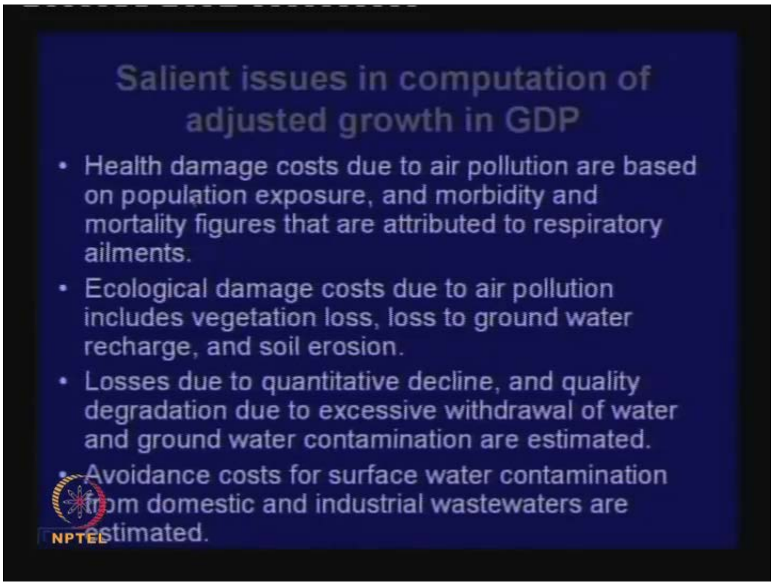

Salient issues in computation of adjusted growth in GDP

- Health damage costs due to air pollution are based on population exposure, and morbidity and mortality figures that are attributed to respiratory ailments.
- Ecological damage costs due to air pollution includes vegetation loss, loss to ground water recharge, and soil erosion.
- Losses due to quantitative decline, and quality degradation due to excessive withdrawal of water and ground water contamination are estimated.
- Avoidance costs for surface water contamination from domestic and industrial wastewaters are estimated.

And if we think of the cost of all kinds of damages to health human health, animal health, plant health, we talked about ecological damages etcetera etcetera.

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- Costs associated with land degradation are productivity losses of land mass under cultivation by assuming aggregate cropping patterns
- Loss of forest services / value is estimated based on charges in forest cover with recourse to the guidelines of the Ministry on benefit cost evaluation of projects involving diversion of forest land mass
- Biodiversity losses are not included in the estimation of total environmental and ecological losses
- Monetized value of natural resources used for growth in GDP not included in calculation.

We may see that, when we are talking about a growth it may be actually a negative growth, not many people are aware that, many such analysis have been done. They are debatable no doubt, but the central idea is very good, you are talking about progress, but you have to pay for that progress and sometimes you have to pay very heavily.

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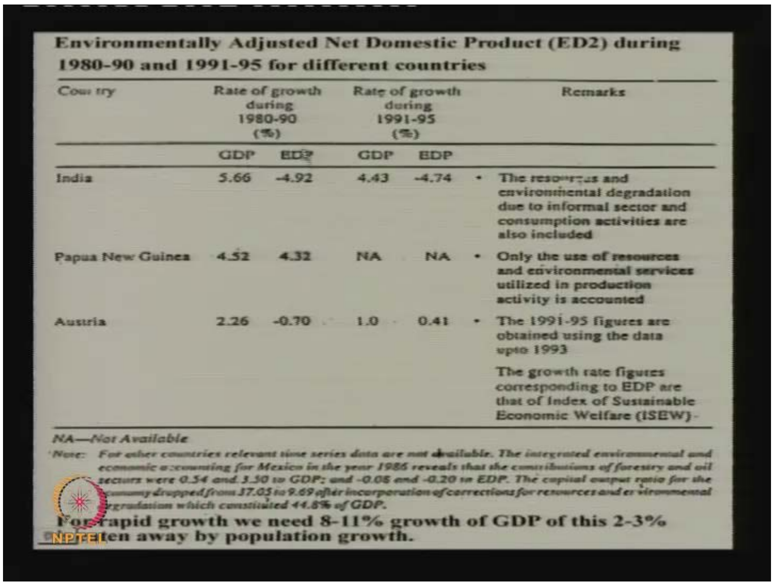

