Non-ferrous Extractive Metallurgy

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Lecture No. # 27

Extraction of Reactor Metals (Contd.)

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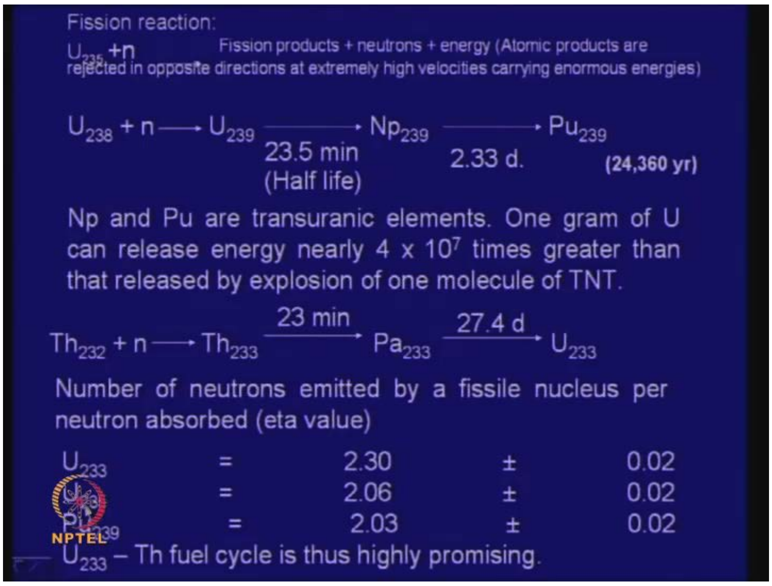

Fission reaction:

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

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

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.

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

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

U_{233} = 2.30 ± 0.02

= 2.06 ± 0.02

Pu_{239} = 2.03 ± 0.02

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

Well friends. In my last lecture, I talked about different isotopes and uranium. And you saw how all talk of nuclear energy production refers to some isotope of uranium. The naturally, the fissionable isotope of Uranium is U 2 235, it is only 0.7 percent, but Uranium 238 which is the bulk of the matter more than 99 percent is a fertile material. It can be converted to Plutonium 239 which is fissionable and we saw that Thorium can be converted to an isotope of Uranium 233 which is fissionable. And if this actually provides us the best route production of nuclear energy because the eta value is the largest. Now, the question is then comes down to this, to start with we need to separate Uranium 235 first from Uranium 238 and we will ignore Uranium 234 which is such a small fraction of naturally occurring Uranium isotopes, then we will ignore them.

So, essentially we come down to separation of Uranium 235 and Uranium 238, how do we do that, how do we separate take out Uranium 235 to start with?

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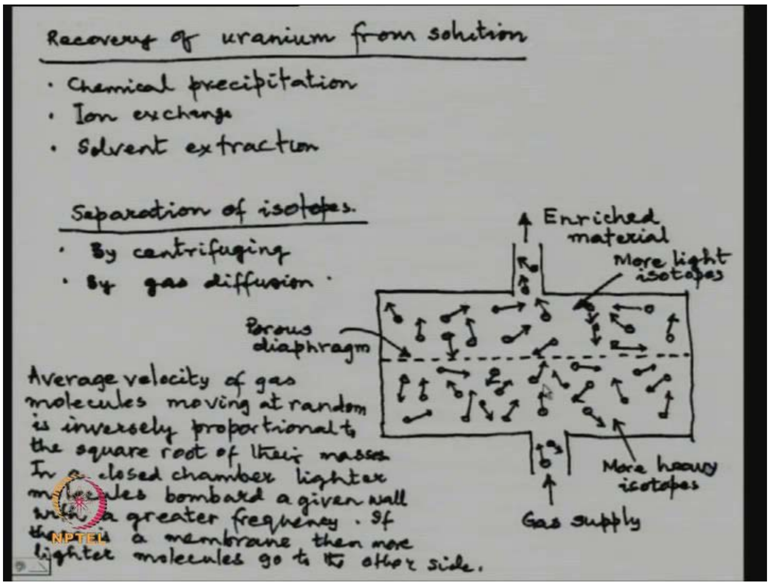

Recovery of uranium from solution

- 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.

Now, essentially we have to first produce a compound pure compound of Uranium. And you know that the chemical properties of isotopes are always similar, no matter of what element you have. If you have different isotopes they will undergo the same reactions, they are the same. Like in hydrogen also you know we have different isotopes.

But when water is reacting all the isotopes react in the same manner. So, when Uranium is reacting as an element, the different isotopes all react in the same manner. So, we have to first produce a pure compound of Uranium. It can be you have to recover Uranium from solution either the acid solution or the alkali solution. We can precipitate an Uranium compound and we can also go through ion exchange and solvent extraction methods to get a pure compound. It is only when you have a pure compound, then we start talking about separating the isotopes Uranium 235 and Uranium 238.

One technique is centrifuging, you must have heard about this word centrifuging. That suppose we have the two isotopes, two compounds in solution. Now, if such a solution is rotate it in a very high speed so like in any centrifuging the heavier once and the lighter once get separated. So, centrifuging can be one way of separating. So, this is often a critical technique in the development of nuclear energy. How do we separate? By centrifuging Uranium 235 and Uranium 238. There is another method of separation which is in this picture that is by gas diffusion.

