Separation of Actinides - II

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Week – 11

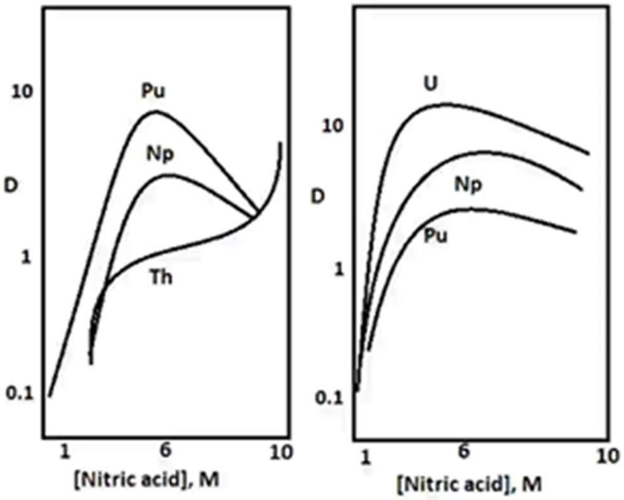
Lecture – 54

So, we were discussing the complexation of actinides and subsequently, we also discussed about the extraction of actinides which has relevance in the nuclear fuel cycle, specifically for the reprocessing of spent nuclear fuel. I will give some more details on this application of complexation and extraction of actinides in this lecture. Now, this is for the extraction of tetra as well as hexavalent actinide ions. Hexavalent ion means, as I have already mentioned, the ionic species is AnO_2^{2+} where 'An' stands for the actinide element. That is to say for uranyl ion, it is UO_2^{2+} and like that for neptunium and plutonium.

The profiles I have shown in this slide are the comparative extraction of the +4 and +6 actinides by TBP where 30% TBP is used here. The solution made in aliphatic diluent like kerosene or dodecane. And the left side figure gives the extraction of tetravalent actinides by 30% TBP.The extraction equilibrium for this is given here.

$M^{4+}_{(aq)} + 4\ NO_3^{-}{}_{(aq)} + 2\ TBP_{(org)} = M(NO_3)_4.2TBP_{(org)}$

COMPARATIVE EXTRACTION OF +4 and +6 ACTINIDES BY TBP



An(IV) extraction by 30%THP AnO_2^{2+} extraction by 30%THP

Trend: $UO_2^{2+} > Pu^{4+} > NpO_2^{2+} > Np^{4+} > PuO_2^{2+} > Th^{4+}$

First equation gives the extraction equilibrium where the tetravalent metal ion in the aqueous phase is forming a complex with 4 nitrates again in the aqueous phase and 2

