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CEA's R&D on advanced fuel treatment with multi-recycling of plutonium and uranium

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Abstract – *The full closure of the fuel cycle stems from the progressive deployment of plutonium and uranium multi-recycling using Fast neutron Reactors (FR) associated with advanced fuel treatment/recycling. On the basis of industrial experience with the present closed fuel cycle and taking advantage of past pilot-scale demonstrations of FR fuel treatment in France, R&D is being conducted in the CEA to move forward in the adaptation and optimization of the overall treatment/recycling process. The main R&D subjects concern increased quantities of fissile material in some key steps of the process: the head-end, because of a growing need for Pu based fuel treatment capacities (LWR and FR MOx), the separation step, because of higher Pu/U ratio, and the conversion and production stages to fabricate MOx fuels from recycled Pu and U. The different features of wastes from FR assemblies compared to those from LWRs may require significant optimizations considering future industrial deployment. The main R&D program orientations and recent achievements are presented in this paper.*

I. INTRODUCTION

Objectives for Generation IV nuclear energy systems were proposed in a 2002 technology roadmap shared by many countries¹. Sustainability, together with economics, safety and reliability, as well as proliferation resistance and physical protection, are important goals for these advanced systems. The objectives were recently confirmed within the Generation IV International Forum (GIF)².

Sustainability can be ensured by repeatedly recycling the fertile/fissile material present in spent fuels with more than 95 wt% of reusable elements. Moreover, only around 0.6% of the extracted natural uranium is used in an open fuel cycle, around 0.8% in the present closed fuel cycle (together with a large decrease of the volume and impact of the final wastes), while there would potentially be more than 80% with a fully closed fuel cycle. The advent of this fully closed fuel cycle requires a Fast neutron Reactor (FR) fleet in order to exploit the energy potential of the fertile ²³⁸U, by far the major part of natural uranium. The vector of this better use is the fissile plutonium simultaneously

generated from ²³⁸U and consumed to produce energy in a fast-neutron spectrum. This sustainable energy production therefore depends on the multi-recycling of plutonium and uranium.

Achieving this type of closed fuel cycle could offer large benefits in terms of resource savings, energetic independence from fossil fuels, low-CO₂ energy production and reduced environmental impact³.

The deployment of this full closure of the cycle is progressive⁴, involving the retrieval of plutonium from Light Water Reactor (LWR) UOX fuel and then its concentration in LWR MOX fuels while at the same time producing additional energy by recycling part of this plutonium in LWRs once or twice before its isotopy precludes its use in this type of reactor. In the present closed fuel cycle, almost 95% of LWR spent fuel is recycled only once in the form of reprocessed uranium and LWR MOX fuel⁵. In the future, the remaining plutonium safely concentrated in spent MOX fuels could actually become the initial mine for the progressively deployed next generation FR fleet. This would mean treating these spent

fuels where Pu is mixed with FP and MA and then manufacturing FR MOx fuels with the recovered and purified plutonium, together with reprocessed uranium and/or depleted uranium from previous nuclear generation systems. Sustainability is ultimately ensured by simultaneously consuming and generating Pu in the FR cores of a reactor fleet in equilibrium, and repeatedly recycling plutonium together with uranium^{6,7}. In this fully closed cycle, only a small input of uranium from the existing depleted uranium stocks is needed, representing the equivalent of more than a thousand years of energy production with the use of FR and multi-recycling.

Significant past experience in FR MOx fuel treatment/recycling is already available, but additional R&D steps are still required to meet the scientific, technical, economical challenges for the progressive deployment of plutonium and uranium multi-recycling. A new R&D phase interconnected with the sodium-cooled FR ASTRID prototype project has been running in the CEA over the last few years, and some recent achievements are presented here.

II. OVERVIEW OF PRESENT AND PAST EXPERIENCE AND THE PRESENT GLOBAL R&D PROGRAM

The CEA's R&D program described below focuses on process and technology dedicated to the next steps of the fuel cycle closure. These include progressive deployment of advanced sodium-cooled FR using MOx fuels. This nuclear system has gained significant experience from previous FR development and can be particularly useful to meet challenges related to Generation IV systems in the near future.

In countries like France, the next steps towards the full closure of the cycle could consist in LWR MOx treatment at higher capacities and symbiotic plutonium recycling in LWR and in FR. AREVA's experience in LWR MOx fuel treatment is an industrial reality⁵ and is not given in detail in the following paragraphs. An even greater experience preexists in LWR MOx fuel manufacturing with the present AREVA MELOX plant, and the following descriptions focus more on FR MOx fuel fabrication.

II.A. RAPSODIE and PHENIX spent fuel treatment at pilot scale

France's past experience in the treatment/recycling of spent FR fuels is quite well documented⁸, and is illustrated in Fig. 1 and 2. It can be summarized as follows.

Research work at the CEA was initially materialized by a first pilot in 1969, where spent fuels from RAPSODIE (mostly) and PHENIX reactors with various characteristics were treated: cooling time as low as 6 months, plutonium content as high as 30 wt% of heavy metals (HM), maximum burnup up to 120 GW.d/ton (oxide), etc. Thanks

to this early experience, the Marcoule Pilot Plant was started in 1973 to test technology for an industrial deployment. The PUREX-based process used enabled the recovery of plutonium and uranium with the relevant purity specifications at a full capacity of 2 tHM/yr. Moreover significant progress was achieved in minimizing the residual content of plutonium in the wastes. At the same time, almost 10 tHM of spent PHENIX MOx were industrially treated in the La Hague Plant together with uranium fuels in order to recycle the plutonium.

