Non-ferrous Extractive Metallurgy

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Module No. # 01

Lecture No. # 28

Extraction of reactor metals (Contd.)

Friends, we are discussing extraction of thorium.

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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.

Let us retrace our steps a bit. I have told you that, essentially to get thorium we have to process beach sands. Now, sun dried beach sands contain small amount of monazite; 0.5 to 5 percent, whole lot of Ilmenite, garnet, zircon, silica and many other things.

And, after we are screened to remove lime shells and trashes, low intensity magnetic separator remove removed Ilmenite, which is highly magnetic. Then, lower intensity magnetic separator will recover monazite. Sorry, the other way, the low intensity magnetic separator will remove Ilmenite, which is highly paramagnetic. And then from the tailings, high intensity magnetic separator removes monazite which is weakly magnetic. Then the other constituents are removed by electrostatic separators, air tables and other things, etcetera, etcetera.

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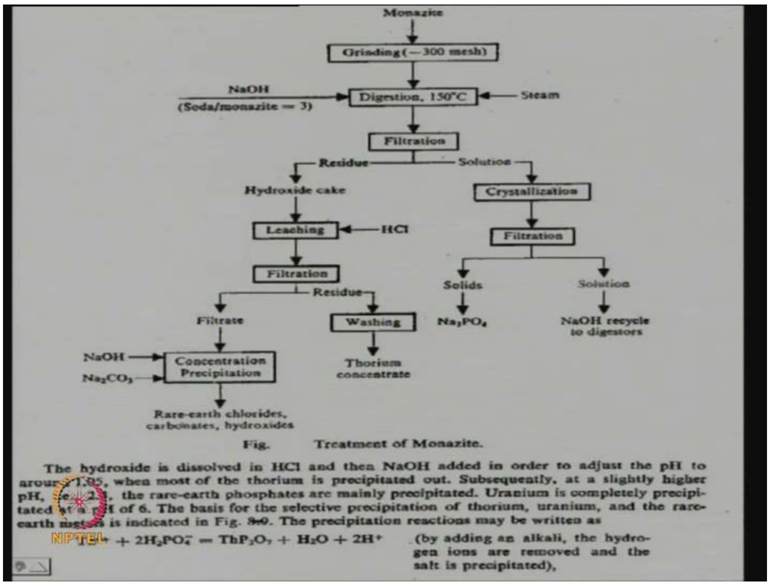

Fig. Treatment of Monazite.

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.[illegible], 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. 8·0. The precipitation reactions may be written as

[illegible] $+ 2H_2PO_4^- = ThP_2O_7 + H_2O + 2H^+$ (by adding an alkali, the hydrogen ions are removed and the salt is precipitated),

The monazite in India; the concentrate is processed through the alkali leaching route. Here the peculiarity is, by leaching we do not take out thorium in the solution. Rather, we produce an insoluble cake, which would have the thorium easily soluble things that we do not want go into the solution from which we recover sodium hydroxide for recirculation.

From in cake after acid leaching, we separate the thorium concentrate. I also mentioned that when you have thorium ions, uranium ions, rare earth ions in solution, then we separate them by adjusting the pH.

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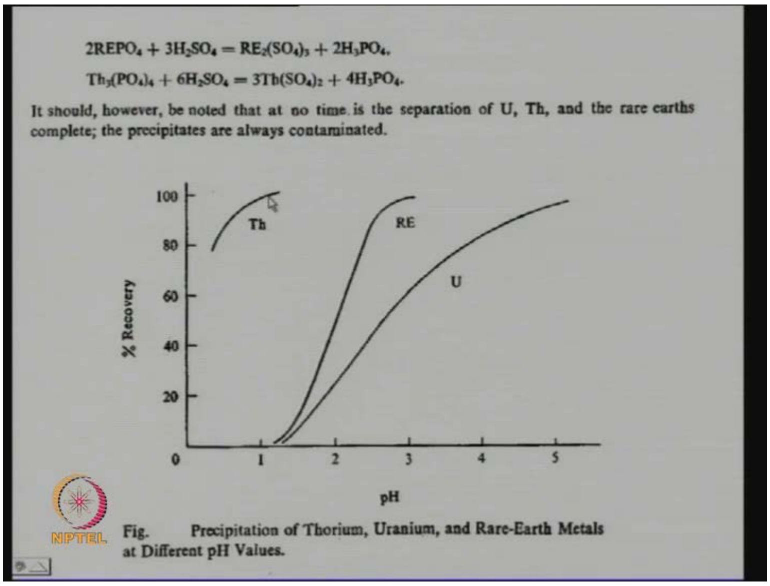

$2REPO_4 + 3H_2SO_4 = RE_2(SO_4)_3 + 2H_3PO_4.$

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

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.

And quite often, at the same pH more than one can precipitate. So, there can be a mixture of things. In the case of thorium, we can have high selectivity of thorium; provided, we keep the pH value very low.

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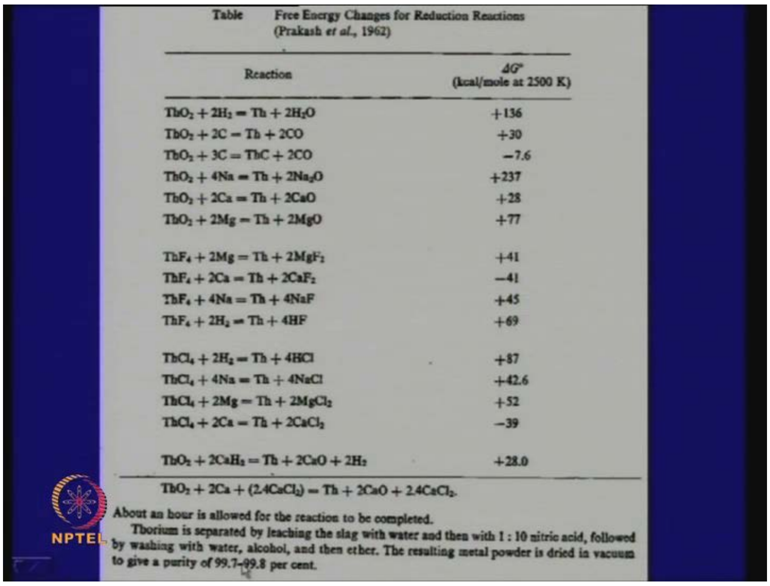

Table Free Energy Changes for Reduction Reactions (Prakash *et al.*, 1962)

Reaction	ΔG° (kcal/mole at 2500 K)
$ThO_2 + 2H_2 = Th + 2H_2O$	+136
$ThO_2 + 2C = Th + 2CO$	+30
$ThO_2 + 3C = ThC + 2CO$	−7.6
$ThO_2 + 4Na = Th + 2Na_2O$	+237
$ThO_2 + 2Ca = Th + 2CaO$	+28
$ThO_2 + 2Mg = Th + 2MgO$	+77
$ThF_4 + 2Mg = Th + 2MgF_2$	+41
$ThF_4 + 2Ca = Th + 2CaF_2$	−41
$ThF_4 + 4Na = Th + 4NaF$	+45
$ThF_4 + 2H_2 = Th + 4HF$	+69
$ThCl_4 + 2H_2 = Th + 4HCl$	+87
$ThCl_4 + 4Na = Th + 4NaCl$	+42.6
$ThCl_4 + 2Mg = Th + 2MgCl_2$	+52
$ThCl_4 + 2Ca = Th + 2CaCl_2$	−39
$ThO_2 + 2CaH_2 = Th + 2CaO + 2H_2$	+28.0

$ThO_2 + 2Ca + (2.4CaCl_2) = Th + 2CaO + 2.4CaCl_2.$

About an hour is allowed for the reaction to be completed.

