

Separation of Actinides - I
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So, after learning the complexation of actinides with inorganic as well as organic ligands, we see their separation chemistry and this has application in the nuclear fuel cycle. Now the separation of actinides in the nuclear industry mostly is based on precipitation, solvent extraction and ion exchange. And the precipitation was used in the Manhattan Project where the plutonium separation was done by the bismuth phosphate process. And there is a schematic of this bismuth phosphate precipitation process is on the right side. You see that mixture of Pu^{4+} , UO_2^{2+} , and the trivalent actinides, trivalent lanthanides and the NpO_2^+ (+5) and the fission products, their mixture to which this bismuth nitrate is added along with H_3PO_4 . You get the precipitation of bismuth phosphate.

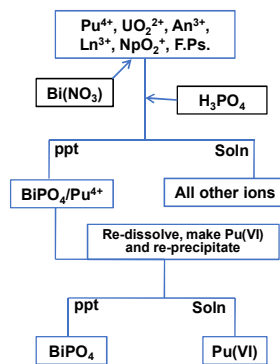
Separation of Actinides

Separation Methods in Nuclear Industry:

- **Precipitation**
- **Solvent Extraction**
- **Ion-exchange**

Precipitation:

- **This method was used for the separation of plutonium in “Manhattan Project”.**
- **Pu(IV) is co-precipitated along with Bi-Phosphate.**



And solution goes and all other ions actually they are coming in a solution while the Pu^{4+} is precipitated. This precipitate can be filtered and then re-dissolved to get a clear solution of Pu(VI) and then this can be again re-precipitated. That is how this bismuth phosphate precipitate of Pu(IV) is done and Pu(VI) goes into the solution. Subsequently, the solvent extraction processes have become more popular in the nuclear industry for both the front as well as the back end of the nuclear fuel cycle.

And in this case what one needs is an extractant which is responsible for forming a

complex with the actinide ion and then which is subsequently partitioned into a diluent phase. So, now this is the organic phase which contains the diluent, the extractant and the metal extractant complex. Whereas the aqueous phase which contains metal ions and other impurity metal ions. Now in case of solvent extraction, I have shown a schematic where actually the mixture of two ions marked with the orange and the red color they are initial in the aqueous phase and you mix the two phases and then you allow to settle. You find that the red pieces they go to the organic phase while the orange pieces they remain in the aqueous phases.

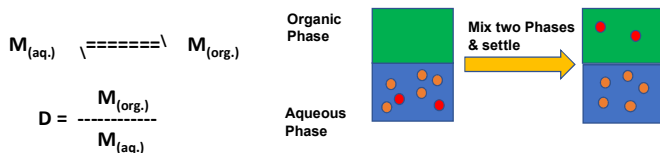
Solvent Extraction

- Solvent extraction is the most commonly used method in nuclear industry both in front as well as back end.
- For metal ion extraction one needs an extractant and a diluent.

Solvent Extraction?

Principle: At a given condition, the distribution of any species in the two phases is constant.

.....Nernst's distribution law.



Extraction of metal ion depends on ligand concentration, metal ion concentration, aqueous phase acidity, etc

So, that is how this separation is done in case of the solvent extraction. So, they follow the Nernst's distribution law where we have this distribution ratio which is defined as the concentration of the metal ion in the organic phase and the concentration of the metal ion in the aqueous phase. The metal ion in the aqueous phase remains in the variety of species including the free metal ion and the complex metal ions with the medium of the aqueous phase that is in case of the nitric acid medium you have the nitrate complexes of the metal ion. On the other hand, the organic phase contains the extractable complex species with the single species or in some cases if you have a mixture of extracted species then you have a mixed species. The extraction of the metal ions depends on the ligand concentration, metal ion concentration, aqueous phase acidity and other conditions like the diluent composition also.

Now for the metal ion extraction the requirement is that we need to neutralize the metal ion charge because the charged metal species is not partitioned into the organic phase and it is mostly present in the aqueous phase because of the hydration sphere of this

metal ions particularly for the actinide ions, very strong hydration spheres. They can never go into the organic phase as such. It is a non-polar organic medium and therefore, the extractant is required to form a complex and also you need a complexing anion. Like if you have a neutral extractant then you need a complexing anion like nitrate ion which makes the extracted species charge neutralized and because of the extractant, the species become hydrophobic and get partitioned into the organic phase. So there are different types of extraction mechanisms, i.e., the solvation, the ion pair, the ion exchange and finally the chelation.