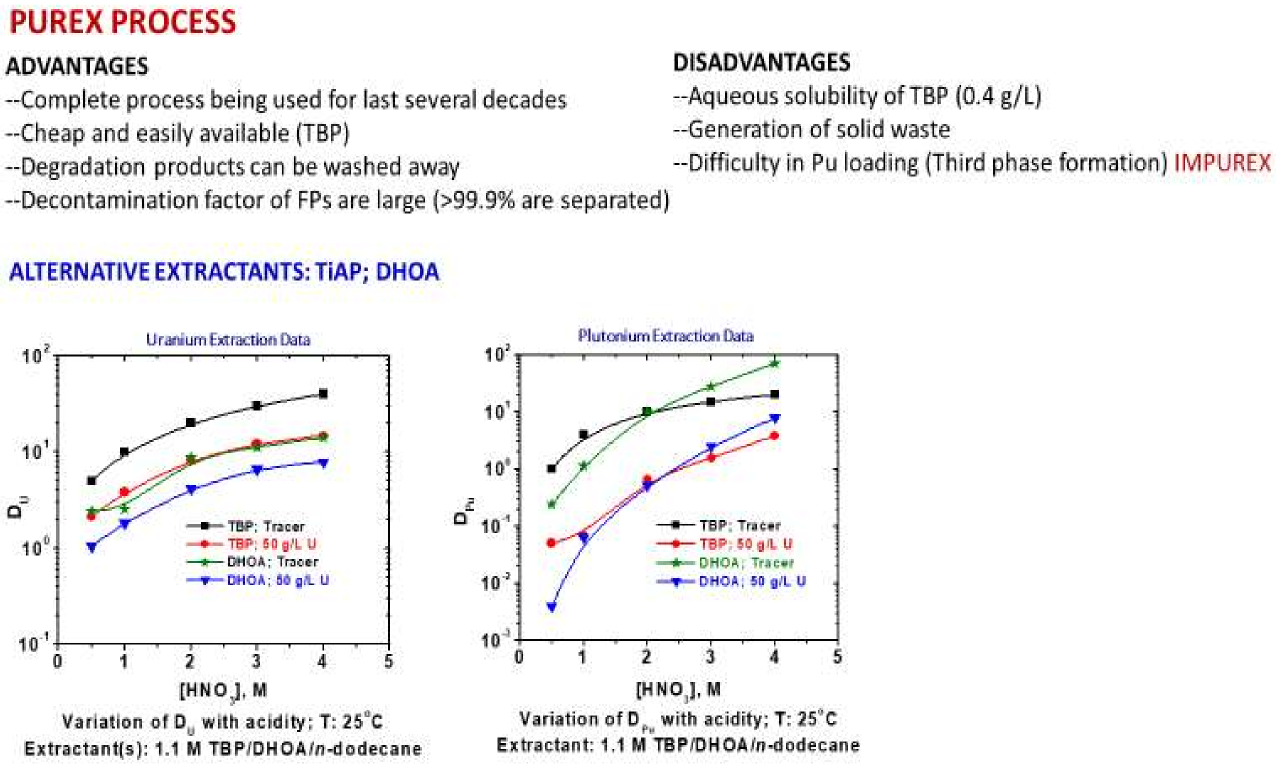
TBP present in the organic phase and resulting in a complex of the type $M(NO_3)_4.2$ TBP which is favorably partitioned into the organic phase. So, the left side profile shows that of the tetravalent actinide ions. You can see that the extraction of Pu(IV) is increasing with increasing nitric acid concentration.You see that this extraction is going up and beyond around 6 M nitric acid it falls which is because of two factors. As I have already mentioned in this extraction equilibrium with increasing nitric acid concentration, the nitrate ion concentration is increasing. Therefore, the formation of this species, i.e., $M(NO_3)_4.2$ TBP is increasing with increasing nitrate ion concentration.That is to say, with increasing the nitric acid molarity this extraction should increase. However, beyond around 6 M nitric acid, the extraction of this tetravalent ion here in this case Pu^{4+} ion extraction is decreasing. That is because of two factors. Number one is that TBP is forming a complex with nitric acid that is $TBP.HNO_3$type species are formed.This can be 1 HNO_3 depending on the higher concentration it can be 2 HNO_3,and like that this adduct species are formed. That reduces the effective concentration of TBP in the organic phase that is why the extraction of$Pu^{4+}$is decreasing. And the second reason is that plutonium at higher nitric acid concentration forms anionic species, i.e., like $Pu(NO_3)_6^{2-}$. So, this type of species are formed at higher nitric acid concentrations maybe something like 6 to 7 M nitric acid or beyond.So, that is the second reason why the plutonium extraction is decreasing. Similar behavior is seen for Np^{4+}ion as well. On the other hand, the Th(IV) extraction is significantly lower as you see here and at higher nitric acid concentration the thorium extraction is increasing. That is because of some salting out effect.

Now coming to the hexavalent actinide ions like uranyl, neptunyl and plutonyl ions, the extraction equilibrium is given by the second equation here.

$$MO_2^{2+}{}_{(aq)} + 2\ NO_3^-{}_{(aq)} + 2\ TBP_{(org)} = MO_2(NO_3)_2.2TBP_{(org)}$$

That is the actinyl ion in the aqueous phase binds with the two nitrate ions present in the aqueous phase and two TBP present in the organic phase to give this extracted species. You can see this two species for the tetravalent as well as the hexavalent ions. You find that the number of TBP molecules are same for both. So that means the organophilicity of this extracted complex due to the presence of TBP is same for the tetravalent as well as the hexavalent metal ions. On the other hand, for the tetravalent metal ion we have four nitrates.So, the nitrate ions are more favorably partitioned into the aqueous phase. So that is the reason why this $M(NO_3)_4.2$ TBP species is partitioned less towards the organic phase compared to the $MO_2(NO_3)_2$. 2 TBP species. That is the reason why uranium(VI) extraction is higher than that of plutonium(IV) extraction from nitric acid medium using TBP.

