

DE LA RECHERCHE À L'INDUSTRIE



Lab-scale implementation of a next-generation uranium and plutonium separation and purification process from spent nuclear fuel using monoamide solvent

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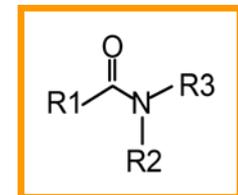
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Study context

- In the back-end spent nuclear fuel cycle, the PUREX process is industrially implemented in the AREVA plant at La Hague for UOX spent fuel reprocessing and recycling.
- Uranium and plutonium are purified by this process thanks to several liquid/liquid extraction steps. TBP (tri-n-butyl phosphate) is the extractant and U/Pu separation is achieved by plutonium reduction which involves reductive reagents.
- In the framework of the development of Gen-IV reactors and the treatment of fuels with increasing Pu content, applying the same chemical process would mean:
 - Quite large increase of reductive reagent consumption,
 - More complex industrial separation workshops.
- New extraction systems such as monoamide solvents have been developed as they exhibit:
 - Good stability towards hydrolysis and radiolysis,
 - High selectivity with respect to fission products^[1-2].



[1] Pathak P. N. *et al.*, *Solv. Extr. Ion. Exch.*, **19**(1), 105-126 (2001)

[2] Condamines N. *et al.*, *Solv. Extr. Ion. Exch.*, **10**, 69-100 (1992)

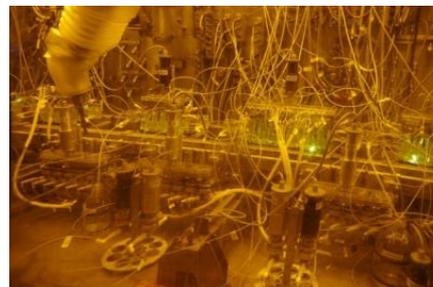
Study context

- In this work, a mixture of N-N-di-(2-ethyl-hexyl)-butanamide (DEHBA - 0.5 mol/L) and N-N-di-(2-ethyl-hexyl)-isobutyramide (DEHiBA – 0.9 mol/L) was tested.
 - See M. Miguiditchian slides in this session.
- The aim of the experiment is to demonstrate uranium and plutonium separation and purification from a genuine spent nuclear fuel in HA conditions.

1



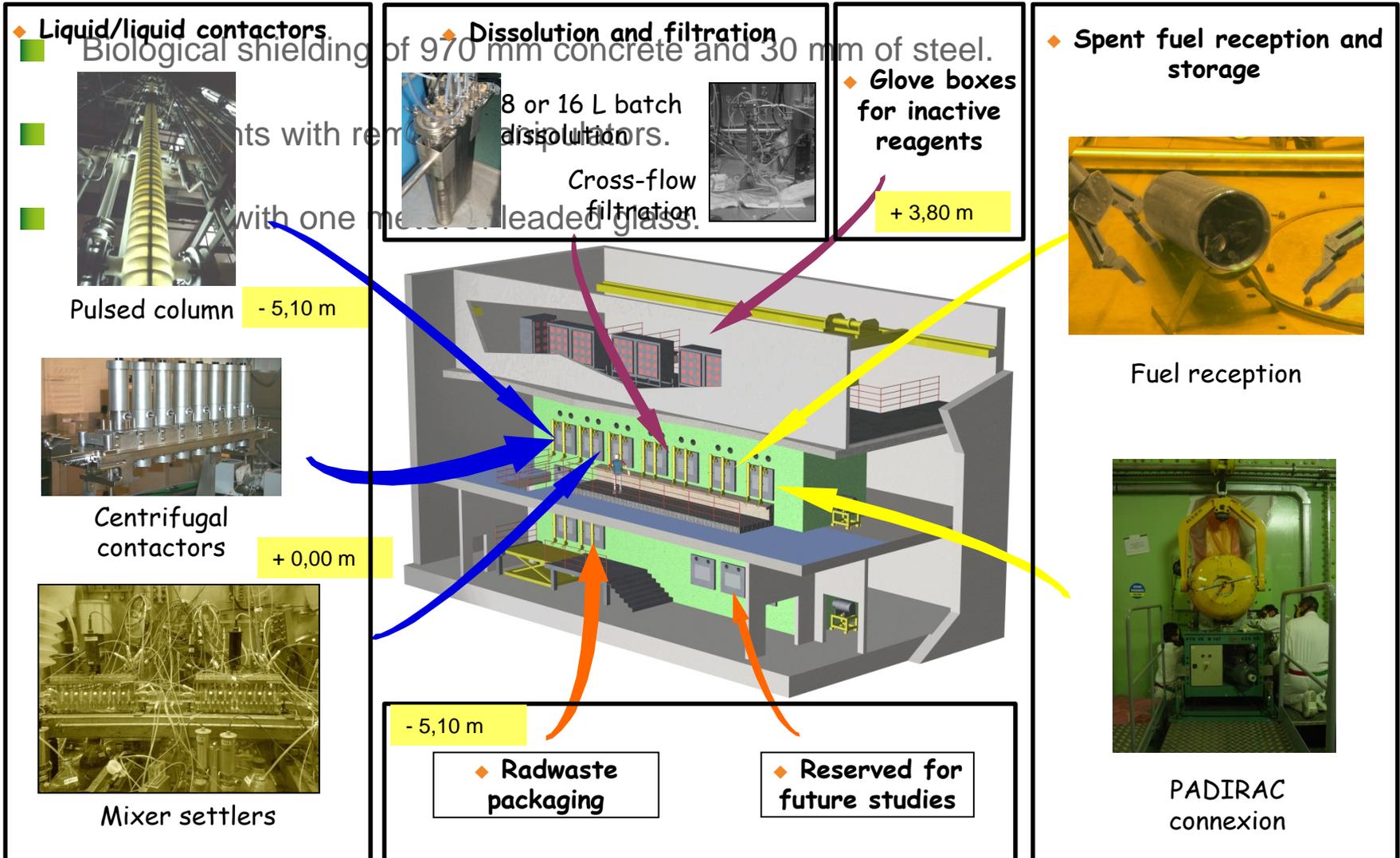
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Dissolution of spent nuclear fuel and filtration of the solution

