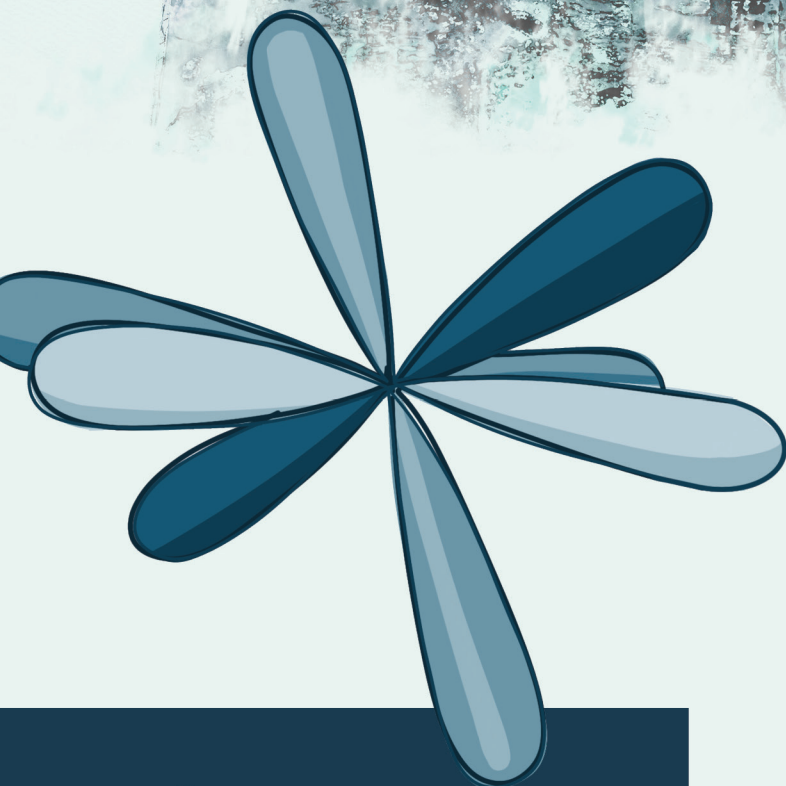


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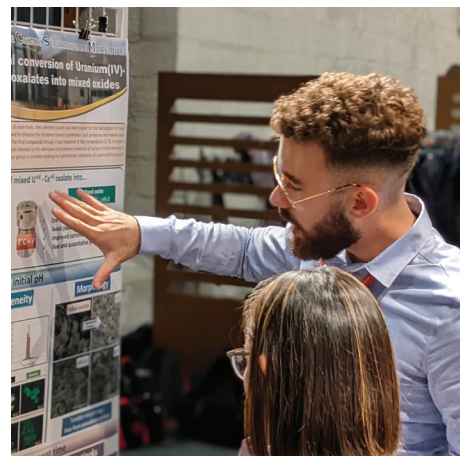
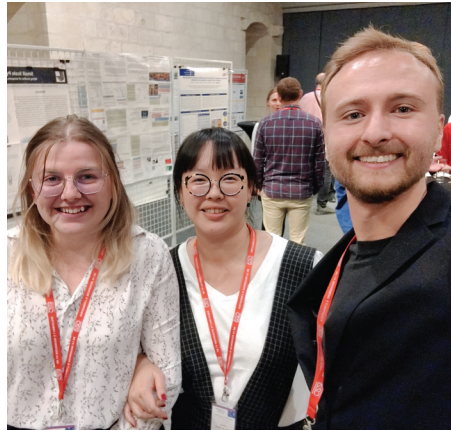
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First Quarter 2024



PLUTONIUM FUTURES 2022 CONFERENCE ISSUE

AVIGNON, FRANCE



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Foreword

Plutonium Futures – The Science 2022 was the eleventh in a conference series initiated by Los Alamos National Laboratory in 1997, with the first meeting held in Santa Fe, New Mexico. 25 years later, in 2022, the conference was held in the Pope's Palace conference center of Avignon, France from September 26th to 29th.

This important conference aims at strengthening international dialogue between scientists on the fundamental properties of plutonium and their technological consequences. It is undoubtedly the largest global conference combining the physics and chemistry of plutonium and the transuranic elements.

After the scheduled 2020 conference was cancelled due to the COVID-19 health crisis, organization was entrusted again to CEA (French Alternative Energies and Atomic Energy Commission) in 2022. Two other historical European partners (Atomic Weapons Establishment and JRC-Karlsruhe), along with the Program Committee and the International Advisory Committee, helped ensure that the conference featured research talks of the highest quality from around the globe. The 2022 conference brought together more than 230 participants, with recognized experts, post-doctoral researchers, and doctoral students who gave 90 talks and 60 poster presentations.

During the conference, scientific exchanges were numerous and constructive, with two parallel sessions focusing on the historical themes of the conference: Condensed Matter Physics, Surface Science and Corrosion, Metallurgy and Materials Science Compounds, Complexes and Coordination Chemistry, Detection and Analysis, Nuclear Fuel Cycle, Environmental Behavior and Chemistry, and Solution and Gas-phase Chemistry. Plenary sessions brought together the communities of chemists and physicists around more general presentations. The poster session, with significant time devoted to discussion, was very popular, particularly thanks to the young researchers who showed great enthusiasm for sharing their research.

The papers selected for this special issue of Actinide Research Quarterly represent some of the many stimulating research talks presented at the conference, addressing the fundamental chemistry of plutonium but also including studies directly linked to the nuclear fuel cycle or the detection and analysis of radioelements.

The success of this conference is the result of the involvement of all the participants, of course, but also the hard work of the people who participated in the organization whom I would like to thank here. I would also like to acknowledge the various committees that helped select the speakers and organize the oral presentations and poster sessions, and we hope to see you all in Charleston, SC for the 2024 edition that will be held from September 8th to 12th, 2024.

— *Philippe Guilbaud, Chair of Plutonium Futures 2022, Research Director and Scientific Assistant of the DMRC, France (Département de recherche sur les procédés pour la Mine et le Recyclage du Combustible; Mining and Fuel Recycling Process Research Department)*

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About the cover:

The image shows the front of the Palais des Papes in Avignon, France—the conference location of Plutonium Futures in 2022.

The palace is one of the largest and most important medieval Gothic buildings in Europe, and the home of six popes in the 14th century. Today, it is an exhibition center and major tourist attraction, featuring in the top ten most visited attractions in France.



Gilles Bordier

Gilles Bordier is a graduate of the Ecole Polytechnique, holds a doctorate in physics, and has recently retired from his position as Deputy Scientific Director in CEA's Energy Division. His work as an engineer and researcher has focused mainly on the nuclear fuel cycle, from uranium enrichment by laser to spent fuel reprocessing and recycling, waste and its conditioning, and on the decontamination and dismantling of facilities, and related research work.

Sustainable Use of Uranium and Plutonium in the French Nuclear Fuel Cycle

G. Bordier, F. Sudreau, A Salvatores, M Phélip

Université Paris-Saclay, CEA, Direction des Energies-DIR, 91191, Gif-sur-Yvette, France

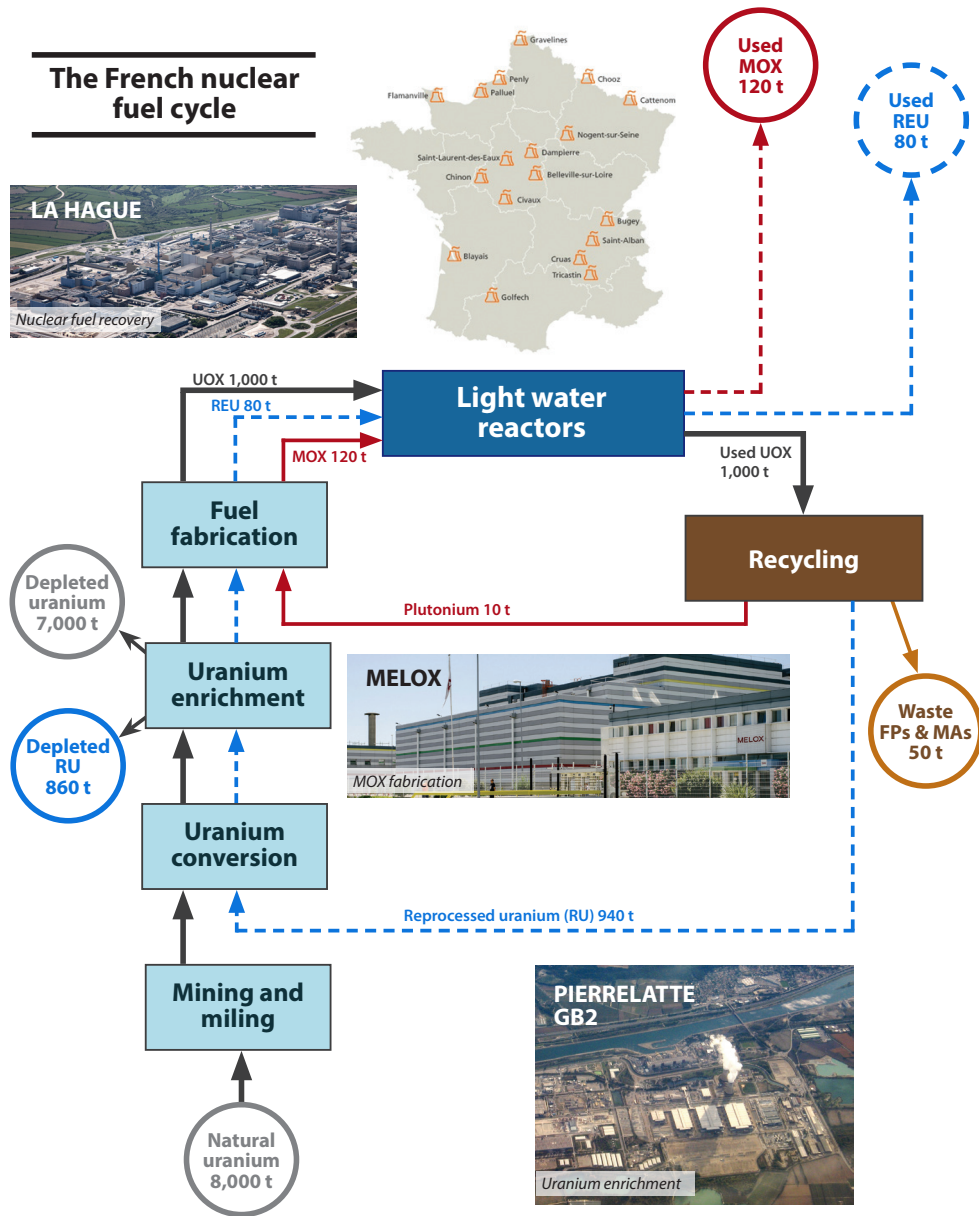
In view of global warming and the world energy crisis, developing a sustainable carbon-free energy mix based on nuclear and renewable energies is mandatory. Improving the use of uranium in nuclear fission reactors involves development of both reactor technology and the accompanying fuel cycle in order to maximize natural fissile resources and reduce the production and impact of waste. This leads to the concepts of plutonium multi-recycling in pressurized water reactors (PWRs) and a closed fuel cycle in fast reactors. Herein, we describe the efforts that are currently underway in France to make these concepts a reality before the end of the century, as well as the associated scientific and technical challenges. We mainly focus on the separation and recycling steps that are at the heart of the Plutonium Futures conference and pay less attention to the front and back end of the fuel cycle.

We begin by detailing the current French fuel cycle, which includes the benefits of plutonium mono-recycling (Part 1). Then we highlight the key points of the French energy policy, translated in the Energy Transition Law for Green Growth and the Multiannual Energy Plan, and its consequences in terms of the nuclear reactor agenda and associated fuel cycles (Part 2). We present both medium- and long-term scenarios to achieve independence from natural uranium and secure long-term sustainability (Part 3). This can be achieved in the long term through plutonium multi-recycling in Generation IV fast neutron reactors (FNRs, Part 5). In the medium term, meanwhile, a step-by-step scenario can be adopted, with benefits gained at each stage, including plutonium multi-recycling in PWRs (Part 4). However, such a trajectory induces new technical issues, related for instance to a continuous increase in the plutonium throughput, thermal power, and radioactivity, and we present some of our promising R&D pathways to overcome these challenges. Finally, we describe the possible management of minor actinides via separation and transmutation for a long-term goal (Part 6).

1. The current French nuclear fuel cycle situation: Back to basics

Fig. 1 shows a simplified description of the current plutonium mono-recycling French fuel cycle, including an optional reuse of uranium from reprocessing, and associated major throughput values. Each year, in order to produce around 1,000 t (metric tons) of uranium dioxide fuels (UOX) for the 56 PWRs in the French fleet, 8,000 t of natural uranium is extracted, purified, and converted into uranium tetrafluoride and then uranium hexafluoride. Uranium hexafluoride is enriched in uranium-235 isotope content from 0.71% (natural uranium) to 3–5% by ultra-centrifugation at the Georges Besse II enrichment plant in Pierrelatte. This produces a tail of around 7,000 t of depleted uranium, with a uranium-235 content around 0.3%—a huge, accumulated resource of 320,000 t of depleted uranium is thus available, either for the current MOX (mixed oxide: a mixture of uranium and plutonium dioxide) fuel fabrication, for possible re-enrichment operations, or for future use in FNRs. The UOX fuel is manufactured with 1,000 t of enriched uranium, then irradiated in the

The French nuclear fuel cycle



French PWRs and finally reprocessed in the UP2-800 and UP3 Orano plants at La Hague after a defined cooling period. This operation allows France to separate around 940 t of reprocessed uranium and 10 t of plutonium annually, while conditioning the remaining 50 t of fission products and minor actinides in 360 t of borosilicate glass containers that are stored at La Hague for transfer to the future deep geological repository, CIGEO, located in a thick Callovo-Oxfordian clay layer at Bure.

Annually, 10 t of plutonium dioxide powders are mixed with depleted uranium dioxide to fabricate MOX fuel pellets by powder metallurgy at the Orano MELOX plant in Marcoule. A total of 120 t of MOX fuel is produced each year and can be used in twenty-four 900 MWe reactors in the French fleet (Fig. 2). After irradiation, the used MOX fuel is stored at the power plants in pools onsite and then at La Hague, waiting for radioactive decay and future reuse. The used MOX fuel contains valuable plutonium, at an average concentration of around 6%, which can be recovered via reprocessing. This has already been demonstrated industrially in France with an operation that used 73 t of MOX at La Hague, which ran from 1992 to 2008. Used

Figure 1. Simplified description of the current plutonium mono-recycling French fuel cycle, including the optional reuse of uranium from reprocessing, and the associated major throughput values. Note that there has been no uranium reprocessing since 2013, but it is planned to restart in 2024.

[RU = reprocessed uranium; REU = re-enriched uranium; MOX = mixed oxide fuel; FPs = fission products; MAs = minor actinides]

Current French nuclear reactor fleet

Installed capacity: 63.2 GWe (1977-1999)
 Currently: 61.4 GWe

32 reactors 900 MWe (29 GWe):

FESSENHEIM (1 2)	[1977, shut down 2020]	UOX (NEU)	4 reactors
BUGEY (1 2 3 4)	[1979 – 1980]	UOX (NEU)	100% UOX (NEU)
CRUAS (1 2 3 4)	[1984 – 1985]	REU (1994 – 2013)	4 reactors 100% REU
TRICASTIN (1 2 3 4)	[1980 – 1981]	MOX: > 1987	24 reactors 70% UOX / 30% MOX
SAINT LAURENT (1 2)	[1981]	MOX: > 1987	
BLAYAIS (1 2 3 4)	[1981 – 1983]	MOX: > 1994	
DAMPIERRE (1 2 3 4)	[1980 – 1981]	MOX: > 1996	
CHINON (1 2 3 4)	[1982 – 1987]	MOX: > 1998	
GRAVELINES (1 2 3 4 5 6)	[1980 – 1985]	MOX: > 2007	
20 reactors 1,300 MWe (26 GWe)		100% UOX (NEU) [>1986]	
4 reactors 1,450 MWe (6 GWe)		100% UOX (NEU) [>1996]	
+(1 reactor 1650 MWe (EPR Flamanville))		[loading 2023]	

Figure 2. The current French reactor fleet includes pressurized water reactors of different power levels. MOX fuel can currently be used in only 24 of the 900 MWe reactors in the French fleet (highlighted in box) but in the near future may also be used in 1300 MWe reactors and, in a more distant future, in EPR2 reactors.

MOX fuel is not considered as nuclear waste in France, but rather as a valuable fissile material—it is envisaged to reuse plutonium either by multi-recycling in PWRs or storing for future use in FNRs. Reprocessed uranium can also be re-enriched up to a commercial assay (re-enriched uranium, REU) and reused in the four Cruas 900 MWe PWRs: uranium recycling was performed for 20 years, 1993 to 2013, and could restart soon. In a mono-recycling strategy, used REU dioxide fuels (80 T/y) are stored in pools.