Now the extraction of the hexavalent metal ions, given in the right side figure, where you find that uranium(VI) extraction is higher than that of neptunium(VI) which is in turn higher than that of plutonium(VI). Now the relative trend of this extraction of the actinide(IV) and actinide(VI) metal ions by 30% TBP from nitric acid medium is given here where you find that the uranium(VI) is extracted higher than that of plutonium(IV) which is extracted higher than neptunium(VI) which is extracted higher than neptunium(IV) which is extracted higher than plutonium(VI) which in turn is extracted higher than thorium(IV). So, thorium(IV) is least extracted out of the actinide ions. Now this has relevance in the PUREX process as I have already mentioned. We come to the advantages of the PUREX process.



PUREX PROCESS

ADVANTAGES

--Complete process being used for last several decades
--Cheap and easily available (TBP)
--Degradation products can be washed away
--Decontamination factor of FPs are large (>99.9% are separated)

DISADVANTAGES

--Aqueous solubility of TBP (0.4 g/L)
--Generation of solid waste
--Difficulty in Pu loading (Third phase formation) IMPUREX

ALTERNATIVE EXTRACTANTS: TiAP; DHOA

Variation of D_U with acidity; T: 25°C
Extractant(s): 1.1 M TBP/DHOA/*n*-dodecane

Variation of D_{Pu} with acidity; T: 25°C
Extractant: 1.1 M TBP/DHOA/*n*-dodecane

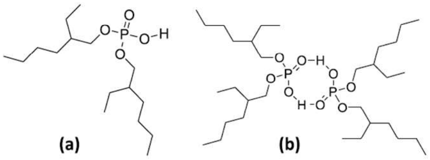
It is a complete process because it has been used for the last several decades. So technology is very well known. TBP which is used as the extractant in case of the PUREX process is cheap and easily available. So, it actually helps in the economy of this process. And this degradation products of the TBP which are monobutyl phosphoric acid and dibutyl phosphoric acid, they can be washed out easily using sodium carbonate solution. Decontamination factor of the fission products are large, that is greater than 99.9% of the fission products are separated during the PUREX process. But there are some disadvantages of the PUREX process as well. That is the aqueous solubility of TBP is quite significant, i.e., 0.4 grams per liter of TBP is going to the aqueous phase which then lead to the generation of solid waste. So, finally after this, the spent solvent has to be managed actually as a solid waste which is the phosphates. And thus, TBP actually this fails the CHON principle. So, the green extractants which would have carbon, hydrogen, oxygen and nitrogen. So, TBP is not that type of extractant as it contains phosphorous. So, it fails the CHON principle of the green extractants. And also, this difficulty in plutonium loading, when you go for the fast breeder reactors, spent nuclear fuel, so in that case plutonium concentration is much higher. Thus, in that case we find the third phase formation in this process. So for that what are the alternatives that we have to go for the processes like one which is called the IMPUREX process.That IMPUREX means it is improved PUREX process. So now in case of the IMPUREX process, the extraction of uranium and plutonium is carried out at a higher temperature, say around 60 degrees Celsius. In that case the plutonium extraction becomes higher and uranium extraction becomes lower. So, in view of that plutonium loading can be increased.

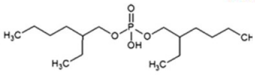
There is another alternative is to go for the branched alkyl group phosphates. So that is like tri-isoamyl phosphate or TiAP which has been tested in different laboratories to show that it is having much higher plutonium loading and third phase formation problem is less. And finally, there is this dialkyl amide like DHOA, that is a dihexyl octanamide. This has been found to be one of the most useful extractants in place of TBP. And for this lot of research has been carried out by the French researchers whohave suggested DHOA, one of the possible replacing extractants for TBP.

I have shown here the profiles of TBP and DHOA in these two figures below. The first figure on the left side gives that of TBP and DHOA for uranium extraction. The data given in the black line is the tracer data for TBP and the green line is the tracer data with DHOA and also the data is there with 50 grams per liter uranium loading. So there you can see that compared to TBP, (the red line), the DHOA extraction data is somewhat inferior. But nevertheless, you can get reasonably good distribution ratio values around 3 to 4 molar nitric acid, even with DHOA, that is dihexyloctanamide.On the other hand, the plutonium extraction data is given in the right side figure where very interesting observation has been made that the TBP and DHOA under 50 grams per liter uranium loading, the data is given as the red line and the blue line, respectively. And you can see that beyond 2 molar nitric acid, the extraction by DHOA is better than that of TBP and also less than 2 molar nitric acid, the extraction of TBP is better than that of DHOA. So this suggests that if you have higher plutonium loading, you can increase the nitric acid concentration and you can have higher extraction of plutonium(IV) and at lower nitric acid concentration, plutonium D values become so less (as shown here) that this plutonium can be stripped efficiently without using a reducing agent as in the PUREX process. This is a big advantage of this di alkylamide extraction DHOA for spent fuel reprocessing. Nevertheless, this has not been used, it is still in the testing stage.

