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Main Results of the French R&D on Minor Actinides Partitioning, a Significant Improvement towards Nuclear Waste Reduction – 15618

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ABSTRACT

In the framework of the successive 1991 and 2006 Waste Management Act, French government supported a very significant R&D program on partitioning and transmutation of minor actinides (MA). This program aims to study potential solutions for still minimizing the quantity and the hazardousness of final waste, by MA recycling. Indeed, MA recycling can reduce the heat load and the half-life of most of the waste to be buried to a couple of hundred years, overcoming the concerns of the public related to the long-life of the waste.

Within this framework, this paper aims to present the most recent progress obtained in CEA on the development of innovative actinide partitioning hydrometallurgical processes in support of their recycling, either in an homogeneous mode (MA are recycled at low concentration in all the standard reactor fuel) or in an heterogeneous mode (MA are recycled at higher concentration in specific targets, at the periphery of the reactor core). Recovery performances obtained on recent tests in high active conditions of the so-called GANEX and DIAMEX-SANEX process will be presented and discussed in light of the potential P&T scenarios. Finally, recent developments regarding the recycling of the sole Am will be presented as well as the results obtained on highly active solutions for this so-called EXAM process.

This set of results gives to the French government a portfolio of potential recycling processes which could be separately and progressively implemented if decided.

INTRODUCTION

Although it could allow mitigating global climate change, nuclear energy is all but widely accepted by the public opinion, in particular since the 11th March Fukushima accident. One of the main issue raised by the public opinion is on the short term, the management of the residual safety risk and on the long term, the radioactive waste management. In particular, the very long time of isolation required by the high level waste is well beyond the common sense of most of the citizens and is seen as unrealistic. Therefore, any technical option which could lead to decrease the waste burden by decreasing the waste lifetime could be a significant contribution to enhance the social acceptance of nuclear energy. Since the early 90's, France identified this issue as a very significant part of the waste management strategy. As early as in 1991, the so-called Bataille's Waste Management Act from 31st Dec.1991 [1], identified partitioning and transmutation of long-lived radionuclides as a key R&D target to improve nuclear energy social acceptance. Since then, France conducted a wide R&D program to identity the main radionuclides of interest, develop dedicated separation processes and address the key issues of their transmutations in nuclear reactors [2]. This paper aims to depict the main output of 20 years of research on the long-lived radionuclides partitioning.

WHY FOCUSING ON THE MINOR ACTINIDES?

Beyond Pu which is already anticipated to be recycled, main contributors to spent nuclear fuel long term radiotoxicity are (i) minor actinides (MA) which dominate by several orders of magnitude the toxicity after some hundreds of years and (ii) long-lived fission products (FP) such as Tc-99, I-129 and Cs-137, which are important in the first hundred years but can also be mobile in the environment later on (Fig.1). R&D was hence initially focused on these elements.

