

URANIUM(VI)/PLUTONIUM(IV) SEPARATION FROM SPENT MOX FUELS USING A SINGLE MONOAMIDE EXTRACTANT: THE PUMAS PROCESS

Solenne Michaud*, Amandine Duterme, Sylvain Costenoble, Fabien Lengrand, Vincent Vanel, Pauline Moeyaert, Pierre Sarrat, Christian Sorel, Manuel Miguiditchian

CEA, DES, ISEC, DMRC, Univ. Montpellier, Marcoule, Bagnols-sur-Cèze 30207, France

* Corresponding Author

Abstract. In the context of the development of generation IV reactors, solvent extraction process is under development for the reprocessing of spent nuclear fuels. A monoamide extractant was found to be a suitable replacement for TBP. This extractant allows plutonium(IV) back-extraction by changing the acidity instead of the plutonium oxidation state. This paper sum up the methodology and the different hot tests performed in Atalante facility to demonstrate uranium(VI)/plutonium(IV) separation from used MOX fuels using this single monoamide extractant with the so-called PUMAS process.

1. Introduction

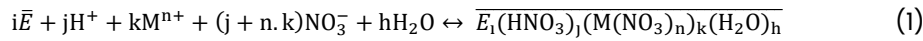
In the framework of plutonium multi-recycling, a new monoamide extractant was designed and selected for mixed oxide fuels (MOX) reprocessing instead of tri-butyl phosphate (TBP) currently used in the PUREX process. This new solvent extraction process allows extraction and purification of uranium and plutonium from the fission products in only one cycle and avoiding the use of redox reagents for the partitioning operation. Indeed, after uranium(VI) and plutonium(IV) extraction from concentrated nitric acid solution, plutonium(IV) is selectively stripped by decreasing the acidity of the aqueous phase [1-3]. In the PUREX process, selective plutonium back-extraction is achieved by reducing the plutonium oxidation state, using reducing agent and nitrous scavengers. Therefore, this monoamide-based process is easier and safer to operate because plutonium is in a stable oxidation state through all the process. Indeed, due to the use of redox reactions in the PUREX process, maloperations can lead to a fast change in the quality of U/Pu separation. However, this new process does not involve redox reactions which means that any disturbances should have a slower impact on the U/Pu separation. This new process will thus be more suitable than the current PUREX process for the recovery of plutonium from Pu-rich fuels (spent light-water reactor (LWR) MOX and Fast Reactor MOX fuels).

A first demonstration of the process scientific feasibility was reached with uranium oxide fuel (UOX) in highly active conditions through pilot tests in the CBP shielded cell [4-5] (Atalante facility). A mixture of two monoamides DEHBA and DEHiBA was used in organic phase but due to the viscosity of the mixture and the complexity of industrial management for two extracting molecules, further studies were performed and led to the selection of a single monoamide molecule. This paper sum up the methodology applied and the hot tests performed in Atalante facility to demonstrate the recovery and purification of uranium and plutonium from MOX fuels using a single monoamide extractant: the PUMAS (Plutonium, Uranium, MonoAmide, Separation) process.

2. Modeling of extraction data

After the selection of the extractant and the optimization of its structure, batch experiments were performed to acquire extraction isotherms of water, nitric acid, uranium(VI), plutonium(IV) and some fission products with this new solvent. Experimental distribution isotherms data were described with a

physico-chemical model based on the application of the mass action law on each extraction equilibrium (equation 1 and 2) and assumptions about the stoichiometry of the complexes formed in organic phase.



$$K_{ijkh}^{eff} = \frac{[E_i(HNO_3)_j(M(NO_3)_n)_k(H_2O)_h]}{[E]^i \cdot a_{HNO_3}^j \cdot a_{M(NO_3)_n}^k \cdot a_{H_2O}^h} \cdot \exp[(S_{ijkh}^+ - i.S_E^+)]. (1 - a_{H_2O}) \quad (2)$$

a_X : activity of electrolyte X; S_X^+ : non-stoichiometric hydration degree (solubilized water of species X for $a_{H_2O} = 1$)

In this model, deviations from ideal behavior in the aqueous phase were estimated by calculating the activity coefficient of each component according to the "simple solutions" concept. In organic phase, deviations from ideality were considered thanks to Sergievskii–Dannus theory [6]. Models parameters were adjusted thanks to an optimization method which minimized the Root Mean Square Deviation (RMSD) between computed and experimental organic concentration.