APPLICATION OF COMPLEXATION AND EXTRACTION OF ACTINIDES

DAPEX Process (HDEHP)





HDEHP

Extraction:

$$UO_2^{2+} + 2(HDEHP)_2 \rightleftharpoons UO_2(HDEHP.DEHP)_2 + 2H^+$$

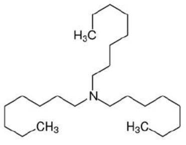
Alkaline Stripping

$$UO_2(HDEHP.DEHP)_2 + 4Na_2CO_3 \rightleftharpoons UO_2(CO_3)_3^{4-} + 4NaDEHP + H_2O + CO_2 + 4Na^+$$

Acid Stripping

$$UO_2(HDEHP.DEHP)_2 + 2H^+ \rightleftharpoons 2(HDEHP)_2 + UO_2^{2+}$$

AMEX Process (TOA)



Trioctyl amine

Amine is better for U uptake from sulphuric acid leach solution

Extraction

$$UO_2^{2+} + SO_4^{2-} + 2(R_3NH)_2SO_4 \rightleftharpoons (R_3NH)_4UO_2(SO_4)_3$$

Stripping

$$(R_3NH)_4UO_2(SO_4)_3 + 4\,HX \rightleftharpoons$$
$$4R_3NHX + UO_2^{2+} = 3HSO_4^- + H^+$$

$$(R_3NH)_4UO_2(SO_4)_3 + 7Na_2CO_3 \rightleftharpoons 4R_3N + UO_2(CO_3)_3^{4-} +$$
$$4HCO_3 + 3SO_4^{2-} + 14Na^+$$

Now coming to the application and complexation of actinides. So for this, there are two more processes, that is the DAPEX process and the AMEX process. These are the front-end processes where the uranium extraction is done from the leach liquor. Uranium from the ores actually you can see that is leached out using either acidic leaching or alkaline leaching. So again using our complexation theory, whatever we have already studied in these lectures, uranium forms good complexes with sulfate as well as carbonate. So that is why dilute sulfuric acid or carbonate solutions are used for the leaching. Now this DAPEX process is actually a dialkyl phosphoric acid extraction process. It is a short form in the DAPEX and the extractant uses HD2EHP (or D2EHPA). This is a phosphoric acid extractant as shown here, structure is given here. This H2DEHP in non-polar diluents forms a dimer as shown the structure shown here.

And then always while writing the extraction equilibrium, we write HD2EHP twice, that means this is a dimeric form of HDEHP as shown in this extraction equilibrium here. UO_2^{2+} plus 2 units of this dimer of HD2EHP is giving this extracted product here. That is the $UO_2(HD2EHP.D2EHP)_2$. That means from here this hydrogen ion is replaced and then this is forming a chelate complex with 2 units of this dimer. So, uranium is here and it forms complex like this binding to these two oxygens (in the dimeric form of ligand). Now this extracted species can be stripped to give the uranium product by acid stripping as well as alkaline stripping. By alkaline stripping as shown here, you can use sodium carbonate and you get uranyl carbonate which are the product. And by acid stripping you can use different acids and you find this reaction here where you have this uranyl ion coming to the aqueous phase.

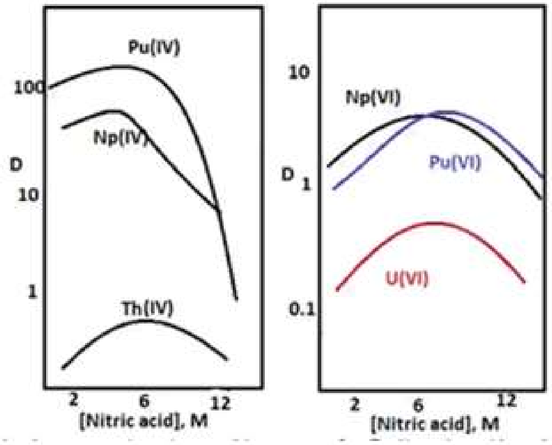
There is another process in the front end where this sulfate leached liquor is actually used for the uranium extraction.That is the AMEX process where one tertiary amine is used, that is tri-octyl amine (TOA). And amine is better for the uranium uptake from sulfuric acid leached solution because the uranyl ion forms an anionic complex in the sulfate medium and that extraction equilibrium is given here. You see that this anionic complex of uranyl ion is actually forming complex by some sort of an ion pair type of extraction mechanism. And you see that R_3NH^+ is actually binding with $UO_2(SO_4)_3^{4-}$. And then this extracted species can lead to the uranium by a stripping mechanism which is given below.