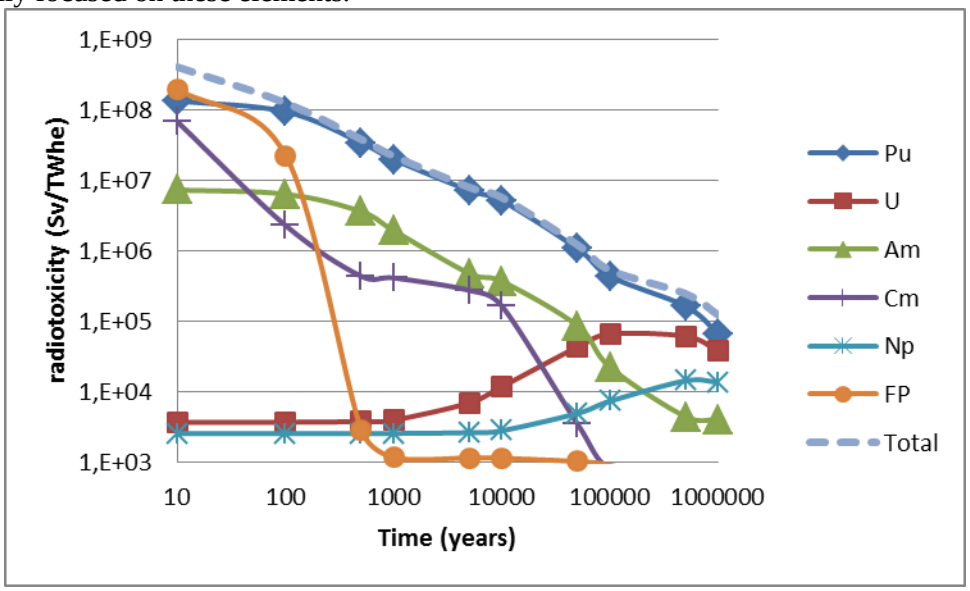


Fig.1: evolution of the radiotoxicity of spent nuclear fuel (Sv/TWh electricity) as a function of time, with the contribution of the different radionuclides. This figures clearly illustrates that long-term toxicity (>300 y) is dominated by the minor actinides, americium (Am) then curium (Cm) [3].

Partitioning and transmutation (P&T) of long-lived fission products (LLFP) was subsequently demonstrated not to be viable mainly because of the transmutation difficulties. Indeed, although cesium and technetium could easily be recovered, their transmutation would require either a prohibitive isotopic separation for Cs, or a metallic fuel for Tc. Finally, transmuting iodine was demonstrated to be difficult due to its high volatility. Based on these results, it was concluded in 2006 that P&T of LLFP is not technically relevant and this program line was abandoned.

The R&D performed on the geological repository also demonstrated that RN inventory is not the only relevant criterion to assess the respective long-term influence of the different RNs. Indeed, long term impact of any geological repository is related not only to the initial toxicity of the waste but also on the relative mobility of the RNs within the geological media. In particular, it has been demonstrated that anionic LLFP (such as I-129, Cl-36, Se-79) are mobile in the deep geological environment since they do not sorb on clay surfaces whereas MA are immobile due to their very low solubilities ($< 10^{-9}$ M) and high sorption ($Kd > 10^5$ $L.kg^{-1}$). From that point of view, decreasing the long term radiotoxicity would not decrease the long-term radiological impact of the repository in normal conditions which is rather governed by the anionic LLFP. However, recycling MA would bring significant improvement:

- It yields to decrease the global waste inventory and toxicity of the waste, which could contribute to decrease the waste burden towards future generations and enhance social acceptance. In particular, it decreases the time needed to reduce the toxicity to the reference level of the initial uranium ore as

evidenced on Fig.2.

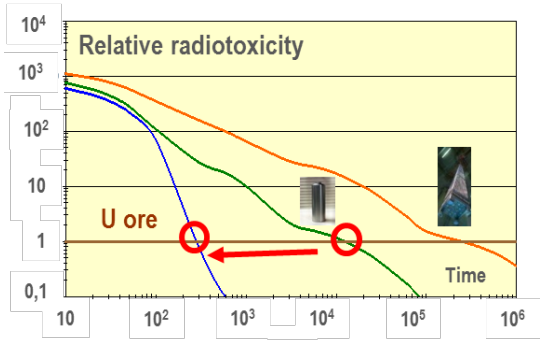


Fig.2: relative radiotoxicity of spent nuclear fuel (orange), nuclear glass produced after the sole recycling of Pu (green) or after the recycling of Pu and MA (orange).

- It yields to improve the performance of the repository in incidental scenario where the geological barrier could not act as a barrier, for instance in case of intruding borehole in or close to a waste canister.
- It also allows optimizing and saving the repository resource due to the reduction of the waste heatpower. Studies performed in the French repository project managed by ANDRA demonstrate that high level waste (HLW) decay heat power has a strong influence on the global surface of the repository due to the low thermal conductivity of the French reference argilites (the so-called Callovo-Oxfordian argilites). MAs are the main long term contributors to the long term decay heat power of the HLW. Recycling MA would hence lead to decreasing the HLW heat loading, and subsequently favors a denser repository. For a given repository, implementing MA recycling technically allows disposing larger amount of HLW and using the repository for a longer period of time. MA recycling is therefore a path towards saving the scarce repository resource, and could contribute to an enhanced acceptance by local communities.

Finally, recent studies evidenced that recycling Cm should be difficult to implement due to the very significant neutron emissions of Cm which would require very thick shielding. In order to overcome this anticipated difficulty, a recent effort was focused on the recycling of sole-Am. In particular, it was demonstrated that most of the gain on the repository surface could be obtained with the sole recycling of Am while avoiding handling Cm all along the fuel cycle. It is the basis for the development of the recent EXAm separation process that will be described later in this paper.

