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Major Hazard and Criticality review of the Euro-Ganex process

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Summary

The European Horizon 2020 GENIORS project aims to improve the current recycling process of spent nuclear fuel and the future recycling strategies to be implemented in the 4th generation of nuclear reactors. Euro-GANEX (Grouped Actinide Extraction) is an advanced aqueous reprocessing flowsheet developed in the field of the SACSESS European project. Though similar to the widely used PUREX process, the GANEX process utilises different chemicals to extract an actinide product rather than plutonium alone, which increases its proliferation resistance and decrease the quantities of actinides sent to high level waste (HLW). This document, which is the D9.5 deliverable, outlines the IRSN independent safety review based on the Euro-GANEX plant design and process flowsheet provided by NNL. This preliminary safety review takes into consideration the conclusion of the previous safety reviews carried out by NNL and IRSN in the framework of the SACSESS project. This review is based mainly upon IRSN's knowledge and experience of reprocessing of light water reactor UOX fuels in La Hague plants and is mainly focused on criticality safety. Besides criticality, other areas/risks (radiation protection, flammability and explosion, chemical compatibility, thermal stability/reactivity, radiolysis, radioactive decay heat ?) were reviewed, even to a lesser extent, these aspects having been discussed in depth in the field of SACSESS project. This report leads to a certain number of recommendations and provides some avenues for R&D aimed at improving the safety of a future industrial reprocessing facility using the EURO-GANEX process.

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MAJOR HAZARD AND CRITICALITY REVIEW OF THE EURO-GANEX PROCESS (D9.5 DELIVERABLE)

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1. INTRODUCTION

The European Horizon 2020 GENIORS project combines the efforts of 24 European partners to improve: the current recycling of spent nuclear fuel, and future recycling strategies to be implemented in the 4th generation of nuclear reactors (expected to enter operation by 2030) [1].

Euro-GANEX (Grouped Actinide Extraction) is an advanced aqueous reprocessing flowsheet developed as part of the European Union's funded SACSESS project [2]. Though it is broadly like the widely used PUREX process, the GANEX process utilises different extraction chemicals to extract transuranic actinide product rather than pure plutonium product. The benefits of this type of extraction are two-fold: the absence of pure plutonium in the product increases its proliferation resistance and the smaller quantities of actinides sent to high level waste (HLW) significantly reduces the heat loading of waste packages. Full recycling of actinides can result in a reduction in the time required for high level waste (HLW) to reduce to reference levels from 100 000 years to 500 years [3]. This increases the quantity of waste that can be incorporated per HLW container, reducing overall strains on storage facilities.

This document, which is the D9.5 deliverable,¹ outlines the IRSN independent safety review based on the Euro-GANEX plant design and process flowsheet [4] provided by NNL (National Nuclear Laboratory). This preliminary safety review takes into consideration the conclusion of the previous safety reviews carried out by NNL and IRSN in the framework of the SACSESS project [2]. This document does not describe the main principle of criticality risks assessments as this point is presented in the SACSESS report [2].

This review is based mainly upon IRSN's knowledge and experience of reprocessing of light water reactor (LWR) UOX fuels in La Hague plants and is mainly focused on criticality safety. In addition to criticality, areas/hazards for consideration are also radiation protection, materials selection/corrosion, flammability and explosion, chemical compatibility, thermal stability/reactivity, radiolysis, radioactive decay heat and management of liquid and gaseous effluents. This work is about the operations from head-end section to co-conversion unit (different process options or alternatives might be also compared) and considers the interface between each process step (mechanical preparation, voloxidation, dissolution, separation, conversion, storage/fuel fabrication, effluent management). Concerning criticality safety, the review either confirms the control modes proposed by NNL in report of Reference [4] report or proposes alternative control methods based on the IRSN's knowledge of the French reprocessing facilities.

First, depletion calculations for a realistic initial composition of MOX fuel in an Astrid reactor are performed. This case is defined thereafter as the "reference depletion calculation". Based on the results of this calculation (in particular the isotopic composition of U, Pu, Cm and Am), simple criticality calculations are performed in order to estimate neutronic properties (infinite multiplication coefficient, Material Buckling) and minimal critical values for mass/dimension/concentration of different fissile media, to compare them to those of the fissile media encountered in the La Hague plants. Some of these calculations take into account incidental situations in the chemical separation unit, especially the separation of actinides (for example, Cm from Pu if chemically or physically feasible).

On the basis of these comparisons, IRSN performs independent safety review of the Euro-GANEX plant design and process flowsheet [4].

¹ It was decided in the MINUTES 1st ExCom (15/06/2017 – Avignon) to cancel deliverables D9.2 because all safety aspects will be put in a single deliverable (DECISION D-EC-1.1: D9.2 is cancelled as it is identical to D9.5)

2. DEPLETION CALCULATIONS

2.1. PRESENTATION OF THE FAST REACTOR

Generation IV SFRs considered in this study is based on the 600 MWe French “low void effect” ASTRID-V1 concept developed by the CEA and its industrial partners [5]. As it can be operated as a plutonium breeder, break-even or burner, this reactor concept has gathered attention for its flexibility. The ASTRID concept is adapted to potential strategy changes. However, for our purpose, only the ASTRID-like break-even design is used.

To reach a negative void coefficient during irradiation, this design is highly heterogeneous. It is radially composed of an internal and an external core with two plutonium contents and several fissile and fertile fuel zones axially. The ASTRID-like break-even design is shown on Figure 1.

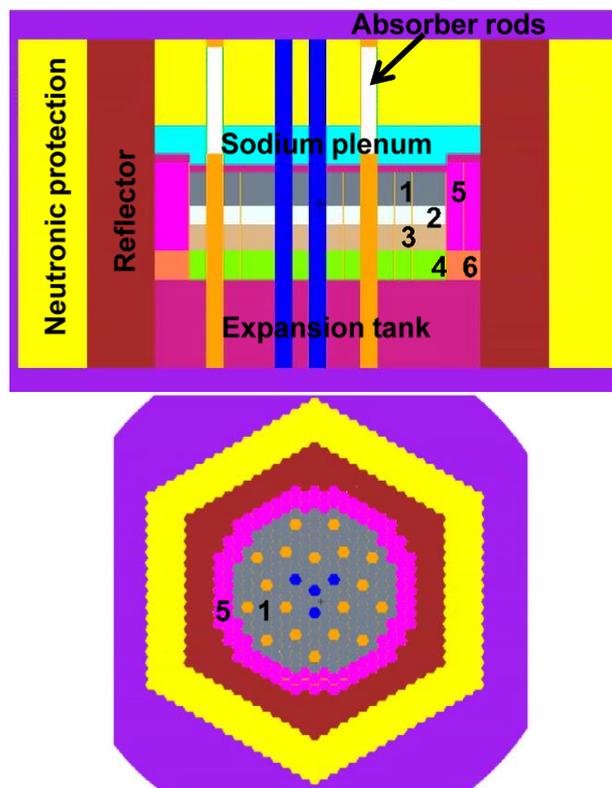


Figure 1: Flowchart of the determination of density mixture for nitrates.

Six fuel zones can be defined in the ASTRID-like design. The three fertile fresh fuel compositions (Zone 2, 4, 6) are always depleted uranium containing 0.2% of ²³⁵U. Then, this SFR design encompasses a wide variation of plutonium isotopic compositions into its three fissile fuel zones (Zone 1, 3, 5).

The compositions for the three fissile fuel zones (Zone 1, 3, 5) used in the reference case are presented in the following table.

Table 1: Composition for fresh fuel considered in the reference study (weight %)

Isotopic composition (weight%) of Pu and Am in fissile fuel zones (1, 3, 5)					
²³⁸ Pu	²³⁹ Pu	²⁴⁰ Pu	²⁴¹ Pu	²⁴² Pu	²⁴¹ Am
2.59	55.2	25.85	7.27	7.87	1.22
Weight ratio PuAm/UPuAm - called T _{PuAm}					
Internal core (fuel zone 1 and 3)			External core (fuel zone 5)		
23.52			20.02		

Full core depletion simulations up to 115 GWd/t have been computed with the VESTA code [6], VESTA fuel depletion simulation is carried out by iteratively coupling a neutron Monte Carlo transport code (MCNP) with a point depletion and decay code (PHOENIX).

Moreover, 1200 ASTRID-like fresh fuel compositions have been sampled inside the ranges presented in Table 2. These ranges cover the possible fresh fast reactor's (FR) fuels that may appear during scenarios by reprocessing LWR UOX and MOX spent fuels with various irradiation histories.

Table 2: Ranges used for fresh fuel considered in 1200 calculations (weight %)

Min/Max isotopic composition (weight%) of Pu and Am in fissile fuel zones (1, 3, 5)					
²³⁸ Pu	²³⁹ Pu	²⁴⁰ Pu	²⁴¹ Pu	²⁴² Pu	²⁴¹ Am
1 / 8	3 / 74	20 / 40	0 / 17	5 / 17	0 / 15
Weight ratio (Pu+Am)/(U+Pu+Am) - called T _{PuAm}					
Internal core (fuel zone 1 and 3)			External core (fuel zone 5)		
15 / 40			15 / 40		

2.2. FUEL COMPOSITION FOR THE REFERENCE CASE

Some results of the fuel composition (Pu isotopes and ²⁴¹Am) for each zone during irradiation for the reference case are presented in Table 3.

Table 3: Fuel composition after irradiation for the 6 zones (weight %)

	Fuel zone	Burn-up (GWd/t)*	²³⁸ Pu	²³⁹ Pu	²⁴⁰ Pu	²⁴¹ Pu	²⁴² Pu	²⁴¹ Am	T _{PuAm}
Fissile zone	1	64	2.0%	52.3%	30.7%	5.3%	8.1%	1.5%	22.8%
		128	1.7%	50.4%	33.5%	5.0%	7.8%	1.6%	22.9%
Fertile zone	2	64	0.1%	87.8%	11.3%	0.7%	0.0%	0.0%	8.2%
		128	0.3%	77.7%	19.7%	1.9%	0.3%	0.2%	13.0%
Fissile zone	3	64	2.1%	52.7%	30.2%	5.4%	8.0%	1.6%	23.1%
		128	1.8%	50.5%	33.3%	5.0%	7.8%	1.6%	23.1%
Fertile zone	4	64	0.0%	94.2%	5.6%	0.2%	0.0%	0.0%	3.8%
		128	0.1%	88.5%	10.7%	0.7%	0.0%	0.1%	7.3%
Fissile zone	5	64	2.1%	54.6%	28.7%	5.3%	7.7%	1.7%	20.2%
		128	1.9%	53.6%	30.7%	4.6%	7.4%	1.8%	20.7%
Fertile zone	6	64	0.0%	95.1%	4.6%	0.3%	0.0%	0.0%	2.7%
		128	0.1%	90.8%	8.5%	0.6%	0.0%	0.1%	5.3%

* Burn up of the full core.

The results for the composition (Pu isotopes and ^{241}Am) of the internal and external core are presented in Table 4. Internal and external core isotopic masses are obtained by weighting compositions of each zones of the core by fuel volumes. This explain why the ^{239}Pu is higher than in fresh fissile fuel (irradiated fertile zones generate plutonium with very high content of ^{239}Pu a seen in Table 3).

Table 4: Fuel composition after irradiation for the external and internal cores (weight %)

Fuel zone	Burn-up (GWd/t)*	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu	^{241}Am	$T_{\text{Pu+Am}}$
Internal core (1, 2, 3 and 4)	0	2.6%	55.2%	25.9%	7.3%	7.9%	1.2%	12.8%
	64	1.7%	59.4%	26.6%	4.5%	6.6%	1.3%	14.6%
	128	1.3%	59.8%	28.2%	3.9%	5.6%	1.1%	16.3%
External core (5 and 6)	0	2.6%	55.2%	25.8%	7.3%	7.9%	1.2%	15.0%
	64	2.0%	56.5%	27.5%	5.0%	7.4%	1.6%	15.6%
	128	1.7%	57.0%	28.7%	4.2%	6.7%	1.7%	16.4%

* Burn up of the full core.

It can be noted that the average content of plutonium obtained ($T_{\text{Pu+Am}} \sim 15\%$ at 64 GWd/t and 16,3 % at 128 GWd/t) is consistent with the fuel feed provided in NNL flowsheets (15,3 %).

The results of the composition of americium and curium are presented in Table 5 and Table 6.

Table 5: Americium composition after irradiation (weight %)

Fuel zone	Burn-up (GWd/t)*	^{241}Am	^{242}Am	$^{242\text{m}}\text{Am}$	^{243}Am	^{244}Am	Am/ (U+Pu+Am+Np+Cm)
Fissile zone 1**	0	100.0%	0.0%	0.0%	0.0%	0.0%	0.29%
	64	56.7%	0.0%	3.1%	40.2%	0.0%	0.62%
	128	46.0%	0.0%	3.4%	50.6%	0.0%	0.77%
Fertile zone 2***	0	-	-	-	-	-	0
	64	92.7%	0.0%	2.0%	5.2%	0.0%	0.00%
	128	85.5%	0.0%	3.3%	11.2%	0.0%	0.03%
Internal core	0	100.0%	0.0%	0.0%	0.0%	0.0%	0.16%
	64	58.6%	0.0%	3.1%	38.3%	0.0%	0.32%
	128	47.2%	0.0%	3.4%	49.4%	0.0%	0.39%
External core	0	100.0%	0.0%	0.0%	0.0%	0.0%	0.18%
	64	66.0%	0.0%	2.8%	31.2%	0.0%	0.39%
	128	56.6%	0.0%	3.4%	40.0%	0.0%	0.49%

* Burn up of the full core.

** the compositions for fissile fuel zones 3 and 5 are similar to those of fissile fuel zone 1.

*** the compositions for fertile fuel zones 4 and 6 are similar to those of fertile fuel zone 2.

One can see that the average content of americium obtained ($T_{\text{Am}} \sim 0,4/0,5\%$ at 128 GWd/t) is consistent with fuel feed provided in NNL flowsheets (0,53 %).

Table 6: Curium composition after irradiation (weight %)

Fuel zone	Burn-up (GWd/t)*	²⁴² Cm	²⁴³ Cm	²⁴⁴ Cm	²⁴⁵ Cm	²⁴⁶ Cm	²⁴⁷ Cm	²⁴⁸ Cm	Cm/ (U+Pu+Am+Np+Cm)
Fissile zone 1**	0	-	-	-	-	-	-	-	0
	64	24.3%	2.1%	67.5%	5.8%	0.3%	0.0%	0.0%	0.1%
	128	9.8%	1.2%	76.5%	11.3%	1.2%	0.1%	0.0%	0.2%
Fertile zone 2***	0	-	-	-	-	-	-	-	0
	64	85.6%	3.2%	10.7%	0.5%	0.0%	0.0%	0.0%	<0.1%
	128	64.4%	4.2%	28.5%	2.7%	0.2%	0.0%	0.0%	<0.1%
Internal core	0	-	-	-	-	-	-	-	0
	64	26.3%	2.1%	65.9%	5.5%	0.3%	0.0%	0.0%	<0.1%
	128	10.7%	1.3%	75.9%	11.0%	1.2%	0.1%	0.0%	0.1%
External core	0	-	-	-	-	-	-	-	0
	64	31.8%	2.1%	61.8%	4.1%	0.1%	0.0%	0.0%	<0.1%
	128	14.2%	1.4%	75.0%	8.7%	0.6%	0.0%	0.0%	0.1%

* Burn up of the full core.

** the compositions for fissile fuel zones 3 and 5 are similar to those of fissile fuel zone 1.

*** the compositions for fertile fuel zones 4 and 6 are similar to those of fertile fuel zone 2.

The average content of curium obtained ($T_{Cm} \sim 0,1\%$ at 128 GWd/t) is consistent with fuel feed provided in NNL flowsheets (0,056 %) as can be seen.

3. CRITICALITY CALCULATIONS

3.1. SIMPLE CRITICALITY CALCULATION FOR THE REFERENCE CASE

Various simple calculations are performed in order to estimate the criticality property of irradiated MOX FR fuel and to compare them to the criticality property of UOX LWR fuel (as these fuels are reprocessed in industrial facilities at the present time). In this part, only the infinite multiplication coefficient (k_{∞}) are studied in an important moderation range (the moderation ratio corresponds to the number of hydrogen nucleus on heavy nucleus) considering water as moderator. These calculations are performed using the APOLLO2-Pij code from the CRISTAL V2 package [7].

3.1.1. k_{∞} FOR THE COMPOSITION OF THE FUEL ZONE AND FUEL ASSEMBLY

This section considers only the composition in uranium and plutonium of the fuel zone and assembly. Indeed, in paragraph 3.1.3 it will be shown that americium tends to reduce the reactivity and that the amount of curium in normal condition does not have a significant impact on reactivity.

Figure 2 shows the k_{∞} for Uranium-Plutonium water moderated system considering a fixed composition for uranium (0.2wt% in ²³⁵U) and plutonium isotopic compositions and a Pu/(U+Pu) ratios based on calculation presented in paragraph 2.1 (either a composition of fresh fuel or at the end of the irradiation). Calculations are performed with the main plutonium isotopes without fission products.

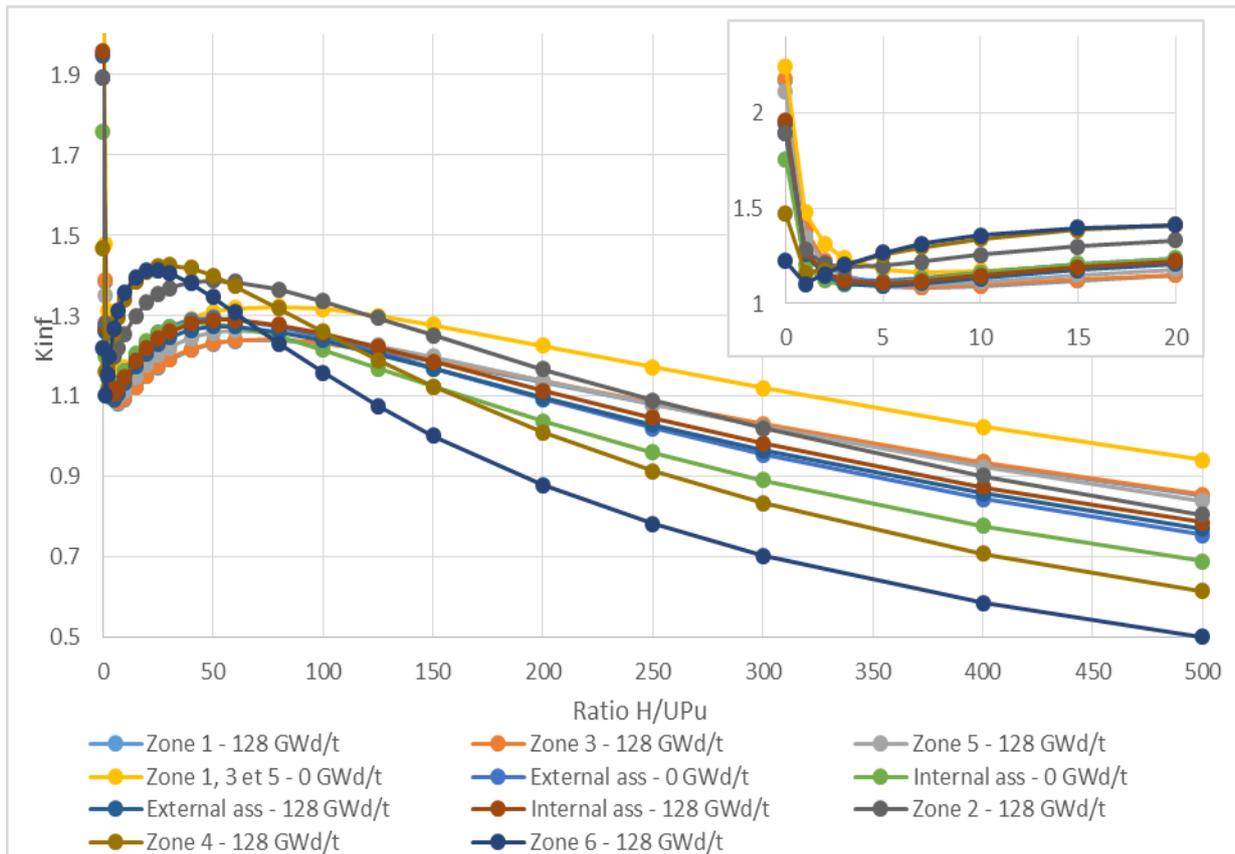


Figure 2: k_{∞} for Uranium-Plutonium moderated by water.

From this figure, the following observations can be made:

- For the external assembly, the reactivity difference between the U+Pu composition for fresh fuel or at the end of irradiation as a function of moderation ratio is not significant;
- For the internal assembly, there are few differences in k_{∞} for low moderation ratio (H/(U+Pu) lower than 50). For higher moderation ratios, k_{∞} of irradiated fuel assembly goes above fresh fuel to reach a maximum of reactivity at the end of irradiation;
- For the internal and external assemblies, there is few k_{∞} difference for low moderation ratio (H/(U+Pu) lower than 50). For higher moderation ratios, the composition of the internal assembly at the end of the irradiation lead to the maximum of reactivity. So, if the whole assembly is dissolved (meaning that we can consider the mean composition), calculations regarding dissolution solution have to consider U+Pu composition of the internal assembly at the end of the irradiation.
- For low moderation ratio, the composition of the fertile zones after irradiation lead to the maximum values of k_{∞} (due to plutonium isotopes production by neutron captures and the fact that fission products are neglected). **Consequently, before dissolution, it could be necessary to consider the composition of these irradiated fertile zones in the criticality safety analysis.**

3.1.2. k_{∞} FOR DIFFERENT COMPOSITION OF PLUTONIUM

The k_{∞} for different compositions of plutonium moderated by water are presented in Figure 3. Except for the yellow curve corresponding to the initial composition of fissile zones, the isotopic compositions of plutonium are those obtained at the end of irradiation (burn-up = 128 GWd/t for the whole core).

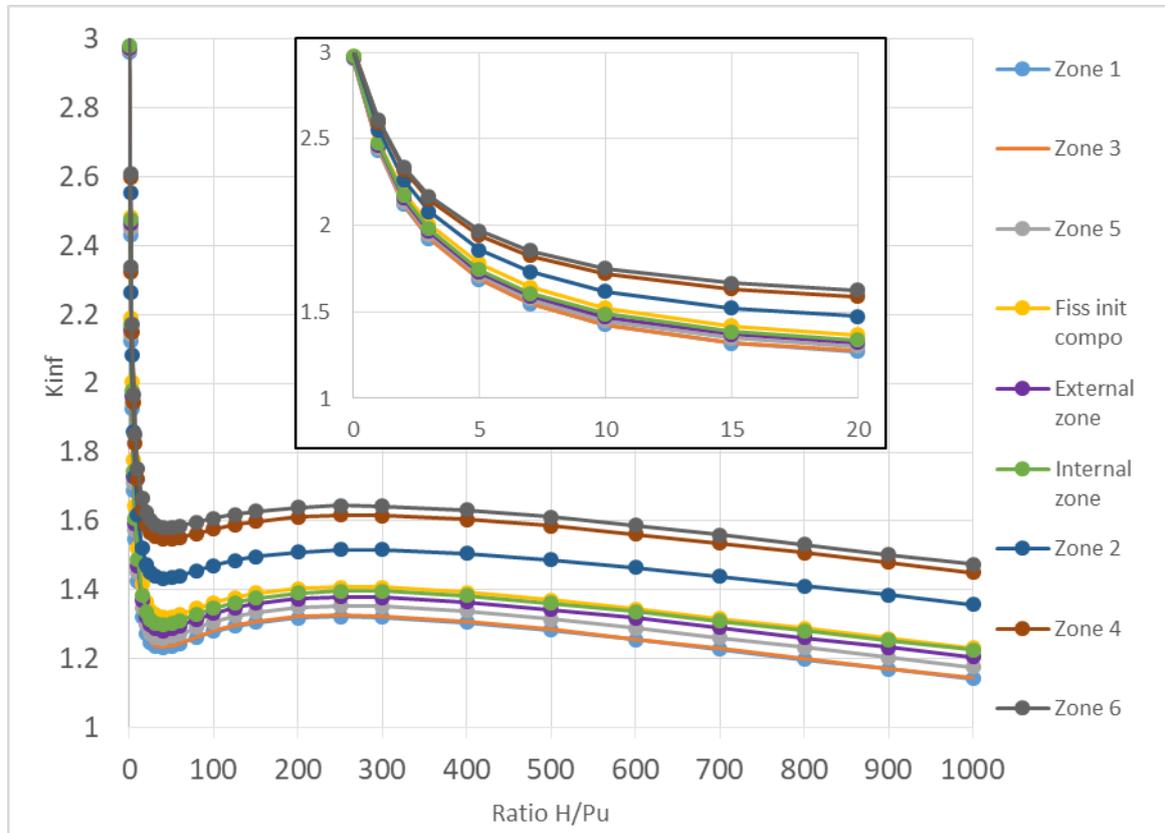


Figure 3: k_{∞} for plutonium moderated by water.

From this figure, the following observations could be made:

- The k_{∞} for the initial plutonium composition of fissile zone are similar to those of the final plutonium composition of the external zone and internal zone. Consequently, after the first separation step (U retrieve from other elements), criticality safety should not be very impacted by the composition of the fuel. In the rest of this study the plutonium composition corresponding to the initial composition will be chosen;
- The k_{∞} for the plutonium from the recycling irradiated fertile zones is more penalizing in terms of reactivity than the plutonium from the fissile zone (higher content of ^{239}Pu in the plutonium). But, in this concept, as the dissolution is performed by fuel assembly, the composition for the plutonium considered in criticality safety should be those of the entire fuel and not only those of the fertile zone. But, if a design of a RNR reactor retains an assembly with only fertile zone, attention should be taken to the composition of plutonium especially after the separation with uranium and fission products.

