



Workshop on

ROLE OF PARTITIONING AND TRANSMUTATION IN THE MITIGATION OF THE POTENTIAL ENVIRONMENTAL IMPACTS OF NUCLEAR FUEL CYCLE

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Overview of Aqueous Methods for Partitioning Minor Actinides and Fission Products

> **T.G.Srinivasan** Indira Gandhi Centre for Atomic Research, Kalpakkam, India





Overview of Aqueous Methods for Partitioning Minor Actinides and Fission Products

T.G.Srinivasan Indira Gandhi Centre for Atomic Research, Kalpakkam, India

- Nuclear Fuel Cycle
- PUREX Process
- Partitioning & Transmutation
- Chemistry of Lanthanides and Actinides
 - ✤ Occurrence
 - ✤ Valency
 - ✤ Hydrolysis
 - Complexation
 - Polymerization
 - Disproportionation
 - Interconversion of valencies
 - Criticality
 - Radiological safety

Extractants and Diluents for Reprocessing, Partioning, An/Ln Separation

- TBP
- Dialkyl Monamides
- СМРО (ОФСМРО, DФСМРО)
- Diamides (TODGA, TEHDGA, DMDOHEMA)
- ✤ TOPO, TRPO
- D2EHPA, DIDPA, DNPPA
 - > Type of species
 - extraction characteristics
 - degradation (radiolysis, chemical and thermal)
 - solvent clean-up
 - > third phase formation
 - > synthesis
- Diluents
- Problems in Repressing and Partitioning
 - Solvent Degradation
 - Third Phase Formation

LLFPs

- Chemistry
- □ Half Life, Decay scheme
- Fission Yield
- □ Fate in Reprocessing

□ Overview of R&D on Partitioning Research on MAs and LLFPs

- Japan
- India
- China
- ✤ Russia
- ✤ Germany
- ✤ France
- ✤ UK
- ✤ USA
- Korea (Essentially Pyro)



ACTINIDE IN SPENT FUEL

	_				UOX	45 GW	d/t										
1				(4 years cooled)												2	
н				U	J	941 kg/tMLI											He
3	4			P	u	11	,3 kg/t	MLI				5	6	7	8	9	10
Li	Be			N	р	61	1 g/tN	ILI				В	С	N	0	F	Ne
11	12	1		A	m	60	05 g/tN	ILI				13	14	15	16	17	18
Na	Mg			CI	m	9	0 g/tM	LI				AI	Si	P	S	CI	A
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Са	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	1	Xe
55	56		72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ва	Ln	Hf	Та	w	Re	Os	lr	Pt	Au	Hg	Т	Pb	Bi	Po	At	Rn
87	88		104	105	106	107	108	109	110								
Fr	Ra	An	Rf	Db	Sg	Bh	Hs	Mt	Uun								

	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
LANTHANIDES	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Τm	Yb	Lu
	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
ACTINIDES	Ac	Th	Ра	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

ACTINIDES MAJEURS

ACTIVATION PRODUCTS

FISSION AND ACTIVATION PRODUCTS

FISSION PRODUCTS ACTINIDES MINEURS

Courtesy : Bernard Boullis, CEA

Element	Nuclide	Sv/Bq (ingestion)
Uranium	²³⁵ U	4.6×10 ⁻⁸
	²³⁸ U	4.4×10 ⁻⁸
Neptunium	²³⁷ Np	1.1×10 ⁻⁷
Plutonium	²³⁸ Pu	2.3×10 ⁻⁷
	²³⁹ Pu, ²⁴⁰ Pu	2.5×10 ⁻⁷
Americium	²⁴¹ Am, ²⁴³ Am	2.0×10 ⁻⁷
Curium	²⁴³ Cm	1.5×10 ⁻⁷
	²⁴⁴ Cm	1.2×10 ⁻⁷
	²⁴⁵ Cm, ²⁴⁶ Cm	2.1×10 ⁻⁷

