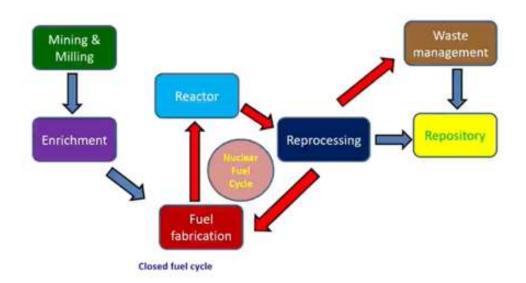
Separation of Actinides - III Prof. P. K. Mohapatra Radiochemistry Division Homi Bhabha National Institute Week – 11 Lecture – 55

One of the major applications of the actinide chemistry has been in the nuclear fuel cycle. As I have mentioned in the previous lecture, how this separation science is important in the front end of the nuclear fuel cycle, where the uranium separation is done from the leach liquor using the DAPEX or the AMEX processes. And in the back end of the nuclear fuel cycle also, the PUREX process is very, very important. Now, I give a brief overview of the nuclear fuel cycle here. So actually it is coming from the mines, we have the uranium ore and it is coming, this is, first we have the mining and then the milling and where we have the uranium product is there. The milling plant, it goes to the fuel fabrication, wherever required enrichment is done.

NUCLEAR FUEL CYCLE



In other cases, directly also natural uranium can be used as a fuel. And this fuel goes to the nuclear reactor and after a particular period of time, the fuel is removed from the nuclear reactor, which is called now the spent nuclear fuel or SNF. The SNF is kept for storage, that's only the storage facility under water. And after a few years time, when the

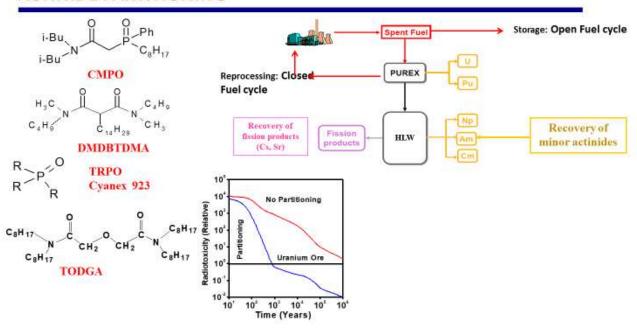
radioactivity has become significantly lesser, then the spent nuclear fuel is used for the nuclear fuel reprocessing.

After reprocessing, there is a waste management step in the nuclear fuel cycle where some of the valuable radio-nuclides are separated before vitrification of the radioactive waste. There is another fuel cycle which is called the open fuel cycle, where this reprocessing is not done and the spent nuclear fuel is directly stored in different parts. It can be directly stored in huge tanks as solution form and also this spent nuclear fuel can be vitrified and kept in the repositories. So these are the basic strategy for the open fuel cycle or the closed fuel cycle. In case of the closed fuel cycle, after the spent fuel reprocessing, the recovered uranium and plutonium are again given to the fuel fabrication, which is in turn given to the nuclear reactor.

And that is how the nuclear fuel cycle operates. Now whatever is coming from the nuclear fuel reprocessing plant that we call as the raffinate and it contains mostly the fission products and also the trans-plutonium elements, that is, americium, curium, etc. and neptunium, which is one of the major minor actinide element, this also is going for the vitrification. Now vitrification means this fission product as well as the activation products are converted to their oxides and glass form is made and the glass should be kept under deep geological repository for a number of years. However, the problem is that some of these minor actinides like Np-237, they have a very long half-life and this has to be monitored, that means these glass blocks have to be monitored for a very long period of time, that is, millions of years.

And also there is a question mark on the integrity of these waste blocks over such a long period of time due to natural calamities like earthquakes or volcanic eruption and also deformation by heat under the repository conditions. So because of that, there is a strategy called partitioning and transmutation or termed as the P&T, which is actually tested at different laboratories in different countries to separate out the long-lived minor actinides. When I call them minor actinides, this is mostly actinides like neptunium, americium and curium. Major amount of these actinides are called as minor actinides and other actinides which we call as the major actinides are plutonium and uranium, which are any of separated by the PUREX process. Now this partitioning and transmutation has two steps.

