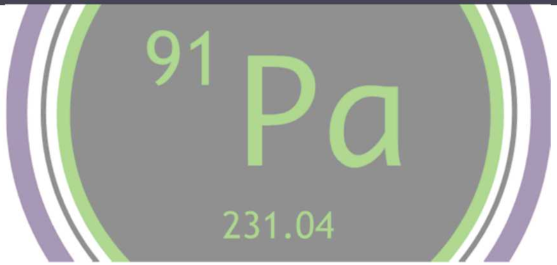
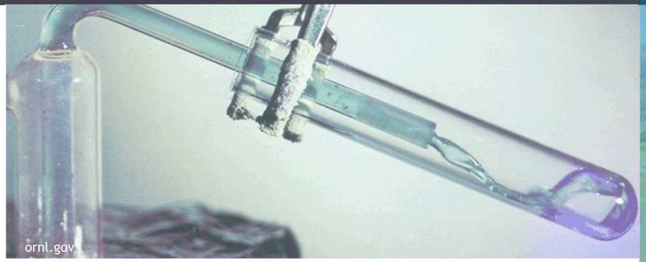
SAND2019-5498C

The Impact of Protactinium

on the Proliferation Resistance of Thorium Power





PRESENTED BY

Eva C. Uribe, Systems Research and Analysis Group

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Overview of the thorium fuel cycle

58 **Ce** cerium	59 **Pr** praesodymium	60 **Nd** neodymium	61 **Pm** promethium	62 **Sm** samarium	63 **Eu** europium	64 **Gd** gadolinium	65 **Tb** terbium	66 **Dy** dysprosium	67 **Ho** holmium	68 **Er** erbium	69 **Tm** thulium	70 **Yb** ytterbium	71 **Lu** lutetium
90 **Th** thorium	91 **Pa** protactinium	92 **U** uranium	93 **Np** neptunium	94 **Pu** plutonium	95 **Am** americium	96 **Cm** curium	97 **Bk** berkelium	98 **Cf** californium	99 **Es** einsteinium	100 **Fm** fermium	101 **Md** mendelevium	102 **No** nobelium	103 **Lr** lawrencium

Uranium-Plutonium Cycle: $\text{neutron} + {}^{238}U \xrightarrow{(n,\gamma)} {}^{239}U \xrightarrow{\beta^-} {}^{239}Np \xrightarrow{\beta^-} {}^{239}Pu$

Thorium-Uranium Cycle: $\text{neutron} + {}^{232}Th \xrightarrow{(n,\gamma)} {}^{233}Th \xrightarrow{\beta^-} {}^{233}Pa \xrightarrow{\beta^-} {}^{233}U$

Advantages and disadvantages of nuclear power from thorium

Advantages	Disadvantages
• Thorium (potentially) more abundant than uranium • ThO_2 has superior stability • Nuclear properties of ^{232}Th and ^{233}U are more favorable for fissile material production and use • Lower production of minor actinides • Produces less plutonium • ^{233}U can be down-blended with ^{238}U • More "proliferation resistant"	• Thorium has no fissile isotopes • ^{233}Pa intermediate absorbs neutrons • ^{231}Pa is long-lived • ThO_2 fuel more difficult to manufacture and dissolve • THOREX reprocessing technology still under development • Remote handling required for fuel fabrication using ^{233}U • ^{233}U is a proliferation concern

Nuclear properties of ^{233}U

neutron + $^{232}Th \xrightarrow{(n,\gamma)} {}^{233}Th \xrightarrow{\beta^-} {}^{233}Pa \xrightarrow{\beta^-} {}^{233}U$

Isotope	^{233}U	^{235}U	^{239}Pu
Critical mass of metal sphere (kg)[a] Isotopic purity and reflector	7.47 98.25 wt% ^{233}U with 4.2 cm Be reflector	20.8 93.5% ^{235}U with 5.1 cm Be reflector	8.39 4.9 wt% ^{240}Pu with 3.69 cm Be reflector
Spontaneous fission rate ($s^{-1} \cdot kg^{-1}$)[b] Isotopic purity	0.5	0.6 1% ^{234}U, 5.5 % ^{238}U	2.5×10^4 6% ^{240}Pu

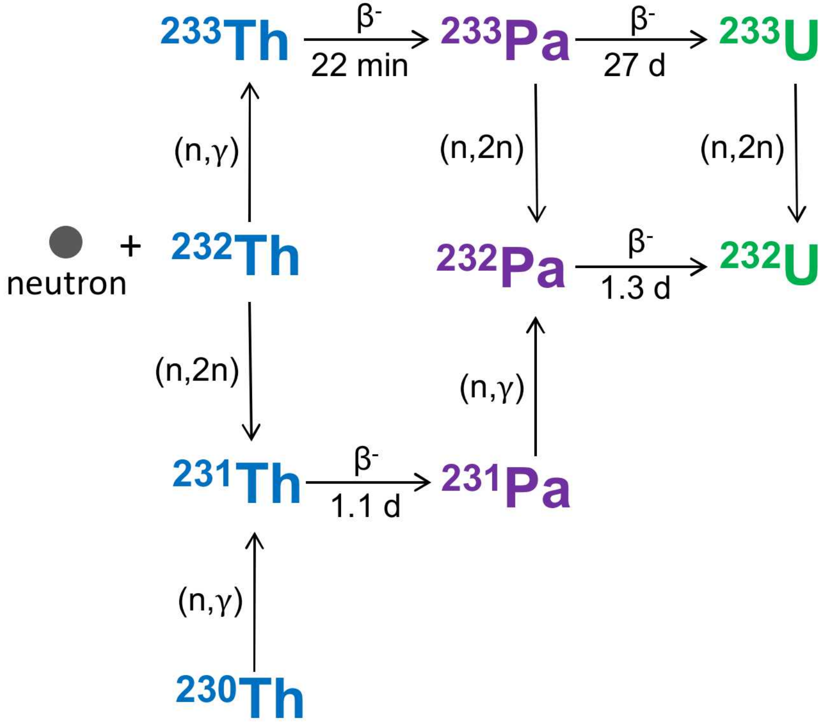
[a]Paxton, H. C. and Pruvost, N. L., Critical Dimensions of Systems Containing U-235, Pu-239, and U-233. LA-10860-MS. Los Alamos National Laboratory, 1986 revision