Liquid-liquid extraction experiments

PRESENTATION OF THE PROCESS SHIELDED LINE CBP



1st STEP: DISSOLUTION AND CLARIFICATION

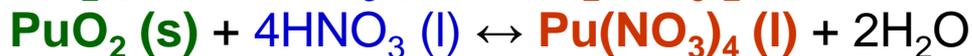
Nature of the spent nuclear fuel

- 1.8kg (U+Pu) coming from different reactors of EDF's French plant units.
- UOX3 fuels (75% mass):
 - Burnup = 65000 MWd/t.
 - Enrichment = 4.95% ²³⁵U.
 - 4 years of cooling.
- UOX fuels (18% mass):
 - Burnup = 37000 MWd/t.
 - Enrichment = 4.95% ²³⁵U.
 - 7 years of cooling.
- MOX fuels (7% mass):
 - Burnup = 25000 MWd/t.
 - Pu enrichment in the range of 6 %.
 - 18 years of cooling.

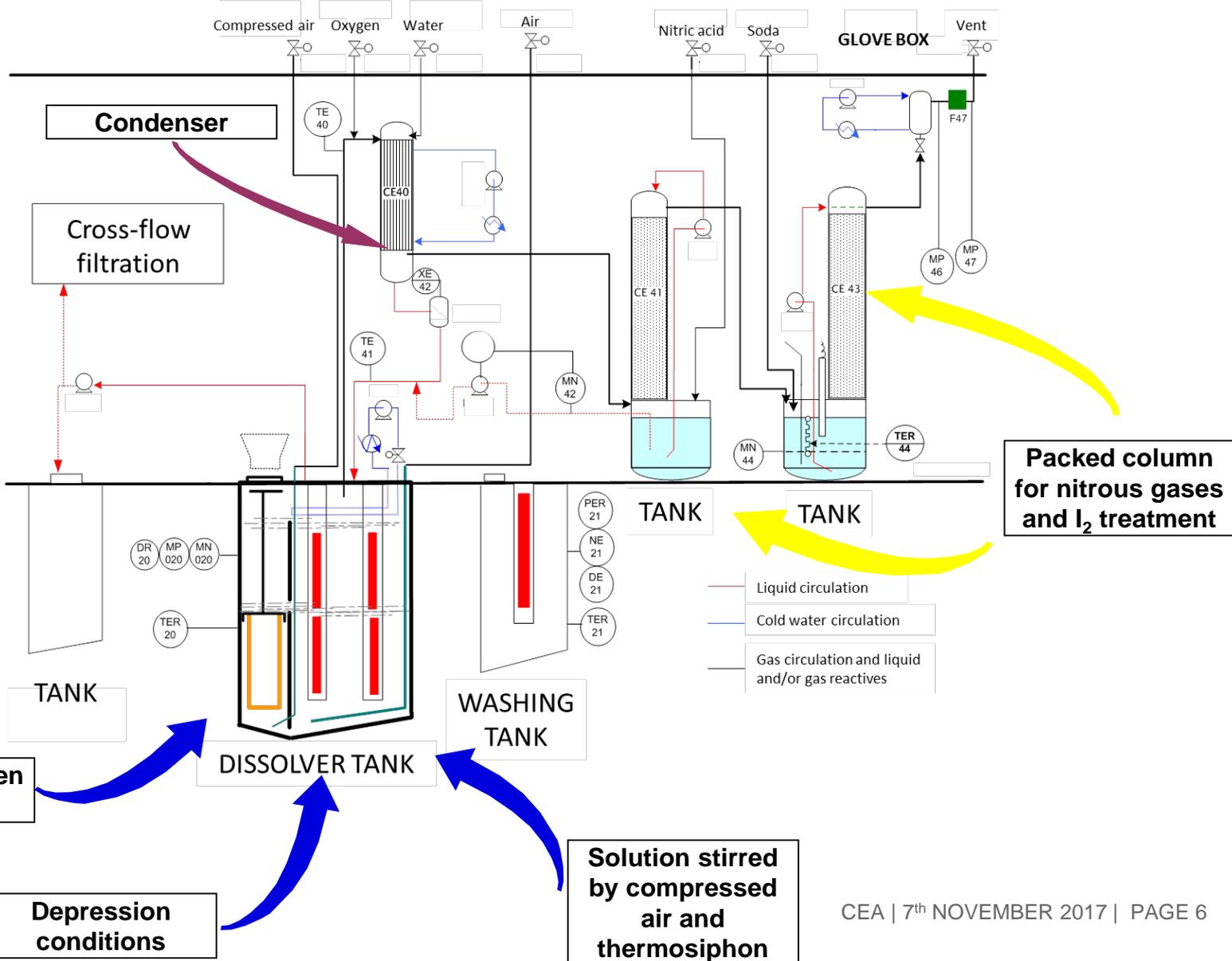


Operating conditions

- Dissolution in boiled nitric acid media with the following reactions.

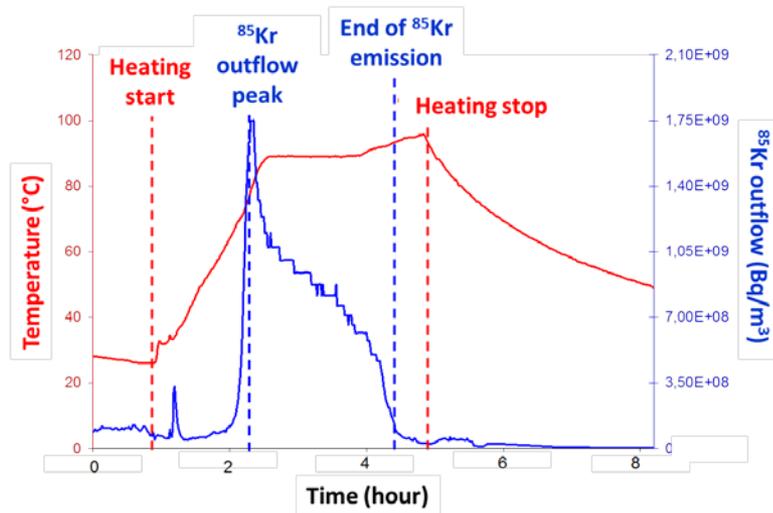


1st STEP: DISSOLUTION AND CLARIFICATION



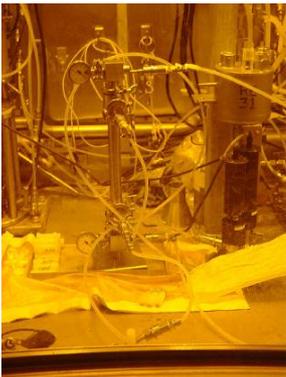
1st STEP: DISSOLUTION AND CLARIFICATION

Monitoring of the process: ^{85}Kr emission



- Kr is trapped into spent nuclear fuel.
- The ^{85}Kr release, measured after gas treatment devices, is controlled during the dissolution.
- The end of emission indicated the end of the reaction.

