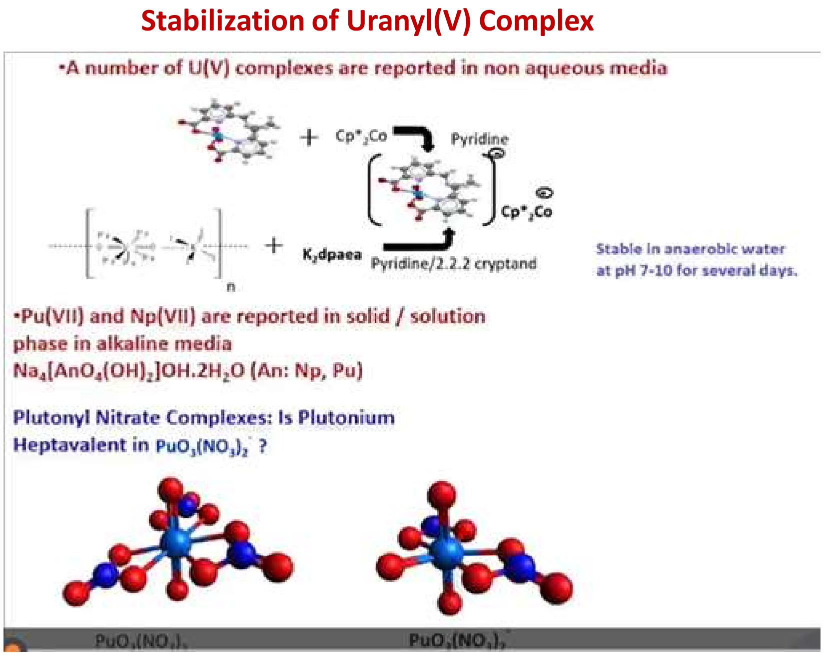
Unusual Oxidation State of Actinides

Prof. P. K. Mohapatra
Radiochemistry Division
Homi Bhabha National Institute

Week – 12
Lecture – 56

In this lecture, we shall be discussing the unusual oxidation states of the actinide ions. Uranium(V) species we have reported before while studying the aqueous ionic species of actinides. Now U(V) that is UO_2^+ ion has a very low stability in the aqueous medium but some of the U(V) complexes given in this scheme you can see these type of complexes they are stable for even seven to ten days. In pH 7 to 10 for several days these type of complexes are stable and the medium where these type of complexes are formed is DMSO, THF or pyridine. In all these cases, this 2,2,2-cryptand plays a very important role while forming this type of complexes because that forms a cationic species with a potassium and then this complex which is having anionic species are mentioned here this forms out of an ion pair and that is how it is stable. Pu(VII) and Np(VII) are already reported in solids or solution phases in alkaline medium.



Stabilization of Uranyl(V) Complex

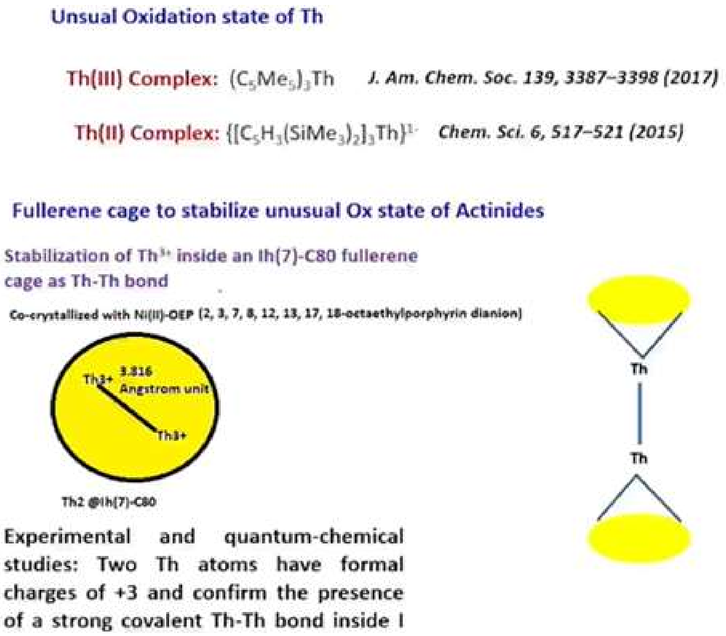
•A number of U(V) complexes are reported in non aqueous media

Stable in anaerobic water at pH 7-10 for several days.