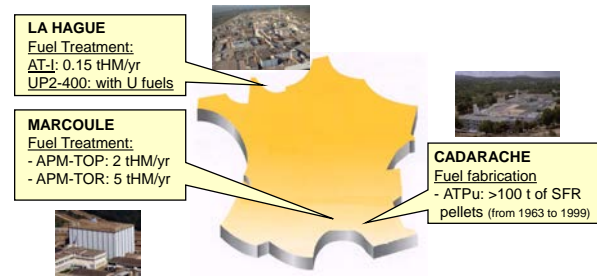


Fig. 1. France's past experience in the treatment and recycling of FR spent fuels.

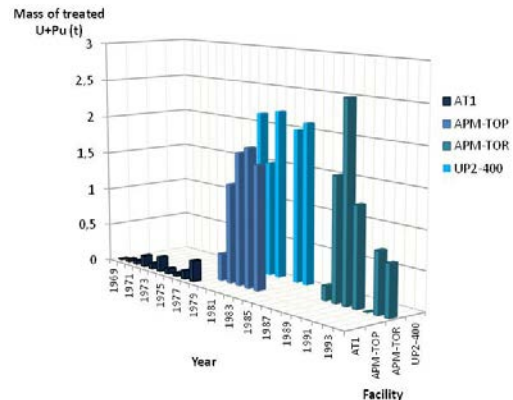


Fig. 2. Amount of RAPSODIE and PHENIX spent fuels treated in pilot plant or industrial facilities (expressed in tons of U+Pu).

Anticipating the deployment of industrial treatment/recycling (associated with a Super-PHENIX fleet project of that time), the Marcoule Pilot Plant was refurbished in the 1980s in order to increase the capacity up to 5 tHM/yr and to test advanced technologies. The objective was to design a future industrial plant dedicated to the treatment/recycling of spent FR fuels (e.g. 150 t HM/yr). The APM-TOR pilot plant was operated until 1994 and treated around 7 tHM of spent FR fuels (mostly from PHENIX).

The equivalent of 25 tHM of spent FR MOx fuels were treated during this period. Part of the recovered plutonium was even recycled twice, prefiguring multi-recycling of plutonium and uranium. This experience is summarized in Table I and represents a solid base for a new R&D phase focusing on present and future objectives for Generation IV nuclear energy systems.

TABLE I

Progress in the Na-FR spent fuel treatment process between 1969 and 1994

| Facility / Process step | AT1 | APM-TOP | APM-TOR |
|-------------------------|---|--|---|
| Dissolution | 1.7 kg U+Pu/batch | 25 kg U+Pu/batch | 55 kg U+Pu/batch |
| Separation (PUREX) | TBP 4 cycles | TBP 3 cycles | TBP 3 cycles (then 2 cycles for Pu) |
| Conversion | Ammonia for Pu and U then oxalic for Pu | Oxalic for Pu | Oxalic for Pu |
| Waste management | Outside the facility. | Cladding rinsing. FP and MA concentration and vitrification. | Cladding rinsing. FP and MA vitrification in a separate facility. Advanced processes planned. |

FR MOx fuel fabrication experience has also been enhanced by more than 30 years of production in the ATPu plant in Cadarache, totaling more than 100 tHM of fuels and mainly devoted to RAPSODIE, PHENIX and Super-PHENIX reactors.

II.B. Overview of the present R&D program for the plutonium and uranium multi-recycling

Regarding the multi-recycling of plutonium and uranium, the main themes of the R&D program running in the CEA^{9,10,11} are illustrated in Fig.3 and concern:

- the head-end, because of the treatment of quite distinct types of MOx fuels (LWR, FR), with increasing concentrations of Pu ;
- separation, because of higher Pu/U ratio;
- conversion and the fabrication stage for MOx fuels using recycled Pu with U;
- effluent and waste management, in particular special wastes from FR assemblies compared to those from LWRs, and considering an industrial scale.

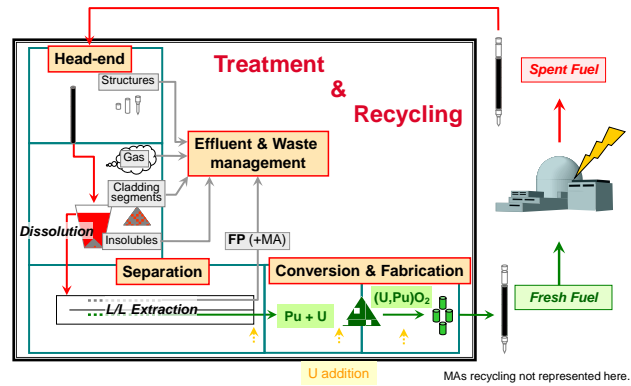



Fig. 3. Main themes of the on-going R&D program regarding plutonium and uranium multi-recycling.

If some adaptations are needed for the treatment of LWR MOx fuels at higher capacities, the ultimate technology challenge remains the treatment at industrial capacity of spent FR MOx fuels with Pu contents of up to 30-35 wt% HM and a relatively large volume of stainless steel sub-assemblies, taking into account the goals defined for Generation IV nuclear energy systems.