Thorium is separated by leaching the slag with water and then with 1 : 10 nitric acid, followed by washing with water, alcohol, and then ether. The resulting metal powder is dried in vacuum to give a purity of 99.7–99.8 per cent.

So, there are ways and means of producing a pure thorium compound. And from that, we get thorium oxide or we can get a halide out of that. Now, we come back to the same question. As we had for extraction of uranium from its compound, how do you proceed to convert the oxide or the halide into the metal? An obvious thing would be metallothermic reaction.

Here are quite a few reactions and the free energy data for that. You know the guide lines. We will have to choose one that would have a negative free energy change. We will also like to have one, which as high exothermicity. And then, we have to worry about the state of the physical state of the reactants and products of the temperature of reaction.

Now, I have given here also some data for carbon reduction of thorium. And, as I keep on mentioning that, for reactive metals like uranium, thorium, plutonium, titanium, in theory carbon reduction is always possible; because if you go back to Ellingham diagrams we have discussed, carbon forms carbon monoxide which becomes increasingly stable as the temperature goes up. Whereas, all oxides becomes more and more unstable at temperature goes goes up.

So, somewhere there is a temperature where carbon monoxide is more stable than the metal oxide. Now for these stable oxides; very highly reactive metal oxides are very stable. But, if you go to high enough temperature, carbon can certainly reduce; so that, carbon monoxide will form taking out that oxygen from the oxide. But then, the problem here is, here if you see the reaction, thorium oxide plus carbon the carbide formation also has minus, delta g is minus means they form carbides.

So, we cannot go for carbon reduction. Of course, we have the similar problem in Ferro alloy productions. So, we had subsequent methods of removing carbon. This is too complicated. It is not desirable to go for a, to produce a carbide containing a metal and then worry about carbon removal. So, we will not touch the carbon reaction at all.

You find here, again here it is a calcium reduction of thorium fluoride which has a negative free energy change; means it is quite feasible as it is. Of course in all cases, we can make them more feasible. If we can dry the reaction to the right by either dissolving the metal or dissolving the other thing into solutions, so that the activities are less, reaction moves to the right.

We are looking at purely a pure compound, pure reductant, pure metal and pure soil being produced. So, it is quite obvious that calcium reduction is thermodynamically most attractive. You see, thorium tetrachloride being reduced by calcium also has a negative free energy change.

Now, we can help this reaction by introducing in the system some other salt to make a lower melting slide. For example, suppose you want to reduce T h O 2 by calcium, the reaction is here; T h O 2 calcium thorium 2Co, the free energy change is positive; means it looks thermodynamically not feasible.

But, suppose we introduce in this system some calcium chloride, so that the calcium oxide that is produced mixes with calcium chloride. In that case, the reaction will be feasible because the activity of calcium oxide will be less. It can move to the right. So, such such tricks we can try.

Provided, calcium oxide and calcium chloride mixed together, of course. Now, thorium oxide is often reduced by this reaction and about an hour is allowed for the reaction to be completed. Then finally, thorium can be separated by leaching the slag with water and then with 1: 10 nitric acid, followed by washing with water, alcohol and then ether. The resulting metal powder is dried in vacuum, and to give a purity of 99.7 to 99.8 percent. So, essentially we fall back on metallothermic reduction of a uranium compound, for a thorium compound, sorry.

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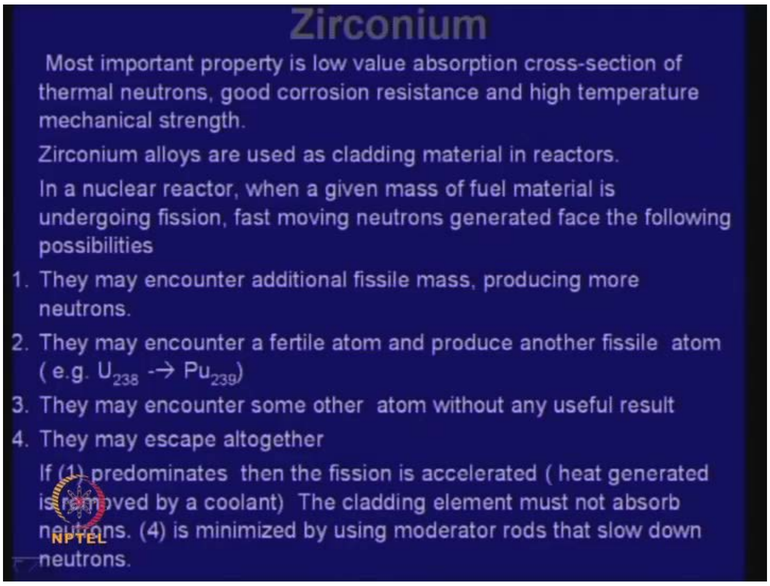

Zirconium

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} -→ 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.

Now, we leave thorium there. We move to zirconium. I had mentioned earlier that zirconium is also a reactor metal, although it has nothing to do with nuclear reactions. But, we call it a nuclear reactor metal because zirconium is vitally needed in the construction of nuclear reactors. We must understand why.

Now zirconium, of course has many applications. The alloys are used. There are alloys by zirconium is used. But, the most important property of zirconium that we want to exploit in nuclear reactors is low value absorption cross-section of thermal neutrons. What does that mean?

That means, when there is a nuclear reaction going on and neutrons are emitted, we do not want the neutrons to be absorbed and lost; because we want the neutrons to be available for carrying on more fission reaction. They should be available to go and impinge on another atom of a fissile atom, so that more neutrons are produced.

Now, when this… we have this fissile material, they have to be contain somewhere. Zirconium is an ideal container material. The fissionable material is contained in zirconium alloy tubes firstly because of low value absorption cross-section of thermal neutrons. It allows the neutrons to pass through. It does not absorb the neutrons. Secondly, it also has good corrosion resistance and high temperature mechanical strength.