3.1.3. k_{∞} FOR AMERICIUM AND CURIUM

Figure 4 present k_{∞} variations for americium, curium, plutonium and a mixture of curium and plutonium. For the element, the isotopic compositions are the following:

- Americium: the composition of zone 1 at the end of irradiation. At this irradiation, the amount of americium is maximal and the amount of fissile ^{242m}Am is maximal;
- Curium: the composition of zone 1 at the end of irradiation. At this irradiation, the amount of curium is maximal and the amount of fissile ^{245}Cm (^{245}Cm is more reactive than ^{243}Cm) is maximal;
- Plutonium: 2 compositions are considered:
 - plutonium composition of fresh fuel (see Table 1). As said in paragraph 3.1.2, for the whole assembly, irradiation do not have a significant impact on k_{∞} for plutonium;
 - plutonium composition of fuel zone 1 at the end of irradiation (see Table 3).
- Curium+Plutonium: composition of zone 1 at the end of irradiation (case with maximal amount of curium).

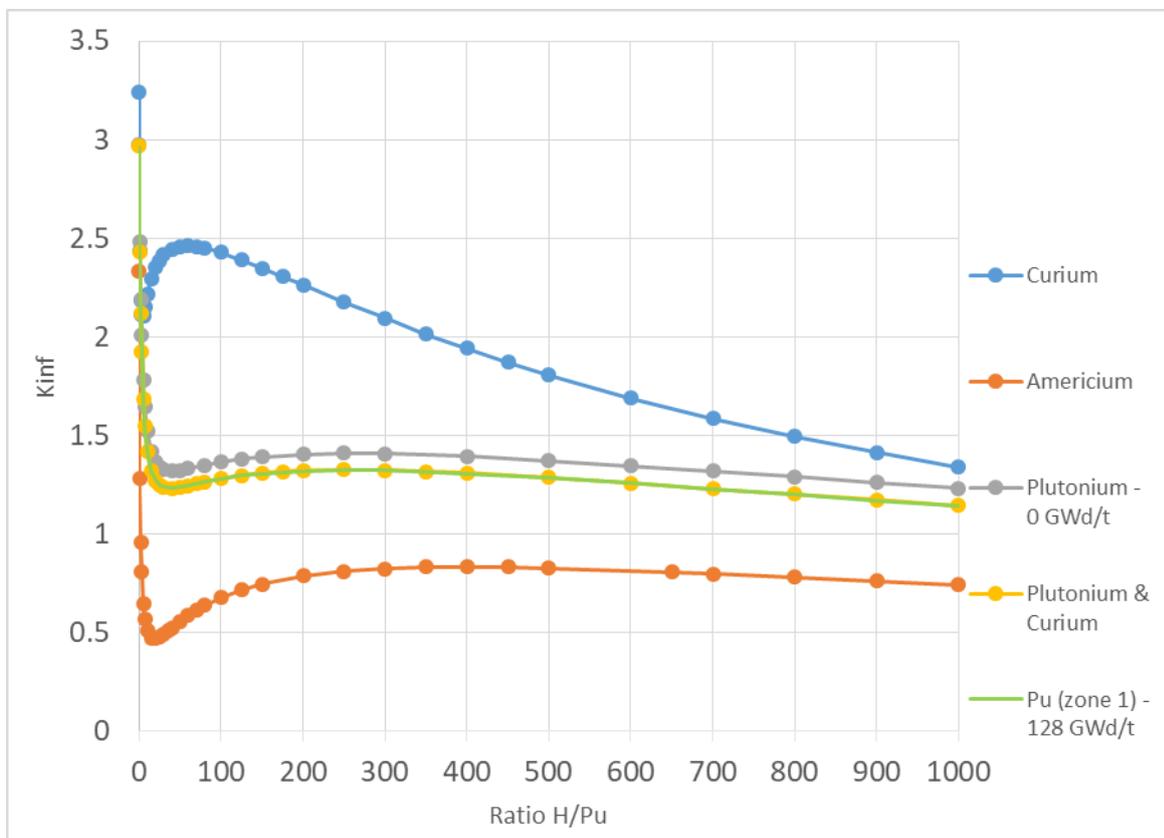


Figure 4: k_{∞} for americium and curium moderated by water.

From this figure, the following observations could be made:

- The k_{∞} for americium is lower than 1 except for very low moderation ratio ($H/\text{Am} < 2$). Indeed, ^{241}Am is only fissile in the fast spectra. For very low moderation ratio ($H/\text{Am} < 2$), it could be noted that k_{∞} is lower than those of plutonium. So, considering the isotopic composition of

americium, americium do not lead to increase in reactivity compared to plutonium for low moderation ratios. Thereafter, the presence of americium is not taken into account;

- Curium has no significant impact on k_{∞} when this element is considered with plutonium with the maximum ratio content obtained at the end of irradiation, even if critical masses of some curium isotopes are lower than the plutonium. This is mainly due to the fact that the amount of curium is limited compare to plutonium (maximum ratio Cm/(Pu+Cm) = 1.1 % at the end of irradiation for fuel zone 1). This conclusion could be questioned if curium is incorporated in higher proportions in the fresh fuel in the frame of minor actinides transmutation;
- The k_{∞} for curium alone is higher than those of plutonium for the whole moderation ratio range. So criticality safety analysis should consider the situations in which curium could be separated from plutonium, if this situation is physically/chemically possible in the process.

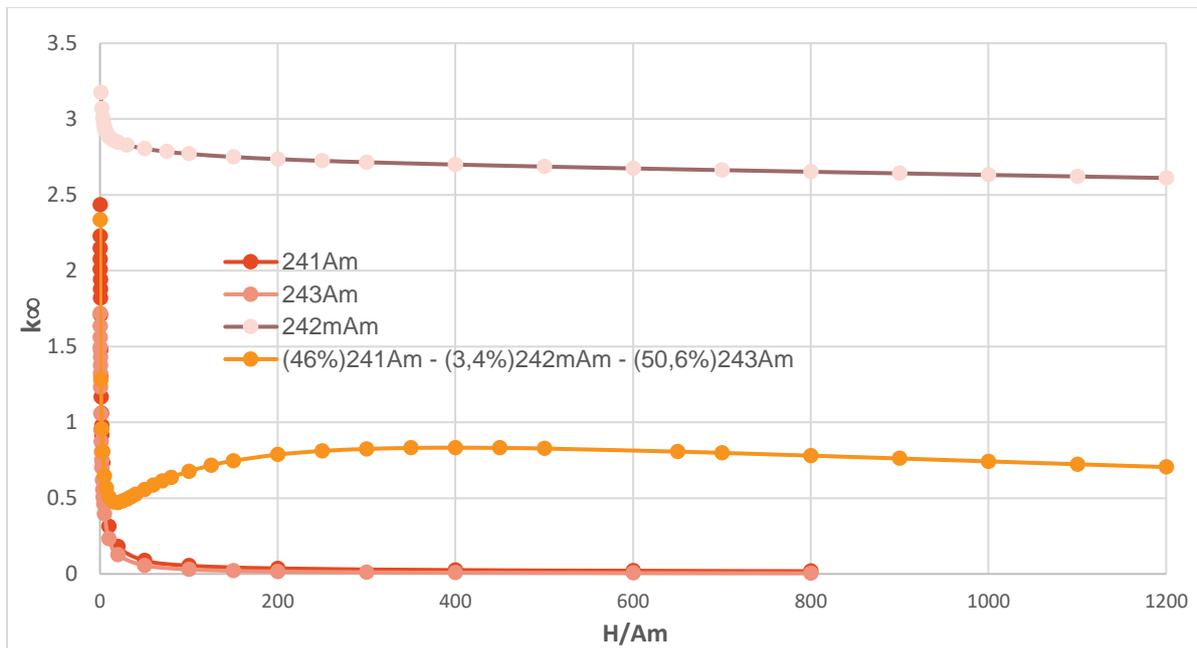


Figure 5: k_{∞} for americium moderated by water.

From this figure, the following observations could be made:

- The k_{∞} for ^{241}Am and ^{243}Am are lower than 1 except for very low moderation ratio ($H/\text{Am} < 2$). Above, this ration, k_{∞} is under 1. Variations of k_{∞} of ^{241}Am and ^{242m}Am in water are very similar, even in k_{∞} of ^{243}Am is slightly lower than the one of ^{241}Am . These two isotopes of Am act as a neutronic poison in solution;
- k_{∞} is above 2,5 when only ^{242m}Am is considered; Fortunately, ^{242m}Am is in very low proportion in the irradiated fuel compare to ^{241}Am and ^{243}Am ;
- due to the low content of ^{242m}Am in the composition in the fissile zone after irradiation, k_{∞} is under 1 once the ratio H/Am is above 2. This is due to ^{241}Am and ^{243}Am neutronic poisonous effect in solution.

Due to its composition, americium acts as a neutron poison in the solution process.

It should be recalled that ^{243}Cm , ^{245}Cm and $^{247}\text{Cm}^2$ are capable to sustain a chain reaction in moderated systems. The subcritical mass limits for ^{243}Cm and ^{245}Cm are even quite very lower than the one of

² Subcritical limit of ^{247}Cm moderated and full reflected by water is 500 g (ANSI/ANS-8.15-2014)

²³⁹Pu (respectively 90 and 23 g compared to 510 g). By contrast, all Cm isotopes are capable of sustaining a chain reaction in non-moderated systems (fast systems). The isotopes ²⁴³Cm and ²⁴⁵Cm are the two main contributors of Cm (composition of fissile zone 1) to k_{∞} in thermal range (moderated medium).

Calculations show that, in the solution, an Am and ²⁴⁵Cm mixture solution remain subcritical as long as the mass proportion of ²⁴⁵Cm in the Am-²⁴⁵Cm mixture remains lower than 15 %.

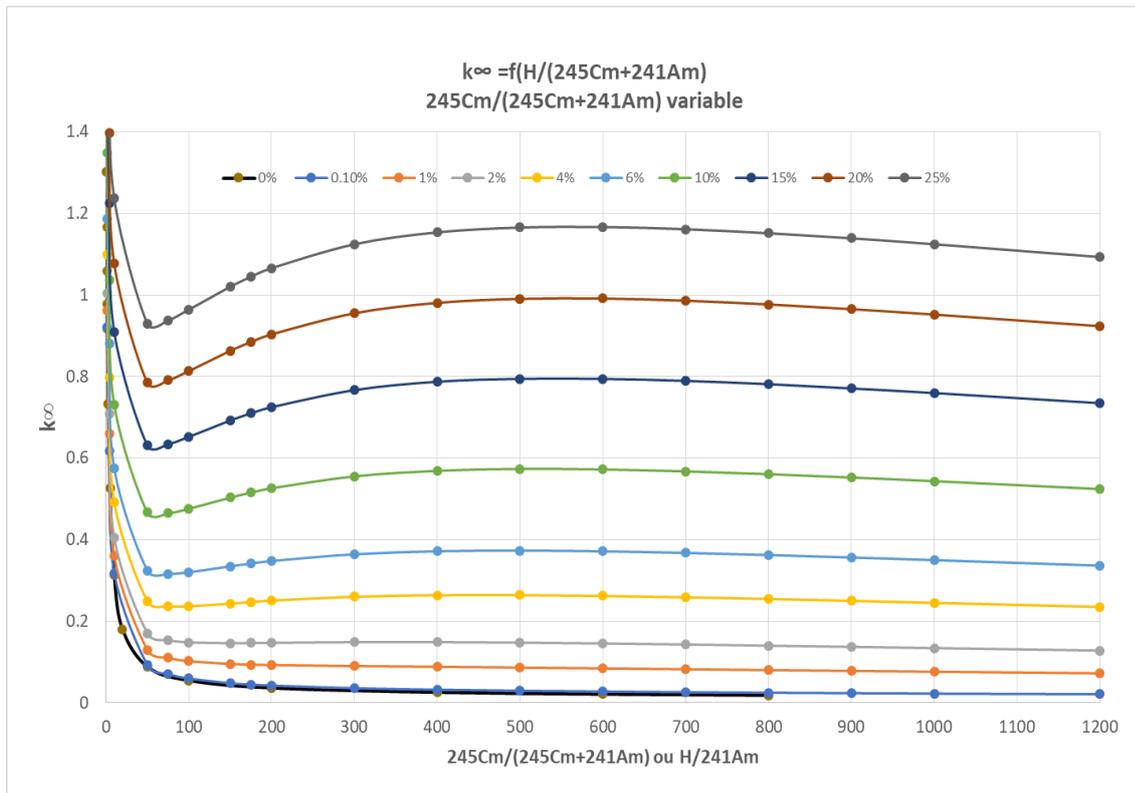


Figure 6: k_{∞} for mixture of ²⁴⁵Cm and ²⁴¹Am moderated by water

Recommendation:

Due to the very low curium critical mass obtained with the expected curium composition, the risk of selective precipitation of curium or separation from other actinides, in particular americium, should be addressed if physically possible.

3.2. COMPARISON OF NEUTRONIC PROPERTIES FOR MATERIAL ENCOUNTER IN EXISTING AND FUTURE REPROCESSING FACILITIES

In this part, a comparison between the fissile material encountered in the existing reprocessing facilities (UOX PWR fuel) and the future reprocessing facilities for MOX FR fuel are performed. This comparison is performed on the bases of:

- k_{∞} and Material Buckling factors obtained with the French APOLLO2-Pij code from the CRISTAL V2 criticality package [7].

- Admissible values of masses, cylinder diameters, plate thicknesses fully reflected by water and infinite medium concentrations ($k_{\text{eff}} = 0.95$) obtained with APOLLO2-Sn code from the CRISTAL V2 criticality package [7].

All calculations were performed taking into account the main actinides ^{235}U , ^{238}U , ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu and ^{242}Pu . Poisoning brought by Fission and Am were not credited.

The fissile material studied are the following:

- oxides (maximum density) moderated by water;
- solutions of dissolution (U or U+Pu nitrate solutions);
- plutonium nitrate solution.

For uranium and plutonium isotopic composition, the following hypothesis are considered:

- For the current reprocessing facilities :
 - For fuel oxide and dissolution solution: the composition of the fissile material before irradiation is considered. Moreover, the enrichment of uranium considered for the design of the La Hague facilities is considered → enrichment of 3.5 wt% in ^{235}U ;
 - For plutonium nitrate solution, a penalizing isotopic weight composition is considered as in La Hague reprocessing plant → $^{239}\text{Pu}/^{240}\text{Pu}/^{241}\text{Pu}/^{242}\text{Pu} = 71/17/11/1$ %;
- For the future reprocessing facilities:
 - For fuel oxide, 2 compositions are considered:
 - Irradiated fertile zone composition. For this case, weight composition of zone 4 at the end of irradiation is considered → $^{235}\text{U}/\text{U} = 0.2$ %, $\text{Pu}/(\text{U}+\text{Pu}) = 7.3$ %, $^{238}\text{Pu}/^{239}\text{Pu}/^{240}\text{Pu}/^{241}\text{Pu}/^{242}\text{Pu} = 0.1/88.5/10.7/0.7/0.0$ %;
 - Fresh fissile zone composition (for the internal zone) → $^{235}\text{U}/\text{U} = 0.2$ %, $\text{Pu}/(\text{U}+\text{Pu}) = 23.3$ %, $^{238}\text{Pu}/^{239}\text{Pu}/^{240}\text{Pu}/^{241}\text{Pu}/^{242}\text{Pu} = 2.6/55.8/26.2/7.4/8.0$ %;
 - For the dissolution solution: weight composition of the internal assembly at the end of the irradiation will be considered → $^{235}\text{U}/\text{U} = 0.2$ %, $\text{Pu}/(\text{U}+\text{Pu}) = 16.1$ %, $^{238}\text{Pu}/^{239}\text{Pu}/^{240}\text{Pu}/^{241}\text{Pu}/^{242}\text{Pu} = 1.3/60.5/28.5/4.0/5.7$;
 - For the plutonium nitrate solution: plutonium weight composition of fresh fuel → $^{238}\text{Pu}/^{239}\text{Pu}/^{240}\text{Pu}/^{241}\text{Pu}/^{242}\text{Pu} = 2.6/55.8/26.2/7.4/8.0$.

For the future reprocessing facilities, the isotopic composition of plutonium is the one obtained in the Astrid core depletion calculation. During the criticality safety analysis, a penalizing composition of plutonium should be considered.

Regarding this point, SACSESS report [8] notes that: *“With regard to criticality risks, the choice of fissile medium or media to be adopted as the reference in GANEX cycle design will be determined mainly by the guarantee of a minimum ^{240}Pu content in the Pu (and, to a lesser extent, the $^{241}\text{Pu}/^{240}\text{Pu}$ and $^{242}\text{Pu}/^{241}\text{Pu}$ ratios) and the maximum Pu content in the solutions. In order to define the contents to be adopted for process equipment design, what are the bounding isotopic characteristics of the fuels to be processed? How is it planned to verify Pu isotopy and the related uncertainty?”*

3.2.1. COMPARISON FOR OXIDE FORM

The comparison for the neutronic properties (k_{∞} and B^2_m) is presented in Figure 7. The comparison of the admissible values (for a $k_{\text{eff}} = 0.95$) is presented in Table 7.

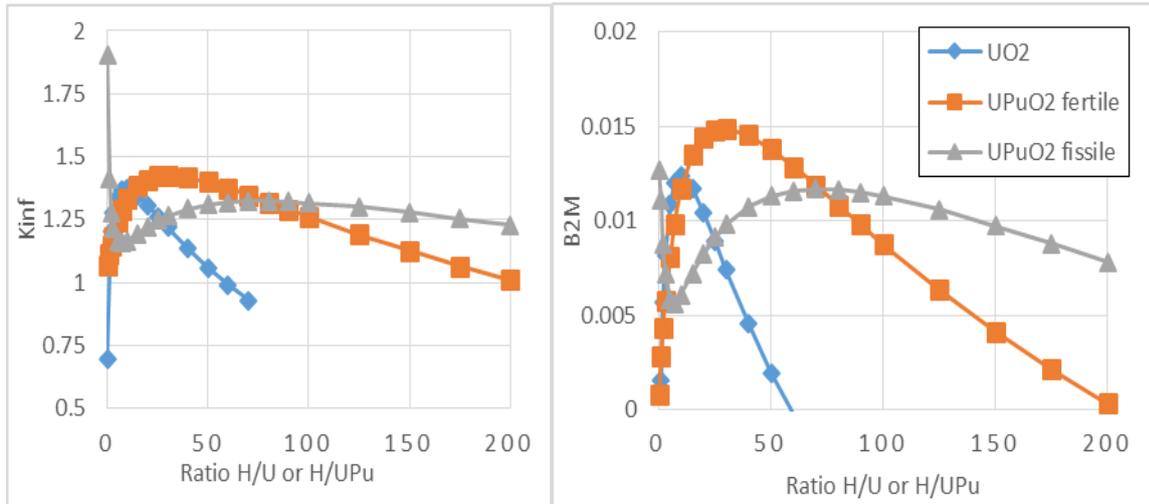


Figure 7: K_{∞} and B^2_m for oxide material.

Table 7: Admissible values for oxide material

	UO ₂ La Hague	UPuO ₂ issue of Irradiated fertile GENIORS	Fresh UPuO ₂ fissile GENIORS
Infinite slab thickness (cm)	12.6	10.4	10.8
Infinite cylinder radius (cm)	13.2	11.51	12.5
UO ₂ or UPuO ₂ mass (kg)	55.7	14.0	8.9

Based on the figure and table above, the following conclusion could be made when materials is in oxide form:

- For criticality safety control mode based on geometry limitation, geometry size of equipment in the future reprocessing plant should be a little smaller than in actual reprocessing plant but the difference will not be significant;
- For criticality safety control mode based on the mass limitation, the fissile mass allowable in the equipment in the future reprocessing plant should be smaller than in actual reprocessing plant;
- UPuO₂ composition issue from Irradiated fertile UO₂ lead to more restrictive dimensions than fresh UPuO₂ fuel composition.

It can be noted that in La Hague plant, the reprocessing of MOX fuel with lower content of plutonium than the present fuel in the rotary dissolver, designed initially for UO₂ fuel, lead already to poisoned nitric acid with gadolinium to allow sufficient treatment capacities.

Recommendation:

The bounding character of fresh fissile fuel with respect to irradiated fertile fuel should be verified particularly in parts of the process where these materials are potentially not yet mixed (shearing, voloxidation, ...).

3.2.2. COMPARISON FOR DISSOLUTION SOLUTION

The comparison for the neutronic properties (k_{∞} and B^2_m) is presented in Figure 8. The comparison of the admissible values (for a $k_{eff} = 0.95$) is presented in Table 8.

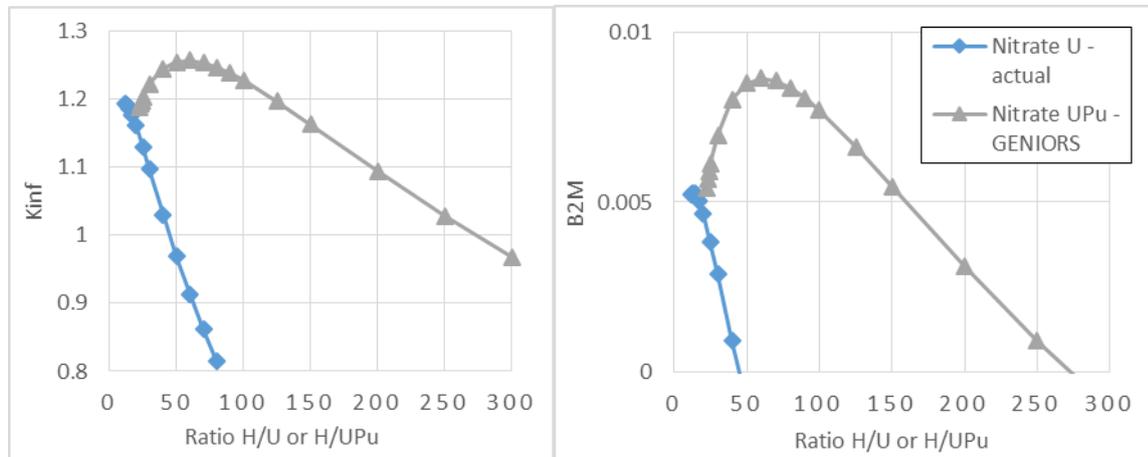


Figure 8: k_{∞} and B^2_m for dissolution solution.

Table 8: Admissible values for dissolution solution

	Nitrate U actual plant	Nitrate U+Pu - GENIORS
Infinite slab Thickness (cm)	24.0	16.3
infinite cylinder Radius (cm)	43.9	32.4
U or U+Pu mass (kg)	136	16
Concentration U or U+Pu (g/L)	444.4	84.2

Based on the figure and table above, the following conclusion could be made for dissolution solution:

- For a criticality safety control mode based on geometry limitation, geometry of equipment in the future reprocessing plant should be smaller than in existing reprocessing plant in dimension. For example, for an infinite slab, the admissible thickness is 1/3 smaller which is significant. Use of neutron poison (Boron or gadolinium for example where it is relevant) could allow to increase these values;
- For a criticality safety control mode based on mass limitation, the mass of materials in the equipment in the future reprocessing plant should be much smaller than in existing reprocessing plant. Analysis associated with uncontrolled accumulations could be more difficult to achieve due to less margins.
- For criticality safety control mode based on the limitation of concentration, the admissible concentration of fissile in the dissolution solution in the future reprocessing plant should be much smaller than in current facilities.

3.2.3. COMPARISON FOR PLUTONIUM NITRATE

The comparison for the neutronic properties (k_{∞} and B^2_m) is presented in Figure 9. The comparison of the admissible values (for a $K_{eff} = 0.95$) is presented in Table 9.

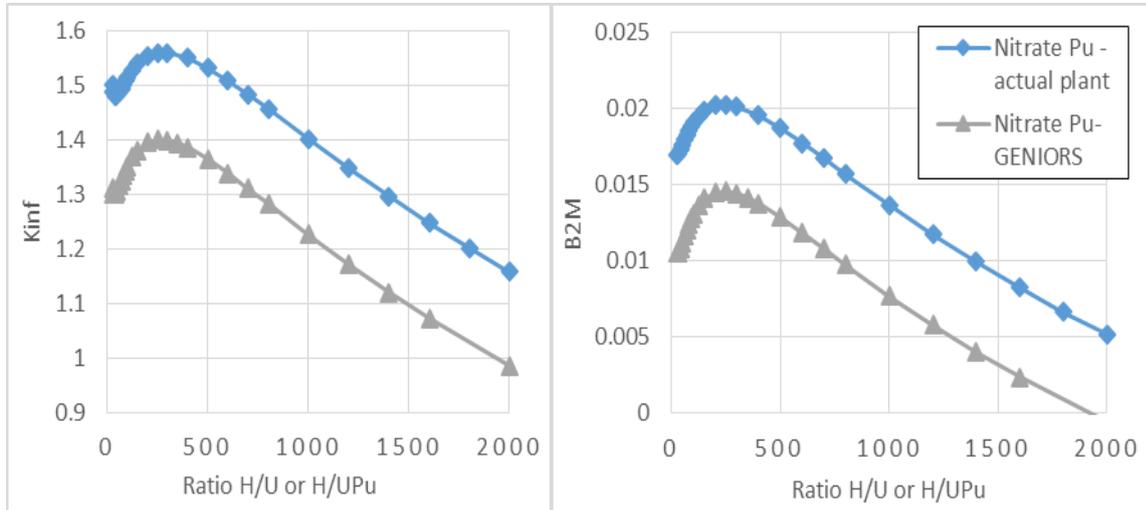


Figure 9: k_{∞} and B^2_m for plutonium nitrate.