Effective dose coefficients of actinides and lanthanides

Element	Nuclide	Sv/Bq (ingestion)
Strontium	⁹⁰ Sr	3.4×10 ⁻¹⁰
Zirconium	⁹³ Zr	8.6×10 ⁻¹⁰
Technetium	⁹⁹ Tc	6.4×10 ⁻¹⁰
Iodine	¹²⁹ I	1.1×10 ⁻⁷
Caesium	¹³⁵ Cs	2.0×10 ⁻⁹
	¹³⁷ Cs	1.3×10 ⁻⁸

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Effect of transmutation on partitioned actinides Courtesy : Enrique M. Gonzalez, CIEMAT



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Actinide Chemistry

• The series of elements beginning with actinium (atomic number 89) and including Th, Pa, U and the transuranium elements through the element lawrencium (atomic number 103). These elements have strong chemical resemblance to the lanthanides (atomic numbers 57 to 71).

• Except for Th and U, actinides are not present in nature in appreciable quantities. The transuranium elements were discovered and investigated as a result of their synthesis in nuclear reactions. All are radioactive.

- Most actinide elements have following in common:
 - Trivalent cations which form complex ions and organic chelates
 - Soluble sulfates, nitrates, halides, perchlorates, and sulfides
 - Acid-insoluble fluorides and oxalates.

• All members of the series can resemble actinium in their chemical and electronic properties; they form separate group within periodic table.

• The actinides display less similarity in their chemical Properties than the lanthanide series, for instance exhibiting a wider range of oxidation states.

• Actinides are metals and all are radioactive. As a result, they dominate the study of nuclear chemistry. The elements emit energy in the form of alpha particles, beta particles, or gamma rays.

• Actinides undergo radioactive decay at different rates; i.e. they have different half-lives. Elements with higher atomic numbers have short half-lives. Some actinides with lower atomic numbers, however, have half-lives ranging between thousands and millions of years.

- Actinides are quite electropositive
- Pa Pu show significant redox chemistry

 e.g. all 4 oxidation states of Pu can co-exist in appropriate
 conditions in (aq)
- stability of high oxidation states peaks at U (Np)
- An³⁺ is the maximum oxidation state for (Cf) Es -Lr
- No²⁺(aq) is especially stable ~ most stable state for No in (aq)
- Redox potentials show strong dependence on pH (data for Ac Cm)

Lanthanide - Actinide contraction

• There is a steady decrease in metallic and ionic radii of lanthanides as the series is traversed from La to Lu. Similar contraction is found for the actinide series

• In multi-electron atoms, decrease in radius brought about by increase in nuclear charge is partially offset by electrostatic repulsion among electrons. Particularly, a shielding effect operates. i.e., as electrons are added in outer shells, electrons already present shield the outer electrons from nuclear charge making them see an lower effective charge on the nucleus

• The shielding effect exerted by inner electrons decreases in order s > p > d > f. Usually in a period as a particular sub-shell is filled up, atomic radii go on decreasing. This effect is particularly pronounced in case of lanthanides as their 4f sub-shells are being filled across the period and they are least able to shield outer(5th and 6th) shell electrons. Thus shielding effect is least able to counter decrease in radii due to increasing nuclear charge

This leads to "Lanthanide contraction". Ionic Radius drops from 1.020 Å in case of Ce(III) to 0.861 Å in case of Lu(III) 14

Shapes of 4f Orbitals



 $f_z 3 = f_{z(2z} 2_{-3x} 2_{-3y} 2_{)} [m_1 = 0]$





 $f_{xyz} \& f_{z(x}^2 - y^2) [m_1 = \pm 2]$



 $f_{xz}^{2} = f_{x(4z}^{2} - x^{2} - y^{2}) \& f_{yz}^{2} = f_{y(4z}^{2} - x^{2} - y^{2}) [m_{l} = \pm 1] \qquad f_{x(x}^{2} - 3y^{2}) \& f_{y(3x}^{2} - y^{2}) [m_{l} = \pm 3]$ 15

Actinide Contraction

Actinide 3+ or 4+ ions with radii similar to their Lanthanide counterparts show similarities in properties that depend upon ionic radius