It is insightful to compare the current plutonium mono-recycling strategy with an open cycle (for a given power generation around 350 TWh/y). Annually, the plutonium mono-recycling strategy allows:

- Savings of 1,000 t natural uranium (8,000 versus 9,000 t)
- Savings of waste storage/disposal capacities [(120 t used MOX + optionally 80 t used REU + 360 t high activity glass) versus 1,000 t used UOX]
- Reduction of the net production of plutonium by ~30% (7 t versus 10 t) since a quantity of recycled plutonium is transformed into fission products in the reactors.

This illustrates the benefits of the current French fuel cycle option. We will now describe the benefits that can be gained going beyond mono-recycling, towards a multi-recycling strategy, and finally towards the closed fuel cycle.

2. The French Energy Transition Law for Green Growth and Multiannual Energy Plan

The Energy Transition Law for Green Growth (2015) and Climate Energy Law (2019) aim to achieve carbon neutrality by 2050 and diversify France's electric mix, with a view to increase energy resilience. The successive Multiannual Energy Plans (MEP 2016–2023 and 2019–2028) set out the government's strategic priorities and measures to be taken in the next 10 years. The latest Multiannual Energy Plan, published in April 2020, reaffirmed that nuclear is a long-term option but as part of a more balanced electricity mix. As such, nuclear power should decrease to 50% of the electricity generation mix by 2035 (down from 62% in 2022). Additionally, the

plan retains the option of building new nuclear reactors and reaffirms the strategy of reprocessing and recycling nuclear fuel until at least the 2040s. Finally, a closed fuel cycle strategy is planned for a more distant period. The total nuclear capacity has been set at a limit of 63.2 GWe, corresponding to the total nuclear power supplied to the grid before the shutdown of the two 900 MWe reactors at Fessenheim in June 2020. Importantly, an increase in renewable energy production was also targeted, with a goal of attaining a 33% share in the electricity mix by 2030, up from 24% in 2022.

More recently, on February 10, 2022, President Macron expressed his wish that, in addition to pursuing the development of renewable energy sources, nuclear energy should be supported and developed to guarantee France's energy independence and achieve carbon neutrality by 2050. The lifespan of the current reactors should be extended in all cases where possible and, furthermore, a new construction program for six EPR2 (European pressurized reactor) type reactors be undertaken and that studies be started for eight additional reactors.

Despite these important commitments, shutting down the oldest reactors of the fleet should have significant consequences on the current plutonium mono-recycling operation, which is performed in 24 of the oldest 900 MWe reactors of the French fleet (Fig. 2). The MEP strategy states that the treatment-recycling plan is “a major challenge for reducing the volume of radioactive waste.” Thus, in order to maintain the current fuel cycle strategy, the use of MOX fuel in the current 1300 MWe reactors has been scheduled, pending the commissioning of EPR2.

Finally, beyond 2040, strategic decisions within the fuel cycle policy will be taken, based on the R&D conducted in the field of fuel cycle closure, with a two-step approach:

- Medium term: plutonium multirecycling in Generation III LWRs using MOX2 fuel assemblies with the aim of stabilizing plutonium and spent fuel inventories. The first objective is to irradiate test fuel assemblies in a PWR reactor, with possible industrial deployment around 2040.
- Long term: complete closure of the fuel cycle with plutonium multi-recycling in FNRs in the second half of the 21st century, which will allow France to reach self-sufficiency and independence from natural uranium.

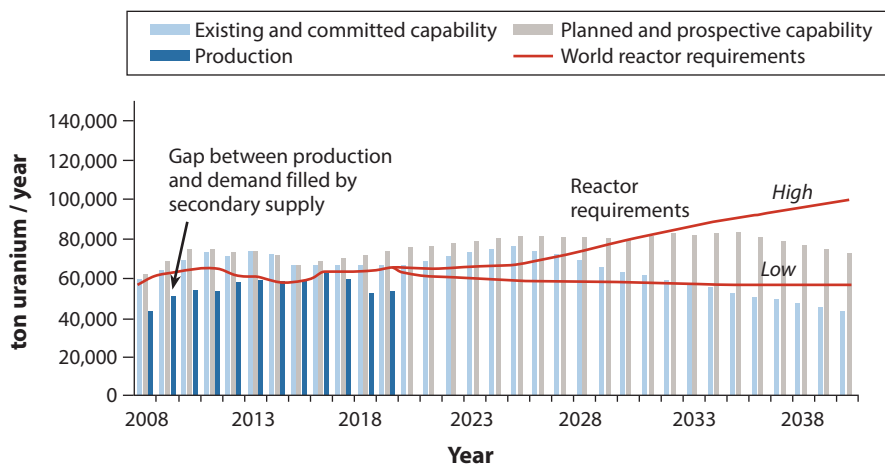


Figure 3. Natural uranium production and demand forecasts to 2040, analyzed in the IAEA NEA 2020 Red Book (Figure 2.10 of the report). The demand for uranium should be covered by the existing, planned, and prospective production capabilities.



3. The need for a closed fuel cycle in the long term and the benefits of a step-by-step deployment

The International Atomic Energy Agency (IAEA)-Nuclear Energy Agency (NEA) 2020 joint publication “Uranium Resources, Production and Demand” (commonly known as the Red Book) analyzes the balance between natural uranium production and demand up to 2040 (Fig. 3) at a reasonable cost (considered as less than \$50/lb U_3O_8). By 2040, the projected demand for uranium is covered by the overall potential production, by totaling the existing, planned, and prospective capabilities at an acceptable cost. However, the situation appears to become more challenging in the second half of the 21st century. This is highlighted in the 2018 meta-study by the IPCC (Intergovernmental Panel on Climate Change) “IPCC Special Report on Global Warming of 1.5°C” (Fig. 4).

The IAEA 2020 Red Book states that meeting the highest projection of nuclear electricity demand by 2040 would require the consumption of approximately 28% of the total listed resources in 2019 at a cost of less than \$130/kg uranium. We conclude that natural uranium resources at moderate cost will probably be lacking before the end of the 21st century; the spot price of natural uranium should make it largely unaffordable sometime in the second half of the century. This explains the French strategy, moving towards a full closure of the fuel cycle before the end of the 21st century. We now explain a possible way to reach this goal.

A closed fuel cycle requires the full deployment of a fleet of fast neutron reactors. Indeed, the fission/absorption ratio of odd and even isotopes of uranium, plutonium, americium, and curium strongly depends on the neutron energy spectrum (Fig. 5). While fissile isotopes of uranium and plutonium are likely to fission in both thermal or fast neutron spectra, the fission/absorption efficiency is strongly reinforced in a fast spectrum for the other isotopes: uranium-238, neptunium-237, plutonium-238, plutonium-240, plutonium-242, americium-241, americium-243, and curium-244.

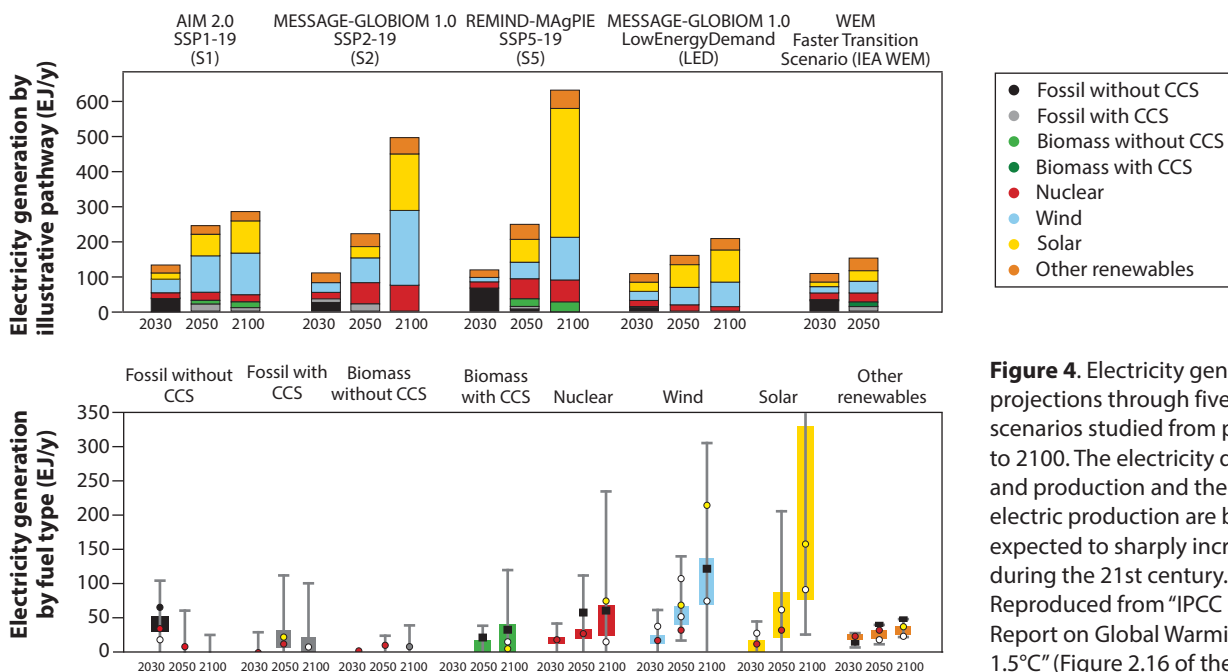


Figure 4. Electricity generation projections through five scenarios studied from present to 2100. The electricity demand and production and the nuclear electric production are both expected to sharply increase during the 21st century. Reproduced from “IPCC Special Report on Global Warming of 1.5°C” (Figure 2.16 of the report).

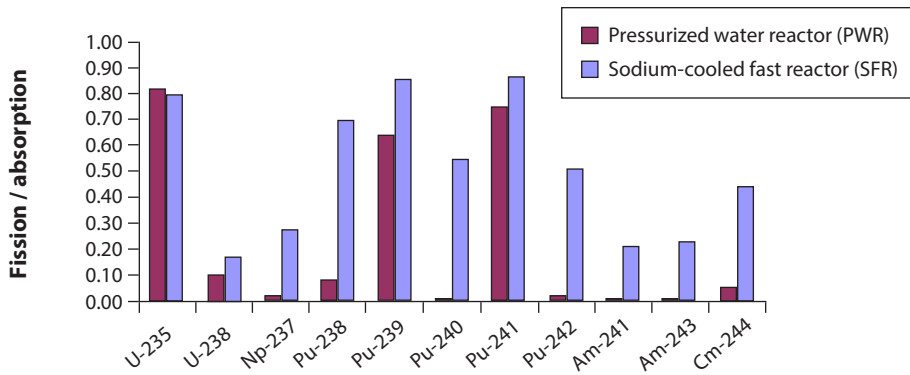


Figure 5. Impact of the neutron energy spectrum on the fission/absorption ratio of actinides isotopes. The fission efficiency is strengthened in a fast spectrum for several isotopes. Reproduced from Robert N Hill, GEN IV Int. Forum, Dec 2016.

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Therefore, the multi-recycling of plutonium in thermal spectrum reactors induces a higher consumption of neutrons and an associated increased production of minor actinides. In contrast, the full deployment of fast neutron reactors (Fig. 6) makes it possible to use every actinide isotope and feed the FNR fleet with only recycled plutonium and depleted fertile uranium (without consuming natural uranium and also avoiding the need to maintain a front-end cycle industry).

There are numerous benefits that could be gained deploying a fast nuclear reactor fleet with a closed fuel cycle strategy: no need for natural uranium supply and front-end operations, zero net production of plutonium, no need for large used fuel storage, and decreased production of minor actinides. Nevertheless, there are some important technological issues to overcome to reach this goal. Indeed, assuming a constant electricity output, plutonium throughput would be expected to increase by a factor of eight to ten compared to the mono-recycling currently used in France. In addition, a complete fleet of fast reactors must be deployed, which entails overcoming technical and financial issues and developing an industrial supply chain for reactor components and fuel (fabrication and processing plants adapted to SFR MOX fuel). Therefore, considering that the risk of a natural uranium shortage should not occur for several decades, France plans to adopt a stepwise approach towards a complete closed fuel cycle, with accumulating benefits at each new stage.

After mono-recycling, a possible next step would be to begin plutonium multi-recycling in PWRs by the 2040s by adapting the MOX fuel assemblies and the fuel cycle processes

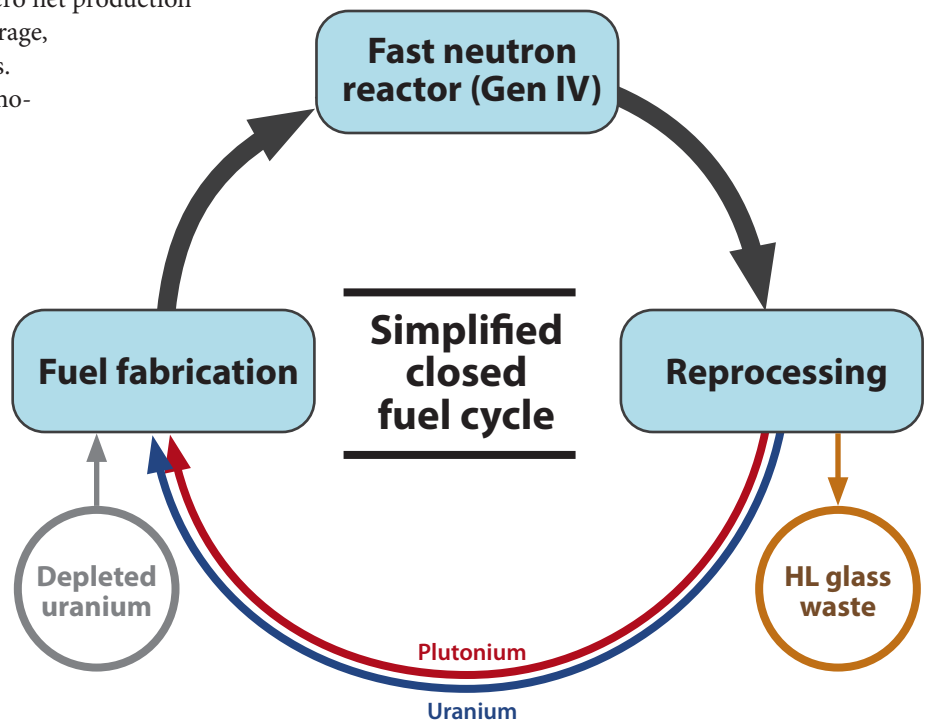


Figure 6. The simplified closed fuel cycle principle, based on the use of fast neutron reactors, has no requirement for natural uranium but only for depleted uranium, which is widely available in France.

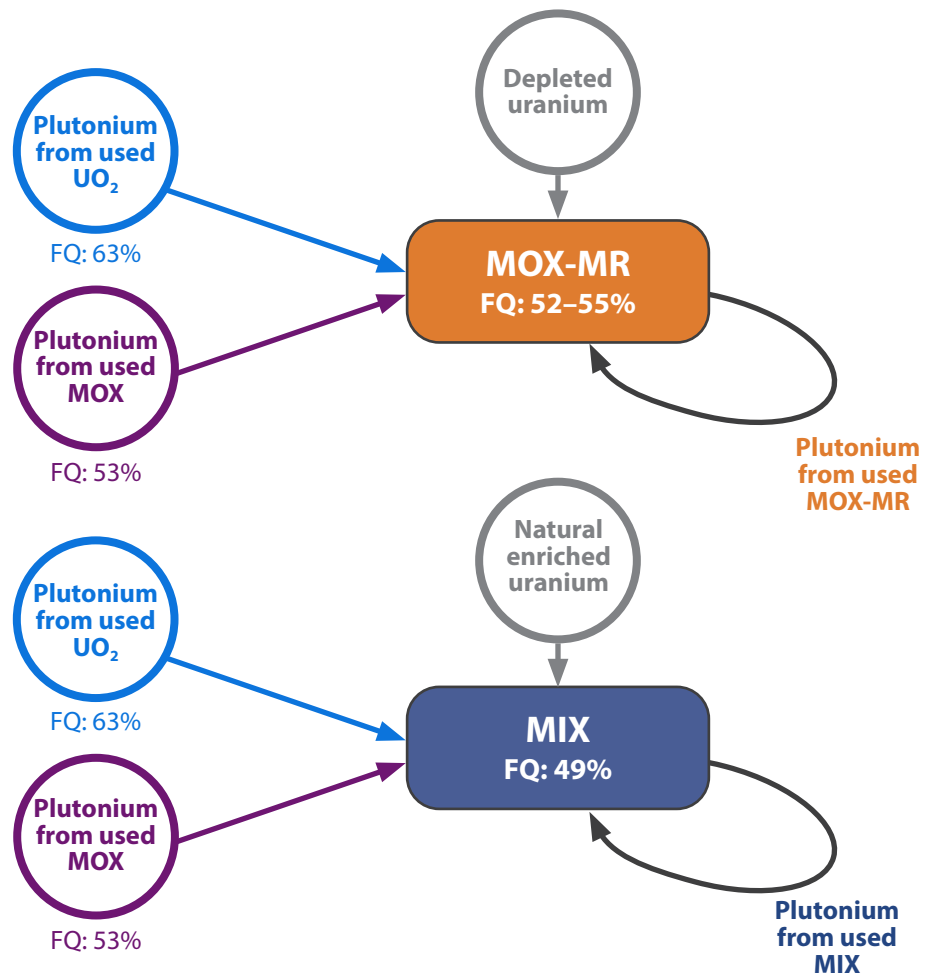


Figure 7. Two different MOX2 fuel concepts to recycle plutonium in pressurized water reactors (PWRs).