Table 9: Admissible values for plutonium nitrate

	Nitrate Pu - actual plant	Nitrate Pu - GENIORS
Thickness of an infinite slab (cm)	7.5	10.4
Radius of an infinite cylinder (cm)	9.2	11.6
Masse of Pu (g)	700	1460
Concentration Pu (g/L)	8.6	12.8

The neutronic properties and the admissible values are smaller for plutonium nitrate from the actual facilities than for future reprocessing facilities. Indeed, in these calculations, a penalizing isotopic composition of plutonium (71/17/11/1%) is considered for existing facilities and compared to future reprocessing facilities for which the isotopic composition comes from depletion calculation. If a penalizing isotopic composition is considered for future reprocessing plant, the difference will be smaller.

3.3 CRITICAL VALUES FOR VARIOUS SOLVENTS OF THE EURO-GANEX PROJECT

The GENIORS project is focused on the determination of new processes for extraction of fissile species in the framework of the reprocessing of new fuel managements. Up to now, the safety demonstration was performed using water as a solvent, postulating that water was conservative.

Density laws were created for these new solvents used in the new processes based on experimental data collected from the GENIORS project chemists [9] to check that if using water in criticality calculations still remain a conservative approach.

Based on these density laws, criticality standards values (infinite slab thicknesses, infinite high cylinder diameters, sphere diameters) were determined for various solvents used in the EURO-GANEX project and compared to those obtained with water as solvent. The reference fissile medium is nitrate of plutonium (GANEX step 2) moderated by water or GANEX solvents or mixed uranyl nitrate and plutonium nitrate (GANEX step 1) with a mass ratio of 0.1805887 between Pu and U+Pu moderated by water or GANEX solvents. The isotopic composition of plutonium and uranium used for this comparison are respectively 71 wt.% ^{239}Pu /17 wt.% ^{240}Pu /11 wt.% ^{241}Pu /1 wt.% ^{242}Pu and (0.8 wt.% ^{235}U /99.2 wt.% ^{238}U). The concentrations of solvent used are those appearing in the flowsheets in Reference [13] and are recalled in report of Reference [11]. In the first approach, no acidity is taken into account (N of HNO_3 contributing to decrease reactivity by its absorption cross-section).

The criticality calculated values are reported in Reference [9], put in the Annex of this report.

The main results are the following:

- With a geometry control mode, water moderation remains always conservative compared to DEHIBA/TPH solvent used in GANEX 1st step, TOGDA+DMDOHEMA/EXXSOL solvent used in GANEX 2nd step and AHA+SO₃-Ph-BTP+HNO₃ used in GANEX 3rd step (see tables below);
- With a concentration control mode, water moderation is not conservative for a range of concentration between around 30 to 100 g U+Pu/l for TOGDA+DMDOHEMA/EXXSOL solvent and between around 30 to 80 g Pu/l for AHA+SO₃-Ph-BTP+HNO₃. Nevertheless, if a certain level of acidity is considered with GANEX solvent/diluent, water becomes conservative again in the entire concentrations range. **Special attention should be taken if the concentration control mode is used with solvent/diluent of GANEX 2nd STEP and 3rd STEP;**
- The decrease of 20% of extractant concentration in the solvent (extractant + diluent) results in a slight reactivity increase.

Table 10: Minimum critical values for optimum moderation

Fissile medium	Moderator	Slab thickness (cm)	Cylinder radius (cm)	Sphere radius (cm)
U+Pu GANEX 1 st step	DEHIBA/TPH	14.2	14.6	21.1
	water	12.5	13.1	19.1
Pu GANEX 2 nd step	TOGDA+DMDOHEMA/EXXSOL	9.1	10.4	15.6
	water	9.0	10.3	15.5
Pu GANEX 3 rd step	AHA+SO ₃ -Ph-BTP+HNO ₃	10.0	11.3	16.8
	water	9.0	10.3	15.5

Recommendation:

Special attention should be taken if the criticality concentration control mode is used with solvent/diluent of GANEX 2nd STEP and 3rd STEP, these latter being not bounding by water moderator in the range of 30 to 100 g/L of Pu without considering a certain level of acidity.

4. INDEPENDENT SAFETY REVIEW

As mentioned in the introduction, this independent safety review is based on the NNL Euro-GANEX flowsheet [4] and follows each step of the process proposed by NNL. To begin with, the overall NNL EuroGanex process examined is presented in Figure 10.

In the next paragraphs, an independent safety review will be performed for the main criticality safety part of this process, taken into account information available on NNL report [4], knowledge and operating feedback of the La Hague facilities and the previous calculation results.

In a final section, comments are also made on other risks (heat release, radiolysis, corrosion, chemical reactivity, exposure to radiation, etc.) and possible alternatives to the processes and technologies selected by NNL, highlighting their advantages and disadvantages from a safety perspective.

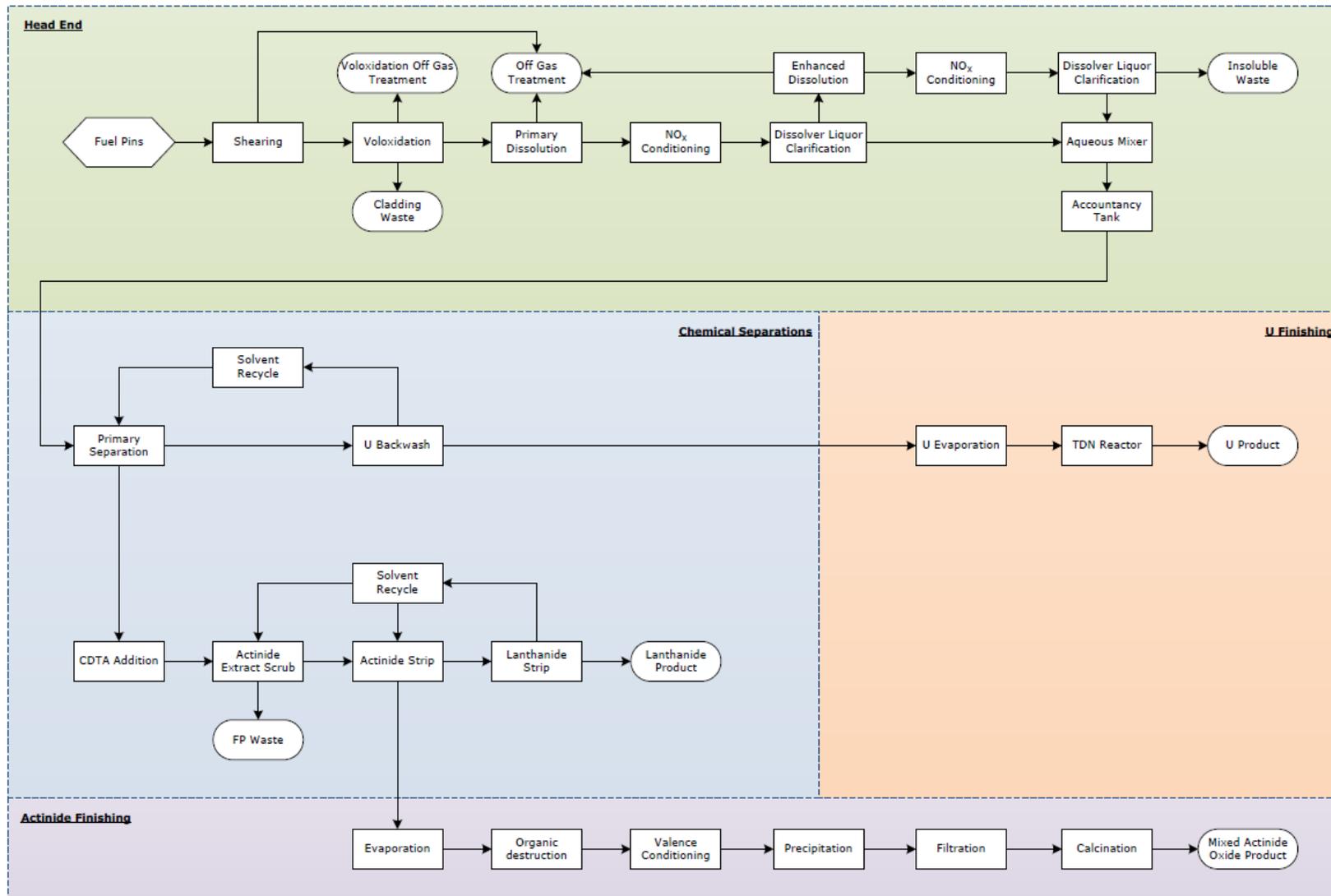


Figure 10: Overall EuroGanex process proposed by NNL in [4].

4.1. CRITICALITY SAFETY

4.1.1. HEAD END PROCESS

4.1.1.1 Shearing

NNL report:

A facility is required to prepare fuel assemblies prior to shearing. This facility will use remote handling devices to remove the outer cladding of the fuel and extract the fuel pin bundle for shearing. Fuel will be fed from the dismantling area to the shear pack equipment. Fuel will be cut into small pieces and fall via a chute into the pre-treatment equipment (voloxidation) whilst off gas released will be routed to the dissolver off gas treatment system.

La Hague knowledge:

During the handling/transfer of the assembly and the shearing operations, the criticality safety control modes used are the limitation of fissile material mass associated with the limitation of moderation. Assemblies introduced in the shear equipment are deemed dry.

But, during the handling/transfer operations, the criticality safety could be also based on the geometry of the assembly (indeed, without deformation, a LWR assembly moderated by water remains subcritical).

During the shearing operation, the limitation of the mass of fissile material integrates the limitation of oxide dust in retention in the shearing equipment. The limitation of the moderation is based on barriers between oil and fissile material and disposition to prevent in leakage of water and nitrous vapors coming from dissolution process.

The chute linking the shearing machine and the dissolver and feeding it with fuel segments has been designed to be safe by geometry. For higher enrichment UOX fuel, the control modes are the limitation of the fissile material mass associated to the geometry.

IRSN safety review:

During the handling/transfer operations, as the section of FR assembly is relatively small, subcriticality of these operations could be provided by assembly geometry and the fact that assemblies are handled individually.

During the shearing operation, the control mode could be based on the limitation of the fissile material mass associated to the limitation of moderation, to relax constraints on fissile material mass. Assembly sheared must be dry. For such case, criticality calculations should be done in order to determine the limitation of fissile material associated to the quantity of moderator which can be present in the shearing equipment. As said in paragraph 3.2.1, the mass of fissile material will be much smaller than in La Hague. To control the oxide mass, disposition should be taken in order to limit the quantity of dust remaining in this equipment (limitation of fissile oxide accumulations). Equipments must be designed, as far as it can, with the objective of limiting the volume available for dust accumulation.

Concerning the transfer of fuel rods segments (chopped fuel pieces) between the shearing and voloxidation process, the criticality safety control mode adopted could be geometry as in La Hague facilities. Nevertheless, if the admissible geometry for such fissile material appears too small for a proper functioning of the process, this control mode could be associated with a limitation of the mass

of fissile material (as in La Hague plant for high enriched UOX fuel or MOX fuel). But, in such case, disposition should be taken into account to detect a clogging of the channel.

4.1.1.2. Voloxidation

NNL report:

Chopped fuel pieces will feed via gravity into a two-stage voloxidation process performed within a single rotary kiln. The feed to the rotary kiln is controlled by the rate of shearing, and thus the criticality safety within the kiln is dependent on a safe-by-mass approach, whereby only a given amount of fuel can occupy the kiln at any point in time.

Voloxidation generally enhances the dissolution rate of the fuel. However it also increases the amount of Pu that remains in the undissolved residues, which can cause problems for downstream units. Sheared oxide fuel is oxidised from UO_2 to U_3O_8 by thermal treatment using oxygen in a furnace or rotary kiln. The fuel pulverises due to a change in crystalline structure which increases its volume. As a result, the cladding is placed under pressure and cracks, releasing the fuel. The product is sieved (the powder product can pass through a sieve where large pieces of cladding can be removed and monitored) to remove cladding, though a small amount of fuel is entrained with the cladding.

La Hague knowledge:

Such process does not exist in La Hague.

IRSN safety review:

A criticality safety control mode based only on the limitation of the mass seems to be too restrictive. Indeed, paragraph 3.2.1 shows that the mass of $UPuO_2$ will be limited to less than 10 kg. A limitation of the mass of fissile material associated to the limitation of moderation could increase significantly the allowable mass of fissile material in the kiln, leading nevertheless in return to constraints concerning moderation. In any case, a control mode by the mass of fissile material requires disposition to control inputs and outputs of fissile material and the potential fissile material accumulation in the kiln.

Based on the knowledge of nuclear facilities, IRSN considers that a criticality safety control mode based on geometry associated if necessary with neutron poison seems to be the more suitable, if it is compatible with the process constraints. This was for example the solution adopted for the calcination kiln of plutonium oxide in La Hague facilities (presence of boron carbide core in the kiln).

4.1.1.3. Primary dissolution

NNL report:

In paragraph 4 of Reference [4], NNL indicates that *“Voloxidised fuel will be gravity fed via a chute into the charge hopper of a rotating wheel dissolver. This technology was selected due to its maturity; it has been operated at the La Hague reprocessing plants UP3 and UP2-800, since 1989 and 1994 respectively, and has the ability to finely control the rate of dissolution whilst maintaining criticality safety. It is believed that the reliability and experience of this type of dissolver offsets the advantages of other designs, despite the fact that some operate with no moving parts, decreasing maintenance requirements”*. Moreover NNL proposes also to retain a standby batch dissolver to maintain dissolution capabilities should a problem with the rotary dissolver arise. This dissolver’s

primary role would be to allow for the dissolution of any chopped fuel which cannot be placed back into storage to make the plant safe should the primary dissolver fail.

Moreover, in paragraph 5 of Reference [4], NNL discuss about different dissolver design options. There are batch dissolution which have been traditionally used in commercial reprocessing plants but continuous concepts have also been developed as those in La Hague.

NNL describes the following two types of continuous rotary dissolver:

- The first, developed at La Hague, adopts a vertical wheel/carousel that has been divided into perforated radial sections. The wheel is suspended above a bath of nitric acid such that the lower sections (where dissolution takes place) are fully immersed in the acid.
- Another type of continuous rotary dissolver resembles that of a helical screw. Fuel enters the dissolver via a chute and is gradually pushed horizontally along the dissolver whilst being contacted countercurrently with nitric acid. When the hulls reach the end of the dissolver they are expelled via a solid waste chute with dissolver product liquor exiting at the opposite end. The screw is designed such that the gaps between adjacent threads essentially form compartments designed to prevent criticality. In addition the spacing between compartments is sized to prevent criticality, though the feed rate to the dissolver could also control how “spread out” fuel is.

The other main type of dissolver are pulsed dissolver. NNL describes the following two types of these equipment:

- One design that utilises pulsing technology is the helical ramp dissolver. This consists of two concentric columns - the central column contains nitric acid, the annular space between the inner and outer column walls houses a helical ramp. Nitric acid is forced from the central column into the outer column at its base with each pulse.
- A pulsed-V dissolver is another example of a pulsed dissolver. It utilises a V-shape to create a bath of liquor which completely immerses the sheared fuel pieces. Agitation is provided via pneumatic pulses which aids fuel dissolution. As the fuel dissolves and the hulls become lighter they overflow out of the dissolver. Due to the relatively small scale of this dissolver it is expected that multiples of them would be connected in series, each dissolving more fuel from the hulls. No evidence has been found supporting the implementation of pulsed-V dissolvers at an industrial scale.

Moreover, NNL explains also that neutron poisons such as gadolinium nitrate can be added to the liquor prior to discharge to the next processing stage to reduce the risk of a criticality hazard.

La Hague knowledge:

As explained in the paragraph below, the dissolver in La Hague plants is a vertical wheel dissolver. During the design of La Hague plants, the dimension of the dissolver has been a compromise between the process constraints (a larger wheel and tank would have been easier to design from an operational point of view) and criticality safety constraints (a smaller wheel and tank would have made the equipment safe by geometry only).

The dissolver criticality safety control modes are the geometry (the wheel, the radial section, the tank), the concentration of the dissolution solution, the mass of fissile material per radial section (if the fuel is high enriched in ^{235}U and the fuel has low burnup) and, sometimes poisoning (gadolinium can be used in some specific cases, as for MOX reprocessing). Moreover, in order to increase the allowable amount of fuel per radial section, La Hague facility takes into account the burn-up credit of irradiated fuel excepted when it is not possible for safety criticality reasons (for example, for LWR MOX fuel with its three zones with different plutonium content, the burn-up measurement is not

validated). When used, the assembly burn-up measure is performed before shearing the fuel assembly, in the monitoring burnup pit.

IRSN safety review:

After voloxidation, there is two ways to do the dissolution, either to dissolve the oxide powder and the oxide in hulls in the same equipment, or to dissolve the oxide powder and hulls in two separate optimized equipments. This paragraph will take into account these 2 possibilities.

As said in paragraph 3.2.2, the dimension for a safe by geometry equipment will be much smaller for the dissolution process of Fast Reactor fuel than of PWR UOX fuels. Due to these results, it appears that it should be very difficult to design a wheel dissolver for both oxide powder and hulls which will be acceptable for both the process and criticality safety, except if a sufficient gadolinium concentration is used to poison the acid solutions, which is not really a suitable solution from a process design point of view. But this type of equipment could be adapted to dissolve the remaining oxide in hulls. In this case, a limitation of the concentration of the dissolution solution and the amount of fissile material in hulls could be considered in addition to geometry.

A helical screw dissolver could be used for both powder and hulls. In order to reach an acceptable section for the process, the center of the helical screw could contain neutron poison core.

Due to his concept, the helical ramp dissolver should not be a good design to dissolve both the powder and the hulls as the diameter of the dissolver seems to be too large. Nevertheless, this kind of dissolver could be used to dissolve oxide remaining in hulls by considering a limitation of the concentration of the dissolution solution and the amount of fissile material in hulls.

For the pulsed-V dissolver, the diameter to be acceptable for criticality safety will be limited for the treatment of both powder and hulls.

Moreover, contrary to La Hague facilities, taking into account the burn-up of irradiated fuel will not lead to a significant reactivity decrease. Indeed, due to its initial high plutonium content, fast reactor fuel assembly reactivity do not decrease at the same rate as LWR UOX fuel assembly (cf. paragraph 3.1.1). Furthermore, only main actinides are taken into account in burnup credit, fission product poisoning being neglected, even if they could bring negative reactivity, due to the difficulty to guarantee their presence.

In conclusion, due to the voloxidation process before dissolution, it appears that separation of the dissolution of powder and hulls seems to be the best option. Indeed, due to the neutronic properties of FR fuel, the powder dissolver geometric dimensions will be inevitably limited. For this operation, a helical screw dissolver with low diameter could be used for criticality safety purpose. For the dissolution of the remaining oxide in hulls, the use of a wheel dissolver like in La Hague facility seems possible, the amount of fissile material in hulls being limited after voloxidation. This hypothesis should nevertheless be ensured during the voloxidation process validation.

4.1.1.4. NOX CONDITIONNING

NNL report:

There is no information about criticality safety of this equipment in report listed in Reference [4]

La Hague knowledge:

This kind of equipment does not exist for the dissolution solution in La Hague. But, such equipment exist for the treatment of plutonium nitrate. In this case, the columns used are safe by geometry.

IRSN safety review:

This column should be safe by geometry taking into account, if necessary, the concentration of the solution. Perhaps, the design of this column could not be acceptable for the process. In this case, either more than one column should be used, or a neutron poison could be used (annular column with neutron poison in the center).

4.1.1.5. DISSOLVER LIQUOR CLARIFICATION

NNL report:

The conditioned liquor will continuously feed a bowl centrifuge (like those adopted on THORP and La Hague). The rotating bowl will spin the liquid, forcing heavy particles to accumulate on the surface of the bowl. Periodically, the bowl is washed using pressurised nitric acid, with solids and insolubles (including insoluble Pu) washed out and eventually diverted to solid waste streams (after having first been treated to remove any Pu). There is the potential for a criticality issue within the first centrifuge due to the expected levels of plutonium. The addition of neutron poisons, careful design of centrifuge geometry and improved acid dissolution could abate this problem however this will need to be addressed in more detail at later design stages.

La Hague knowledge:

In La Hague, the criticality safety control modes for bowl centrifuge are the geometry, the fissile concentration and the limitation of the mass of fissile material in undissolved material. The periodicity of washing operation depends on the quantity of plutonium in the undissolved material.

IRSN safety review:

The amount of plutonium in the undissolved material is higher than the quantity of uranium. This is already the case for irradiated UOX fuel reprocessing and this effect is amplified with MOX fuel and will be even more during the MOX FR fuel reprocessing. As the amount of plutonium in undissolved material will be much higher than in La Hague due to the higher initial content of plutonium, the criticality control modes adopted in La Hague will not be suitable for GENIORS process.

As said in the NNL report, the addition of neutron poisons could be used for such equipment (boronated stainless steel in the bowl centrifuge for example). The use of neutron poison and the more accurate modelling of the equipment could be used in the design of such equipment. If the geometry of the equipment remains too limited, even with neutron poisons, the use of multiple centrifuges will have to be considered. This problem needs to be addressed.

4.1.1.6. ENHANCED DISSOLUTION

NNL report:

Two Ag(II) dissolvers will be utilized to dissolve any insoluble Pu remaining after acid dissolution. Each of them will operate on a batch basis such that as one undergoes dissolution the other will be filling with feed slurry from the washing of the first clarification centrifuge.

La Hague knowledge:

Such dissolution is encountered at La Hague to dissolve reject from the manufacture of MOX pellets or MOX or PuO₂ powders. The criticality control modes adopted are the geometry associated with heterogeneous poisoning (use of an external inox-cadmium-inox "sandwich" structure in contact with the dissolver walls). When processing MOX pellets/powders, these control modes are complemented by the limitation of the mass of oxide treated (batch treatment). But, the amount of material treated by batch in this type of equipment is limited.

IRSN safety review:

Due to the neutronic properties of undissolved material (which will be less reactive than PuO₂ powder), it will be possible to design an Ag(II) dissolvers safe by geometry with neutron poison in the equipment side walls. In order to increase the geometry size of this equipment (and to increase the amount of material treated by batch), criticality safety analysis could take into account the composition of undissolved material, in particular if a maximum content of plutonium can be guaranteed and if some compounds in the undissolved material are neutron poison.

4.1.1.7. ACCOUNTARY TANK

NNL report:

The dissolution liquors are mixed and monitored in the criticality safe (by geometry) buffer tank prior to being sent to the chemical separation area of the plant.

La Hague knowledge:

In La Hague, this buffer tank are safe by concentration.

IRSN safety review:

Due to the amount of plutonium in the dissolution solution (U+Pu concentration around 188 g/l to compare with the admissible infinite medium concentration of 84.2 g/l), the control modes for the buffer tank should be the geometry with neutron poison eventually integrated in geometry to increase the admissible equipment size.

As seen in Figure 8, the maximum of reactivity is reached for a relatively low moderation ratio $H/(U+Pu)$ (between 50 and 100 which correspond to around a U+Pu concentration between 450 and 250 g/l). The concentration of one of the accountary tank feed been close to 190 g/l following the NNL flowsheet, the limitation of the concentration in this tank will certainly not lead to a significant increase of the geometry of the tank.

4.1.2. CHEMICAL SEPARATIONS

NNL report:

In paragraph 5 of Reference [4], NNL presents three main types of solvent extraction equipment used in the nuclear industry:

- **Mixer-settlers:** the mixer-settler is one of the simplest contactor designs available. They have been adopted in early reprocessing plants such as the Windscale and Magnox reprocessing plants at Sellafield, UK. Mixer settlers are an extremely mature technology and can be built into banks of significant size to improve extraction efficiency. However, the design involves mechanical drives which can fail and cause maintenance issues. In addition, it can be difficult to design the equipment to criticality safe geometries; therefore some sort of neutron poison may have to be added to the liquor.
- **Pulsed columns:** THORP utilises pulsed columns in its primary separation solvent extraction cycle. These were originally adopted due to additional design constraints introduced by the higher fissile content of the fuel relative to earlier reprocessing plants which posed a criticality hazard. In addition, the combination of higher activity and the long residence times within the settling section of mixer settlers would have resulted in high levels of solvent degradation. The geometry of the column is such that a criticality cannot happen under any circumstance.
- **Centrifugal contactors:** Relative to the other types of solvent extraction equipment, centrifugal contactors are very compact in size and can occupy significantly less plant footprint for a given level of extraction.

Centrifugal contactors have been selected as the solvent extraction technology throughout the plant, due to the enhanced performance offered whilst occupying a relatively small footprint. In addition, this technology has been proven extensively in other industries and is increasingly being used in nuclear environments.

La Hague knowledge:

In La Hague facilities in activity, the 3 types of solvent extraction equipment are used:

- **Mixer-settlers:** the mixer-settler is principally used in backwash process (for example: uranium and solvent backwash process). These equipment are safe by geometry taking into account, if necessary, the limitation of concentration of plutonium. These equipment are used when the radioactivity of the solution is not high in order to prevent solvent degradation;
- **Pulsed columns:** pulsed columns are utilized during the primary separation cycle as in THORP. These columns are safe by geometry taking into account the presence of a neutron poison core (placed in the center of the annular pulsed columns) and considering only plutonium in the solution (which takes into account a deviation of the process).
- **Centrifugal contactors:** centrifugal contactors are used only in the purification/concentration of plutonium solution. These equipment are safe by geometry taking into account the presence of neutron poison (inner parts of the centrifugal contactors made of boron stainless steel).