$$(R_3NH)_4UO_2(SO_4)_3 + 4\,HX \rightleftharpoons 4R_3NHX + UO_2^{2+} = 3HSO_4^- + H^+$$

$$(R_3NH)_4UO_2(SO_4)_3 + 7Na_2CO_3 \rightleftharpoons 4R_3N + UO_2(CO_3)_3^{4-} + 4HCO_3 + 3SO_4^{2-} + 14Na^+$$

You can have either this stripping mechanism or by the carbonate method also you can have the stripping of uranium. So, that is how this uranium stripping is done. Now comparative extraction of this +4 and +6 actinides by tri-octyl amine (TOA) and xylene as the solvent system. I have summarized here for both the tetravalent as well as hexavalent actinide ions.

COMPARATIVE EXTRACTION OF +4 and +6 ACTINIDES BY 10% TOA / XYLENE



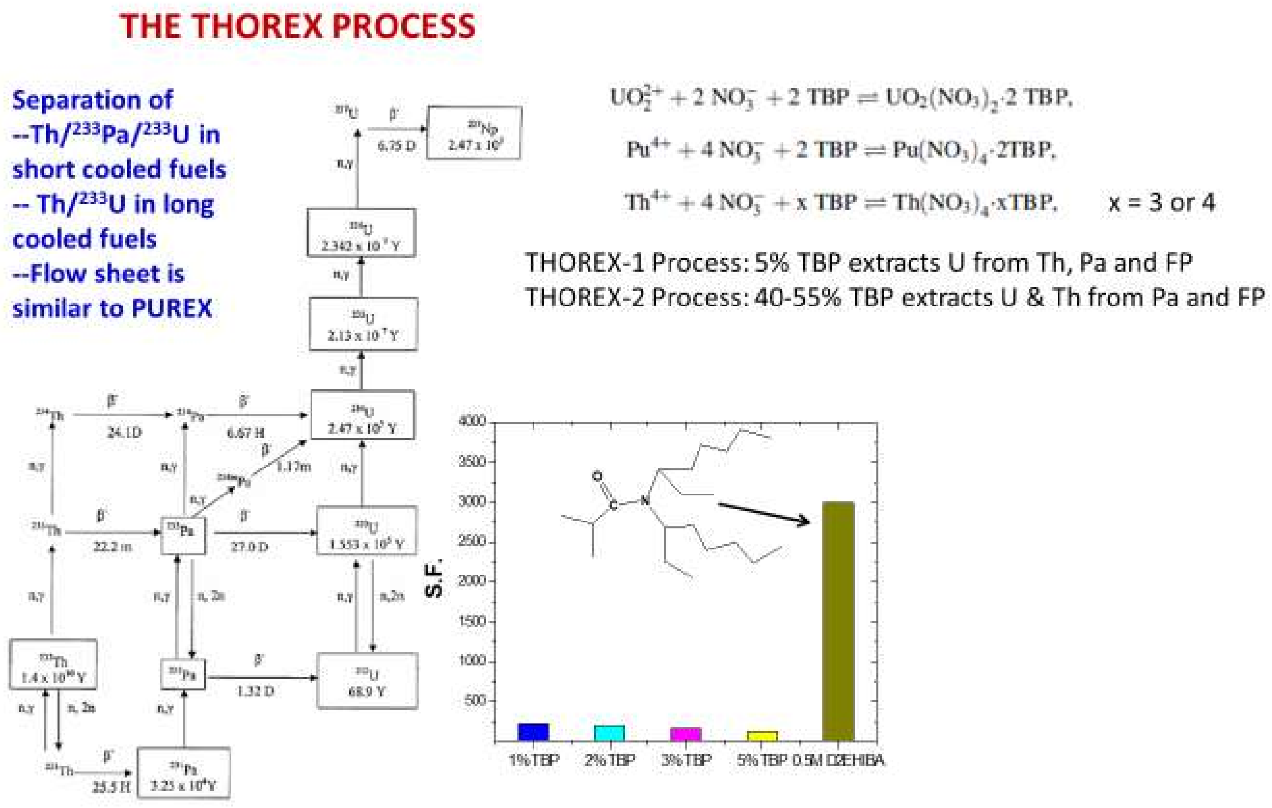
An(IV) extraction by 30%THP AnO_2^{2+} extraction by 30%THP

Trend: $Pu^{4+} > U^{4+} > NpO_2^{2+} > PuO_2^{2+} > UO_2^{2+} > Th^{4+}$

You can see here that the left side figure gives the extraction profiles using 10 percent tri-octyl amine and xylene.And you see that the plutonium(IV) extraction is higher than that of neptunium(IV) than that of thorium(IV) as shown here. These extraction profiles are there shown here. And uranium(IV) profile is not very clearly shown here.