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to progressively larger quantities of plutonium, of reduced fissile quality and more highly irradiating. This should not only allow used fuel and plutonium inventories to be stabilized, but also prepare the reprocessing and recycling industry for a future closed fuel cycle.

Before achieving full closure of the fuel cycle, the final intermediate step will be the progressive replacement of the EPRs in the fleet with FNRs. This will gradually decrease the production of minor actinides, and therefore also the volume of glass waste canisters and associated disposal footprint.

4. Multi-recycling of plutonium in PWRs (EPRs)

Here we examine in more detail the origin of the plutonium amounts used in the PWR multi-recycling stage. Fission quality (FQ) of a plutonium batch is defined as its proportion (percent contained) of fissile isotopes of plutonium (plutonium-239, plutonium-241). Plutonium derived from UOX fuel typically has an FQ of 63%, whereas that from used MOX reprocessed fuel is lower, 53% or less. Each cycle in a multi-recycling scheme in a PWR will also decrease the FQ. Therefore, in order to maintain a given burn-up reactivity, it is mandatory to compensate for the decreasing FQ. This can be achieved by using one of two MOX2 fuels concepts (Fig. 7).

The MOX-MR scheme mixes plutonium batches coming from reprocessed used UOX, current MOX used fuels, and a minor amount of multi-recycled plutonium, leading to an FQ ranging from 52.5 to 55%. The plutonium is then blended with depleted uranium dioxide. The lack of reactivity in these assemblies is accounted for by adjusting the reload size: MOX-MR assemblies are therefore very similar to current MOX assemblies.

The MIX scheme uses a similar source of plutonium batches but mixed to give a slightly lower FQ, ranging from 53 to less than 50%. The lower neutron reactivity is compensated for by using enriched uranium dioxide instead of depleted. Because both schemes use additional supplies of uranium, the system is not free from front-end operations at this stage (namely, natural uranium mining, purification, and enrichment).

It is possible to reach a steady state with zero net production of plutonium in the PWR fleet by operating an appropriate mix of UOX (naturally enriched uranium oxide, NEU) and MIX amounts (Fig. 8). Let γ represent the share of the MIX fuel assembly throughput in PWR cores ($\gamma = \text{MIX}/(\text{MIX}+\text{UOX})$) and x and x' the average plutonium contents in the fresh MIX fuel (x) and in the used MIX fuel (x') (averaged values of the three different fuel zones in the fuel assembly). To comply with the safety constraints in the core, the local plutonium content in the fresh fuel must not exceed 12%. Incorporating a wide safety margin from this limit, a value of 8% has been chosen. The plutonium concentration in used UOX fuel is around 1% and x' is roughly 6%.

Basic calculations lead to the share of the MIX fuel $\gamma \approx 1/3$, which means that, in order to reach a zero net production of plutonium, one third of the fuel used in the PWR fleet should be MIX fuel and two thirds should be UOX fuel. It is also easy to calculate the mass throughput of plutonium ($m_{\text{Pu}}^{\text{MIX}}$) and compare it with the current plutonium mono-recycling value ($m_{\text{Pu}}^{\text{mono}} \approx 10 \text{ T/y}$). Assuming a constant value of electricity production, it follows that the ratio $m_{\text{Pu}}^{\text{MIX}}/m_{\text{Pu}}^{\text{mono}} \approx 2.7$ or $m_{\text{Pu}}^{\text{MIX}} \approx 27 \text{ T/y}$. It is worth noting that attaining a steady state, which means zero increase of the used fuel and plutonium inventories, leads to a large increase in the quantity of circulating plutonium.

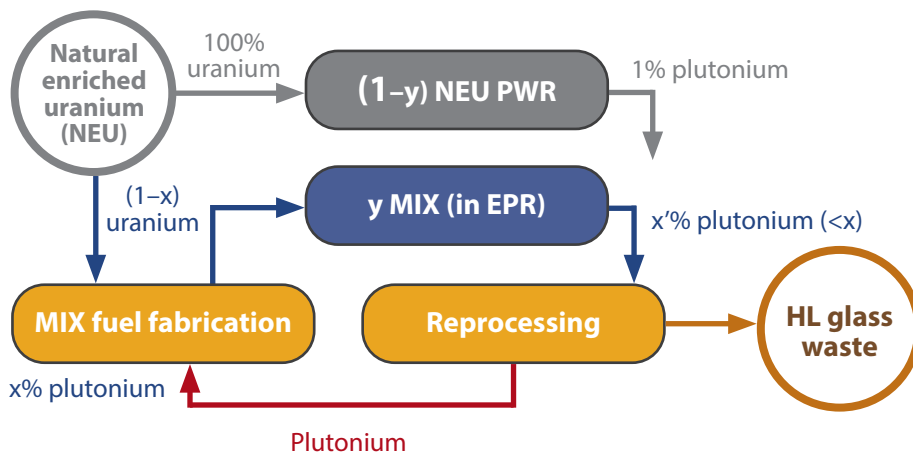


Figure 8. Schematic representation of a steady state (in total plutonium amounts, including every isotope) in a mixed fleet using a share of naturally enriched uranium dioxide and of MIX (U,Pu)₂ fuels. [PWR = pressurized water reactor; EPR = European pressurized reactor]



Furthermore, the average plutonium FQ slightly decreases with each cycle (see “Pu multi-recycling scenarios towards a PWR fleet for a stabilization of spent fuel inventories in France” by Courtin et al., published in the Journal of Nuclear Science and Technology in 2021) and consequently there is an increase in isotopes with even-numbered mass numbers (plutonium-238, plutonium-240, and plutonium-242). This has several consequences: increasing the thermal power and radioactivity, as well as increasing the production of minor actinides and the accompanying production of helium. This has been taken into consideration in plans to adapt the fuel cycle process to a multi-recycling scheme, with specific R&D studies already performed, as we show below through two examples.

Fabrication: Cryo-milling process development

To limit the release of helium and other gaseous fission products (which leads to a pressure increase in the fuel rod), an ongoing goal of CEA (French Alternative Energies and Atomic Energy Commission) and Orano R&D is to optimize the grain size and increase (U,Pu)O₂ homogeneity through advanced fabrication processes. There are three major steps in the MOX fabrication process: powder preparation (with a feed of plutonium dioxide and uranium dioxide powders), pellet shaping, and sintering. Grain size optimization and oxide homogeneity may be achieved by adapting either the first step, powder preparation, or the last, sintering. The first pathway we have studied is changing the current roller-ball mill process into a new cryo-milling approach (Fig. 9).

Experiments show that total cryo-milling may reduce the time required for powder preparation, increase homogeneity, and lead to several other operational benefits such as reduced waste production.

Reprocessing / dissolution: Voloxidation step

To validate these initial results, complementary experiments were performed. Using larger grain sizes of fuel, with potentially greater amounts of plutonium, slows down the dissolution of used fuel pellets in nitric acid at the front-end reprocessing

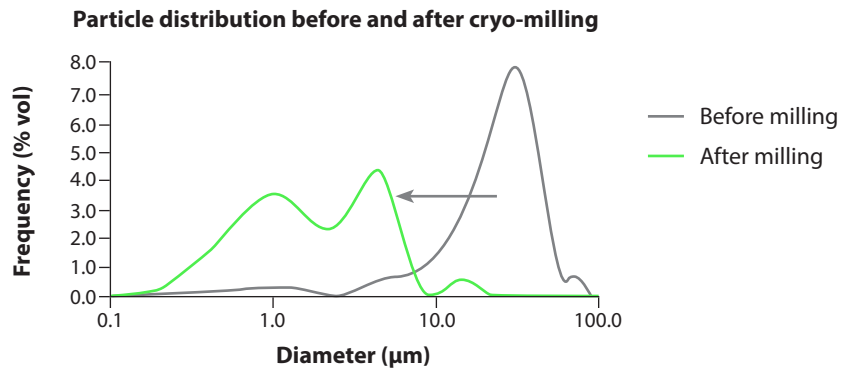


Figure 9. The principle of the cryo-milling process for PuO₂ + UO₂ powders. Initial results show promise—the powder particles are reduced in diameter and obtained in a much shorter time by cryo-milling compared to traditional ball milling (reproduced from the CEA-ORANO article “Cryo-milling process for MOX nuclear fuel,” Robisson et al., GLOBAL 2022).

step. Slower dissolution is also observed with MOX fast-neutron fuel pellets, owing to the significantly higher plutonium content required for achieving a fast-neutron spectrum. To facilitate the dissolution of these pellets, CEA and ORANO are currently studying the voloxidation pathway. Voloxidation induces an over-oxidation of UO_2 into U_3O_8 , leading to swelling of the uranium lattice and a fragmentation of the oxide. The larger surface area of the oxide significantly increases the rate of dissolution. The impact of this oxidizing treatment and the behavior of plutonium at the dissolution step is currently under study and could also be beneficial for SFR fuels. These studies aim to increase the TRL (technology readiness level) of the nuclearized voloxidation process.

5. Long-term closed fuel cycle in fast neutron reactors

A simplified view of the closed fuel cycle scenario is shown in Fig. 6. Fast neutron reactors allow higher burn-up values, roughly 150 GWd/T (versus 50 GWd/T for the current PWR fleet) but they require higher plutonium contents, typically 22 to 28%. Assuming that electricity production is fixed at the current value (around 380 TWh/y) and considering the above increased burn-up value, this gives an annual MOX fuel throughput value for FNRs of around 400 T/y (versus 1200 T/y for the current fleet), which also roughly yields the amount of depleted uranium consumed each year. Considering the above range of plutonium content, we obtain the value of annual plutonium throughput at roughly 90 to 110 T/y plutonium in the FNR fleet and fuel cycle plants. We conclude that, compared to the current plutonium mono-recycling value (around 10 T/y), the inventory of plutonium in the closed fuel cycle is multiplied by a factor of roughly eight to ten and by a factor of three compared to the multi-recycling of MIX fuel in PWRs, which is a considerable challenge. More precisely, the challenges and R&D goals associated with a closed fuel cycle are the following:

- Larger quantities of MOX fuels to be treated. Therefore, it is mandatory to develop simplified extraction processes (see below).
- Increased plutonium content in the MOX fuels. This makes dissolution slower and less efficient (see the voloxidation pathway above).
- Strongly increased burn-up values. This tests the integrity of the materials used in the reactor. Oxide dispersion strengthened (ODS) ferritic steel is being developed as an advanced cladding tube because of its excellent swelling resistance and high temperature strength. This work is important in the framework of the collaborative European MATISSE project, which aims to develop materials for safe and sustainable nuclear power.
- Increased content of fission products and platinum-group metals in the used fuel (associated with high burn-up values). This would likely require some improvements in high-level waste conditioning (N.B., in this definition, the radioactivity of high-level waste is of the order of several GBq/g).

CEA, with the support of partners Orano and EDF, are conducting several R&D projects to develop future closed fuel cycle processes. As an example of one of these projects, we describe the principle of a simplified separation for fast MOX fuel reprocessing (see Sorel et al., Proceedings of the GLOBAL 2017 conference, Paper A221.). Due to the limited selectivity and properties of the TBP extractant molecules used in the PUREX process, the current plutonium/uranium separation combines two steps: an initial extraction cycle (with a specific redox operation to re-extract plutonium from the organic phase), followed by two cycles for uranium and plutonium purification. The use of new, highly selective mono-amide type



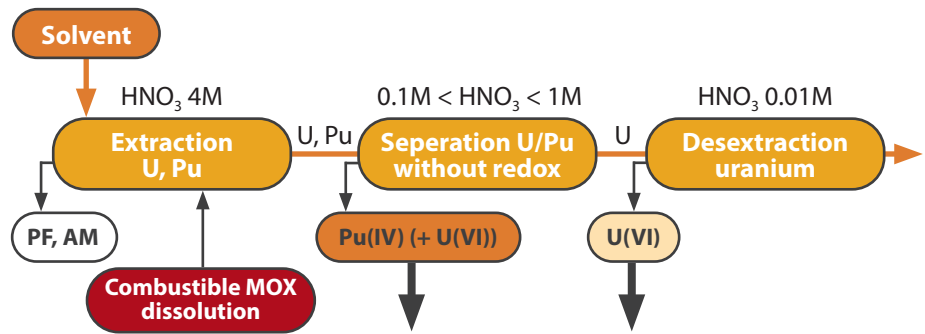


Figure 10. Simplified monoamide-based separation process: a single cycle without REDOX operation (reproduced from C. Sorel et al., Proceedings of the GLOBAL 2017 conference, September 24-27, Paper A221).

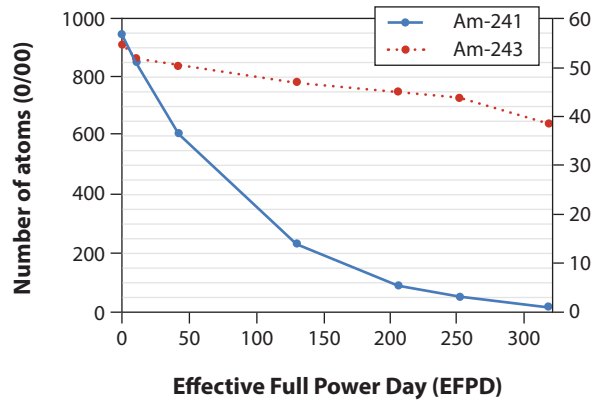


Figure 11. The transmutation of americium in fast neutron reactors is feasible, as proven with ECRIX irradiated pellets: evolution of 1000 americium atoms during irradiation in the Phenix SFR (reproduced from Tome 2: La séparation et la transmutation des éléments radioactifs à vie longue, December 2012).

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solvents (DEHiBA, DEHBA, etc.) simplifies and reduces the process to a single extraction cycle, with no redox operation as plutonium and uranium are simply re-extracted by decreasing the acidity of the aqueous phase (Fig. 10). This simplified process has been successfully tested in shielded cells in the Atalante hot facility in Marcoule, France, first with surrogate solutions and then on real PWR MOX fuel dissolution solutions.

CEA, supported by Orano and EDF, continues to study new molecules to improve extraction schemes and separation coefficients for different elements. These studies will also address the separation process as a whole, including aspects such as the implementation of industrial equipment and the management of secondary flows in scrubbing operations that remove degradation products, in order to improve the TRL of this process.

6. A path towards transmutation of minor actinides

Beyond the multi-recycling of plutonium, which is clearly a high priority, the separation and transmutation of minor actinides is a more distant future goal. This aims to decrease the short- and medium-term thermal power of high-level waste, to

reduce the volume of waste delivered to a disposal facility, and reduce its long-term radiotoxicity. The French reference path involves using sodium-cooled fast reactors (SFR) to transmute americium and even curium. Molten salt reactors are a new option that we also currently study, with some potential benefits (e.g., no handling of solid fuels and targets) but also with a low TRL at present.

A great deal of experience has been gained following both the first Waste Management Act (1991–2006) and the second Waste and Radioactive Products Management Act (2006–present). CEA has used two major R&D facilities for this separations research: the PHENIX SFR (closed in 2009) and the Atalante hot facility, both in Marcoule, France. The first step is to separate americium and curium from fission products and other actinides uranium, neptunium, and plutonium, using a chained PUREX/DIAMEX/SANEX process. Following this, doped targets or fuels are fabricated using the minor-actinides and then they are finally irradiated in a fast neutron reactor (Fig. 5). The feasibility of the transmutation process has been proven through several experiments, in particular for americium-241, and also to a lesser extent americium-243 (see the ECRIX results in Fig. 11). These results and more information can be found in the second volume of CEA experimental work published in 2012 (“Tome 2: La séparation et la transmutation des éléments radioactifs à vie longue”). Despite their proven feasibility, these processes would need some improvements before moving towards a potential industrial use.