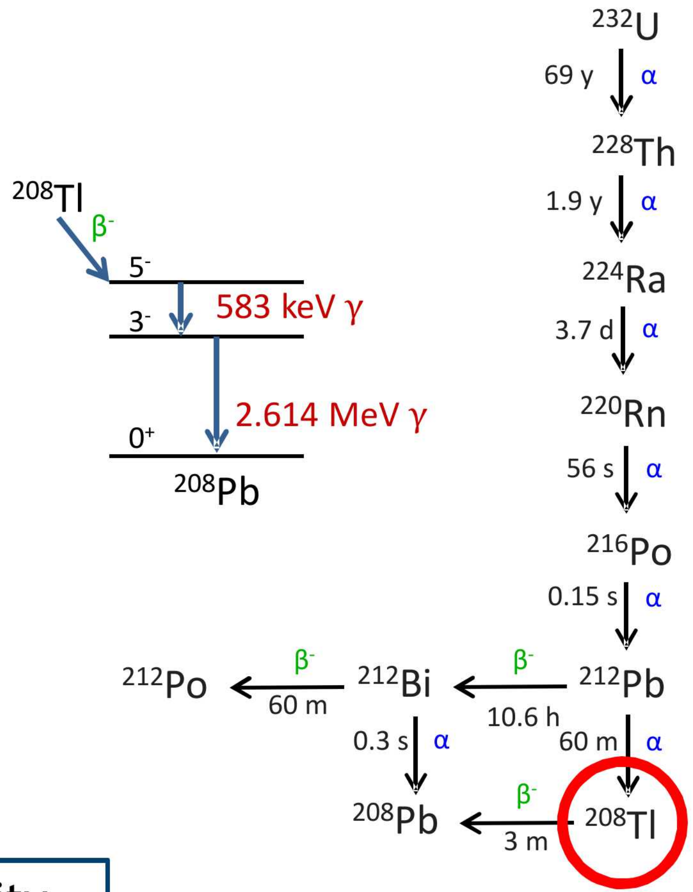
[b]Kang, J. and von Hippel, F. N. U-232 and the Proliferation Resistance of U-233 in Spent Fuel, Science and Global Security, 2001, 9, 1-32

Are thorium reactors proliferation resistant?

Reason 1: They produce less weapons-usable plutonium compared to conventional light water reactors

Reason 2: Thorium fuels will contain a ^{232}U that decays to ^{208}Tl, which emits highly-penetrating γ rays





IAEA Significant Quantity
^{233}U = 8 kg

IAEA Safeguards Glossary 2001 Edition, International Nuclear Verification Series No. 3, IAEA, Vienna (2001)

How can we compare the *attractiveness* of nuclear materials?

Bare critical mass of metal (kg)

Heat (W/kg)

Spontaneous Neutron Rate (n/s•kg^{-1})

Dose Rate (rad/h)

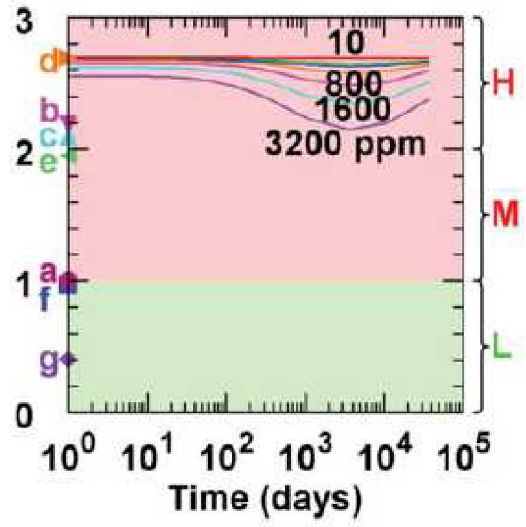
$$FOM = 1 - \log_{10}\left[\frac{M}{800} + \frac{Mh}{4500} + \frac{MS}{6.8} + \frac{M}{50}\left(\frac{D}{500}\right)^{1/\log_{10} 2}\right]$$

d) ^{233}U (10 ppm ^{232}U)

b) HEU (93%)