Actinides: Electronic subshells are filled in a manner analogous to the lanthanide series

	Ac	Th	Ра	U	Np	Pu	Am	Cm
Z	89	90	91	92	93	94	95	96
M(g)	6d7s ²	6d ² 7s ²	5f ² 6d7s ²	5f ³ 6d7s ²	5f ⁴ 6d7s ²	5f ⁶ 7s ²	5f ⁷ 7s2	5f ⁷ 6d7s ²
M⁺(g)	7s²	<mark>6d7s</mark> ²	5f ² 7s ²	5f ³ 7s ²	5f ⁵ 7s?	5f ⁶ 7s	5f ⁷ 7s	5f ⁷ 7s ²
M ²⁺ (g)	7s	5f6d	5f ² 6d	5f ³ 6d?	5f ⁵ ?	5f ⁶	5f ⁷	5f ⁸
M ³⁺ (g)		5f	5f ²	5f ³	5f⁴	5f ⁵	5f ⁶	5f ⁷
M ⁴⁺ (g)			5f	5f ²	5f ³	5f ⁴	5f ⁵	5f ⁶

Actinides: Electronic subshells are filled in a manner analogous to the lanthanide series

z	97	98	99	100	101	102	103
M(g)	5f ⁹ 7s ²	5f ¹⁰ 7s ²	5f ¹¹ 7s ²	5f ¹² 7s ²	(5f ¹³ 7s²)	(5f ¹⁴ 7s²)	(5f ¹⁴ 6d7s ²
M⁺(g)	5f ⁹ 7s	5f ¹⁰ 7s	5f ¹¹ 7s	(5f ¹² 7s)	(5f ¹³ 7s)	(5f ¹⁴ 7s)	(5f ¹⁴ 7s²)
M ²⁺ (g)	5f ⁹	5f ¹⁰	5f ¹¹	(5f ¹²)	(5f ¹³)	(5f ¹⁴)	(5f ¹⁴ 7s)
M ³⁺ (g)	5f ⁸	5f ⁹	5f ¹⁰	(5f ¹¹)	(5f ¹²)	(5f ¹³)	(5f ¹⁴)
M ⁴⁺ (g)	5f ⁷	5f ⁸	(5f ⁹)	(5f ¹⁰)	(5f ¹¹)	(5f ¹²)	(5f ¹³)

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+2 oxidation state

- Unusual oxidation state
- Common only for the heaviest elements
- No²⁺ & Md²⁺ are more stable than Eu²⁺

+3 oxidation state

- The most stable oxidation state for all trans-Americium elements (except No?)
- General properties resemble Ln³⁺ and are size-dependent
- Stability constants of complex formation are similar for same size

An³⁺ & Ln³⁺

- Isomorphism is common
- later An³⁺ & Ln³⁺ must be separated by ion-exchange/SX

+4 oxidation state

- Very important, stable state for Pa, U, Pu
- Am, Cm, Bk & Cf are increasingly easily reduced only stable in certain complexes e.g. Bk⁴⁺ is more oxidizing than Ce⁴⁺
- Hydrolysis / Complexation / Disproportionation are all important in (aq)
- +5 oxidation state
 - Principal state for Pa
 - \Box Pa⁵⁺ chemistry resembles that of Nb⁵⁺ / Ta⁵⁺
 - For U, Np, Pu and Am the AnO₂⁺ ion is known (i.e. quite unlike Nb/Ta)

+6 Oxidation state

- AnO_2^{2+} ions are important for U, Np, Pu, Am UO_2^{2+} is the most stable
- Few other compounds *e.g.* AnF_6 (An = U, Np, Pu), UCl₆, UOF₄ etc..., U(OR)₆
- +7 Oxidation state
 - Only the marginally stable oxo-anions of Np and Pu, e.g. AnO₅³⁻