This thermodynamic model of the extraction equilibria was integrated into the PAREX+ simulation code [7]. In addition, mass transfer kinetics were measured and also implemented in the PAREX+ code. Thanks to all acquired data in the models and the enhanced numerical methods in PAREX+ code, the process flowsheet was optimized to obtain uranium and plutonium at very high purity and to achieve high recovery efficiencies.

3. Flowsheet calculation

PUMAS flowsheets can be divided into four sections (Fig. 1). The first one is devoted to uranium and plutonium extraction at high nitric acid concentration and fission products scrubbing. The last stages of the fission products scrubbing step are used to decrease the acidity in organic phase before uranium/plutonium partitioning. The former section is operated at low acidity and a uranium scrubbing is added to extract uranium in organic phase minimizing any uranium leaks in the plutonium product. In the third section, uranium is stripped from the solvent at very low acidity before the solvent clean-up step allowing its recycling.

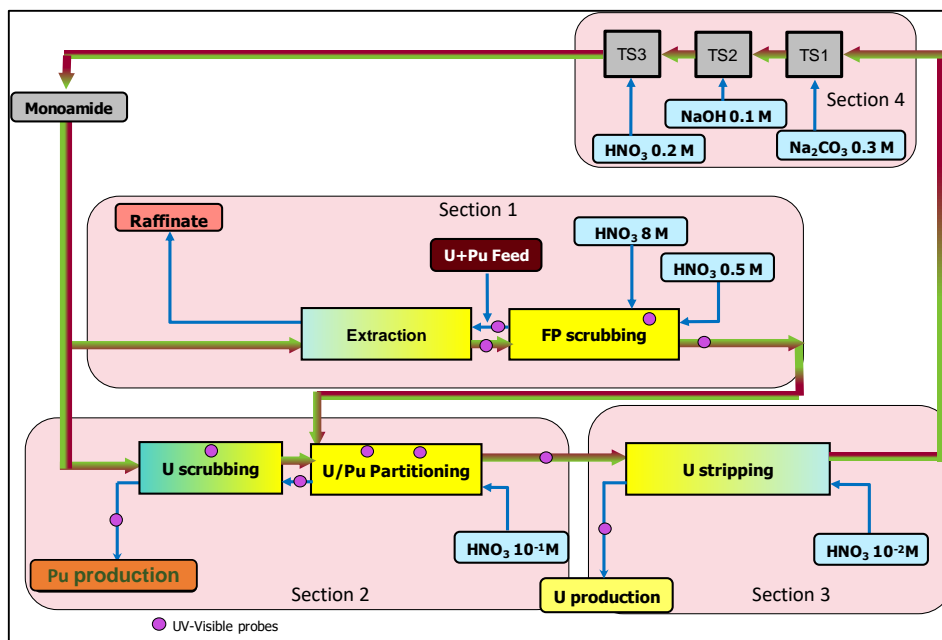


Fig. 1. Global flowsheet of the different tests

The first three sections are operated in laboratory-scale mixer-settlers whereas centrifugal contactors are used in the solvent clean-up step in order to take into account the emulsifying nature of the systems.

To follow the evolution of uranium and plutonium concentration on-line, both in the organic and the aqueous phase during the trial, UV-Visible probes were implemented. About eleven probes, three in organic phase and eight in aqueous phase, were used and strategically located. Laboratory analysis were also punctually performed by K-edge and X-ray fluorescence to complete the trial monitoring.

4. Hot tests results

Four hot pilot tests were successfully performed with this single monoamide extractant. The first test was conducted in 2018 with a surrogate LWR MOX feed (Pu/U=9.5%) in a alpha-shielded line (atalante facility) to confirm the uranium/plutonium partition feasibility and compare experimental data with calculated values obtained with the PAREX+ code (Fig. 2, Fig. 3 and Fig. 4). During this trial, a good hydrodynamic behavior was observed. Uranium and plutonium were quantitatively extracted in organic phase from the MOX fuel feed. No uranium nor plutonium leaks were observed in the raffinate of the extraction step. However, a small leak of plutonium was measured in the uranium product.

The comparison between measured and calculated aqueous concentration profiles obtained at the end of the trial showed a good agreement for nitric acid, uranium and plutonium (Fig. 2, Fig. 3 and Fig. 4). A little under-estimation of calculated aqueous uranium concentration in the U/Pu partitioning section (Fig. 3) and calculated aqueous plutonium concentration in the FP scrubbing section (Fig. 4) was observed.