Clarification of the dissolution solutions

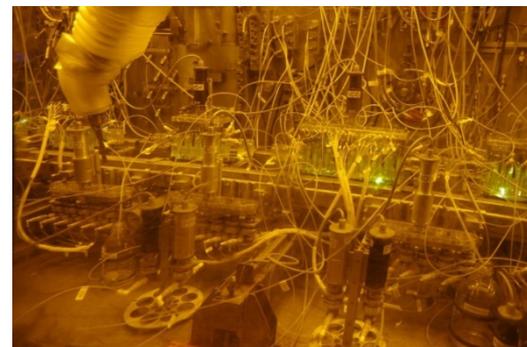
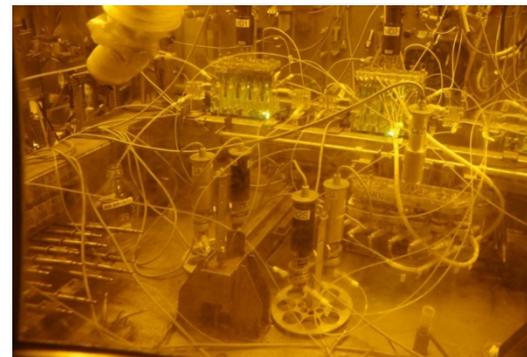
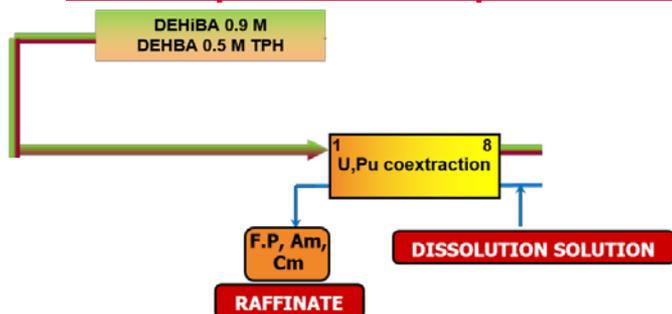


- Indispensable step prior to directing them to downstream operations (avoiding any risks of equipment plugging or solvent degradation).
- Performed by tangential filtration through membrane.
- Production of 10L of dissolution solution without fines.

Main properties of the clarified solution

Element	Concentration (g/L)	Radioelement	Activity (Bq/L)
U	184	¹⁰⁶ Ru	1.35*10 ¹¹
Pu	2.85	¹³⁴ Cs	4.90*10 ¹¹
Tc	0.210	¹³⁷ Cs	1.23*10 ¹²
Np	0.125	¹⁴⁴ Ce	1.10*10 ¹¹
Zr	0.989	¹⁵⁴ Eu	1.68*10 ¹¹
Ru	0.524	¹⁵⁵ Eu	4.50*10 ¹⁰
Mo	0.939	²⁴¹ Am	9.90*10 ¹⁰
Pd	0.437		
Sr	0.255		

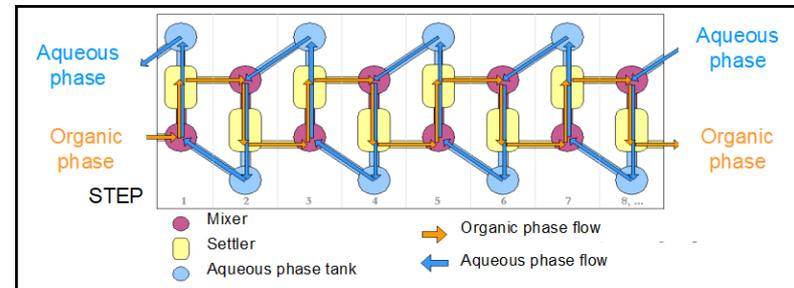
Principle of the process



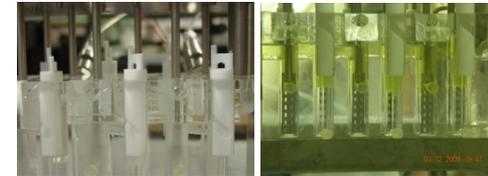
- 1-Coextraction of U(VI), Pu(IV) at relatively high nitric acidity.
- 2-U/Pu purification vs fission products (F.P. scrubbing) at moderate acidity completed with a section at low acidity for U/Pu partitioning preparation.
- 3-U/Pu partitioning at low acidity with U scrubbing step to adjust Pu/U ratio.
- 4-Np, Tc scrubbing by reduction with U(IV).
- 5-U stripping.
- 6-Solvent clean-up before recycling the organic phase.

Process devices

- PMMA mixer-settler extractor batteries where the aqueous and the organic phases flow countercurrently.