So, all these make it an ideal material. Of course not pure zirconium, some other things are mixed with it to form an alloy which will stand high temperatures, which will not be corroded, which will not be which will stand all the radiations in the nuclear reactors. And most important, it will not absorb the neutrons because they would allow the neutrons to pass from one place to another, one pile to another pile to carry on the fission reaction.

Now, try to understand what happens in a nuclear reactor. In a nuclear reactor, when a given mass of fuel material is undergoing fission, fast moving neutrons generated face the following possibilities. They have been generated at one place by a fission reaction. Then, see what happens to these neutrons that have that have come out of the fission reactions.

First, they may encounter another additional fissile mass producing more neutrons. This is what we want for the fission reaction to be carried on. Whatever neutrons that have been made available by fission reaction we want; they should encounter additional fissile mass and produce more neutrons. And, this must go on.

There is a second possibility that the neutrons that have come up encounter a fertile atom, not a fissionable material. A fertile atom and produce another fissile atom. Like, when you are starting we cannot have pure uranium 235. You have an enriched material; uranium 235 as well as uranium 238. The neutrons if they impinge on addition uranium 235, more neutrons will be produced. But, instead of that, if the neutrons from efficient reaction impinge on uranium 238, then that uranium 238 gets converted to plutonium 239. So, the neutrons have achieved a useful function. It has not taken part into more fission reaction, but it has produced a fertile mass.

Now, it is possible that this neutrons may encounter some other atom without any useful result; means it goes and hits some other mass, which is neither fissionable nor it is a fertile materials. In case you are losing that neutron neutron, it does not serve any purpose.

There is a fourth possibility that the neutrons may escape altogether without serving useful purpose. It neither encounters a fissile mass to generate more neutrons. It does not encounter a fertile material to produce a fissionable in the mass. It is not lost into something useful, some other material. But, it simply escapes to system. It goes out of the system.

Now, if the first thing predominates; means one predominates, then the fission is accelerated because from one neutron, we are producing two neutrons; they are producing some more neutrons. The heat generated is removed by a coolant. This generates the lot of heat. Because every neutron, a every fission reactions; it means generation of neutrons, thermal neutrons also the fissile materials split into two equal masses, which going opposite directions with high energies. And this, there is a lot of heat generated by that process. The material in a cladding material like zirconium alloy; zirconium alloy stands that heat. But, at the same time we have to takeout that heat because that is the energy, which you are going to use from a nuclear reactor.

So, that is removed by a coolant. A liquid will flow all around the doors, tubes, which contain whereon when the nuclear fission reaction is taking place. That liquid will come out with all the energy heated form from which energy will be taken out. This could be heavy water; it could be other things.

The cladding element which is made of zirconium alloy must not absorb neutrons; because if it absorbs neutron it goes against the fission reactions. So, it must not absorb neutrons. What about this possibility? That, some neutrons may escape altogether; means there lot of tubes, cladding elements, where fission reaction is taking place. Coolant is flowing between them. Now, what happens if some neutrons escape altogether? We have to; we have to eliminate that possibility. To do that, there are some moderator rods that are inserted now and then. Their function is to slow down neutrons. Some neutrons which are moving so fast that it may escape the system. They are not allowed to escape the system. They are slowed down. So that, they eventually go on heat, another fertile mass or they go on heat a fissionable mass. They are not allowed to escape all together. They are slowed down by using a moderator. And, beryllium has that function. It can slow down the thermal neutrons. And, that is why it is also a nuclear material.

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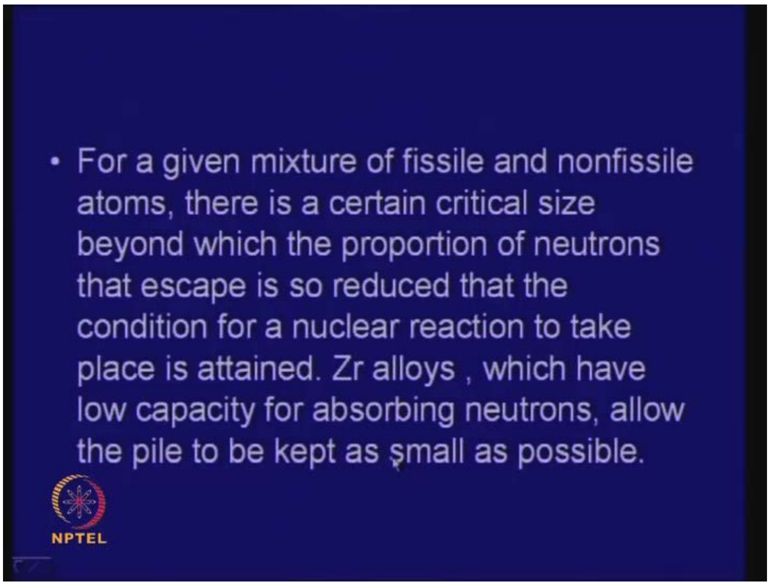

- For a given mixture of fissile and nonfissile atoms, there is a certain critical size beyond which the proportion of neutrons that escape is so reduced that the condition for a nuclear reaction to take place is attained. Zr alloys , which have low capacity for absorbing neutrons, allow the pile to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

Now, you never have a mass which is all fissile material. No, that is not possible. You can enrich a mixture of uranium 235 and 238, so that there is more uranium 235. It becomes a mixture of fissile and non fissile atoms. Uranium 238 is not fissile. From there, we will produce small amounts of uranium to plutonium 239 that will be fissionable, provided you can extract it and get a good amount of heat at one place. But, for a given mixture of fissile and non fissile 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.

You must understand that what makes a nuclear reaction possible. A nuclear reaction is possible when you are generating more and more neutrons very rapidly in an accelerated fashion. And, that will be ensured by non escape of neutrons out of the system. Whatever is being generated must be used to go on heat another fissile mass, so that more neutrons are created.

And, there is a certain critical size. If the size is too small, then no matter what you try. The thermal neutrons just do not have enough of mass around to get all absorbed. It will escape the system. So, there has to be a critical mass for a given mixture of fissile and non-fissile material. In that mass, it will now be possible to ensure that the neutrons do not escape all together. That will take part in fission reactions and there will be nuclear reactions. So, zirconium alloys which have low capacity of absorbing neutrons, allow the pile to be kept as small as possible because if the zirconium alloys were not there, then the piles cannot be that small.