•Pu(VII) and Np(VII) are reported in solid / solution phase in alkaline media
$Na_4[AnO_4(OH)_2]OH.2H_2O$ (An: Np, Pu)

Plutonyl Nitrate Complexes: Is Plutonium Heptavalent in $PuO_3(NO_3)_2^-$?

Some of the examples are given here this type of species which is mentioned are there. Now Plutonium Nitrate complex which is reported whether plutonium is heptavalent in the $PuO_3(NO_3)_2^-$ this type of species the structure which is given below. So here it has been proven theoretically that plutonium may be heptavalent in this type of complexes.



Unsual Oxidation state of Th

Th(III) Complex: $(C_5Me_5)_3Th$ *J. Am. Chem. Soc. 139, 3387–3398 (2017)*

Th(II) Complex: $\{[C_5H_3(SiMe_3)_2]_3Th\}^{1-}$ *Chem. Sci. 6, 517–521 (2015)*

Fullerene cage to stabilize unusual Ox state of Actinides

Stabilization of Th^{3+} inside an Ih(7)-C80 fullerene cage as Th-Th bond

Co-crystallized with Ni(II)-OEP (2, 3, 7, 8, 12, 13, 17, 18-octaethylporphyrin dianion)

Th2 @Ih(7)-C80

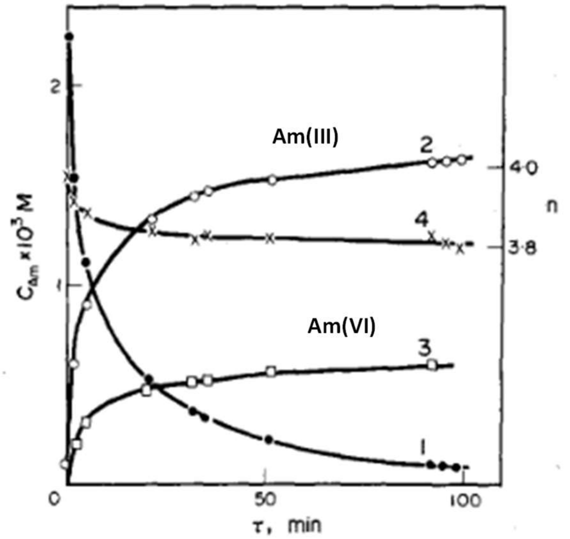
Experimental and quantum-chemical studies: Two Th atoms have formal charges of +3 and confirm the presence of a strong covalent Th-Th bond inside I

Now unusual oxidation state of thorium: as we know, thorium has +4 as the most common oxidation state and because of the f_0 configuration, it has very stable oxidation state and we have most of the thorium complexes in the +4 states. But there are some reports of Th(III) complexes. This is the tris-cyclopentadienyl thorium this complex reported where thorium is in the +3 oxidation state and also analogous complex is also formed and where thorium is having +2 as the oxidation state. So, these are some of the unusual oxidation states of thorium. There are many other examples but I have quoted only these two here and also there is an interesting species of Th^{3+} in the C_{80} fullerene structure as given here. In this case you have two Th^{3+} ions going inside the fullerene case and they are getting stabilized due to the thorium- pi electron interaction within the fullerene system as shown here. Very stable complex formation is there where the thorium to thorium bond distance is around 3.816 Å as shown here and this has been proven both by experimental as well as quantum chemical studies.

AMERICIUM (IV)

In 3-8 M phosphoric acid, Am(IV) disproportionates

$$3Am^{4+} + 2H_2O \rightarrow 2\ Am^{3+} + AmO_2^{2+} + 4H^+$$



AMERICIUM (VI)

Am(III) is oxidized to AmO_2^{2+} ion by Ammonium Persulphate. Then TBP extraction of AmO_2^{2+} was done.

Am(IV): As I have already mentioned in previous classes, the most stable oxidation state of americium in aqueous solutions is the +3 state. Now Am(IV) formation is very difficult because immediately it is disproportionated as shown here in the low acid concentrations. So,

$3\ Am^{4+} + 2\ H_2O <=> 2\ Am^{3+} + AmO_2^{2+} + 4H^+$

Now this Am(IV) species this has disproportionated and this diagram is given here where the starting concentration of americium is 10^{-3} M, i.e., a millimolar solution of Am(IV) has been taken and that disproportionates. You can see here with the Am(VI) and Am(III). The concentration of Am(III) is roughly twice that of Am(VI) which is satisfying the equation given above. The profiles of americium species are presented in the figure given here. Am(VI), as I have mentioned before, is used in the SESAME process for the separation of americium and curium. So Am(III) is oxidized to Am(VI) or AmO_2^{2+} plus ion by ammonium persulfate and then TBP extraction of Am(VI) can be done in the similar manner as the uranyl ion extraction is done from the nitric acid media.