HOMOGENEOUS RECYCLING: GANEX SEPARATION PROCESS

First option to recycle MA is to recover them altogether with the other actinides by a dedicated separation process referred to as GANEX (Grouped ActiNides EXtraction). Transmutation is therefore achieved by diluting the minor actinides in the whole core by producing MA-bearing fuels with a limited MA content. This approach does not require producing specific fuels but significantly impacts the fuel cycle since every fuel elements contain MA, which require specific shielding during fabrication processes.

The GANEX process hence aims at the recovery of all transuranium elements from the spent nuclear fuel dissolution solution. It consists of two steps: selective extraction of uranium, and then partitioning of actinides from fission products and lanthanides.

- The selective separation of uranium(VI) is operated by a hydrometallurgical process using a monoamide extractant DEHiBA (N,N-di-(ethyl-2-hexyl)isobutyramide) diluted in an industrial

aliphatic solvent HTP. Based on batch experimental results, a physicochemical model was developed to describe the extraction of U, (Np), Pu, and Tc by DEHiBA. With the help of this model, a flowsheet was designed and tested in 28 mixer-settlers (laboratory scale) on a genuine High Liquid Waste (HLW) in the CBP hot cell (Atalante facility) in June 2008. After running 60 hours, more than 99.99% of the initial uranium was recovered with a good purity versus transuranium elements and fission products [4].

- The GANEX 2nd step process consists of a grouped separation of transuranium elements (Np, Pu, Am, and Cm) by solvent extraction. The DIAMEX-SANEX process, initially developed for the partitioning of trivalent minor actinides (Am and Cm), was optimized to handle neptunium and plutonium along with americium and curium. Based on the experimental distribution ratios of actinides and major fission products, the initial DIAMEX-SANEX process was modified to allow the grouped actinide extraction GANEX by adjusting experimental conditions (selection of complexing agents, optimization of reagent concentrations) [5].

In terms of results, Np, Pu, Am and Cm were recovered altogether in a single flux (actinide product) and the losses of transuranium elements in the different outputs and in the solvent were estimated at a value lower than 0.5% (essentially neptunium) at the end of the test, corresponding to a recovery yield of actinides higher than 99.5%.

HETEROGENEOUS RECYCLING: DIAMEX/SANEX PARTITIONING PROCESS

Second option to recycle MA is the heterogeneous recycling option in which the MA are recovered in a dedicated flux independently on the other actinides. This process is referred to as the Enhanced Partitioning and is based on the so-called DIAMEX/SANEX separation processes and its derivative. These separation processes are proposed as a complementary step to the PUREX process. Transmutation is therefore achieved by producing dedicated fuel with a significant MA content (in the range 20% - see later) which is emplaced at the periphery of the core in blankets or targets.

Considering enhanced separation, a lot of work has been performed since 1991 by CEA to improve the recovery of trivalent actinides and their separation from lanthanides and fission products. Especially, a great number of N-bearing extracting molecules have been developed and tested to enhance the performances of An(III)/Ln(III) group separation.

The first quantitative recovery of trivalent actinide Am and Cm to be successfully tested on a genuine PUREX raffinate was performed in 2005 by using a combination of two separation processes.

- The DIAMEX process which uses the diamide molecule DMDOHEMA to extract trivalent actinides and lanthanides from nitric acid solutions with acidity ranging from 4 to 5 M. The stream of trivalent elements was then recovered by a stripping stage using low acidity nitric acid.
- The SANEX process was developed perform the An(III)/Ln(III) group separation. The principle of the SANEX process is to coextract trivalent elements from an acidic solution with a mixture of the extracting molecules DMDOHEMA and HDEHP and to strip selectively An(III) in a buffered solution at pH = 3 containing a polyaminocarboxylate compound. The performances of this process were good and more than 99.9 % of Am and Cm were recovered with a decontamination factor towards lanthanides elements close to 80.

As satisfactory results were obtained with this two steps process, work has been done to improve the separation flowsheet and led to consider again the DIAMEX/SANEX one step process which has been previously validated in 2001[6] and improved in 2008 [7] when studying the GANEX process. This process is more compact as the PUREX raffinate is directly contacted in the extraction stage with a mixture of DMDOHEMA and HDEHP. An(III) are then selectively stripped from the loaded phase with a buffered

complexing solution. To obtain a good recovery of An(III), a molybdenum back extraction from the organic phase has to be performed before An(III) stripping. The principle of the DIAMEX/SANEX process is presented in Fig.3.