Environmentally Adjusted Net Domestic Product (ED2) during 1980-90 and 1991-95 for different countries

Country	Rate of growth during 1980-90 (%)		Rate of growth during 1991-95 (%)		Remarks
	GDP	EDP	GDP	EDP	
India	5.66	-4.92	4.43	-4.74	• The resources and environmental degradation due to informal sector and consumption activities are also included
Papua New Guinea	4.52	4.32	NA	NA	• Only the use of resources and environmental services utilized in production activity is accounted
Austria	2.26	-0.70	1.0	0.41	• The 1991-95 figures are obtained using the data upto 1993 The growth rate figures corresponding to EDP are that of Index of Sustainable Economic Welfare (ISEW)

NA—Not Available

Note: For other countries relevant time series data are not available. The integrated environmental and economic accounting for Mexico in the year 1986 reveals that the contributions of forestry and oil sectors were 0.54 and 3.50 to GDP; and -0.08 and -0.20 to EDP. The capital output ratio for the economy dropped from 37.05 to 9.69 after incorporation of corrections for resources and environmental degradation which constituted 44.8% of GDP.

For rapid growth we need 8-11% growth of GDP of this 2-3% eaten away by population growth.

I have given some figures again I said, they are debatable that in the 90's somebody showed that we were claiming more than 5 percent annual growth rate in GDP, but it was actually a minus figure if you took into account all the cost of the development.

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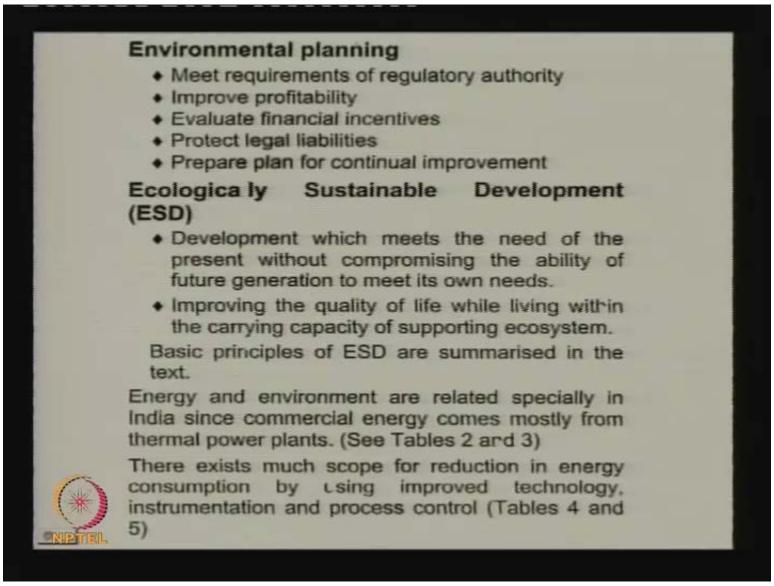

Environmental planning

- Meet requirements of regulatory authority
- Improve profitability
- Evaluate financial incentives
- Protect legal liabilities
- Prepare plan for continual improvement

Ecologica lly Sustainable Development (ESD)

- Development which meets the need of the present without compromising the ability of future generation to meet its own needs.
- Improving the quality of life while living within the carrying capacity of supporting ecosystem.

Basic principles of ESD are summarised in the text.

Energy and environment are related specially in India since commercial energy comes mostly from thermal power plants. (See Tables 2 ard 3)

There exists much scope for reduction in energy consumption by using improved technology, instrumentation and process control (Tables 4 and 5)

So, how do we handle the situation, for that we have to be smart, we have to think of ecologically sustainable development that we have development, but it must be sustainable ecologically.

