Accountable Nuclear Material Production from Fissile Isotope Precursors in Advanced Fuel Cycles:

The Case of Protactinium

Eva C. Uribe,[1] S. Matt Gilbert,[1] Louise G. Evans,[2] Nicholas Luciano,[2] Richard Reed,[2] Natalie McGirl,[2] Jeffrey Powers[2]

[1]*Sandia National Laboratories*

[2]*Oak Ridge National Laboratory*

Abstract

Introduction of thorium into nuclear fuel cycles has been proposed as a way to improve fuel efficiency and reduce production of long-lived radioactive waste from nuclear power. Protactinium-233 is a short-lived precursor to the fissile isotope uranium-233, and forms upon neutron irradiation of thorium-232. Protactinium-233 β- decays with a 27-day half-life to uranium-233, which is an accountable nuclear material under international nuclear safeguards. However, protactinium-233 itself is not an accountable nuclear material; therefore, there are no conceptual approaches for monitoring protactinium-233 during thorium irradiation and spent fuel reprocessing. In this paper, we argue that technological advances in nuclear fuel cycles, particularly those related to rapid or online spent fuel partitioning, may result in the need to monitor fissile isotope precursors to meet accountancy and timeliness goals for nuclear materials. First, we will describe a "Goldilocks" approach used to identify protactinium-233 as a high-priority fissile precursor material. We then approximate the quantity of protactinium-233 generated in an example thorium-fueled reactor from first principles, showing that sufficient quantities of protactinium-233 will be generated to impact uranium-233 materials accountancy, depending on spent fuel partitioning timelines. Finally, we suggest a framework for developing safeguards approaches for nuclear materials and their precursor material counterparts that may apply to isotope pairings beyond protactinium-233 and uranium-233.

Introduction

Advances in spent fuel reprocessing technologies that allow for partitioning of elements at very short or zero cooling time (i.e., online reprocessing of fluid-fueled reactors) may present both challenges and opportunities for nuclear material accountancy within domestic and international safeguards regimes. Opportunities may arise from the availability and relevancy of novel, short-lived signatures, such as radioactive emissions or isotopic ratios, that may be visible to monitoring equipment required for routine facility operational monitoring.

On the other hand, early partitioning of fissile precursors from their fissile isotope daughters may result in the generation of distinct process streams containing fissile material, which must be accounted for separately and potentially under difficult conditions (e.g., high-heat, high-radiation, corrosive environments, with heavy shielding present, and with no prospect of direct observation or inspection). We define *fissile precursors* as those isotopes that spontaneously decay to fissile isotopes that are defined as *direct use* nuclear material by the International Atomic Energy Agency (IAEA) [1]. In this paper, we will discuss the gap we observe between current international safeguards nuclear material definitions and the potential need to detect, account for, and verify fissile precursors; we examine the case of protactinium-233, which beta decays to uranium-233; and we discuss a framework for international safeguards approaches that may be applied to protactinium-233 or other fissile precursors.

What defines a fissile precursor material of interest?

The technical objective of IAEA safeguards is "the *timely detection* of diversion of *significant quantities* of nuclear material from peaceful nuclear activities…and deterrence of such diversion by the risk of *early detection*" [1] (emphasis added). Table 1 shows significant quantities for different types of nuclear material [1] and lists select precursors.

Table 1. Significant quantities defined by the IAEA and select nuclear material precursors

Material		Significant Quantity	Applies to…	Select Precursors (half-life, decay mode)
Direct use	Plutonium[a]	8 kg	Total element	Neptunium-239 (2.356 days, β^-)
	Uranium-233	8 kg	^{233}U	Protactinium-233 (26.975 days, β^-) Neptunium-237 (2.14E+06 yrs, α)
	High enriched uranium ($^{235}U \geq 20\%$)	25 kg	^{235}U	Protactinium-235 (24.44 mins, β^-) Plutonium-239 (24110 yrs, α)
Indirect use	Low enriched uranium ($^{235}U < 20\%$)	75 kg	^{235}U	-
	Natural uranium	10 MT	Total element	-
	Depleted uranium	20 MT	Total element	-
	Thorium	20 MT	Total element	-

[a] For plutonium containing less than 80% plutonium-238.