IRSN safety review:

IRSN agrees that centrifugal contactors are the best equipment from criticality safety point of view: these equipment could be safe by geometry taking into account neutron poison materials. Furthermore, under normal operation conditions, the amount of fissile material in the equipment is limited. One of the concerned identified is that, given their internal size, these equipment could be

subject to clogging. It might be the case particularly during principally the primary separation and, perhaps, also during the Fission Products and actinides separation process.

Moreover, for the backwash process (for example uranium backwash), the liquid flow rate of centrifugal contactors could be too important to detect the presence of unwanted element (for example plutonium). In this case, the use of mixer-settlers allows more time to detect a deviation of the process.

In conclusion, choices adopted in La Hague plants seem, at first sight, the more suitable:

- Pulsed columns in the primary separation and perhaps separation of fission products. These equipment will be safe by geometry taking into account the presence of a central neutron poison core (placed in the center of the annular pulsed columns). Moreover, the solvent degradation will be limited in this equipment as the time presence of solution in this equipment is limited;
- Mixer settlers in backwash process. These equipment will be safe by geometry taking into account, if necessary, the limitation of concentration of plutonium. In the absence of such equipment, the tank which receive the solution (for example the aqueous uranium) should respect the exigence of accountary tank (see paragraph 4.1.7);
- Centrifugal contactors in actinide strip and lanthanide strip. As in La Hague, these equipment will be safe by geometry taking into account the presence of neutron poison. As seen in paragraph, 3.2.3, the geometry of these equipment should be larger for plutonium from irradiated MOX FR than from plutonium used for La Hague equipment's plant design (due the degraded quality of plutonium). If the central contactor appear too small to treat a sufficient actinide solution flow, several processing lines could be necessary.

Recommendation:

If centrifugal contactors are used in all phases of separation, clogging risk must be addressed, particularly for primary separation.

4.1.3. URANIUM FINISHING

NNL report:

Two buffer storage and preparation tanks will receive aqueous uranyl nitrate (UN) from the uranium backwash contactor bank. The tanks will be geometrically safe for criticality safety. The liquor will be monitored to check its enrichment level, with samples taken to confirm these measurements, as the enrichment must be sufficiently low to prevent criticality problems downstream.

In THORP, the U-rich aqueous stream from chemical separation flows to a safe-by-shape buffer tank which allows for monitoring, sampling and blending with low enriched uranium (from an external source). The blending of uranium is crucial so that the concentration of fissile ^{235}U will be sufficiently low post concentration via evaporation to avoid the risk of criticality. The criticality safety philosophy changes from safe-by-shape to safe-by-mass at the evaporation stage. The solution flows through a steam strip column prior to feeding the evaporator.

La Hague knowledge:

In La Hague facilities, there is no risk of criticality due to the limitation of uranium enrichment at 2wt% in ^{235}U (samples confirm this enrichment prior to chemical separation) and that uranium remain in nitrate form. In case of precipitation, the mass of uranium to have a criticality risk is so high that it is not credible to have such mass of precipitates.

Before the uranium finishing part, there is a mixer settler safe by geometry and concentration to prevent the presence of plutonium (the abnormal presence of plutonium is control by monitoring).

IRSN safety review:

If the enrichment of uranium in ^{235}U is limited to 1 wt% (which is the case for MOX fuel), there is no risk of criticality even in oxide form. In such case, uranium finishing equipment could be design without criticality geometry constraints. A specific equipment shall be provided in the uranium backwash process (for example a mixer settler safe by geometry and concentration of plutonium) to ensure, with the appropriate controls (samples analysis for example), the absence of significant amount of plutonium and curium with uranium in the uranium finishing part.

4.1.4. ACTINIDE FINISHING

NNL report:

The description of the actinide finishing process from NNL report in Reference [4] is the following.

The mixed actinide finishing section of the plant is expected to mimic that of the plutonium finishing line of THORP. Similar to U finishing, the mixed actinide finishing is expected to occur in either large gloveboxes or cells. The addition of a solvent destruction and evaporation stages have been deemed necessary due to the more dilute stream (relative to THORP) expected to arise from the chemical separation area.

Actinide-bearing aqueous liquor will be homogenised and sampled in product storage buffer harp tanks before leaving the chemical separation area. The liquor is then transferred via reverse flow diverters (RFD's) to the steam strip column which destroys any entrained organics before passing into the evaporator.

The evaporator is expected to be of a similar design to that used in the uranium finishing section. However care will have to be taken to ensure that the evaporator remains safe in terms of criticality geometries, and that the evaporation does not produce an over-concentrated product which in turn would present a criticality hazard.

The concentrated liquor will be metered via continuous volume feeders (CVFs) into a conditioning vessel where hydrogen peroxide is added to modify the valence of the actinides such that the crystals produced during precipitation will be of the correct size and shape.

In THORP, two dilution vessels add nitric acid to the feed to reduce the concentration of plutonium for the precipitation stage. It is expected that these units will not be necessary due to the dilute plutonium concentration in the feed from chemical separation - the concentration of plutonium will be controlled by the extent of evaporation. Trace heated pipes pre-heat and carry the liquor, via a CVF, to precipitation. Liquor is continuously fed into the precipitation vessels along with pre-heated oxalic acid (four vessels are used in parallel in THORP, it is assumed this will be sufficient capacity for this plant). The oxalic acid reacts to form plutonium oxalate precipitate at approximately 60°C. The vessels are stirred such that a vortex is formed, the precipitate slurry overflows from the lip of the vortex and falls on to a flat-bed rotary vacuum filter. The slurry is vacuum dried and the filter cake washed with dilute nitric acid and demineralised water before being removed using a screw feeder. The moist cake is removed to the drying furnace. The remaining oxalate mother liquor (OML) is removed and evaporated to form a concentrated mother liquor (CML) which in turn undergoes evaporation again to destroy residual oxalic acid. It is then stored prior to re-use within the process. The plutonium oxalate is fed through the drying furnace using rotating screws against a contra-flow of process air and argon. The off gas is passed through a filtration unit to remove particulates before

passing to the glovebox ventilation system. The drying process converts plutonium oxalate to dioxide powder which is then fed into a calcination furnace for surface area adjustment using process argon. Product powder flows into a hopper and feed tube to the batch blending unit, which homogenises the powder prior to sampling and packaging.

La Hague knowledge:

Plutonium finishing process in La Hague is similar to those of THORP excepted that the concentration of plutonium is not produced by an evaporator but by the chemical separation: a chemical separation process is performed only on plutonium feed in order to purify it and to concentrate it.

In La Hague facilities in activity, equipment which contain the main flow of plutonium are safe by geometry taking into account of the presence of neutron poison:

- Tank: either annular tank with a sandwich plate of inox/cadmium/inox and bitumen in the center, or tank with vertical inox tubes of borated polyethylene plaster;
- Furnace: the center of the screw contain B₄C.

Even the hopper, the feed tube, the batch blending unit and oxide packaging box are safe by geometry.

Concerning CML, equipment are safe by geometry taking into account the presence of neutron poison until a measure of the plutonium concentration is performed (under abnormal situation, the plutonium concentration could be non-negligible). After this measure, the criticality safety control mode is the concentration of plutonium.

IRSN safety review:

The design of plutonium finishing in La Hague (IRSN does not know the design of THORP), safe by geometry, taking into account the presence of neutron poison if necessary to increase the size and the available volume, leads to a minimum of operational constraints.

IRSN recommends that the design of the actinide finishing process should consider, as far as possible, geometry as the main control modes of criticality safety.

Perhaps, due to the higher amount of plutonium treated in the MOX FR reprocessing plant than in UOX LWR reprocessing plant, it should be necessary to have several processing lines.

4.1.5. CONCLUSION

This chapter presents the IRSN independent safety review based on the Euro-GANEX plant design and process flowsheet provided by NNL [4] and focused on criticality safety.

The main following points could be noted:

- Shearing process: the control mode could be based on the limitation of the mass of fissile material associated to the limitation of moderation but, the mass of fissile material should be limited. Perhaps, Disposition should be taken in order to limit the quantity of dust present in this equipment.
- Voloxidation: the control mode could be based on the limitation of geometry associated, if needed, to the presence of neutron poison.
- Primary dissolver: a separate dissolution for powder and hulls could be a good solution for criticality safety. In this case, powder could be dissolved in a safe by geometry equipment

(for example a helical screw dissolver), and hulls could be dissolved in a wheel dissolver like in La Hague.

- Dissolution solution tank: due to the amount of plutonium in the dissolution solution, the control modes for the buffer tank should be the geometry associated to the presence of neutron poison.
- Chemical separation: the 3 types of equipment could be used (pulsed columns in the primary separation and perhaps separation of fission products, mixer settlers in backwash process and central contactors in actinide strip and lanthanide strip).
- Uranium finishing: if the enrichment of uranium in ^{235}U is limited to 1 wt% there will be no risk of criticality.
- Actinide finishing: the control mode could be based on the limitation of geometry associated, if needed, to the presence of neutron poison.

This analysis lead to some recommendations which are listed below.

Recommendations:

- **Due to the very low curium critical mass obtained with the expected curium composition, the risk of selective precipitation of curium or separation from other actinides, in particular americium, should be addressed if physically possible.**
- **The bounding character of fresh fissile fuel with respect to irradiated fertile fuel should be verified particularly in parts of the process where these materials are potentially not yet mixed (shearing, voloxidation, ...).**
- **If centrifugal contactors are used in all phases of separation, clogging risk must be addressed, particularly for primary separation.**
- **Special attention should be taken if the criticality concentration control mode is used with solvent/diluent of GANEX 2nd STEP and 3rd STEP, these latter being not bounding by water moderator in the range of 30 to 100 g/L of Pu without considering a certain level of acidity.**

4.2. COMMENTS ON OTHER RISKS AND PROCESS ALTERNATIVES

4.2.1. INTRODUCTION

In order to assess the feasibility of the industrial implementation of the EURO-GANEX plant, to evaluate in a very preliminary way the safety of the processes and technologies proposed by NNL [2] (including possible alternatives), and to identify the necessary R&D actions, IRSN relied on the operating feedback from French pilot installations and French reprocessing plants in operation or shut down that have processed fast neutron fuels (AT1, APM, UP1, UP2, UP3, UP2-800), on projects of plants that have not been deployed dating from the 1980s (PURR, MAR 600, etc.), on R&D work in progress at CEA, on regulations concerning nuclear installations, and on a certain number of bibliographical elements, in particular taken from [14]. The main risks addressed are related to heat release, radiolysis, corrosion, explosion and chemical reactivity. A few targeted comments are also made on criticality risks, in addition to the elements provided in paragraph 4.1 of this report.

Preliminary, it should be noted that the SFR MOX fuels reprocessing should not be a breakthrough in comparison with the processes used in the current plants, even if R&D works have still to be carried out to define the necessary adaptations, taking into account the specificities of these fuels. On the other hand, the design and operation of plants will be affected by the choice of recycling option for minor actinides, due to their radioactivity and thermal power, with consequences that will be all the more important as their content in fuels (in homogeneous mixture) or in fertile blankets will be high.

In the case of homogeneous recycling, the minor actinides being diluted in the SFR fuel elements to a few weight percent (1 to 4% of MA or Am), the entire nuclear fleet and the fuel cycle as a whole will be affected. If the whole manufacturing process will be impacted by the presence of these actinides, the main consequences in the processing plant will concern the separation and conversion stages for which minor actinides will be in a concentrated form. Thus, major changes in these installations will probably be necessary because of the need to control operator dose uptake and heat releases and to limit source terms in accident situations.

On the other hand, the recycling of minor actinides in heterogeneous mode (especially americium), implemented in more compact installations and, in principle, more easily adaptable to their handling, should limit their flow. The loaded blankets could thus be manufactured in dedicated plants, different from the MOX fuel fabrication plants of the fissile core. These plants could be coupled to reprocessing plants in which the irradiated blankets would be dissolved in the flow of "standard" fuels, thus benefiting from a dilution effect limiting the operating constraints.

For information, the values of thermal power and total neutron emission of a spent SFR MOX-MA fuel (Pu content 17.6%, minor actinide content 3.9%, irradiation rate 100 GWj/t, cooling 5 years) are respectively of the order of 3 kW and 4.10^{+9} n/s per assembly. These values linked mainly to the curium presence are about three times higher than those corresponding to SFR-MOX fuel with the same irradiation characteristics and three times lower than those corresponding to blankets loaded with 20% minor actinides³. Finally, the quantities of homogeneous spent nuclear fuel to be treated per year in a EURO-GANEX-type plant would be of the order of 450 tML for a 60 GWe SFR fleet at equilibrium.

³ Values provided by the CESAR-5 depletion code and resulting from studies of SFR deployment scenarios carried out by the CEA within the framework of the PNGMDR and taking into account the situation of the French nuclear fleet.

4.2.2. HEAD END PLANT

4.2.2.1. STORAGE, DISASSEMBLY, STRIPPING AND SHEARING

Given the operating feedback of the Creys-Malville (APEC) storage pool and the La Hague centralized storage pools (these last installations having already received spent fuel assemblies of the Superphénix or Phénix type), no obstacle can be identified currently concerning the possibility of receiving and storing under water, in a safe way, on the the processing plant site itself, SFR MOX-MA fuels in the form of assemblies or reconditioned fuel pins, previously washed to remove all traces of residual sodium. In particular, the necessary pool and cooling capacities (a few thousand tons to be stored at most, i.e., about 10 MW to be released) remain consistent with the current characteristics of the La Hague plants (8 to 16 MW authorized per pool, 8 kW maximum per PWR-type assembly). Moreover, unlike the blankets loaded with minor actinides, the residual thermal power of SFR MOX-MA fuels should not require disassembly them at the reactor site before transport to the reprocessing plant.

Compared with the MOX-SFR fuels processing, the implementation of transmutation in homogeneous mode should not significantly influence the design of head-end plant units dedicated to the mechanical disassembly operations, oxide-cladding separation or shearing, even if these operations require, in any case, significant technological developments. Indeed, it should be remembered that the MOX-SFR fuels processing requires equipment that allows to remove the hexagonal steel tube containing the fuel pins, the structural elements (top and bottom nozzles) and the spacer wires of the pins, since shearing of the whole element is impossible. In the context of the Phénix fuel reprocessing campaigns carried out at Marcoule in the 1980s, various means were developed to remove the end pieces and extract the pins bundle as a whole or by layer (opening of the hexagonal tube by mechanical milling on two opposite angles and then separating the two half-tubes, cutting by sawing, milling, laser, or "cracking"), with new techniques being also possible (water jet with abrasive, nitrogen jet, etc.) The fuel pins can then be sheared, depending on the desired processing capacity, individually, in layers or bundles, or even continuously using rotary shears or shears equipped with one or more blades. These shearing methods make it possible to avoid a significant dispersion of fuel powders, to resort to an extremely massive shear and to control more easily the problems of formation of foams and important gas emissions (NO_x) in the dissolver. R&D could thus be carried out to make these operations compatible with the industrial processing requirements (reliability, rate, etc.), including improving the disassembly of some fuel elements parts, facilitating the extraction of pins and limiting the volume of structural waste sent to the dissolver. In addition, the different options for managing the spacer wires⁴ and the risk of pins pinching during shearing, which can lead to difficulties in dissolving the fuel (blocking of the ends of the fuel segments that are not very favorable to the nitric acid solution diffusion), should be evaluated.

The presence of minor actinides in these fuels will nevertheless lead to the implementation, in the disassembly-shearing units, of adapted radiological protection to take into account the greater neutron emission of these fuels compared to standard SFR assemblies. The numerous maintenance operations associated with fuel disassembly could also lead to higher operators dose uptake when large quantities of minor actinides are present. As mentioned in paragraph 4.1, SFR MOX-MA fuels shearing should lead to lower fissile material mass limits and higher cleaning frequencies of the

⁴ Feedback from the Marcoule pilot workshop shows that the spacer wire removing operation, which also makes it possible to remove the expansion chambers of the pins (which leads to a gain in the treatment capacity of the dissolver and a reduction in the quantities of corrosion products in solution), is complex, the choice of whether or not to carry out this operation being linked to the operation of the shears and the dissolver.

equipment. The shearing machine should therefore be designed to eliminate or limit the accumulation of fuel powder inside this piece of equipment.

4.2.2.2. DISSOLUTION-CLARIFICATION

With regard to the dissolution of fuels incorporating minor actinides, and in the same way as for the standard MOX-SFR fuel, the requirement to dissolve almost all the uranium, plutonium and minor actinides contained in these fuels (the targeted recovery yield for these transuranics is greater than 99.9%) and the requirement for the cladding material to withstand corrosion in the dissolution medium will have to be considered in terms of process performance and safety. Thus, the R&D to be carried out could be oriented along two main lines, taking into account the specificities of these fuels:

1. the implementation of a two-stage dissolution: a "controlled" primary dissolution followed by a separation and "thorough" rinsing of the hulls and a complementary dissolution (or "digestion") of the separated dissolution residues allowing to recover the insoluble fissile materials and thus to obtain satisfactory dissolution yields,
2. the design of "powder" dissolver, a more compact, requiring the implementation of an upstream voloxidation or oxide/cladding separation step.

In particular, the homogeneous fuels, whose overall reactivity should remain similar to that of standard fuels (cf. paragraph 4.1.)⁵, could be processed in the same types of equipment envisaged for the standard fuels (discontinuous dissolver with flat tank and vertical tubes, wheel dissolver, continuous helical dissolver, screw dissolver, pulsed dissolver, powder dissolver, etc.).

Concerning the fuels used in homogeneous transmutation mode, the results acquired during irradiation experiments carried out in the 1980s and more recently in the 2010s in the PHENIX, JOYO, ATR and HFR reactors (SUPERFACT-1, Am1, AFC-2C and 2D experiments) show that these fuels, manufactured mainly by powder metallurgy, have physical properties and thermal behavior (melting point, microstructure evolution, helium production, radial redistribution of actinides, etc.) that are finally quite close to those of standard fuel, up to burnup rates close to 20 at%. Thus, the behavior of homogeneous fuels during the primary and complementary dissolution stages should in principle be not very different from that of standard MOX-SFR fuels (formation of mixed compounds or intermetallic alloys, effect of « erasure » of Pu-rich manufacturing heterogeneities linked to irradiation...)⁶. **This hypothesis should nevertheless be confirmed on the basis of dissolution tests aimed at verifying the good behaviour of these fuels during reprocessing with representative irradiated samples (dissolution kinetics and yield, final insolubility of the fuel, etc.).**

Moreover, the masses and characteristics of the dissolution fines formed during the dissolution of standard MOX-SFR fuels and of spent homogeneous MOX-MA fuels should differ little (for similar operating conditions), the very significant masses of fission products formed in these fuels being in

⁵ The overall reactivity (k_{∞}) of homogeneous MOX-MA fuels containing up to 4% of minor actinides is not expected to change significantly compared to that of standard SFR fuels, because americium, compared to plutonium, tends to decrease this reactivity, and curium has no significant influence as long as it is not separated from americium.

⁶ The very high operating temperature of the SFR MOX fuel will lead to the formation of mixed or intermetallic compounds (in the form of nodules or inclusions) that may include plutonium (Ru_3Mo_5 , $RuTcMo_5$, Pd_3Sn type compounds), which are more refractory to dissolution in a nitric medium. These phenomena could be all the more marked as the burnup are high (above 100 GWj/t), or even very penalizing in terms of fuel treatability (very slow dissolution kinetics of the oxide linked to its significant restructuring at the end of its life, requiring the implementation of extremely aggressive dissolution and reattack conditions to dissolve insolubles). Moreover, the final plutonium insolubility of irradiated SFR MOX fuel will also be linked to the presence of plutonium-rich clusters in the new fuel, the characteristics of which depend on the manufacturing process used. Consequently, this process must guarantee the most perfect possible homogeneity of the oxide, and in particular the absence of aggregates of PuO_2 or mixed oxides with a content higher than 30-35%.

particular very close for identical irradiation conditions. In this respect, it should be recalled that the Phénix fuels reprocessing feedback shows that the masses of fines formed during dissolution are very important (12 to 15 kg per ton of (U+Pu) for maximum burnup of 80 to 100 GWj/t) and could reach several tens of kg per ton for higher burnup, associated with a very high specific activity. These masses of fines will also depend on the operating conditions adopted during the primary dissolution, a too high final U+Pu concentration favoring the formation of these compounds. Their presence in the solutions transiting through the circuits and process equipment, located upstream of clarification, could be the cause of significant operating difficulties (clogging of ejectors or flow rate measurement equipment during transfers, deposits in the transfer pots, seal pots, buffer tanks, etc.) leading to potentially dosing interventions for the operators. In addition, these residues have a much wider granulometric spectrum than the UOX fine, and their precise characterization on the physico-chemical and radiological levels is therefore necessary for the definition of future transfer and clarification equipments.

The masses of zirconium and plutonium molybdate precipitates formed during dissolution will also depend on the irradiation characteristics of the fuel, the type of dissolver used, and the dissolution conditions. These compounds can clog the dissolvers, induce risks of corrosion under deposition and clogging of circuits during transfer operations, and lead to a significant loss of plutonium into the structural waste (hulls). These phenomena require periodic rinsing of the equipment and the use of specific reagents; these operations are restrictive from maintenance and radiation protection point of view and require the implementation of special measures to prevent criticality risks. **Studies should therefore be carried out to understand the conditions of formation of these precipitates and to optimize the conditions of dissolution as well as the thermal-hydraulic characteristics of future dissolvers to prevent these phenomena (high acidity, temperature close to boiling, homogeneity of the solution, absence of local over-concentration or hot spots, etc.).**

With regard to the two-stage dissolution scheme, the conditions of the primary dissolution (acidity, residence time of the hulls, temperature) will necessarily be more aggressive to ensure satisfactory efficiency of fissile material recovery, but will nevertheless have to be adapted to take into account the need for the stainless steel cladding material to withstand the potentially very corrosive dissolution environment. Indeed, the characteristics of the steel cladding of irradiated SFR MOX fuels (local accumulation of corrosive FP at the oxide-cladding interface, internal corrosion...) lead to a strong decrease in their resistance to corrosion in a nitric environment and to a release of corrosive ions (Fe, Ni, Cr...). These ions will lead to increased risks of dissolution of dissolver structural materials (risks reinforced by the presence of Pu(VI) and Np(VI) ions in solution, which are very strongly oxidizing)⁷ but also of FP solution evaporators and storage tanks for concentrated effluents, notably by intergranular corrosion. **The choice of materials constituting the future dissolvers, digesters and boiler-equipments located downstream of the dissolution will thus have to take into account these more aggressive dissolution environments, the operating feedback from pilot or industrial units and the results of the R&D that will have to be carried out (knowledge of the different mechanisms of corrosion/aging and types of possible damage⁸, modelling of these mechanisms, optimisation of the compositions and structures of the existing steels, development of passivating treatments, development and qualification of innovative materials, research into their limits of use with regard to generalised or localised corrosion,...).** As an example, zirconium

⁷ This phenomenon will require the implementation of a step of reduction of the oxidizing species present in solution (injection of nitrous vapors for example) before the chemical separation operations. This step will be all the more essential as the concentrations of Np(VI) in solution will be higher during the treatment of homogeneous MOX-MA fuels.

⁸ Generalized, localized or intergranular corrosion phenomena (presence of oxidizing ions or halogens in solution or in vapour phase...), corrosion by galvanic coupling or under deposition (presence of platinoids, reduction of nitric acid into nitrous acid...), tribocorrosion (friction/erosion), mechanical fatigue or induced by thermal cycles.

702 or titanium alloys, such as Ti-5Ta-1,8Nb, seem to be well adapted and could be retained as a constituent material of the dissolver and the digester.

The breaking up or desintegration of the cladding, in case of exacerbated corrosion, could also lead to clogging and overloading of the clarification equipments. In addition, the presence of corrosion products in significant quantities in the solution to be vitrified could require the use of a new glass matrix. Operating feedback from Phénix fuel reprocessing shows that the austenitic steels successively used for pins cladding (316 hyperquenched and cold worked, 316Ti and 15/15Ti cold worked) have a fairly good behaviour to dissolution, contrary to the ferritic steels originally used. International studies show that ODS type steels (ferritic/martensitic steels reinforced by oxide dispersions) would be likely to have a better resistance to swelling and creep under irradiation. **Studies should therefore be conducted to better evaluate the corrosion behavior of these new cladding materials in dissolution environments.**

For the complementary "digestion" of the dissolution fines, the use of complexing or oxidizing agents (concentrated nitric acid, hydrofluoric acid, oxidation by Ag(II) or Ce(IV) in the presence of ozone, etc.) could be envisaged, depending on the nature and quantities of plutonium-rich insolubles recovered after primary clarification. In this respect, the use of nitro-hydrofluoric acid in the digester could lead to the production of extremely corrosive fluoride ions, the management of which in the process could be very restrictive and require the addition of complexing agents (aluminium nitrate). Oxidation by Ag(II) or Ce(IV), regenerated with ozone, thus seems more attractive than the electrogeneration process currently used in the La Hague plants. However, it will be necessary, during the operation, to destroy the excess ozone and to trap the volatile ruthenium (RuO₄) present in the gaseous effluents, then to reduce, at the end of the operation, the oxidizing species present in solution (Pu(VI), excess Ag(II),...) by injection of nitrous vapors, in order to protect the downstream stainless steel equipments from corrosion. **Studies should be carried out in this sense.**

Other studies would also be necessary to ensure that an oxidizing treatment of the hulls would not lead to prohibitive corrosion phenomena, the objective of these "advanced" rinses being to perfect, on the one hand, the dissolution of possible oxide particles rich in Pu trapped in these wastes, and on the other hand, their decontamination in alpha emitters.