7. Summary

The use of nuclear energy will increase and diversify in the coming decades: it is therefore necessary to preserve natural uranium resources in a competitive world. France has chosen to recycle reusable fissile materials by mono-recycling of plutonium and by commissioning feasibility studies on multi-recycling and fuel cycle closure, which are underway. The multi-recycling of plutonium in PWRs would be a first step before the complete closure of the cycle using FNRs, thus allowing France’s independence from natural uranium resources.

This path towards multi-recycling and closing the fuel cycle before the end of the 21st century requires developing new processes; in particular, accounting for the increasing throughput of plutonium (by a factor of three to ten), but also its changes in isotopic composition, thermal power, and radioactivity, and the future diversity of fuels.

To make these developments possible, CEA with its industrial partners Orano, EDF, and Framatome, are conducting several important R&D programs on innovative reprocessing and fuel fabrication processes, in order to prepare the French nuclear industry for future fuel cycle goals.

Further reading:

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Brice Ravat

Brice Ravat is an actinide materials scientist working at the French Atomic Energy Commission (CEA) Centre de Valduc. He has more than 20 years of experience in plutonium materials science and metallurgy. He has worked on self-irradiation damage, phase transformation and properties of plutonium alloys. Currently, his research interests are mainly focused on the study of the oxidation mechanisms and reactivity of plutonium alloys.

Gallium Alloying Behavior During Oxidation of Delta Phase Plutonium Alloys

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Plutonium is one of the most complex elements in the periodic table, displaying highly unusual behavior and a total of six allotropic phases between room temperature and its low melting point (640 °C) at ambient pressure. The high-temperature δ -phase (face-centered cubic) of plutonium is the most interesting phase for metallurgical applications as it is the most ductile compared to the other phases—in particular the α -phase (simple monoclinic), which is the stable phase at room temperature and relatively brittle. Notably, the δ -phase can be stabilized at room temperature and pressure by alloying with gallium in small amounts. Although δ -phase plutonium oxidizes at a lower rate than other phases, it still remains very sensitive to corrosion, which may be severe in long-term storage under an inadequately controlled atmosphere.

High temperature oxidation of δ -phase plutonium under an oxygen atmosphere leads to the formation of an oxide scale composed of an outer layer of face-centered cubic PuO_2 and an inner layer of Pu_2O_3 . This inner layer of Pu_2O_3 exhibits a polymorphic character as both cubic and hexagonal (α - and δ -phases) crystallographic structures may be present. The overall oxide scale growth kinetics consists of an initial parabolic growth stage mainly resulting from the thickening of the Pu_2O_3 layer, followed by linear growth of PuO_2 . Furthermore, oxidation leads to an unexpected destabilization of the δ phase with the appearance of a pure phase of plutonium during oxidation, corresponding to the emergence of a gallium-depleted layer below the oxide scale as well as an enrichment of this element on the outer surface of the scale. Although formation of Ga_2O_3 is suspected, the formation enthalpy of PuO_2 is energetically more favorable than that of Ga_2O_3 . Alternatively, gallium may be incorporated into plutonium oxide scale: ab-initio calculations indicate that it is energetically favorable to place gallium atoms in plutonium substitutional sites of PuO_2 lattice.

The exact role played by the gallium solute element during oxidation is not yet understood. Several important questions need to be answered: Does the gallium diffuse through the oxide scale up to the scale/gas interface in order to be oxidized instead of plutonium atoms? This would have the effect of limiting the formation of the plutonium oxide. Also, does the gallium remain inside the oxide scale and where exactly? At present, there is limited experimental data for gallium behavior and consequently many questions remain unanswered.

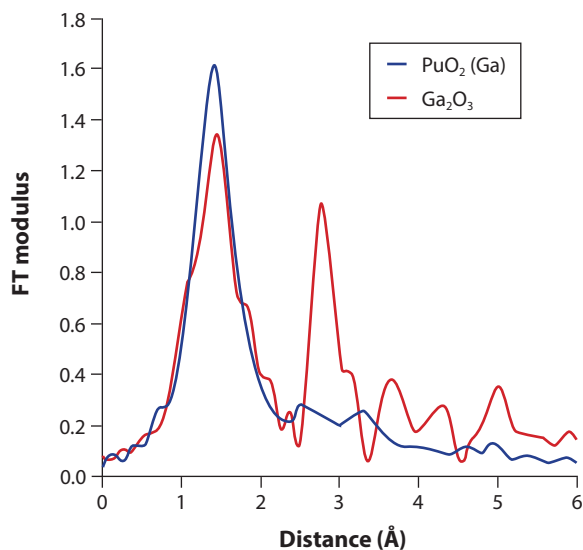


Figure 1. Fourier Transforms (FTs) of the averaged EXAFS spectra, recorded in fluorescence mode at the Ga K-edge for an incidence angle of 3° with PuO_2 lattice (blue line) and $\beta\text{-Ga}_2\text{O}_3$ as standard material (red line). (Note that FTs exhibit pseudo radial distribution functions from which real inter-atomic distances cannot be read directly).

Experimental characterization of the gallium local environment

To provide a better understanding of gallium behavior during oxidation, we investigated how gallium atoms are localized in the plutonium oxide crystalline lattice, focusing on the characterization of the atomic local environment around the gallium atoms within a PuO_2 layer. Therefore, EXAFS (extended X-ray absorption fine structure) measurements were performed on an oxidized $\delta\text{-PuGa}$ 1 at.% alloy at the MARS (multi-analysis on radioactive samples) beamline located at the SOLEIL synchrotron facility near Paris, France. Measurements were performed in fluorescence mode at the Ga K-edge (10,367 eV) in grazing incidence geometry (to analyze the PuO_2 layer) and at the Pu $L_{3\text{-edge}}$ (18,057 eV) in a normal incidence-grazing-exit geometry to reduce the so-called self-absorption effect.

In the Fourier transform (FT) of the Ga K-edge-averaged EXAFS data (which can be considered as a pseudo-radial distribution function, Fig. 1), only a well-ordered first coordination shell seems to be detected. Thus, the local order around the gallium atoms may be reduced to first-nearest neighbors (1NN). Next, Ga_2O_3 was analyzed as reference standard material to check if gallium was present in the oxide scale as Ga_2O_3 . Comparing the EXAFS spectra shows that the 1NN shells of both compounds are similar, indicating that gallium in the oxide scale is likely surrounded by oxygen atoms with Ga–O distances close to those in Ga_2O_3 . However, the 2NN contribution in the EXAFS spectrum of Ga_2O_3 corresponding to gallium cations is clearly missing in the EXAFS spectrum of the PuO_2 layer. This demonstrates that gallium is not present as Ga_2O_3 (precipitates or layer). Therefore, gallium atoms are very likely incorporated in the PuO_2 lattice and surrounded by oxygen atoms. However, since no 2NN shell appears in the EXAFS spectrum at the Ga K-edge, the local structure around gallium atoms may be significantly disordered and remains unresolved. Consequently, the best way to determine this local structure was to analyze EXAFS data using the reverse Monte Carlo (RMC) method, which allows exploration of numerous local atomic configurations.

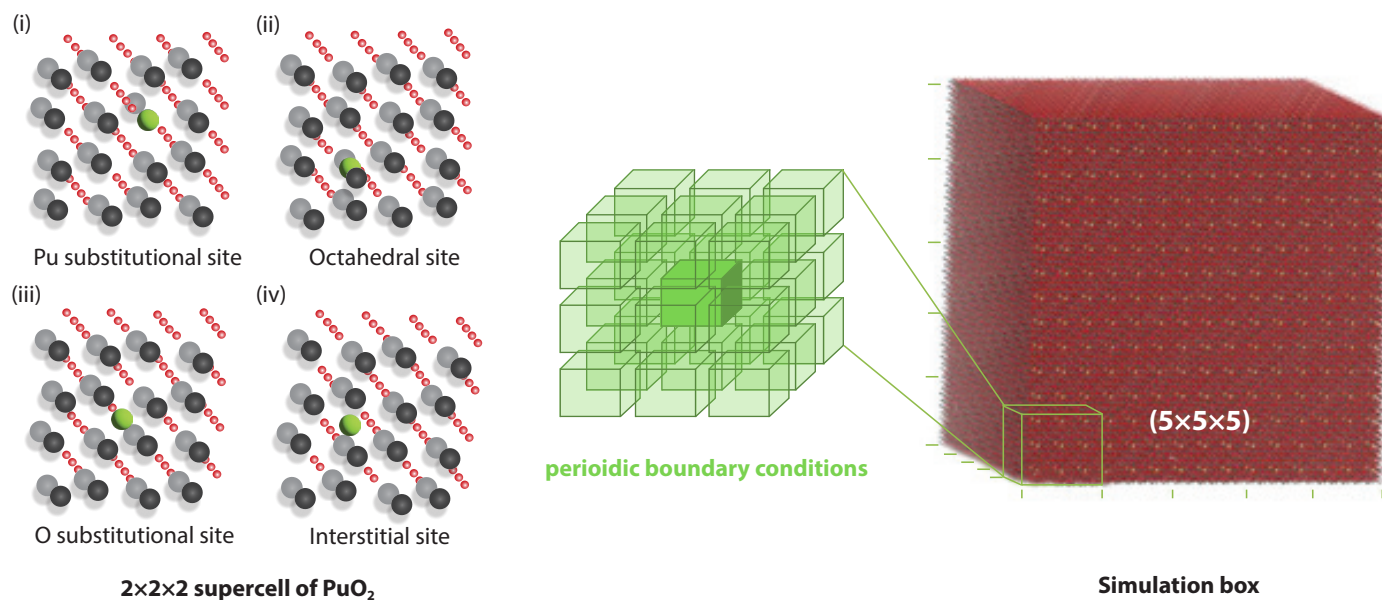


Figure 2. Initial structure $2 \times 2 \times 2$ supercells of PuO_2 containing one gallium atom (green sphere) in the following positions: (i) plutonium substitutional site, (ii) octahedral site, (iii) oxygen substitutional site, and (iv) interstitial site (with coordination to two neighboring oxygen atoms). The RMC calculations were performed using periodic boundary conditions (PBC) with a $5 \times 5 \times 5$ simulation box size containing 12,000 independent atoms including 125 Ga atoms.

Reverse Monte Carlo simulation

The RMC method, as implemented in the EvAX software package, is an atomistic simulation technique based on an evolutionary algorithm (EA) that allows the 3D atomic structure to be reconstructed by minimizing differences between experimental and simulated EXAFS spectra. Both Ga K-edge and Pu L_3 -edge EXAFS spectra were simultaneously analyzed using this RMC/EA method. For this simulation, a structural model consisting of a $2 \times 2 \times 2$ supercell of PuO_2 was built by incorporating one gallium atom inside the lattice in one of the four possible crystallographic sites: a plutonium substitutional site, an octahedral site, an oxygen substitutional site, or an interstitial site (with coordination to two neighboring oxygen atoms), as shown in Fig. 2. At each iteration, during the simulation, a new atomic configuration was generated by randomly displacing all of the atoms. After this, the corresponding Ga K-edge and Pu L_3 -edge configuration-averaged EXAFS spectra were calculated.

At the end of the simulation, the final atomic configuration that gave the best agreement with the experimental EXAFS data was saved and used to calculate the partial radial distribution functions (RDFs) $g(R)$ around the gallium and plutonium atoms for further analysis. Good agreement between the experimental and theoretical EXAFS spectra was obtained with the Pu L_3 -edge (Fig. 3a) whatever the initial gallium position in the PuO_2 lattice. This means that the long-range order of the PuO_2 crystalline structure lattice is not significantly affected by the presence of gallium. The final RDF $g_{\text{Pu-X}}(R)$ (Fig. 4a) exhibits enlarged peaks which do not perfectly match the positions of atoms in the different crystallographic sites of the ideal crystalline lattice. This broadening is however characteristic of the effects of vibrational motion of the atoms since EXAFS experiments were performed at room temperature.

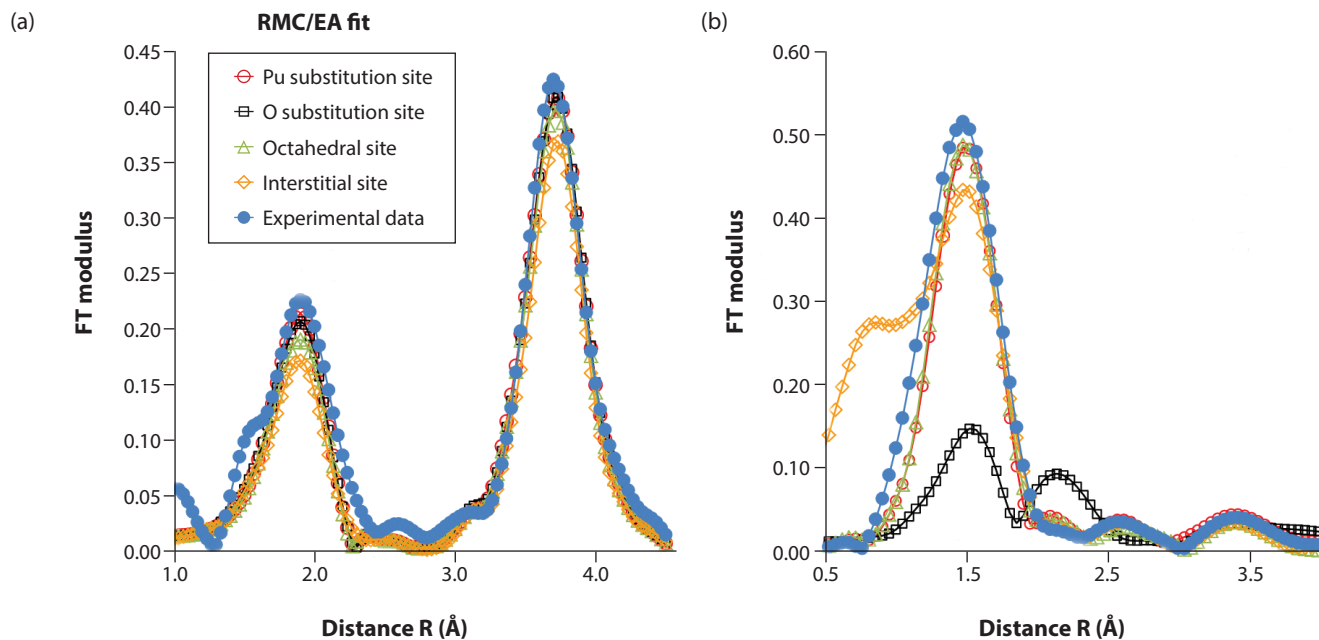


Figure 3. Experimental and calculated Pu L₃-edge (a) and Ga K-edge (b) EXAFS spectra FTs. RMC/EA simulations were performed from supercells of PuO₂ containing initially one gallium atom within the lattice either in: plutonium substitutional site, octahedral site, oxygen substitutional site, or interstitial site (with coordination to two neighboring oxygen atoms).

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With the Ga K-edge data, a good agreement between experimental and theoretical EXAFS spectra was obtained only for the PuO₂ structures with the gallium atom in the plutonium substitutional site or the octahedral site (Fig. 3b). The RDF $g_{\text{Ga-X}}(R)$ for gallium (Fig. 4b) in the plutonium substitutional site exhibits a large local disorder around the gallium atoms, with a splitting into two main contributions of the 1NN shell peak corresponding to eight oxygen atoms, initially located at 2.34 Å. The former consists of two thin peaks at a distance of 1.83 and 1.91 Å, each corresponding to one oxygen atom. The latter is shifted to longer distance by 0.4 Å and includes a series of four peaks at 2.35, 2.54, 2.77, and 2.96 Å, corresponding to the remaining six oxygen atoms of the initial 1NN shell. The loss of local order around the gallium atoms is experimentally responsible for the extinction of the second contribution of the experimental Ga K-edge EXAFS spectrum FT (Fig. 1). The RDF $g_{\text{Ga-X}}(R)$ for gallium in the octahedral site after the RMC/EA simulation also exhibits changes of the same scale. In addition, the study of gallium, oxygen, and plutonium atom displacements reveals that gallium atoms are no longer located in their initial high symmetry site. The gallium atoms move to be closer to two oxygen atoms and further from the other six oxygen atoms.

In parallel, DFT calculations highlighted that placing the gallium atom in the plutonium substitutional site appears to be energetically favorable because of its atomic radius in addition to the positive electron interaction effects, as it maintains the electronic structure of PuO₂.