Metal ion Extraction

Requirements

Neutralization of metal ion charge by extractant or complexing anion to make the species hydrophobic

- Solvation
 - TBP, ether, TOPO
- Ion-Pair
 - TOA, TLA
- Ion-exchange
 - D2EHPA, Aliquat 336
- Chelation
 - HTTA, DBM

Extractant properties

- Insoluble in water
- Freely soluble in org. solvent (immiscible with water)
- Should form a reversible complex with metal ions
- Faster complexation kinetics.
- Should have good stability
- Ease of availability/low cost

Diluent properties

- Non-polar
- Low aqueous solubility
- Easy phase separation
- Low viscosity

The extractants can also be classified as neutral, acidic as well as basic extractants. The basic extractants are the amines like trioctylamine or trilaurylamine I have mentioned here or the ion pair extraction. The neutral extractants can be TBP, diethyl ether or trioctyl phosphine oxide. So in those cases you need necessarily a counter anion that is the nitrate ion which can form charge neutralized complex along with these neutral donor ligands and that is how the extraction is done. In case of (diethyl) ether you need to do the extraction into the organic phase by something called salting out.

We have to add large concentration of salts so that it partitions favorably into the organic phase. We also have these acidic extractants: some of them are like thenoyl trifluoroacetone or HTTA, di-benzoyl methane or DBM. They are actually acidic extractants and they are existing in the enol form and that's how they give away one proton and then form charge neutralized complex with the actinide ion. Similar also is the case for the di-2-ethylhexyl phosphoric acid or D2EHPA. This can form charge neutralized complex with the actinide ions, i.e., this does not need a counter anion with the D2EHPA. Most of the cases, there are of course cases where you need counter anions with D2EHPA

as well. Now this Aliquat 336 is actually a liquid anion exchanger and in this case the extraction is taking place by ion exchange, i.e., the chloride part of this extractant is exchanged with anionic complex. Now coming to this extractant properties, most of these extractants should be insoluble in water and freely soluble in the organic solvent. This is the prime requirement. Otherwise, the complex will be present in the aqueous medium and not partition into the organic phase. There are of course some extractants which have reasonably good solubility in the aqueous medium as well like the crown ether or acetyl acetone which have good aqueous solubility and in those cases the partition is there to the aqueous phase to some extent, but major amount of the complex is partitioned into the organic phase.

That is how the extraction is achieved and the extractant should form a reversible complex with the metal ion so that you can strip it out at a later stage so that you first have the extraction of the metal ion and then you can strip it into the aqueous phase in a subsequent step so that the overall process (cycle) is complete. Then this kinetics of this extraction should be faster. If it is slow complexation kinetics with this extractant then it will take a unusually large time for this extraction to be complete.

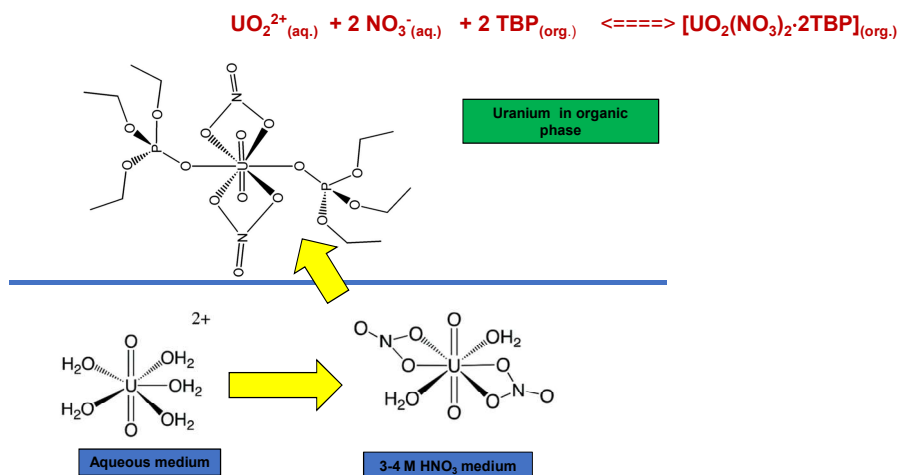
It is not practically viable to use such extractants for application purposes. Now these extractants should have a good stability. Now when I talk about the stability, generally it should have the hydrolytic stability, i.e., if in the acid medium, the acid hydrolysis of this extractant should not be taking place. And in the case of actinides, because most of the actinides are radioactive so the extractants should also have radiation stability. And finally, the extractant should be of low cost and easily available.