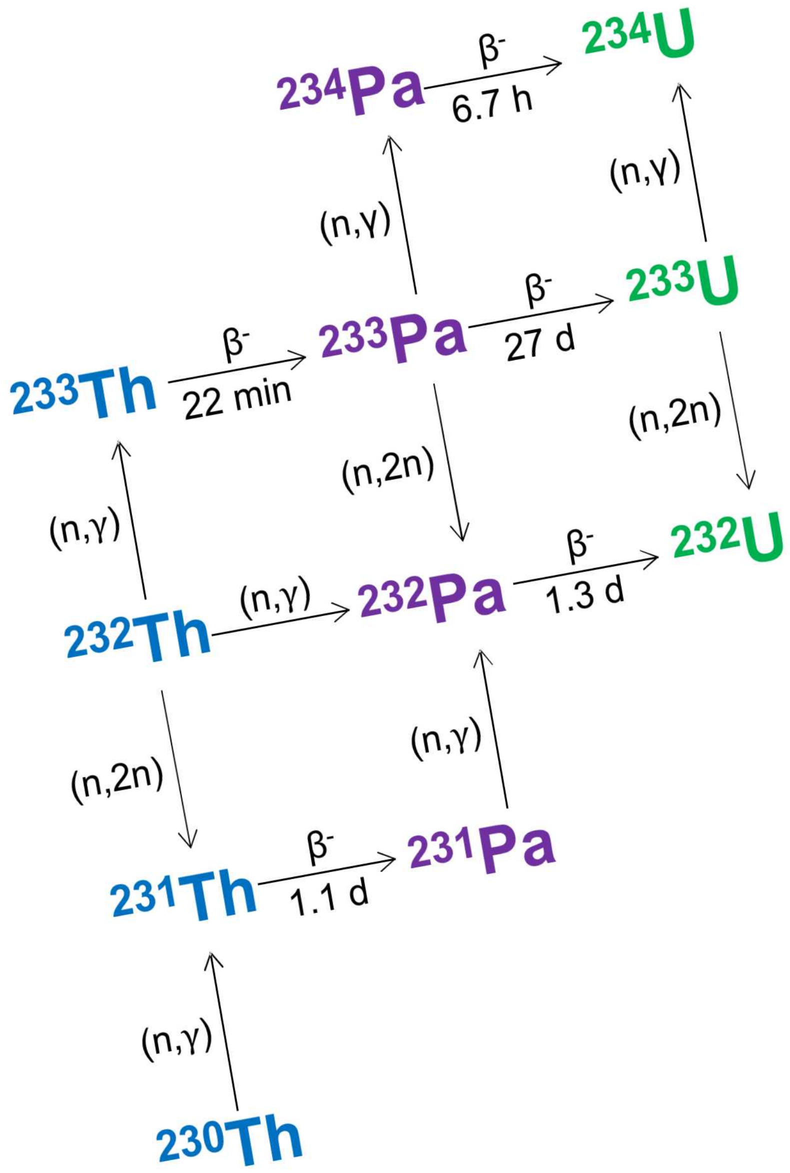
c) ^{237}Np

e) Weapons Grade Pu



Bathke, et al. The Attractiveness of Materials in Advanced Nuclear Fuel Cycles for Various Proliferation and Theft Scenarios, *Nuclear Technology*, **2012**, 179, 5-30

Chemical reprocessing can further reduce the ^{232}U concentration

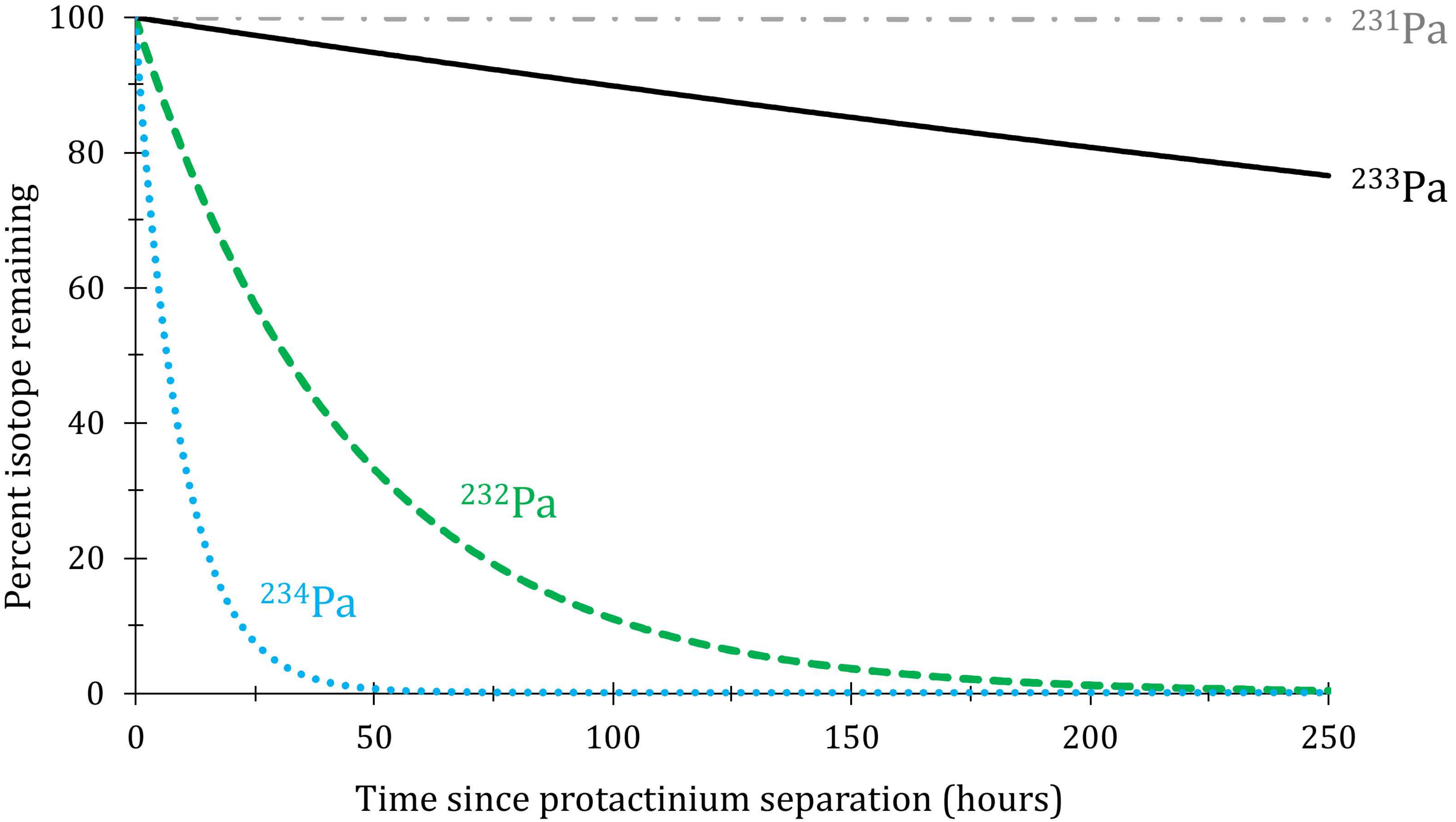

234Pa
β-
6.7 h
234U
(n,γ)
(n,γ)
233Th
β-
22 min
233Pa
β-
27 d
233U
(n,γ)
(n,2n)
(n,2n)
232Th
(n,γ)
232Pa
β-
1.3 d
232U
(n,2n)
(n,γ)
231Th
β-
1.1 d
231Pa
(n,γ)
230Th

$^{234}Pa \xrightarrow{\beta^-} {}^{234}U$ $t_{1/2}$ = 6.7 hours

$^{233}Pa \xrightarrow{\beta^-} {}^{233}U$ $t_{1/2}$ = 27 days

$^{232}Pa \xrightarrow{\beta^-} {}^{232}U$ $t_{1/2}$ = 1.3 days

$^{231}Pa \xrightarrow{\alpha} {}^{227}Ac$ $t_{1/2} = 3.276 \times 10^4$ years



100
80
60
40
20
0
0
50
100
150
200
250
Percent isotope remaining
Time since protactinium separation (hours)
231Pa
233Pa
232Pa
234Pa

The unique chemistry of protactinium

“Pa(V) in aqueous solution is rarely present as a single species, but rather exists as a mixture of several complexes or hydrolyzed species.