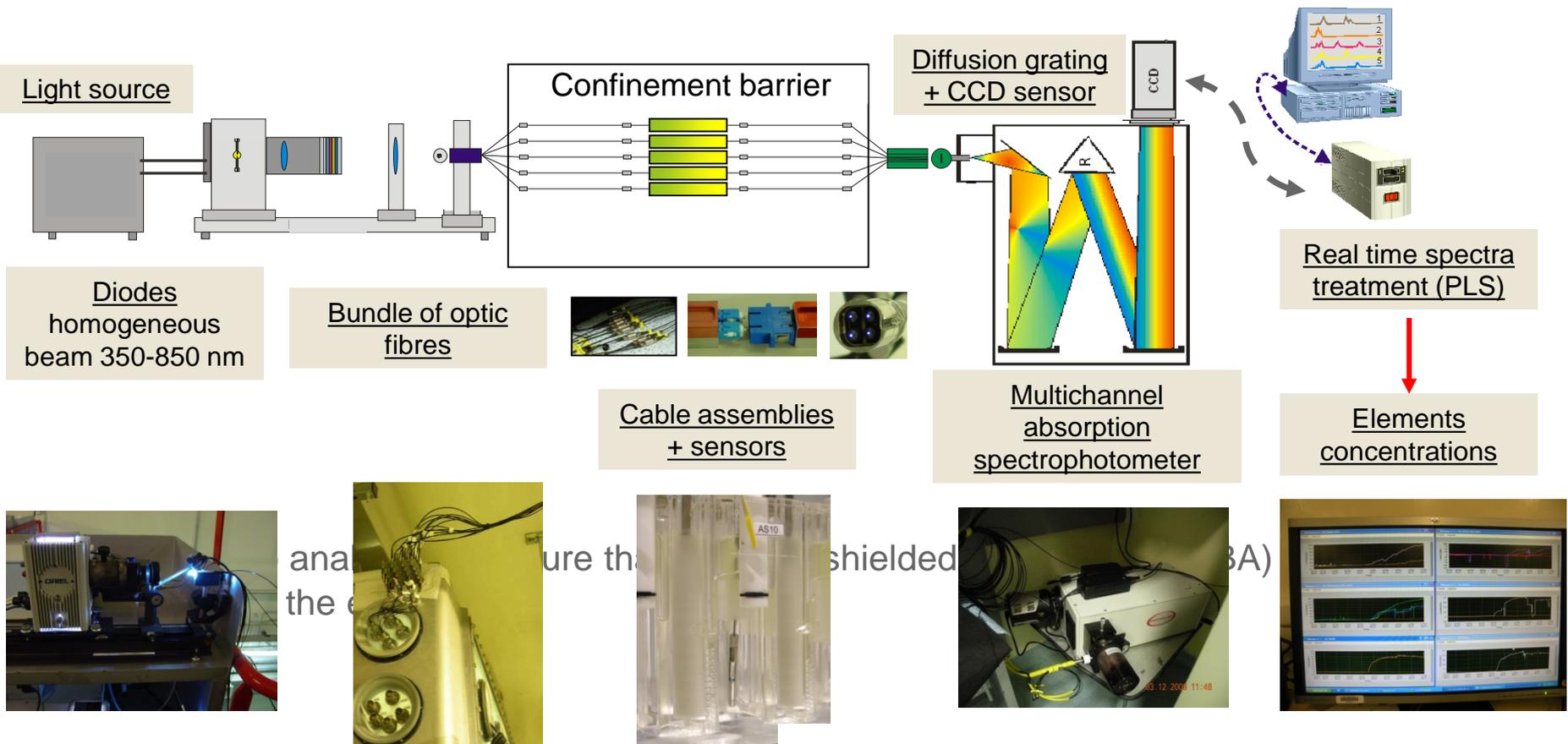


- Solutions mixed by stainless steel perforated paddle impellers (1700 to 3000 rpm).
- Interphases in settler compartments adjusted with titane slides.
- All reagents are introduced by rotary piston pumps located outside the confinement barrier.
- Flow rate measurements are performed thanks to Coriolis mass flowmeter and controlled by a specific supervision application.



Analytical measurements

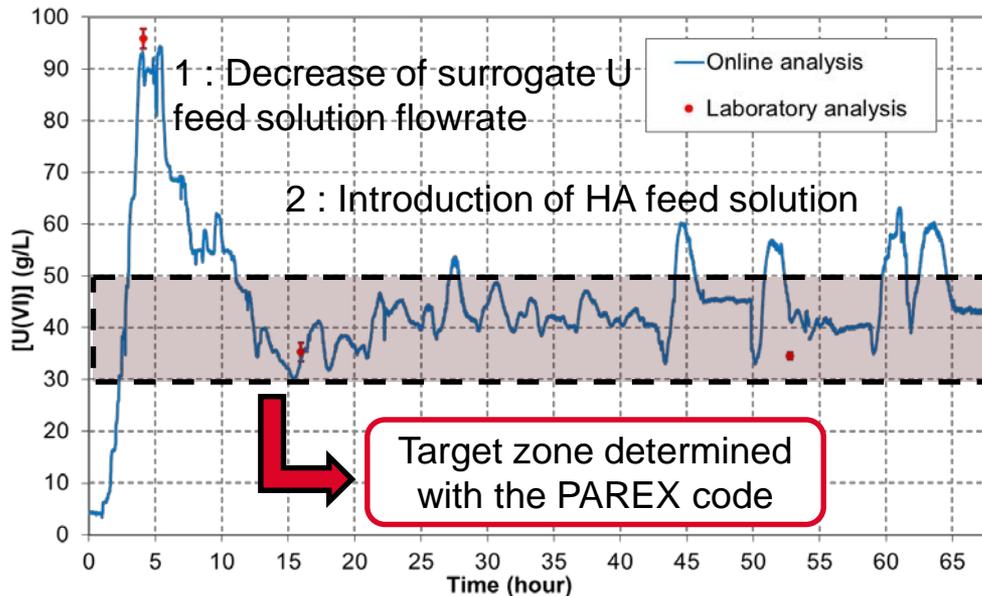
- On-line and *in situ* UV-visible spectrophotometric measurements implemented to follow elements (U, Pu, Am...) concentrations in organic and aqueous phases.