That is how the process cost can be reduced. Now along with the extractant as I mentioned we also need a diluent. So, diluents should have these following properties like it should be non-polar, it should have low aqueous solubility, it should be having easy phase separation ability and the diluents also should have low viscosity. Some of the diluents are highly viscous like the room temperature ionic liquids. That is why those are not proposed for the separation in a large scale because the time required for separation will be much larger.

Some of the extractants like Aliquat 336 is very viscous so it needs to be diluted properly with a suitable diluent so that extraction can be done in a favorable kinetics so that separation can be done in an acceptable time limit. I give some example here. Actinide extraction by solvation. Now the solvation is done here mostly by TBP. There are also other examples of this, viz. uranium extraction by diethyl ether, methyl isobutyl ketone (MIBK or hexone) and butex.

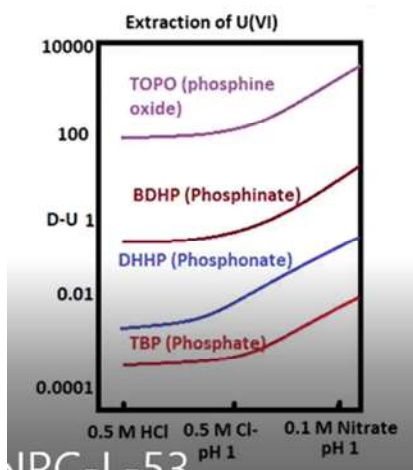
Actinide ion Extraction by Solvation

Example: Extraction of uranium by diethylether, MIBK, Butex, TBP, etc.



So, these are some of the extractants which has been used in the middle of the last century where these uranium extraction studies were carried out in different laboratories. And this is the extraction equilibrium what I have shown here is for the TBP where the uranyl ion (UO_2^{2+}) is present in the aqueous phase. It can form a complex with two nitrates to neutralize its charge that is $\text{UO}_2^{2+} + 2 \text{NO}_3^-$ becomes $\text{UO}_2(\text{NO}_3)_2$ but as such species cannot get partitioned into the organic phase that is why you need two TBP also in the organic phase which is coming to the aqueous phase. So, in such case what happens is that TBP is partitioned into the aqueous phase, forms a complex with the $\text{UO}_2(\text{NO}_3)_2$ species and finally you get this complex species which is $\text{UO}_2(\text{NO}_3)_2 \cdot 2 \text{TBP}$ which is stable in the organic phase. The schematic has been shown here in the aqueous phase where we have this hydrated uranyl ion which is forming a complex with a nitrate ion to give this type of species at 3 to 4 molar nitric acid. Now the TBP, which is there in the organic phase, can get partitioned slightly to the aqueous phase and incidentally TBP has a reasonably good aqueous solubility and then this TBP present in the aqueous phase can form a complex with the $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$ species. These two H_2O molecules are replaced by the TBP and then you have this species which is present in the organic phase.

Actinide ion Extraction by Solvation



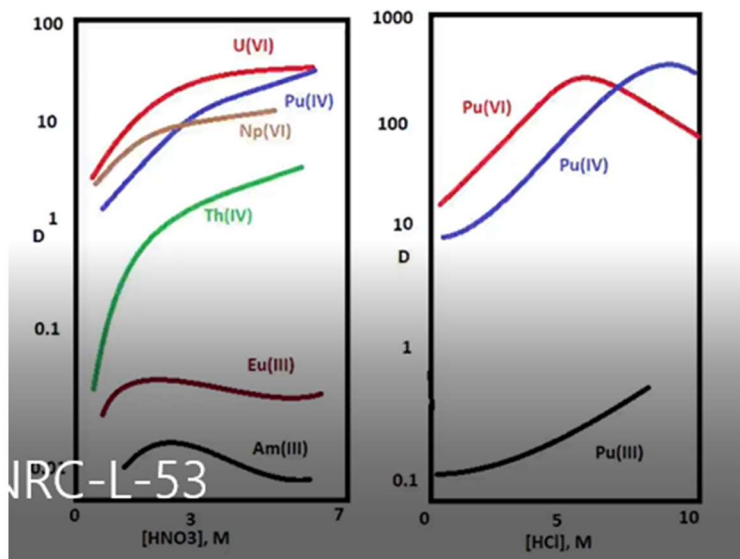
Comparison of U extraction with 0.1 M phosphate, phosphonate, phosphinate and phosphine oxide in kerosene