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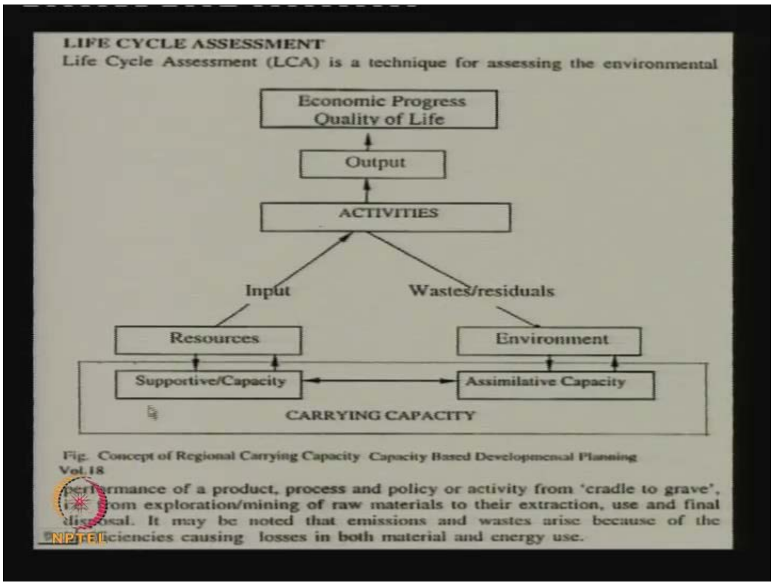

LIFE CYCLE ASSESSMENT

Life Cycle Assessment (LCA) is a technique for assessing the environmental

Fig. Concept of Regional Carrying Capacity Capacity Based Developmental Planning Vol.18

performance of a product, process and policy or activity from 'cradle to grave', i.e. from exploration/mining of raw materials to their extraction, use and final disposal. It may be noted that emissions and wastes arise because of the inefficiencies causing losses in both material and energy use.

And that is defined as that you enjoy life, but you also ensure that your future generation also enjoy the kind of life you are enjoying. So, like if you have a bank (( )) leave on interests not on capital. I have talked about carrying capacity, the sustainable development.

Then I have talked about analyze what we mean by development. And for sustainable development, we need to go for reuse, reduction of material use, recirculation both for materials (( )) energy. And we have to be aware of certain terms like life cycle assessment (( )) assessment and and after we have done that, I have given you some guidelines as to how in the industry, they introduce environmental policies, what are the procedures, they need to adopt? What are the environmental aspects you have to consider, and how they can quantify the effect on environment using some criteria.

And in terms of area affected, severity, duration, frequency and give a total score, because one we have a high score we have we have to be more careful. Then something about waste management, environment management system and environment management audit I have discussed. How we should produce in an industry.

I have taken example of the aluminium industry and I mentioned what is the local effect, what is the regional effect, what is the global effect, given some more details. And finally, I ended up by saying a few things which have been the basis of discussions in Copenhagen in Denmark recently, that we have to do something about CO 2 emission various countries are setting various targets mostly voluntary we still have not got a legal frame work. And everywhere, we have the talk about carbon footprint that has to be reduced people want to get carbon credit.

And I have said, it is possible to be smart and progress without increasing per capita energy consumption. And finally, I have ended my lecture by saying that, the time has come to very seriously think about making use of alternate energy sources better technologies like high pressure grinding roles you know grinding takes 3 to 4 percent of the energy use of the whole world. In mineral industries, copper industry 75 percent of the energy goes for grinding only. So, we must have better techniques, and I have given examples of how energy can be saved.

Then I have given two, three problems to discuss the concept of life cycle assessment. And I have ended by some remarks on nuclear reactors, because some countries are getting their energy supply, electricity supply by using nuclear reactors. And we have to depend perhaps more and more on nuclear reactors, because then we will have a CO 2 free source; not nuclear reactor, there could be many other alternate energy sources.

So, friends I have done, what I could in the course of this 40 40 odd lectures. I hope you have got some idea about the basic principles of non ferrous extraction and basic features of extraction of various metal extraction processes. I hope you are enthused enough to go back to some books, and read more about these things in the literature that is available; thank you very much.