ANALYTICAL CHEMISTRY OF ACTINIDES

A. Gravimetry

Th, U, Np and Pu form insoluble precipitates with hydroxide, oxalate, iodate, fluoride or peroxide. Or by organic reagents such as cupferron, benzoic acid, hydroxyquinoline, etc

Th:

--The inorganic precipitates can be heated in a furnace to yield the oxides. The organic precipitates can be directly filtered, dried and weighed.

--Interference may be there from Zr, Ti, Hf and REE

UO22+:

Precipitation by carbonate free ammonia (ADU) which can be converted to U3O8 upon heating

Np4+:

Oxalate or peroxide precipitation can be done from HCl / HNO3 medium

Pu4+:

Precipitated as insoluble peroxide, hydroxide or oxalate.

--Pu valency adjustment is required

Now coming to the analytical chemistry of actinides we should be in a position to analyze the actinides. Those of them are highly radioactive, there is not a problem because we can go for the radiometric method of estimation but those with relatively lower radioactivity there are other methods for analysis. So, I will be giving a general method of analysis for some of the early actinides like thorium, uranium, neptunium and plutonium. These four actinides I am mostly discussing here. These actinides form insoluble precipitates in their +4 oxidation state with hydroxide, oxalate, iodate, fluoride or even peroxide. It can also be done by organic reagents such as cupferron, benzoic acid or hydroxyquinoline and those precipitates can be filtered and estimated by the gravimetric method.

For Th^{4+}, the inorganic precipitates as I have already mentioned such as the thorium hydroxide or peroxide or oxalates they can be heated in a furnace to yield the oxide that is ThO_2 and the organic precipitates they can be directly filtered, dried and weighed to give the exact amount of thorium. There may be interference if there are other tetravalent ions present in the solution like zirconium, titanium, hafnium or even some trivalent metal ions that is the rare earth element. Uranium precipitation can be done by carbonate free ammonia to yield ADU or ammonium diuranate which is the ammonium diuranate which can be converted to U_3O_8 upon heating and then by weighing this we can find out how much is the uranium present in this final product. Neptunium in this case in the +4 oxidation state can be precipitated as oxalate or peroxide from hydrochloric acid or nitric acid medium. Same way Pu^{4+} can be precipitated as its insoluble peroxide, hydroxide or oxalate. Plutonium valency adjustment is required in this case as I have already mentioned . Nitrite ion can be used for the oxidation of Pu^{3+} to Pu^{4+} or the reduction of PuO_2^{2+} to Pu^{4+} ion.

B. Spectrophotometry

Th:

Thoron can be used to obtain red coloured complex of Th4+ with λ_{max} at 545 nm. Interference from Zr, Ti, other tetravalent actinides
Arsenazo III: Absorbs at 650 nm. But interference by U, Pu etc.

U:

Absorbs in the range of 400-450 nm (ϵ = 30). Used for 1 mg/mL solutions.
--SCN complex is intense yellow λ_{max} at 375 nm (ϵ = 3850). Interference from transition metals.
--DBM λ_{max} at 417 nm (ϵ = 3850)
--Br-PADAP gives complex with λ_{max} at 575 nm (ϵ = 74000