The *timeliness* portion of the safeguards technical objective depends on the chemical form and isotopic purity of the nuclear material under safeguards and is also informed by diversion assumptions made by the IAEA for planning purposes as they formulate quantitative safeguards goals [2]. In defining detection timeliness goals

for various types of nuclear material, the IAEA considers the time it would take to convert a material into a form that could be used to manufacture components of a nuclear explosive device.

There are three distinct categories with different timeliness goals. *Direct use material* is "nuclear material that can be used for the manufacture of nuclear explosive devices without transmutation or further enrichment." Examples include plutonium (containing less than 80% plutonium-238), highly enriched uranium, and uranium-233. Direct use material is further classified as either *irradiated* (containing significant amounts of fission products mixed with the fissile material, e.g., plutonium in spent nuclear fuel) or *unirradiated* (material for which manufacturing an explosive device component would take minimal time and effort, such as separated plutonium or unused highly enriched uranium). Unirradiated direct-use material has a timeliness goal of one month, while irradiated direct-use material has a timeliness goal of three months [1]. *Indirect use material* is "all nuclear material except direct use material," [1] including depleted, natural, and low enriched uranium, and thorium. These materials all require significant time and effort involving irradiation, processing, and/or isotopic enrichment to generate direct use material [1]. Indirect use material has a timeliness goal of one year. The IAEA uses these timeliness goals to determine frequency of inspections and other activities at a facility to provide for early detection of nuclear material diversion.

We pose the research question: how should the fissile precursors listed in Table 1 be categorized? They are not directly used for the manufacture of nuclear explosive devices, which suggests that they are not direct use material themselves. Furthermore, it is not clear that protactinium-233, protactinium-235, and neptunium-239 would even be considered "nuclear material," which the IAEA defines as "any source material or special fissionable material," of which these isotopes are neither, so long as they remain in their undecayed forms. However, if fissile precursors are purified from fission products, they decay to unirradiated direct use material *without* substantial time, effort, processing, or isotopic enrichment. In a sense, we think of purified fissile precursors that are present (e.g., separated pure protactinium-233) as being "*future* unirradiated direct use nuclear material" (e.g., pure, unirradiated uranium-233). This implies that timeliness goals for detection of diversion of significant quantities of direct use nuclear material via isolation of their fissile precursors may be guided by the timeliness goal for unirradiated direct-use material, that is, one month. Based on these definitions, there is a gap in the language conventionally used that may prevent proper categorization of fissile precursors. The IAEA *Safeguards Glossary* [1] does note that americium and neptunium are sometimes referred to as "alternative nuclear material" because they have fissionable isotopes (and fissile in the case of neptunium) and may be separated [1]. Perhaps fissile precursors merit a similar distinction, although for the different reason that they decay to direct use material over time.

Not all fissile precursors are of equal concern. There are two fundamental questions that determine the relevancy of a fissile precursor to nuclear material accountancy. First is the timescale of its radioactive lifetime, from the time it is produced to the time it decays. Second is the quantity of material present on that timescale, and whether it approaches the significant quantities shown in Table 1. If a fissile precursor is too short-lived (or *too hot,* i.e., highly radioactive) it may decay before it can be separated, in which case no separate or special monitoring is needed for the fissile precursor. The interpretation of this metric will necessarily shift as reprocessing technologies advance and provide for increasingly shorter partitioning times. If a fissile precursor is very long-lived (or *too cold,* i.e., less radioactive), then it may not decay rapidly enough to accumulate significant amounts of direct use material on meaningful human timescales. This *Goldilocks* framework is summarized in Figure 1.