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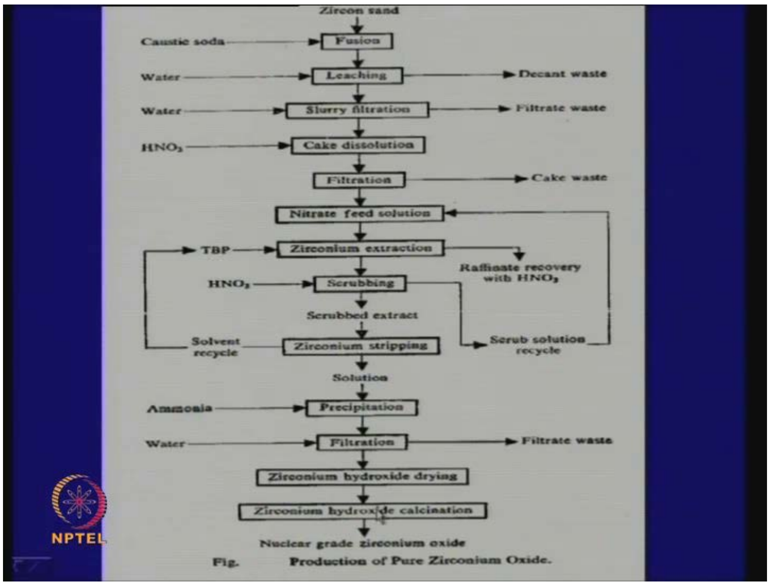

Fig. Production of Pure Zirconium Oxide.

Now, how do you produce pure zirconium oxide? It has to come from zircon sand. Again, here the technique is slightly different. We do not leach zircon sand by an alkali. This is a classical chemistry method that you fuse zircon sand with caustic soda. And, after we got a mass, solid mass, that will be leached. So, there is a solid state reaction followed by leaching. And then, of course we cannot waste. There will be a solid filtration, there will be a cake, which is basically a zirconium hydroxide that will go through some other steps like tributyl phosphate, solvent extraction method, some scrubbing, finally zirconium stripping, solution. Then, ammonia will finally precipitate a zirconium hydroxide, which will be dried to get zirconium hydroxide that will be calcined to produce pure grade zirconium oxide.

So, we are starting with zircon sand, made an alkali, fusion with alkali, a cake. That goes through some reactions and finally a solvent extraction process, so that, finally we produce nuclear grade zirconium oxide. So, these are the standard steps.

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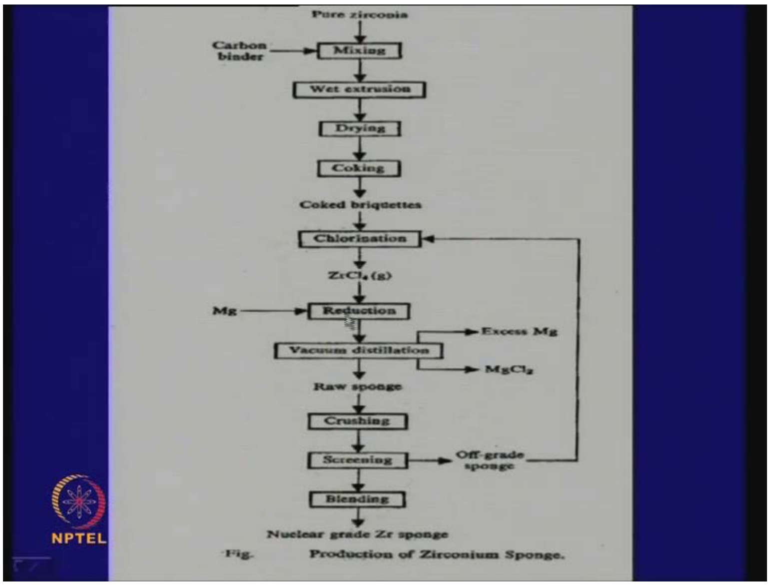

Fig. Production of Zirconium Sponge.

And, once you got pure zirconia, we can produce from that zirconium sponge metal. It is called zirconium sponge because it will have lot of holes, like your sponge iron. And finally, it has to be consolidated.

How do we produce this sponge? It is very simple. It will, with carbon binder there will be weight extrusion, drying, coking, coked briquettes. So, essentially we are reducing by carbon, zirconia Z r O 2 plus carbon. It will now be chlorinated. So, it is chlorinated in presence of carbon.

So, zirconium oxide; I have mentioned it is too stable on oxide, without carbon it cannot be chlorinated. In presence of carbon it will be chlorinated. We will find this carbon is coming from recirculation. We will produce zirconium tetrachloride gas. It will be reduced by magnesium in the gas phase.

And then finally, we will produce zirconium which will go for vacuum distillation to get rid of the excess magnesium that we have used in the reduction process. We get a raw sponge. It will be crushed, screened, then blending, a nuclear grade zirconium will come. And, from all this, half grade sponge will be re-circulated for chlorination.

So, again here, we have following a chlorination route. But, from the chloride we are going for again metallothermic reduction by magnesium. It is done in gas phase.

Zirconium tetrachloride gas may be after this magnesium gas. It has to be obviously done in a close reactor.

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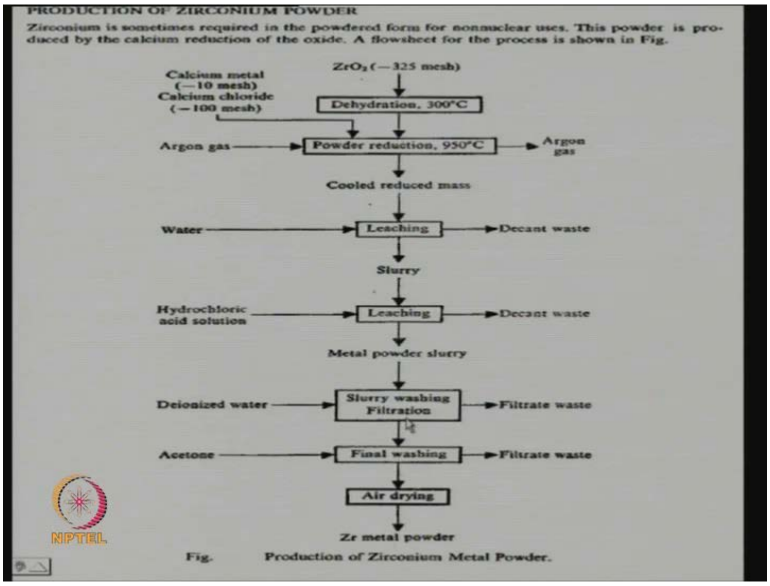

PRODUCTION OF ZIRCONIUM POWDER

Zirconium is sometimes required in the powdered form for nonnuclear uses. This powder is produced by the calcium reduction of the oxide. A flowsheet for the process is shown in Fig.

Fig. Production of Zirconium Metal Powder.

Sometimes, we produce zirconium powder. I will go through the steps just to; I do not think there is anything that needs any special mention. zirconium is sometimes required in the powdered form for non nuclear uses. This powder is used, produced by calcium reduction of the oxide. For nuclear grid, we went for magnesium reduction. Now, we are going for calcium reduction.