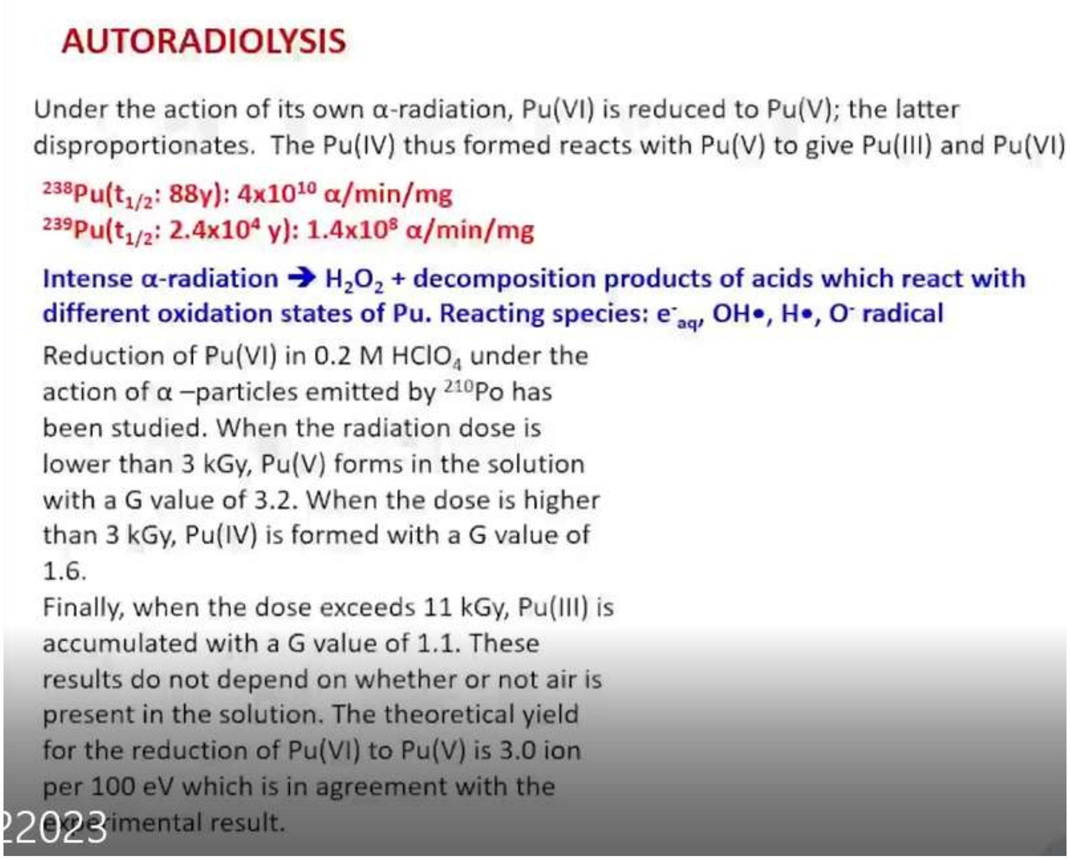
Np:

Np(IV) at 964 and 704 nm (ϵ = 120). Np(V) at 983 nm and Np(VI) at 1230 nm.
--Arsenazo III forms green coloured complex with Np(IV) in HCl / HNO3 with λ_{max} at 665 nm. But quantitative reduction has to be ensured.
--Np(IV) also forms colored complex with Thoron (λ_{max} at 540 nm).

Pu:

Pu species give characteristics absorption bands. Pu(III): 603 & 560 nm; Pu(IV): 470 and 700 nm. Pu(VI): 953 and 833 nm
--Thoron and Arsenazo III can also be used.

The other popular method of analysis of the early actinides like thorium, uranium, neptunium and plutonium is spectrophotometry. For thorium, very specific agent is there, i.e., Thoron; which can be used to obtain the red corner complex of Th^{4+} with a λ_{max} at 545 nanometer. However there can be interference from zirconium, titanium or other tetravalent actinides. Arsenazo III is also used for the estimation of Th^{4+} where it absorbs at 650 nanometer but there can be serious interference by other actinides like uranium and plutonium which also form complexes giving rise to color and observing at again close to 650 nanometer. Uranium can be analyzed spectrophotometrically by different methods. Uranium itself absorbs in the range of 400 to 450 nanometer that means the yellow colored uranyl nitrate solution can be used for its estimation with a epsilon value of around 30 and around 1 milligram per ml solution is used for this purpose. If the concentration is less than 1 milligram per ml, then we go for other more sensitive methods like the thiocyanate complex formation is done of uranyl ion which gives an intense yellow colored solution with a λ_{max} at around 375 nanometer with epsilon value of 3850. So, that means nearly two orders of magnitude as compared to the only uranyl nitrate solution. But the interference with thiocyanate can be there from the transition metals and the iron thiocyanate complex also forms intense red color and it can interfere with the uranium estimation. Di benzyol methane method or DBM this forms a complex with the uranyl ion with a lambda max value at 417 nm with epsilon value again very close to this thiocyanate complex that is 3850. Br-PADAP is another ligand which is used for complex formation with the uranyl ion. It has a lambda max value of 575 nm with epsilon value of 74,000. So it's a very high absorption is there and it's a very low concentration of uranium can be estimated by this method. Np(IV) can be estimated if it is there in the nitric acid solution at 964 and 704 nm. These are the characteristic bands of Np(IV) with epsilon value close to 100. Np(V): it has a sharp band at 983 nm and Np(VI) has again the sharp band at 1230 nm. Arsenazo III forms a green colored complex with Np(IV) in hydrochloric acid or the nitric acid medium with a λ_{max} at around 665 nm. But quantitative reduction has to be ensured otherwise there will be errors in the results. So neptunium oxidation state has to be maintained at +4 state by using reagents like ferrous sulphamate which we have already discussed. Np(IV) also forms a colored complex with Thoron with λ_{max} at around 540 nm. It can interfere with the estimation of thorium and the same way thorium also can interfere with an estimation of neptunium by Thoron. Plutonium: Plutonium species give characteristic absorption bands. Pu(III) has characteristic bands at 603 and 560 nm. Pu(IV) at 470 and 700 nm and Pu(VI) at 953 and 833 nm. Thoron and Arsenazo III can also be used for the estimation of Pu^{4+} ion. But the results can be erroneous if some of the actinide ions like Th^{4+} and Np^{4+} is present in the solution.