We obtained a good agreement between structural analysis and DFT calculations when incorporating a gallium atom into the plutonium substitutional site of the

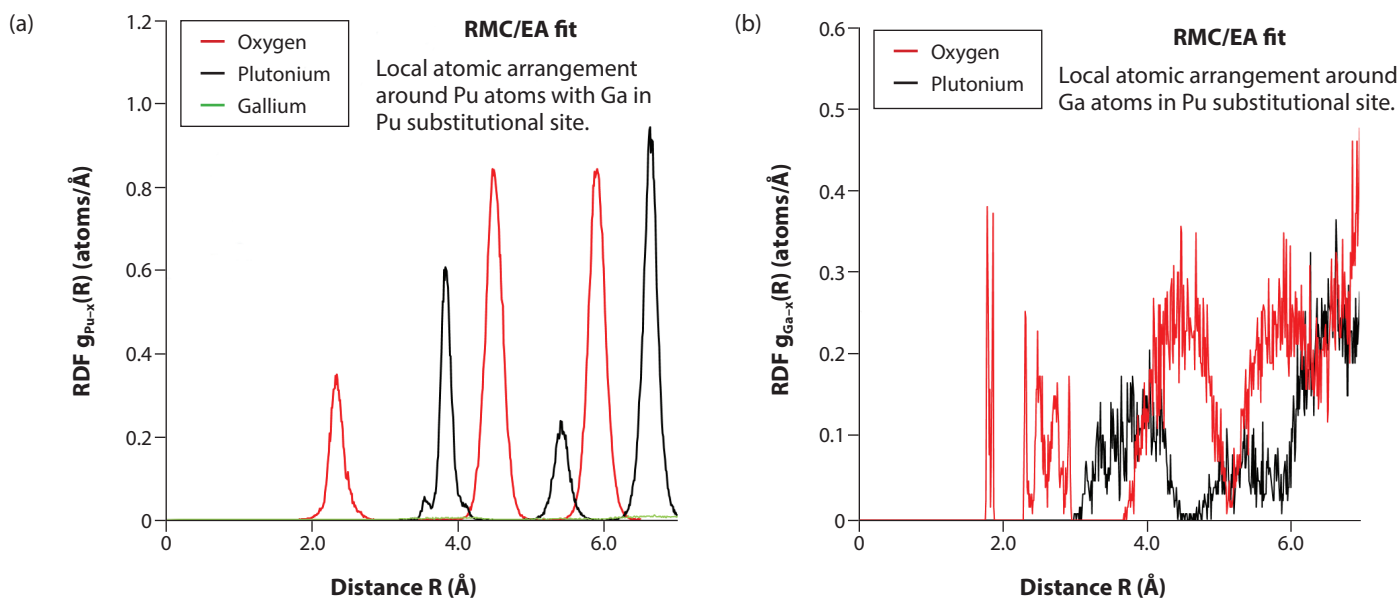


Figure 4. Radial distribution functions (a) $g_{\text{Pu-x}}(R)$ and (b) $g_{\text{Ga-x}}(R)$ corresponding to the final atomic configuration obtained after RMC/EA simulation giving the best agreement with the experimental EXAFS. Calculation was performed from supercells of PuO_2 containing initially one gallium atom in a plutonium substitutional site.

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PuO_2 lattice. Thus, during the oxidation process, gallium atoms likely diffuse into the plutonium substitutional site in the PuO_2 layer. There is a driving force corresponding to an energy gain when incorporating gallium atoms into plutonium vacancies, which supports this process. Therefore, plutonium vacancies must exist, possibly resulting from self-irradiation of plutonium and also from the oxygen gradient inducing point defects in the oxide scale.

Summary

High temperature oxidation of PuGa alloys under oxygen atmospheres leads to the formation of an oxide scale composed of an outer layer of PuO_2 and an inner layer of Pu_2O_3 . This leads to a surprising destabilization of the δ phase, suggesting that it also modifies the structure of the alloy. Coupling of EXAFS experiments with reverse Monte Carlo (RMC) simulations permitted us to characterize the atomic local environment around the plutonium and gallium atoms in the outer PuO_2 layer formed on δ -PuGa 1 at.% alloy. The results have highlighted the presence of gallium in the plutonium oxide scale. However, no formation of gallium aggregates or gallium oxides was detected. Instead, RMC analysis of experimental data indicates that gallium atoms are present within the PuO_2 lattice. More precisely, the results showed that gallium atoms may occupy a plutonium substitutional site or octahedral site. This incorporation leads to a large local disorder with displacement of gallium atoms from their initial high symmetry crystallographic site. A noteworthy agreement is obtained by DFT calculations when incorporating gallium in a plutonium substitutional site in the PuO_2 lattice. In conclusion, diffusion of gallium atoms into plutonium vacancies in the PuO_2 lattice is likely to be the main process responsible for the observed δ -phase destabilization.

Transferrin and Fetuin: Potential Vectors for Plutonium Accumulation in the Liver and Skeleton

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Metallic cations are essential in biological systems, in particular in the role they play in proteins. About half of the proteins expressed in humans interact with metals—the complete set of these biomolecules containing a metal is referred to as the metallome. Even though most metals essential to the metallome are found in the upper part of the periodic table, they can be replaced by other metals that carry out no physiological function, inducing a variety of physiological and toxicological effects. These metals devoid of physiological function include the actinides, notably plutonium. From a physics standpoint, due to the instability of all of its isotopes, plutonium presents a radiological toxicity that is totally independent of its chemical properties. Chemically, plutonium is a hard acid according to the Pearson classification and therefore it exhibits special affinity for hard bases such as hydroxides, carbonates, carboxylates, or phosphonates, and consequently for certain groups found in proteins, such as tyrosine, aspartate, or histidine.

Plutonium(IV) presents very low clearance and is very strongly retained in the human body. Biodistribution studies indicate that more than 80% of the plutonium retained is partitioned between two main organs: the skeleton and, preferentially, the liver. Human epidemiological data are very scarce—fortunately—but this paucity means that the toxicity of plutonium has had to be estimated using experiments performed on animal models. Furthermore, it remains difficult to quantify plutonium in the skeleton due to individual variability (age, health status, etc.), the small size of bone samples available for analysis and their heterogeneous origin (sternum, femur, ribs, etc.), and the time elapsed between autopsy and postmortem sampling. All of these parameters require extrapolations that contribute to the overall heterogeneity of the results.

As early as 1965, transferrin (Tf) was one of the very first target proteins identified; its modes of interaction with the actinides remain widely explored to this day. But transferrin by itself cannot explain why plutonium accumulates in the bones. Bone is composed of a network of collagenous and non-collagenous proteins permeated with a mineral matrix of hydroxyapatite. While fetuin-A (Fet) and albumin represent more than 25% of the non-collagenous proteins present in the serum, fetuin-A is four times more concentrated than albumin in the calcified matrix.

Given the special properties of these two proteins—one of them produced by the liver (transferrin) and the other ending its lifespan in the bone matrix (fetuin-A)—we considered it relevant to study their affinity for plutonium and examine whether they could enter into competition with each other.



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Jean Aupiais is currently Senior Scientist at CEA (the French Alternative Energies and Atomic Energy Commission) DAM Ile-de-France and Professor of Radiochemistry at the National Institute of Nuclear Science and Technology. His research interests are focused on actinide speciation by means of hyphenated techniques, thermodynamics of actinides in solution, and detection of radionuclides at the ultratrace scale.

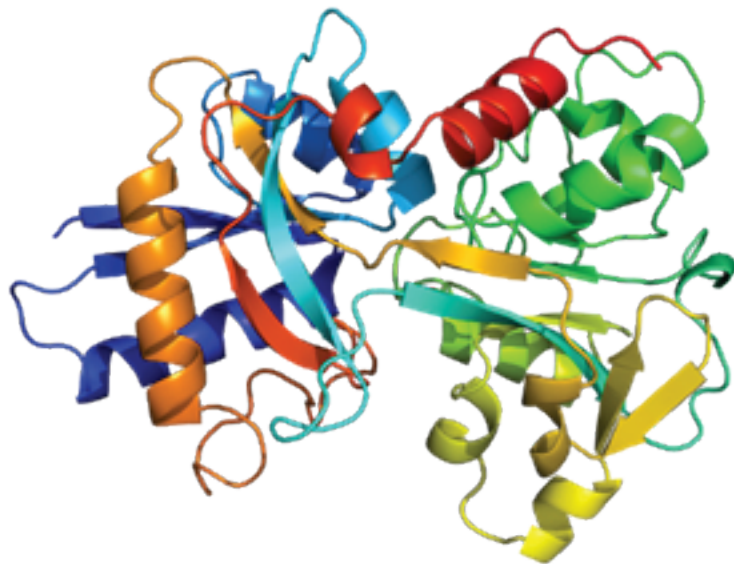


Figure 1. Transferrin is a glycoprotein with a molecular weight of approximately 80 kDa (kilodalton). Its concentration in the blood is approximately 2.5 mg/mL ($\approx 30 \mu\text{M}$). It is responsible for transporting iron in the blood to the organs, particularly the liver. Two binding sites are found on the two lobes of this protein: the C-lobe ($\log_{10} K(\text{Fe}^{\text{III}}) = 21.4$) and the N-lobe ($\log_{10} K(\text{Fe}^{\text{III}}) = 20.3$). The carbonate anion, which acts as a synergetic anion, is necessary for cation fixation and thereby enables the closure of the lobes. Only the diferric form (referred to as holotransferrin) adopts the conformation required for internalization in the cell. The free form (without iron, known as apotransferrin) and the monoferric form, which together represent 70% of total blood protein, can bind with plutonium. The half-life of transferrin in the blood is roughly eight days.

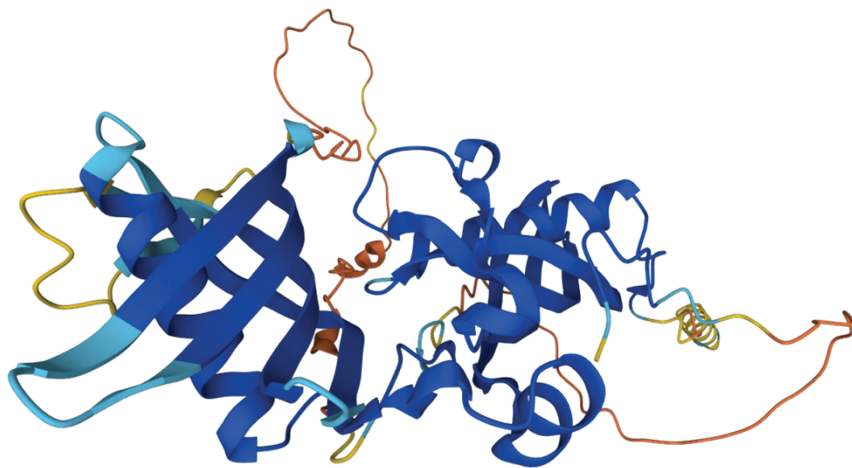


Figure 2. Human fetuin (also known as fetuin A or $\alpha 2$ -HS-glycoprotein) is a protein with a molecular weight of 48 kDa, but its highly glycosylated nature can increase its apparent weight to approximately 56 kDa. It consists of three domains: two cystatin domains known as D1 and D2, and an unstructured domain (D3). Fetuin is a plasma protein derived from the liver. It is abundant in fetuses and young children, decreasing over time to about $15 \mu\text{M}$ in adults. Its function is to control the formation of calcium phosphate clusters by binding them and transporting them to the bone matrix, while its life cycle comes to an end 1.5 days after its release into the bloodstream.

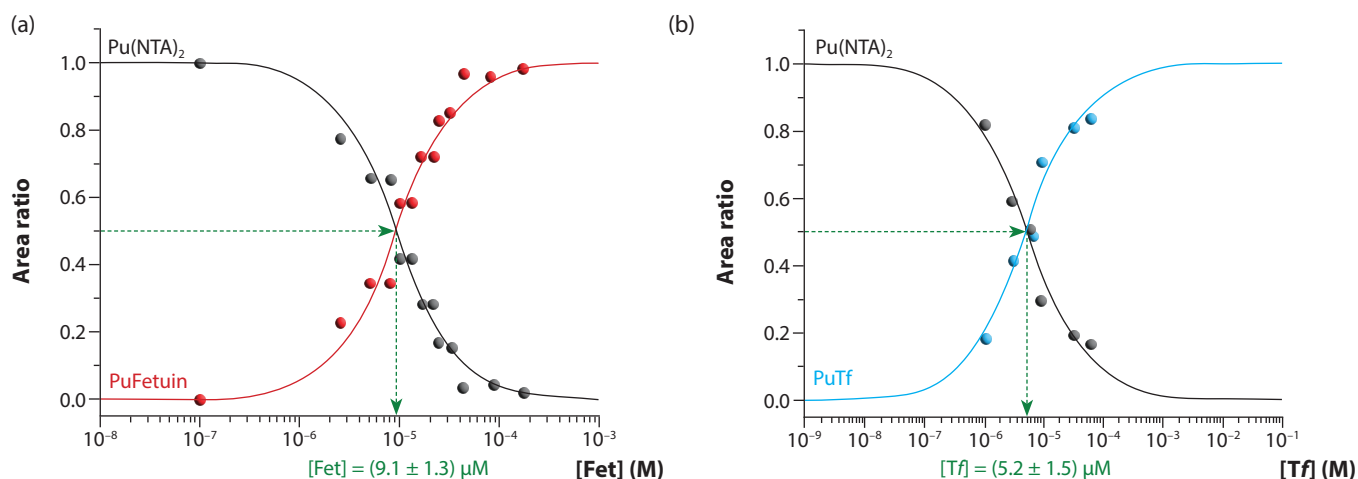


Figure 3. Effect of increasing (a) Fet and (b) Tf concentrations on the Pu(NTA)₂ complex (NTA = nitrilotriacetic acid). The relative area of Pu(NTA)₂ (black spheres) is shown as a function of the relative area of PuFetuin (red spheres) or of PuTf (apo form, blue spheres). By locating the point at which both species present the same concentration, i.e., [Fet] = (9.1 ± 1.3) μM and [Tf] = (5.2 ± 1.5) μM, it becomes possible to calculate the binding constant:

$\log K = 26.20 \pm 0.24$ for fetuin and 26.44 ± 0.28 for transferrin.

Serum proteins: Transferrin and fetuin

Transferrin was discovered by Holmberg and Laurell in 1947. This glycoprotein of approximately 80 kDa in molecular weight (Fig. 1) can bind up to two Fe(III) cations in two different lobes (known as the C-lobe and the N-lobe), which leads to the closure of the lobes, the recognition of transferrin by its receptor, and the cellular internalization of the transferrin. Ongoing studies have established the interaction of this protein with actinides in oxidation states III, IV, V, and VI and identified its behavioral similarities with Fe(III). The binding sites of actinides are common to those of Fe(III), involving histidine, tyrosine, and aspartate groups.

Fetuin-A is a non-collagenous protein of approximately 48 kDa (Fig. 2), discovered by Pederson in 1944. It can bind to a great many receptors with various functions; recently, its strong affinity for uranium(VI) was demonstrated. It possesses three known binding sites for this actinide, including a site with particularly high affinity that has not yet been clearly identified, but appears to be located in the first cystatin domain (D1). Its affinity for plutonium has been unknown up to the present time.

Stability constants of transferrin and fetuin with plutonium

It is extremely difficult to study plutonium(IV) in physiological environments due to competing hydrolysis reactions. For plutonium(IV) to be stabilized at physiological pH (7.4), it must be protected by a chelate whose affinity for plutonium overcomes the issue of hydrolysis reactions. We opted for the use of nitrilotriacetic acid (NTA), which at a concentration of 2 μM makes it possible to study the binding process with transferrin and fetuin up to a pH of 7. This investigation relies on capillary electrophoresis (CE) coupled to inductively coupled plasma (ICP) mass spectrometry, a method based on the competition between the Pu(NTA)₂ complex and the proteins, whose concentrations range from 0.1 μM to 0.1 mM. Examples of these variations are provided in Fig. 3, while typical electropherograms are shown in Fig. 4.