- High oxidation states are more stable in basic conditions
- Even at low pH hydrolysis occurs: e.g. Pa^{5+} hydrolyses easily; potentials that indicate it to be most stable oxidation state are recorded in presence of F⁻ or $C_2O_4^{2-}$
- Tendency to disproportionation is particularly dependent on pH e.g. at high pH, $3Pu^{4+} + 2H_2O = PuO_2^{2+} + 2Pu^{3+} + 4H^+$
- Early actinides have a tendency to form complexes
- Complex formation influences reduction potentials e.g. Am⁴⁺(aq) only exists when complexed by fluoride (15 M NH₄F(aq))

Ion	Colour	Stability
Md ²⁺		easy to oxidize, but stable to water
No ²⁺		stable
Ac ³⁺	colorless	stable
U ³⁺	claret	evolves H ₂ on standing; easily oxidized by air
Np ³⁺	blue- purple	stable to water; easily oxidized by air
Pu ³⁺	blue- violet	stable to water & air; readily oxidized
Am ³⁺	pink	stable; difficult to oxidize
Cm ³⁺	pale yellow	stable; chemical oxidation not possible

Ion	Colour	Stability
Bk ³⁺	green	stable; can be oxidized to Bk4+
Cf ³⁺	green	stable
Es ³⁺		stable
Fm ³⁺		stable
Md ³⁺		stable, but easily reduced to Md ²⁺
No ³⁺		easily reduced to No ²⁺
Lr ³⁺		stable

Ion	Colour	Stability
Pa ⁴⁺	Colour- less	stable to water; easily oxidized
U ⁴⁺	green	stable to water; easily oxidized by air to UO ₂ ²⁺
Np ⁴⁺	yellow- green	stable to water; slowly oxidized by air to NpO ₂ ⁺
Pu ⁴⁺	tan- brown	stable in 6M acid, disproportionates at higher pH
Am ⁴⁺	pink?	only stable as fluoride complex; easily reduced
Cm ⁴⁺	pale yellow	only as fluoride complex; stable only 1 hr at 25°C
Bk ⁴⁺	yellow	marginally stable; easily reduced
Pa ⁵⁺	Color- less	stable; readily hydrolyzed

Ion	Colour	Stability
UO ₂ +		unstable to disproportionation (least at pH 2-4)
NpO2+	green	stable; disproportionates at high acidity
PuO ₂ ⁺	pink- purple	tends to disproportionate (least at low pH)
AmO ₂ ⁺	yellow	disproportionates in acid; reduced by its a-decay
UO ₂ ²⁺	yellow	stable; difficult to reduce
NpO2 ²⁺	pink-red	stable; easy to reduce
PuO ₂ ²⁺	orange- pink	stable; easy to reduce; reduced by its α -decay

Ion	Colour	Stability
AmO ₂ ²⁺	rum- brown	easy to reduce; rapidly reduced by its a -decay
NpO ₅ ³⁻	deep green	only in alkaline solution
PuO ₅ ³⁻	deep green	only in alkaline solution; oxidizes water

Hydrolysis

- Hydrolysis of actinides is an important phenomenon in solution chemistry, reprocessing, and waste management
- □ Hydrolysed actinides are insoluble and migrate less unlike complexed actinides (Cl^- , CO_3^{--} , NO_3^{--})
- Like complexation hydrolysis is also valence dependent (IV) > (III) > (VI) > (V)

Complexation

- Complexation of actinides is extremely important like hydrolysis
- The complexation depends upon the ionic potential of the cation and the anion
- Complexation markedly affects the formal redox potentials of ions and hence allows to manipulate redox reactions (e.g. Davies & Gray method for U(VI),
 - Reduction of Pu in SO_4^{2-} medium)
- Among the actinide ions the complexation varies in the order, (IV) > (III) > (VI) > (VI) > (V)
- For the same actinide cation the complexation decreases in the order,

and

$$CO_3^{--} > SO_3^{--} > C_2O_4^{--} > SO_4^{--}$$

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Problems in solvent extraction

- Radiation, Chemical and Thermal degradation of solvent
 - Lower DFs from FPs
 - Phase Separation
 - Emulsion and precipitation
 - Flooding
- Third Phase formation
 - Criticality
 - Flooding
 - Red oil formation leading to explosion