Of the fissile precursors listed in Table 1, protactinium-233, protactinium-235, and neptunium-239 are not otherwise categorized as direct use or alternative nuclear materials. Because the half-life of protactinium-233 is 27 days, it persists long enough that approaches designed solely for accounting for uranium-233 may fail to account for protactinium-233 if these isotopes are separated during the first few months after irradiation of thorium-containing fuels. The 27-day half-life of protactinium-233 is relatively long compared to its counterparts in the uranium-plutonium fuel cycle, i.e., neptunium-239 (2.4-day half-life) and protactinium-235 (24.44-minute half-life), the fissile precursors of plutonium-239 and uranium-235, respectively. The shorter

half-lives of neptunium-239 and protactinium-235 likely preclude any meaningful scenarios where the fissile precursors are separated from their daughters, at least with reprocessing technologies currently under development. In contrast, the half-life of protactinium-233 is long enough to be effectively isolated, yet also short enough to allow for full decay to uranium-233 after approximately one year. Thus, we will focus on protactinium-233 as a special case study for the remainder of this paper.
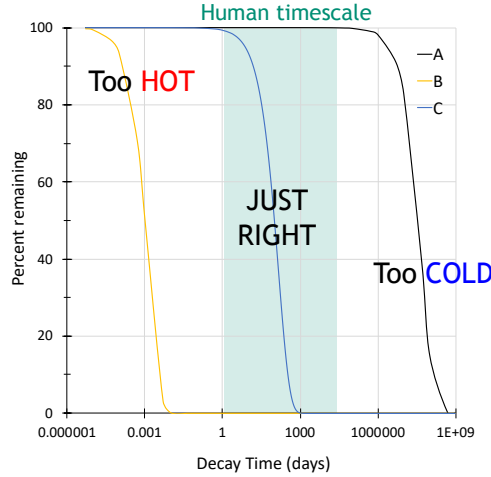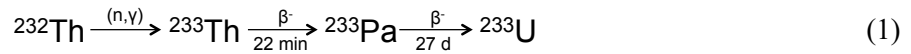

Figure 1. Goldilocks framework for identifying potentially safeguards-accountable fissile precursors

Approximation of Protactinium-233 Quantities in Thorium Fuel Cycles

Protactinium-233 is generated during neutron irradiation of thorium-232 (Equation 1).

$$^{232}\text{Th} \xrightarrow{\text{(n,γ)}} {}^{233}\text{Th} \xrightarrow[\text{22 min}]{\beta^-} {}^{233}\text{Pa} \xrightarrow[\text{27 d}]{\beta^-} {}^{233}\text{U} \qquad (1)$$

The protactinium inventory in a typical reactor at equilibrium using only thorium-232 as a fertile material and in-grown uranium-233 as a fissile material can be estimated from first principles. Assuming the rate of protactinium-233 decay is equal to the rate of uranium-233 fission, no excess production of uranium-233 (i.e., breeding ratio of 1), and constant power entirely driven by fission of uranium-233, then given:

$$\lambda_{Pa} = \frac{\ln(2)}{T_{1/2}} \qquad\qquad R = \frac{PM}{EN_a} \qquad\qquad I_{Pa} = \frac{R}{\lambda_{Pa}} \qquad (2)$$

where R is the fission rate for uranium-233, I_{pa} is the protactinium-233 inventory, P is the reactor power, M is the molar mass of uranium-233 (233 g/mol), $T_{1/2}$ is the half-life of protactinium-233, E is the average energy per fission of uranium-233 (200 MeV/fission), and N_a is Avogadro's number, the following equation can be derived showing a linear relationship between the protactinium-233 inventory and the thermal power of the reactor:
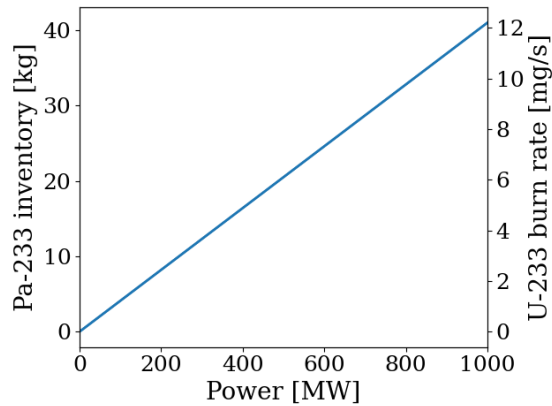
$$I_{Pa} = \frac{MT_{1/2}}{EN_a\ln(2)} * P \qquad (3)$$

Figure 2. Protactinium-233 inventory as a function of reactor thermal power output (Equation 3).