This flowsheet was then applied to the treatment of actual high active solutions in the CBP hot cell :

- in 2020 and 2023, for recovering and purifying plutonium from a mixture of several solutions.
- in 2021, for recovering plutonium from a feed produced by the dissolution of a LWR MOX fuel.

A good hydrodynamic behavior was observed for these three trials. In 2020, 16 liters of dissolution liquor with Pu/(U+Pu) ratio of 2.5% were treated and excellent recovery yields of uranium and plutonium (> 99.9%) were achieved. The Pu/U ratio in the plutonium output was adjusted by minor variations of flowrate. Without redox reactions, process monitoring is simplified and a good performance stability was underlined during about 200 hours. Despite a very small aqueous phase carry-over in organic phase, good decontamination factors (DF) were measured in agreement with formal requirements ($DF_{134Cs} \sim 3.8 \times 10^4$, $DF_{137Cs} \sim 3.4 \times 10^4$). However, no Pu/Np nor U/Tc separation was achieved.

In 2021, the first treatment of a MOX fuel (9 liters of dissolution liquor with Pu/(U+Pu) ratio of 5,8 %) was carried out by adopting a separate management of plutonium and uranium (more restrictive in terms of process control). Excellent recovery yields of uranium and plutonium (> 99.9%) were achieved and good stability of the solvent was obtained. As the previous trial, consolidation of process robustness was tested using optimisation of Pu/U ratio, in the plutonium output by minor flowrates adjustments. The flowsheet was also optimized to reduce phase entrainment and thus to increase decontamination of plutonium towards fission products. Indeed, high decontamination factors were obtained ($DF_{134Cs} > 1.29 \times 10^5$, $DF_{137Cs} \sim 1.88 \times 10^5$). Good agreement between experimental and calculation profiles for HNO₃, uranium and plutonium was achieved but neptunium and technetium were not separated from plutonium and uranium respectively.

In 2023, 7 liters of dissolution liquor with Pu/(U+Pu) ratio of 7.2 % were treated. The flowsheet included for the first time a technetium barrier in order to separate technetium from uranium. Excellent recovery yields of uranium and plutonium (> 99.9%) were achieved. This trial highlighted the capacity of this new extractant to deal with high Pu/U ratio. As shown before, no Pu/Np separation was reached. Specific trials are planned in Atalante facility in order to manage neptunium behavior in the PUMAS process.

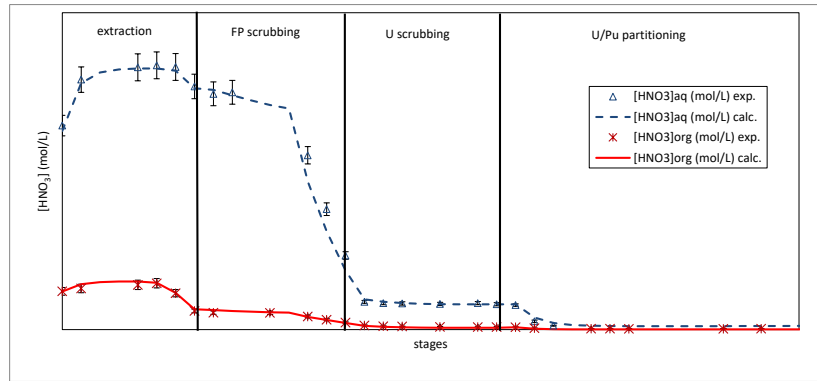


Fig. 2. Comparison of experimental (exp) and calculated (calc) aqueous (aq) and organic (org) nitric acid concentration profiles

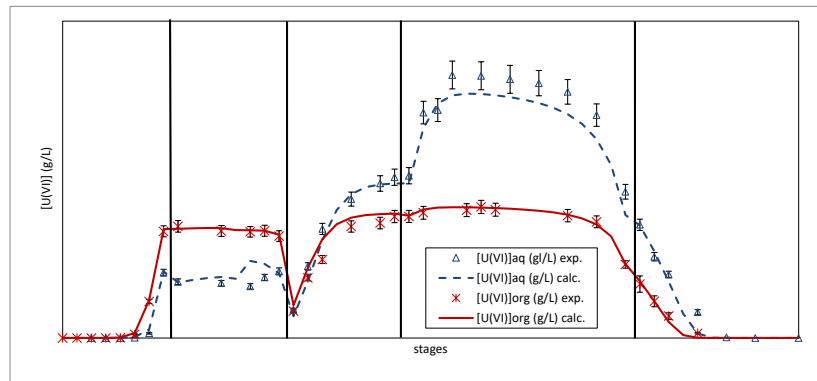


Fig. 3. Comparison of experimental (exp) and calculated (calc) aqueous (aq) and organic (org) uranium(VI) concentration profiles