Actinide Third Phases



Courtesy : University of Nevada



Pu(IV)



Np(IV)



Pu(VI)



Np(VI)

Criticality Parameters for some actinides

Parameter	Form	U-235	U-233	Pu-239
Mass (kg)	Solution	0.82	0.59	0.51
	Metal	22.8	7.5	5.6 (α) 7.6 (δ)
Diameter of Infinite	Solution	5.4	4.4	4.9
Cylinder (Inches)	Metal	3.1	1.9	1.7
Solution Volume (lit)	Solution	6.3	3,3	4.5
Conc. (g/l)	Solution	12.1	11.2	7.8

Radiological Safety Parameters

S.No	Nuclide	ALI (Bq)	DAC (Bq/m³)
1	²³⁹ Pu	625	0.26
2	²³⁷ Np	1333	0.555
3	²⁴¹ Am	740	0308
4	²³⁸ Pu	666	0.277

Isotopes of high risk nature in repositories

Fission Products :

 129 I > 99 Tc > 135 Cs > 93 Zr > 126 Sn (in the order of toxicity)

Activation products ¹⁴C and ³⁶Cl

¹³⁷Cs and ⁹⁰Sr with low half lives (~30 years) do not require trasmutation

129**T** Half Life : 1.6*10⁷ a Fission yield %: (0.913 / 1.596)

ALI by Ingestion : $2*10^5$ Bq/year Emission : β^- 3.151 keV, γ 37.6 keV

- Has the highest toxicity among FPs equivalent to those of actinides
- High mobility element, enters the biosphere easily
- During aqueous reprocessing, iodine is removed from the dissolver solution with a yield of 95-98%
- To improve the separation yield, more complex chemical treatments are necessary
- Setter separation yields achievable with pyrochemical processes
- Conditioning in the form of AgI, PbIO₄, developed yet not effective to exclude migration into environment due to extremely long half-life

⁹⁹Tc Half life : 2.1*10⁵ a Fission yield % : 5.774 / 5.998

ALI by Ingestion : $3*10^7$ Bq/year Emission : β^- 1.42 keV, γ 140.51 keV

- The radiologic significance of ⁹⁹Tc is important if the repository surroundings are slightly oxidic
- In reducing conditions ⁹⁹Tc is remarkably stable and insoluble as technetium metal or TcO₂ suboxide
- Partitioning of ⁹⁹Tc is not an easy task because it occurs as insoluble metal in the alloy form with other elements and as soluble TcO₄⁻ ion in solution
- Separation from aqueous effluents is possible in an advanced PUREX scheme, but recovery from insoluble residues is difficult, with the present recovery yield at best reaching 80%
- Improving this yield significantly implies the development of new separation technologies such as the not yet proven conversion of the technetium into a single chemical species
- Alternatively, a group separation together with the platinum metals may be carried out using pyrometallurgical processes
- If separated in metallic form, transmutation appears to be feasible because of its stability and relatively large neutron capture cross-section

¹³⁵Cs (T_{1/2} = 2.3*10⁶ a)
 ALI by Ingestion : 3*10⁷ Bq/year
 Fission yield % : 6.35 / 7.495
 Emission : β⁻1.081keV, γ 787.2, 846.1keV

- Cesium occurs in the form of the isotopes 133 (stable), 135 and 137
- ✤ In terms of radiologic significance, ¹³⁷Cs is the major constituent of HLW
- The activity of the long-lived ¹³⁵Cs in HLW is a million times lower However, once released from a matrix as glass, cesium is very mobile
- Transformation of ¹³⁵Cs to stable ¹³⁶Ba is possible from a neutronics point of view, but impracticable due to the requirement of close to 100% isotopic separation efficiency (traces of ¹³³Cs in the target would generate new ¹³⁵Cs during the irradiation)

⁹³Zr (T_{1/2} = 1.5*10⁶ a),
FY% : 6.14 / 3.734
Emission : β⁻ 1.583 keV, γ 30.77keV