“…may yield **ambiguous or mutually contradicting** interpretations…”

“It exhibits an extraordinarily high tendency to undergo hydrolysis, to form polymers, and to be adsorbed on almost any available surface.”

“…many reports of **erratic and irreproducible behavior** of protactinium as well as for its frustrating habit of disappearing in the hands of inexperienced or unwary investigators.”

“The known world supply of the isolated elements and its compounds did not exceed one or two grams until the late 1950s.”

“Laboratory work with protactinium has been largely abandoned…”

“The **mystery and witchcraft** mostly came from protactinium’s confusing chemical properties, not quite truly actinide, yet not quite transition metal.”

B. Myasoedov, H. Kirby, and I. Tananaev, *Chemistry of the Actinides and Transactinides*
H. W. Kirby, *The Radiochemistry of Protactinium*, National Academy of Sciences National Research Council
R. Wilson, “Peculiar Protactinium,” *Nature Chemistry,* 4, 586 (2012)

The unique chemistry of protactinium

58 **Ce** cerium	59 **Pr** praesodymium	60 **Nd** neodymium	61 **Pm** promethium	62 **Sm** samarium	63 **Eu** europium	64 **Gd** gadolinium	65 **Tb** terbium	66 **Dy** dysprosium	67 **Ho** holmium	68 **Er** erbium	69 **Tm** thulium	70 **Yb** ytterbium	71 **Lu** lutetium
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Actinium	$[Rn]6d^1 7s^2$
Thorium	$[Rn]6d^2 7s^2$
Protactinium	$[Rn]5f^2 6d^1 7s^2$
Uranium	$[Rn]5f^3 6d^1 7s^2$

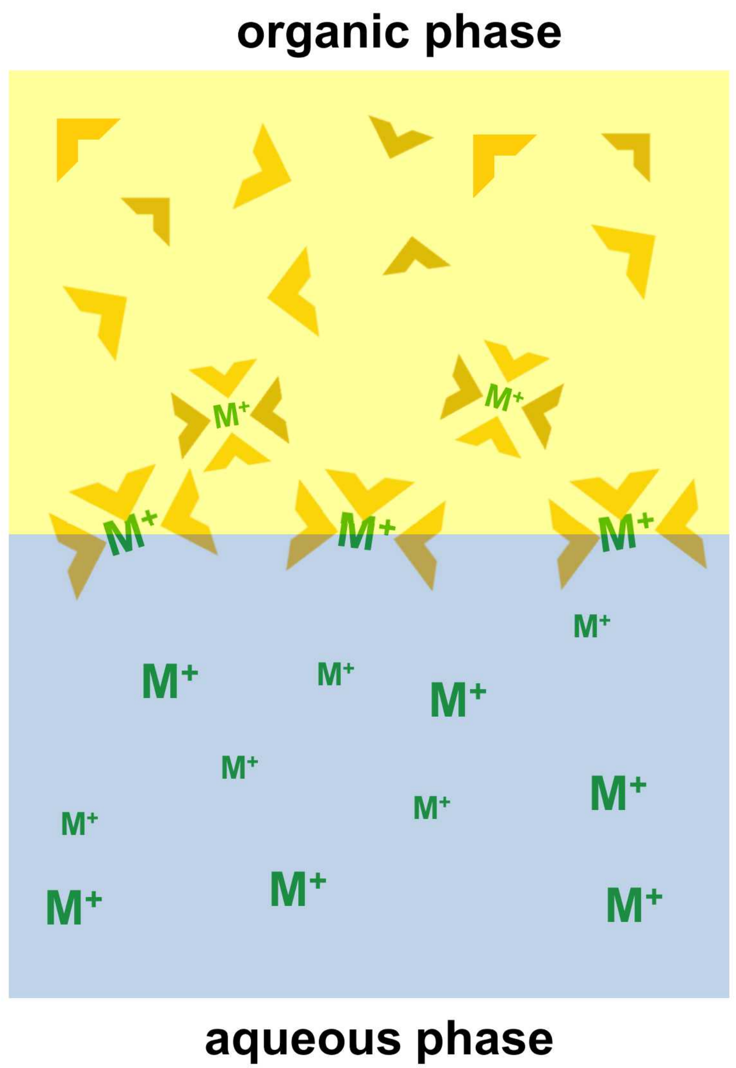
Element	Oxidation state*	Ionic form
Th	+3, **+4**	**Th^{4+}**
Pa	+3, +4, **+5**	**PaO^{3-}**
U	+3, +4, +5, **+6**	**UO_2^{2+}**
Np	+3, +4, **+5**, +6, +7	NpO_2^{+}
Pu	+3, **+4**, **+5, +6**, +7, +8	PuO_2, PuO_2^{+}, PuO_2^{2+}
Am	**+3**, +4, +5, +6	Am^{3+}

*Most stable oxidation state in aqueous solutions bolded.

Cotton, S. *Lanthanide and Actinide Chemistry*; John Wiley & Sons, Ltd: Sussex, 2006.