In a finely ground zirconium, after the dehydration, power reduction, powder reduction will be done by calcium metal in presence of calcium chloride. The same technique; so, it is a calcio thermal reduction in presence of calcium chloride. The calcium chloride is simply to produce a lower melting slag. So, it is to dry the reaction to the right. Then, the powder reduction will takes place around 950 degrees in argon gas. We have a cooled reduced mass, leaching, slurry. Again leaching by hydrochloric acid, we get metal powder slurry because you already have the zirconium in the reduced mass. The hydrochloric acid solution is simply taking away all the mud leading the metal powder.

And then, de-ionized water, final washing, air drying, zirconium metal powder. So, all these are examples of metallothermic reduction. Here, sometimes when magnesium in gas phase, sometimes by calcium in gas phase, we are adding calcium chloride to drive the reaction to the right. It is very simple principles of how you manipulate the free energy change for the reaction. If there is not enough heat, we have to supply heat. Otherwise, things can be can move on on their own.

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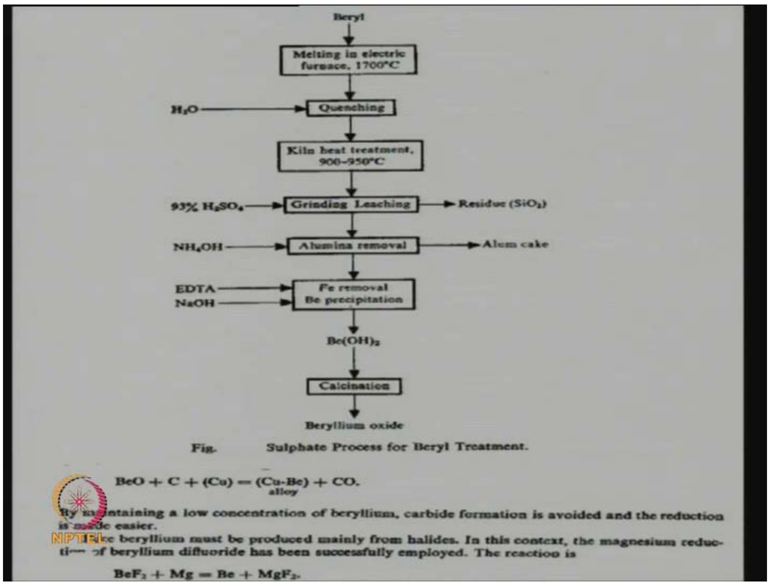

Fig. Sulphate Process for Beryl Treatment.

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

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

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

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

Now, we will come to the production of Beryllium. Now Beryl, I have… beryl is a… let me tell you what beryl the… yes.

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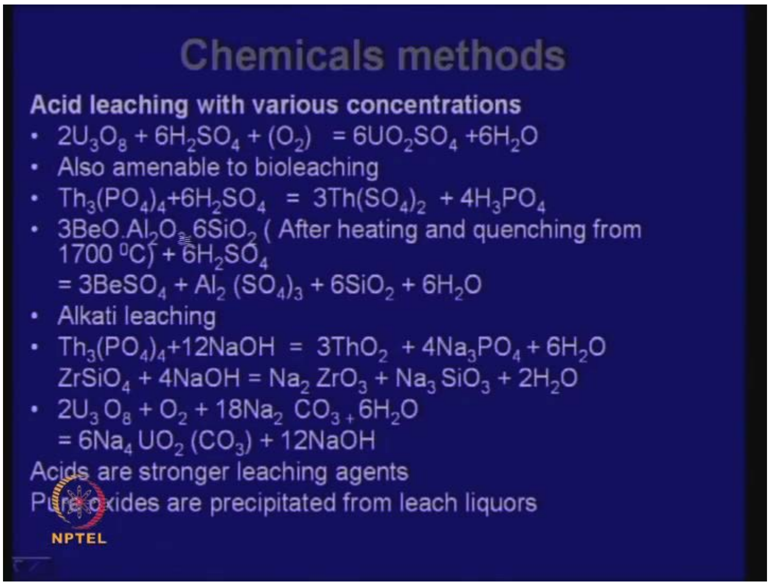

Chemicals methods

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 °C) + $6H_2SO_4$
  $= 3BeSO_4 + Al_2(SO_4)_3 + 6SiO_2 + 6H_2O$
- 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

This is beryl; 3 B e O Al 2 O 3 6 S i o 2. Beryl is a very interesting mineral. And sometimes, hexagonal crystals of this beryl are also found in the mines. But then, we are not talking about that now. We we are just trying to say beryl, as we find in mines.

This beryl… crystals can be picked up. Actually beryl is a very hard substance, the mineral. And, the way it is processed is very interesting. Beryl is heated to high temperature and then the whole thing is put into water. So, then there are co-inch cracks. Otherwise, it is very hard to crush and grind beryl. And, but by this heating and quenching, you create internal cracks. Then it becomes very easy to bring down the size. So, that is what is done. And after, melting in electric furnace, then quenching kiln treatment. We do grinding, leaching and all that in sulphuric acid, then ammonia treatment, we remove iron and beryllium is precipitate. Finally, beryllium hydroxide. So, these are chemical steps we have to produce beryllium oxide.

Then, there is a very interesting situation here. In the case of beryllium, we need not go through the halide route. And very often, beryllium can be reduced by carbon in presence of copper to produce copper beryllium alloy.

Now, try to understand why we do that. Firstly, if we have copper in the system and we are producing beryllium as an alloy, then this reaction is driven to the right because the activity of beryllium becomes less than 1. And, if it becomes less than 1, then it may not form beryllium carbide also, in case there was a possibility.

There is another advantage. In the industry, beryllium, copper beryllium alloys are needed. Actually, a lot of beryllium is used as copper beryllium as springs. Copper beryllium alloys make beautiful springs, which retain their springiness.

So, it is double advantage. You are getting a productive one. At the same time, the product makes it easy for the process to occur. So, beryllium oxide is reduced by copper and reduced by carbon in presence of copper. We produce beryl, copper beryllium alloy and C O.

So, now by maintaining a low concentration of beryllium, carbide formation is avoided and the reaction is made easier. Now, we have to ensure that the beryllium concentration alloy is not high. Then, again we get into the question of forming beryllium carbide.

But, it is a beautiful example of manipulating a reaction to get the product you want and avoid getting a product you do not want. Normally if you take the beryllium oxide, you reduce by carbon. According to Ellingham’s diagrams, there is a temperature beyond which carbon monoxide will be more stable. You can refer to the diagram and get the temperature. But, the product would be not pure beryllium, but beryllium and lot of beryllium carbide as well.

How do we avoid the carbide formation? By not producing pure beryllium. We produce copper beryllium alloy and also ensure with the beryllium, concentration is low. So, the beryllium carbon reaction will not take place.