Irradiated FR fuels, either standard or experimental one such as the PHENIX pins currently discharged from reactor (Fig. 4), are particularly valuable starting material for long-term R&D in order to acquire complementary basic data, to perform parametric studies considering the variability of FR fuels (wt % Pu, average and local burnup, design,...) and to test advanced process in hot cell laboratories.



| % Pu _{ini} | Av. BU Phénix (GWd/t HM) | End of the irradiation campaign |
|---------------------|--------------------------|---------------------------------|
| 20.8% | 156.1 | 13/11/1998 |
| 28.7% | 1.8 | 06/04/2009 |
| 28.3% | 121.8 | 09/01/1995 |
| 29.1% | 124.9 | 06/04/2009 |
| 28.2% | 143.4 | 13/11/1998 |

Fig. 4. Examples of experimental and standard irradiated PHENIX fuels selected for the on-going R&D phase in the ATALANTE facility for the multi-recycling of Pu and U.

Recent results from experimental studies are given in the next section to illustrate first achievements and further R&D orientations dealing with the processing of materials or solutions with higher concentrations of plutonium, and the management of FR specific wastes.

III. RECENT R&D ORIENTATIONS AND RESULTS

The priority targets of the current CEA R&D program related to the multi-recycling of plutonium and uranium are listed below:

- an industrially scalable head-end process with compact technologies for MOx dissolution and full Pu recovery in solution,
- a simplified separation of plutonium and uranium with a higher Pu/U ratio,
- a high-capacity process for co-converting plutonium and uranium into mixed oxide and an automated and flexible MOx fabrication process avoiding cumbersome powder milling,
- an optimized management of the effluents and specific wastes generated by spent FR fuels.

III.A. Head-end of the treatment

Recent R&D work on the head-end of spent fuel reprocessing has been driven by an AREVA project in a new shearing and dissolution facility in the La Hague plant (Fig.5). This facility is notably designed to dissolve LWR or FR MOx fuels, with industrial capacity. The constraints related to i) higher Pu concentrations in the fuel rendering it more resistant to nitric acid and ii) an equally low level of residual plutonium which must be ensured in the solid wastes (fine particles, cladding,...) despite a far higher Pu content in the initial fuel, require the same degree of R&D as that devoted to a Generation IV plant.

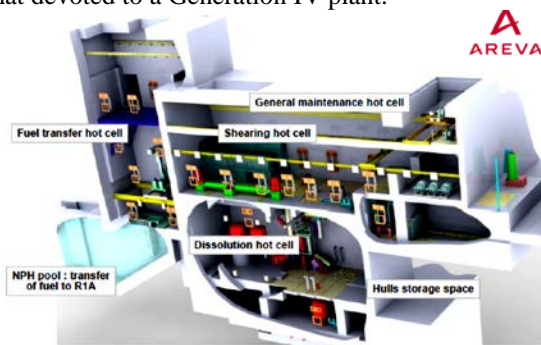


Fig. 5. 3D view of AREVA's new shearing and dissolution facility currently at the project stage in the La Hague plant. It is named TCP (polyvalent fuel treatment), and is dedicated to a wide range of fuels including LWR and FR MOX¹².

The TCP process is shown in Fig. 6. It includes complementary process steps dedicated to the most challenging fuels to be treated in order to recover the residual Pu possibly still contained in the fuel cladding after prior rinsing and in the fine particles undissolved in the previous dissolution step.

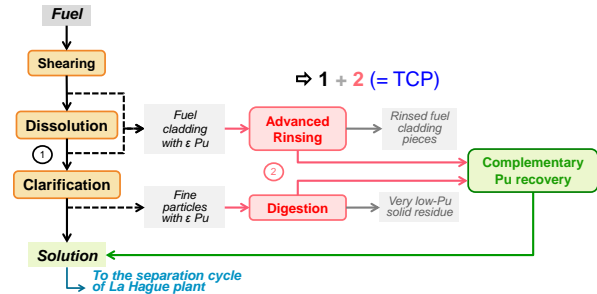


Fig. 6. Simplified scheme of the TCP process including an additional plutonium recovery (if needed) from undissolved solid particles and fuel cladding.

Before digesting these particles in order to retrieve their residual Pu in solution, they must be separated from the large volume of solution produced in the batch dissolver. To achieve high separation yields, knowledge of the particle characteristics is essential. However, these characteristics are very specific to the initial fuel. Targeted investigations into irradiated fuels are performed in the CEA ATALANTE facility (Fig. 7) in order to complete databases in order to optimize the separation system and operation.

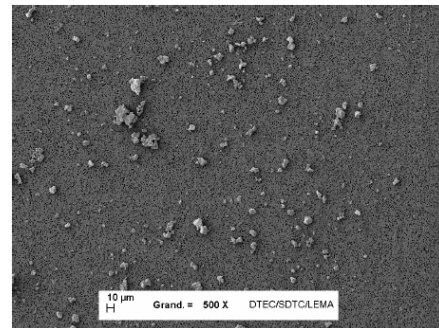


Fig. 7. SEM image of solid residues separated after the dissolution of a specific spent MOX fuel.

The digestion process is based on the principle of oxidizing dissolution like that used in the Pu Dissolution Unit (URP) of the UP2/800 La Hague plant. It is currently being optimized at laboratory scale in order to extend its use to a wide range of particles potentially containing Pu (oxide, mixed oxide, metallic...).



Fig. 8. View of the experimental setup used to digest dissolution-resistant solid residues containing some plutonium (ATALANTE C11/C12 shielded cells).

This type of oxidizing dissolution for Pu-containing particles is very efficient for the recovery of residual plutonium, with nearly 100% yield and quite short reaction time (Fig. 9).