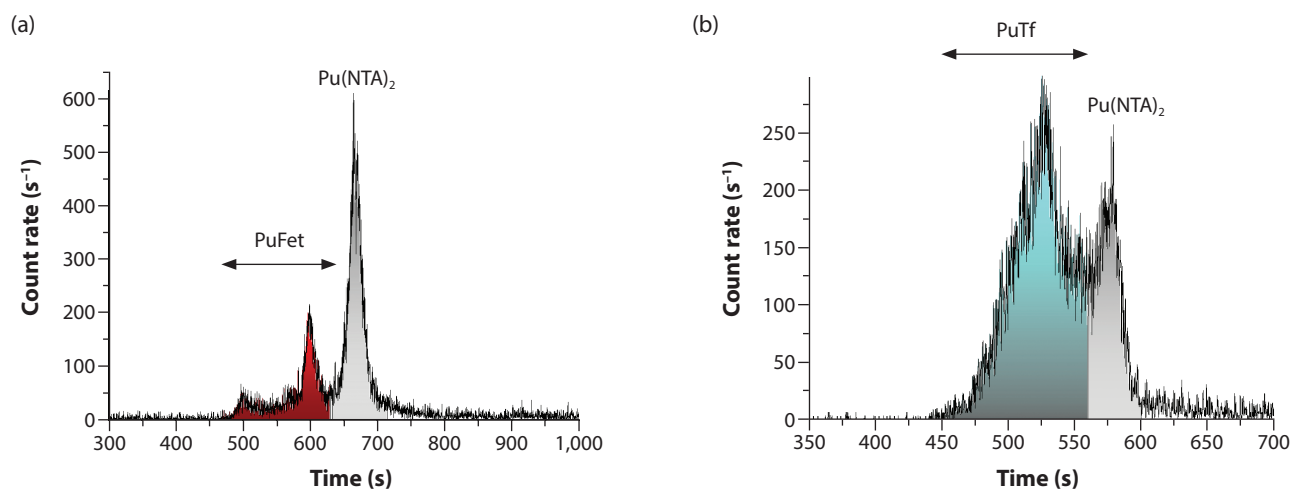


Figure 4. Electrophoregrams obtained via CE-ICPMS coupling for (a) a [Fet]/[NTA] ratio of 4 and (b) a [Tf]/[NTA] ratio of 5. Two peaks are associated with fetuin (which presents two different conformations with the same affinity for plutonium(IV)), while only one peak is detected for transferrin (only one conformation of the apo form). It can be noted that for similar protein concentrations (8 μM for Fet, and 10 μM for Tf) and an NTA concentration of 2 μM , Tf binds to plutonium(IV) more strongly than does Fet.

Fetuin and transferrin as potential vectors for Pu accumulation in the liver and bones

The theoretical biodistribution of plutonium between the liver and the bones can be estimated using the relative affinities of transferrin and fetuin for plutonium. Based on average blood concentrations of fetuin-A (15 μM) and unsaturated transferrin (70% of 30 μM), the relative distribution of plutonium between these two proteins depends on the ratio of their binding constants ($10^{26.44}/10^{26.20}$) and on the ratio of their concentrations in the bloodstream ($70\% \times 30 \mu\text{M}/15 \mu\text{M}$). The value of this ratio is about 2.5, i.e., a relative distribution of 71% for Pu-Tf and 29% for Pu-Fet. This partition agrees with experimental observations favoring the liver, but the concentrations of these proteins can vary from one individual to another. Because transferrin concentrations in healthy subjects range from 25 to 51 μM (or from 17.5 to 35.7 μM for the unsaturated forms), the resulting Pu-Tf/Pu-Fet ratios range from approximately 2 to 4, corresponding to partitions between 67/33 and 80/20. A similar observation can be made for fetuin, whose concentration can vary between 8 and 21 μM in healthy subjects.

These results must be compared with the *in vivo* data available in the literature. Stather and Nenot collected data with approximately 200 samples showing that the distribution between the liver and bones was between 0.57 and 0.23 $\text{pCi}\cdot\text{kg}^{-1}$, respectively, giving a partition of 71/29—identical to the result calculated using binding constants. In addition, five studies carried out in the 1970s using 25 autopsies of highly contaminated workers revealed an average relative distribution of 72% in the liver and 28% in the bones, but with significant variation among individuals (16–95% for the liver; 5–85% for the bones).

Thus, the physiological variations of transferrin and fetuin concentrations among individuals can, to a certain degree, also help explain these heterogeneous plutonium distributions. Importantly, fetuin-A concentration in infants and young children can exceed 20 μM , possibly explaining the greater plutonium accumulation observed in the bones of young organisms.

Conclusion

Because capillary electrophoresis is a non-intrusive technique (speciation is preserved), its coupling with ICP-MS provides an ideal tool for studying plutonium-protein interactions. Studies focusing on the interactions of plutonium with transferrin and fetuin-A proteins at near-physiological pH have been successful, supplying valuable information indicating that the driving force between these two proteins is primarily thermodynamic. This observation has led us to propose that the fate of plutonium in a body depends mainly on the relative concentrations of these two proteins in the bloodstream. Fetuin-A is highly concentrated in the bone matrix and its strong affinity for plutonium could now provide a convincing explanation for plutonium accumulation in the bones. We therefore suggest that fetuin-A is one of the carriers (serum citrate is another) that transport plutonium to the bones.

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Jean Aupiais presenting in the Environmental Behavior and Chemistry session at Plutonium Futures 2022.



Roxanne Tuthton

Roxanne Tuthton received a Ph.D in Applied Physics from the Colorado School of Mines in 2017. She was a postdoctoral research associate at Los Alamos National Laboratory from 2018 to 2020 and transitioned to a staff scientist position in T-4 in January, 2020. Her background is in density functional theory (DFT), density functional perturbation theory (DFPT), and molecular dynamics (MD) calculation methods. As an early-career scientist at LANL, she has collaborated on numerous projects involving the modeling of actinides and other strongly correlated systems.

Electronic Structure Modeling Strategies for Actinides

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Electronic structure theory is an essential tool in condensed matter research. It has been implemented in modeling tools such as quantum Monte Carlo, density functional theory (DFT), and tight-binding. It is widely used in modeling materials that span the periodic table. However, in materials where the lattice, charge, orbital, and spin degrees of freedom are strongly correlated, standard electronic structure theories fail. This is partially because most electronic structure modeling is based on the Schrodinger equation, and so cannot fully take into account relativistic effects. Another aspect is that standard techniques have a simplistic treatment of electron-electron correlations. For heavier atoms, actinides especially, this is a significant disadvantage. There are several ways around these issues: we can include a Coulomb parameter for the electron interactions, use mean-field theory models to capture correlations and spectral properties, and we can reformulate the mathematics in terms of the Dirac equation to better understand relativistic effects (there have been efforts in this direction using the RSPt code described by John Wills et al. in *Full-Potential Electronic Structure Method* published by Springer in 2010). The challenge of accurately modeling the electronic behavior of actinides has had significant attention from a small community of dedicated researchers due to its importance in quantum and nuclear materials science. In our research, we have explored several tools for addressing electronic behavior in actinides, and we have compared methods of modeling strongly correlated electrons for accuracy and efficiency. Which tool is the best? Ultimately the answer to this depends on the questions we are asking.

The plutonium challenge

The mysteries around f electron behavior have stimulated numerous contributions to literature over the years and produced even more questions. This is particularly true of plutonium, which has been the focus of a great number of studies due its complexity, exotic physics, and central importance in key areas of nuclear science and engineering. Plutonium has six allotropic phases, each of which present challenges to the task of theoretical modeling. The 25% volume contraction between the α and δ phases, the questions around magnetic ordering, and the quantum entanglements between localized and itinerant electrons are a few of the frequently examined questions surrounding this exotic material. By pursuing the goal of describing plutonium metal and its alloys, researchers have made considerable advances in electronic structure modeling for f electron materials and compounds over nearly four decades.

A compendium of techniques

In 1985, Wienberger used a relativistic KKR-Greens function technique to examine the electronic structure of δ -plutonium and several plutonium alloys. In the 1990s, pioneering DFT calculations began a long sequence of studies that would explore the effectiveness of various approximations including exchange

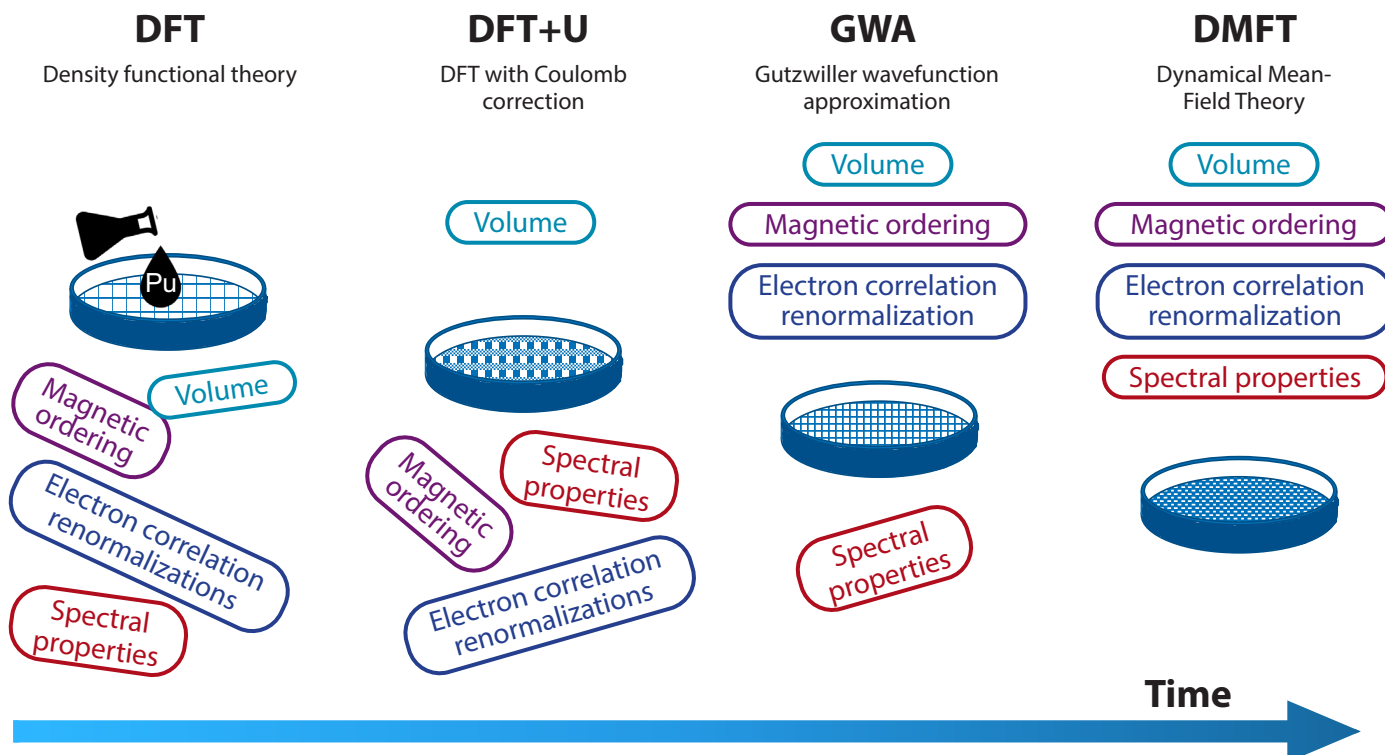


Figure 1. Electronic structure methods: Conceptually each of the methods are represented by strainers with increasingly fine meshes. The finer the mesh, the more sophisticated the method’s treatment of electronic correlations. The fastest method is DFT then the increasingly sophisticated methods are DFT+U (shorthand for LDA/GGA+U), the GWA, and DMFT. The more information the method can calculate, the more time it requires.

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correlation functionals, orbital polarization, and Coulomb interactions. The 2000s was dominated by investigations into the magnetic ordering of plutonium’s electrons. Though no long-range magnetic ordering has been observed for any phase of plutonium, theoretical calculations performed using DFT, within either the local density approximation (LDA) or generalized gradient approximation (GGA), can only reproduce the characteristic volume expansion for δ -plutonium by including artificial orbital polarization. This is also the case for DFT with the addition of a Coulomb parameter (LDA/GGA+U) to simulate static electron-electron interactions (see Further Reading for more information).

Around the same time, mean-field theory methods showed promising results modeling quantum entanglements between the localized and itinerant electrons by treating the electron-electron interactions as dynamic fluctuations. For example, dynamical mean-field theory (DMFT) is able to describe the electronic characteristics of plutonium, including its volume contraction, in good agreement with photoemission data as well as predict the valence fluctuations validated by neutron spectroscopy without resorting to adding orbital polarization. This has led to two debated explanations of the role of magnetism in plutonium. The first is the “disordered local moment” described by Niklasson et al. in “Modeling the actinides with disordered local moments” published in *Physical Review B* in 2003. This is also known as the “static” model, which describes the orbitals as individual localized magnetic moments that are spatially and temporally disordered such that any

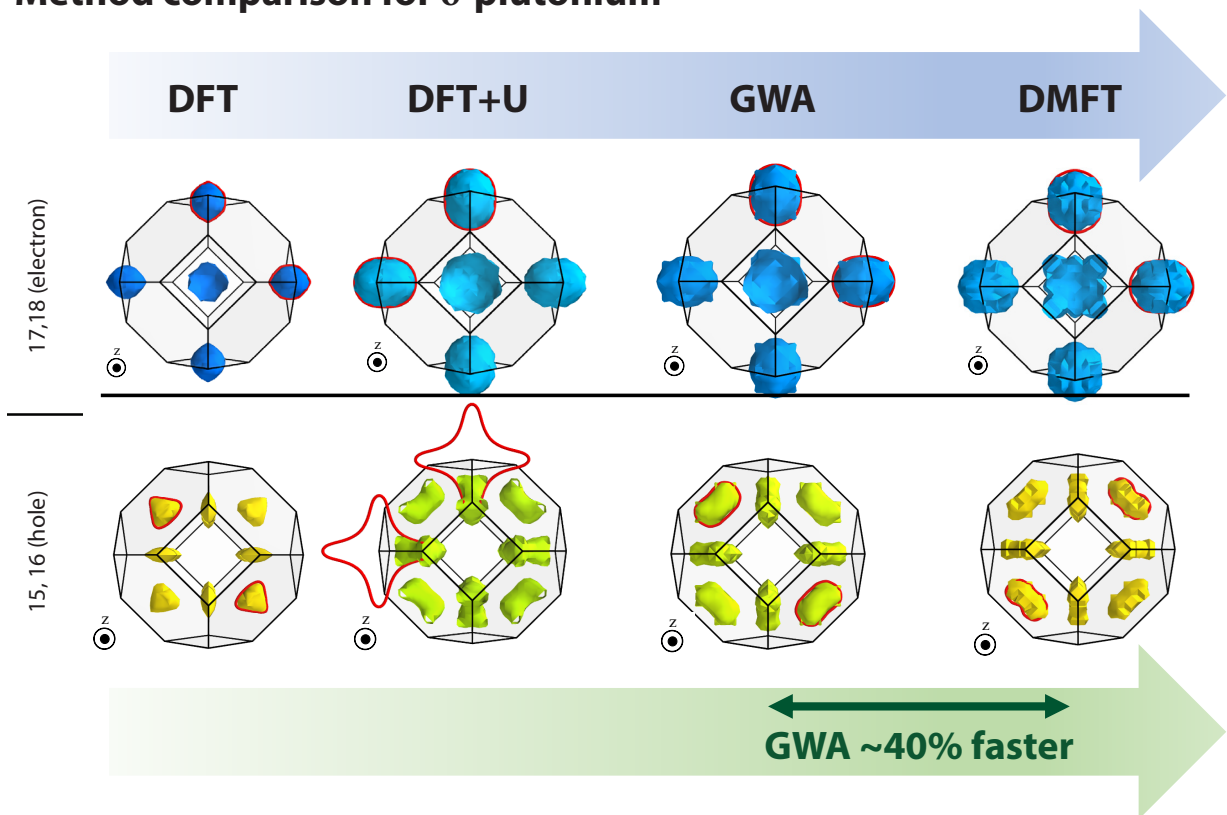
Method comparison for δ -plutonium

Figure 2. Fermi surface comparisons: Fermi surfaces were calculated for δ -plutonium using four electronic structure methods. Each calculation was performed with spin-orbit coupling and without orbital polarization. The calculations performed with the GWA were comparably accurate compared to DMFT and they required roughly 40% less computational time. A full analysis of the results can be found in Tutchtou, et al., Phys. Rev. B 101, 245156 (2020).

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long-range magnetic ordering is obscured by averaging over time. The second is the “valence fluctuation,” or dynamic, model as captured by DMFT and notably described in “The valence fluctuating ground state of plutonium” by Janoschek et al. in Science Advances in 2015. This method predicts quantum entanglements between the localized magnetic moments and the itinerant conduction electrons resulting in valence fluctuations that effectively screen the magnetic ordering below the material’s Kondo temperature. Effectively, the mean-field theory approach more accurately describes the physics of strongly correlated electrons, which is a key piece of the plutonium mystery that many studies have been exploring.