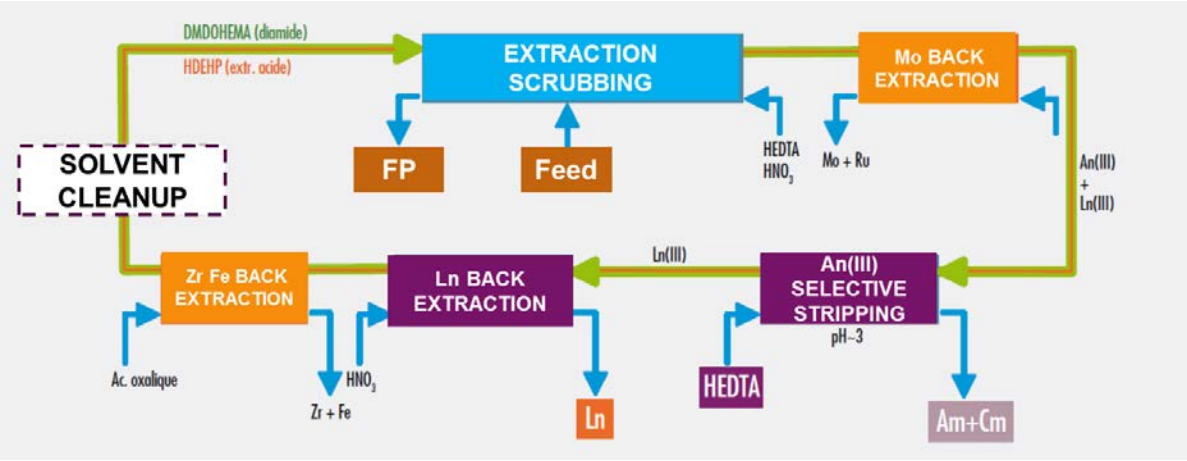


Fig.3: the DIAMEX/SANEX process flowsheet [6].

Further improvements have been developed by CEA and a simplification of the DIAMEX/SANEX process has been proposed with the use of the extracting molecule TODGA belonging to the diglycolamide family [8]. This process has been tested in 2009 on a genuine PUREX raffinate in the CBP cell of the Atalante facility. Even if the process is simpler due to the use of only one extracting molecule, a high sensitivity of the Am-Cm back extraction step to pH and temperature is to be mentioned.

The EXAm Process

As curium is a radioactive element which could bring difficulties when dealing with fuel or target fabrication, the option of a recovery of sole americium has been also studied. The principle of the EXAm process is based on the extraction of americium together with some light lanthanides having close values of distribution coefficients in high nitric acidity, while curium and other lanthanides remain in the aqueous phase [9]. Furthermore, the TEDGA amide molecule is added in the aqueous phase, in order to increase the selectivities Am/Cm and Am/heavy Lns, because of the preferential complexation of curium and heavy lanthanides by this amide: global efficiency of the process is largely improved, with a corresponding decrease of the number of the necessary separation stages [10]. Then, americium is selectively stripped from light lanthanides like in the GANEX 2 step as described on Fig.4.

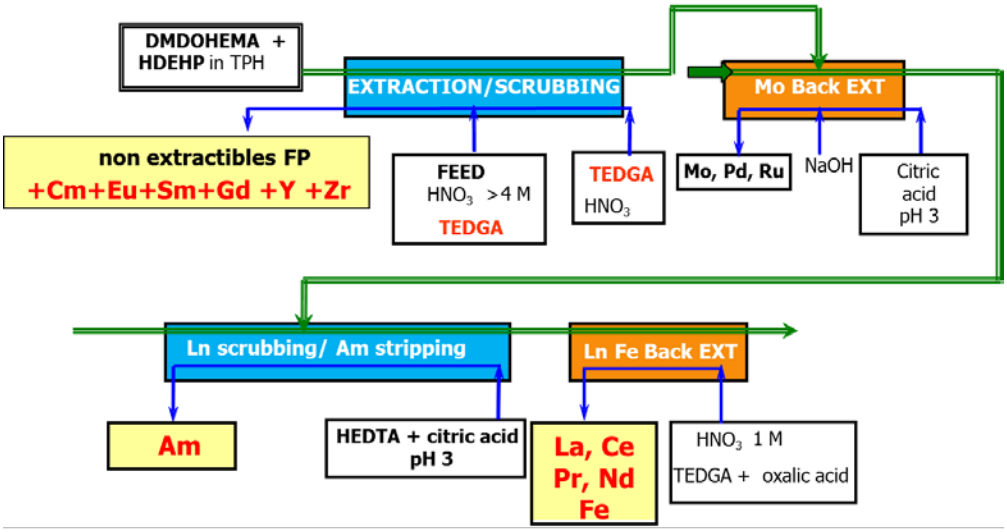


Fig.4: The EXAm process flowsheet [9]