ACTINIDE PARTITIONING



One is called the actinide partitioning, where the minor actinides are separated from the raffinate, which is concentrated to be termed as high-level waste. This high-level waste contains more than 97% of the radioactivity which are involved in this nuclear fuel reprocessing. And this high-level waste is the major source of this minor actinide and also the fission products like Cs-137 and Sr-90, which give a lot of dose to the working personnel (MANREM). So the strategy is to separate the minor actinides and also that of the fission products like cesium and strontium are shown here in the schematic. That is how this MANREM problem or the dose to the working personnel can be minimized.

And these actinides which are separated, they have the advantage that is as the figure is given here. See the, as a function of time, up to a million years, relative radiotoxicity is plotted here. If you do not have this nuclear reactor or the nuclear energy program, then the dose is actually, which is the background, which is from the uranium ore only. And if you do not have this actinide partitioning and whatever activity is coming, starting from the initial period of this nuclear fuel, you have a very high level of radio toxicity, that is around 10⁴. And over the period of time, it will decrease, but to come to the background level of the uranium ore, it will take nearly 10⁶ years.

But if you go for this partitioning, that is, you separate the minor actinides, that is neptunium, curium and americium from the high level waste, then this radio toxicity can fall relatively faster. And in about 1000 years, you will have this radio toxicity coming to that of the background level, that is that of the uranium ore. So now this minor actinide partitioning has been one of the challenging topics and different labs are working on this.

The Americans started research into the minor actinide partitioning using several phosphorous based compounds. Most prominent of them is called the CMPO.

TRUEX PROCESS

--Extractant: Octyl-Phenyl-N,N-diisobutyl carbamoyl methyl phosphine oxide (0.2 M)

-- Phase modifier: TBP (1.2 - 1.4 M)

-- Diluent: Paraffinic hydrocarbon

-Extraction trend: Pu4+ > UO22+ > Am3+

--Used for the separation of trivalent lanthanides and actinides as well. Known as the SETFICS (Solvent Extraction of Trivalent felements Intragroup separation in CMPO-complexant System) Process

-Complexing agent: DTPA - NaNO3: Selective stripping of An(III)

DISADVANTAGES

- -- P based extractants
- --Stripping issues

The structure is given here, which the full form is carbamyl methyl phosphine oxide. And subsequently, they have developed a process called the TRUEX process. This process name is TRUEX process, that is trans uranium extraction, TRUEX process. Subsequently, the French people, they have developed an extractant, which are called the malonomides or tetra alkyl malonomides. One example is given here, that of the DMDBT DMA or dimethyl dibutyl tetradacyl malonamide.

This is falling in the same class of malonamide extractants and the French people have developed the process called the DIAMEX process, which is a diamide extraction process, which is very, very popular in the European Union laboratories. However, these processes are not yet used for the waste management of the minor actinide. At the same time, these Chinese people, they have tried TRPO or trialkyl phosphine oxide. The commercial reagent, which is available is the Cyanex 923 and the structure of this extractant is given here, where R is the alkyl group. This has been used for the actinide partitioning from nitric acid media.

TRPO PROCESS

- -- Process developed at China
- -- Cyanex 923 (commercially available) cheap extractant
- --Extraction of actinides is possible by tuning the HNO3 concentration
- --Competition of nitric acid for the extractant
- -- Denitration of feed is required
- --Increase in waste volume

DIDPA PROCESS

- --Phosphoric acid extractant developed in Japan
- --Mixture of DIDPA and TBP is used
- --HLW acidity needs to be brought down to 0.5 M
- --Dinitration is needed and waste volume is large
- --An(III) and Ln(III) can be separated using DTPA as the complexing agent
- --Pu is stripped by oxalic acid and UO22+ by Na2CO3

DIAMEX PROCESS

- -- CHON ligands (French researchers)
- -- Alternative to TRUEX process
- --Third phase formation at higher nitric acid concentrations
- -- Larger extractant concentration is used

The Japanese people have also used another extractant, which is called the DIDPA, the diisodecyl phosphoric acid. Finally, another Japanese group has come up with an extractant called the diglycolamide or the DGA. The structure of this is given here (in slide No. 2), is a tetra-octyl diglycolamide or TODGA. By far, this TODGA has been one of the most efficient extractants for the actinide partitioning. So I will be just briefly mentioning about these different processes.