Now, centrifuging made use of the fact that one isotope is heavier than the other isotope. Gas diffusion also make use of the same fact that one isotope is heavier than the other isotope. Let me first tell you how it is done then we will come to the principle. Essentially, there is gas diffusion will be in the gas phase. The Uranium compound in a gas phase is supplied from one side in a chamber, where there are two compartments separated by a porous diaphragm. Now, when you talk about a porous diaphragm, we are talking about porosities of the atomic sizes, it is a very fine diaphragm.

What happens in this? That in the gas phases the all the isotopes forming the particular compound. A compounds with different isotopes, they are all moving around in different direction with different speeds. But eventually, after a while what will happen is the lighter atoms will more selectively go through the pores in the diaphragm. And the gas that goes to the other side will be richer in lighter isotopes so, we get an enriched material in terms of Uranium 238. So, Uranium 235 Uranium 238 and Uranium 235 isotopes in the gas supply gets differentiated because the lighter once will penetrate this pores preferentially and so we get an enriched material which would have a higher proportion of Uranium 235 then and compare to what there was previously of course, this has to be repeated many times. This is a very simplified way of presenting it why should this happen? I have written it here very briefly.

You know in a gas, the average velocity of gas molecules can be calculated in many ways. If we assume a Gaussian distribution, you can think of a more probable velocity, you can think of an ultimated average, but more meaningful is the root mean square velocity. So, we say that average velocity of gas molecules moving at random is inversely proportional to this square root of their masses. In a close 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.

So, all the gas molecules that a bombarding this membrane at random all the time moving among themselves, colliding with each other. There is a velocity distribution amongst all these input gas molecules also. There is a distribution of velocities because their constant be colliding with each other. But there is an average value, that average value for the lighter isotopes is higher. So, because they there is a average velocity is higher, there is they would be bombarding this membrane more frequently. And therefore, more the lighter isotopes will go through to the other side that is how from a normal proportion we get an enriched material so more U 235 will be here in one stage.

Now, how it is exactly done in multiple stages and what are the other inter case is of this thing we need not study. But basically it is done by centrifuging or by gas diffusion. Different countries adopt for different methods and perhaps some countries employ both the methods. I do not know exactly how it is done in India which is applied where. But basically the reason why I am mentioning it to you is that the nuclear metallurgy is based on the central theme. That you have to have Uranium and to start with you must have a method of separating the isotopes of Uranium. One isotope which is lighter is fissionable; it will give fission reaction when bombarded with thermal neutrons.

Those thermal neutrons can be used to bombard the isotope which is higher in valued U 238. It will get converted to Plutonium 239 which is fissionable and then apart from this if you have thermal neutrons bombarding Thorium 232 we can produce another isotope of Uranium. We says Uranium 233 which can also undergo fission reaction and do that far more effectively than either Uranium 235 or Plutonium 239. So, it is basically the interplay of all these things.

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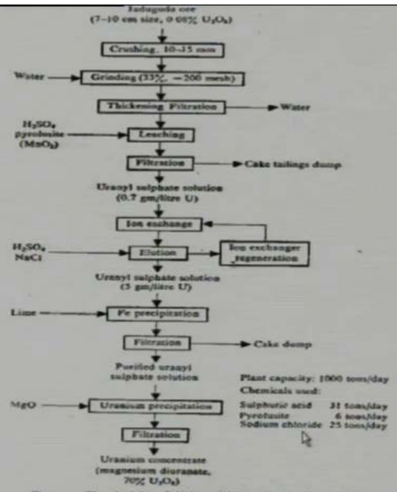

Plant capacity: 1000 tons/day
Chemicals used:

Sulphuric acid	31 tons/day
Pyrolusite	6 tons/day
Sodium chloride	25 tons/day

Fig. Chemical Beneficiation of Jadugada 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 ~ 2.2, P_2O_5 ~ 1.0
S ~ 0.8]

Now, I mention to you that we are actually when we are talking about Uranium, we are not talking about an ore like bauxite or hematite where things are high grade, we are talking about ores where the a metallic value percentage is very low. For example, I am talking about here the chemical beneficiation of Jaduguda Uranium ore we have in Jaduguda, in Bihar. Uranium deposits, ore deposits which contain Uranium, there are one or two other places, but they are not yet so important. Now, here the ore analysis is like this Uranium is only in the form of U 3 O 8 is only this actually 0.0, it is not sorry, correct, it should be 0.06 to 0.07 is as small as that please correct it or check my in the book I have mentioned, there is something wrong here.

Silica most of it is Silica then there is iron oxide, there is alumina, there is TiO 2, there is MnO, there is calcium, there is magnesium, there is some P 2 O 5, but essentially it is a siliceous material containing small percentages of U 3 O 8. So, it is point take it has point remove it 0.07 0.08 percent, what you do with such an ore? It is such a low grade ore, but there are processes of getting a concentrate and pure U 3 O 8, let see how it is done. Again do not be scared by the flow sheet it is only talks about the logical steps. As always when we start with this ore, the ore particles would be 7 to 10 centimeter size. You know big particles which are basically siliceous material going to be small amounts of Uranium.