AUTORADIOLYSIS

Under the action of its own α-radiation, Pu(VI) is reduced to Pu(V); the latter disproportionates. The Pu(IV) thus formed reacts with Pu(V) to give Pu(III) and Pu(VI)

^{238}Pu($t_{1/2}$: 88y): 4x10^{10} α/min/mg
^{239}Pu($t_{1/2}$: 2.4x10^4 y): 1.4x10^8 α/min/mg

Intense α-radiation ➔ H_2O_2 + decomposition products of acids which react with different oxidation states of Pu. Reacting species: e^-_{aq}, OH•, H•, O^- radical

Reduction of Pu(VI) in 0.2 M $HClO_4$ under the action of α –particles emitted by ^{210}Po has been studied. When the radiation dose is lower than 3 kGy, Pu(V) forms in the solution with a G value of 3.2. When the dose is higher than 3 kGy, Pu(IV) is formed with a G value of 1.6.

Finally, when the dose exceeds 11 kGy, Pu(III) is accumulated with a G value of 1.1. These results do not depend on whether or not air is present in the solution. The theoretical yield for the reduction of Pu(VI) to Pu(V) is 3.0 ion per 100 eV which is in agreement with the experimental result.

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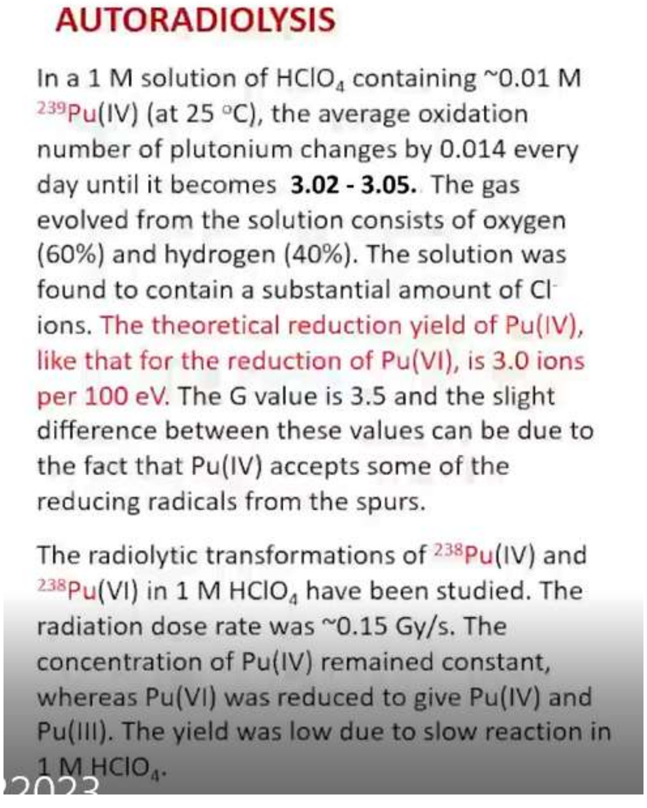
Now coming to another important topic is the autoradiolysis. You know most of the actinides they are undergoing alpha decay and under the action of its own alpha radiation the actinides can undergo oxidation and reduction reactions. So, I have taken this only the case of plutonium which is one of the most important actinides. And plutonium oxidation state, how it is changing because of this radiations emitting from the plutonium. I will be discussing that in this section. So, because of this alpha radiation Pu(VI) is reduced to Pu(V) which in turn disproportionates. Pu(IV) which is formed from the disproportionation reaction and it reacts with the Pu(V) again to give the Pu(III) and Pu(VI). So that is how Pu(VI) if it is present under the autoradiolysis it can go to the all the four oxidation states like 6, 5, 4 and 3 and after some time, we have the mixture of Pu(VI), Pu(IV) and Pu(III) because Pu(V) is immediately disproportionating. Plutonium, mostly consists of the two alpha emitting nuclei that is ^{238}Pu and ^{239}Pu with half-lives of 88 years and 2.4x10^4 years but other plutonium isotopes are also giving alpha but these two are the most important that is why I am considering these two isotopes of plutonium. And the alpha which is emitting from them you can see if you have one milligram of plutonium-238 this gives 4x10^{10} alpha per minute and if you have one milligram of plutonium-239 it gives 1.4x10^8 alpha per minute. So, because of this intense alpha radiation there is going to be radiolysis of water which forms species like hydrogen peroxide and also species like hydrated electron, OH radical, H radical, O^- radical and also O_2H which also gives different products which can oxidize or reduce the plutonium ions. Also, the decomposition products of the acids in which the plutonium solution is made like whether it is a hydrochloric acid, perchloric acid or nitric acid those radiative degradation products of the acids also will be playing a part in the redox chemistry of plutonium in this medium.