From the dissolution process safety point of view, it should be emphasized that studies aimed at better understanding the mechanisms of dissolution of the irradiated oxide (dissolution kinetics, origin of local insolubilities, characterization of dissolution residues rich in Pu, modeling, etc.) and at better understanding the conditions of formation of precipitates likely to be deposited in the equipments and to promote the entrainment of fissile material with the hulls, should be particularly well developed. Indeed, this data will be very important to guide the design choices for the equipments of future generations of plants, to establish a safe operating range for the continuous dissolution and digestion stages, to justify the choice of the most suitable criticality control modes for the equipments, taking into account the targeted treatment capacities (cf. paragraph 4.1.), and to guarantee the compatibility of the structural wastes with the future treatment and conditioning systems.

From a technological point of view and as mentioned in the report on Reference [2], several types of discontinuous and continuous dissolvers could be used.

The main disadvantage of batch dissolvers like flat tank with vertical tubes or pit dissolver, is the presence of a static hulls layer of significant height in the dissolution tubes, which can lead to dissolution and rinsing difficulties (less efficient thermosiphon, trapping of oxide grains in the hulls

layer, more difficult dissolution for partially sealed hulls, risk of local overconsumption of nitric acid in the dissolution tube and hydrolysis of the Pu, poorer decontamination due to the limited efficiency of static rinsing, etc). Similarly, in case of difficulties in priming the thermosiphon, this type of dissolver could lead to significant phenomena of precipitation and localized accumulation of zirconium molybdate and plutonium. Consequently, it would seem preferable to evolve this concept towards solutions allowing homogenization and continuous agitation of the hulls in the dissolution medium (alternate motion dissolver, drum dissolver, etc.), the dissolver hulls emptying device having to be decoupled from the fuel supply system to avoid any contamination.

A concept of a continuous helical dissolver with a safe geometry and greater unit capacity has already been developed in the past at CEA. In addition to its advantages from the criticality safety point of view, this type of dissolver appears to be significantly less cumbersome than the wheel dissolver of the existing plants in La Hague, since its characteristics should make it possible to reduce the size of the dissolving cell and to facilitate controls during operation and maintenance interventions. In addition, the operating mode of this dissolver, which requires a steady supply of fuel, should make it possible, in principle, to avoid clogging problems, to better decontaminate the hulls, to control the phenomena of foam formation and the gaseous releases during dissolution and thus to facilitate the design of the off-gas treatment and of the process ventilation ensuring the dynamic containment of this equipment.

For the complementary oxidative dissolution of the dissolution fines, operation could be carried out in a digester consisting of a safe geometry flat zirconium tank (with poisoning of the acid solution) and equipped with a recirculation loop, supplied with ozone, allowing the generation of the electrochemical mediator (Ag^{2+}). The digester vent could be connected to a off-gas stream decontamination device and then connected to the dissolver off-gas treatment.

Regarding the thorough rinsing of hulls, operations could be carried out in the dissolver after emptying the dissolving liquor and/or in a safe by geometry specific hulls rinser, such as a continuous helical rinser for example.

Regarding the one-step dissolution scheme, a concept of a "powder" vortex dissolver with a subcritical geometry, small size, high treatment capacity and allowing quantitative recovery of plutonium could be considered. However, this concept would require the oxide to be separated from the cladding and reduced to powder, which would simplify the design of the dissolver, allow the use of lower volume devices with high evaporation rates, reduce the residence time of the fuel, make the process rigorously continuous, improve the dissolution conditions of the oxide powder, design a more efficient gas treatment, eliminate the constraints related to the necessary proper behavior of the cladding in the dissolution medium and finally, adopt sufficiently aggressive attack conditions to reach the targeted dissolution yield in a single step. Under these conditions, only one clarification step would be necessary.

Mechanical oxide/cladding separation processes by shearing, grinding and sieving have been studied in the past, notably in France, and could be re-examined to confirm their feasibility, other techniques being also possible (magnetic separation...). One of the main advantages of these processes is their relative compactness compared to industrial disassembly and shearing equipments. However, these processes do not allow, at the present stage of their development, to recover the totality of the irradiated oxide (adhesion of residual oxide fragments) and require, consequently, to be supplemented by a hot nitric acid rinsing (or an oxidizing rinsing) of the fuel segments and of cladding splinters allowing to perfect their decontamination.

As mentioned in the report in Reference [2], these mechanical treatments could be completed by a thermal treatment of the oxide and the cladding segments (or voloxidation), already developed in the 1970s by the Oak Ridge National Laboratory (ORNL) (successive cycles of oxidation at 400-500 °C under O₂ and reduction under H₂). A last reduction step would allow the recovery of the irradiated fuel in the form of UO₂, the latter dissolving more rapidly than U₃O₈ and UO₃ in nitric medium. Finally, the voloxidation step would be followed by a mechanical separation step of the oxide powder and residual cladding fragments (sieving, etc.). **The possibility of eliminating the rinsing step of the cladding fragments should nevertheless be confirmed.**

Voloxidation could nevertheless lead to the release of a more or less significant fraction of the gaseous, volatile or semi-volatile radionuclides present in the spent fuel (³H, ⁸⁵Kr, ¹⁴C, ¹²⁹I, Cs, Ru, Rh, Tc, Rb, Mo, Se...), this fraction depending on the operating conditions adopted (temperature, furnace atmosphere...). Consequently, a specific gas treatment should be designed to trap and separate each of these radionuclides, the “dry” option being in principle preferred (molecular sieve, zeolite, etc.). The conditioning for these different wastes should also be defined. In addition, this thermal treatment could also influence the final solubility of the irradiated oxide (possible increase in the quantities of Pu-rich insolubles, linked to the successive reactions between the chemical forms UO₂, U₃O₈ and UO₃) and lead to the production of fine particles whose pyrophoric character would have to be evaluated, as well as the risk of dust explosion. From the technological point of view, these operations could be carried out in large capacity rotary furnaces. Two separate furnaces could be necessary for the successive stages of oxidation and reduction of the fuel. The foreseen technological difficulties (treatment capacity of the furnaces, etc.) and the associated risks (corrosion/abrasion, confinement of fine oxide powders issue conversion, pyrophoricity, criticality, hydrogen risk, etc.) should be the subject of specific developments and studies. In particular, for this type of furnace, criticality could be controlled by limiting the geometry of the apparatus associated with neutron poisoning, as control by limiting only the mass could turn out to be too restrictive (cf. paragraph 4.1. above).

Regarding the powder dissolver design, the residence time of the dissolution liquor will depend on the characteristics of the acid solution, the granulometry of the oxide powder, the kinetics of the chemical dissolution reaction (in principle fast) and the targeted dissolution yield. Under these conditions, the solid hold-up of such an apparatus should be very low, of the order of a few kg of (U+Pu), authorizing in principle the design of a dissolver of safe geometry. Modeling studies would in any case be necessary to design such an equipment (dissolution tests of powders in batch and continuous conditions, modeling of dissolution kinetics, etc.). If the design of such an equipment does not lead, in first analysis, to prohibitive difficulties, the hydraulic behavior and the agitation of the solution should nevertheless be the subject of specific studies to guarantee a sufficient homogenization of the oxide in the dissolution medium. In particular, the regular feeding of the fuel should make it possible to control the overpressure phenomena linked to the reactivity of the powder during dissolution and to facilitate the design of the gas treatment. In this respect, it should be ensured that the conditions of powder supply to the dissolver and the conditions of withdrawal of the dissolution solution will make it possible to limit the risks of clogging or wet deposits related to the rise of vapors in the oxide fuel introduction tube, as well as the risks of entrainment of solid particles downstream from the dissolution step. Finally, thanks to the short residence time of the solution, to the vortex phenomenon and to optimized heating conditions, this type of dissolver should be in principle much less prone to accumulation, precipitation, fouling and deposits than the current dissolvers, the dissolution medium having to be in principle more homogeneous in temperature and concentration. Finally, the nature of the material constituting the dissolver tank will have to be adapted to the dissolution conditions and to the nature of the surrounding environment.

Regarding the clarification stage, and as mentioned in the report in Reference [2], the equipment of this unit should also remain similar in principle to that developed for the treatment of UOX fuel and equipping the existing plants (Thorp and UP3 centrifuges). However, their design will have to take into account the much larger masses of plutonium-rich fines and insolubles in the primary dissolution liquors, and the high radiological activities and specific decay heat that will depend on the cooling time of the reprocessed spent fuels.

Concerning the risks linked to heat release, in the case of prolonged immobilization of the centrifuge bowl and the impossibility of carrying out the cleaning and rinsing step, the heating time of the cake of fines could be considerably reduced (a few tens of hours) because of its very high thermal power (a few hundred watts per kg of fines if the SFR MOX-MA fuels treated are slightly cooled), and this heating would lead to the release of volatile ruthenium (RuO_4) from about 120°C . Releases into the process ventilation circuits would then be much greater than in the case of treatment of UOX fuels. These characteristics could require changes in the design of the clarification units and their operating conditions (modification of the centrifuge bowl, improvement of the reliability and robustness of the rinsing system, increase in rinsing frequencies, addition of mitigation means likely to reduce radiological releases, etc.). With regard to the prevention of criticality risks (cf. paragraph 4.1. above) and taking into account the Pu content expected in MOX-AM dissolution fines (at least ten times higher than that of UOX fines), the control mode for future centrifuges could be the limitation of the geometry associated with internal poisoning, which would require an evolution of the existing equipment (installation of neutron absorbing core in the middle of the bowl for example).

In terms of prospects, the efficiency of dissolution liquors centrifugation being, in principle, limited because of the partly colloidal nature of the dissolution fines, the R&D to be carried out and in particular the precise physico-chemical characterization of these residues after primary and complementary dissolution should make it possible to direct the choice of the clarification devices towards even more effective, reliable and robust separation solutions and technologies. Some concepts could be revisited (pulsed filter, microfiltration, flocculation or electro-flocculation, electromagnetic filtration, ultrafiltration, etc.) by highlighting their advantages and drawbacks. Indeed, the achievement of the highest possible separation factor between the insoluble and the dissolution solution, associated with a marked improvement of the rinsing conditions of the fines, will be essential to minimize the risks of plutonium entrainment in the downstream flows, accumulation of fines in the transfer circuits and solvent extraction equipment, and increased degradation of the solvent used in the separation units (clogging of circuits, deposits likely to form hot spots favoring corrosion, formation of stable emulsions and interphase jellyfish, dissemination of iodine with the fines in the downstream part of the process...). Moreover, an efficient clarification seems essential to ensure an efficient and enough decontamination of U, Pu and MA in one or two cycles. The respect of these requirements will be more important as the spent fuels to be treated will not be cooled much, and the efficiency of the clarification must also be maintained over time (evolution of the characteristics of the reprocessed fuels expected during the transition phase of the nuclear reactors fleet). **A major R&D effort should therefore be made to limit the dissolution fines at the clarification stage, to control their transfer to the conditioning units, and to improve the safety and operating performance of future reprocessing plants.**

Concerning the storage of aqueous suspensions of fines awaiting conditioning, the design of the equipment would also have to be adapted to the much larger masses of fines to be stored (heat transfer, agitation, dilaceration, etc.), and a specific approach might also be necessary if the plutonium content of these residues were too high to achieve a sufficiently high H/Pu ratio to guarantee their subcriticality in an infinite medium.

As regards the risks of exposure to ionizing radiation, the dissolution-clarification units will be relatively unaffected by the treatment of SFR MOX-MA fuels, given that radiation shielding is already sized with regard to gamma emissions from fission products. The equipment of the dissolution, clarification and balance units will nevertheless be subjected to a source of neutron emission that is greater than for standard SFR MOX fuels (up to a factor of about 5). The installation of appropriate radiation shielding could therefore prove necessary.

In the same way, for SFR MOX-MA fuels, the constraints linked to the heat release from the dissolution solutions before or after clarification will be greater than in the case of processing SFR MOX, PWR MOX or PWR UOX fuels (by a factor of about 3 to 6), as the heat power density of the solutions can be of the order of 4 W/L for an equivalent heavy metal concentration of 200 g/L. Consequently, these power densities will lead, in case of loss of the cooling systems, to a significant reduction of the time available before the boiling temperature of the solutions is reached. Similarly, these characteristics will lead, in case of loss of the production and distribution systems of the dilution air of the hydrogen produced by radiolysis, to a significant reduction of the time available before reaching the lower flammability limit of the air/hydrogen mixture (4%) in the process equipment. **Also, the reliability and robustness of these systems, which are essential elements of the safety of the installations, will have to be reinforced.**

Concerning more particularly the risks of explosion linked to the hydrogen produced by radiolysis, taking into account the Pu and minor actinide contents and the much higher activities for SFR MOX-MA fuels, the values of hydrogen radiolytic yield ($G(H_2)$) adopted in the safety analysis of the current reprocessing plants, in normal operating and accidental conditions (loss of agitation and total loss of dilution air) could no longer be adapted. **These $G(H_2)$ values should therefore be determined experimentally at the laboratory scale and then at the pilot or industrial scale to evaluate the radiolysis gas flow rates to be taken into account in future safety demonstrations.** In addition, the studies carried out should also aim to better understand the effect of radiation on $G(H_2)$, in particular the combined influence of alpha and beta emitters (actinides and fission products), as well as the underlying mechanisms of formation/recombination of radiolysis hydrogen involving the chemical matrix (effect of high nitrate and nitrite contents, recombination/catalysis by certain FPs, effect of the solution height...).

4.2.3. CHEMICAL SEPARATIONS

The chemical separation stages of the EURO-GANEX process, integrating the problems of effluent management, have already been the subject of a safety review conducted by NNL and IRSN in the framework of the SACSESS project [8] [10]. Only the points considered most important are listed below, although further additional comments have been made.

4.2.3.1 REMINDER OF THE DEVELOPMENT STAGES OF THE EURO-GANEX PROCESS

In order to carry out the "grouped" separation of MA and plutonium, a two-stage concept, called GANEX, was initially developed by the CEA. It is only compatible with the homogeneous transmutation mode. In this concept, the minor actinides (Np, Am and Cm) are not only no longer separated from each other but are extracted and managed jointly with uranium and plutonium, which can offer in particular an increased resistance to proliferation risks. However, this concept requires the handling of radioactive materials containing curium, which induces very important thermal and radiation

protection constraints relating to the fabrication process, the handling in the reactor, and transport of the fuels. One of the difficulties of this concept is that it leads to the treatment, in the same feed stream, of materials whose concentration levels are very different, the concentration of uranium being in particular much higher than that of plutonium and minor actinides (one to two orders of magnitude). It thus appeared necessary to separate, during a first stage, a large part of the uranium in order to allow the solvent, used during the second stage, to retain a sufficient loading capacity to extract, in a grouped and selective manner, the plutonium and the minor actinides. In addition, this strategy makes it possible to recycle the uranium in the required proportions.

Regarding the different options related to the GANEX concept and developed at the European level, the research conducted since the late 2000s in the framework of the ACEPT, SACSESS and GENIORS projects have led to the development of the EURO-GANEX reference flowsheet, constituting a variant of the CEA process. The first cycle is quasi-similar to the GANEX 1 flowsheet proposed by the CEA. This first stage consists of a preliminary separation of the uranium (VI) present in the dissolution solution by means of a monoamide, DEHiBA, without necessarily adding plutonium complexing or reducing reagents for the plutonium. The structure of this molecule, a strong extractant of An(VI) and of uranium in particular, was optimized in order to increase the U(VI)/Pu(IV) selectivity while ensuring a good loading capacity to take into account the high concentrations of uranium to be extracted. This molecule also has a good resistance to radiolysis (the degradation products of DEHiBA, which are less troublesome than those of TBP, do not form a precipitate with Pu) and a low solubility in the aqueous phase, which is more than two orders of magnitude lower than that of TBP in nitric acid (this limits the loss of solvent and means that it is not necessary to install a diluent wash system upstream the An-Ln section). The extracted uranium stage with DEHiBA diluted in OK is followed by a scrubbing stage with hydrazine to improve the decontamination of the solvent loaded, in order to re-extract Np and Tc. The uranium stream is then backwashed with diluted nitric acid, the uranium being stripped back to the aqueous phase, before final concentration and storage (an additional purification cycle is maintained as a precaution on the uranium concentrate). It should be noted that the re-extraction of uranium is easier than with TBP (limitation of the flow rate of the aqueous backwash nitric acid solution), the implementation of a concentrating backwash stage being possible by simply heating this section. Finally, the regeneration of the solvent is obtained by contacting with nitric acid (in the presence of hydroxylamine nitrate) and then with sodium carbonate to remove the degradation products and residual cations. The solvent is then reacidified.

The GANEX 1st cycle was the subject of important studies and tests on simulated uranium solutions and then on real active solutions (feedstock consisting of a UOX-type dissolution solution) until 2008. The results of the research show that the uranium recovery rates are greater than 99.9%, with decontamination factors regarding Pu and FPs equal to or greater than those of the uranium flow produced at the first U-Pu cycle of the La Hague existing plants. These tests also made it possible to confirm, on the one hand, the possibility of improving the uranium decontamination factors of uranium with respect to Pu and extractable FPs (Ru in particular) by increasing the saturation of the solvent, and on the other hand, the beneficial influence of hydrazine, introduced into the uranium scrubbing section, on the decontamination of the uranium stream regarding Pu. At the present stage of development, the decontamination factors regarding FPs and actinides targeted for uranium could be sufficient with a single separation/purification cycle, especially for Pu, Np, Tc, Ru, and certain metallic impurities (Mo, Zr, Fe, etc.). **However, the possibility of eliminating the second uranium purification cycle should be confirmed, in particular in the case of the reprocessing of slightly cooled SFR MOX-MA fuels.**

Although the scientific feasibility of the GANEX 1st cycle can be considered as acquired, additional work remains to be done, notably concerning the implementation of the process in continuous solvent

extraction system (pulsed columns, etc.) and the regeneration of the solvent by the development of a specific treatment. Indeed, DEHiBA is temperature sensitive and therefore incompatible with the evaporation and distillation process currently used in the La Hague plants (TEO units). **Consequently, the industrial feasibility of the GANEX 1st cycle has yet to be demonstrated.**

The second EURO-GANEX cycle consists of only three stages, excluding solvent treatment. The first stage consists in co-extracting directly transuranics and lanthanides from aqueous outlet stream coming from the 1st cycle uranium extraction section using a mixture of DMDOHEMA and TODGA diluted in Oderless Kerosene (OK), the feedstock containing a complexing agent (CDTA) to avoid in particular the extraction of Zr and Pd. Indeed, the use of the only diglycolamide TODGA, which is a very powerful complexing agent of actinides (III), (IV) and (VI), requires to use it in low concentration, which consequently limits the loading capacity of the solvent. The diamide DMDOHEMA, playing the role of phase modifier, was thus added to the extractant system to reduce the extraction capacity of TODGA and to facilitate the stripping of actinides, and to avoid the formation of a third phase with high acidity and high actinide loading and to increase correlatively the extraction capacity of the solvent in plutonium. This extraction step is followed by a scrubbing of the loaded solvent with a nitric acid solution to complete the decontamination in FP, except for lanthanides (Zr, Mo, Fe, Sr, Pd). The second step consists in selectively stripping all the actinides back in an acid medium in the presence of a mixture of selective hydrophilic complexing agents constituted by BTP (in the SO₃-Ph-BTP form) and acetohydroxamic acid (AHA). The last step consists in stripping the lanthanides in a weakly acidic medium in the presence of a strong complexing agent, glycolic acid (pH 4 medium). The aqueous actinides stream produced is then concentrated and mixed with the aqueous uranium stream from EURO-GANEX first cycle before co-conversion. Finally, a treatment of the solvent (not yet optimized) is also necessary before its recycling.

The EURO-GANEX flowsheet was tested in "active" at ITU Karlsruhe in 2014 using an SFR fuel dissolution solution, demonstrating its scientific feasibility. The overall actinide recovery rate reached 99.8%, with less than 0.1% of lanthanides accompanying the actinides loaded aqueous solution. Current development work concerns the replacement of the TODGA/DMDOHEMA mixture by a single organic molecule (mTDDGA or PTEH), which simplifies solvent management and increases plutonium extraction capacity, and the replacement of the hydrophilic SO₃-Ph-BTP by another sulfur atoms-free complexing agent, which can have an impact on the quality and yield of the co-conversion step (a test is planned for 2021 with the molecule pitridiol). These new extractants are selected in particular on the basis of their resistance to radiolysis, the identified degradation products having, if possible, to keep their extraction capacity towards actinides and not to induce phenomena that are prohibitive for the safety of the process (formation of explosive or flammable gaseous products, degradation products becoming hydrophilic extracting back the fissile actinides, etc.). Otherwise, these products would have to be eliminated, making the process more complex. The optimization of the extractants must also take into account the influence of the temperature on the distribution coefficients and the separation factors An(III)/Ln(III). Indeed, if these coefficients are too sensitive to temperature, this parameter would have to be controlled extremely precisely at the different separation stages, which could also make the process more complex and lead to safety issues (criticality risks, etc.).

Finally, it should be emphasized that the EURO-GANEX concept may appear to be a breakthrough towards the current PUREX process (or the future COEXTM process), due to its specificities and the fact that it replaces the entire reference U-Pu extraction cycle. In this sense, this process could present more "industrial" risks than the sequential (SANEX-DIAMEX) or individualized (EXAm) separation processes, with a direct impact on the supply of the SFR reactor fleet in the event of a major hazard at the treatment plant (no reversibility possible), since all these processes have not reached a sufficient technological readiness level yet.

4.2.3.2. CONSOLIDATION OF THE EURO-GANEX PROCESS IN RELATION TO SAFETY

The main objectives of the R&D programs aimed at specifying the conditions for the industrial implementation of minor actinide separation processes are recalled below, as these studies must be carried out while taking into account the various aspects related to safety:

- development of even more selective extraction systems that produce less effluent, control of elementary phenomena and understanding of mechanisms,
- simplification of the processes, in particular by reducing the number of elementary steps,
- study of more “concentrating” flowsheets leading to a reduction of flows, of the consumption of reagents and of the size of the solvent extraction equipments (concentration of the FPs loaded aqueous solutions from the 1st EURO-GANEX cycle...),
- development of simulation models of separation processes, integrating the phases of phenomenological analysis, modelling, numerical resolution, validation and improvement of these models; the objective is to have a calculation code which makes it possible to appreciate the operating margins of the various flowsheets, to carry out sensitivity analyses and to define the operating modes as well as the associated means of monitoring techniques (choice of instrumentation, identification of the sensitive parameters, choice of the appropriate status indicators to detect any disturbances or deviations, etc.),
- choice and adaptation of the equipments towards the physical or chemical characteristics of the new extractants implemented (taking into account the presence of solids, extraction kinetics, physico-chemical characteristics of the phases such as the aptitude for separation or the generation of the emulsion, the resistance to irradiation and to the temperature of the solvent, the hydrodynamic behaviour of the extractors...) and qualification of all the selected technologies,
- studies of the conditions of regeneration of the solvents (extractants and diluents) and approach of the long-term behavior of these systems with regard to the phenomena of radiolysis and hydrolysis (irradiation loop with long-term tests, measurement of the effectiveness of the chemical treatments intended to eliminate the degradation products generated, evaluation of the need for complementary (second level) regeneration treatments, definition of the methods of management of the used solvents...).

Concerning the last point, the implementation of a separation process such as EURO-GANEX on an industrial scale requires indeed to be able to recycle the organic phase as long as possible. One of the main stakes linked to its development remains the definition of extractants (DMDOHEMA, TODGA, DEHIBA...), associated with the choice of a diluent (TPH, OK...), sufficiently resistant to hydrolysis and radiolysis phenomena induced by the high acidity and the very high alpha radioactivity of the solutions to be treated (possible presence of highly degraded plutonium with significant levels of ²³⁸Pu, high levels of minor actinides linked to the implementation of “concentrating” flowsheets...). The development of an appropriate first- or even second-level solvent treatment is therefore essential to eliminate the various acidic degradation products generated in the organic phase as well as possible. Indeed, these compounds, formed after rupture in various places of the extractant molecule by radiolysis and hydrolysis under the effect of radiation and the strongly acidic environment, are very diverse and can prove to be troublesome for the operation of the process (modification of the extraction capacities and the physico-chemical properties of the solvent, modification of the hydraulic behaviour of the contactors, reactivity and exothermicity, phenomena of retention during washing, risks of precipitation, formation of third phase...).

It is therefore necessary to identify the various compounds formed, to understand their metabolism and to appreciate their nuisance on the process (behavior of the solvent in stationary regime and stability of the performances of the implemented separation flowsheet). As an example, the

degradation of the diamide DMDOHEMA leads to the formation of: 1/ light products such as carboxylic acids, alcohols and amines which can in principle be eliminated by washing, 2/ monoamides and secondary diamides with less good extraction capacities but which can be eliminated by secondary treatment, 3/ bi-functional compounds (of the amide-acid type), which are undoubtedly the most troublesome and which require a specific treatment to eliminate them.