But the right hand side figure shows the uranium(VI), neptunium(VI) as well as plutonium(VI) extraction profiles as a function of the nitric acid concentration. And you see that with increasing nitric acid concentration the extraction increases and then subsequently it falls down that is because of the competition between the nitrate ion with that of the anionic complexes of the actinyl ions.

So, these actinyl ions form anionic complexes as I have mentioned, i.e.,like $PuO_2(NO_3)_n^{(n-2)-}$. This type of species it can form. And then with a increasing nitric acid concentration you can find that this species is forming to a large extent and then that is how it is getting extracted and subsequently at higher nitric acid concentration because of the competition with the nitrate ion so it actually falls. Now this trend of this actinide ions or the actinyl ions with the amine extractants like tri-octyl amine is given here. So, where this tetravalent plutonium is extracted to a much larger extent than that of a uranium tetravalent and which is in turn larger than that of the neptunium(VI) that is NpO_2^{2+} ion which is larger than the PuO_2^{2+} ion and which is larger than the uranyl ion and finally the Th^{4+} ion extraction is very very less.



THE THOREX PROCESS

Separation of
--Th/^{233}Pa/^{233}U in short cooled fuels
-- Th/^{233}U in long cooled fuels
--Flow sheet is similar to PUREX

$$UO_2^{2+} + 2\,NO_3^- + 2\,TBP \rightleftharpoons UO_2(NO_3)_2\cdot 2\,TBP,$$

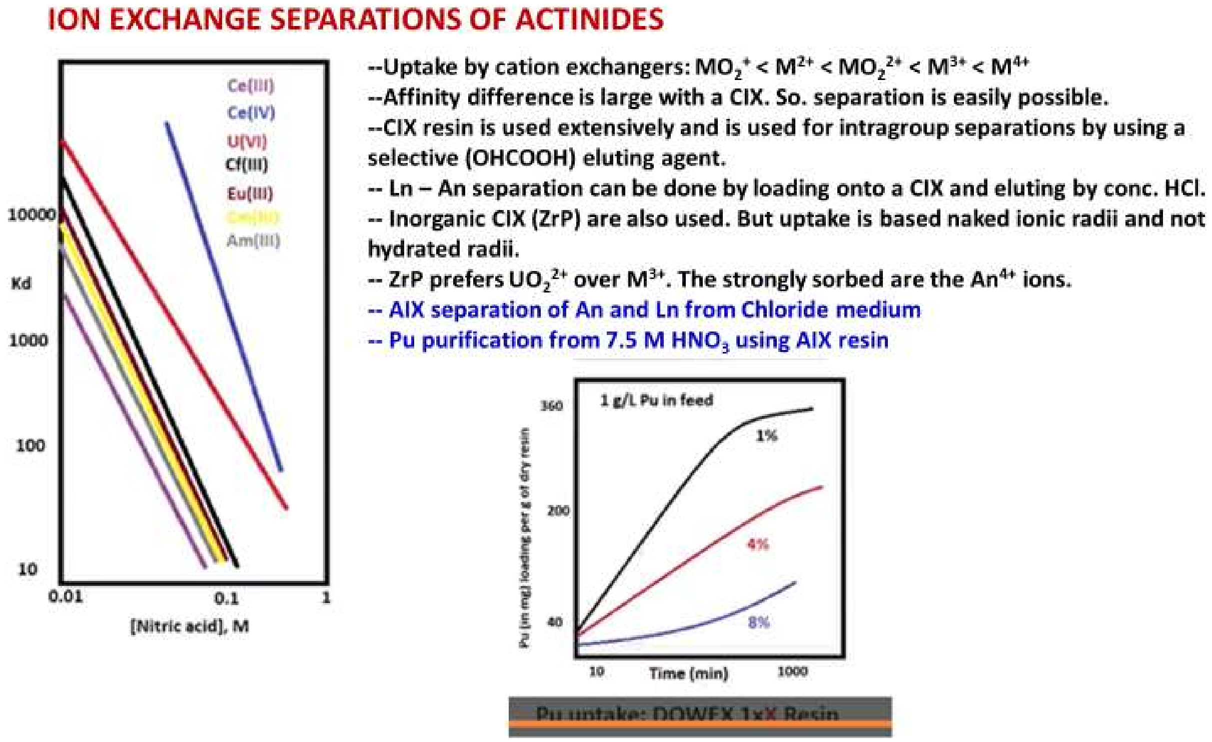
$$Pu^{4+} + 4\,NO_3^- + 2\,TBP \rightleftharpoons Pu(NO_3)_4\cdot 2TBP,$$