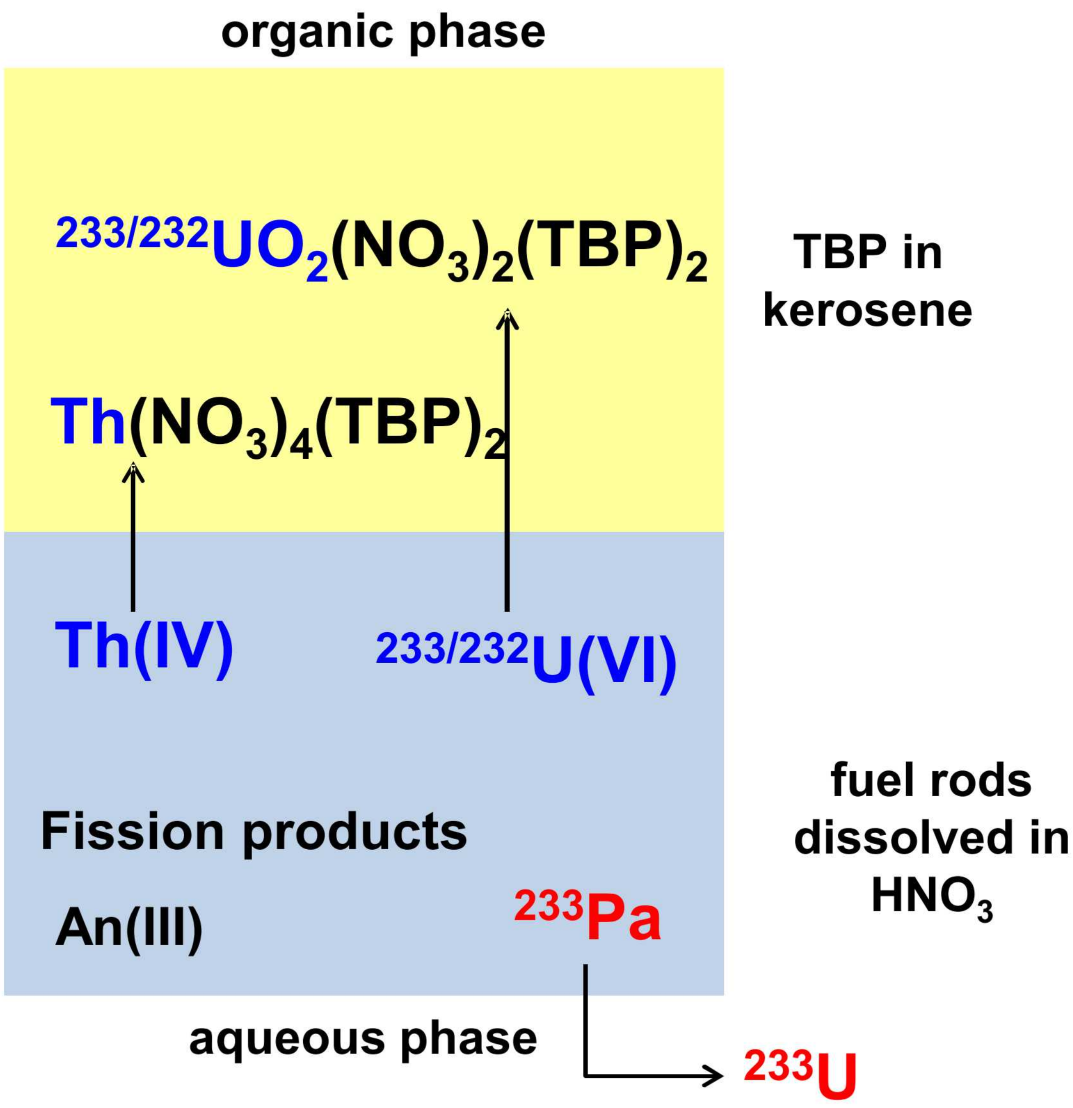
What happens to protactinium during spent fuel reprocessing?

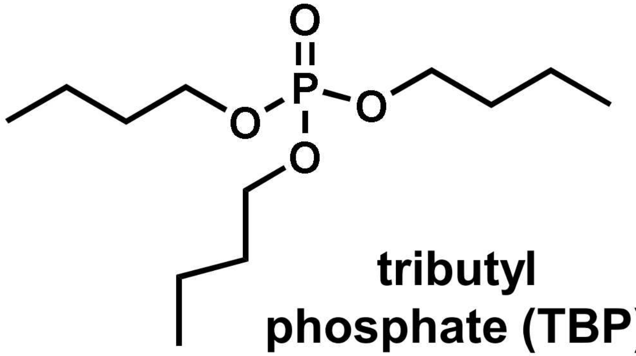
Aqueous reprocessing: THOREX



Solvent Extraction
(liquid-liquid extraction)

Aqueous reprocessing: THOREX





tributyl phosphate (TBP)

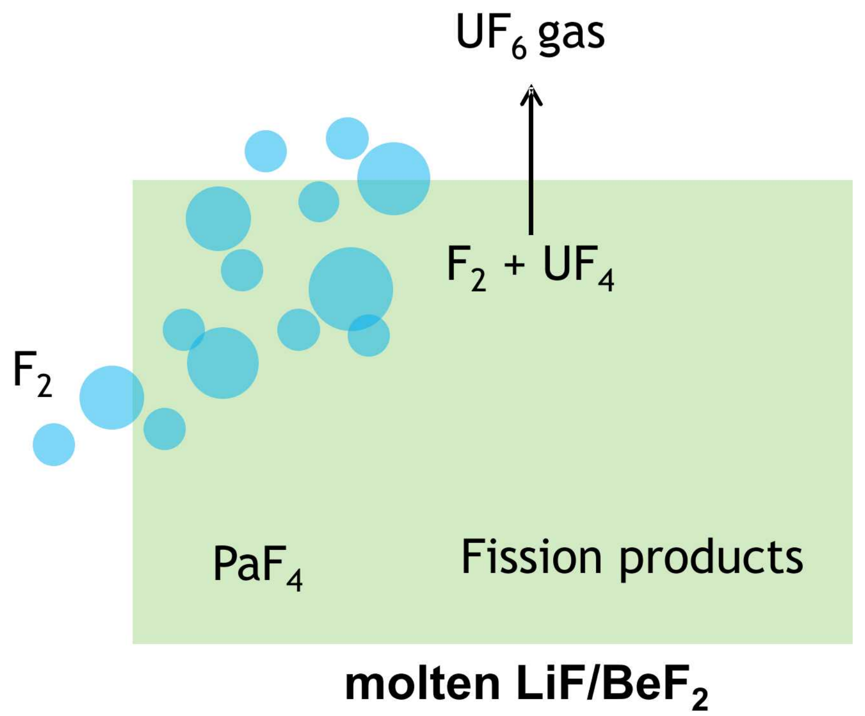
Molten salt reprocessing

Where is the protactinium?