First is the TRUEX process, which I mentioned for the CMPO. Structure of CMPO is given here. The extractant used is 0.2 molar, but as it forms third phase with the diluent and also on nitric acid concentrations, which is prevailing in the high level ways, that is 3 to 4 molar. So TBP has been used as a phase modifier.

And 1.2 to 1.4 molar TBP has been used along with the 0.2 molar CMPO as the TRUEX solvent. The diluent in this case is a paraffinic hydrocarbon. The extraction trend is that plutonium 4 plus is extracted higher than that of the uranyl, which is higher than that of the americium 3 plus. Nevertheless, the extraction of americium is significantly high.

You get a distribution ratio of around 25 to 30 using the solvent mentioned above, i.e., the TRUEX solvent. And this solvent extracts not only americium 3 plus, it also extracts the trivalent lanthanide ions because this extractant cannot distinguish between the trivalent actinides and lanthanides. And then there is a process called SETFICS, which is a Solvent Extraction of Trivalent F-elements Intragroup Chemical Separation in the CMPO

complex and system, where DTPA sodium nitrate has been used for the selective stripping of the actinide ions, that is the trivalent actinide ions. So, the SETFICS is used in conjunction with the TRUEX process for a direct separation of the trivalent actinides from the lanthanides. Now we will be coming to the trivalent actinide-lanthanide separation in a more detailed manner in this lecture.

The disadvantages of this TRUEX process or the CMPO process, with the phosphorus-based extractants are used, that is both CMPO as well as TBP, they are containing phosphorus, so that is how they are leading to large volume of solid waste production. And also there are stripping issues, that means it is not so easy to strip the trivalent actinides. So subsequently researchers have developed a buffer medium which is used for the stripping of the trivalent actinides. But the hexavalent actinides like uranyl ion is stripped very comfortably by sodium carbonate solution and Pu⁴⁺ is stripping of the tetravalent and hexa-valent actinide ion.

But for the trivalent actinide ion, there is some problem for stripping using the CMPO extraction system. Similar to the CMPO extraction system, this phosphine oxide, trialkyl phosphine oxide process or TRPO process has been developed at China. Here this complexing group is the phosphoryl group, similar to that of the CMPO. But the Cyanex 923 which is commercially available and also is a cheap extractant compared to CMPO, which has a problem that you cannot carry out the extraction from the actual high level waste condition that is 3 to 4 molar nitric acid. So what has to be done is that the feed has to be diluted to tune in the extraction of the actinides from the high level waste.

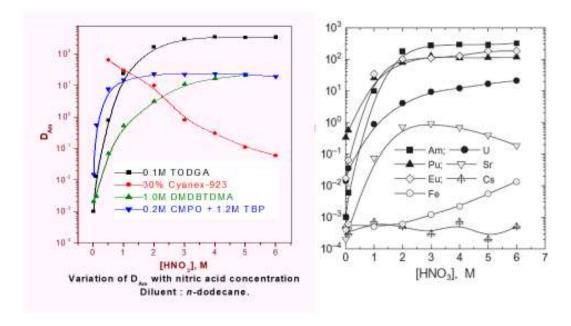
So the disadvantage is that you need to dilute the feed which is resulting in lot of waste volume. And also, if the nitric acid concentration is little higher, then extraction of the trivalent metal ions is less. Nevertheless, the extraction of tetravalent and hexavalent actinide ions is not a problem to high nitric acid concentration because this trialkyl phosphine oxides, they are very strong extractant of the tetravalent as well as hexavalent actinides. Another process as I mentioned by the Japanese group is the phosphoric acid base extractant that is called the DIDPA process or the di-isodecyl phosphoric acid. The structure of the extractant is given here.