The first level solvent treatment, proposed in the report [2], is composed of an acid wash (which could also be replaced by an acid complexing agent of the carboxylic acid family⁹) and an alkaline wash to eliminate, on the one hand, the radioemitting cations (ruthenium...) forming basic complexes with the degradation products of the solvent and, on the other hand, the non-lipophilic acidic compounds resulting from the reagents introduced or the degradation of the solvent. The use of a reducing reagent (hydroxylamine or NH_2OH) is proposed in the EURO-GANEX flowsheet to reduce the traces of Pu(IV) and Np(VI) into Pu(III) and Np(V), these species being less extractable in the solvent and thus more easily back re-extracted in aqueous phase. In this respect, the effluents of the solvent treatment being in principle directed towards vitrification, non-saline and incinerable reagents should be sought to limit the quantities of sodium in the glass matrix (partial or total replacement of Na_2CO_3 , NaOH reagents...). **Consequently, the verification of the efficiency of this treatment and the absence of significant drift in the hydraulic and chemical behaviour of the extractant-diluent system should be the subject of long term irradiation tests** (several hundred hours) simulating as well as possible the real degradation conditions of the solvent in the plant (coupled acid hydrolysis and gamma radiolysis). These tests should also be carried out in the presence of the organic reagents used, these last ones being able to be partially extracted and their behavior modified under the effect of the radiolysis. In addition, tests to characterize the effect of alpha radiolysis¹⁰ and the possible catalytic effect of certain fission or corrosion products should also be carried out. These tests in an irradiation loop would thus make it possible to simulate the result of several years of operation in the plant and to verify the absence of accumulation of degradation products harmful to the process.

However, a second level of treatment could be necessary in case of insufficient elimination of certain "heavy" degradation products which could accumulate in the long term, this phenomenon could be prohibitive for the process. This type of treatment is also essential to separate and recover the pure diluent necessary for the "diluent washing" operations of the extraction cycles¹¹, to concentrate the extractant and to readjust the solvent concentration before its recycling. However, the choice of possible processes is limited by the fact that most of the extractants under development are temperature-sensitive, which excludes in particular the vacuum distillation techniques currently used in the La Hague plants to treat and regenerate spent solvents. Studies should therefore be carried out to evaluate the potential development of other techniques such as, for example, evaporation by

⁹ The acid complexing agent must have a low extractability in the organic phase, be composed only of C, O, H and N atoms (principle of the "CHON" molecule giving only gaseous products after degradation) and form complexes with the soluble cations in the aqueous phase that are stronger than those formed with the solvent degradation products. The family of carboxylic acids meets most of these criteria.

¹⁰ Solvent irradiation loops generally operate with ^{60}Co sources (gamma emissions) and are therefore only partially representative of the effect of alpha radiolysis, which is particularly important in the case of organic solutions loaded with actinides.

¹¹ The washing of extraction raffinates and backextraction solutions with diluent could be eliminated if the solubility in the aqueous phase of the new extractants used proved to be very low. It should be emphasized that this type of equipment constitutes one of the main barriers to prevent the risk of sending significant quantities of solvent to the evaporators, as such a situation could lead, on the one hand, to significant foaming phenomena which could disturb the proper course of the denitration reaction and oblige the operator to reduce the feeding rates (reduction in evaporation capacities), and on the other hand, to violent exothermic reactions between the solvent and the nitrates (formation of "red oil" compounds) in the event of a combined loss of extraction of the process gases (process ventilation system).

liquid film under vacuum, the "flash distillation"¹² technique or extraction by supercritical CO₂¹³ allowing the preferential solubilization of certain compounds.

The methods of management of the used solvents and of the possible organic residues resulting from the second-level treatments should also be defined, by evaluating in particular the different possible thermal treatments for the organic liquids or residues (pyrolysis, incineration, mineralization in the presence of an electrogenerated oxidizing mediator, wet oxidation, hydrothermal oxidation in supercritical water, etc.)¹⁴. The safety issues associated with these different processes should be addressed, particularly with regard to the risks of ignition and explosion. Their impact on the release of radioactive effluents (possible presence of iodine in organic residues, etc.) and chemical releases should also be evaluated.

Thus, these different first and second level treatments should make it possible to minimize the effluents generated and to recycle the organic phase over long periods without any prohibitive addition of new solvent (guarantee over time of a sufficient decontamination factor of the extractant and diluent brought by the treatment units). Indeed, the organic phase must keep its extracting and hydrodynamic properties and not accumulate degradation products that could be potentially exo-ergic (formation of alcohols, nitro derivatives, carboxylic acids, amides or secondary amines...). The accumulation of such products could, under these conditions, constitute hazards for the downstream stages involving heat sources (transfer of solvent by steam ejector, evaporation-concentration, other thermal treatment...). In addition, it should also be shown that these degradation products and those of other reagents or complexing agents used (CDTA, BTP, AHA, glycolic acid...) will not be able to complex fissile actinides or other metal cations and lead to the formation of precipitates in the extractors, tanks or evaporators (limitation of extraction and re-extraction yields, loss of actinides in the extraction raffinates and the unloaded solvent, etc), or even in the dissolvers in the case of extensive recycling of nitric acid in the head-end plant or in the chemical separation units. These phenomena could call into question the prevention of criticality risks in these units.

Moreover, the treatment of SFR MOX-MA fuels that have not been cooled much (of the order of 3 years or less) could only exacerbate these phenomena, mainly at the level of the first cycle of U-Pu co-

¹² Flash evaporation or "flash distillation" is characterized by the absence of energy input in the evaporator. The feed, possibly overheated, undergoes an isenthalpe expansion through a valve at the inlet of the evaporator. The resulting pressure drop leads to partial vaporization of the solvent, as well as cooling and concentration of the solution.

¹³ Supercritical fluid extraction is a process that allows the extraction of a solute using a supercritical fluid acting as a solvent, usually CO₂, maintained above its critical points (T > 31°C and P > 74 bar for CO₂). The solute is then separated from the supercritical fluid by precipitation, after return of the fluid to the gaseous state (decrease of pressure and temperature), this one losing its solubilization power. Compared to other extraction techniques using organic solvents, the kinetics of extraction by supercritical CO₂ is faster and the temperature of implementation is lower, which makes it possible to separate thermosensitive compounds.

¹⁴ Pyrolysis corresponds to the thermal decomposition of organic materials or liquids in a low oxygen atmosphere (temperature 300 to 800°C and O₂ content 0 to 15%) whereas incineration requires higher temperatures of about 850 to 1000°C (O₂ content 20%). These processes produce immobilized ash, generally in a cement matrix. The CEA, CENTRACO and ORANO have significant experience in the incineration of organic solvents (TBP, TLA, etc.) and the mineralization of organic residues by pyrolysis (TEO units). In addition to taking into account the ignition properties of the treated solvents (flash point, auto-ignition temperature...), the main risk to be analyzed is the risk of explosion related to a loss of tightness of the pyrolyser or the incinerator (air inlet).

The Ag(II) mineralization of contaminated organic effluents is an efficient method of destruction which nevertheless presents slow reaction kinetics, the treatment capacities being limited by the imposed current intensities. This process leads to the formation of alkyl nitrates and organic nitrates. These compounds must be destroyed by an additional treatment to ensure the safety of the process (combustion of reaction gases...).

Wet oxidation (WVO) is characterized by an oxidation of organic waste in water at high temperature and under pressure in the presence of O₂ or H₂O₂. However, the subcritical oxidation (area below the critical point of water) generates reaction intermediates of low molecular weight requiring the addition of a catalyst (copper...) to decompose them.

Finally, the process of mineralization of organic solvents by hydrothermal oxidation (OHT) uses the properties of water in the supercritical state (P > 221 bar and T > 374°C) to destroy the used solvents and transform them into carbon dioxide and water. The hydrothermal oxidation reaction, implemented in a homogeneous phase in a tubular reactor, is a fast kinetic reaction. Its yield is higher than 99% for solvents such as TBP, TLA or dodecane. The destruction of DMDOHEMA diamide by the OHT process has also been the subject of feasibility studies at CEA. This process induces risks of fire and explosion that must be analyzed, and the reactor must respect the pressurized equipment regulations.

extraction and the minor actinides grouped separation cycles. This could lead to greater degradation of the solvents used, to disturbances in the operation of the solvent extraction equipments (formation of interphase precipitates or stable emulsions in significant quantities in the pulsed columns in the case of insufficient clarification, risks of clogging and hot spots in the transfer circuits, etc.), high residual activity of the solvents after treatment, entrainment of the organic phase in the aqueous phases, significant leakage of plutonium or minor actinides into the unloaded solvent, difficulties in operating the FP evaporators, and finally, significant losses of solvent in the process. These phenomena could thus make it very difficult to reprocess these fuels with high throughput.

In addition, the implementation of more "concentrated" separation flowsheets for minor actinides, allowing in principle a reduction in the volume of effluents produced, the size of the solvent extraction system and the reagents consumption, would require an additional stage of concentration of the actinides loaded aqueous solution coming from the first EURO-GANEX cycle before feeding the second cycle. However, this new step would be likely, depending on the concentration rate and the final acidity targeted for the raffinates¹⁵, to lead to the formation of precipitates (metal cations or FP that are not very soluble in nitric acid solution) and would therefore require prior clarification of the fission product and actinide concentrates obtained (reduction of the risks of clogging and increased degradation of the solvents at the interfaces of the liquid-liquid contactors) to verify the absence of plutonium and minor actinides in the precipitates, which should also be characterized, and to define an appropriate management method for these compounds. These operations will, in fact, make the process flowsheets more complex by introducing new risks that would have to be managed (effects of thermal releases at the level of the solid-liquid separation equipment, management of the separated precipitates, taking into account the risks of criticality, etc.), the feasibility of these operations remains to be demonstrated (clarification efficiency, compatibility of the physico-chemical characteristics of the concentrates with the co-extraction and re-extraction stages, hydrodynamic behaviour of the liquid-liquid contactors, significant radiolysis of the solvent from the first stages of separation, etc.).

Losses of uranium and plutonium and of minor actinides in the treatment plants are estimated at 0.1% when they are recycled. It should be emphasized that the definition of sufficiently selective extracting molecules and the achievement of high separation yields for plutonium and minor actinides are major objectives, since the mass inventory of these radionuclides in the waste will be directly conditioned by the separation factors obtained. These factors will also have a direct impact on the characteristics of the manufactured fuels, in particular with regard to the risks of exposure to ionizing radiation (significant increase in equivalent dose rates due to neutron emission in the manufacturing plants, etc.). Similarly, obtaining sufficient decontamination factors for actinides (Pu, Am, Cm) with respect to extractable FPs (lanthanides, Zr, Mo, Ru...) is essential to limit the radiation protection constraints during the fabrication of SFR MOX-AM fuels, the impact of FPs on the neutronics of the reactor core, their chemical interactions with the fuel cladding during irradiation in the reactor, and their rate of release into the fuel matrix in an accidental situation.

As already mentioned, the modeling studies of the EURO-GANEX process will make it possible to carry out analyses of the operation and sensitivity of the flowsheet implemented in the future workshops and will therefore be particularly important (studies of disturbances, steady and transient states calculations, identification of the most sensitive operating parameters and evaluation of the margins, identification of the status indicators of the process and of the relevant monitoring points, definition

¹⁵ The maximum allowable concentration levels for EURO-GANEX first cycle raffinates should depend on the physical or chemical limits that would then be reached.

of the means and operating modes best adapted to the process, etc.)¹⁶. Indeed, this type of process could present a strong sensitivity to certain operating parameters, the plutonium and minor actinide contents of the reprocess streams, of which some isotopes can have very low critical parameter values, being moreover important.

The developed models will have to be based on the integration of the most developed and reliable phenomenological models possible (partition coefficients of the species, complexation reactions, interphase transfer kinetics, kinetics of the oxidation-reduction reactions, hydrodynamics of the chemical reactors, thermal phenomena...). These models will have to be validated for each step of the separation processes, in order to allow an extrapolation to the industrial scale of the flowsheets tested at the laboratory level. Numerical simulations based on theoretical chemistry could also progressively alleviate the need to acquire certain experimental data. In addition, it still seems very difficult to do without tests on real solutions on a pilot or even semi-industrial scale to definitively validate the industrial implementation of these very evolving processes, taking into account, on the one hand, the complexity and the diversity of the phenomena involved in these very high activity media, and on the other hand, the effect of scale (presence of very radioactive fines in solution, degradation of the solvent by radiolysis, formation of interphase cruds (jellyfish), ageing and clogging of the pulsed columns playing on their hydrodynamic functioning...).

Concerning in particular the operation of the separation processes at the plant, the main elements to be followed are the major actinides (U, Pu), the minor actinides (Am, Np), and certain lanthanides (Nd, Sm). If on-line monitoring by spectrophotometry is already partly operational for U, Pu, and Am, the development of analytical techniques and on-line nuclear measurements for the other elements mentioned, in particular curium, also appears indispensable, as does the monitoring of certain cations with particular behavior (Mo, Pd, Ru, Fe, Tc) and the measurement of acidity in high activity. **The launching of prospective studies on these different aspects thus appears necessary.**

In addition, it seems useful to recall the importance of the choice of the diluent within the framework of the development of a new solvent. If the extractant is composed of complex organic molecules, functionalized, of high molar mass and presenting a strong chemical affinity for the metal ions to be extracted (esters, amines, amides, phosphates, etc.), the diluent is in general a molecule little or not functionalized and of rather low molar mass (linear or branched alkane, etc.). The physical and chemical properties of the extractant can be, in particular, modified by the choice of the diluent, the latter giving to the solvent useful hydraulic properties (effect on the disengagement and the decantation of the phases...). In addition, the physical characteristics of the diluent (volatility, flammability...) must necessarily remain compatible with the control of fire and explosion risks and present a low sensitivity to chemical attacks (HNO₃...) and to α and $\beta\gamma$ radiations (just like the extractant). Finally, the diluent (alcohol, polar molecule, alkane...) can play a role of phase modifier and allow in particular to reduce the risks of formation of third phase and the risks of criticality induced. Some extractants such as diamides can indeed present limits of formation of third phase, in terms of concentrations of nitric acid and metal cations, more or less high which can make the operating conditions of the process rather constraining. Diluents such as aliphatic carbides with linear structure (n-dodecane...) generally favor third phase phenomena, unlike branched compounds which are (or have been) more widely used (hyfran 120, TPH, ISOPAR L...).

¹⁶ As a reminder, the conventional approach will be to carry out sensitivity analyses of the proposed separation flowsheet in order to detect any "sensitive" operating parameters, for which a slight variation could have a significant impact on process operation, performance and safety, as well as relevant follow-up points (or status indicators) for observing process status. Steady then transient-state calculations are required next (with combination of single deviations if necessary) to evaluate the dynamics with which any disturbances will affect outlet streams and any leakage of fissile materials and to verify that the selected status indicators provide sufficiently early detection and warning of any malfunctions.

In terms of technical analysis intended to develop a first image of a future industrial EURO-GANEX separation unit, the solvent extraction operations can generally be implemented in continuous contactors (pulsed columns) or contactors divided into compartments (mixer-settlers or centrifugal extractors), the choice of the type of contactor for each operation must be carried out according to the rules in use and taking into account the feedback from the current plants (UP3, THORP...). At first glance, it does not seem necessary to develop specific extractors for the separation processes of minor actinides. The number of stages of the contactors and the height of the pulsed columns bodies can be estimated from the theoretical number of stages necessary for a given operation. The diameter of the pulsed columns can also be estimated from the aqueous and organic flow rates used for each operation, taking into account the criticality safety constraints for the larger diameter columns (annular columns of safe geometry with a central neutron absorbing core).

NNL has chosen centrifugal extractors for the first and second EURO-GANEX cycles [2] mainly because of their performance and compactness. Pulsed columns could nevertheless be retained for the first EURO-GANEX cycle, insofar as these extractors are relatively well adapted to the presence of finely divided solids in the clarified dissolution solutions constituting their feedstock (dissolution fines of a more or less colloidal nature having passed through the clarification and leading to the formation of interphase cruds) and in spite of the fact that the interfacial exchange area created in this type of apparatus is relatively limited in comparison with the other types of extractors. In this respect, it should be emphasized that although centrifugal extractors allow to gain in size and volume of equipment, to limit the radiolysis of the solvent (short residence times), to reduce the quantities of fissile materials used in the separation unit and to reach quickly the equilibrium of the cycle, their main disadvantages are a lack of tolerance to solids in the feed solution (risks of clogging and hot spots...), which makes them in principle incompatible with its treatment, even if it is clarified (UP2 plant operating feedback). Moreover, the « mechanical » heating of the solvent in this type of equipment could lead to a risk of ignition, as well as a rapid evolution of the system in the event of a malfunction (loss of flow...) with almost immediate repercussions on downstream operations (risks of criticality...).

Pulsed columns could also be selected for the second EURO-GANEX cycle. In this respect, studies would nevertheless be necessary to verify that the characteristics of the phases present would allow satisfactory hydrodynamic behavior of these extractors (sufficient interfacial area and material transfer kinetics between aqueous and organic phases, correct countercurrent circulation of the two phases, absence of risk of formation of stable emulsions, aptitude for phase separation, etc.)¹⁷. On the other hand, the uranium backwash section of the 1st EURO-GANEX cycle and the associated second uranium purification cycle (assuming that the latter is still necessary in view of the FP decontamination factors already obtained in the first cycle) could be carried out in banks of mixer-settlers, similarly to 1st cycle operated in the current La Hague reprocessing plants.

Finally, concerning the solvent treatment operations implemented, these are usually carried out in mixer-settlers, similar basic washing and acidification operations, with possible addition of complexing or reducing agents, being implemented to purify the extractants (DEHIBA, DMDOHEMA/TODGA). As indicated in the report [2], centrifugal extractors could nevertheless be retained in order to improve the settling of the phases.

¹⁷ In particular, the solvents of the amide family have different physico-chemical characteristics from those of TBP which can influence the operating conditions of the extractors (lower interfacial tension, higher viscosity, reduced phase density difference but adjustable by the concentration of extractant, different wettability of the plates of the pulsed columns, etc).

4.2.3.3. PRELIMINARY RISK ANALYSIS

It should be remembered that the design and operation of the chemical separation units, like the head-end plant and the other units, will be affected by the choice of the minor actinide recycling method, with consequences that will be all the more significant as the minor actinide content of the fuels and blankets will be high.

Concerning the risks of exposure to ionising radiation, as for the head-end plant units, the chemical separation units will be little affected by the presence of minor actinides, as the radiation shielding are already designed with regard to gamma emissions from fission products. However, the dose equivalent rates at the various workstations as well as the preliminary designing of the radiation shielding, will have to be refined during the detailed design stages of the future workshops. On the other hand, the equipment of the separation units containing the separated actinides (Pu-Am-Cm-Np) in a concentrated form and the actinides finishing equipment will require the addition of suitable radiological protection.

In the same way, the constraints linked to heat release and radiolysis gases will also be much more important in these units and will require a reinforcement of the cooling and dilution air production systems, ultimate measures having to be defined to compensate for the total loss of these systems.

Concerning the risks of explosion linked to radiolysis phenomena, the values of apparent radiolytic yields of hydrogen (or other potentially flammable/explosive gas) to be retained in normal operation and abnormal or accidental conditions (total loss of dilution air or process ventilation, loss of agitation or pulsed air in the equipment, etc.) to assess the radiolysis gas flow rates to be considered in future safety analyses must be determined experimentally at laboratory scale and confirmed at pilot or industrial scale. The $G(H_2)$ yields will have to be evaluated in particular for the following solutions:

- Pu-MA-FPs extraction raffinates from the U extraction and Pu-Np-Tc scrubbing sections of the first EURO-GANEX cycle¹⁸;
- The FPs raffinates from the TRU extraction and TRU stripping sections of the second EURO-GANEX cycle¹⁹ ;
- The Pu-MA loaded aqueous solutions from the An stripping and the FPs raffinates from Ln stripping sections of the same second cycle²⁰;
- Basic effluents from solvent treatments²¹ ;
- Loaded solvents²².

With regard to the first cycle of the EURO-GANEX process in particular, the introduction of hydrazine nitrate (anti-nitrous reagent) into the uranium backwash section (improvement of Np and Tc back re-

¹⁸ Compared to the raffinates from the first PUREX and COEX™ extraction cycles, the raffinates from the first EURO-GANEX cycle contain, in addition to the FPs and minor actinides present in the spent fuel, all the plutonium produced during irradiation. These solutions are therefore subject to much higher alpha radiolysis. They may contain degraded solvent (DEHIBA/OK) traces (content depending on solubility of the solvent in the aqueous phase and mechanical entrainment at the outlet of the extraction column).

¹⁹ These raffinates contain only FPs and should be more diluted than raffinates from the 1st PUREX (or COEX™) extraction cycles (higher aqueous flows required for scrubbing and backwashing operations). They may contain potentially degraded organic chemical reagents (CDTA, etc.), as well as trace concentrations of degraded solvent (DMDOHEMA, TODGA, OK, etc.) (content depending on solubility of the solvent in the aqueous phase, mechanical entrainment and efficiency of the diluent wash operation).

²⁰ These aqueous actinides stripping solutions have high alpha activities (high radiolysis) and may contain potentially degraded organic chemical reagents (AHA, BTP...) and trace solvent degradation products (content depending on solubility of solvent in aqueous phase, mechanical entrainment and efficiency of diluent wash operation).

²¹ The composition of these effluents is not yet known (acid and/or alkaline washes, sodium-free reagents, complexing agents, etc.). They contain the degradation products of the solvents taken up by these washes (compounds of an acid nature, etc.).

²² The solvents used in the EURO-GANEX process will, once loaded, undergo significant radiolysis $\alpha\beta\gamma$ due to the presence of Pu, Am and FP (lanthanides and other extractable FP).

extraction) could lead to the formation of azothydric acid (N_3H), which is highly volatile and explosive in the gaseous or liquid phase, in the presence of nitrous acid in solution. This unstable compound should in principle follow the loaded solvent (DEHiBA/OK) to uranium backwash section and then be back re-extracted in an alkaline medium at the solvent treatment level as sodium azide. If the principle of the treatment of basic effluents implemented in the La Hague plants is retained, these effluents would in principle be concentrated and then reacidified before vitrification, this last operation being able to release N_3H in the gaseous phase at a level close to the explosiveness level. Studies should therefore be carried out to confirm the risk of formation of nitric acid in the event of the use of hydrazine in the first EURO-GANEX cycle, to specify its behaviour at the various stages of the process, including those relating to the management of basic effluents, and to define, if necessary, prevention measures to reduce the risk. These measures should be similar to those already implemented in current plants (destruction of N_3H formed by sending NO_x in the uranium backwash section, limitation of the nitrogen content of basic effluents before concentration, destruction of residual nitrogen before acidification of concentrates, elimination of any concentration and accumulation process of N_3H in the process equipment, elimination of the risks of distillation by evaporation-condensation, etc.).

Concerning the criticality risks, the compatibility of the EURO-GANEX process with the flowrates of fissile materials to be reprocessed will have to be assessed. As a reminder, the multi-recycling of plutonium and the reprocessing of SFR MOX or MOX-MA fuels will involve much higher flowrates of Pu than those associated with the treatment of light water reactor fuels. The flowrate of Pu is multiplied by a factor of about 10 for a throughput of about 450 t per year. Moreover, if the co-conversion of uranium and plutonium is retained, this would lead, up to the final stages of the treatment process, to volumes of fissile solutions much higher than the current volumes obtained in the La Hague plants.

Furthermore, the equipment design for criticality risk requires an isotopic composition bounding real compositions but also a bounding moderator. For example, in the La Hague plants, water is considered as the moderator in situations excluding any precipitation phenomenon (Pu nitrate solution in particular). Given the use of new extractant systems, specific studies were conducted by IRSN as part of the GENIORS project to obtain the necessary data to verify the bounding nature of water moderation and to define actinides density laws with these new extractants (need to define the relationship between fissile material concentration and hydrogen quantity, organic phase according to the quantity of extracted fissile material, etc.). They are the subject of the reports listed in Reference [9], [11] and [12].

Regarding the sensitivity studies of the separation flowsheets, and as previously mentioned, steady and transient-state calculations will have to be carried out to assess the kinetics with which disturbances will affect the outlet streams and possible leakage of fissile material, the occurrence of possible malfunctions having to be detected sufficiently early on the basis of the monitoring of predefined status indicators. For example, the process deviations likely to lead to Pu leakage in the uranium-loaded solvent leaving the uranium extract section of the first EURO-GANEX cycle and in the unloaded solvent leaving the actinide strip section of the second EURO-GANEX cycle must be identified and the kinetics of the increase in Pu concentration for these different deviations specified. Depending on the type of extractors selected, this type of information could make it possible to assess the possibility of relaxing the equipment designing constraints by jointly controlling the geometry and concentration at these stripping stages. If not, a constraining dimensioning in terms of equipment size should be retained. As an example, the mixer-settlers bank of the first EURO-GANEX uranium backwash section (if this type of equipment were to be retained) would be of safe geometry, and this control mode could be associated with the limitation of the plutonium concentration.

The criticality safety analysis would also require the definition of process discontinuities (buffer tanks, etc.) and the necessary controls on transfers ending up in an unsafe equipment geometry (sampling for analysis, interlocks, etc.).

Finally, as mentioned above, some actinides have very low critical parameter values (for example, the minimum critical masses of certain Cm isotopes considered separately are of the order of a few tens of grams, regardless of the large uncertainties that may be attributed to them). **It would therefore be advisable to identify as soon as possible the process stages likely to accumulate, concentrate or precipitate chemical elements, in normal or abnormal operation (equipment rinsing, etc.), at values close to the maximum admissible masses and concentrations.** This could constitute a prohibitive difficulty. **Regarding the Cm issue, specific studies relating to nuclear measurement techniques should be carried out in order to compensate for the current lack of on-line monitoring of this minor actinide.**

4.2.4. URANIUM AND MIXED ACTINIDE FINISHING

4.2.4.1. PROCESS ADOPTED BY NNL

For the uranium finishing unit, NNL opted for a preliminary treatment stage by steam stripping of the uranyl nitrate solution from the uranium backwash section of the first EURO-GANEX cycle (recovery of the traces of residual solvent). This first stage is followed by an evaporation/concentration stage under reduced pressure at 90 °C (final uranium concentration of the order of 1,000 g/L) and then by a direct denitration stage in a fluidised bed at 300 °C (with the addition of sulphuric acid) of the concentrate obtained to produce UO₃ powder.