It will be crushed into 10 to the power 10 to 15 centimeter size, then crushing is to that kind of sizes then we go for grinding, you can never take a big particle and grind it. The both the things are combination, but when we come to from big particle to sizes like this we call it crushing and we crush particles further, then you call it grinding. Grinding means we are going to minus 200 or minus 300 mesh. If also in the case of sulfides, we have to go to that kind of thing for floatation. Why do we grind to that size? Because when you grind, your leaching reactions will be more effective. There is a far greater surface area orders will react much more effectively with acid or alkali like in a sugar when it is much finery it dissolves faster.

So, now here in Jaduguda we are going for a H 2 SO 4 leaching. Of course, after grinding with we can infiltration etcetera, these are simply process of getting get because when we do the grinding we do wet grinding we have putting water. Because when there is a even in at home when you do some masala and grinding you put some water because in presence of water grinding is often more effective, why it is so? I will discuss it now, but there are fundamental reasons for that. So, when you have lot of excess water that will, will have to go. So, we remove that water by thickening filtration step then we go for leaching, sulfuric acid why do we put pyrolusite MnO 2, MnO 2 is an oxidizing agent.

So, it makes the action of acid even more strong, then we will have filtration a cake which is the insoluble material go Uranium sulfate will be in solution. See, from an ore which are so little bit of Uranium. Now, we have got Uranium where you have 0.7 gram per liter of Uranium which is fairly large you at least you have got the mock out of this system. Now, it has to go through this iron exchange, elution techniques you know it is a solid through which it will go, it will get absorbed then it will be eluded out. So, we have discussed that. So, an in iron exchange the iron exchange regime is constantly regenerated and we get after illusion a solution where Uranium sulfate goes up to 5 grams per liter then we go through some chemistry step. If we add 9, iron will be precipitated. It will be separated out as a cake, purified Uranium sulfate solution then by adding MgO, we will produce after filtration Uranium concentrate which will be 70 percent U 3 O 8.

So, you see how beautiful these steps are. You are starting with a raw material which has 0.07 percent. Uranium and all the other thing that you do not want and from there by this steps you are come up with a concentrate which 70 percent U 3 O 8 70 percent. Now, what operates I wrote this quite some time ago, the plant capacity was 1000 tons per day, chemical used by sulfuric acid pyrolusite sodium chloride, just to give you this scale of operation.

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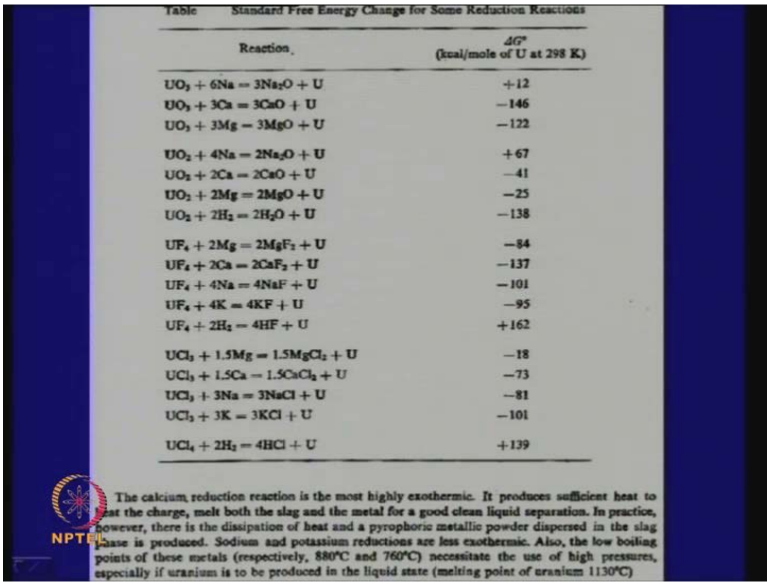

Table Standard Free Energy Change for Some Reduction Reactions

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
$UO_2 + 2H_2 = 2H_2O + U$	−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)

Now, from that oxide, we have to go to some more purification steps to produce a pure oxide and finally, produce UO 2 or chlorinate to UCl 2 or fluorinate 2 UF 2. I am not going to go in to though that exactly I will do that I think it is not necessary. But you get the idea. You start with a low grade ore, you produce an oxide 70 percent U 3 O, there is some other things you have to purify it further then you have to convert it to by some simple chemical steps to pure U O 2. You can chlorinate it, by using Carbon and Chlorine or Carbon and Fluorine try the chloride or fluoride.

Now, in theory then once you have the Chloride or Fluoride we can go for metallothermic reduction. You can go for metallothermic reduction of the oxide also, like in the case of ferroalloys you will remember. In ferroalloys when we produced by Carbon reduction there was a danger of Carbon contaminations. So, you produce high Carbon ferrochrome and to, but we could avoid having Carbon in ferroalloys if we went for metallothermic reduction, here also. If we have a pure oxide, you can reduce by Sodium or Calcium reduces the metal, no problem. Also fluoride and Chloride can be produced by metal.