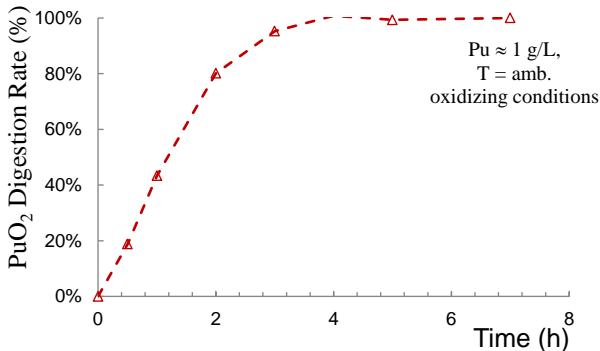


Fig. 9. View of the experimental setup used to digest dissolution-resistant solid residues containing plutonium (ATALANTE' C11/C12 shielded cells).

III.B. Separation

In the La Hague plants (UP2-400, then UP2-800), more than 60 t of Pu and U from LWR MOX fuels have been separated and purified using TBP without any issues. The U+Pu flow was diluted with uranium in order to meet the criticality safety requirements specified for the plant's present separation cycles. Separation of Pu and U from MOx fuels (LWR and FR) without prior dilution of the flow with uranium was tested at pilot-scale in the Marcoule Pilot Plant (1.5 kg of U+Pu/h). Purification criteria for U and Pu products were achieved using three TBP cycles (Fig. 10), and it was found that just two were sufficient for plutonium, given the supplementary decontamination provided by the oxalic precipitation step of the Pu conversion into oxide.

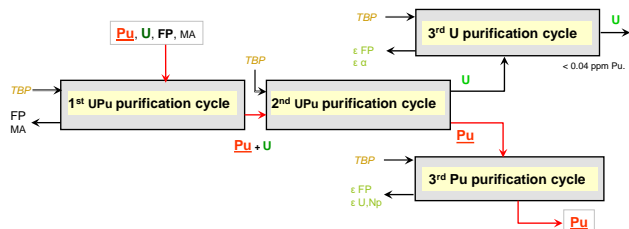


Fig. 10. TBP separation process used in the Marcoule Pilot Plant (TOR).

In the context of the Generation IV systems, separation processes that do not produce separated plutonium are encouraged. Again using TBP, recent R&D progress has demonstrated the possibility of separating the recyclable actinides and producing purified plutonium accompanied by uranium (Fig. 11).

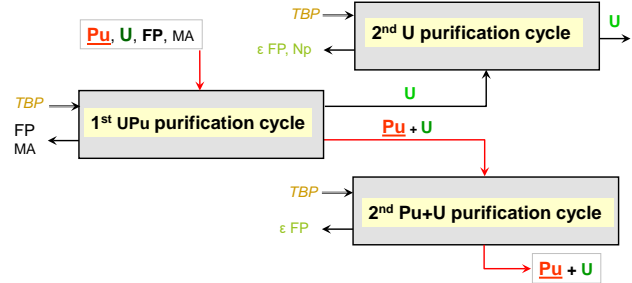


Fig. 11. Separation scheme for Pu and U considered as a starting point for the next R&D steps.

The principle of a TBP process is based on the Pu redox, i.e. because of Pu selectivity depending on the Pu oxidation state, either Pu(III) or Pu(IV). This redox is controlled with a reducing and/or anti-nitrous reagent (e.g. U(IV), hydrazine,...) or oxidizing reagent (nitrous gas or NOx). Table II illustrates the increased use of these redox reagents when switching from UOX treatment to that of MOx for the same daily capacity. When reaching the industrial MOx treatment capacities required for a Generation IV plant, this could become a significant economic and/or technical constraint.

TABLE II

Indicative data regarding redox reagent use in the TBP separation cycles when MOx fuels are treated without dilution with UOX flow.

| Redox reagent use | U(IV) | Hydrazine | NOx (= nitrate waste) |
|------------------------|-----------|-----------|-----------------------|
| TBP with UOX (present) | Ref. | Ref. | Ref. |
| TBP with LWR/FR MOX | X 10 à 15 | X 5 à 7 | X 5 à 7 |

There has been continuing interest within the separation community for alternative extracting systems. In the CEA, some of this interest has been redirected to the assessment of past or novel extracting systems limiting the use of redox reactions. Amides, for example, are well-known extracting molecules able to achieve this type of actinide separation without redox¹³. Basic studies are in progress (e.g. Fig. 12 and Fig. 13) in order to better understand the selectivity of targeted molecule families towards plutonium, uranium and other actinides and fission products, either structurally or thermodynamically, and to acquire kinetic data.

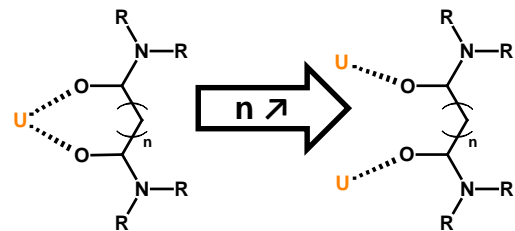


Fig. 12. Example of basic research on tetraalkylamides with a view to better understanding the selectivity of this type of extractant for Pu and U from a structural standpoint¹⁴.

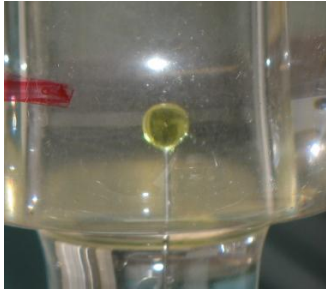


Fig. 13. Application of the single drop method to solvent extraction kinetic data acquisition to assess an advanced extracting system for Pu and U separation¹⁵.