Now fortunately this alloy that we are producing; itself, is of use in the industry. So, we are killing couple of birds with one stone. Bringing copper, make the reaction feasible at a lower temperature, 1, bringing copper, reduce the activity of beryllium, reduce quite a bit by making it a dilute solution of beryllium in copper. Then, beryllium carbide does not form. Also, by carbon reduction in presence of copper produces an alloy which you need in the industry. So, we have killed, done three things by one, which is a beautiful example.

Now, of course, this is when you want to produce copper beryllium alloy. Now, you might like to produce a pure copper, a pure beryllium. In that, this process will not work because you cannot pure… beryllium, you cannot produce by a carbon reduction.

So, we want to go again to the halides root. Pure beryllium must be produced mainly from halides. In this context, magnesium reduction of beryllium difluoride has been successfully employed; the reaction is B e f 2 plus Mg… B e plus M g F 2.

So, you see for all these cases; uranium, plutonium, thorium, beryllium, we have always aimed at producing a pure oxide, then try to reduce the oxide metallothermically or convert the oxide into a halide and try to reduce metallothermically. Question is can we use an electrolytic method?

Now, I should tell you once again that very rarely can an oxide be dissolved in a halide. Only exception is Al 2 O 3 dissolving in a molten salt like cryolite. There are few other examples of an oxide dissolving in salt, but oxide dissolve in other oxides. And generally, it will be, if these are acid oxides stable there will be in basic the basic oxide there will go in to acid oxide like silicates, phosphates, aluminates. Now, they are highly viscous. You cannot think of using them for electrolysis. But fluorides and halides, certainly you can you can, if you can make uranium halide, plutonium halide, thorium halide or beryllium halide, you can produce the metal electrolytically. But, then the question is what is easier to do. In many cases, metallothermic reduction is easier. And, that is why metallothermic reduction is what we do.

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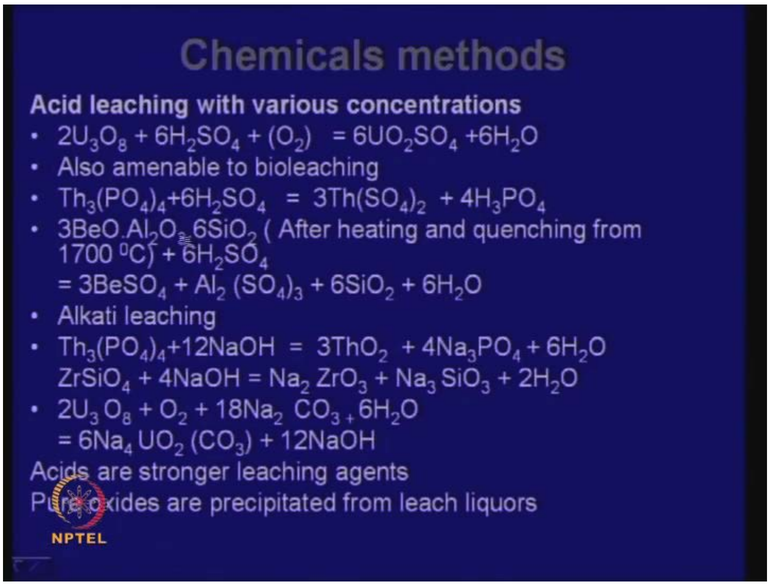

Chemicals methods

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

Now, now I move to a metal which is of vital importance, which is titanium. India actually should be a country that should produce a lot of titanium metal because we are rich in ilmenite deposits. Unfortunately, we have so far produced only pure T i O 2 from ilmenite. That ilmenite is F e O T i O 2 and from that, we remove that F e O part, produce T i O 2 which is rutile. We call it artificial rutile. When we produce from ilmenite, it goes into the paint industry because T i O 2 is absolutely white. So, this makes the basis for paint making.

But, from T i O 2 to T i is not an easy step. So, although we know it, a pilot plant has been run for a long time in Hyderabad, D M R L Hyderabad and I will talk about that. We still have not will able to have in India a commercial process for production of titanium. Why do we need titanium? Titanium is known for a very high strength to weight ratio. It is nearly double that off steel; means, we can get the same strength as steel using only half the weight of titanium. So, titanium, aluminium alloys have now become irreplaceable when we come to making of aircrafts or aerospace, where we need lighter weights, but strength.

It has some other advantages. Its corrosion resistance is better than that of 18-8 stainless steel. So, on one hand we have a material which is strong. And, in comparison to steel for the same kind of strength, its weight is half, then it is also a highly corrosion resistant; has better than 18-8 stainless steel.

There is another advantage. It retains, the titanium alloys retains strength even at high temperatures and show less creep with not many steels can do. Steels may have the strengths. It may have the corrosion resistance, but it will be, it will have more weight and it will have very difficult to have high temperature resistance to creep. And, you know what creep is? Creep is under a load, if a material slowly deforms. So, titanium alloys even under load at high temperatures will resist deformation. There will be no creep. And, that is why it finds now applications in jet engine components. Forty five percent of titanium is going into jet engine components, in air frames, in missiles and spacecraft twenty percent.

That is the relative consumptions of titanium. It does not mean twenty percent of space craft is made of titanium and aluminium alloys. No. It shows its total consumption of titanium- means forty five percent in jet components; air frames twenty five percent; missiles and spacecraft twenty percent. But, it is there, everywhere.

You cannot think of aero, applications in aerospace without titanium, aluminium alloys. So, we need to produce titanium in our country. So, you need to know little bit about how titanium can be produced.

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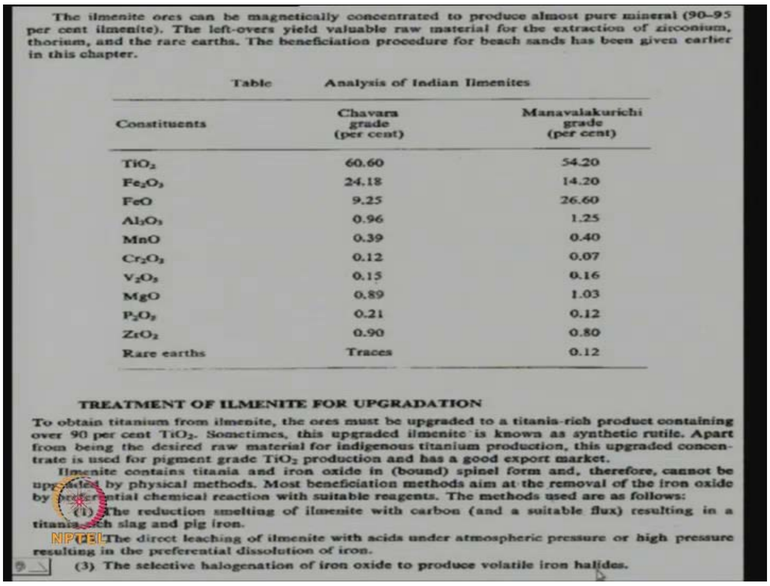

The ilmenite ores can be magnetically concentrated to produce almost pure mineral (90–95 per cent ilmenite). The left-overs yield valuable raw material for the extraction of zirconium, thorium, and the rare earths. The beneficiation procedure for beach sands has been given earlier in this chapter.