But then we have to see three things that I have mentioned earlier. First of all we have to look at the free energy of formation. We will like to only go for those reactions where free energies of formations are negative. Now, here it is positive means to make it fusible it can be made fusible. We have to drive the reaction to the right, if we take Uranium into some kind of an alloy or if we take out Na 2 into some kind of a slag this reaction may go to the right. Because remember delta g naught standard free energy change does not change too much of temperature. But in some other cases it is already highly negative so, the reaction is thermodynamically very fusible. So, you find it is highly negative when there is a Calcium reduction or Magnesium reduction.

In this scales also negative values are there for calcium reduction, magnesium reduction also there is hydrogen reduction. But in a trying to reduce an oxide by hydrogen it is a very tricky thing because you know the lots of precautions are necessary. Normally, one avoids hydrogen in a pyrometallurgical process. Coming to reduction of Fluorides you find Magnesium, Calcium have negative free energy change sodium also Potassium also again in the case of Fluoride, Magnesium, Calcium, Sodium, Potassium they all are negative values.

Now, what do we choose? We have so many choices to produce Uranium by metallothermic reduction of oxide, metallothermic reduction of fluoride. Also chloride now there are the other criteria will come into picture, what is this physical state of the reducing agent, what is the physical state of the products, where slag metal separation will be easy? Etcetera. For example, offend you can say that if you want to reduce by hydrogen, then you are talking about a close reactor. After all how will you keep hydrogen? And obviously if you can increase pressure of hydrogen, thing should become easier but, you need a brome you need a close reactor.

Here, we are talking only about delta g naught values, we are not talking about what is the heat available from the reaction. If there is a lot of heat coming out as exothermic heat that reaction would be preferable with some others. Some of these factors I am discussing in the right of at the bottom, read this. The Calcium reduction reaction is the most highly exothermic not shown here, but Calcium always exothermic reduction is highly exothermic. It produce a sufficient heat to heat with the charge melt both slag and the metal for a good clean liquid liquid separation.

In practice however, this is one in theory there is good in practice however there is dissipation of heat. Because no matter where you do it, you cannot really keep all the exothermic heat with you, there will be lot of dissipation. And because of dissipation a pyrophoric metallic powder dispersed in the slag phase is produced. See for example, you talk about the Calcium reduction of Uranium trichloride. You have produce Calcium chloride which is in the liquid slag and Uranium, Uranium is not going to be liquid is very the melting point is very high.

It will not be in consolidated form there will be a powders dispersed in Calcium chloride phase which is not a very happy situation, but this is nothing you can do about it. And this metallic powder you mine it pyrophoric so long it is dispersed in the slag it is, but it can very easily react with atmosphere. Now Sodium and Potassium reductions are less exothermic also, the low boiling points of these metals like 880 and 760 necessitate the use of high pressures. So, like hydrogen if we want to try to reduce by Sodium and Potassium we will also need a close reactor.

Because at the temperatures where we want to produce a liquid slag, there would become volatile so, it will not occur it will not be favorable. Specially, if Uranium is to producing the liquid state melting point of Uranium is 1130 degrees. If you have want to produced in solid state (( )) but, ideally you would like to produce a liquid Uranium and liquid slag which will cover the Uranium so that Uranium will not get reoxidized. Now, if you want to produce liquid Uranium, you need 1130 degrees you cannot use Sodium or Potassium as reducing agent.

Because they become volatile one at 880 degrees another is 760 degrees so, you need a closed chamber. So, all these parameters rule them out. You need convenience you need something which is in practice can be carried out without too much of hassle that is why we have to fall back on Calcium or Magnesium. And we have seen the Calcium is very highly exothermic so, we will called Calcium reduction, that is how we choose a metallothermic process from a choice of so many. So, the free energy of formation is not the only guide it is one guide, but there is also heat of reaction, there is also physical state of reactants and products all these are important.

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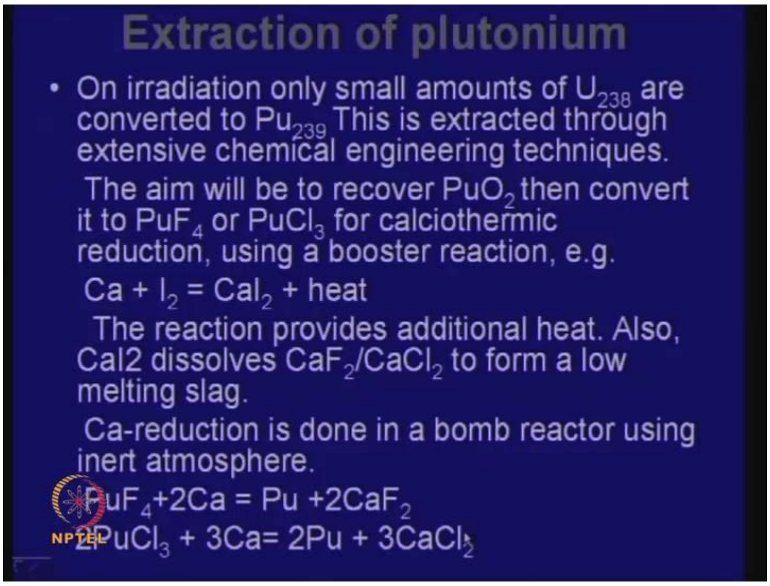

Extraction of plutonium

- 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.