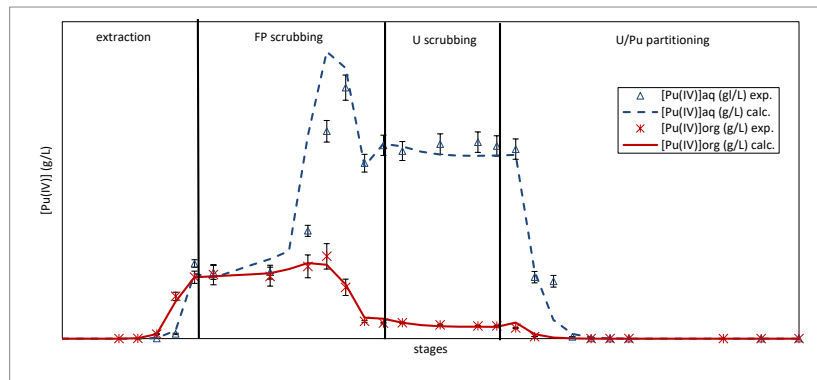


Fig. 4. Comparison of experimental (exp) and calculated (calc) aqueous (aq) and organic (org) plutonium(IV) concentration profiles

5. Conclusion

All trials performed in Atalante facility showed the feasibility of quantitatively recovering uranium and plutonium from UOX and LWR MOX fuels using a new redox free process based on a single monoamide extractant.

The model developed to design the flowsheets was validated. The combination of on-line analysis with accurate estimation by the model was very powerful to drive the process.

Recovery ratios (99.9%), purity rate and decontamination factors ($\sim 10^5$) were achieved in accordance with formal requirements except for Pu/Np and U/Tc separation which should be managed

specifically. Fig. 5 depicted the global flowsheet intended : technetium barrier was added as well as a second step dedicated to Pu/Np separation.

These successful tests allow to pursue the development of this process and scaling up flowsheets for industrial purposes.

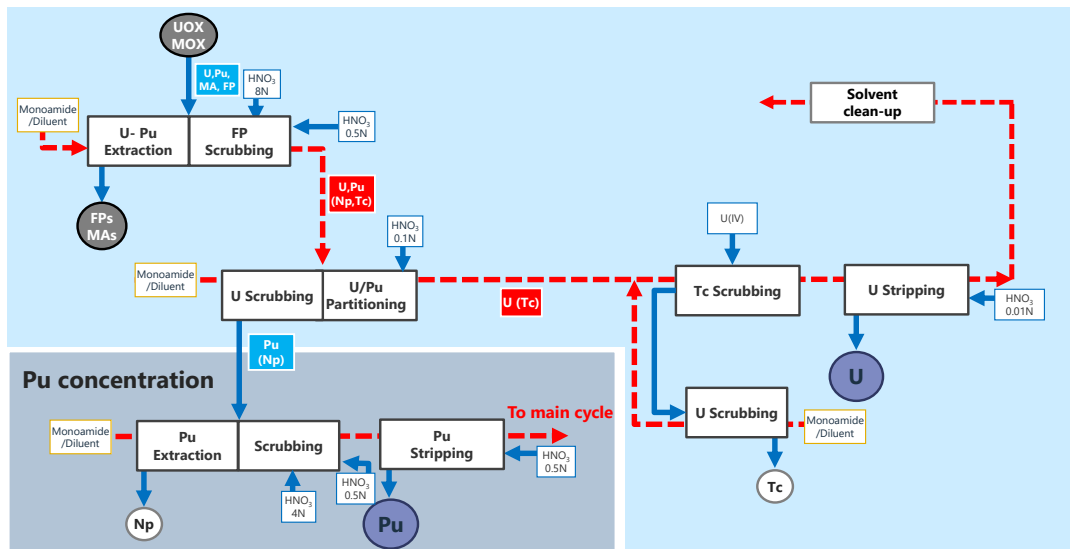


Fig. 5. Flowsheet of U/Pu separation and decontamination versus fission products using a single monoamide

Acknowledgments

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