Now this is an example of these phosphate complexes and I was talking about this TBP is an organic phosphate and there are other phosphates or phosphorous ligands like which are having phosphoryl groups like in case of phosphate, phosphonate, phosphinate as well as phosphine oxide and these are shown in this figure where we are comparing the extraction of uranyl ion from different aqueous conditions that you see here that the phosphate that is the TBP is giving the lowest distribution ratio values. In all cases, you find that the extraction of TBP is lower than the other extractants but nevertheless depending on the concentration the TBP extraction can be made high but in all these cases the concentrations are much lower the anionic complexing ion here in this case it is either sulfate or fluoride or nitrate. Sulfate data is not given in the figure for simplicity but we are also studying these extraction studies at a much lower concentration of nitrate that is 0.1 M nitrate that is why this extraction of uranium is very very low with nitrate and TBP.

But if you have a phosphonate that is this ligand DHHP or di-hexyl hexyl phosphonate, in this case, you have the extraction of uranium significantly higher than that of TBP and you get the condition where you have the TBP extraction of uranium **D** at around 0.01 and it has increased to little less than that of 1. Now same also you get for the phosphinates so these phosphinates form stronger complexes so this BDHP in this case the extraction of uranium becomes significantly larger than that of the phosphonate DHHP and you get more than 10 as the distribution ratio of uranium under the condition where the extraction of uranium was around 0.01 with TBP. So for phosphinate you have higher extraction and if you go to phosphine oxide, i.e., tri-octyl phosphine oxide (TOPO) then you get the distribution ratio of uranium around 1000 or maybe little more than that. So this suggests that it depends on the basicity of these extractants and tri-octyl phosphine oxide is a strong base and it forms a stronger complex that is how the uranium extraction

is much higher with TOPO. Also I have shown here a comparison of actinide extraction by TBP. So this trivalent actinide ion extraction I have shown in the right side, i.e., of Pu(III) from HCl medium and that of Am(III) from the nitric acid medium in the left side figure and you can see that in the hydrochloric acid medium the extraction of trivalent actinide is significantly larger compared to that with the nitric acid medium.

Actinide ion Extraction by TBP



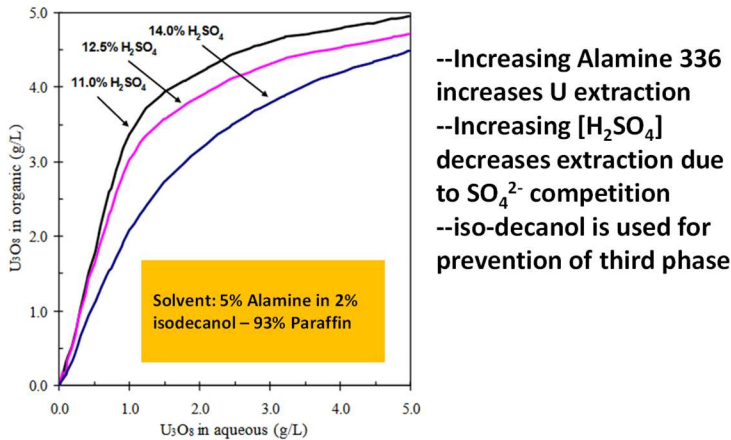
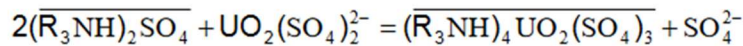
Trivalent actinide ion extracted from HCl medium