  $PuF_4+2Ca = Pu +2CaF_2$

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

Now, we will talk about extraction of Plutonium. I have mentioned and I have mention it again. That Plutonium does not exist in nature; it is produced by neutron bombardment of Uranium 235 which is fissionable. But then when Uranium 235 is undergoing fission, it does not mean the all of Uranium 235 at a time is going to produce a neutrons are produced. And those neutrons when you bombard Uranium 238 to produce Uranium 239 not all that Uranium 239 is becoming Uranium 230, it is Plutonium 239 that does not happen.

When the thermal neutrons coming from the fission of Uranium 235 are allow to bombard Uranium 238. Only tiny fractions of that Uranium 238 will get convert to Plutonium 239. This Plutonium 239 has to be separated from eradiated mass, eradiated 238. It does not mean the rest of it uses, it has to be eradiated again that is a separate matter. Now, this is an enormous task, I do not know how many of you are studied in the story of Madame Curie. When she first madam Curie and Pierre Curie when they first produced radium, they have to process tons of pitch blend, day in and day out through many steps in chemistry and chemical engine to finally, produce that element which as called radium.

Similarly, in case of Plutonium also there is small fractions of Plutonium produced because of eradiation of Uranium 238 and they have to be extracted. Now, chemical engineers have perfect with the metal, it is a very complicated process which are discussed in my book. Do this then do that then do this it is a matter of knowing where to find it as I have mentioned, you need not know. By this should know where to find it when you want to know. I have given you one reference, but there are many other books. Specially, those monographs published from B A R C, you will find the production of Plutonium 239.

It itself is a very interesting material. There are several isotopes of Plutonium 239 I think there are 6 of them may be. And this highly a toxic material the tiniest amount of Plutonium in the air what is it drinking water system can bringing deaths of 100s or 1000s of people so it has to be handled very very carefully in glove boxes and complete isolation. It is a signs by itself, it is a technology by itself, but our scientists and engineers have learn to do this. So, I am not going to the inter cases of isolation of Plutonium from eradiated mass of Uranium 238, please read it up. I will just come to emphasize as to how the same kind of principles will be considered, when you want to produce Plutonium from a compound.

Now first of all the aim of the all these isolation techniques would be to use chemical engineering techniques to produce PuO 2 then convert it to PuF 4 or PuCl 3 again for calciothermic reduction. Again various consideration show that Calcium reduction in is the best way of going at it. In theory there can be many you can talk about metallothermic reduction of the oxide or several metallothermic reactions for the halides Chlorides and Fluorides, but Calcium seems to be the best pet.

Now, here one special technique is used which is also of general application in many cases. During the reduction of PuF 4 or PuCl 3, we also used what we known as a booster reaction. Booster reaction boosts the availability of heat and it does some other things how does it boost. The booster reaction is that when we are adding Calcium as a reducing agent, we also add some iodine. So, at the temperatures were reduction takes place Calcium reacts with iodine to produce Calcium iodide Ca I 2 is highly exothermic it produces heat.

So, it supplies heat for calciothermic reduction so that the metal and the slag they melt. In addition it does another trick it produces Calcium iodide which dissolves Calcium fluoride or Calcium chloride whatever is being produced to form a low melting slag. See the trick by making Calcium and iodine react we have first of all supply the heat. So that the Plutonium that is produced and the salt slag that what I call is produced they can melt easily. At the same time we ensure that the salt we have producing that the Calcium fluoride or Calcium chloride that F and Cl is coming from the Plutonium compound. They form a low melting slag because they will dissolve in Calcium iodide.

So, Calcium iodide plus CaF 2 or CaCl 2 of being mixture we would have a lower melting point so a lower melting slag will be found. So, we have a low melting slag and a metal. This Calcium reduction is done in a bomb reactor in an inert atmosphere because Plutonium is very highly reactive with this any oxygen it will go back to that oxide form. Essentially, the reactions could be Plutonium PuF 4 Calcium reduction Plutonium CaF 2 or Plutonium trichloride can also be reduction and it will be Calcium chloride. And as I said when there is a Calcium iodide in the system, the chloride and fluoride will mix with Calcium iodide to form a low melting slag. This is the basically the trick.

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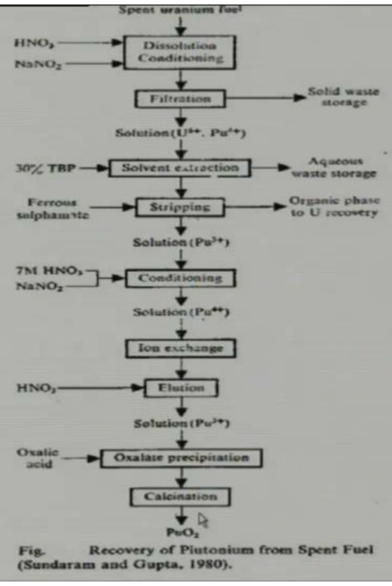

Fig. Recovery of Plutonium from Spent Fuel (Sundaram and Gupta, 1980).