So again, this forms third phase. So that is why the mixture of DIDPA and TBP is used. And the high level waste acidity has to be brought down to around 0.5 molar, otherwise the extraction is not very efficient. In this case also, the feed has to be denitrated, otherwise the waste volume will be very, very large.

The trivalent actinides and trivalent lanthanides can be separated from the DIDPA extract using DTPA as the complexing agent. And the plutonium is stripped by the oxalic acid and

uranyl ion by sodium carbonate. The CMPO process or the TRUEX process, the TRPO process and the DIDPA process, all these three processes are having phosphorous based extractants. And that is why there is a problem of solid waste generation. And in view of this, the CHON type of ligand has been used by the French research groups and that is how this DIMEX process was evolved.

So, they are used as I already mentioned, the malonamides or the tetraalkyl malonamides, so which are usually alternative to the TRUEX process and very, very efficient. The major problem with the DIMEX process is the third phase formation at higher nitric acid concentrations. Acid itself forms third phase and also the larger concentration of the extractant is required to carry out the extraction of it. So finally, as I mentioned, this diglycolamide is considered the most promising extractant out of all these extractants. So TODGA has been tested and a comparative evaluation of TODGA, Cyanex 923 which is used in the TRPO process, DMDBTDMA which is used in the DIMEX process and CMPO plus TBP which is used in the TRUEX process has been given in the left-hand side figure where the distribution ratio of americium as a function of nitric acid concentration is given.



The diluent for all cases is n-dodecane and as you can see with our 0.1 molar TODGA, the extraction of americium has been most efficient compared to the other three types of extractants. And as you can see here in case of the Cyanex 923, the extraction of americium becomes very very less with increasing nitric acid concentration. Now when we go for this TODGA type of extractant or this DGA type of extractants, the extraction mechanism is relatively unusual we can say as compared to that of the all previous extractants I have discussed that is CMPO, TRPO, and diamide and also DIDPA in which case the extraction trend follows that of the ionic potential of the metal ions that is Pu(IV) is extracted higher than that of Pu(VI) which is in turn extracted higher than that of Am³⁺. In all cases,Am³⁺

extraction has been the lowest out of these three metal ions and in case of TODGA, we will find that this extraction trend has become different. That is Am3+ extraction has become more than that of Pu⁴⁺ which in turn has been more than that of the uranyl ion. The relative extraction profiles of these metal ions is given in the right hand side figure and see here this americium extraction is much higher than that of Plutonium extraction presented by the red line and also the trivalent lanthanide extraction that is the europium ion extraction is marginally larger than that of americium extraction and Plutonium extraction is less than that. On the other hand, the uranium extraction is significantly lower which is shown here. And the fission products like strontium and cesium are very very poorly extracted which is not shown in this figure. Now once these actinides are partitioned, i.e., separated from the high level waste what we get in the product is the lanthanides that is the trivalent lanthanides the trivalent actinides. and

So, along with Am(III), Cm(III) we have a whole lot of trivalent lanthanides which are also extracted and this trivalent actinides and lanthanides separation is therefore one of the very very important steps in the radioactive waste management program. This, as I have already mentioned, (means) that before vitrification we have to do the partitioning and transmutation if we have to bring down the surveillance period from millions of years to around thousand years or so. So, for that, lanthanide actinide separation has to be done. Now why lanthanide actinide separation has to be done? As I already mentioned in the previous slides that this lanthanide extraction is comparable to that of actinides that is the trivalent actinides and lanthanides have very large neutron absorption cross sections. So that is how this when you are using these actinides for burning in a reactor.

Why Ln/An Separation?