Now I have discussed earlier also in one of the previous lectures that is Am(III) extraction with TBP from nitric acid medium is very very insignificant and if it is possible it is only by salting it out in the absence of nitric acid. So that is by taking large concentration of sodium nitrate you can carry out the extraction of Am(III) using TBP. Now, europium also is extracted poorly but higher than that of Am(III) so you get slightly higher extraction of europium compared to americium maybe around one order of magnitude higher but then at higher concentration of nitric acid maybe around 5 to 6 molar you can have a good separation of americium from europium. Thorium extraction, because it is a tetravalent ion, with nitric acid is very good and plutonium extraction (Pu⁴⁺) is even more than that of thorium because of the ionic potential. U(VI) extraction is much larger than that of Pu(IV) in view of the fact that Pu(IV) can form stronger complex but uranium extraction is much higher than that of Pu. In most part of this figure, I have shown that which is because U(VI) has 2 nitrates and Pu(IV) has 4 nitrates and that is how under TBP present in these two species that is U(VI) extraction species and Pu(IV) extraction species have 2 TBP in each case. So, the hydrophobic part is same but the hydrophilic part is much

higher for Pu(IV) that is the nitrate ion that is how the extraction of Pu(IV) is lower than that of U(VI). Pu(IV) extraction is lower than that of Pu(VI) and same also for Np(VI). That means it is more than that of Pu(IV) up to maybe around 2 to 3 molar nitric acid. However, beyond that Np(VI) extraction is lower than that of Pu(IV) but Np(VI) extraction is lower than that of U(VI). That is because of the less strong complex formation of Np(VI) as compared to U(VI). Now, in case of the chloride medium as you see in the right side of the figure, Pu(IV) extraction is lower, Pu(VI) extraction is higher similar to what we have seen in case of the nitrate medium for U(VI) and Pu(IV) but the distribution ratio values indicate that this plutonium extraction is relatively larger than that of what we see in the nitric acid medium.

ION-PAIR EXTRACTION

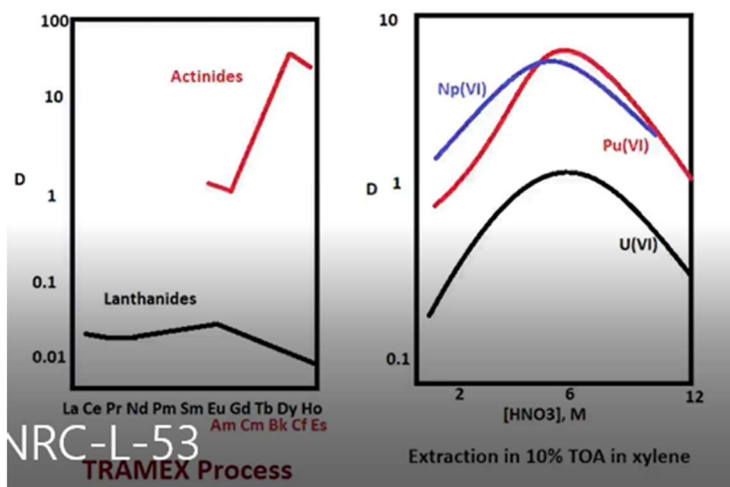
The AMEX (Alamine 336) process of U extraction in the front end of nuclear fuel cycle



Now coming to the ion pair extraction, I give some example where the Alamine 336, the commercial extractant, it is (called) tricaproyl amine. It extracts the uranium which has application in the front end of the nuclear fuel cycle and as I have mentioned the sulphate complexation the anionic sulphate complexes have formed and which is extracted by the sulphate form of this amine which is protonated. So, you have $(R_3NH^+)_2 \cdot (SO_4)^{2-}$ this type of species is there and this where in uranyl sulphate also forms an ion pair and the sulphate from the amine part which is going to the aqueous phase and this is soluble in the organic phase. Now increasing the Alamine 336 concentration increases the uranium extraction, increasing the sulphuric acid concentration decreases the uranium extraction as shown in this figure. Here the solvent used is 5% Alamine in 2% iso-decanol and 93% paraffin and the sulphate concentration increase suggest lower extraction that is because of competition

between sulphate as well as the anionic uranyl sulphate species indicated here. In this extraction method isodecraanol is used as a phase modifier that is used to prevent the third phase formation.