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.

[illegible] 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, ilmenite is F e O T i O 2. This is the ore mineral of titanium. There is also rutile, which is pure T i O 2; means mineral is pure T i O 2. But, ilmenite is usually far more common than rutile. But, wherever you find ilmenite or rutile, you are not going to get a necessarily very high grade of that mineral. As I said, in the case of beach sands, for example, forty five, fifty percent was ilmenite, then there are whole lot of other things. But, still that ilmenite was far more than monazite or other things. So, ilmenite is not that rare a mineral, plus you have seen that it is highly magnetic. So, it can be separated it out by low intensity magnetic separators. So, there it is very quite easy in the industry to produce ilmenite concentrates. It is not difficult at all.

Now for artificial rutile or production of T i O 2, they have to reduce the F e O part and you know it it is not very difficult. Even at moderate temperatures under reducing conditions, T i O 2 will not be reduced. If Fe O part will get reduced to iron, that iron is leached out. There are several processes of leaching.

Actually, it is a kind of process of corrosion, like iron is corroded. But, similarly some oxidizing medium iron will be taken, had as an iron hydroxide and it will be removed. We would be left out with T i O 2, which will go for paint industry.

Now, the… as I said here, the ilmenite ores can be magnetically concentrated to produce almost pure mineral (90-95 percent ilmenite). The left overs yield valuable raw materials. Always ilmenite is associated with lots of other valuable minerals. And, for the extraction of zirconium, thorium, rare earths, etcetera, etcetera they have all come from the rest of it.

And so, the beneficiation procedure for beach sands we have discussed, we have discussed several times they have I mentioned of processing of beach sands, which give us ilmenite, monazite, garnet and then other other rare earths, etcetera.

Now Indian ilmenites; I am giving the approximate analysis of two ilmenite containing beach sands. Analysis of ilmenite; there is one in Chavara, there is a 60 percent T i O 2, then there is F e 2 O 3 F e O and then whole lot of other things, including rare earth traces. Then, there is another one Manavalakurichi. I think it is in Kerala. We have T i O 2, then we have F e 2 O 3, we have F e O. So, in different parts of India there are beach sands, which all contain ilmenite, but with different kinds of impurities. So, their treatment procedures are not all identical. Now, here is something I have written for treatment of ilmenite for upgradation. Let me read that.

To obtain titanium from ilmenite, the ore must be upgraded to a titanium rich product containing over 90 T i O 2. So, first, again we have to try to produce an intermediate concentrate, which is very rich in T i O 2. And, we are saying 90 T i O 2. The upgraded ilmenite is known as synthetic rutile. As I said, rutile is pure T i O 2 discussed synthetic rutile.

Now, apart from being the desired raw materials for indigenous titanium production, this upgraded concentrate is used for pigment grade T i O 2 production and has a good export market. That T i O 2 we have, we have done some value addition. From ilmenite, if we have produced synthetic rutile, we had met some value addition because synthetic rutile T i O 2 will fetch much more value than ilmenite as such. it has an export market. But, if you can reduce T i O 2 to titanium, then you can add far more value. This, at this moment we are not able to do, but sooner or later, India will have to do this.

Now, ilmenite contains titania and iron oxides as I have shown, in bound form. We cannot say ilmenite is a mixture of f I F e O and T i O 2. It is a compound F e O T i O 2, a bound form; we call it a spinel. And therefore, it cannot be upgraded by physical methods. We cannot physically remove F e O and T i O 2. We have to go for a chemical processing.

Most beneficiation methods aim at removal of iron oxides by preferential chemical reaction with suitable reagents as I mentioned. The methods used are as follows. The reductions smelting of ilmenite with carbon and a suitable flux resulting in a titania rich slag and pig iron. Now, there are three basic methods which I have listed here for removing F e O and T i O 2, or rather the iron value and the titanium value.

Now, in our industries today, what we are doing is because we are mostly interested in the… to producing synthetic T i O 2, we reduce the F e O part to iron and then we rust it. The process is called rusting of that iron to produce an oxide. And then, T i O 2 is separated from what is now discarded. So, if you go to Indian rare earths in Chattarpur which is near Bhubaneswar, they are producing synthetic rutile. There are dumps of a rejects, which contain fifty percent iron. So, it is almost a raw material for iron production for some other countries, not for our countries. In our country, we have rich iron ores. And, they do not know what to do with it. These are one of the big environmental issues in non-ferrous metal industry.

I have mentioned one about red mud. that in, when you are trying to produce aluminium from Al 2 O 3, bauxite will be leached by sodium hydroxide, so that aluminium is taken into solution as sodium aluminate. The insoluble is called red mud are simply disposed and kept aside in big big places, which occupy whole lot of places. This red mud has iron oxide, some T i O 2, some vanadium, other things. It has a lot of iron oxide; 40 percent or so, iron.

Similarly, we have a, we have also here an environmental issue. If you are simply going for T i O 2 production, we are not interested in the Fe O part. We reduce first, so that to break the chemical bonding between F e O and T i O 2. Iron comes out, then that iron that has come out we rust it; means, we oxidized it by various oxidizing as it make hydroxide. And from, that is thrown out. We are losing that iron value for moment.

So, there is a process where they say, no, let us not do that. Let us reduce F e O T i O 2, the whole thing by carbon using a suitable flux. So, produce pig iron like iron smelting. Your goal is to produce pig iron. And, there would be a slag which will be a rich in T i O

2. So, we go for a pyro metallurgical process of reduction by carbon of F e O T i O 2 using a flux, which you will produce a slag; like flux means, you have to put quartz, you have put lime stone. The product will be pig iron. And, T i O 2 going to the slag phase. So, the pig iron will fetch value.

And now, titanium will have to be extracted from that titany titany ferrous slag. Now, we have changed, gone from ilmenite where titanium was bound with F e O to titanium in a slag phase. But, the advantage there is, we have produced pig iron in the process which we will have a market.

From that slag, we will have to take out titanium; which can be done by halogenation. We can, we can halogenate and we can chlorinate that slag to get a titanium tetrachloride out of that. Or, some other process we can check out. So, that is number one way of handing ilmenite to get titanium.