Fluoride volatility

- UF_4 and PaF_4 dissolved in molten salt (LiF/BeF_2)
- Fluoride gas bubbled through molten salt
- UF_4 oxidized to volatile compound, UF_6
- PaF_4 stays dissolved in molten salt?

$$F_{2(g)} + UF_{4\,(ms)} \rightleftharpoons UF_{6(g)}$$



"Accelerator-driven Systems (ADS) and Fast Reactors (FR) in Advanced Nuclear Fuel Cycles: A Comparative Study,: Nuclear Energy Agency Organization for Economic Co-Operation and Development, 2002

Molten salt reprocessing

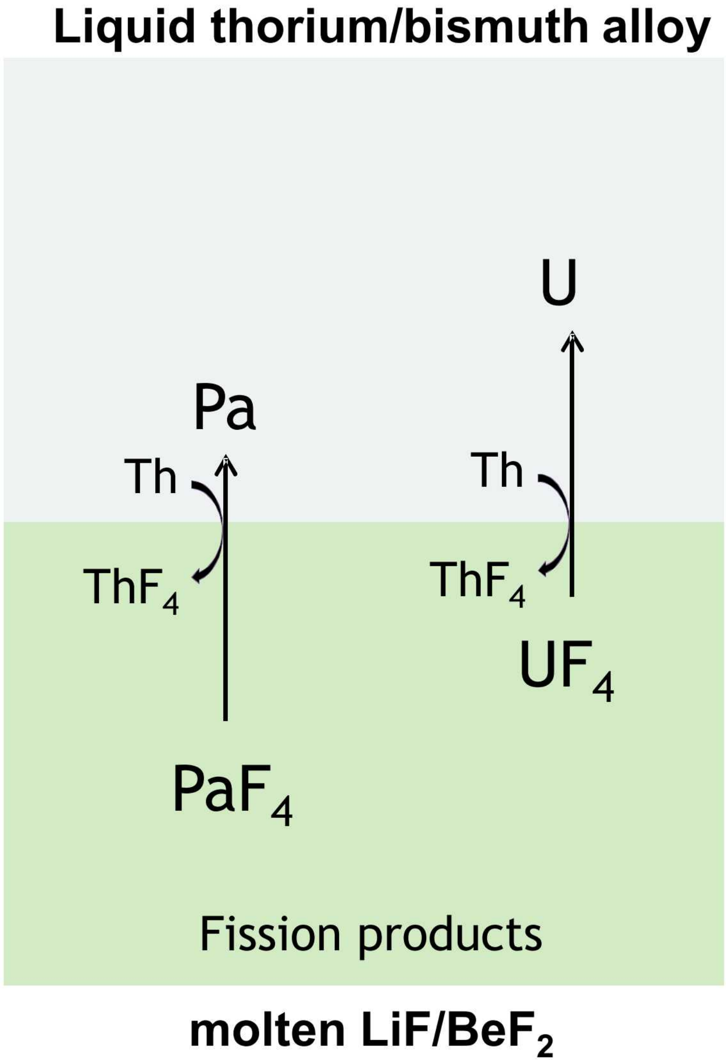
Where is the protactinium?

Liquid bismuth extraction process

- Designed to separate fission products from U and Pa
- UF_4 and PaF_4 dissolved in molten salt (LiF/BeF_2)
- UF_4 and PaF_4 reduced to U and Pa metal, and co-extracted into liquid bismuth.
- Protactinium is less-readily reduced than uranium

$$UF_{4\,(ms)} + Th_{(Bi)} \rightleftharpoons ThF_{4\,(ms)} + U_{(Bi)}$$

$$PaF_{4\,(ms)} + Th_{(Bi)} \rightleftharpoons ThF_{4\,(ms)} + Pa_{(Bi)}$$



W. R. Grimes, "Molten Salt Reactor Chemistry," *Nuclear Applications & Technology*, 8 (1970) 137-155
M. E. Whatley, et al., "Engineering Development of the MSBR Fuel Recycle," *Nuclear Applications & Technology*, 8 (1970) 170-178
M. W. Rosenthal; P. R. Kasten, R. B. Briggs, "Molten Salt Reactors – History, Status, and Potential," *Nuclear Applications & Technology*, 8 (1970) 107-117

Summary & Conclusions

1. Thorium fuel cycles are not inherently proliferation resistant
   - Depends on reprocessing involved
2. Protactinium has distinct and unusual chemistry
   - During spent fuel separations, the partitioning of U and Pa may be hard to avoid
3. Several unanswered questions:
   - How much Pa is produced in different fuel cycles?
   - Does Pa tend to behave more like lanthanide fission products or more like uranium during separations?
   - Should the International Atomic Energy Agency monitor or safeguard ^{233}Pa in addition to ^{233}U?

Thank you for your attention

Questions or comments?

Backup Slides

Leading thorium fuel cycles

TABLE 1. LEADING THORIUM FUEL CYCLES

Fuel Cycle	Country/ Developer	Reactor
Multi-stage fuel cycle—continuous recycle of ^{233}U	India	Heavy water reactor (Stage 1), sodium-cooled fast reactor (Stage 2), advanced heavy water reactor (Stage 3)
Once-through or continuous recycle in pressurized water reactor	ThorEnergy (Norway), WASB (USA)	Pressurized water reactor
Continuous recycle of ^{233}U in MSR	Thorcon (USA-Indonesia), Flibe (USA), China	MSR (thermal fuel salt)