ION-PAIR EXTRACTION OF ACTINIDES



TRAMEX Process: 0.6 M Alamine 336 in xylene. Aq.: 11M LiCl + 0.2 M HCl

Extraction in 10% TOA in xylene

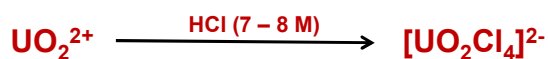
We also have this ion pair extraction of actinides. I have made a comparison of this for the extraction of U(VI), Np(VI) and Pu(VI) from nitric acid medium using 10% trioctylamine in xylene. Trioctylamine is a tertiary amine and this data is presented in the right side figure. You can see here that the neptunium extraction is highest at a lower acid concentration, i.e., < 6 M nitric acid concentration. The Np(VI) is extracted to a larger extent compared to that of plutonium extraction. Plutonium extraction is larger compared to that of the uranium extraction and you get this type of curves are formed here that means at higher concentration of nitric acid there is a competition between the nitrate ion and that of the anionic complexes formed. So that is how this ion pair extraction of the actinides are taking place from the nitric acid medium with xylene (as diluent). For neptunium and plutonium in the hexavalent state they are forming anionic complexes to a significantly higher extent as compared to that of uranium and that is the reason of this extraction.

Now another application of this ion pair extraction of actinides is the separation of trivalent actinides and lanthanides as shown in the left side figure. 0.6 M Alamine 336 is used which is tricaproyl amine which is a tertiary amine. Alamine 336 is used in xylene and you see the aqueous medium is 11 M lithium chloride containing 0.2 M HCl. HCl is

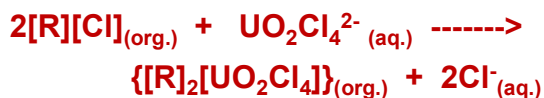
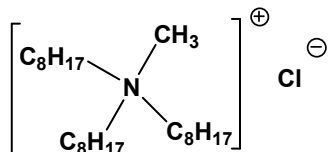
added to prevent the hydrolysis of the metal ions and the extraction of actinides is significantly larger compared to that of the lanthanides and that is how this trivalent actinides can be separated from the trivalent lanthanides which have relatively lower distribution ratio values. And this is used initially for the separation of trivalent actinides and lanthanides.

Metal ion Extraction by Ion-Exchange

Example: Extraction of uranium by Aliquat 336



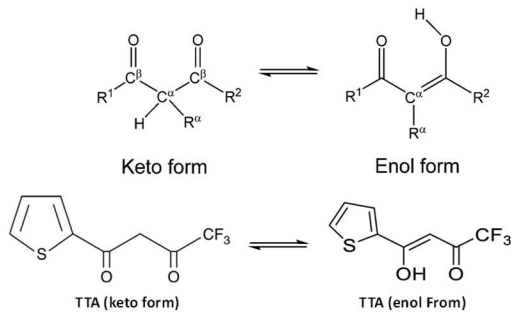
Aliquat 336
(Liquid Anion Exchanger)



Here, Cl⁻ of Aliquat 336 in the organic phase is exchanged with the UO₂Cl₄²⁻ of aqueous phase.

Now metal ion extraction by ion exchange: Here, I have given an example of extraction of uranyl ion by Aliquat 336 from hydrochloric acid medium (7 to 8 M). Uranyl ion forms species like this UO₂Cl₄²⁻ and this anionic species gets exchanged with Aliquat 336 (chloride ion) that is what is shown here. This aliquat 336 is a tricaprile methyl chloride and this actually for simplicity purpose we have shown here only 3 octyl groups but it can be anywhere between hexyl to octyl in a commercially available region. Now the chloride of the Aliquat 336 is exchanged with the UO₂Cl₄²⁻ species present in the aqueous phase and that is how uranium is extracted using Aliquat 336.

Importance of beta-diketone ligands in solvent extraction



- Dissociation of $-OH$ group in the enol will depend on pK_a values of the beta-diketones.
- By substituting the R group, pK_a values can be tuned, thus the selectivity for tri-, tetra and hexavalent cations.