- -- Lns have very large n absorption cross sections
- --Form separate phase during vitrification
- --Separation can decrease the waste volume significantly
- -- The An(III) can be used for transmutation of heterogeneous recycling

Processes for Ln/An Separation

TRAMEX (CI⁻),

TALSPEAK, TRUSPEAK, Reverse TALSPEAK, ALSEP (N): Amino polycarboxilate

SANEX-I, II, III (N): Aromatic heteropolycyclic

SANEX-IV (S): Dithiophosphinates

GANEX, Euro-GANEX (N): Aromatic heteropolycyclic

R-SANEX, 1c-SANEX (N): Aromatic heteropolycyclic

i-SANEX (N): Aromatic heteropolycyclic (Aq. Soluble)

Nuclide	Cross section, barn
Xe-135	2.65×10^{6}
Sm-149	4.01×10^4
Sm-151	1.53×10^4
Gd-157	2.54×10^{5}
Gd-155	6.07×10^4
Pm-147	1.68×10^{2}
Eu-151	9.2×10^{3}

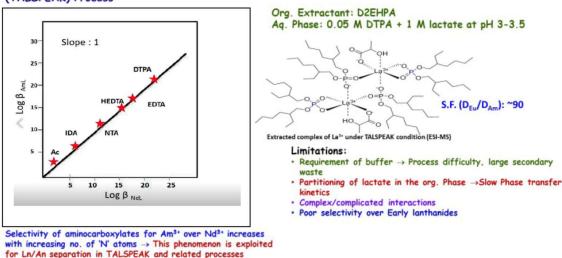
So, this lanthanides will be acting as neutron poisons and they will be bringing

down the efficiency of the reactors. Also, as I have given here this table in the right hand side and see some of the lanthanide isotopes their cross section is given in bars; see that these are very very high neutron absorption cross sections. So they act as neutron poisons and they decrease the reactor efficiency. Also, if the lanthanides are not separated from the actinides, i.e., if you carry out the vitrification of the radioactive waste then lanthanides they form separate phase during vitrification and they complicate the vitrification process.

Also, lanthanides have a significantly larger volume than that of the actinides. By saying larger volume what I mean is the amount of lanthanides produced in the nuclear fission is much much more than the amount of minor actinides like an americium and curium which are formed by the neutron capture reactions. Maybe about 1000 times higher we get the lanthanide from the fission. So, that is how if your lanthanides are separated from the trivalent actinides then the waste volume can be brought down very very significantly. That means in a very small volume we can contain the radioactive waste (when) trivalent lanthanides are removed from the radioactive waste.

The trivalent actinides can also be used like Am(III) can be used for the transmutation or heterogeneous recycling that is how we can disintegrate these trivalent actinides. Now the processes which are used for the lanthanide-actinide separation, I have already discussed the TRAMEX process where the tertiary amine extraction that is tertiary amine is used for the extraction of the americium and curium in the trivalent state from strong chloride medium that is around 11 M lithium chloride and that is how the separation is done. The trivalent actinides are extracted to a much larger extent than that of the trivalent lanthanides. There is also another process called the TALSPEAK process. I mentioned about this TALSPEAK process which I will be mentioning in the next slide.

Trivalent Actinide Lanthanide Separation with Phosphorus-reagent Extraction from Aqueous Komplexes (TALSPEAK) Process



Also, there are processes like TRUSPEAK which is coupled to the TRUEX process, and reverse TALSPEAK and ALSEP processes which I am not going to discuss here, but I will be giving details of the TALSPEAK process where aminopolycarboxylates are used for the complexation of the trivalent actinides. So, in this case the trivalent lanthanides are there in the organic phase and trivalent actinides are brought into the aqueous phase by selective complexation with aminopolycarboxylates. This is again the application of the actinide complexation what we have studied using the multipodant carboxylic acid ligands. There are also nitrogen donor extractants for this lanthanide-actinite separations and there are processes called SANEX or the Selective Actinide EXtraction. So, there are several SANEX processes, SANEX 1, 2, 3 which use nitrogen donor ligands that is the aromatic heteropolycyclic ligands are used.