While DMFT offers more accurate results than DFT, it is a computationally expensive and time-consuming calculation (Fig. 1). An alternative mean-field theory approach uses the Gutzwiller wavefunction approximation (GWA) first described in 1965 by Martin C. Gutzwiller in Physical Review. Like DMFT, this method has been used to successfully calculate the volume dependence in plutonium phases without the addition of artificial orbital polarization. The combination LDA (or GGA) and GWA formulation has the same mathematical structure as LDA combined with DMFT, with the difference that it assumes infinite quasiparticle lifetimes. This makes the GWA method less accurate for calculating quantum entanglement effects

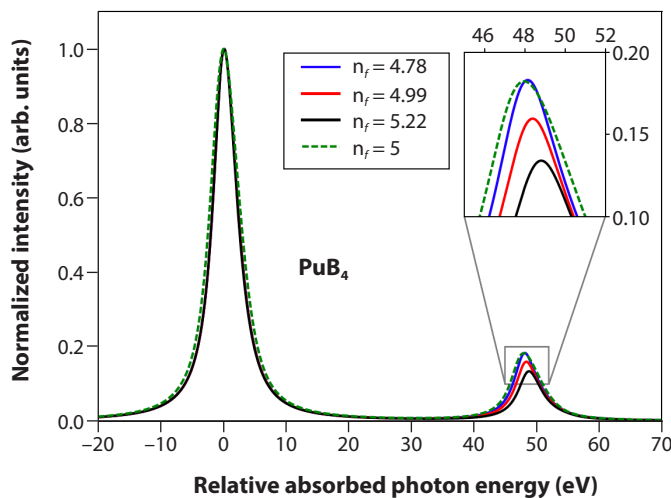
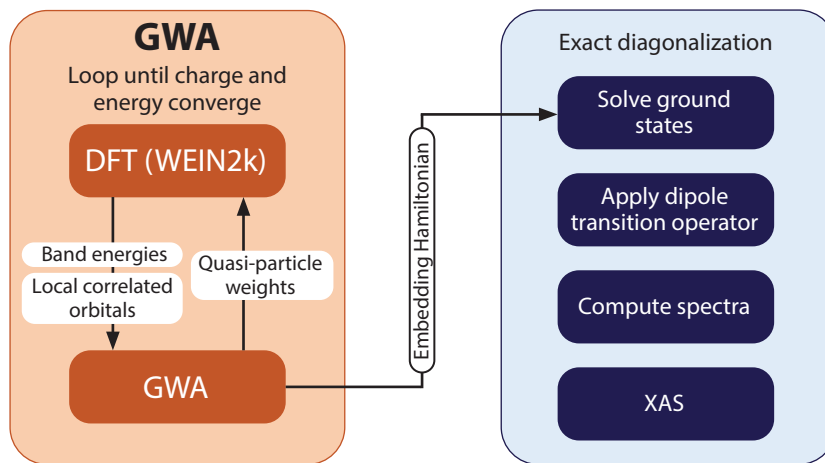


Figure 3. Beyond electronic structure: The flexibility of the GWA method allows us to extend our calculations beyond basic electronic structure calculations. On top is a diagram of the computational workflow from the Cygutz GWA implementation described in Lanatà, et al., *Phys. Rev. X* 5, 011008 (2015) through the exact diagonalization process to calculate the X-ray absorption spectra for PuB_4 , shown below. The details of this calculation are fully explored in Chiu, et al., *Phys. Rev. B* 102, 085150 (2020).

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than DMFT, however it is significantly less computationally demanding and does capture important physics of the electron-electron correlation effects. However, the GWA method is still significantly more time consuming than DFT or the LDA+U methods that require orbital polarization to capture key features of plutonium. There is, therefore, a need to consider strategies to perform calculations on plutonium and other actinide materials. It is relatively common for researchers to use a DFT method with an anti-ferromagnetic configuration for plutonium phases as an approximation for the correlation effects. This technique is essentially understood to give the correct volume expansion for the wrong reason, but it is much more flexible for complex simulations where supercell structures are required to examine alloys, surfaces, lattice dynamics, etc. It can also be used for DFT-based molecular dynamics calculations that may help to understand details of interatomic interactions.

Choosing the right method

The question, then, is which tool or method is appropriate for the questions we are trying to answer. With the more comprehensive techniques we may be able to get more complete data, but the price is time and computational resources, so we need to be strategic and choose the best method based on the requirements of the material and what we want to know about it. For heavier elements, plutonium especially, DFT will not be able to capture a significant scope of the electronic behavior, but if a large supercell is necessary to model an alloy, defect, or any dynamics, DFT may be the only practical option. Adding a Coulomb interaction with a DFT+U method and/or orbital polarization may be useful approximations that improve the overall results, but we will still miss important physics. With the GWA and DMFT, we start to see results that match experimental observations. Using the GWA, we sacrifice some of the spectral information by approximating infinite particle lifetimes but we save time compared to DMFT (Fig. 1). So, depending on what we need to know for a given calculation, the GWA can be a strategic choice for plutonium and other strongly correlated materials.

As an example, each of the discussed methods has been applied to δ -plutonium in “Electronic correlation induced expansion of Fermi pockets in δ -plutonium,” published in Physical Review B in 2020. In this work, we examined the Fermi surfaces to study the electronic correlations in momentum space (Fig 2). We included spin-orbit coupling in all methods, but no orbital polarization. Both the GWA and DMFT were able to capture the electronic correlations, but the GWA was roughly 40% faster than DMFT. This is also applicable to other strongly correlated materials including actinide and lanthanide compounds and alloys. Another advantage of the GWA is that because the computational expense is less intense, we can use the results to go beyond the electronic structure to model more complex material characteristics such as X-ray absorption spectra. We showed this with PuB₄ in the 2020 Physical Review B article “Hybridization effect on the x-ray absorption spectra for actinide materials: Application to PuB₄” by Chiu et al., where the end result can be directly compared with experimental results (Fig. 3). There are additional opportunities to use the GWA to explore novel quantum materials in which strong electronic and spin correlations play key roles in superconductivity.

Summary

The methods discussed here are not the only first principles modeling techniques that can be used to calculate the electronic structures of strongly correlated materials. The challenge of these types of complex materials has and will continue to require a full exploration of the capabilities of many different techniques and tools. DMFT is a powerful method that is able to capture the physics of strong electronic correlations, but it is also computationally demanding and limited to structures that can be represented by relatively small unit cells. The GWA is slightly less accurate but allows for much more efficiency in terms of computational resources. This creates space for some flexibility in the types of physics and structures that may be studied. DFT, while not able to capture much of the physics of the electron-electron correlations, is still a useful tool to address a great deal of the groundwork research that still needs to be performed for the actinides. Rather than discarding the results we have obtained using DFT, we can use what we learn from the compendium of theory techniques and interpret the data from each method according to its limitations. The tools for truly accurate modeling of *f*-electron materials and strongly correlated systems are still being formed. It is necessary to use and expand the tools that we have to study the electronic structures of these materials and take the next step in accurate first principles modeling.

Acknowledgments

Thanks to Wei-Ting Chiu, Jian-Xin Zhu, R. C. Albers, G. Kotliar, and, F. Ronning, Giacomo Resta, Tsung-Han Lee, Eric D. Bauer, Richard T. Scalettar, Q. Si, J. Singleton, P. Wolfle, N. Harrison, J. M. Wills, and G. Zwicknagl for helpful discussions. This work was carried out under the auspices of the U.S. Department of Energy (DOE) National Nuclear Security Administration under Contract No. 89233218CNA000001. The Fermi-surface topology analysis work was supported by the LANL LDRD Program. The DFT + DMFT simulation work at high temperatures was supported by the NNSA Advanced Simulation and Computing Program. It was, in part, supported by the Center for Integrated Nanotechnologies, a DOE BES user facility, in partnership with the LANL Institutional Computing Program for computational resource.



Roxanne Tutchton presenting in the Condensed Matter Physics session at Plutonium Futures 2022.

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Ping Yang

Ping Yang serves as the Deputy Director of the G.T. Seaborg Institute for Transactinium Science and a Staff Scientist in the Physics and Chemistry of Materials group of the Theoretical Division at LANL. Yang's research aims to elucidate the fundamental electronic structure and reactivity of actinides complexes, nanoparticles, and surfaces. She holds a keen interest in leveraging high-performance computing frameworks and data science to develop new computational techniques for simulating complex actinide systems over long timescales, and to accelerate f-element separation.

Simulating Dynamic Actinide Systems: Perspective on Methodologies

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Great strides have been made in the last few decades to shed light on the fundamental electronic structures of actinide complexes and materials. First-principles calculations, including density functional theory (DFT) and wavefunction-based methods, have been instrumental in predicting structures, elucidating the role of d- and f-orbitals in bonding, and in extracting electronic structure information from the complex spectroscopic data of actinide materials and molecular systems.

While great advances have been made in the fundamental understanding of actinide complexes and materials through first-principles calculations, the field continues to evolve with a growing need for new approaches to give faster and more chemically realistic dynamical simulations, beyond static calculations. Some of the challenges include understanding the chemical coordination environment of actinides and lanthanides in solution, mass transport in actinide/lanthanide separation processes, surface reaction mechanisms, electrochemistry, and phase transitions in actinide materials and their mechanism as a function of temperature and pressure. Fig. 1 highlights two complex examples of surface and solution chemistry of uranium for which we have limited understanding at the molecular level. The dynamic simulations are essential for a deeper understanding of these complicated processes in actinide science, however, they also bring new challenges, particularly in developing an accurate description of the diverse and dynamic nature of redox-active actinides. In this article, we present a brief overview of the current methodologies for simulating dynamic actinide systems and offer our perspective on the future directions in which this field could beneficially evolve.

Molecular dynamics

Molecular dynamics (MD) simulation is an extremely powerful technique because it gives a realistic picture and sampling of the atomic conformation space. Besides being a phase space sampling technique, yielding coordinates and momenta, this technique allows for the study of time-dependent phenomena such as diffusivities, solubilities, ligand residence times, and ligand exchange dynamics. MD simulations have been a crucial tool to address dynamic effects in many research areas, for example in materials science and biological systems, leading to groundbreaking discoveries.

Conceptually, molecular dynamics is very intuitive. Given the potential energy of a system, typically as a function of the positions of all the nuclei, the forces on each atom are calculated. Setting initial conditions with the atomic coordinates and velocities, the equations of motion are numerically integrated in discrete steps of time, giving the trajectory of all the atoms in the system. Techniques for integrating

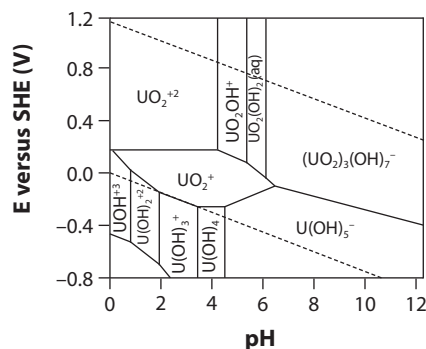
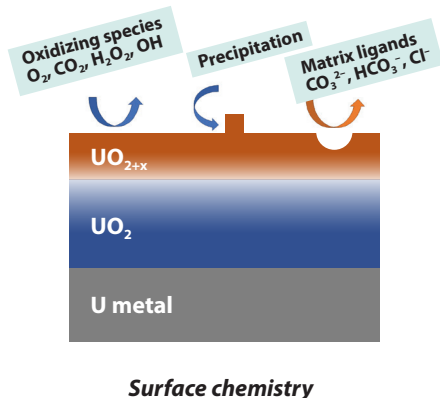


Figure 1. *Left:* Schematic diagram of the complex surface chemistry of uranium. *Right:* A plot of electric potential versus pH for an aqueous solution of uranium (reproduced from Paquette and Lemire, Nucl. Sci. Eng., 1981, 79, 26). These examples illustrate the variety of factors that can affect chemical reactions in actinide science. Our understanding of these processes at the molecular level remains poor, however, especially compared to analogous reactions with elements from other groups of the periodic table.

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the equations of motion in different thermodynamic ensembles were developed more than 70 years ago and algorithms for evolving the trajectories are in a highly optimized state, allowing for large-scale simulations. When using molecular dynamics to study actinide sciences, additional complexities stem from the redox sensitivity inherent to most actinide systems. Multiple oxidation states can coexist or change during the reaction process, requiring a description of the change in oxidation states for the same element in one simulation cell. In these situations, elements of the quantum-level theory should remain, in spite of the approximations, to capture events such as charge transfer and redistribution processes dynamically.

Depending on the level of theory at which the potential energy surfaces are calculated, the simulations can be largely divided into three categories: first-principles MD, semi-empirical MD, and classical MD, with increasing levels of approximation. All three levels have their pros and cons, going from more accurate and portable yet very computationally time consuming, to computationally fast at the expense of introducing approximations.

A range of approximations exist in the literature and here we remark on two approaches: the development of empirical functions—simple functions of the nuclear positions—and semi-empirical formulations which preserve the electronic degrees of freedom that are removed in the empirical approach, albeit with parameterized dependence. Both have their advantages and disadvantages, stemming from the simplifications incurred. Empirical methods gain speed at the expense of removing electrons from the system, whereas the semiempirical methods retain the electronic effects however at higher computational cost.

Quantum mechanical potential energy surfaces

The most accurate methods to compute potential energy surfaces are quantum-mechanics-based. Whereas solving Schrödinger's equation for more than a handful of atoms is unfeasible, DFT provides a reasonable alternative. To obtain the forces on the atoms requires computing the molecular orbitals for all the electrons in the



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system and then using these electronic states to calculate the energy gradient as a function of the nuclear positions. Currently, the two most widely used methods in this domain are the DFT-based Car-Parrinello Molecular Dynamics (CPMD) and Born-Oppenheimer Molecular Dynamics.

Electronic structure methods are very attractive because they are completely transferable (do not depend on what molecule one is studying) and the charge state of the atoms naturally arises from the simulation. Hence, first-principles MD simulations have been successfully applied to various systems to provide atomic pictures, such as molten salts and fast chemical reactions which can reach equilibrium at short timescales.

While accurate, these simulations are computationally demanding and very difficult to scale to take advantage of high-performance computers. Currently, modern methods that can accurately simulate systems containing heavy elements are limited to roughly 200 atoms (Fig. 2), taking on the order of three minutes for one calculation of the atomic forces, limiting its applicability to very short MD trajectories (picoseconds) with wall-clock simulation times reaching weeks. To achieve a reasonable sampling, trajectories on the order of hundreds of picoseconds are needed, involving approximately 200,000 calculations of the forces (taking over 400 days!). The short timescale may not provide sufficient statistical information, leaving critical questions unanswered, particularly in areas such as surface corrosion processes, which involve phenomena such as oxygen migration that often occur at nanosecond timescales or longer.

Furthermore, the time-per-force computation scales with the cube of the number of atoms in the system, or $O(N^3)$, therefore, trajectories incorporating thousands of atoms are unfeasible with this level of theory. While these approaches provide valuable insights into short-range interactions, they present challenges in fully capturing the complexities of actinide systems. For example, the limited length scale in these simulations often fails to adequately represent the second or third coordination shells.

The key computational expense is the calculation of the total energy of the system and its derivatives, i.e., the forces on each atom. Therefore, the time to compute

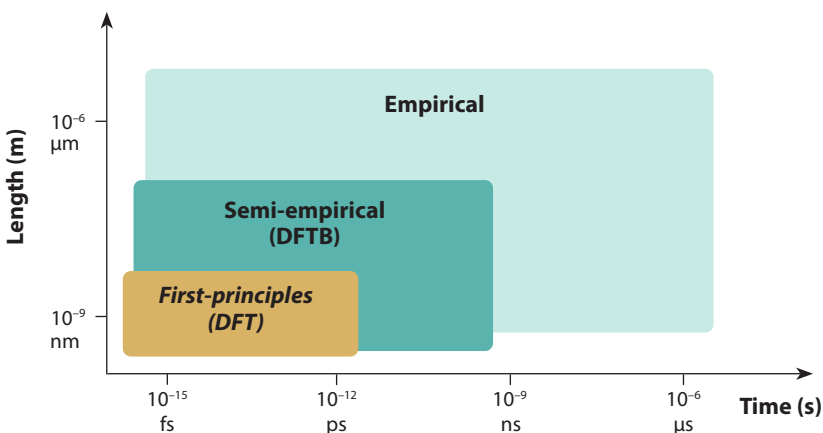


Figure 2. Various methods for molecular dynamics simulations and their time-length scales.

the forces is pivotal in the usefulness of the MD technique. To address these shortcomings that derive from the high computational demand of the first-principles methods, approximated forms of the energy function have been developed.

Empirical potential energy surfaces

The key ingredient for an MD simulation is the potential energy function $U(\mathbf{R})$; the quality of the simulation will only be as good as the accuracy of this function. The large-scale MD simulations found in the literature are based on empirical interatomic potentials, i.e., functions of the inter-nuclei positions, \mathbf{r}_{ij} . These functions are developed empirically and fitted to physical properties (e.g., diatomic dissociation curves, samplings of potential energy surfaces by massive ab initio calculations, radial distribution functions, etc.). These empirical potentials combined with the latest algorithmic developments of computation and parallelization are very fast. Simulations of, for example, shocks through materials can be performed with millions of atoms for extended timescales to visualize reorganization of materials and defect formation. These large simulations most often involve light elements in systems such as explosives or biological matter, where the interatomic interactions are simpler than those among f-elements, and mature potentials have been developed.