◆ ⁹³Zr is somewhat similar to ¹³⁵Cs, it has also a very long half-life and a small isotopic abundance (about 14% of the total Zr)

An isotopic separation would be necessary, and its transformation to stable ⁹⁴Zr would be very slow because the thermal capture cross-section is about five times smaller than that of ¹³⁵Cs ¹²⁶Sn (T_{1/2} = 1.0*10⁵ a)
ALI by Ingestion : 3*10⁶ Bq/year
FY% : 0.138 / 0.287
Emission : β⁻ 30.0 keV, γ 87.57 keV

- ¹²⁶Sn is partly soluble in HLW from aqueous reprocessing but occurs also as an insoluble residue, similar to technetium
- Isolation involves a special treatment of the HLW, and the use of isotopic separation techniques
- Transmutation of ¹²⁶Sn is questionable due to the very low neutron capture cross-section

TBP

- The workhorse of aqueous reprocessing industry for 50 years!
- economical
- easy commercial availability
- good stability
- Drawbacks
 - aqueous solubility
 - third phase formation
 - deleterious degradation products

N,N Dialkyl Monamides (DOHA,DHOA etc.,.)

□ Easily incinerable to atmospheric elements (CHON Principle)

Non-deleterious degradation products

• amines and carboxylic acids

Drawbacks

Viscosity of metal solvate

phase separation behaviour

third phase formation

Diamides (DBDMTDMA,TODGA,TEHDGA, DMDOHEMA)

- □ Easily incinerable to atmospheric elements (CHON Principle)
- Non-deleterious degradation products
 - □ amines and carboxylic acids
- Drawbacks
 - Viscosity of metal solvate
 - phase separation behaviour
 - third phase formation

CMPOs

- Excellent extraction characteristics at high acidity
- Stripping at low acidity
- Widely studied
- A boon for complete polishing of aq. Solutions wrt actinides of almost all valencies

Drawbacks

- Leaves phosphate on final disposal
- □ Third phase formation (severe in Diphenyl version)
- Complicated synthesis
- Difficult purification
- Degradation products deleterious
- Requires large concentration of modifier

TRPO, TOPO

□ TOPO is a solid

□ synthesis is not as easy as TBP yet simple

Drawbacks

third phase / precipitate formation

Deleterious degradation products

 \Box not very economical

D2EHPA (HDEHP), DIDPA, DNPPA

- □ Acidic compounds
- Hence extraction requires low acidity
- purification difficult
- Deleterious degradation products

Drawbacks

- leaves phosphate on final disposal
- phase separation behaviour
- □ third phase formation
- no selectivity

SOLVENT EXTRACTION VS EXTRACTION CHROMATOGRAPHY

- □ Continuous counter current extraction
- □ Large throughput
- □ Fast process

- □ Large theoretical plates, hence better separations
- □ Batch process, hence less throughput
- Large solid substrate waste
- □ Slow process

Diluents in reprocessing and partitioning

- Kerosene
- ✤ N-paraffin mixtures (NORPAR, HNP, NPH etc.,.)
- Isoparaffin mixtures (ISOPAR-L,M, SHELL SOL-T, HPT (TPH) etc.,.
- Aromatics (DEB, DBB)
- Fluorinated compounds (TCE, CCl₄, Fluoropol-732)
 - ✤ safety (FP, BP)
 - economics (cost easy availability)
 - engineering (hydrodynamics, viscosity, density)
 - * Are they really inert?

SI Units

Physical Quantity	SI Unit	Non SI Unit	Relationship
Activity	Bq	Сі	1 Bq=2.7*10 ⁻¹¹ Ci
Absorbed Dose	Gray (Gy) 1 Gray = 1 J/kg	rad	1 Gy = 100 rads 1 rad = 0.01 Gy
Dose Equivalent	Sievert (Sv) 1 Sv = 1 J/kg	Rem	1 Sv= 100 rems 1 rem = 10 mSv
Exposure	Coulomb/kg	Roentgen(R)	1C/kg = 3876 R



Thank You