So, the reduction of Pu(VI) in 0.2 M perchloric acid under the action of the alpha particles which are emitted by ^{210}Po this has been taken because more number of alpha particles are emitted from ^{210}Po and this can be used as an intense alpha source. So, in this study, when the radiation dose is lower than 3 kGy (kilo Gray) then Pu(V) forms in the solution with a G value of 3.2. So the G value means with 100 eV radiation how many products are formed that is 3.2 is the average value formed and when the dose is higher than 3 kGy then Pu(IV) is formed with a G value of 1.6. Finally when the dose exceeds 11 kGy, Pu(III) is accumulated with a G value of 1.1. So, these products are formed from the radiolysis of Pu(VI) in the presence of ^{210}Po (and) this does not depend whether this reaction is taking place in the presence of air or not.



AUTORADIOLYSIS

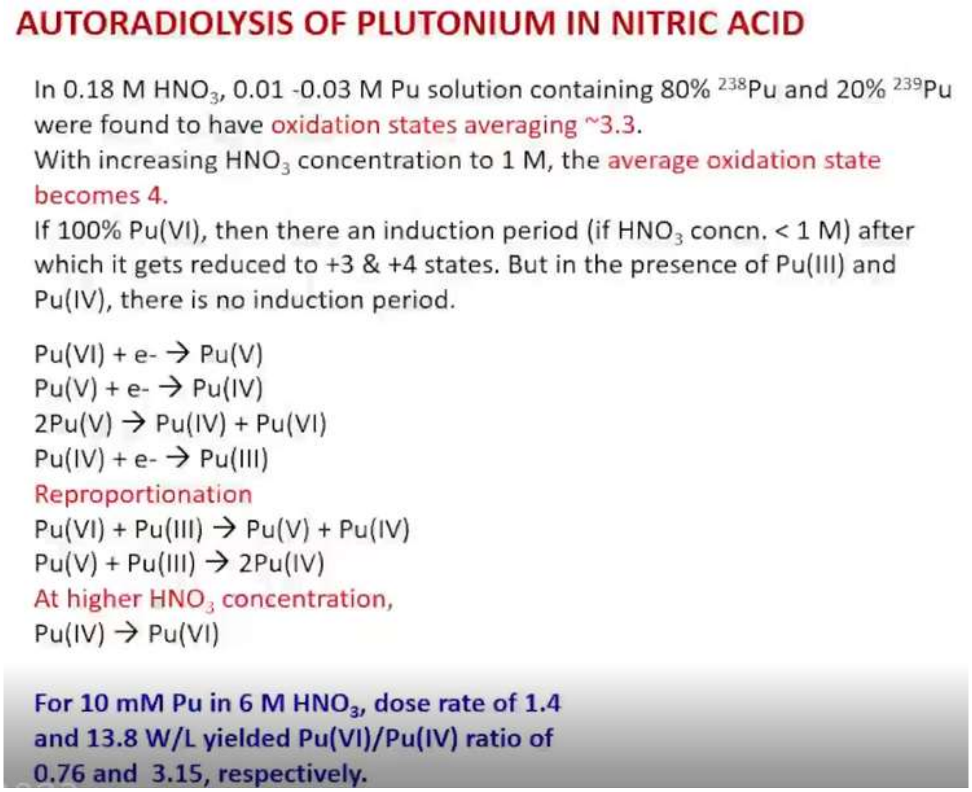
In a 1 M solution of $HClO_4$ containing ~0.01 M ^{239}Pu(IV) (at 25 °C), the average oxidation number of plutonium changes by 0.014 every day until it becomes **3.02 - 3.05.** The gas evolved from the solution consists of oxygen (60%) and hydrogen (40%). The solution was found to contain a substantial amount of Cl^- ions. The theoretical reduction yield of Pu(IV), like that for the reduction of Pu(VI), is 3.0 ions per 100 eV. The G value is 3.5 and the slight difference between these values can be due to the fact that Pu(IV) accepts some of the reducing radicals from the spurs.