This process has been validated on a genuine PUREX raffinate in 2010. Performances were in accordance with the predicted values of the simulation code and an Am recovery yield higher than 99 % was obtained. The decontamination factor of americium form curium was higher than 500 and DF(Am/Nd) around 340.

Even if the performances of this process are good, work is now underway to improve its compactness essentially with the aim of its potential application at industrial scale. The way which has been selected is to treat a concentrated PUREX raffinate. As the concentrations of elements are increased in the feed solution, studies have been launched to adapt the process to these new operating conditions. Especially, due to the loading capacity of the extracting system, the concentration factor of the PUREX raffinate should not be higher than 3.5 [11]. The increase of elements concentrations in the feed brings modifications of the process parameters to maintain the separation performances, especially the effect of a higher TEDGA concentration and the pH stabilization in the molybdenum scrubbing stage have been intensively studied [11][12].

A first test of the EXAm process dedicated to the treatment of concentrated solutions has been run on a surrogate spiked solution on april 2014 [11]. Am recovery is about 99.4 % and the efficiency of the supplementary TEDGA scrubbing stage was satisfactory. The molybdenum scrubbing stage is well mastered and a good adequation between the thermodynamical model [12] and experimental results is obtained.

The Integrated Experiment for Am Transmutation

To check the feasibility of an Am transmutation cycle, CEA is currently developing a demonstration experiment which aims to demonstrate the feasibility and efficiency of the whole recycling process: initial irradiated fuel dissolution, Am recovery thanks to EXAm, fabrication of $UAmO_2$ pellets and fabrication of an experimental fuel pin to be irradiated in the ATR US reactor, and finally the treatment of irradiated targets to recover Am. The first steps of this experiment: fuel dissolution and production of a raffinate with the PUREX process have already been performed in the ATALANTE facility in 2011. The next step is planned in 2015 and consists in the concentration of the PUREX raffinate and its treatment with the EXAm process to recover 4 g of americium. Then, the Am production solution of the EXAm process will be concentrated to reach the Am concentration required by the conversion process which consists in a U(IV)-Am(III) oxalate precipitation. The oxalate is then calcinated to produce $UAmO_2$ oxide powder. The production of $UAmO_2$ pellets is expected at the end of 2015 and a pin fabrication in 2016.

Complementary Studies

To support the development of these processes, with an increasing complexity, many laboratory studies have been launched since 1991 and concern various fields of the extraction chemistry and chemical engineering. It mainly deals with (i) thermodynamical and kinetics data acquisition for actinides, lanthanides and fission products other a wide range of concentrations, (ii) complexation studies of studied elements with complexing agents and extracting molecules, (iii) comprehensive studies of metal to ligand interactions, (iv) modeling of extraction mechanisms, (v) selection of organic extracting molecules fitting to numerous criteria as: easy synthesis, low production cost, good loading capacities, good extraction and back extraction kinetics, good hydrolytic and radiolytic stability, ability to be recycled, definition of solvent clean-up processes, recyclability of the various reagents and their behavior when considered as waste.

A systematic scientific approach has been implemented to settle and validate the described processes. It includes the following steps:

- The design and the synthesis of new molecules fulfilling the required criteria to develop a separation process,
- Assessment of the extracting and complexing properties of the molecules,
- For an identified promising extracting system, acquisition of all the thermodynamic and kinetic data needed to define a complete separation scheme. These data are used to elaborate a phenomenological modelling of the system,
- Design of flowsheet based on the modelling and test at a small scale level with counter-current equipments (mixer-settlers or centrifugal contactors) on inactive or surrogate solutions spiked with minor actinides and fission products to check hydrodynamic behavior and performances of the system,
- Implementation of long term tests on the MARCEL irradiation loop to study the behavior of the solvent under hydrolysis and radiolysis degradation (hydrolysis effect, combined hydrolysis and radiolysis effects, impact of the solvent clean-up), the kinetics of solvent consumption, the degradation products accumulation and their impact on the process performances,
- Finally, the last step is the implementation of the whole flowsheet in hot cell on a genuine feed solution. This last test leads either to the validation of the concept and its associated flowsheet or to complementary studies to improve it.