A key step is to assess these potential extracting system candidates with specifications as high as those applied to the TBP system over the past decades. It is a long-term route considering safety, technical, economic issues. Confronting real dissolution liquors is necessary, and has been initiated in the ATALANTE facility with a view to measuring decontamination factors and to assessing plutonium and uranium partitioning using alkyl-amide systems (Fig. 14).

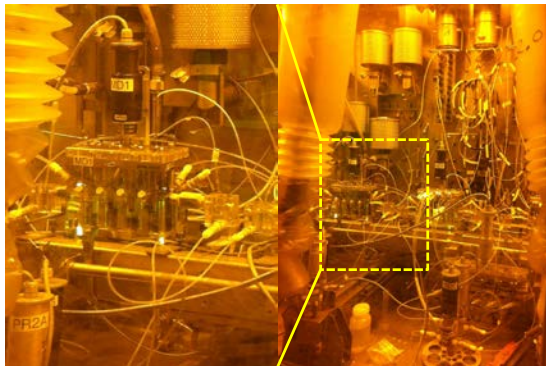


Fig. 14. View of the mixer-settler batteries used to test advanced separation processes for Pu and U recovery and purification taking into account higher Pu/U ratios (ATALANTE CBP shielded cells).

At an intermediate stage, hydrolysis and radiolysis resistance assessment of a new extracting system is an essential step in extracting molecule screening. An irradiation system coupled to a process loop has recently been refurbished for long-term behavior assessment of novel extracting systems when accumulating high dose rates and for solvent regeneration studies using appropriate washing (Fig. 15).



Fig. 15. Pictures of the new γ cell irradiator coupled to a process loop used to test the irradiation resistance of new extracting systems for Pu and U separation.

III.C. Conversion into oxide and MOx fabrication

After separating plutonium together with some uranium, the next step concerns the conversion of both actinides into a solid form usable for FR MOx fabrication. This co-conversion process into a mixed oxide powder could significantly simplify the mixing operation by powder metallurgy in order to achieve the final homogeneous metallic composition of the fuel pellets. It had already been performed in the past by co-milling PuO_2 and UO_2 single oxide (Fig. 16, left). In the future, premixing Pu and with some U in solution, then co-solidifying both actinides will be able to be achieved by various routes such as coprecipitating methods¹⁶. A gentler mixing of $(\text{U,Pu})\text{O}_2$ with the required amount of remaining UO_2 can be more easily designed (Fig. 16, right) leading to potential simplification of the fabrication scheme. By coupling this mixture mode to a reject pellet recycling management without a milling step (i.e. by a wet route, consisting in a dissolution at the head end of the treatment), benefits could include a lower dust buildup and thus a lower radiation exposure risk due to retention in glove-boxes. R&D is in progress in order to optimize dissolution of this type of non-irradiated $(\text{U,Pu})\text{O}_2$ material, also using an oxidizing method (see III.A)

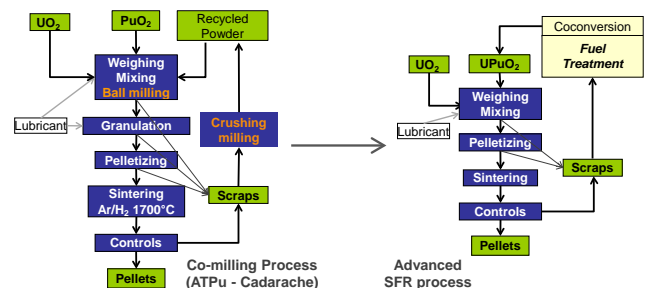


Fig. 16. FR MOx fuel fabrication: Co-milling Process (CFCa/ATPu - Cadarache) (left) and a simplified route under development within an integrated treatment and recycling process (right).

Compared to the present experience in the La Hague plant (R4/T4 workshops), the main technical challenge is related to higher metal flows at the conversion step due to increased amounts of plutonium in the cycle and the accompanying uranium (“no plutonium alone” as desired for Generation IV cycles). No previous experience is available with such a flow and technical progress is needed to keep the conversion line compact (limited number of reactor vessels and calcination furnaces, while meeting criticality safety requirements).

III.D. Waste Management

Considering the evolution of the FP distribution when deploying uranium and plutonium multi-recycling (Fig. 17), vitrified high-level waste packages can still be considered suitable for MA and FP containment in a geological depository. The main adaptation could concern the vitrified matrix formulation and process adjustment due to increased amounts of platinum group elements. Long-term radiotoxicity and heat-generating capacity could also be significantly decreased by recycling all or part (e.g. americium) of the MA in the future. MA partitioning and transmutation R&D is not described in this paper.

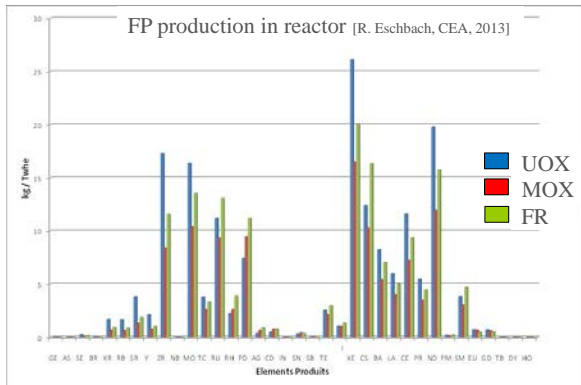


Fig. 17. Indicative data for FP distribution in UOX, LWR MOx and FNR MOx fuels (5 y. cooling time).