The radiolytic transformations of ^{238}Pu(IV) and ^{238}Pu(VI) in 1 M $HClO_4$ have been studied. The radiation dose rate was ~0.15 Gy/s. The concentration of Pu(IV) remained constant, whereas Pu(VI) was reduced to give Pu(IV) and Pu(III). The yield was low due to slow reaction in 1 M $HClO_4$.

The theoretical yield for the reduction of Pu(VI) to Pu(IV) is 3 ions per 100 eV which is in agreement with the experimental results obtained in this study as mentioned above. Continuing in this auto radiolysis in a 1 M of perchloric acid containing 0.01 M ^{239}Pu in the +4 oxidation state at 25 degrees, the average oxidation number of plutonium changes by 0.014 every day until it becomes 3.02 to 3.05. The gas evolved from this solution which consists of oxygen and hydrogen which is coming from the radiolysis of water. Also, the solution is found to contain a substantial amount of chloride ion which is coming from the radiolysis of perchloric acid. The theoretical reduction yield of Pu(IV) like that of Pu(VI), just discussed in the previous slide, is around 3 ions per 100 eV. The G value of 3.5 which is experimentally same is because of the slight error due to the Pu(IV) reduction from the radicals from the spores actually coming because of the alpha particles. The radiolytic transformations of ^{238}Pu which is giving significantly more number of alpha particles again in the +4 oxidation state and in the +6 oxidation state was studied in 1M perchloric acid and the radiation dose was around 0.15 Gy/s. The concentration of Pu(IV) remained constant in this case whereas that of Pu(VI) was reduced to give Pu(IV) and Pu(III). The yield in this case was low due to the slower reaction in 1M perchloric acid.

Autoradialysis of plutonium in nitric acid medium:

Nitric acid medium also leads to the autoradialysis of plutonium similar way as I mentioned for the perchloric acid.



AUTORADIOLYSIS OF PLUTONIUM IN NITRIC ACID

In 0.18 M HNO_3, 0.01 -0.03 M Pu solution containing 80% ^{238}Pu and 20% ^{239}Pu were found to have oxidation states averaging ~3.3.
With increasing HNO_3 concentration to 1 M, the average oxidation state becomes 4.
If 100% Pu(VI), then there an induction period (if HNO_3 concn. < 1 M) after which it gets reduced to +3 & +4 states. But in the presence of Pu(III) and Pu(IV), there is no induction period.

$Pu(VI) + e^- \rightarrow Pu(V)$
$Pu(V) + e^- \rightarrow Pu(IV)$
$2Pu(V) \rightarrow Pu(IV) + Pu(VI)$
$Pu(IV) + e^- \rightarrow Pu(III)$
Reproportionation
$Pu(VI) + Pu(III) \rightarrow Pu(V) + Pu(IV)$
$Pu(V) + Pu(III) \rightarrow 2Pu(IV)$
At higher HNO_3 concentration,
$Pu(IV) \rightarrow Pu(VI)$

For 10 mM Pu in 6 M HNO_3, dose rate of 1.4 and 13.8 W/L yielded Pu(VI)/Pu(IV) ratio of 0.76 and 3.15, respectively.

In 0.18 M nitric acid if we have a solution of 0.01 to 0.03 M plutonium which contains around 80% ^{238}Pu and 20% ^{239}Pu, then it was found to have average oxidation state of 3.3 with increasing the nitric acid concentration to with 1M the average oxidation state has changed to around 4. If 100% Pu(VI) was taken, then there is an induction period initially if the concentration of the nitric acid was less than 1M and subsequently the Pu(VI) was found to be reduced to the +3 as well as +4 oxidation states but in the presence of Pu(III) and Pu(IV), there is no induction period that is to say if the Pu(VI) also contains some amount of Pu(III) and Pu(IV) to start with, then there is no induction period and we have immediately this reduction redox reactions taking place.