Now, let me just give a hint of the enormous complexity of how Plutonium is recovered from this spent fuel means, from the you have U 230. So, you have a spent Uranium fuel is treated by hydrogen HNO 3 NaNO 2 it goes through filtration step, solution would have both Uranium as well as plutonium solvent extraction by tributyl phosphate. And then stripping will bring Plutonium in the solution organic phase will have the Uranium which will be needed again, but we have taken as the Plutonium they two go through iron exchange, elution etcetera. Finally, an oxalate will be precipitated by adding oxalic acid, calcinations will produced PuO 2. it is not very easy it is very easy to show all these that is from this spent fuel. This is the way they will get the tiniest fractions of Plutonium which have come as a result of the reaction of U 238 that has given rise to plutonium.

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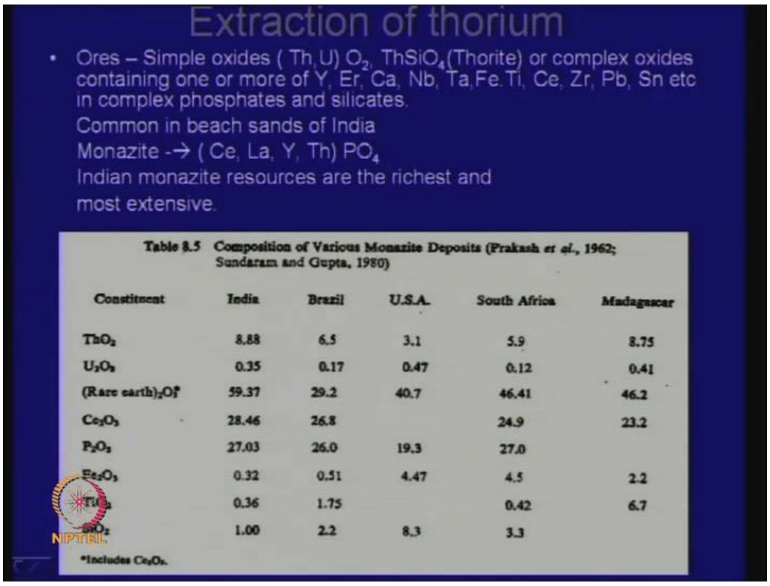

Extraction of thorium

- 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.

Now, we will be come to Thorium. Now, Thorium has other uses it can going for making ceramics. It could have some alloying applications, but we are looking at it from the point of view of nuclear metallurgy. There as I said Thorium is not fissionable, but it can be convert it Thorium 232 to an isotope of Uranium. We does not exist in nature Uranium 233 which would be fissionable. And it is the most effective fissionable material because it consumes some neutron, but produces much more neutron than the other cycles. Now, the Thorium ores are in plenty in our country and we are very lucky that way. And that is why they are found in the beach sands of south India, both western coast and eastern coast, they have different composition of course, and they are export is band, it is been band for a long time.

In those in the beach sands, Thorium exists the some simple oxides like; Thorium, Uranium O 2 or Thorium SiO 4 called Thorite. Or there can be very complex oxides containing one or more of all these materials Yttria Er Calcium, Niobium, Tantalum, Iron, Titanium, Cerium, Zirconium lead tin in complex phosphates and silicates in a very complex manner. In common in beach sands of India we have a thing called monazite.

Monazite is usually written like this Lanthanum, Cerium, Yttrium, Thorium PO 4. Indian monazite resources are the richest and most extensive in the world.

And, we are hoping the someday we will come to this Thorium cycle and we will produce from Thorium U the U 233 which will give us the nuclear energy in future. But to come to that we have to first are Uranium 235 and Plutonium 239 initial stages we need those. Now, here is a table, which gives the composition of various monazite deposits in different countries. These are the countries India, Brazil, U S A, South Africa Madagascar and these are the main countries. We will find in our Monazite the Thorium ThO 2 content is very high U 3 O 2 is low.

The lots of rare Earths, rare earths are very important elements. Actually, rare earths go for making films you know the lighters you have there made of rare Earth materials metals, there is C C 2 O 3 P 2 O 5 Fe 2 O 3 TiO 2 and silica. Of course, this monazite is associated with TiO 2 in separately that to that I will concept but, then in monazite can there can also be small amounts of TiO 2 that is the TiO 2 been shown. So, anyway the someone substance is Indian monazite is supposed to be very rich in Thorium content and rare Earth content.

And this monazite will come from processing of beach sands which have discussed in one or two lectures. That beach sands we process in Kerala also in Orissa for getting TiO 2 we are looking at Ilmenite. Ilmenite is FeO TiO 2 we take out Ilmenite then produce artificial Rutile is remove FeO 2 and produce TiO 2. But then the rest are not to be wasted, that is where we have monazite we have rare earths we have many other things. But it will all coming from beach sands and I mention some of the beach sands look black because of the very high TiO 2 content. So, this TiO 2 that is being shown in this table is only the TiO 2 that is associated with monazite fraction.

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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.

Now, the monazite comes from separation techniques employed on beach sands. Again there are beach sands of Kerala, there are beach sands in Madras, Chennai, there are beach sands in Orissa coast. These beach sands when sun dried has composition in this range there are mostly Ilmenite 60 75 percent Ilmenite that is what makes it black Ilmenite is FeO TiO 2. And I remember mentioning also that in the place where olive Ridley turtles come to lay eggs. And they come in 1000s and it is now a protected area, it is we believe some of we are worked on the how the olive Ridley turtles come to the beach, if this sand is absolutely black, it is so rich in Ilumenite.