$$Th^{4+} + 4\,NO_3^- + x\,TBP \rightleftharpoons Th(NO_3)_4\cdot xTBP, \qquad x = 3 \text{ or } 4$$

THOREX-1 Process: 5% TBP extracts U from Th, Pa and FP
THOREX-2 Process: 40-55% TBP extracts U & Th from Pa and FP

Now the one thing which is very common in the nuclear fuel cycle is that we have to go for alternative fuel elements that is the fissile element that is uranium-233 which will be used in our future reactors by our AHWR process that is why it is very important and for that this is the decay scheme which is shown here (left part) how this thorium-232 which is irradiated in the nuclear reactor and to give the product that is uranium-233 and also along with uranium-233 we have uranium-232 which has decay products which give hard gamma rays and that is how this separation of uranium-233 is very very important and also from the bulk of thorium this uranium-233 separation is required this uranium-233 can be used in the reactors. So, the extraction can be done by TBP similar to the PUREX process and as mentioned in this case uranyl ion is extracted by 2 nitrate and 2 TBP giving this species $UO_2(NO_3)_2.2TBP$ plutonium gives the species $Pu(NO_3)_4.2TBP$ and Th^{4+} when it is there so this extraction is not same as that of plutonium but more number of TBPs are required because thorium has a lower ionic potential so the complex formation is relatively lower compared to that of Pu^{4+} that is why more number of TBP molecules are required to form organophilic complex that is how this type of species which I have shown here that is $Th(NO_3)_4.x$ TBP where x can be either 2 or 3 depending on the TBP concentration. Now there are 2 types of TBP based THOREX processes one is called the THOREX 1 process where 5 percent TBP is used for the extraction of uranium from thorium, proctactinium and the fission products and there is another process called the THOREX 2 where 40 to 55 percent TBP is used for the extraction of uranium and thorium from again protactinium and the fission products. So, the first process that is the THOREX 1 it is having much lower concentration of TBP that is how thorium extraction is prevented and only uranium is extracted and for THOREX 2 process both uranium and thorium can be extracted. However, the separation factors which are obtained in case of this TBP based separation processes are relatively less as shown in this figure it is much less than 200 the separation factor that is the distribution ratio of uranium divided by that of thorium. On the other hand, one of these dialkyl amides which is a branched dialkylamide the structure is given here this is termed as di-2-ethyl hexyl isobutyramide or DEHiBA.

So, this gives a very favorable separation factor for uranium(VI) vis-a-vis that of thorium(IV) and you get separation factor in excess of 3000 as shown here in this figure. So, suggesting that this branched dialkyl amides can be used for the THOREX process as well. Now, we are discussing about the solvent extraction based separation of actinides. Now, there are also ion exchange resins they are also used for the separation of actinides. So, the separation again by different ion exchangers follows the same trend as we have seen in the case of the complexation of actinides with different ligands.



ION EXCHANGE SEPARATIONS OF ACTINIDES

--Uptake by cation exchangers: $MO_2^{+} < M^{2+} < MO_2^{2+} < M^{3+} < M^{4+}$
--Affinity difference is large with a CIX. So. separation is easily possible.
--CIX resin is used extensively and is used for intragroup separations by using a selective (OHCOOH) eluting agent.
-- Ln – An separation can be done by loading onto a CIX and eluting by conc. HCl.
-- Inorganic CIX (ZrP) are also used. But uptake is based naked ionic radii and not hydrated radii.
-- ZrP prefers UO_2^{2+} over M^{3+}. The strongly sorbed are the An^{4+} ions.
-- AIX separation of An and Ln from Chloride medium
-- Pu purification from 7.5 M HNO_3 using AIX resin