The development of accurate empirical potentials for the actinides can be surprisingly difficult because a single function of \mathbf{r}_{ij} needs to be derived that accurately mimics the radial, angular, and polarization nature of all the electrons combined. One approach taken in the past to tackle these difficulties has been to consider whole molecular units, such as UO_2^{2+} , H_2O , etc. However, for example, if the pH of the solution were to change, requiring H_2O dissociation into OH^- and H^+ , this would call for further development of the model. Capturing changes in oxidation state with these approaches is difficult, although techniques have been developed that introduce charge as a dynamical variable and electronegativities as parameters, although this approach has not been used for simulating actinides, as far as we are aware. On the other hand, situations such as ion migration and coordination present more benign modeling conditions and lend themselves to study via empirical potentials, with all the advantages of computational speed that this confers. To make the development of empirical potentials for actinides approachable, research groups have explored a few methods such as simulating the interaction of the late actinides as spherical units via 12-6-4 Lennard-Jones type functions or reducing the complicated electronic structure of the actinide ion by folding it into simulations of the UO_2^{2+} ion as a unit. More sophisticated polarizable force fields have been developed for some actinide ions and applied to simulate liquid-liquid separation.

In the last five years, the field of machine learning (ML) has been making inroads into the parameterization, or training, of interatomic potential energy functions. Success has been reported for light elements but the application of these approaches to the f-elements is in its infancy. The ML universal potential M3Gnet has been trained throughout the periodic table, including the actinides. These potentials show great promise for their speed and we expect to see them becoming very useful in the foreseeable future.

In the chemical reactions of actinide and lanthanide systems, it is imperative to include a description of charge transfer and chemical bond dissociation/formation for accuracy and interpretability. To capture effects that are purely electronic in nature, methodologies are needed that explicitly include the electronic degrees of freedom, even if in parameterized form. The first-order approximation of such approaches comes from the self-consistent-charge (SCC) methods which we discuss next.

Semi-empirical methodologies

A middle road between first-principles and empirical methods is a family of semi-empirical methodologies that preserve the electronic degrees of freedom that were removed in the empirical potentials described above. They reduce the computational cost to 1/100th or 1/1000th of their parent quantum methods, hence they are able to describe the charge transfer process and bond-breaking and forming.

The semi-empirical methodologies are based on a functional Hamiltonian and approximated wavefunction equation, albeit with certain approximations (see below). Minimum basis sets methodologies with parameterized Hamiltonians based on Hartree-Fock have been derived starting with the Huckel model and a number of improvements that applied for light elements. This development has not however been extended to the 5f-elements, and would prove a challenge given the complicated electronic structure of the 4f- and 5f-elements and the drastic simplification implied by the minimum basis assumption.

Density functional tight binding (DFTB) is an attractive approach to achieve a rapid calculation of forces in the same manner as the empirical potentials while retaining the electronic degrees of freedom explicitly, as with DFT. In simple terms, this approach uses a similar formulation to DFT, in the sense that the governing equations are also a diagonalization of a Hamiltonian problem, although in order to speed up the calculation, the Hamiltonian is parameterized for the different types of interactions and as a function of the relative interatomic distances. Hence, matrix elements between two basis functions, which would involve computing the double volume integral, are reduced to a simple arithmetic calculation (function of \mathbf{r}_{ij}), decreasing the computational cost enormously. Implementations of DFTB have been reported to be as efficient as linear scaling between the computational cost (hours to run the calculation) and the number of particles (atoms or electrons). This could enable large-scale, long-duration simulations required for realistic molecular dynamics simulations of solution environments. These time-saving improvements are encouraging, allowing DFTB to reach thousands of atoms in a realistic MD simulation. Furthermore, because DFTB is quantum mechanical in nature it captures many-body effects, formation of covalent bonds, charge transfer between species of different electronegativities, and spin polarization (open-shell atoms). Hence, it is well suited to the simulation of interactions in liquids.

As highlighted above, the elements of the Hamiltonian matrix are parameterized, that is, written as a function of the interatomic separation vectors. Here lies the main difficulty of making DFTB usable, in the production of such functions that accurately capture the behavior of the Hamiltonian for an arbitrary atomic configuration. We should add that, because the parameterization is for matrix elements, one would expect the development of accurate parameterizations to be easier than parameterizing a whole interaction empirical potential, although this is far from a trivial exercise. A scaling difficulty still remains because the Hamiltonian matrix elements are for pairs of atoms. Therefore, the parameterization of DFTB will correspond to pairs of atom types. For example, H-H, O-O, and O-H parameterizations are required to simulate an aqueous medium, yet, unlike with an empirical potential, these parameters will also be useful if the medium contains OH, O₂, H₂O₂, etc. If one wanted to simulate uranyl ions (UO₂²⁺) in water, parameterizations of U-O, U-H, and U-U terms should be added to the previously stated ones. For each new element to be included in a simulation, all the pairs of terms should be parameterized in advance. Without the parameterization for specific atom types, no MD trajectory can be simulated.

Currently, only a few groups around the world are dedicating efforts to developing parameterizations for DFTB, and the accuracy of each set of parameters will depend on how the group developed it. At least one DFTB parameterization currently exists for each element in the periodic table—except for the 5f-elements. Unfortunately, there is a dearth of models available for simulating f-block elements with only two sets of parameters published to date, namely, interactions of Pu–H, developed for solid-state simulations, and the U–O–H system, for aqueous solution chemistry of uranium. These are the first attempts to obtain promising results, but improvement is still needed. Furthermore, parameterizations of interactions with other elements, such as U–C, U–N, U–Cl, etc., and not only uranium but all the 5f-elements are very much needed to study actinide complexes and model chemical processes with the solvents used in the laboratory.

Outlook

Our understanding of the intricacy of actinide systems has come a long way, yet numerous questions remain unresolved. As we progress, it is essential to address the urgent need for methodological advancements to navigate the challenging time and length scales we encounter, ensuring a thorough statistical sampling of phase space.

To be predictive for actinide chemistry across a wide spectrum of chemical systems, we are in serious need to expand the chemical space of the above parameterized methodologies such as DFTB and empirical potentials. This is essential to properly capture charge transfer and chemical reactivity. However, in expanding the parameter space to encompass a wider range of chemical reactions the number of high level (DFT, multi-reference, etc.) calculations will rapidly increase and with it the computer time demanded. To reduce this burden and increase efficiency, we see the incorporation of advanced machine learning techniques, such as active learning,



Ping Yang presenting in the Compounds, Complexes, and Coordination Chemistry session at Plutonium Futures 2022.

and physics- and chemistry-informed techniques, to be an essential step in the training process.

Furthermore, exploring kinetics simulations beyond sampling is vital as it elucidates reaction pathways for rare, rate-determining events, yet is understudied. A pivotal, but unaddressed question involves determining the influence of particular actinides on both the kinetics and complex reaction networks. For example, variations in f-element configurations across the series may significantly influence reaction outcomes, leading to a diversity of products. Therefore, the role and effects of 5f electrons across the actinide series remain an open question.

Finally, coupling machine learning techniques with methodologies development, as well as with simulation techniques, will enable multi-fidelity and multi-scale simulations. Such approaches appear promising not only to increase the prediction accuracy but also to improve the time and length scales, facilitating more effective simulations of the complex chemistry and materials of actinides.

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Enrique Batista presenting in the Solution and Gas-Phase Chemistry session at Plutonium Futures 2022.



Interview: Poster prize winner Julien Margate

Thank you for agreeing to this interview! Please tell us about yourself, what is your current position?

My name is Julien Margate, I am 26 years old and I come from Paris, France. I am currently doing a PhD in the physical chemistry of actinides at the Institute for Separation Chemistry in Marcoule (ICSM) in the Laboratory for Sonochemistry in Complex Fluids (LSFC). My thesis is conducted under the supervision of Sergey Nikitenko and Matthieu Virot from ICSM and is carried out in collaboration with Philippe Moisy and Thomas Dumas from CEA Marcoule. I am in the third and final year of my thesis, which deals with the preparation, structural characterization, and reactivity of actinide peroxides. My research involves studies with uranium, which are performed at ICSM, while experiments with plutonium are performed at the Atalante facility in a dedicated glove box.

What does your research into uranium involve?

My research focuses first on the formation of uranyl peroxide. Recent studies show that the formation of mineral uranyl peroxides, metastudtite and studtite, can be observed in geological storage conditions (by oxidation of uranium dioxide) or following a nuclear accident, e.g., Fukushima. The formation of uranyl peroxides resulting from radiolysis can thus lead to the corrosion of nuclear fuel and the release of radionuclides in the surroundings. Sonochemistry, which deals with the effect of powered ultrasound on chemical reactions, is known to share some similarities with radiolysis particularly through the in-situ generation of hydrogen peroxide resulting from water molecule splitting. Therefore, this approach can be used as an original alternative to evaluate the effect of hydrogen peroxide on actinide materials, and has been investigated for several years by the ICSM sonochemistry group. Careful choice of parameters can give a dramatic spike of hydrogen peroxide production under mild conditions with observation of additional physical effects, e.g., erosion of solids, mass transfer, fragmentation, etc.

Tell us more about your investigations using sonolysis

I have been studying the sonolysis of uranium dioxide in pure water and slightly acidic media under oxygenated atmosphere. After the preparation of well-characterized uranium dioxide platelets using the oxalic route, we observed complete conversion into metastudtite under ultrasound. Detailed investigations on the remaining solutions using UV-Vis. absorption spectroscopy and ICP-OES and solid residues using SEM, XRD, and FTIR techniques allowed us to attribute this behavior to the sonochemical generation of hydrogen peroxide. The formation of crystalline studtite structures was observed on the surface of uranium dioxide platelets with a preservation of morphology, suggesting a complex formation mechanism other than classical dissolution/reprecipitation. Interestingly, under specific sonochemical conditions, center-holed platelets are observed. We proposed a mechanism based on a sonocapillary effect giving rise to circulation of the reactants within the oxide. This led to a publication in the Journal of Hazardous Materials in 2023 and a poster prize at the conference Plutonium Futures 2022.



Julien with colleagues at the poster session of Plutonium Futures 2022.

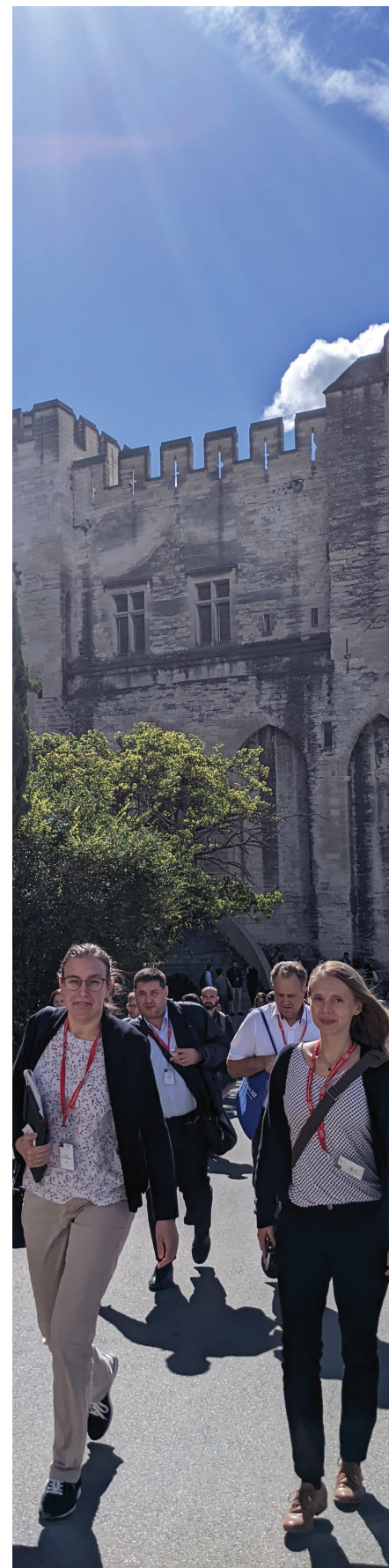
Can you tell us about your plutonium work?

My plutonium studies examine the formation of plutonium peroxide species. Over five decades ago, the formation of plutonium peroxy complexes was described through the addition of hydrogen peroxide to acidic plutonium(IV) solutions, leading to the creation of colored complexes, which transition from brown to red as the concentration of hydrogen peroxide increases. Excessive quantities of hydrogen peroxide relative to plutonium result in the formation of green precipitates, which have been used as precursors for plutonium dioxide or in waste management processes. Various structures have been proposed for these complexes and solid compounds, but definitive evidence has remained elusive until now. During my thesis, we synthesized a new peroxy-based compound of tetravalent plutonium by adding dilute solutions of plutonium(IV) previously stabilized in nitric media into highly concentrated hydrogen peroxide solutions at a pH of 1–2. The as-prepared solution of green color was found to be very stable. Vibrational and spectroscopic investigations confirmed the peroxide and polynuclear structure of the compound. The latter bears striking similarities to the green solid compound used historically in the nuclear industry and during the Manhattan project. This discovery sheds new light on a chapter of science deeply intertwined with the history of nuclear research. A publication on this work is currently under submission.

How did you become an actinide scientist?

I started my academic journey by pursuing a degree in chemistry with a specialization in physical chemistry and spectroscopy at the University of Paris-Saclay in France. I successfully graduated with distinction, obtaining a comprehensive understanding of physical chemistry, complemented by a robust grounding in geoscience. As my academic path unfolded, I directed my focus towards nuclear sciences, choosing relevant study projects and optional subjects to align with this interest.

Diving into the realm of scientific research, I undertook multiple internships in research laboratories, exploring diverse areas such as materials under irradiation, spectroscopy, and geochemistry. Subsequently, I enrolled in the nuclear engineering master's program at University of Paris-Saclay and the ChimieParisTech engineering school. This internationally renowned program, conducted in partnerships with



research institutes such as IJClab and CEA, as well as prominent nuclear industry players like EDF, CEA, Orano, and Framatome. Delivered in English, this program attracts high-caliber students worldwide and covers a broad spectrum of nuclear-related topics, ranging from the nuclear fuel cycle to reactor physics, nuclear power plant design, and waste management. During this program, I learned a lot about nuclear science, including radiochemistry, chemistry under radiation, nuclear physics, and nuclear engineering, and received the EDF Excellence Scholarship. In my final year, I specialized in actinide chemistry and chemistry under radiation, and I proudly completed my master's degree with honors.

What first drew you to study plutonium?

I find this a complex question. I have always loved science and how it shapes our world. When I was studying physical chemistry, I got into some cool subjects like the physicochemistry of d- and f-block elements, nuclear physics, and radiation chemistry. That is when I discovered a real interest in actinide chemistry. After doing research at IJCLab (Laboratoire de Physique des deux Infinis Irène Joliot-Curie) in Orsay, France, during an internship, my interest in this field got even stronger. Therefore, I decided to pursue a master's in nuclear studies based on my professors' advice. I delved deeper into nuclear sciences, focusing on fundamental physicochemistry, especially in radiation and actinide chemistry. Later on, I chose to continue with research, going for a PhD. I got a thesis topic on actinide peroxides at CEA Marcoule, recommended by one of my professors. It perfectly matched my interests, so I went for it. This topic examines the chemistry and structure of actinide peroxides, with a focus on uranium and plutonium due to their use in industries and the military. Lastly, what makes plutonium truly beautiful is not just its scientific importance but also the mesmerizing colors it displays in different oxidation states. From vibrant yellows to striking reds and purples, these colors result from the interplay between plutonium's electronic structure and its surroundings, adding an artistic touch to its exploration in the periodic table.

Julien is finishing his PhD this year and looking for a post-doc abroad in actinide chemistry, possibly in the United States.









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Actinide Research Quarterly is published by Los Alamos National Laboratory and is a publication of the Glenn T. Seaborg Institute for Transactinium Science, a part of the National Security Education Center. ARQ (est. 1994) highlights research in actinide science in such areas as process chemistry, metallurgy, surface and separation sciences, atomic and molecular sciences, actinide ceramics and nuclear fuels, characterization, spectroscopy, analysis, and manufacturing technologies.

LA-UR-24-23342

Address correspondence to:

Actinide Research Quarterly
c/o Editor
Mail Stop T-001
Los Alamos National Laboratory
Los Alamos, NM 87545

ARQ can be read online at:

www.lanl.gov/arq

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Los Alamos National Laboratory is operated by Triad National Security, LLC, for the National Nuclear Security Administration of U.S. Department of Energy (Contract No. 89233218CNA000001).

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