And I think because it is so black, it absorbs sunlight and remains quite warm. Even during the month of February, this sand is a warm and I think it is very good for incubation of the eggs of this olive Ridley turtles. I think that is one reason why the olive Ridley turtles come to that Gahirmatha beach. Now, the government of India are nobody with their senses will try to take out that portion of the beach sands because you will be interfering with the entire ecology of this system. But, fortunately we do not know how much of what is there, although there has been some work, but there are other beaches were also. We have the very rich in Ilumenite and other things.

So, but as I said the is the blackness is because of the richness of the iron the Ilumenite content. And that is why the olive Ridley turtles go there. Anyway coming back to the sun dried beach sands which are available plenty around our coast line. Ilumenite is 60 to

75 percent mostly Ilumenite then there is garnet 5 to 6 percent Zircon which is oxide to Zirconium oxide 2 to 4 percent Rutile. Rutile is only TiO 2 not no FeO in it 0.5 to 5 percent monazite it varies from place to place. 8 to 28 percent silica and other is this monazite that we are talking about now. About this Ilumenite fraction I will talk later when we talk about titanium and we have discussed it once.

Now, after screening it has to be first Sun the Sun dried beach sands are screen to remove lime shells in all kinds of things. There are shells all over the coast line, all the sea creatures come and live the shells. So, the lime shells will go there are also trashes they have to be removed. Then it will go through low intensity magnetic separator. Ilumenite will can be removed with low intensity magnetic separation because is highly magnetic it will do not need strong magnetic field. Ilumenite can be very nicely separated is highly paramagnetic. Then from the tailings high intensity magnetic separator removes monazite, monazite is weakly magnetic. That is how we will get monazite out of the trashes.

Now, there are other constituents which are removed by electrostatic separators or air tables. Air tables is another or separating depending on their density particles size etcetera. Then after you are separated monazite essentially by magnetic separation, it has to go for chemical treatment. Which has I mentioned can be by acid leaching or it can be by alkali leaching.

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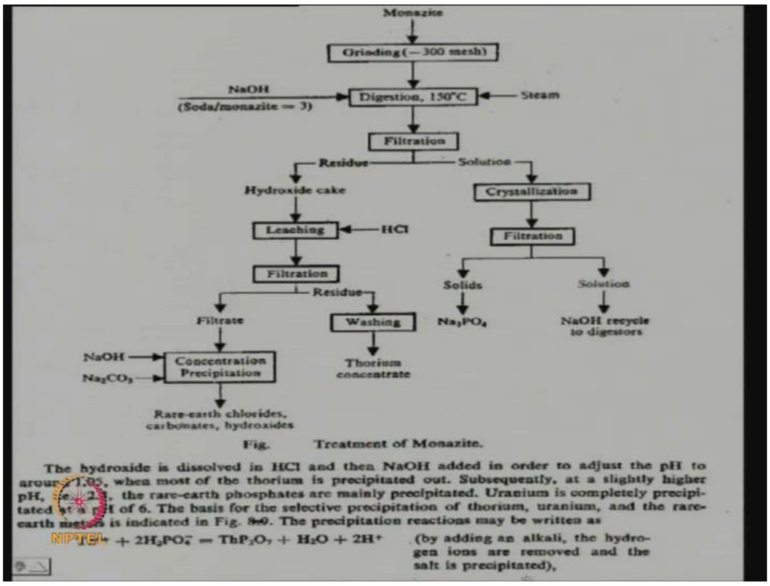

Fig. Treatment of Monazite.

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. 8-9. 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), In our country, for reasons that I do not know they have our people have opted for alkali leaching of monazite. And their flow sheet is like this, I will quickly go through. We have produce monazite from beach sands by separating it out by high magnetic, high intensity magnetic separator. Then it will go through grinding, we do not need crushing because beach sands are already small particle size, but we need grinding to take it to minus 300 mesh. When you are going for alkali leaching actually, you need finer particles because as I said alkali is not has from a reagent as acid in terms of leaching. So, we need very fine particles.

And then the digestion would be at higher temperature 150 degrees which means you need autoclaves, why we need it? Because we are going for alkali leaching and alkalis are weak leaching agents, you need higher temperatures, you cannot go to temperature higher than 100 degrees you need autoclaves where there is higher pressure and your boiling point of water will be raised. Recall the leaching of Alumina in Sodium hydroxide. There also we need autoclaves and sometimes we needed high in a pressure so that the temperature exceeded 200. There also alkali leaching which goes up to temperatures likes this.

In this case the digestion is done at around 150 degrees with excess soda; soda by monazite is equal to 3. If we filtrate we get a residue and you get a solution, what will go in the solution? That so crystallize in filtration we will find that we have thinks that we are not interested in that from this we actually recover NaOH that can be recirculated. But it is the insoluble’s which now has what we want so this is a very special kind of an alkali leaching, where the solution is not what interested as. But it is the residue that gives an hydroxide cake which would be leached by HCl. Which after filtration will give us a Thorium concentrate and a filtrate will give us a fraction where we have rare earths chlorides carbonates and hydroxides.