For a validated concept which feasibility has been proven, further studies are then launched with the aim to

optimize and simplify the process to adapt it to industrial constraints (flexibility, robustness, costs...).

CONCLUSION

Since 1991, France has significantly invested in the development of partitioning processes which are able either to recover the minor actinides together with plutonium, or in a dedicated flux. This wide research program yields to a portfolio of different types of partitioning processes that have been proven to be efficient at the laboratory scale on kilograms of spent nuclear fuel: GANEX to recover Am, Cm and Np with Pu, DIAMEX/SANEX and SANEX/TODGA to recover Am and Cm together, finally EXAm to recover the sole Am. Fig.5 is showing the evolution of MA recycling processes developed by CEA. All these processes were demonstrated to be efficient enough to allow an efficient recycling of the minor actinides. Furthermore, specific researches were also conducted to extend this knowledge towards an industrial feasibility: all the extracting molecules were demonstrated to be relatively easily synthesized at the industrial scale with a reasonable cost. They have also been demonstrated to be resistant enough to undergo years of irradiation in highly acidic media while relevant treatment processes to eliminate the potential degradation products have been developed. Furthermore, specific chemical engineering modeling tools have been developed for each of them which allowed both the development of optimized separation scheme and flowsheets, and the assessment of the robustness of the processes towards any evolution of the parameters (sensibility studies). Relevant key on-line measurements have been identified and addressed to the R&D which still needs to be amplified in this direction.

Recovering the minor actinides is hence demonstrated to be industrially feasible in case any decision should be taken towards its implementation. Coupled with the development of fast reactors, this would allow to successfully transmute the minor actinides by fission reactions. Such fuel cycle option would clearly not improve the technical and economic efficiency of the electricity production. However, it is a very serious mean to decrease the residual long-term radiotoxicity and heat power of the waste, which itself size the repository density. Hence, recycling the minor actinides would allow decreasing the time needed for the waste to have a radiotoxicity down to that of the initial uranium ore, *i.e.* from hundreds of thousands of years to roughly three hundreds years. Such a fuel cycle option would hence bring back the nuclear waste within the Human history. Regarding the serious difficulty for the public opinion to grasp the issue of waste management, it could be a very significant improvement towards an increased acceptance of the nuclear energy, which is a key issue to address if such an energy should develop on the long-term.

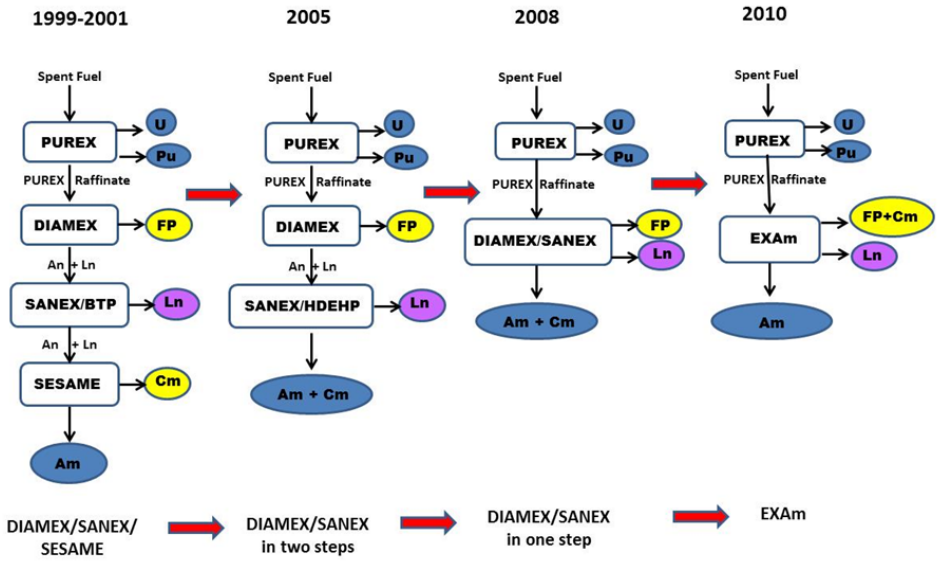


Fig.5: The MA partitioning routes successively developed by CEA in order to get a portfolio of different MA partitioning processes.

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