Figure 2 provides an upper bound of the protactinium-233 inventory required to sustain the fuel assuming all power results from fission of uranium-233. Some of the protactinium-233 will be lost to other neutron absorption reactions, such as ^{233}Pa(n,γ)^{234}Pa or ^{233}Pa(n,2n)^{232}Pa. These pathways represent potential loss of protactinium inventory because protactinium-232 (1.3-day half-life) and protactinium-234 (6.7-hour half-life) decay to uranium-232 and -234, respectively. Additionally, thorium reactors are likely to contain mixtures of uranium-233, uranium-235, or plutonium resulting from either neutron capture or supplementary feed. Table 2 shows an upper bound of the protactinium-233 inventory at reactor equilibrium, and at decay times of three months, six months, and one year for fuel mixtures resulting in various levels of power derived from uranium-233 fission.

Table 2. Protactinium-233 inventories at various fuel compositions and cooling times

Power from ^{233}U Fission (% of 1 GWth)	Quantity ^{233}Pa (kg/GWth) at reactor equilibrium	Quantity ^{233}Pa at +3 months cooling (kg/GWth)	Quantity ^{233}Pa at +6 months cooling (kg/GWth)	Quantity ^{233}Pa at +12 months cooling (kg/GWth)
10%	4	0.38	0.036	3.4×10^{-4}
20%	8	0.76	0.073	6.7×10^{-4}
50%	20	1.9	0.18	1.7×10^{-3}
100%	40	3.8	0.36	3.4×10^{-3}

Ongoing work to conduct higher fidelity fuel inventory modeling reveals the extent to which other factors, including fuel composition, neutron energy, breeding ratio, and loss of protactinium-233 to neutron absorption reactions influence the quantity and isotopic composition of protactinium produced. However, we observe that power production from uranium-233 is the strongest determinant of protactinium-233 inventory across various reactor types [3].

Safeguards framework for fissile precursor materials

Based on these calculations, we identified four potential fuel cycle case studies. Each case study would require distinct monitoring and safeguards approaches for meeting material accountancy and timeliness goals for safeguarding uranium-233. These four case studies are summarized in Table 3.

Case 1: Solid fuel, no reprocessing

In the case of a once-through thorium fuel cycle, separation of protactinium from uranium does not occur. Over several years in storage, the vast majority of protactinium-233 decays to uranium-233. The protactinium-233 that remains in the spent fuel is in secular equilibrium with neptunium-237. Additional monitoring of protactinium beyond what is done to account for uranium-233 is not necessary in this case. The primary safeguards objective is to maintain continuity of knowledge of the spent nuclear fuel assemblies to ensure that no chemical reprocessing occurs. However, uranium-233 is still present in the spent fuel and must be accounted for. Monitoring and accounting of the uranium-233 would likely resemble established practices used to monitor plutonium in spent nuclear fuel.

Table 3. Summary of fuel cycle case studies and their associated safeguards objectives

Solid fuel, no reprocessing	Solid fuel, long-cooled reprocessing
• Verify no reprocessing has occurred (continuity of knowledge) • Verify ^{233}U content using burnup codes, gamma confirmatory measurement • Item-based safeguards	• Verify no short-cooled reprocessing has occurred (continuity of knowledge) • ^{233}Pa is sufficiently dilute in THOREX processing streams to allow termination of safeguards on these streams of ^{233}U • Bulk material accountancy for ^{233}U
Solid fuel, short-cooled reprocessing	**Molten salt fuel, continuous reprocessing**

• ^{233}U safeguards may require:
    ○ Verification of ^{233}Pa inventory in multiple process streams
    ○ Detection of loss or diversion of 8 kg ^{233}Pa in 1 month
    ○ Monitoring loss of protactinium to aqueous raffinate in THOREX processes [4]
 	
• Inventory measurements must compare to total ^{233}Pa + ^{233}U from burnup codes
 	