Example: Acetyl acetone, $pK_a = 8.8$, Thenoyl trifluoroacetone (TTA), $pK_a = 6.2$

- TTA is widely used to extract tri-, tetra- and hexavalent actinides (example Pu) by suitable tuning of aq. pH
- At 1 M HNO_3 ($pH = 0$), it extracts only Pu(IV).
- At $pH = 2$ it will extract Pu(VI)
- At $pH > 4$, it extracts Pu(III)

Another class of this extractant is this beta diketones which are again acidic extractants and they form actually chelate complexes where this beta diketone like thenoyl trifluoroacetone (TTA) or HTTA, simply TTA which is written here and they form generally present in the keto form and they are in equilibrium with the enol form and at a given condition the aqueous phase containing the metal ion (for example let us take the plutonium ions) then this enol form of TTA forms a complex with the plutonium ions and that is how the plutonium ions can be extracted into the TTA medium. So, by adjusting the conditions of the aqueous phase this plutonium extraction can be achieved. If you are having plutonium in the +4 oxidation state and the aqueous phase is 1M nitric acid then only Pu(IV) will be extracted. That is how the Pu(VI) and Pu(III) species can be left behind in the aqueous phase. Now subsequently, if you want to extract the Pu(VI) from the aqueous phase leaving behind the Pu(III) then you adjust the pH of the aqueous phase to 2 that is how by TTA extraction, Pu(VI) can be separated from the aqueous phase and finally whatever you are having in the aqueous phase is a Pu(III). Or you can simply extract the Pu(III) into the TTA phase by pH value around 4 to 5. So if you go to beyond pH 6.2 then it will have hydrolysis of TTA as well and that will create problems in the metal ion extraction.

Reprocessing of spent fuel: PUREX Process

Tri(n-butyl)phosphate (TBP)

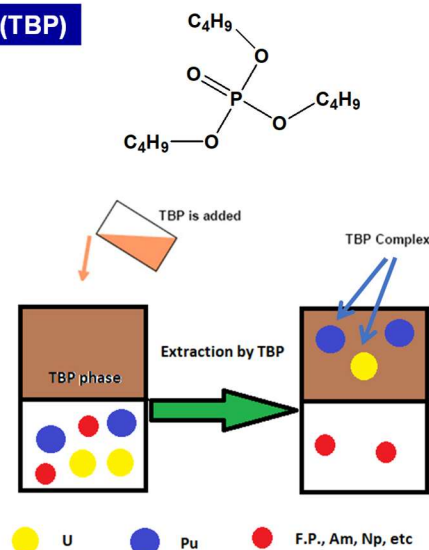
❖ **PUREX Process:** Plutonium Uranium Reduction Extraction Process

❖ **Extractant:** 30% TBP in *n*-dodecane

- Supply and cost
- Good physical properties
- Reasonable stability
- Non toxic nature
- Adequate selectivity and fast kinetics

❖ **Separation Scheme:**

- Co-extraction of Pu(IV) and U(VI)
- Partition of Pu(III) from U(VI) & U(IV)



Now finally we come to the reprocessing of this spent fuel. This is the application of the TBP extraction and I have discussed for uranium and also for plutonium. So this process is called the PUREX process or **P**lutonium **U**ranium **R**edox **E**xtraction process. Now where this TBP (the structure which is given here) forms a complex with Pu(IV) and also with U(VI) that is the uranyl ion and both these metal ions are extracted into the TBP phase which is taken in *n*-dodecane.