Successive steps of the trial

- Acid equilibria of the flowsheet (6 hours).
- Uranium equilibria (15 hours):
 - Acid feed solution replaced by a surrogate uranium feed solution.
 - Solvent saturation control with the help of online spectrometry completed with lab-analysis.
- HA trials (50 hours):
 - Surrogate replaced by the dissolution solution.

Example of monitoring (aqueous scrub outlet)



1 – Decrease of surrogate feed flowrate

2 – Introduction of genuine feed solution

Main conclusions

- Treatment of approximatively 5 litres of HA feed solution.
- Good hydrodynamic behaviour.
- Recovery yield > 99.99% for U and > 99.96% for Pu.
- Constant Pu/U ratio in the Pu outlet during the trial.
- Good DF of U and Pu towards F.P.

	T0 + 52H	T0 + 62H	T0 + 69H
[U] (g/L)	1.23	1.85	1.79
[Pu] (g/L)	3.41	4.89	5.05
[U]/[Pu]	0.34	0.38	0.35

Element	Uranium		Plutonium	
	Result	Target ^[3]	Result	Target ^[4]
Pu (Bq/g)	1.5.10 ⁵	125	-	-
Np (Bq/g)	17	125	Not separated	
Tc (µg/g)	5	5	609	6000
¹⁰⁶ Ru (Mev/g)	1.9.10 ²	3.0.10 ²	1.3.10 ⁴	1.0.10 ⁵
γ act. (Mev/g)	5.8.10 ²	3.0.10 ²	4.0.10 ⁴	1.0.10 ⁵

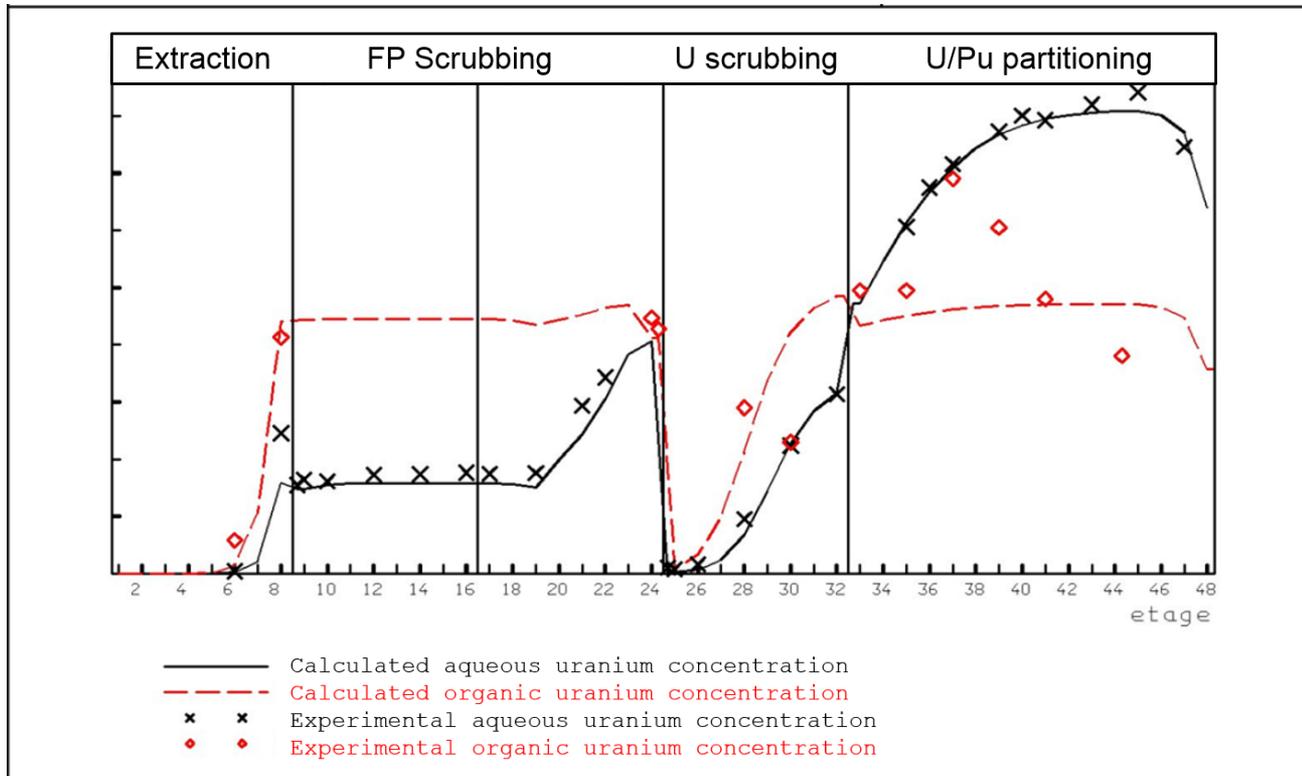
[3] ASTM C788-03(2015)
[4] ASTM C757-90 (1996)e1