• Not cost-effective for commercial purposes
	• Fission products and potentially ^{233}Pa removed continuously
	
	• ^{233}Pa held outside of the neutron flux to decay to ^{233}U, which is fed back into core
	
	• ^{233}U safeguards require:
	    ○ Verification of ^{233}Pa inventory in multiple process streams
	    ○ Detection of loss or diversion of 8 kg ^{233}Pa in 1 month

Case 2: Solid fuel, long-cooled reprocessing

Closed thorium fuel cycles that would reprocess solid oxide fuels after 3-5 years of cooling time would also not require separate monitoring of protactinium. Long cooling times allow nearly all of the protactinium-233 to decay to uranium-233. The 40 kg produced in a 1-GW$_{th}$ reactor powered entirely by fission of uranium-233 will decay to less than one microgram (which would result in approximately one tenth of a billionth of a significant quantity of uranium-233) after two years. Therefore, after several years of cooling, additional monitoring of protactinium is not necessary. With standard THOREX reprocessing, significant fractions of the protactinium remaining may separate from uranium into the aqueous raffinate waste [4], and later decay to uranium-233. However, even assuming that all of the protactinium remaining is isolated from uranium during reprocessing, it would be dilute enough to be practically irrecoverable.

Case 3: Solid fuel, short-cooled reprocessing

In contrast to the previous case study, closed thorium fuel cycles that would reprocess solid oxide fuels after short cooling times may require additional monitoring of protactinium, depending on the precise cooling time used and the makeup of the fleet of reactors feeding the reprocessing plant. Typical spent fuel cooling times are 3-5 years or longer. Fuel cooled for shorter than six months will have high releases of volatile radioactive species, including iodine-131 (8-day half-life) [5]. For this reason, we assume that 6 months (180 days) is the shortest cooling time that would be considered for commercial purposes. However, even if an operator declares that these fuels will be reprocessed after a cooling period of 6 months or longer, it will likely be necessary to verify that reprocessing is not being conducted on a shorter timescale than declared. For consideration of protactinium-233 diversion, this is especially important in the first 6 months because it is over this timeframe that isolation of meaningful quantities of protactinium becomes less feasible from a practical standpoint. To illustrate this point, consider a 1-GW_{th} reactor deriving 20% of its power output from uranium-233 fission. The total protactinium-233 inventory at reactor equilibrium will be approximately 8 kg. After three months of cooling, this has decreased to approximately 0.8 kg, which would require extracting the entire protactinium contents of 10 1-GW_{th} reactors to yield one significant quantity of resulting uranium-233. An additional three months of cooling time reduces this quantity to 0.08 kg, which would require a supply of 100 1-GW_{th} reactors to obtain one significant quantity of uranium-233.

Case 4: Molten salt fuel, continuous reprocessing

Molten salt reactor concepts with continuous removal of fission products and protactinium are the most likely scenario where additional monitoring of protactinium-233 may be required to meet nuclear material accountancy and timeliness goals for uranium-233. In the single fluid MSBR concept developed by Oak Ridge National Laboratory [6], protactinium would be separated from the fuel salt at regular intervals, held outside of the reactor's neutron flux to decay to uranium-233, and then fed back into the core as driver fuel. One of the primary advantages of molten salt reactors is that the liquid form of the fuel is not limited by irradiation damage in the same way as solid fuel, and so it does not need to be replaced as often, provided there are mechanisms for removing fission products. These features would allow a molten salt reactor to operate continuously for many years. Breeding fissile material, and therefore separation of protactinium-233, is consistent with this advantage (i.e., it is justifiable for commercial power generation purposes).

At chemical equilibrium, a 2250 MW_{th} molten salt reactor would contain approximately 90 kg protactinium-233 in its salt processing system at any given time. In this case, the primary safeguards objective is to verify protactinium-233 inventories at various stages to enable timely detection of loss or diversion of a significant quantity of uranium-233. Inspectors would also have to verify that a reactor is not being operated to allow for slightly higher breeding ratios than declared, which would enable removal of material from salt processing streams. This places a high reliance on design information verification throughout the planning and construction phases of the plant, to look for ways that the facility could be misused, followed by periodic design information verification throughout the plant's lifetime to ensure that nothing about the plant's fundamental design or operation has changed.