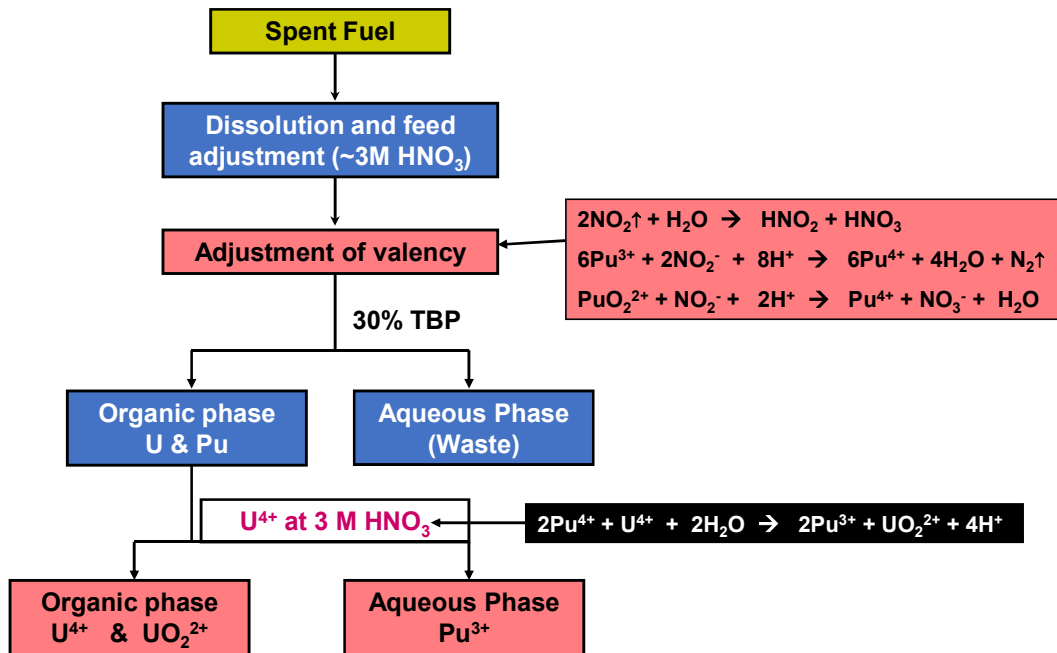
The major advantage of this PUREX process is that the organic solvent containing the TBP it extracts only U(VI) ion as well as Pu⁴⁺ ion and then these are extracted leaving behind the fission products like Cs⁺, Sr²⁺ and also the trans-plutonium elements like Am³⁺, Cm³⁺ etc. And fission products they contain most of the elements also that is how this trivalent actinides and lanthanides are directed to the radioactive waste stream and the separation scheme is actually the co-extraction of Pu(IV) and U(VI) by the TBP and in a subsequent state this plutonium and uranium partitioning is done by reducing plutonium to the +3 oxidation state. So now the steps will be discussing in a next slide but here one thing I would like to mention that only 30 percent TBP is used because to use high concentration of TBP then there are problems like there will be viscosity of this medium increased and also the metal and loading can be significantly higher and that will create problem in the operations in the plants. So the major problem in case of this that TBP undergoes the radiolytic as well as hydrolytic degradation and continuous use in the plant and the degradation products of TBP are the monobutyl phosphoric acid (MBP) or the dibutyl phosphoric acid (DBP). They form strong complexes with plutonium and that is how it is not possible to recover plutonium from the extracted phase.

So because of that this degradation products that is the MBP and DBP they can be

separated from the TBP phase by giving alkali wash or the sodium carbonate wash. That is how the degradation products are removed and this TBP can be recycled. And subsequently after a long time use, this TBP which is a spent solvent we can call this is again if given for the cementation in the waste management. So that is how this TBP is finally separated from this plant and also this kinetics of this extraction of uranium and plutonium is relatively fast.

TBP is non-toxic and it has a very low cost. In view of this several good physical properties this TBP is used in the reprocessing plant worldwide in the last several decades and also one of the major advantage of the TBP is that this decontamination factors for the efficient products are very very high. Now the schematic of the PUREX process is given here that you have the spent fuel and which is dissolved and the feed adjustment is done to 3 M nitric acid. Finally, the plutonium valency adjustment is a must. So plutonium as you know it exists in different oxidation states like +3, +4, +5, and +6. But +5 stability is much much less because of the disproportionation.

Scheme of PUREX Process



U & Pu recovery and decontamination from fission and activation products is necessary

That is how this Pu(III) and Pu(VI) they are actually adjusted to Pu⁴⁺ oxidation state by the nitrite ion as shown here. You get this nitrite ion by dissolving this NO₂ gas as shown here in the first equilibrium and in the second one the Pu³⁺ is converted to Pu⁴⁺ and the third equilibrium shown here suggests plutonyl ion that is PuO₂²⁺ plus is converted to Pu⁴⁺ up there. So nitrite ion is actually doing the dual role that is this oxidizing plutonium 3

plus and also reducing plutonium in the six plus state. Using 30% TBP, the organic phase is having both uranium and plutonium as the extracted species that I have already discussed before. Now subsequently the aqueous phase which is coming out of this extraction cycle this will have all the fission products and also the trans plutonium elements like americium, curium etc.

Then this organic phase containing the uranium and plutonium extract in TBP is actually given a partitioning stage where U^{4+} is passed and then Pu^{4+} is reduced to Pu^{3+} so it goes to the aqueous phase and the uranium which is there in the organic phase is subsequently recovered and then purified for further use. Thank you.