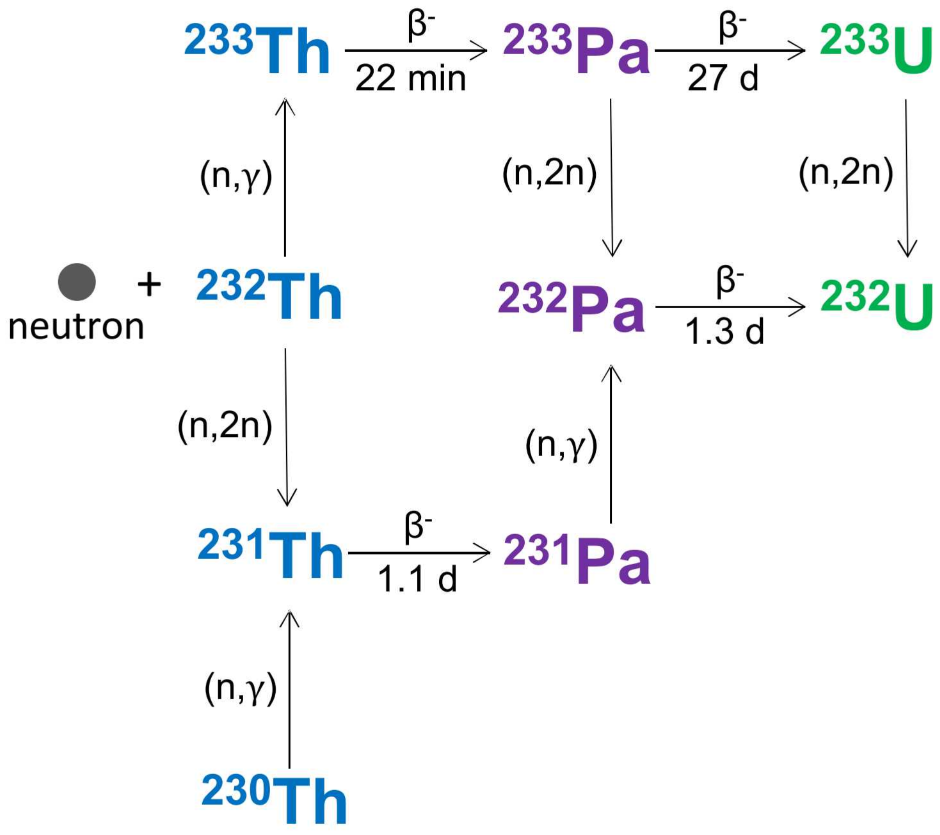
L. G. Worrall, et al. "Safeguards Challenges and Safeguards Technology Needs Assessment for Leading Thorium Fuel Cycles," *Proceedings of the IAEA Symposium on International Safeguards,* Vienna, Nov. 5-8, 2018.

Molten salt projects (liquid fuel)

Name	Developer	Power, MWt	Fuel/carrier/moderator
Thermal Spectrum Liquid Fuel MSRs			
Thorium Molten Salt Reactor, Liquid Fuel (TMSR-LF)	Shanghai Institute of Applied Physics (SINAP), China	395	ThF_4-$^{233}UF_4$/^7LiF-BeF_2/graphite
Integral Molten Salt Reactor (IMSR)	Terrestrial Energy, Canada and the United States	400	UF_4/fluorides/graphite
ThorCon Reactor	ThorCon International, Singapore	557×2	UF_4/NaF-BeF_2/graphite
Liquid-Fluoride Thorium Reactor (LFTR)	Flibe Energy, United States	600	ThF_4-$^{233}UF_4$/^7LiF-BeF_2/graphite
FUJI-U3	Japan	450	ThF_4-$^{233}UF_4$/^7LiF-BeF_2/graphite
Advanced Molten-salt Break-even Inherently-safe Dual-mission Experimental and Test Reactor (AMBIDEXTER)	Ajou University, Korea	250	$^{233}UF_4$-ThF_4/^7LiF-BeF_2
Transatomic Power MSR (TAP)	Transatomic Power, United States	1 250	UF_4/FLiNaK/SiC clad $ZrH_{1.6}$
Compact Used fuel BurnEr (CUBE)	Seaborg Technologies, Denmark	250	SNF/fluorides/graphite
Process Heat Reactor	Thorenco, United States	50	UF_4/NaF-BeF_2,/Be rods
Stable Salt Thermal Reactor (SSR-U)	Moltex Energy, United Kingdom	300-2 500	UF_4/fluorides/graphite
Fast/Epithermal Spectrum Liquid Fuel MSRs			
Molten Salt Fast Reactor (MSFR)	SAMOFAR, France – EU – Switzerland	3 000	ThF_4-UF_4/^7LiF-
Molten Salt Actinide Recycler and Transformer (MOSART)	Kurchatov Institute, Russia	2 400	$TRUF_3$ or ThF_4-UF_4/^7LiF-BeF_2 or NaF-^7LiF-BeF_2
U-Pu Fast Molten Salt Reactor (U-Pu FMSR)	VNIINM, Russia	3 200	UF_4-PuF_3/^7LiF-NaF-KF
Indian Molten Salt Breeder Reactor (IMSBR)	BARC, India	1 900	ThF_4-UF_4/LiF-
Stable Salt Fast Reactor (SSR-W)	Moltex Energy, United Kingdom	750-2 500	PuF_3/Fluorides
Molten Chloride Fast spectrum Reactor (MCFR)	TerraPower, United States		U-Pu/Chlorides
Molten Chloride Salt Fast Reactor (MCSFR)	Elysium Industries, United States and Canada	100-5 000	U-Pu/Chlorides
Dual Fluid Reactor (DFR)	Dual Fluid Reactor, Germany	3 000	U-Pu/Chlorides

Name	Developer	Power, MWt	Fuel/carrier/moderator
Solid Fuel MSRs (all thermal spectrum)			
Molten-Salt Reactor with Micro-Particle Fuel (MARS)	Kurchatov Institute, Russia	16	TRISO-coated LEU/FLiBe/Graphite pebble bed
Advanced High Temperature Reactor (AHTR)	ORNL, United States	3 400	Coated U particles in blocks or plates/FLiBe/Graphite
Small Advanced High Temperature Reactors (SmAHTR)	ORNL, United States	125	Coated U particles in blocks or plates/FLiBe/Graphite
Pebble Bed – Fluoride Salt-Cooled High Temperature Reactors (PB-FHR)	UC Berkeley, MIT and UW, United States	242	TRISO-coated LEU/FLiBe/Graphite pebble bed
Thorium Molten Salt Reactor, Solid Fuel (TMSR-SF)	SINAP, China	395	TRISO-coated U-Th/FLiBe/Graphite pebble bed
Indian High Temperature Reactor (IHTR)	BARC, India	600	TRISO-coated U-Th/FLiBe/Graphite pebble bed

Source: 2017 GIF Report: https://www.gen-4.org/gif/upload/docs/application/pdf/2018-09/gif_annual_report_2017_210918.pdf



Isotope	Half-life	Decay Mode	Source
^{231}Pa	3.28×10^4 y	α	^{235}U decay chain
^{232}Pa	1.32 d	β^-	Neuron absorption by $^{231/233}Pa$
^{233}Pa	27 days	β^-	Neutron absorption by ^{232}Th
^{234m}Pa	1.16 min	β^-	^{238}U decay chain