2nd STEP: LIQUID-LIQUID EXTRACTION EXPERIMENTS

Process simulation

- At the end of the test, both aqueous and organic phases were sampled and analyzed to obtain data at the stationary state.

URANIUM PROFILES

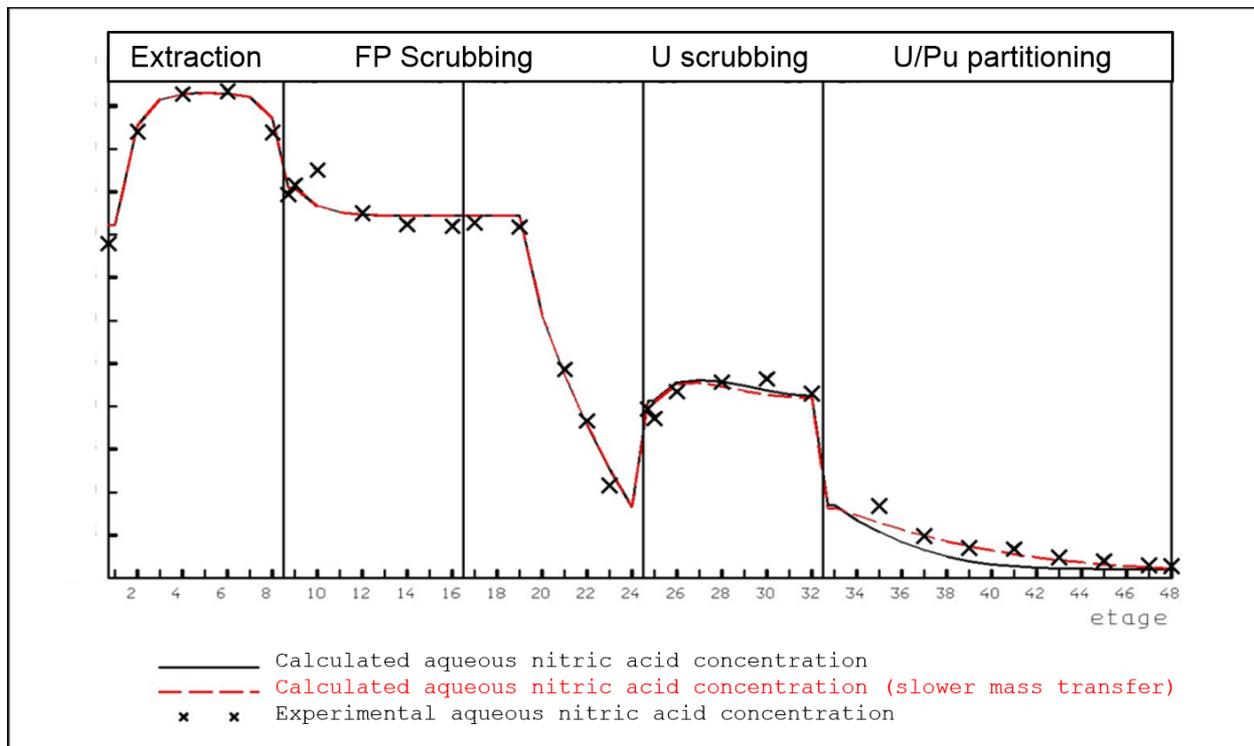


- Very good simulation of U behaviour in the different steps of the process.

Process simulation

- At the end of the test, both aqueous and organic phases were sampled and analysed to obtain data at the stationary state.