And also there is another process called the SANEX 4 which is based on the sulfur donor ligands which is a dithiophosphonate type of ligand. Then there is also what is called a regular SANEX or R-SANEX, 1C-SANEX or a 1C-SANEX which I am not going to discuss here which uses aromatic heteropolycyclics. And there is another one called an innovative SANEX process where aromatic heteropolycyclic ligands are used which are aqueous soluble. So, I will be briefly mentioning about these processes which have been studied by the European Union and also other countries including India.

So, first I come to the TALSPEAK process. So here the extractant is HDEHP which is di-2-ethyl hexyl phosphoric acid as I mentioned in the DAPEX process. And we have the solution of this HDEHP and the complexing medium which is that is the aqueous medium is 0.05 molar DTPA. This is their amino polycarboxylic acid that is diethylene triamine penta acetic acid and 1 molar lactate that is a 1 molar lactic acid at pH 3 to 3.5. The separation factor of Eu and Am; the ratio of their distribution ratio values is around 90 which is obtained in case of the TALSPEAK process. This has originated in the United States of America and has been other countries also have carried out lot of research in the

TALSPEAK process. This is a species of this whatever is shown here from ESI-MS this species has been shown here where the complexes of the trivalent lanthanides has been shown here with the HDEHP extractant and also this Am they form the complexes with the amino-carboxylate ligands. As I have already mentioned during the complexation lectures depending on the type of this carboxylic acid extractants this log beta value of the actinides can be fine-tuned as per the requirement so that you get benefit during the complexation. So here you can see that this acetate is given here and compared to that nitrilo triacetic acid and the EDTA (ethylene diamine tetraacetate) and also DTPA (diethylene triamine pentacetic acid) are better.

So, DTPA forms a very strong complex with the trivalent actinides the stability constant much higher than that of the trivalent lanthanide ions. You can see here these values given for the neodymium here and that of the trivalent actinide here. So you see this value for DTPA which is much higher for the trivalent aminidium than that of the neodymium that is how the secretion is done. Now the limitation of this TALPEAK process is there is a requirement of buffer because we need to work in the pH range that is pH 3 to 3.5. There is a process difficulty that is a large amount of secondary base generation. Then partitioning of lactate in the organic phase which has a very slow phase transport kinetics and these interactions are quite complex and complicated and poor selectivity over the early lanthanides. Whatever we have shown it is for Eu / Am or Nd/ Am or seen these figures I have shown. But if it is early lanthanides then there is a selectivity not as good as you put it here. Then coming to the soft donor ligands, those having sulfur or the nitrogen donors.

Soft donor ligands (lipophilic)

As I mentioned in the beginning of our this actinide complex chemistry that some of these trivalent actinides they in fact act as soft metal ions. So that means when we consider soft-soft interaction on the basis of the HSAB concept or the hard soft acid-base concept then they should be forming stronger complexes with the soft donor ligands. There will be some covalent interactions. So that is how the soft donor ligands are used for this complexation with trivalent actinides. I have given example of some soft donor extractants that is a cyanex 301 structure is given here.

This is a dithiophosphonic acid with two sulfurs which can be binding with the trivalent actinide. And also there is another laboratory synthesized sulfur based ligand which is this bis chlorophenyl derivative of this cyanex 301. And this has given a separation factor beyond 10 to the power 3. The major problem of the sulfur donor ligands are their stability because the sulfur can get exchanged or degraded and you get the oxygenated products in those cases. So the stability of this extractant is one of the big problem when you are using the sulfur donor extractant.

On the other hand, this nitrogen donor extractants which are mentioned here for the SANEX 1 process that is a selective actinide extraction process 1. The terpyridine is the extractant is here and the separation factor between trivalent actinide and trivalent lanthanide that is americium 3 and europium 3 distribution ratio values is less than 10. When we have this SANEX 2 extractant, this extractant whatever shown here structure is again a heteropolycyclic extractant which is nitrogen donors, 3 nitrogen donors are there and it has separation factor of around 10. And subsequently around 1999, there was a report

in which this BTP type of extractants has been reported with the separation factor greater than 100. So but the major problem with all these nitrogen donor ligand is that this their poor solubility in common organic diluents like n-dodecane which are used in the nuclear fuel cycle.