Then, there can be direct leaching of ilmenite with acids under atmospheric pressure or high pressure resulting in preferential dissolution of iron. This has also been tried. To remove iron, first we thought… reduce, take out iron oxidized separate, but there are also processes. But, the ilmenite is directly leached and you know acids are very strong reagents, preferentially they could, they will dissolve the iron part leaving aside the titanium part. Then, it is also possible to directly go for selective halogenation on the ilmenite, so that iron oxide will produce volatile iron halides under certain temperature, leaving T i O 2 behind. So, there are different approaches of separating iron from T i O 2. Eventually, we need to produce T i O 2 or a halide of titanium from which we produce the metal.

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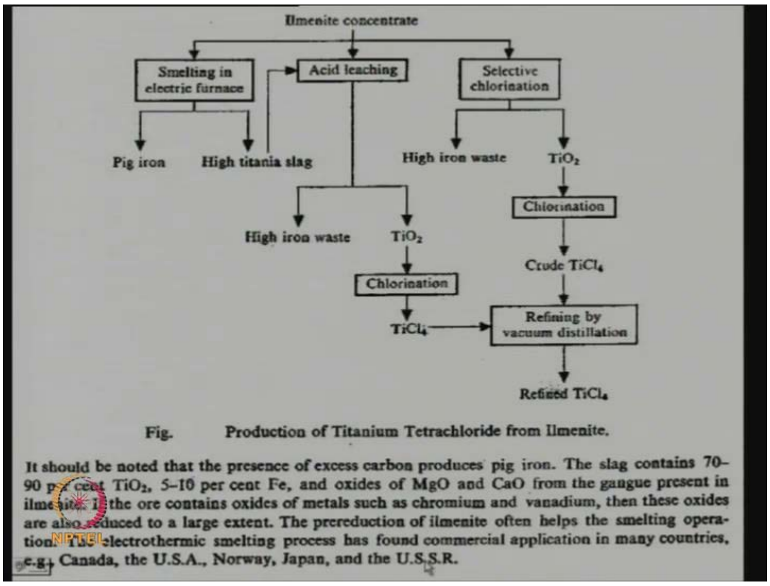

Fig. Production of Titanium Tetrachloride from Ilmenite.

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 also 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, e.g., Canada, the U.S.A., Norway, Japan, and the U.S.S.R.

Now, here is what we have mentioned. But, I just now mentioned. I have put in a flow sheet form. We produce an ilmenite concentrate, and then we have the following choices. We go for smelting in an electric furnace, which we will produce pig iron. And, we produce high titania slag. Just like an electric furnace operation. We can go for acid leaching. This high titania slag can also go for acid leaching, instead of the ilmenite concentrate being done. We can do this, take out the pig iron part of pig iron, then this slag itself is leached so that, we can produce a high iron waste.

Here, this iron is being wasted. If we go from this slag to acid leaching, we are only wasting the iron that has entered the slag phase. But, we have taken out most of the iron here. It is pig iron. But, if you go for direct acid leaching, we will produce a high iron waste. And then, we will have T i O 2 which you go for chlorination to produce T i C l 4. Or, we can go straight for chlorination of the ilmenite concentrate. That would also produce a high iron waste that will go to waste unfortunately. But, it will produce leave behind T i O 2 which can be chlorinated to produce crude T i C l 4. It will be refined by vacuum distillation. This will also be vacuum distillation; so, T i C l 4. So, these are the three steps.

The advantage here is, you produce iron as a valuable product is pig iron. in these things, steps, we are actually rejecting iron as a waste and it is very difficult at this moment to do something about. That is where you find in India; rare earths, dumps of wastes, an iron rich waste, which have come out of that ilmenite.

So far, no use for it. it also, other things, it has other valuables also in that. But, eventually here also we are going for production of a halide. Now, it should be noted that the presence of excess carbon produces pig iron. Here, we need lot of excess carbon to produce pig iron. The slag contains 70 to 80 percent T i O 2. It will be very viscous slag; 5 to 10 percent iron, which we are going to lose here. There will be oxides of M g O and C a O from gangue present in ilmenite. If the whole contains oxides of metals such as chromium and vanadium, which are very often present, then these oxides are also reduced to a large extent. And, if they are reduced, they will enter the pig iron. I think it pig iron will contain that chromium.

If not reduce, vanadium may not be reduced. it will go into the slag phase. The pre reduction of ilmenite often helps the smelting production. Prereduction means, if we initially reduced ilmenite as I had mentioned into F e and T i O 2, then go for smelting. Sometimes smelting becomes easier because we have already taken out iron from the F e O part.

The electrothermic smelting process has found commercial applications in many countries; Canada, U S A, Norway, Japan and U S S R. Actually, it is Canada which first introduced method. That makes better use of the metallic value. we take out iron also, you take out titanium and you are not to you are not to worry about generating lot of waste because in this case we are not generating that iron wastes with these roots are generating.

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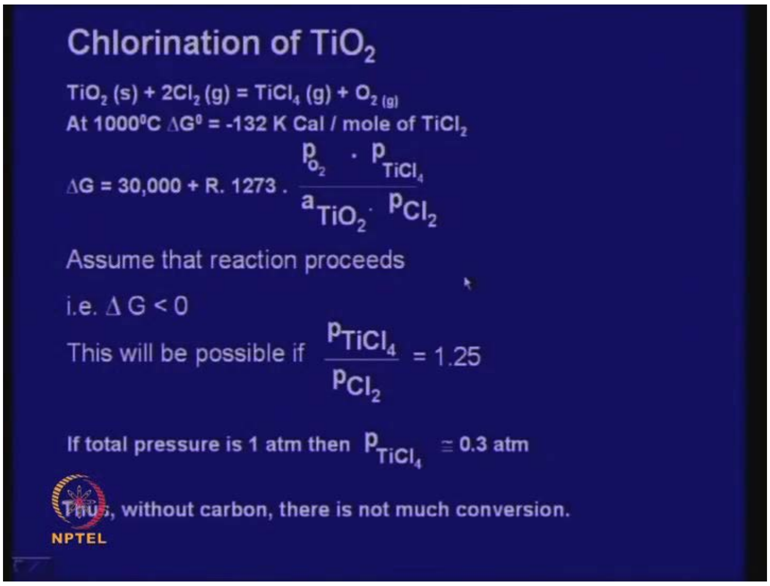

Chlorination of TiO_2

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

At 1000°C $\Delta G^0 = -132$ K Cal / mole of $TiCl_2$

$$\Delta G = 30{,}000 + R.\,1273\,.\,\frac{p_{O_2}\,.\,p_{TiCl_4}}{a_{TiO_2}\cdot\,p_{Cl_2}}$$

Assume that reaction proceeds

i.e. $\Delta G < 0$

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

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

Thus, without carbon, there is not much conversion.

Now, in the next lecture I will come to chlorination of T i O 2. It is a very very interesting step. And because you are talking about chlorination so often in the past, may be if I talk about the chlorination of one oxide, I would I would able to show the example of chlorination of all similar, such similar oxides. So, I will continue with chlorination of T i O 2 in the next lecture. Thank you very much.