NITRIC ACID PROFILES

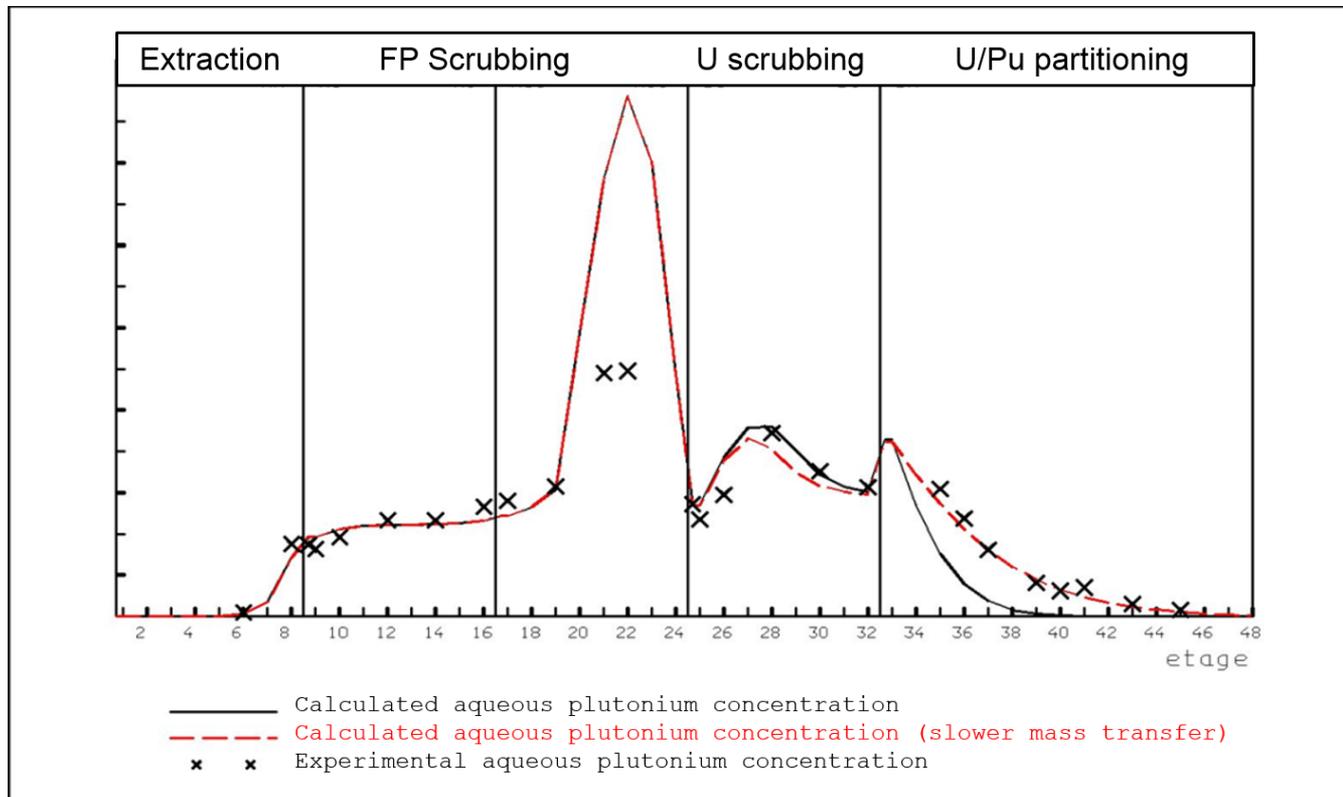


- Very good simulation of HNO_3 behaviour in the three first steps of the process. In the U/Pu partitioning part, a deviation is observed that can be simulated by taking into account a slower mass transfer kinetic.

Process simulation

- At the end of the test, both aqueous and organic phases were sampled and analyzed to obtain data at the stationary state.

PLUTONIUM PROFILES



- Like HNO_3 profiles, the Pu behaviour simulation can be improved by taking into account a slower mass kinetic transfer.

CONCLUSION AND PROSPECTS

Successful experimental demonstration in HA conditions of the use of monoamides as an alternative to TBP for spent nuclear fuel reprocessing

- Efficient recovery of U and Pu
- Good decontamination factors of U and Pu towards FP after one cycle
- No reducing agent for the U/Pu partitioning

Validation of the model developed to design the flowsheets

- Good representation of nitric acid and actinides concentration profiles
- Combination of online analysis with accurate estimation by the model was very powerful to monitor the process

Process optimizations

- Replacement of the mixture of monoamides by a single molecule with a less viscosity
- Improvement of Np management
- Decontamination of uranium towards technetium without any redox agents

Thank you for your attention

Acknowledgements

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