The actinide finish operations are assumed to be identical to the Pu finish operations as implemented in the THORP plant. These operations consist of precipitating Pu and Am nitrates by adding oxalic acid in a vortex precipitator, filtering the resulting oxalates in a rotary filter and then thermally decomposing them in a calcination furnace (under air/Ar) to transform them into (Pu,Am)O₂ oxide. The UO₃ and actinide oxide powders are then stored before being sent to the SFR MOX-AM fuel fabrication plant (powder metallurgy route). Prior to these different operations, the actinide solutions are treated by steam stripping, concentrated by evaporation and then undergo a valence conditioning by adding H₂O₂ [2].

These processes are compared hereafter with oxalic co-conversion and direct co-denitration processes, as well as with new co-conversion routes such as sol-gel co-gelation and fixation on porous or organic medium, which are being studied with the aim of simplifying and improving the techniques for manufacturing fuels dedicated to the transmutation of minor actinides. In particular, safety aspects are addressed.

4.2.4.2. URANIUM, PLUTONIUM AND MINOR ACTINIDES COCONVERSION UNIT

It should be remembered that even if the implementation of the co-precipitation step may seem simple, it is necessary to control all the physico-chemical and chemical engineering parameters (concentration of actinides in the effluents, precipitation conditions, effect of radiolysis...) that can

affect the chemical composition of the precipitate and its physical characteristics (flowability, granulometry, filterability, microstructure...), and that the conditions for obtaining these characteristics must be perfectly reproducible. Thus, the co-conversion process allows both to obtain a better homogeneity of the plutonium in the fuel (improved solubility of Pu) and to simplify the manufacturing operations (simplification or even suppression²³ of the grinding operations of the powders generating fine contaminating particles).

Taking into account the experiments carried out at CEA at the laboratory scale and the industrial experience of the oxalic conversion units of the La Hague plants, no redhibitory point with regard to the demonstration of the feasibility of the co-conversion of U and Pu by the oxalic route (the aim of COEX™ process is to produce a mixture of mixed oxide (U,Pu)O₂ from U(IV) and Pu(III)) has been identified at this stage. However, although the analyses of nuclear risks and risks linked to the chemistry of the process do not seem to reveal any prohibitive difficulties, the throughput required on an industrial scale for U and Pu recycling in the form of MOX fuel could lead to the need of re-examining all the stages of co-conversion, particularly from the technological point of view, and even to study alternative routes.

Taking into account the knowledge and experience gained from the COEX™ process studies, oxalic co-precipitation could also be used for the co-conversion of streams containing minor actinides, the objective being to obtain a solid oxide solution (U,Pu,Am)O₂, with about 20% Pu and MA weight content, ensuring an optimal homogeneity of minor actinides in the fuel. The use of this type of homogeneous precursor should thus simplify the shaping steps by directly targeting the final actinide composition (elimination of mechanical mixing steps at the fuel fabrication level).

The choice of the degree of oxidation of the various actinides to be converted into oxide is an important parameter to obtain a solid phase of controlled composition, within which the distribution of the elements is the most homogeneous possible. A mixture of An (IV)-An (III) should therefore be retained, aiming at an equivalent reactivity between the different elements in the chemical system considered. Obtaining the degree of oxidation (IV) of uranium is thus necessary for a quantitative and homogeneous precipitation of this element, the other actinides (Pu, Am, Cm) being used in degree of oxidation III. Tests of co-conversion carried out at CEA using uranium and curium have nevertheless shown a rapid oxidation of U(IV) into U(VI) under the effect of very important alpha radiolysis in solution, a phenomenon that can prove to be prohibitive on an industrial scale.

In this respect, as indicated in the report in Reference [2], the An loaded aqueous solutions from the An stripping stage of the second EURO-GANEX cycle must be concentrated before being co-converted into oxide, in order to reduce the volumes of stored effluents and to obtain precipitation yields that will limit the losses of actinides in the oxalic mother liquors. The solution for the production of actinides (Pu,Am) is indeed not very concentrated, being of the order of a few g/L at the most, according to the more or less "concentrating" process flowsheet adopted, the co-conversion operation requiring to have actinides concentrations in solution of the order of a few tens of g/L at the most. As mentioned above, an operation of valence conditioning of the solutions (U-Pu-Am) is also necessary before co-conversion, the mixed oxalates of uranium, plutonium, and minor actinides having to be formed from uranous nitrate (U (IV)) and trivalent actinide nitrates (Pu (III), Am (III), Cm (III)) or tetravalent actinides (Np (IV)). **Given the characteristics of the concentrated solutions, research should be carried out to evaluate the possibility of co-precipitating mixtures of uranium (IV) and**

²³ The co-grinding operation could be omitted if the mixed oxide powder has the intended final composition.

actinides (III) under "exacerbated" ²⁴radiolysis conditions, since the absence of prohibitive points cannot yet be established. Uncertainties remain in particular concerning curium.

In addition, the organic reagents used in the EURO-GANEX process (complexing agents or reducing agents) lead to the generation of effluents with a high carbon content, and these effluents need to be concentrated to meet the specifications of the downstream transformation steps, and in particular the conversion. Consequently, complementary studies should be carried out to evaluate the impact of the reagents (and their degradation products) present in the solution for the backextraction of minor actinides (Pu,Am) feeding the co-conversion stage. For example, DTPA could partially complex uranium (IV), thus preventing it from precipitating quantitatively in the form of oxalate. This could lead to a lack of uranium in the final oxide and to a questioning of the reference fissile medium for the prevention of criticality risks. The appearance of precipitates could also be linked to the formation of by-products from the radiolytic degradation of DTPA during the storage phases, which could again call into question the prevention of criticality risks. In this respect, the risks of selective accumulation of a risky species (Pu or Cm) should be evaluated and the means of monitoring and detecting these possible accumulations implemented, taking into account the high neutron emissions foreseeable from these solutions.

The possibility of destroying these troublesome organic compounds by means of "oxidizing" processes (mineralization using hydrogen peroxide or ozone, denitration, electrolysis, etc.) or more simply by steam distillation, or by taking advantage of the effect induced by the thermal releases and radiolysis during the stages of concentration and storage of actinide solutions, should therefore be examined in particular. The various processes that could be envisaged could be assessed against to different criteria (effectiveness, simplicity, safety, discharges, etc.).

The importance of acquiring the best possible knowledge of the chemical behavior of the species present in solution must be emphasized again in order to evaluate the risks related to the reagents, their degradation products and the reactions implemented during the different stages of the process. In this respect, it should be emphasized that the processes for separating minor actinides do not use oxidizing-reducing reagents as in the PUREX process, which eliminates the risks related to the characteristics of this type of reaction (chemical reactivity, exothermicity, explosion, corrosion, etc.).

Regarding the technological aspects, a thermosiphon evaporator with a feed rate of a few m³/h, allowing to concentrate the actinide solutions before co-precipitation, could be used. The volumes of concentrate and distillate could be estimated from the following data: a purification factor of 106, a maximum thermal power of the concentrate solution of the order of 10 W/L (equivalent to that taken into account in the evaporators and the FP storage tanks of the La Hague plants), and a maximum final concentration of the order of 100 g/L, identical to that used for U-Pu co-conversion. **Given the concentrations of fissile actinides expected in solution, the evaporator should be designed with a safe geometry from the criticality point of view.**

In addition, a composition of the oxide powder formed close to that targeted in the SFR MOX-AM fuel should be retained because of the associated handling constraints, due essentially to the high thermal release of these powders. From the point of view of the process, this "direct" route could also lead to better redox stability of the solution to be co-precipitated and to better control of radiolysis phenomena and heat release, given the lower concentrations of minor actinides.

²⁴ As an example, an in-line mixing allowing to compensate the effects of radiolysis on the stability of the actinides oxidation degrees after valence conditioning (presence of free radicals, HNO₂ and H₂O₂ in solution) could be considered.

In the case of the mixture of uranium, plutonium, and minor actinides, the reduction of the plutonium, which could be carried out by adding uranium (IV), would remain necessary before the co-precipitation stage, the elimination of the uranium (VI) being supposed to be possible by extraction with the monoamide DEHiBA (a solvent also used in the first EURO-GANEX cycle).

Since the oxalic conversion process is supposed to be used for the production of minor actinide oxides, equipment similar to that used for the U-Pu stream could be used for the EURO-GANEX process. In this regard, it is necessary to recall the importance of obtaining a homogeneous precipitation of uranium, plutonium, and minor actinides in solution from the point of view of prevention of the risks of criticality, this requirement constituting a key point for justifying the reference fissile medium used to size the equipment for co-conversion. Without such a guarantee of homogeneity, the prevention of criticality risks as planned would be called into question.

As for the operations at the end of the plutonium process, the number of equipments (precipitators, filters and calcination furnaces) can be estimated based on the quantities of oxide to be produced. For the plants corresponding to homogeneous recycling, the number of equipments, which is very important, is comparable to that envisaged for the conversion of the mixture of uranium and plutonium (that is, nearly 2 t/d of oxide (U,Pu,Am)O₂ to be produced by the "direct" route for for a 60 GWe SFR fleet at equilibrium). Consequently, as for the production of uranium and plutonium oxide, only a change of technology or even of process would make it possible to reduce the number of devices and thus to facilitate their operation, since their technical and industrial feasibility is not acquired at this stage. In addition, the high thermal and radiolysis gas releases due to actinides will impose significant additional constraints on the design of equipment and associated safety functions (cooling, dilution of radiolysis gases). The demonstration of the technical feasibility and safety of the process of co-conversion of minor actinides thus remains uncertain for the moment.

Regarding the risks of exposure to ionizing radiation, the equipment for co-conversion and storage of materials in oxide form will be subject to an even greater neutron flux than in the case of U-Pu co-precipitation, because of the presence of minor actinides. This will require an appropriate reinforcement of the radiological shielding of the cells in which the process equipment will be installed (thick walls of light materials such as polyethylene or water to stop the neutrons...). **Thus, co-conversion operations can no longer be carried out in glove boxes and will require an even higher degree of automation with remote maintenance of the equipment. In any case, the choice and sizing of radiation shielding will have to take into account ambitious dose objectives, integrating an optimization approach into the design.**

Finally, concerning the risks of explosion linked to radiolysis phenomena, the values of radiolytic yield in hydrogen (or other potentially flammable/explosive gas) in the concentrated solutions of Pu and MA before co-conversion, to be retained under the conditions of the process in normal operation and accidental conditions, will have to be determined experimentally. These values will make it possible to evaluate the flow rates of radiolysis gas to be taken into account in future safety analyses.

4.2.4.3. PROCESS ALTERNATIVES

Direct denitration processes allow, in principle, to pass, in a single step, from the actinide nitrate solution to the oxide (by evaporation of the solutions and then thermal decomposition of the nitrates) without generating liquid effluents that cannot be directly recycled.

These processes require little equipment (compactness of the production facilities) and are relatively simple to operate (no valence conditioning of the actinides in the feed solution, no co-precipitation/filtration upstream, no use of hazardous chemicals other than nitric acid, relative simplicity of process control, little maintenance, etc.). On the other hand, direct denitration does not provide additional decontamination factors (the initial nitrate solution must have the required purity for the final oxide), the volume of gaseous effluents to be processed is very important and the design of a denitration gas treatment on an industrial scale could present difficulties (gas-powder separation, risks of clogging of the filters, contamination control, waste management). Moreover, the denitration reactors or furnaces can present important "hold-ups" with risks of accumulation of fissile materials. From the point of view of criticality, control by limiting the mass of fissile materials may prove too restrictive, with the need to establish input/output material balances and to monitor accumulation phenomena. Consequently, the design of equipment with a safe geometry seems more appropriate, and this control method can be associated with neutron poisoning if necessary. Finally, as regards the characteristics of the powders produced, this type of process does not have the flexibility of precipitation methods. These characteristics are generally subdued and not very compatible with a direct shaping of the fuel.

Regarding the oxides obtained by oxalic co-conversion and in the current state of development, the mixed oxide powders produced by direct denitration must undergo an additional mechanical grinding/granulation step to compensate for their poor aptitude for ceramisation (lower density, formation of agglomerates or undeformable aggregates...), which limits the interest of this route, particularly with regard to the risks of dissemination of radioactive materials and exposure to ionising radiation. In any case, the direct denitration route should still require extensive R&D to improve these aspects and be able to be industrialized. Finally, from the safety point of view, the examination of the operating feedback from pilot or industrial scale denitration units shows that the risks of thermal runaway and explosion linked to TBP/nitrate reactions should be examined in depth (several accidents have occurred, notably in the United States). Indeed, under the operating conditions of these processes, reactions between, on the one hand, the solvent (TBP/diluent mixture) and its degradation products, and on the other hand, nitric acid, its derivatives and U and Pu nitrates, can lead to the formation of unstable organic nitro compounds, called "red oils", which can decompose violently and lead to the production of potentially explosive gases. However, new co-denitration routes in the presence of organic additives are being developed, notably at CEA, and seem to show encouraging results.

New wet synthesis routes, in particular the sol-gel co-gelation and fixation on a porous or organic support, could be adopted in order to simplify and improve the techniques for manufacturing fuels dedicated to the transmutation of minor actinides. These new processes, which have already been tested on a laboratory scale, should make it possible, as for the mixed oxide (U,Pu)O₂, to eliminate the risky steps where powders are handled, which would be a major advantage for the fabrication of fuels bearing minor actinides.

Sol-gel processes have the advantage of an easy shaping of the solid compound synthesized during gelation, the very principle of this step allowing to obtain homogeneous compounds thanks to the perfect mixing of the elements in solution and to facilitate the formation of solid solutions during the later phase of thermal treatment. Optimized, this technique allows to obtain, after washing, drying and calcination, spherical particles of homogeneous composition resulting from the co-condensation of the heavy metals involved. The different reference sol-gel processes (GSP external gelation²⁵ or

²⁵ GSP for « Sol-Gel Microsphere Pelletisation »

HMTA internal gelation²⁶ processes) should in principle be well adapted to the co-conversion of actinides, accompanied by a shaping of the material, the initial mixing of heavy metals in solution and the intermediate gel stage minimizing the generation of contaminating and irradiating dust.

Indeed, the perfect homogeneity of mixed oxide microparticles based on U (VI) and Am (III) or other actinides (SUPERFACT and MARINE experiments, PELGRIMM project, etc.) elaborated by external or internal co-gelation in the ITU/Karlsruhe and PSI facilities has been confirmed. The studies carried out at CEA on the internal co-gelation of mixtures of U (VI) and Am (III) have also confirmed the homogeneity in composition of the microspheres obtained. The experiments carried out showed nevertheless that the characteristics of the spherules obtained were extremely sensitive to the chemical composition of the actinide solutions and that it was still difficult to decide on the formation of solid solutions. Moreover, this process requires a high concentration of actinides (of the order of 1 mol/L) in a weakly acidic medium, thus leading to extremely high levels of radiolysis and to the instability of these solutions (interaction on the speciation of the elements, risk of precipitation of actinide hydroxides, etc.). The management of ammonia effluents from gelation is also a delicate point to evaluate because of the simultaneous presence of nitrate and ammonium ions and numerous organic compounds from the reagents introduced.

These processes therefore have a certain number of disadvantages: a virtual absence of additional decontamination factors, a relative complexity of the many operations to be carried out in solution and at the solid stage, compared to other co-conversion processes, greatly increased thermal and radiolytic effects linked to the high concentrations of actinides in solution, and a relatively complex management of concentrated ammonia effluents, loaded with additives residues and various degradation products (in particular ammonium nitrate)²⁷. From the safety point of view, in addition to reducing the risks of dissemination of radioactive materials and exposure to ionizing radiation with respect to the powder metallurgy processes mentioned above, the risks, especially of fire and explosion, associated with the different stages of the process and with the management of concentrated ammonia effluents will nevertheless have to be examined in depth.

In conclusion, the sol-gel processes, although complex, seem well adapted to the supply of precursors for the fabrication of SFR MOX-AM fuels. In particular, they make it possible to minimize the generation of contaminating and irradiating dust during the fabrication of fuels. However, the lack of experience associated with the elaboration of materials based on minor actinides, elements that are difficult to hydrolyze and that induce increased radiolytic and thermal effects, does not allow a statement to be made, at this stage, on a possible transposition of these processes to the industrial fabrication of fuel or transmutation targets. In particular, there are still strong uncertainties as to the demonstration of the absence of major technological difficulties integrating safety constraints. **Consequently, significant R&D and technological developments should still be carried out to acquire the missing data at each stage of the process (from the preparation of the initial actinide solution to the treatment of effluents and the recycling of reagents or additives), to optimise and simplify these processes and to anticipate the fuel fabrication capacities required on an industrial scale.**

²⁶ The internal gelation process consists in mixing at low temperature a concentrated solution of metal ions with a gelation additive consisting of a solution of HMTA (HexaMethylTetraAmine) and urea. This stock solution is then dispersed as drops in an organic solvent. Under the effect of temperature, the HMTA-urea mixture decomposes, leading to an increase in pH responsible for the hydrolysis of the metal cations. After gelation, the microspheres are recovered, washed, dried and finally calcined.

²⁷ Several solutions exist to eliminate the ammonium nitrate present in these effluents (recycling in the form of solutions of ammonia and nitric acid via electrolytic treatment or extraction by an ion exchange resin, direct decomposition by photochemistry or oxidation-degassing...) but these processes would have to be developed and their safety should be examined.

The process of fixation on ion exchange resins (or WAR process) consists of fixing, by ion exchange, actinide cations on calibrated carboxylic resin spherules previously sorted. The cation-loaded resin is then washed and dried, followed by an oxidizing heat treatment leading to the formation of spherical cores of metal oxides after the carbonaceous material has been completely removed. A reduction step at high temperature is then necessary to finish synthesizing the solid solution of mixed oxides and adjust its oxygen stoichiometry. These non-powdered precursors can be used to manufacture pellets or even vibrocompacted fuel pins (VIPAC type).

The physico-chemical characteristics of the solids produced can be modulated according to the type of macromolecular skeleton of the resins used, monodisperse particle size distributions or calibrated particles can be produced with sizes ranging from micrometers to a few millimeters. The porosity of the final particles depends very strongly on the heat treatment applied. The spherules thus produced present an excellent flowability and an organization in the form of agglomerates of low mechanical resistance which limits the dissemination of fine particles during their handling while allowing their pressing in the form of pellets.

As for the oxalic route, this route requires solutions of actinide nitrates at concentrations of about twenty to thirty g/L. A preliminary concentration of the solutions resulting from the separation steps is thus not necessary, thus reducing the thermal constraints and those related to radiolysis. However, the fixation of actinides on the carboxylic resin requires, in order to reach a high loading rate, to operate on weakly acidic actinide solutions, since these conditions can induce risks of hydrolysis of the metal cations, in the first place uranium (IV). The characteristics of the mixed oxide micro-balls (morphology, microstructure and nature) will also depend closely on the conditions of calcination of the loaded organic resin, its initial spherical shape having to be preserved.

In conclusion, the "resins" route, because of the characteristics of the mixed oxide micro-balls obtained, is of real interest. Nevertheless, this process, tested at the laboratory scale, still requires significant R&D to optimize the fixation of uranium and minor actinides and to verify the absence of segregation between these elements, to develop the necessary technologies, and to lead to an industrial implementation. From the point of view of safety, this process should make it possible to reduce the risks of dissemination of radioactive materials and of exposure to ionizing radiation in comparison with powder metallurgy processes. The risks of chemical reactivity between the nitrates and the organic resins should nevertheless be analyzed, also integrating the management of the waste produced.

4.2.4.4. SPECIFIC COMMENTS ON URANIUM FINISHING

As mentioned in the previous paragraphs, at the end of the EURO-GANEX extraction cycles, the uranium should in principle be sufficiently purified to meet the specifications of the UNIREP standard. In fact, the results of the tests of the first CEA-GANEX cycle obtained in the laboratory showed that the uranium could be recovered selectively with decontamination factors regarding FPs at least equal to those obtained for the uranium loaded aqueous solution leaving the first extraction cycle of the PUREX process. The possibility of retaining only one purification cycle for uranium should nevertheless be confirmed on the basis of tests carried out on real solutions from the treatment of slightly cooled down fuels (verification of the achievement of the required DFs, especially for ^{106}Ru). A second purification cycle could therefore be retained as a precautionary measure, with an intercycle concentration step being necessary. The stage at the end of the uranium finishing process would

include a stage of concentration of the uranyl nitrate solution at 400 g/L and then storage of this solution.

With respect to the steps of intercycle concentration and final concentration of the uranium, the risks of thermal runaway between the nitrates, the uranium, and the residual DEHiBA/OK solvent present in the uranium loaded aqueous solutions from uranium backwash section (a "red oil" type phenomenon) should be analyzed. This evaluation would require:

1. to characterize thermochemically the DEHiBA/OK/HNO₃/H₂O/NU system, considering the solvent degradation products (determination of thermal kinetics data in adiabatic calorimetry, enthalpies of reaction, etc.);
2. to acquire the basic data necessary to evaluate the risks of sudden arrival or accumulation of organic phases in the evaporators (presence or not of diluent washing or solvent flushing, solvent solubility limit in aqueous phase, phase inversion phenomenon, solvent vapour entrainment, chemical and radiolytic degradation kinetics, etc.),
3. to determine the conditions for starting a possible runaway reaction from the characteristics of the incoming phases and the industrial equipment (heating mode, heat losses, presence of vents, etc.), then to deduce the maximum acceptable variation ranges of the control parameters (quantity of organic phase, temperature, acidity, pressure, etc.) that will guarantee the safe operation of the process.

Part of the reprocessed uranium stream is used in the form of U (IV) in the separation and conversion processes, as a reductant or diluent of plutonium. This uranium is thus integrated into the formation of (U,Pu, Am)O₂ powders. The production of U (IV) could be carried out, as for the present plants, by reduction of the uranyl nitrate solution with hydrogen in the presence of a catalyst (platinum). The production capacity of U (IV) necessary would nevertheless be important (of the order of a hundred kg per hour at the most), and the risks linked to the preparation of uranyl nitrate must be considered.²⁸

4.2.5. EFFLUENT MANAGEMENT

In addition to the processes for separating minor actinides, operations to manage liquid effluents should be implemented in order to recycle nitric acid in the process and to limit as much as possible radioactive and chemical discharges (nitrates, etc.).

A management of aqueous effluents, similar to that implemented in the La Hague plants, would make it possible to direct most of the radioactivity of the radioactive liquid effluents produced towards vitrification. It would then be based on a set of concentration and rectification operations making it possible to produce, on the one hand, purified nitric acid recycled either in the head-end plant (tritiated nitric acid fed to the dissolvers) or in the heart of the process (non-tritiated nitric acid fed to the various separation cycles), and, on the other hand, a concentrated solution of fission products that would be stored before being vitrified.

²⁸ As a reminder, the process of catalytic reduction of U (VI) to U (IV) in the presence of pressurized hydrogen and a catalyst (platinum), as at the La Hague plants, is conceivable for this stage, but this process can lead to risks of explosion (creation of an air-hydrogen mixture in the installation's pipe systems, rupture or failure of a component causing a hydrogen leak) The presence of uranous nitrate stored in large quantities can also lead to similar risks linked to the sudden reoxidation of U (IV) into U (VI) (absence, for example, of hydrazine, used as a stabilizer, in these solutions). Feedback from the La Hague plants shows that these risks are controlled. Other processes are nevertheless possible (electrolytic reduction, etc.), but their safety remains to be evaluated.

Thus, the treatment scheme for liquid effluents, characterized by the presence of organic chemical reagents, should not be very far from that implemented in the present plants, but should nevertheless be adapted to take into account the development and optimization studies of the processes for separating minor actinides. This flowsheet would include, on the one hand, the stages of concentration of intermediate-level effluents and recovery of tritiated acid, fed by the distillates from the fission products concentration step, and on the other hand, the operations of concentration of high-level effluents and recovery of non-tritiated acid fed by the flows charged with technetium and neptunium. However, the feed rates for the medium-activity effluent units and for the recovery of tritiated acid would be much greater in a EURO-GANEX-type plant than in the present plants. Indeed, the volumes of effluents to be treated would be much greater than those generated by the PUREX or COEXTM processes because additional aqueous flows would be necessary to carry out the stripping operations that take place at the level of the different minor actinides separation flowsheet. Additional evaporation-concentration capacities would therefore have to be implemented.

Regarding the basic effluents coming from the solvent treatments of the extraction and purification cycles implemented in the current plants, these are concentrated by evaporation then undergo, after reacidification, an oxidizing treatment (mineralization by H₂O₂) before being directed towards vitrification. The purpose of this treatment is to destroy the organophosphorus products present in the basic effluent concentrates thus produced, the latter being responsible for clogging and foaming phenomena in the calciners' feed equipment of the vitrification unit. Additional safety measures have been put in place to take into account the exothermic reaction of elementary decomposition of hydrogen peroxide into water and oxygen (conditions of agitation and temperature, volume of H₂O₂ additions and interval between two additions, monitoring of the progress of H₂O₂ decomposition, etc.).