One of the reduction reactions is Pu(VI) picks up one electron and gets reduced to Pu(V) same way Pu(V) gets reduced to Pu(IV) and Pu(V) is disproportionating to Pu(IV) and Pu(VI) and again Pu(IV) is reduced to the Pu(III). There is also a reproportion reaction where Pu(VI) combines with a Pu(III) to give Pu(V) and Pu(IV) and also Pu(V) reacts with Pu(III) to give two ions of Pu^{4+}. At higher nitric acid concentrations, Pu(IV) is getting converted to Pu(VI). For a 10 millimolar solution of plutonium in 6M nitric acid, the dose rate of 1.4 watts per liter yielded a Pu(VI) to Pu(IV) ratio of 0.76 which significantly gets enhanced to around 3.15, i.e., the ratio of Pu(VI) to Pu(IV) becomes 3.15 if the dose rate was increased to 13.8 watts per liter of the solution.

APPLICATIONS OF ACTINIDES

1. Nuclear energy (U-235, U-233, Pu-239)
2. Power sources

	Specific power (W/g)	Comment
^{227}Ac	2.127	Limited use: heavy shielding
^{228}Th	26.05	Limited use: heavy shielding
^{238}Pu	0.54	Has been used as power source
^{242}Cm	120	Short half life

3. Medical use

Pu-238 is used as a pace maker

Ac-225 is used in alpha therapy

4. Neutron sources

Am-Be n source (2×10^6 n per Ci of radionuclide)

Cf-252 n source (4.4×10^9 n per Ci of radionuclide)

Now, coming to the applications of the actinides, one of the major applications of the actinides is in the nuclear energy that is U-235, U-233 and Pu-239. So these are the fissile isotopes of the actinides which are used in the nuclear energy. Also, the actinides are used as the power sources that is to say some of the actinide isotopes are the radionuclides like ^{227}Ac and ^{228}Th, ^{238}Pu with ^{242}Cm they are used as power sources. ^{227}Ac which has a specific power density of 2.127 W/g but it has a limited use, it requires heavy shielding for its application as a power source. Similarly, ^{228}Th which has a specific power density of 26.05 W/g this also has a limited use and it also requires heavy shielding while applying it for as a power source. ^{238}Pu has a specific power density of 0.54 W/g and this has been used as a power source in space shuttles. ^{242}Cm which has a specific power density of 120 W/g has relatively short half-life of around 2.2 years or so. So it also has a very good use as a power source. There are some of the other applications of the actinides like ^{238}Pu is used as a pacemaker. Actinium-225 is used in the alpha therapy as we know these days for the cancer therapy even though we are using previously that beta gamma emitting radionuclides the alpha therapy or the alpha emitting radionuclides are finding a great application because of very very specific way it destroys the tumor cells due to high linear energy transfer of the alpha particles. So in this way, actinium-225 is one of the very useful radionuclides used in the alpha therapy.

Actinides are also used as neutron sources. There are examples where the americium-beryllium (mixture or equivalent) which are used as neutron sources giving 2x10^{6} neutrons per curie of the radionuclide. There are also examples of plutonium-beryllium source being used for the neutron generation. Californium-252 which is having a spontaneous fission, it gives neutrons from the spontaneous fission reaction and it has 4.4x10^{9} neutrons per curie of the radionuclide.

There are also applications of the actinides like americium-241 is used in smoke detectors. Thorium is also used in gas metals. Now to summarize the actinides are produced in the nuclear reactors. They also can be produced by heavy ion reactions in accelerators. In these actinides they have very interesting chemical properties. Apart from being used in the nuclear power industry they also have several other uses and as I mentioned ^{238}Pu is a very popular radionuclide as a power source and (is produced by neutron capture of) neptunium-237 which is there in the radioactive waste that is the high level liquid waste. There is proposal in different countries to separate the ^{237}Np radionuclide from the high level waste (and) irradiate it in a reactor to get 238 plutonium which can have used as power source. Then also we have seen how these actinides have very very interesting chemical properties because of their multiple oxidation states.

Many cases the unusual oxidation states like Np(V), Pu(V), U(V) they get disproportionated under the given chemical conditions to give other more stable oxidation states like the pentavalent and hexagonal states. That is how the chemistry of these actinides depending on the aqueous medium in which these type of oxidation states are present so that their chemistry can be studied. And mostly as we have seen the chemistry of actinides in the +4 as well as +6 oxidation states are important so far as the nuclear well reprocessing is concerned. And other actinides are present mostly in the +3 oxidation states like the trans plutonium elements and the minor actinide like neptunium which also is present in the +4 as well as +6 oxidation states can be separated by using several separation methods on the radioactive waste feeds. The use of the actinides also I have mentioned that is how we come to the end of this actinite part of this lecture series.

Now we'll be covering actinides in the environment and then the transactinides. Thank you.

Contact Detail:
Email: mpatra@barc.gov.in
Phone: 022-25594576