Intermediate-level waste packages for metal pieces could evolve due to an increased amount of stainless steel pieces from spent FR subassemblies. From a process point of view, the full recovery of residual plutonium accompanying some of these metal species after the dissolving of MOx fuels could raise renewed interest for a melting process instead of a compacting one. The development of a molten process could indeed offer benefits in simultaneously recovering residual plutonium from fuel cladding and undissolved particles (Fig. 18, method 3). Past experience at laboratory scale demonstrated the obtaining of alpha-emitter decontamination factors of up to 2000 through the use of a dedicated slag intended to extract Pu from the molten metal bath¹⁷. A more conventional compacting method is also applicable, such as that planned for the future TCP workshop in the La Hague plant (cf. § III.A). Recovery of residual plutonium from solid wastes produced by spent FR fuel shearing and dissolution would then be ensured by a hydrometallurgical route (Fig. 6 and Fig. 18, method 2).

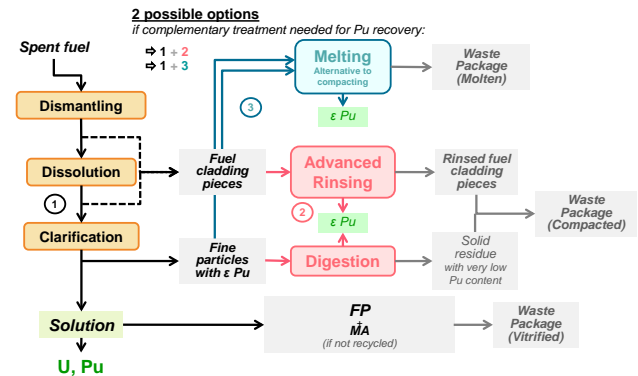


Fig. 18. Examples of potential evolution in the management of intermediate/high-level long-lived wastes together with additional Pu recovery from solid wastes.

Concerning the volatile radionuclides, the assessment of alternative ways of management to those used at present could be of interest to minimize gaseous releases still further. This issue is not specifically related to Pu and U multi-recycling but more generally to Generation IV systems promoting as low as reasonably achievable environmental and/or radiological impact. It could consist in trapping then conditioning this type of radionuclides in order to minimize effluent release at the treatment facility. It would involve finding suitable technical solutions to immobilize them safely and without added impact, either in surface or sub-surface repositories for relatively short-lived radionuclides or in deep geological repositories, as for ¹²⁹I.

This element represents one of the greatest technical challenges case. The half-life of ¹²⁹I is 16 x 10⁶ years. Concentrating iodine in a matrix designed for geological repositories requires the definition of extremely durable materials and a demonstration that the potential radiological impact of this management route (involving concentrating and conditioning) is lower than that of a continuous controlled release where an extremely high isotopic dilution is ensured. Present R&D is thus firstly devoted to a better understanding of the incorporation mechanisms of iodine into a targeted conditioning matrix with a view to assessing the possibility of achieving a containment time of up to the order of magnitude of the ¹²⁹I half-life. One example of the on-going studies is illustrated in Fig. 19. Preliminary results reveal some potential to achieve very low leaching rates, even if further assessments and impact studies are still required¹⁸.

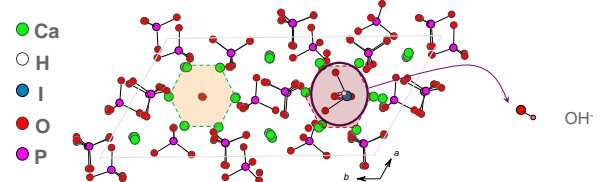


Fig. 19. Optimized geometry of iodate-substituted Ca-hydroxyapatite and of the substitution mechanism¹⁹.

Another example concerns ¹⁴C. Present R&D is focused on a better understanding of the distribution of this radionuclide during spent fuel dissolution. Precise measurements of ¹⁴C in gas, in hulls and in unclarified dissolution solution have recently been performed, as a preliminary to studying potential improved or alternative ways to manage this radionuclide in a Generation IV plant²⁰.

III.E. Process Monitoring and Control

Increasing Pu flows in the treatment/recycling facility mean more stringent process monitoring and control. Two R&D axes have been defined in order to design an advanced system: real-time and on-line measurement of key physical-chemical parameters of the process ([U], [Pu], [H⁺], flow rates...) and process simulation. These two axes must then be coupled to a data reconciliation algorithm in order to feed the Process Monitoring and Control (Fig. 20). One advantage, for example, would be the ability to provide a rapid response (quasi on-line if needed) to a process drift or disturbance.

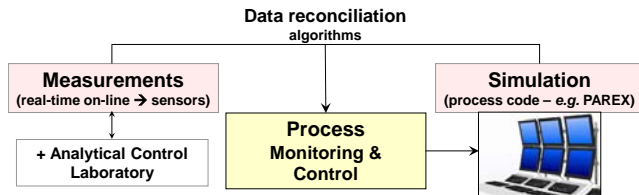


Fig. 20. Scheme of an advanced Process Monitoring and Control system based on a qualified process code, real-time measurements and data reconciliation.

The feasibility of this approach has recently been assessed at the laboratory scale during a separation experiment with irradiated fuel (Fig. 14). Combining the use of real-time on-line measurements by specifically designed UV-visible probes and the PAREX process code²¹, the flow rates were regulated continuously together with the acidity concentration in the extraction mixer-settlers. It was then possible to reach a higher reactivity for adjustment of the outlet U(VI) concentration in the separation process, either at the start of the run or following hydrodynamic disturbances (Fig.21). These on line measurement results were consistent with those received from the control laboratory, but after a significantly longer time.