So you have to use very complicated solvent combinations for this separation using this nitrogen donor extractants. That is how in the last decade or so there has been development to have aqueous soluble heterocyclic compounds like one is shown here that is SO₃-Ph- BTP. This BTP is the extractant which is shown here. This is R-BTP that the alkyl group is termed as R here and this is the reagent which is used structurally for the separation of lanthanides and actinides where this BTP derivative is a sulfonated BTP which is aqueous soluble and this process is called innovative SANEX (iSANEX) process where the separation factor is reported to be greater than 1000. Now after this trivalent actinides are separated from this trivalent lanthanides then this americium can be burnt in the reactor by the heterogenous recycling but always americium is associated with curium.

So recently there is a strategy which is evolving is americium and curium separation. Why americium curium separation is required? Because some of the isotopes of curium like ²⁴²Cm and ²⁴⁴Cm, they have high neutron and heat emission so it can complicate the fabrication of nuclear fuel. The separation can decrease the waste lifetime and also the radio toxicity if the curium can be separated and also this can decrease the long term waste heat power and share repository resources. After this curium is separated from the americium then this americium along with plutonium and uranium can be used for any heterogeneous recycling in reactors together they can be used as a fuel. Now the strategy is that we can separate the specially designed complexing agent.

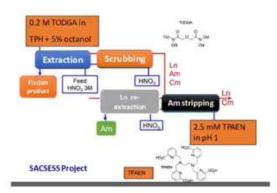
One complexing agent is called TPAEN. It is a complicated name but I will read out. It is a N,N,N',N'-tetrakis-6-carboxy pyridinyl methyl ethylene diamine and the structure is given here. So this is the extractant which has been synthesized by the French research groups and they have used it for the separation of trivalent curium and trivalent americium.

AM-CM SEPARATION

Why Am-Cm separation?

- -- Decreases waste lifetime & radiotoxicity
- --Decreases long term waste heat power & saves repository resources
- --Strategy is to separate Am and opt for heterogeneous recycling (U + Pu + Am)

0.2 M TODGA in TPH + 5% octanol



Strategy

- --Separation using specially designed complexing agents such as TPAEN (N,N,N'N'-tetrakis[(6-carboxypyridin-2-yl)methyl] ethylenediamine). SF_{Cm/Am} as high as 3.7 was reported
- --Selective oxidation of Am (SESAME) to the +6 state (electrochemical) followed by TBP extraction

Usually the Am-Cm separation factor is around maybe 1.1, 1.2 by any process you try to do it but by the specially designed complexing agent they have found that the separation factor between Cm and Am can be as high as 3.7. There are some reports very recently the Russian group they have developed an extractant which can give a separation factor as high as 7 but this is very very recent testing is going on in Moscow State University but this method which has been reported by the French group also is quite good for carrying out separation of curium and americium. There is another way to separate americium and curium where Am(III) is oxidized selectively to the plus 6 state by electrochemical method followed by a TBP extraction. As I have already mentioned several times these actinyl ions are extracted to a much much larger extent than that of the Am³⁺ ion.

So, that is how americium 3 plus is oxidized to the americyl ion that is AmO₂²⁺ ion by electrochemical method then it can be extracted selectively by the process which is called the SESAME process. So this is a newly developed process which is called SESAME process which is selectively it can separate Am. Now this is such that given a flow sheet of this americium curium separation method where TODGA has been used as the extractant in the organic phase and TPAEN has been used as the complexing agent. They have seen that this separation factor of around 3.7 to 4 can be obtained when you have 2.5 millimolar of TPAEN in pH 1. Americium can be recovered from that and curium stripping can be done. This is part of this project of the European Union which is called the SACSESS project. Thank you very much.

Contact Detail:

Email: mpatra@barc.gov.in

Phone: 022-25594576