Now, here this is a very interesting point. Now, you see you do not always leach to take out the values you are interested in solution. The idea of leaching is separation of the metallic values you are interested in and the things you are not interested in. Normally by leaching we take the metallic value into solution like in the case of alumina. When you leach by Sodium hydroxide aluminum becomes Sodium aluminate in solution, what does not dissolved contains Iron, Titanium etcetera. Here it is opposite. What does not dissolve forms a cake, which has the metallic values Thorium and rare earths? It happens in alkali leaching process. may not happen in acid leaching. That is one advantage for us which is attractive people.

So, once you have a hydroxide cake, that has to be leached by HCl and after filtration there will be a residue which will be Thorium concentrate because this acid has not dissolved Thorium, but it has dissolved the rare Earth chlorides carbonates hydroxides. So, we separate here Thorium and rare earths the rest of the things are not of much interest to us. Excepting that in this process we can use regenerates sodium hydroxide which will be recycle to register. Now, let me read what at the, what is there at the bottom.

The hydroxide is dissolved in HCl then NaOH is added to adjust the pH 2 around 105. Now, we are going through a selective precipitation process, now we are going into pure chemistry. That once we have the Thorium concentrate which is in hydroxide or other hydroxides we can take them into solution and precipitate one after another by simply controlling the pH of the solution. Typical chemistry we have done such chemistry experiments, if I read it out it will become clearer.

The hydroxide cake is dissolved in HCl and then NaOH is added in order to adjust the pH 2 around 1.05 when most of the Thorium is precipitated out. Subsequently at a slightly higher pH that is 2.3, rare earth phosphates are mainly precipitated. Uranium if there is completely precipitate of pH of 6. The basis for the selective precipitation of Thorium, Uranium rare earth metals is indicated in figure. And essentially Thorium ions reacting with this Thorium phosphate now, by adding an alkali the hydrogen ions are removed and the salt is precipitated. Now, I would just finished by saying it is a typical chemistry thing, you have in solution Thorium some Uranium, rare Earths.

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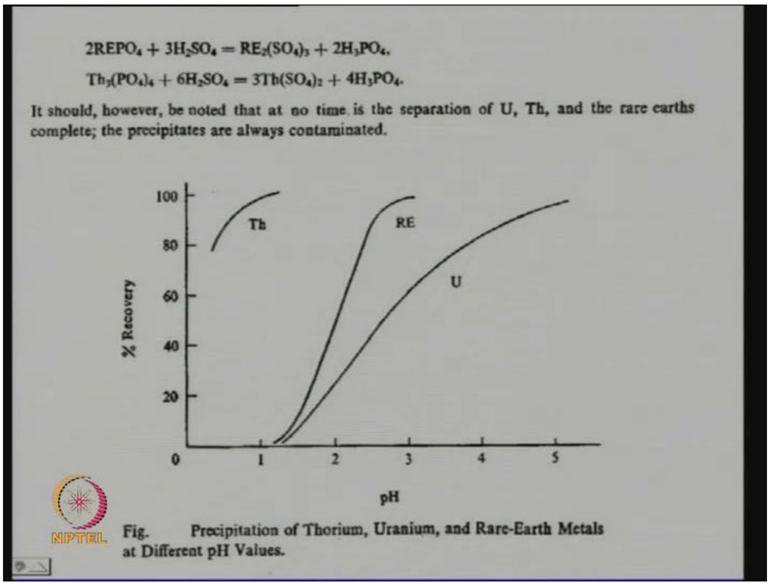

$$2REPO_4 + 3H_2SO_4 = RE_2(SO_4)_3 + 2H_3PO_4.$$

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

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.

They can be precipitate out of solution simply by adjusting the pH. This one example, there can be many such examples. Typical reactions I have mentioned here the rare earth phosphates in H 2 SO 4 will form this, Thorium phosphate will form this. At no time is separation of Uranium, Thorium and rare earths can be complete when we are trying to precipitate there. Like Thorium is precipitated at pH 1 means, highly acidic solution. Rare earths at a slightly higher pH, Uranium at even at higher pH.

Supposing the pH was adjusted here, then percentage recovery of Uranium would be this and percentage recovery of rare earths would be this percentage Thorium would be here even above that. Which means very rarely it is totally selective here, a lot of rare earths will come lot of Uranium will also come. If you are somewhere here neither rare earths nor Uranium is being precipitated by you can take out almost 100 percent Thorium. So, almost 100 percent Thorium can be taken out without any rare earths or Uranium. But rare earths and Uranium precipitation it is not that selective, no matter where you go unless, you go very pH value of something like this you will have some rare earths.

So well I will stop here for now just by saying. As we did in the case of Uranium and Plutonium, here also we have to when you come to Thorium you have to produce a compound. And the compound can be an oxide or a fluoride or a chloride. Then we have to think about again a metallothermic reduction. Again we will think of the same criterion free energy, change enthalpy, change physical state of reactants, physical state of the products which will be convenient in practice.

So, I will discuss that for Thorium and you will find things will be so similar to what we have discussed for Uranium, similar principles operate everywhere. And the that is why it is necessary to try to find out where are the similarities, where are the dissimilarities. That is that is the bases of knowing the settle differences in the extraction processes. Thank you. I will continue with that in the next lecture.