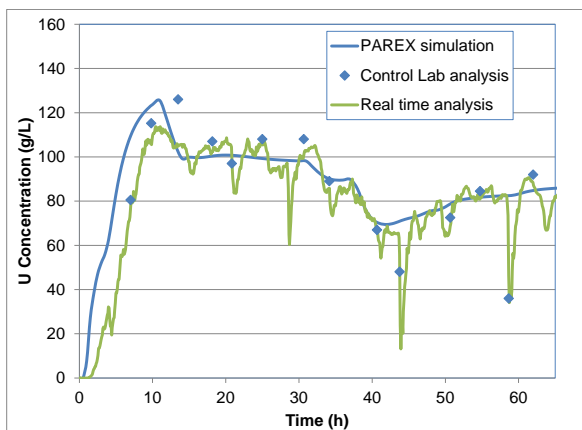


Fig. 21. Illustration of on-line real-time analysis of U(VI) using optimized UV-visible probe (green line) compared to U(VI) concentration simulated by the separation code PAREX (blue line), during a separation experiment (ATALANTE C17 laboratory).

In this approach, sensor design, optimization and miniaturization adapted to very aggressive and radioactive environments are key points. Considering fuel treatment by a

hydrometallurgical process, a microsensor combining microfluidics and detection in a single chip would be very useful. In the example described in Fig.22, the sensor principle consists in a single chip with optical guides and two channels designed to let the solution to be controlled circulate. The two channels are connected to each other by a 2 mm wide area where the interaction between the incident light and the solution film is optimized. The measurement by this innovative miniaturized sensor is based on visible absorptiometry, a detection technique commonly used for actinide measurement and speciation²².

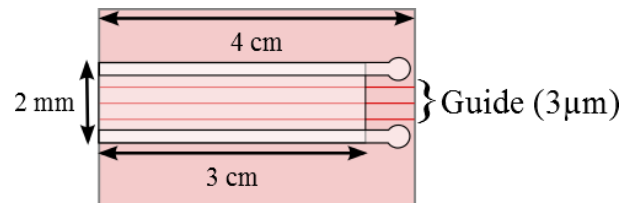


Fig. 22. Principle of a micro sensor using visible absorptiometry for actinide monitoring in solution.

In parallel, process codes are continuously being developed in order to simulate each step of the process, following the example of the PAREX code for the separation for actinides using various extraction systems.

IV. CONCLUSIONS

The French R&D program for multi-recycling of plutonium and uranium has been structured in order to accompany the progressive deployment of a fully closed fuel cycle, for an optimized use of natural resources and a sustainable nuclear energy production.

Considering i) past experience on previous-generation sodium fast reactors, ii) present experience on the LWR closed UOX fuel cycle, and above all iii) the internationally defined Generation IV goals, this R&D focuses firstly on a hydrometallurgical treatment of spent LWR MOx at increasing capacities in order to recover Pu for the production of MOx fuels dedicated to the first FR units. Secondly it examines the repeated treatment/recycling of spent FR MOx fuels, the ultimate goal of the fully closed fuel cycle.

The specific properties of these MOx fuels compared to UOx have led to developments devoted to process steps where higher plutonium concentrations and/or flows require modification, optimization and/or innovation. These include the head-end of the treatment, the separation, the conversion into oxide together with the fuel fabrication, and the waste treatment prior to conditioning, as illustrated by recent achievements. The design differences between LWR and FR fuels will also require specific management for the activated and/or contaminated structure materials of FR fuel assemblies.

The activity in this field is organized around two main projects: the polyvalent head-end fuel treatment in the AREVA facility at La Hague plant (TCP) which will, in the near future, enable advanced shearing and dissolution capacities for spent fuels (including LWR and FR MOx) and the development of the ASTRID fuel cycle which should lead the way for the progressive deployment of a fully closed cycle (Fig. 23).

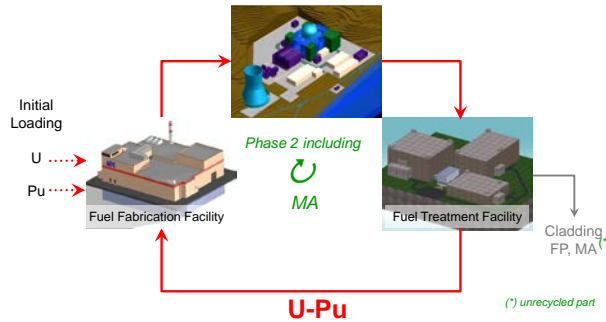


Fig. 23. The ASTRID fuel cycle.

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ABBREVIATIONS

LWR: Light Water Reactor.
 FR: Fast Reactor.
 UOx: Uranium Oxide fuels.
 MOX: Mixed plutonium-uranium Oxide fuels.
 TBP: Tri Butyl Phosphate.
 FP: Fission Products.
 MA: Minor Actinides.
 PGM: Platinum Group Metals
 TCP: Traitement des Combustibles Particuliers or Flexible Recycling Unit for Special Fuels.