Conclusion

Detection, monitoring, and material accountancy approaches for fissile isotope precursors may need to be developed as technology advances to allow for reprocessing fuels with increasingly short or zero cooling times. We conclude by making a number of recommendations and observations for further consideration.

The definition of "short" for short-cooled reprocessing of spent fuel depends on the half-life fissile precursor. For protactinium-233, we have determined that anything additional monitoring approaches may need to be developed if reprocessing is to take place within the first six months after irradiation. However, in the future, comprehensive safeguards approaches for reprocessing facilities may need to include detection of undeclared

reprocessing of short-cooled fuels. These may include detection of volatile fission products, rather than direct monitoring of the fissile precursor, which may be difficult under the intense radioactivity of short-cooled fuel.

For materials accountancy for short-cooled fuels, we recommend that fissile isotope and fissile precursor pairs be considered in aggregate. Inventory measurements made during spent fuel reprocessing should be compared to burnup calculations that reflect the combined total quantity of a fissile precursor and the fissile material. For example, the total inventory of uranium-233 should be the sum of protactinium-233 and uranium-233, because this is the total quantity of uranium-233 that will be present after the protactinium-233 decays in approximately 9 months (or ten half-lives). Under this approach, a uranium-233 inventory declaration would be incomplete without a caveat explaining how much protactinium-233 is present in the material balance area or at the key measurement point.

A similar approach would be to establish a concept of "material balance in future," where operators would report the current quantity of a direct use nuclear material made in an inventory measurement *and* report the quantity of the direct use material that will exist at some future time point, when all its precursors will have decayed. This would require introducing inventory measurement capabilities to include assay of any fissile precursors present. Finally, a third approach could be flowsheet verification of fissile precursors, similar to the approach taken for americium-241 and neptunium-237. Under this approach, fissile precursor isotopes would not be directly measured, but operators would declare flowsheet information, which would be independently verified for correctness and completeness.

Protactinium-233 is a special case, as thorium molten salt fuel cycles have specifically proposed its isolation. For these fuel cycles, additional monitoring may be required to verify that protactinium-233 is not being mishandled or misused, as part of uranium-233 nuclear material accountancy. It is not yet clear if the best approach constitutes direct measurement or monitoring of protactinium-233 inventories. Future work should investigate protactinium inventories within specific molten salt reprocessing plant concepts, as well as the sensitivity of alternative diversion indicators, such as a decrease in power output of the reactor or the release of volatile fission products. While continuous or rapid online fuel reprocessing technologies represent the most difficult cases for developing in-depth monitoring approaches, they are also in the earliest design stages, and therefore present the greatest opportunity for implementation of practical and transparent safeguards designs.

Acknowledgments

References

[1] "Safeguards Glossary 2001 Edition," International Atomic Energy Agency, Vienna, Austria, 2001.

[2] V. Fortakov, "Nuclear Verification: What it is, How it Works, the Assurances it Provides," *Technical Workshop on Safeguards, Verification Technologies, and Other Related Experience, International Atomic Energy Agency*, Vienna, Austria, 1998.

[3] E. C. Uribe, "Protactinium Production in Leading Thorium Fuel Cycles," UC Berkeley Nuclear Science and Security Consortium , 2021. [Online]. Available: https://www.youtube.com/watch?v=_CcHF9Lr7FM [Accessed 15 June 2021].

[4] E. C. Uribe, "Protactinium Presents a Challenge for Safeguarding Thorium Reactors (SAND2018-8490 C)," *IAEA Symposium on International Safeguards*, Vienna, Austria, 2018.

[5] M. Benedict, T. Pigford and H. Levi, Nuclear Chemical Engineering, 2nd Edition, New York: McGraw-hill Book Company, 1981.

[6] R. C. Robertson et. al., "Conceptual Design Study of a Single-Fluid Molten Salt Breeder Reactor (ORNL-4541)," Oak Ridge National Laboratory, Oak Ridge, TN, 1971.