The unique chemistry of protactinium

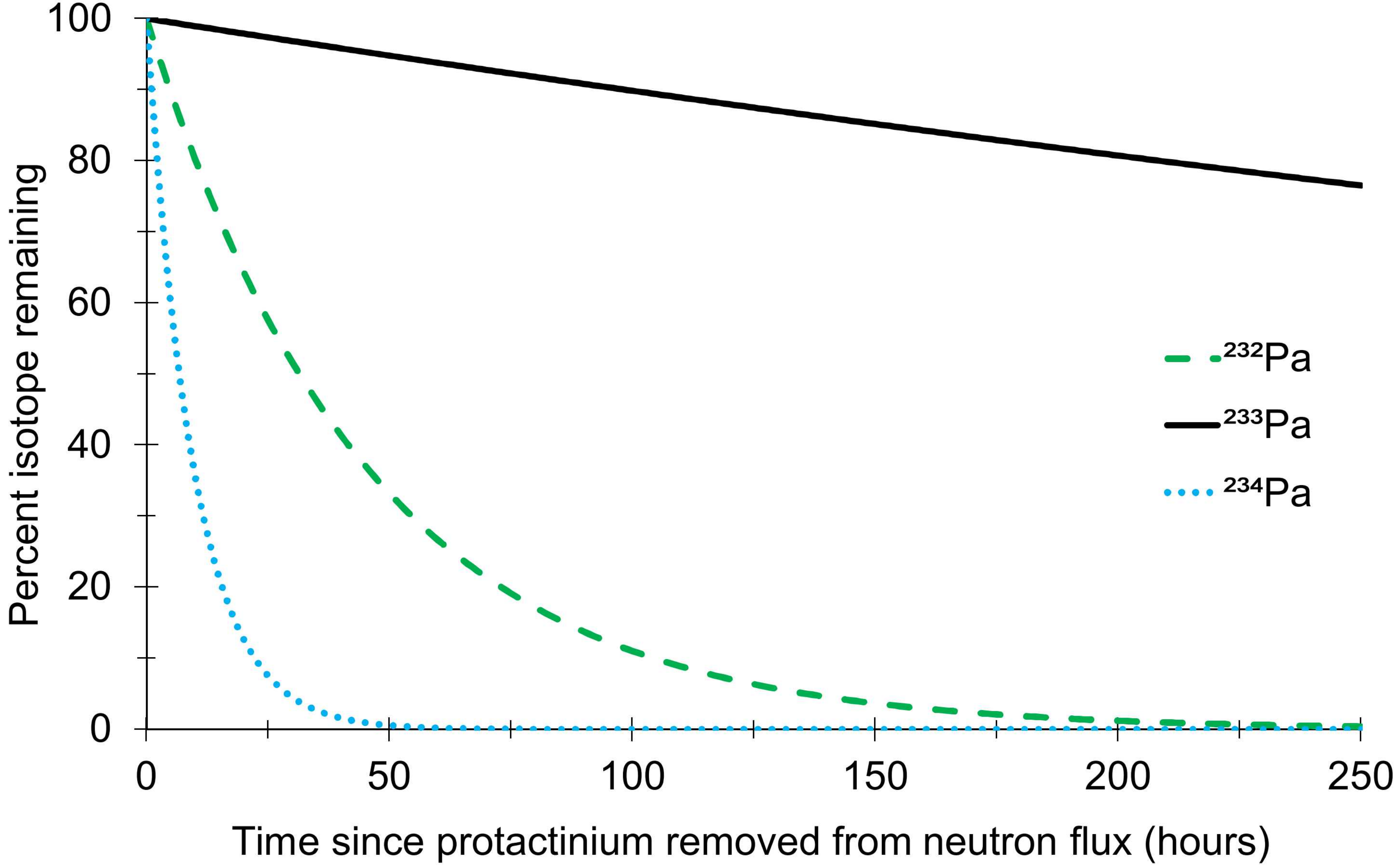
58 Ce cerium	59 Pr praesodymium	60 Nd neodymium	61 Pm promethium	62 Sm samarium	63 Eu europium	64 Gd gadolinium	65 Tb terbium	66 Dy dysprosium	67 Ho holmium	68 Er erbium	69 Tm thulium	70 Yb ytterbium	71 Lu lutetium
90 Th thorium	91 Pa protactinium	92 U uranium	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr lawrencium

Element	**Oxidation state***	**Ionic form**
Th	$^{+}3$, **$^{+}4$**	**Th^{4+}**
Pa	$^{+}3$, $^{+}4$, **$^{+}5$**	**PaO^{3-}**
U	$^{+}3$, $^{+}4$, $^{+}5$, **$^{+}6$**	**UO_2^{2+}**
Np	$^{+}3$, $^{+}4$, **$^{+}5$**, $^{+}6$, $^{+}7$	NpO_2^{+}
Pu	$^{+}3$, **$^{+}4$**, **$^{+}5$**, **$^{+}6$**, $^{+}7$, $^{+}8$	PuO_2, PuO_2^{+}, PuO_2^{2+}
Am	**$^{+}3$**, $^{+}4$, $^{+}5$, $^{+}6$	Am^{3+}

Compounds and properties of Pa(V) species in selected aqueous media	
HNO_3 media	$[Pa(OH)_n(NO_3)_m]^{5-n-m}$, $[Pa(NO_3)_m]^{5-m}$ anionic above 4M HNO_3, fair stability
H_2SO_4 media	$[PaO_x(OH)_{4-2x}SO_4]^{-}$, $PaO(HSO_4)_2^{+}$, $[PaO(SO_4)_m]^{3-2m}$ soluble in 2.5M
HF media	$[PaF_m]^{5-m}$, $[Pa(OH)_nF_m]^{5-n-m}$, $HPaF_7^{-}$ soluble in all concentrations

*Most stable oxidation state in aqueous solutions bolded.

Cotton, S. *Lanthanide and Actinide Chemistry*; John Wiley & Sons, Ltd: Sussex, 2006.


100
80
60
40
20
0
Percent isotope remaining
0
50
100
150
200
250
Time since protactinium removed from neutron flux (hours)
232Pa
233Pa
234Pa