REFERENCES

1. U.S. Nuclear Energy Research Advisory Committee (NERAC) and the Generation IV International Forum (GIF), *A Technology Roadmap for Generation IV Nuclear Energy Systems*, GIF-002-00 (2002).
2. OECD Nuclear Energy Agency for the Generation IV International Forum, *Technology Roadmap Update for Generation IV Nuclear Energy Systems* (2014).
3. C. POINSSOT, S. GRANDJEAN, M. MASSON, B. BOULLIS, "Improving the Actinides Recycling, a Key Step towards a More Sustainable Nuclear Energy", *WM2015 Conference*, March 15 – 19 2015, Phoenix, Arizona, USA (2015).
4. B. BOULLIS, "Plutonium Management in France: Future Possible Scenarios", *Pu Futures The Science*, Sept. 8 – 11 2014, Las Vegas, USA (2014).
5. J.J. BRUEZIERE et al., "Used MOX Recycling Experience", *this conference* (2015).

6. C. POINSSOT, C. ROSTAING, S. GRANDJEAN, B. BOULLIS, "Recycling the actinides, the cornerstone of any sustainable nuclear fuel cycles", *Procedia Chemistry*, **7**, 349 – 357 (2012).
7. C. POINSSOT, S. GRANDJEAN, M. MASSON, B. BOULLIS, D. WARIN, « Improving the actinides recycling in closed fuel cycles, a major step towards nuclear energy sustainability », *GLOBAL 2013 conference*, 30 Sept. - 4 Oct., 2013, Salt Lake City, Utah, USA (2013).
8. M. MASSON, A. TRIBOUT-MAURIZI, S. GRANDJEAN, C. POINSSOT, D. WARIN, B. BOULLIS, "French experience and R&D challenges for SFR MOX spent fuel treatment" *International Conference on Fast Reactors and Related Fuel Cycles: Safe Technologies and Sustainable Scenarios (FR13)*, March 4-7 2013, Paris, France (2013).
9. S. GRANDJEAN, C. POINSSOT, M. MASSON, D. WARIN, B. BOULLIS, "French R&D Program for Multi-Recycling of Plutonium", *International Conference on Fast Reactors and Related Fuel Cycles: Safe Technologies and Sustainable Scenarios (FR13)*, March 4-7 2013, Paris, France (2013).
10. S. GRANDJEAN, M. MASSON, C. POINSSOT, L. PARET, D. WARIN, B. BOULLIS, « Towards the multi-recycling of plutonium and uranium: CEA's R&D program on advanced fuel treatment/recycling », *GLOBAL 2013 conference*, 30 Sept. - 4 Oct., 2013, Salt Lake City, Utah, USA (2013).
11. S. GRANDJEAN, N. REYNIER-TRONCHE, A. SALVATORES, N. HERLET, X. HERES, J-P. DANCAUSSE, M. MASSON, C. POINSSOT, L. PARET, D. WARIN, B. BOULLIS, " Overview of the CEA's R&D dedicated to the treatment/recycling of Pu-based fuels (towards Pu multi-recycling)", *Pu Futures The Science*, Sept. 8 – 11 2014, Las Vegas, United States (2014).
12. J. J. BRUEZIERE, L. DURAND, M. MAURIN, N. BERTRAND, A. TRIBOUT-MAURIZI, "Flexible Recycling Unit for Specific Fuels", *GLOBAL 2013 conference*, 30 Sept. - 4 Oct., 2013, Salt Lake City, Utah, USA (2013).
13. C. MUSIKAS, P. ZORZ, "Method of extracting U(VI) and/or Pu(IV) present in an aqueous acid solution by means of a mixture of N,N-dialkylamides, for use in the reprocessing of irradiated nuclear fuels", *EP0381579B1* (1990).
14. S. WAHU, J-C. BERTHET, P. THUERY, D. GUILLAUMONT, M. EPHRITIKHINE, R. GUILLOT, G. COTE, C. BRESSON, *Eur. J. Inorg. Chem.*, **23**, 3747-3763 (2012).
15. A. LELIAS, R. BERLEMONT, M. MIGUIRDITCHIAN, "A comparative study of uranium and plutonium transfer during liquid-liquid extraction", *ISSP16 conference*, 21-25 July 2014, Germany (2014).

16. S. VAUDEZ, R. C. BELIN, L. AUFORE, Ph. SORNAY, S. GRANDJEAN, "A new fabrication route for SFR fuel using (U, Pu)O₂ powder obtained by oxalic co-conversion", *Journal of Nuclear Materials*, **442**, Issues 1–3, Pages 227-234 (2013).
17. CEA e-den "A Nuclear Energy Division monograph", *Nuclear Waste Conditioning*, Ed. CEA Saclay and Groupe Moniteur (Éditions du Moniteur), ISBN 978-2-281-11380-8 (2009).
18. L. CAMPAYO, S. LE GALLET, D. PERRET, E. COURTOIS, C. CAU DIT COUMES, Y. GRIN, F. BERNARD, *Journal of Nuclear Materials*, **457**, 63–71 (2015).
19. D. LAURENCIN, D. VANTELON, V. BRIOIS, C. GERVAIS, A. COULON, A. GRANDJEAN and L. CAMPAYO, *RSC Adv.*, **4**, 14700 (2014).
20. M. CROZET, G. FERLAY, "Carbon 14 distribution during spent fuel dissolution - Application to a UOx3", *this conference* (2015).
21. S. MICHAUD, M. MIGUIRDITCHIAN, G. DEBLONDE, B. DINH, X. HERES, G. ANDREOLETTI, *Procedia Chemistry*, **7**, 251 – 257 (2012).
22. E. JARDINIER, L. COUSTON, J.E. BROQUIN, D. BUCCI, F. CANTO, A. MAGNALDO, "Optical waveguide comprising a nano-channel and optofluidic sensor using such an optical waveguide", *WO2014082988 A1 patent* (2014).