Pu uptake: DOWEX 1xX Resin

Now, as we know in case of the ion exchange resins we have one called a cation exchange resin where we have strong acid cation exchange resin. So, in that case we have this sulfonate group which is there which is actually replaced and that is how we have this sulfonic acid group which is there where the hydrogen ion is replaced by the cationic species of actinides. And also we have this anion exchange resin where the anion of this resin which is there like the chloride ion is replaced by the anionic complex of the actinides. So, the uptake by the cation exchangers (the cation exchange resins) is given here is first is the tetravalent actinide ions which form strong complex and it's uptake is definitely much much larger than the other type of actinide ions. So, it is followed by that of the trivalent actinide ions followed by the actinyl ions (+6) that is MO_2^{2+} which is higher than that of the actinide plus 2 (M^{2+}) metal ions and finally, that of the actinyl (+5) metal ions.

Now, based on this cation exchange the resins the separation of actinides has been attempted. We have already given one example where this DOWEX 50x8 resin has been used for the intragroup separation of lanthanides and actinides where this complexing agents like alpha hydroxy isobutyric acid has been used as the eluting agent that is one of the application of this ion exchange resins. And also as I have seen case of the ion exchange resins the affinity difference between the cations is very large in case of the cation exchange resin. So, the separation is relatively easy. On the other hand, the disadvantage is that many of these actinide ions can be sorbed onto the cation exchange resin to different extents making it difficult for their separation or the separation can be done by tuning the ligand property so that you have the element containing a selective ligand for a particular actinide ion that can bring down the metal ion from the loaded regime.

So, as some example I want to give for this organic ion exchange regime cation exchange resins I have already given this intragroup separation. Also, lanthanide-actinide separation can be done loading the lanthanide and actinide ions onto the cationic ion exchange regime and eluting by concentrated hydrochloric acid. Better results has been obtained to take the ethanolic solution of this hydrochloric acid also to get better separation of these lanthanides and actinides. This is in addition to what I have already discussed in the intragroup separation where this hydroxy-carboxylates like alpha-hydroxyl butyric acid has been used. We also use inorganic cation exchange resins like zirconium phosphate (ZrP) which also take up the metal ions very efficiently, but in this case the uptake is slightly different than what has been there for the organic cation exchange resins.

So, for organic cation exchange resins which are mostly the gel type resins in that case the separation is done based on the hydrated radii of the metal ions. On the other hand inorganic ion exchange resins like zirconium phosphate (ZrP), the uptake is based on the naked ionic radii of the metal ion. The left side figure gives the uptake of actinide ions onto zirconium phosphate from nitric acid molarity you can see from starting from 0.01 to 1 molar nitric acid concentration. And we have seen this americium(III), curium(III) californium(III), cerium(III), europium(III), cerium(IV) and uranium(VI) uptake by this inorganic ion exchange resin.

And you see here that the uptake of the trivalent ions are relatively less compared to that of the actinyl ions. So, that is you see that this uranyl ion is preferred by the zirconium phosphate over the trivalent actinide ions like americium(III), curium(III), etc. This ion exchange resin also has been used for the separation of actinides using anion exchange resins. Now, in that case this actinide and lanthanide separation I have mentioned previously the TRAMEX process where we have used the strong chloride medium (around 11 molar lithium chloride) has been used where the actinides form stronger complexes than that of the lanthanides. And the extraction has been done into amine extractant and that is how the separation of actinides is done from the lanthanides.

Also, anion exchange resin can be used for the selective uptake of uranium from hydrochloric acid medium where uranium forms anionic species like UO2Cl4 2- and many of our rare earth plants where uranium also is one of the products they use this method from hydrochloric acid medium they try to recover uranyl ion by this anionic complex of uranyl ion. Plutonium also forms anionic complexes and these also are separated by using anion exchange resins and this plutonium(IV) is the species which forms as I mentioned $Pu(NO_3)_6^{2-}$, these type of anionic species are formed, with Pu^{4+} ion and this purification of plutonium in our PUREX process is finally done by taking Pu(IV) in 7.5 M nitric acid and using anion exchange resin like DOWEX 1x8 or DOWEX 1x4. And given a profile of this plutonium uptake by anion exchange resin from the nitrate medium see that this cross linking of the anion exchange resin has a role. Increasing the cross linking the uptake of plutonium has decreased. It is given here 3 different cross linking: 1 percent, 4 percent and 8 percent. And you see that with 8 percent cross linking that is DOWEX 1x 8 resin, the uptake of plutonium has been much lower than that of a 4 percent cross linked resin which is much lower than that of 1 percent cross linked anion exchange resin. Thank you.