The transposition of these treatments to the case of basic effluents from solvent treatments of minor actinide separation units could nevertheless require adjustments. Indeed, these effluents will contain not only the acidic organic degradation products of the new solvents (DMDOHEMA, TODGA, DEHiBA...) but also, according to their solubility in the organic phase and their specific behavior, the reagents introduced at the level of the separation cycles and the solvent treatments (complexing agents, reducing agents, non-saline compounds, etc.), as well as their decomposition products. These compounds should therefore be eliminated before concentration, and oxidizing treatments can also be implemented (use of hydrogen peroxide, ozone, etc.). This approach would, however, require assurance that these treatments would be effective in eliminating the various compounds, that they would remain compatible with the vitrification process of the effluents, and that they could be carried out under satisfactory safety conditions (control of the risks of overpressure or runaway reaction, consideration of the risks of precipitation of fissile materials, etc.). Finally, in the case of the use of hydrazine nitrate at certain stages of the separation processes, the risks of explosion linked to the formation of azothydric acid should be re-examined if this anti-nitrous agent were placed in the presence of nitrous acid (case of the first EURO-GANEX cycle).

As for the fission products concentration stage, this operation should be carried out, as in the present plants, by evaporation, the nitric acid being destroyed by the addition of a formaldehyde solution (denitration reaction) in order to maintain an acidity of the solutions close to 2N. This would limit the risks of corrosion of inner surface of the evaporator wall and precipitation of the fission products. The tritiated nitric acid distillates would be recycled in the plant via the tritiated acid recovery unit after concentration-rectification. After a period of storage in cooled tanks, the fission product concentrates would be fed to the vitrification process.

In a EURO-GANEX plant, the FPs loaded aqueous solution would be made up of the combination of solutions from the extraction-scrubbing sections and Mo and the Ln stripping sections of the two cycles of the grouped separation process. The fission product concentrations of these solutions to be fed to the evaporators would therefore be much lower than those of the extraction raffinates from the first U-Pu coextraction cycle. Taking into account the nominal capacity of the evaporators in the current La Hague plants (a little less than 300 L/h), it would be necessary to install more than twenty evaporators. The development of larger capacity evaporators would therefore seem to be essential in order to reduce the number of concentrator lines.

This study also shows that the concentration factors of FP solutions would be limited by the iron content of the concentrated solutions (maximum iron concentration taken as 10 g/L to take into account the risks of evaporator corrosion), the final concentration rate leading to a volume of about 2,000 L/tMLi. This would lead to significant storage capacity requirements (about ten 120 m³ tanks), the power density of the stored solutions being nevertheless lower, of the order of a few W/L. In this respect, it should be emphasized that increasing the size and number of evaporators and storage tanks would lead to a significant increase in the activity contained in this equipment and, given the evolution of the characteristics of concentrated FP solutions (much higher alpha emitter contents,), the radiological consequences in the event of an accident would be much greater, requiring reinforcement of the prevention and mitigation measures adopted at the design stage (loss of cooling, leakage from an evaporator or storage tank, etc.).

While the design of such treatment units, very similar to those installed in current plants, does not reveal any prohibitive points at this stage, the definition of the methods for managing liquid effluents, linked to the implementation of advanced processes for separating minor actinides, and the assessment of the associated risks still require major studies and research. In particular, the definition of potential risks inherent in the management of liquid effluents and the concentration of fission products would require mastery of the chemistry and safety parameters of the processes implemented and, in particular, an evaluation of:

- the impact on these operations of the use of new solvents (DMDOHEMA, TODGA, DEHiBA...) and organic reagents (complexing or reducing agents) in the processes for separating minor actinides, taking into account their decomposition and degradation products and their behavior in the process;
- the risks of creating loops of accumulation of disturbing ions in the process linked to the advanced recycling of nitric acid (depending on the composition of the fuels treated, the new solvents and reagents used, the associated impurities, etc.), the latter being able to have an impact in particular on the corrosion of the materials constituting the evaporators;
- the risks of overpressure and explosion in evaporators concentrating acid or basic aqueous effluents, possibly of large capacity (possible violent reactions of the "red oil" type between the new extractants and diluents and nitrates or other oxidants, etc.);²⁹
- these evaluations will require in particular to characterize each system from a thermochemical point of view and to acquire the basic data necessary to evaluate the risks of sudden arrival or accumulation of organic phases in the evaporators as well as the conditions of starting a possible runaway reaction from the characteristics of the phases introduced and of this equipment, then to deduce from this the maximum acceptable ranges of variation of the control parameters (quantity of organic phase, temperature, acidity, pressure...) making it possible to guarantee the safe operation of the process;

²⁹ According to recent research work carried out by the CEA, ORANO and the IRSN, the risks linked to "red oil" compounds in acid recovery units are considered to be higher than in other evaporation units, because of the higher acidities reached in solution (12-13N). In addition, the behavior of the solvent accompanying the aqueous flows is more delicate to comprehend in the equipment (evaporation-concentration unit coupled with a rectification unit).

- the risks of criticality in this same equipment, including the dissolvers receiving the recycled tritiated nitric acid (possible precipitation of fissile actinides in the presence of certain reagents and associated degradation products, complexing ions, etc.).

In this regard, it would be appropriate to evaluate the compatibility of aqueous effluents from separation processes with the current management option for liquid effluents, to define the additional treatments needed, to ensure the safety of these operations, and to verify the compatibility of the flows produced with the planned elimination ways (vitrification) or the existing outlets (discharges...)

For example, if the concentration-denitration process implemented in the current plants (use of formaldehyde) were to be renewed, it would be advisable to ensure the absence of anti-nitrous compounds (hydrazine, hydroxylamine, amines, amides, etc.) in the aqueous solutions to be concentrated, the presence of such compounds being able to considerably increase the induction period of the denitration reaction, or even to inhibit this reaction,³⁰ and to lead to an accumulation of formaldehyde in the evaporator. This situation could lead to a risk of runaway reaction with important consequences in the installation (severe overpressure in the evaporator, siphoning of the solutions towards other units, rise of active solutions in zones accessible to the operators via the instrumentation pipes, risks of irradiation and contamination, etc.).

Finally, with regard to the risks of explosion linked to the radiolysis phenomena, the values of radiolytic yield in hydrogen (or other potentially flammable/explosive gas) to be retained under the conditions of the process, in normal operation and accidental conditions, making it possible to evaluate the flow rates of radiolysis gas to be taken into account in future safety analyses, will have to be determined experimentally for the concentrated solutions of PF and the basic effluents after oxidizing treatment and concentration.

4.2.6. CONCLUSION

The reprocessing of fuel assemblies loaded with minor actinides should be carried out in plants designed to accept the various types of spent fuel to be recycled, the treatment operations being supposed to be based on hydrometallurgical processes of the same type as those used in the existing plants in La Hague. The future reprocessing plant should be divided into workshops for separating the oxide fuel from the cladding and dissolving it, separating the desired elements (U, Pu, and MA) via solvent extraction cycles, converting these separated elements into oxide, and conditioning the structural waste and the fission products.

The analysis carried out by IRSN, which was based in particular on the R&D under way at CEA and on that carried out in the framework of the SACSESS and GENIORS projects, made it possible to define some preliminary design elements by analogy with the operations and equipment used in the La Hague plants. However, the necessary process evolutions highlight major constraints and difficulties for their implementation on an industrial scale. Continued R&D activities are therefore necessary, both scientifically and technologically. In particular, many questions remain unanswered due to the specificities of homogeneous fuels and the lack of data characterizing them. Some remarks are mentioned in this chapter.

³⁰ A solution of sodium nitrite (NaNO₂) is added to the evaporator at the start of the concentration cycle to initiate the reaction between nitric acid and formaldehyde, the nitrites acting as a catalyst. In the presence of anti-nitrous agents (inhibitors), these nitrites could be partially destroyed thus delaying the start of the reaction.

Regarding the irradiation experiment programs underway on homogeneous fuel pellets or pins, these should make it possible to make progress on the demonstration of the feasibility of these concepts. However, the feasibility of the treatment of these fuels should be confirmed on the basis of dissolution tests carried out on representative irradiated samples, in particular concerning their solubility after irradiation, the behaviour of cladding materials in the dissolution media and the masses of fines formed. These data should make it possible, in particular, to define the dissolution conditions for this type of MOX fuel loaded with minor actinides.

Transmutation of minor actinides in homogeneous mode implies the implementation of a grouped separation process (EURO-GANEX flowsheet), extracting together the plutonium and the minor actinides. This process would completely replace the core of the PUREX or COEX™ process, which could present more "industrial" risks.

A lot of work has been done at the laboratory level to progress in the definition of new selective extractants. However, the scientific feasibility of these processes has only been demonstrated for a certain number of routes that are considered, in the current state of knowledge, to be more robust. Other optimization or alternative routes are nevertheless being studied. Their qualification and industrial implementation should still require a long R&D process, in particular to simplify the separation flowsheets and to acquire the necessary consolidation elements (equipment and technological development, simulation and process control, operation of extraction cycles over time, effluent management, etc.). Complementary studies will also be necessary to evaluate the compatibility of aqueous effluents from separation processes with the planned liquid effluent management options (verification of the absence of impact of organic reagents and their degradation products on concentration operations, definition of complementary treatments, compatibility of the flows produced with the planned elimination ways and outlets, safety of operations, etc.).

The oxalic route could be considered at present as the reference route for the co-conversion of uranium, plutonium, and minor actinides, since in principle it makes it possible to obtain a solid solution that ensures optimal homogeneity of the minor actinides in the fuel oxide. The use of this type of homogeneous precursor would also simplify the shaping steps by directly targeting the final actinide composition. However, if current technologies are retained, the high processing capacity required for the recycling of these elements in SFR would lead to the implementation of too many equipments with regard to the thermal constraints. Consequently, all the steps of the co-conversion process should be re-examined from a technological point of view to have an industrially viable solution and a safe process. From the point of view of the process, there are also strong uncertainties about the possibility of co-precipitating mixtures of uranium (IV) and actinides (III), especially given the "exacerbated" radiolysis conditions in solution. The absence of redhibitory points on the scientific and technological level cannot yet be fully demonstrated at this stage, concerning the precipitation of all the minor actinides.

Other routes, such as sol-gel processes or the process of fixation on ion exchange resins, are being examined with the aim of simplifying and improving the techniques for manufacturing fuels dedicated to the transmutation of minor actinides and americium in particular. These processes make it possible to obtain cohesive spherical microparticles that further reduce the risks of dissemination of radioactive materials. Nevertheless, significant R&D is still necessary to overcome the difficulties identified, optimize these alternative processes, develop the necessary technologies and achieve industrial implementation.

From the safety point of view, given the nuclear characteristics of the minor actinides present in solid or liquid form in the various process equipments, the reinforcement of safety systems (containment,

cooling, dilution air for the hydrogen from radiolysis) and the installation of appropriate radiological protection would be necessary, especially for the minor actinide conversion stage. Since the recycling of plutonium already requires the use of equipment with a safe geometry, the risks of criticality during the treatment of SFR MOX-MA fuel assemblies should be controlled without particular difficulty.

In addition, the increase in the content of insoluble elements (platinoids, plutonium formed successively by transmutation and decay, etc.), and even of cladding corrosion products (due to aggressive dissolution conditions), in the fission product solutions could require changes in the vitrification process and in the current specifications for vitrified waste, and the possibility of managing the dissolution fines separately (conditioning in a specific matrix, etc.) should be examined.

Finally, the use of additional and more harmful radioactive materials in the fuel cycle leads, on the one hand, to an increased need for separate storage of fuels and materials, and, on the other hand, to an increase in hazards and risks, accident situations to be considered and source terms. In addition, the doses received by operators are potentially higher in accident conditions and waste management is more complex.

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6 ANNEX**Report****Comparison of criticality standards values for various solvents in
the framework of the EURO-GANEX Project**

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Comparison of criticality standards values for various solvents in the framework of the EURO-GANEX Project

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1. INTRODUCTION

The GENIORS project is focused on the determination of new processes for extraction of fissile species in the framework of the reprocessing of new fuel managements. Up to now, the safety demonstration was performed using water as a solvent, postulating that water was conservative as moderator. The aim of the present work is to build density laws for other solvents used in the new processes and in a further report, to check whether or not water is conservative as moderator when compared to them.

This report is part of the D9.5 deliverable (working package 9) of the GENIORS Project. This task takes part into the GENIORS Project [1], which is a European project dedicated to the management of nuclear fuel for future cycles. It is expected to provide the EU with science-based strategies for nuclear fuel management and contribute significantly to its energy independence. In the longer term, the project's results will facilitate radioactive waste management by reducing its volume and radiotoxicity, and support a more efficient utilisation of natural resources.

In a first part, we will describe why density laws are needed in criticality safety and what they look like. Then, we will focus on the strategy to establish density laws involving new solvents with the data collected from GENIORS chemists.

Finally, results of criticality standards calculations are presented in the deliverable D9.5 "Major hazard and criticality review of the Euro-GANEX process".

2. DEFINITION OF A DENSITY LAW

Density laws are intimately linked to the French criticality safety practice. Indeed, in French criticality safety studies, the bulk density of solutions is rarely known. One only has access to the concentration in the main specie (fissile very often), the acidity and the temperature. Density laws are used to determine the bulk density of the solution and then have access to the solvent content.

They take the shape of mathematical relationships linking concentration, acidity and temperature to the density or to the moderation ratio (H/X where X is the atomic concentration in fissile specie and H the atomic concentration in hydrogen).

$$\rho=f(C(X), \text{Acidity}, T^{\circ}\text{C}) \quad (1)$$

Different types of density laws exist:

- Theoretical ones,

- Experimental ones,
- Semi empirical ones.

The choice of the density law is intimately linked to the conservatism associated with a criticality study.

In fact, $k_{eff} \left(k_{eff} = \frac{\nu \times \Sigma_{eff}}{\Sigma_a + Leakages} \right)$, which is the main physical parameter in criticality, is the ratio of the production of neutrons ($\nu \Sigma_{eff}$) versus the absorption (Σ_a) and leakages from the system and characterizes the propensity of a chain reaction to self-sustain. Then, the higher the density is, the lower the leakages and, at fixed concentration in fissile specie, the higher the moderation of neutrons. Consequently, for many configurations assessed in criticality safety, maximizing the density leads to an increase of reactivity.

A scale of conservatism for density laws can be established versus the density of the electrolyte corresponding with the fissile specie and the density of the solvent. The higher the electrolyte density, the more conservative the density law is.

2.1. THEORETICAL DENSITY LAWS

Theoretical density laws are used to “cover” fictitious fissile media, for instance metallic uranium in solution. They are voluntarily conservative and are based on the volume additive principle consisting in saying that the volume of a solution is the sum of the solute volume and the solvent one, which remains true as long as the concentration in fissile specie remains low and the interactions between molecules of solute remain limited.

2.2. EXPERIMENTAL DENSITY LAWS

Experimental density laws correspond to a really existing mixture. They are based on experimental measurements. And interpolations are performed between various measurements. They are used for uranium oxifluoride for instance.

2.3. SEMI EMPIRICAL DENSITY LAWS

Semi-empirical density laws use measurement values and a physical model that postulates the values of densities at concentration different from the ones corresponding to the measurement points.

They are used for uranium uranyl nitrate, plutonium nitrate for instance.

3. STRATEGY TO ELABORATE THE DENSITY LAW

3.1. METHODOLOGY

A first methodology based on the volume addition of mixtures having the same solvent activity was investigated (“isopiestic” concept) [2, 3]. The idea was to apply the same methodology as for mixtures involving nitrates. Such works were based on PhD works performed before 2000 by Nicolas Charrin [4] at CEA Marcoule. These works were realized within collaboration between INSTN Saclay and CEA Marcoule. However, discussions with French and international experts (Jean-Pierre Simonin from CNRS and Philippe Guilbaud from CEA) during the GENIORS meetings showed that measurements of organic solvents activities proved to be really tough if not impossible. As a result and given that the range of concentrations in fissile species of the process was limited to low concentrations (< 150 g/L), a standard volume additive law could be envisioned, without deviating so much from a theoretical behaviour. This methodology was therefore selected for the realization of criticality standards calculations.

3.2. VOLUME ADDITIVE LAW

The volume additive principle consists in postulating that the volume of a mixture is the sum of the volumes of each constituent: fissile species (solute), acid and solvent (extractant + diluent).

It is always true at low concentrations since low molecular interactions are observed. However, the rule is less and less followed while the solute concentration increasing. A volume contraction, due to specific interaction between the solute and the solvent, can occur and leads to higher densities than expected.

3.2.1. GANEX 1ST STEP

In the first step of the GANEX process [5], the separation of uranium and plutonium is at stake. As illustrated in Figure 1, the process is fed with 103 g/L of uranium, traces of Tc and Np and 22.7 g/L of plutonium in 5 mol/L of nitric acid. The plutonium along with neptunium, americium and lanthanides are extracted in the solvent (extractant and diluent) and uranium remains in the water part. DEHIBA is used as the extractant and TPH behaves as the diluent.

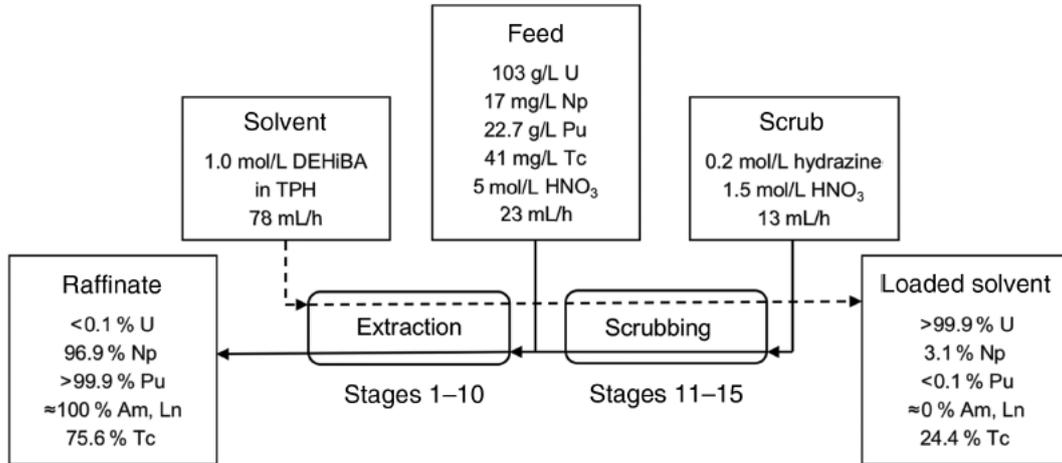


Figure 1: GANEX 1st step process.

For the purpose of our study, nitric acid will be first neglected since it contributes to decrease the reactivity as, for the same concentration in fissile specie, it decreases the number of water molecules and adds more nitrogen, which is a neutron absorber. The plutonium weight isotopic vector is a vector traditionally used in French criticality studies to bound plutonium media encountered in the nuclear fuel cycle. It is the following: 71 wt% ²³⁹Pu, 17 wt% ²⁴⁰Pu, 11 wt% ²⁴¹Pu and 1 wt% ²⁴²Pu. This choice is purely arbitrary but we need to fix an isotopic vector to make a comparison. In the next deliverable, this assumption will be evaluated in terms of criticality-safety comparing with a more realistic isotopic vector that is representative of burnt fuel.

Uranium is assumed to be natural uranium with an enrichment of 0.7 %. Room temperature (20 °C) is retained.

The density of the solution is calculated using formula (2).

The density of the extractant-diluent (DEHIBA-TPH) is calculated using formula (3).

$$\rho_{solution} = C(UO_2(NO_3)_2) + C(Pu(NO_3)_4) + \rho_{extractant-diluent} \times \left(1 - \frac{C(U)}{\rho(U)} - \frac{C(Pu)}{\rho(Pu)}\right) \quad (2)$$

$$\rho_{extractant-diluent} = \left(C(extractant) + \rho_{diluent} \times \left(1 - \frac{C(extractant)}{\rho(extractant)}\right)\right) - 0.00072 \times (T - 25) \quad (3)$$

With C(extractant), the concentration in DEHIBA in g/cm³, $\rho_{diluent}$ being the density of TPH at 25 °C.

T is the temperature in °C.

$\rho(\text{extractant})$ is the density of DEHIBA at 25 °C.

It should be noted that the molarity in extractant is assumed to be constant and equal to 1 mol/L.

3.2.2. GANEX 2ND STEP

In the second step of the GANEX process [5], uranium has been separated from plutonium. As illustrated in Figure 2, the process is fed with 10 g/L of plutonium in 5.9 mol/L of nitric acid and 0.055 mol/L of CDTA (trans-1,2-cyclohexanediaminetetraacetic acid). In this step of the process, plutonium is separated from neptunium, americium and lanthanids.

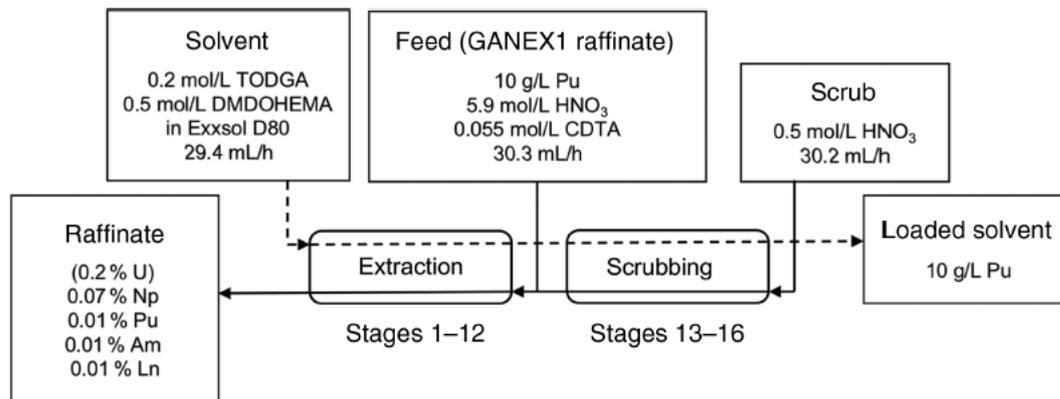


Figure 2: GANEX 2nd step process.

Once again, for the purpose of our study, nitric acid will be first neglected since it contributes to decrease the reactivity. The plutonium weight isotopic vector is a vector traditionally used in French criticality studies to bound plutonium media encountered in the nuclear fuel cycle. It is the following: 71 wt% ²³⁹Pu, 17 wt% ²⁴⁰Pu, 11 wt% ²⁴¹Pu and 1 wt% ²⁴²Pu.

Room temperature (20 °C) is retained.

Uranium and CDTA will be neglected since their content is very low. Neglecting uranium contributes to an increase of reactivity since plutonium is more conservative than uranium in terms of criticality.

The density of the solution is calculated using formula (4).

The density of the extractant-diluent (TODGA/DMDOHEMA-EXXSOL) is calculated using formula (5).

$$\rho_{solution} = C(Pu(NO_3)_4) + \rho_{extractant-diluent} \times \left(1 - \frac{C(Pu)}{\rho(Pu)}\right) \quad (4)$$

$$\rho_{extractant-diluent} = \left(C(TODGA) + C(DMDOHEMA) + \rho_{diluent} \times \left(1 - \frac{C(TODGA)}{\rho(TODGA)} - \frac{C(DMDOHEMA)}{\rho(DMDOHEMA)}\right) \right) \quad (5)$$

With $\rho_{diluent}$ being the density of EXXSOL in g/cm³ at the desired temperature in °C.

T is the temperature in °C.

$\rho(\text{extractant} - \text{diluent})$ is the density of the solvent in g/cm³ at 20 °C.

$C(TODGA)$ is the concentration of TODGA in g/cm³.

$C(DMDOHEMA)$ is the concentration of DMDOHEMA in g/cm³.

$\rho(TODGA)$ is the density of TODGA at the desired temperature in g/cm³.

$\rho(DMDOHEMA)$ is the density of DMDOHEMA at the desired temperature in g/cm³.

It should be noted that the molarity in TODGA and DMDOHEMA is assumed to be constant and equal respectively to 0.2 mol/L and 0.5 mol/L.

3.2.2. GANEX 3RD STEP

In the third step of the GANEX process [5], uranium has been separated from plutonium. As illustrated in Figure 3, the process is fed with 10 g/L of plutonium in 0.5 mol/L of nitric acid and 0.055 mol/L of SO₃-Ph-BTP and 1 mol/L of AHA. In this step of the process, a more achieved separation is performed to set apart lanthanides from other constituents.

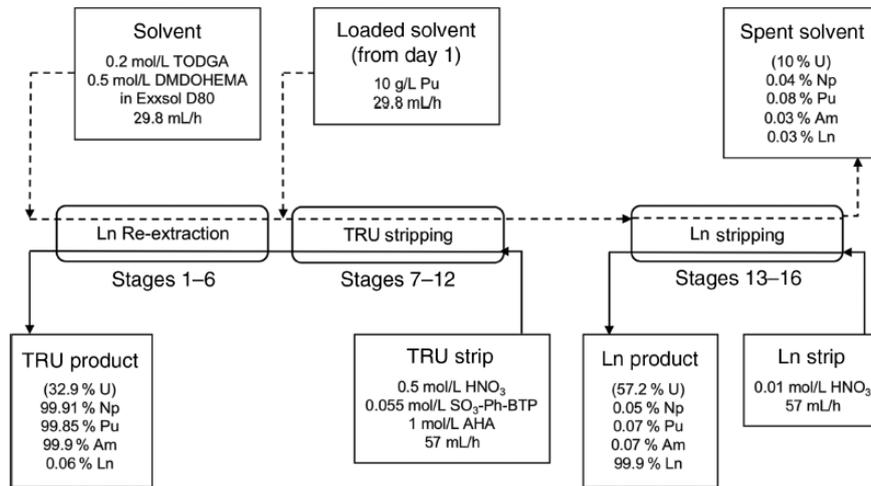


Figure 3: GANEX 3rd step process.

Contrary to the previous step, nitric acid has not been neglected in a first approach. The isotopic vector of plutonium is a vector traditionally used in criticality to bound plutonium media encountered in the nuclear fuel cycle. It is the following: 71 wt% ²³⁹Pu, 17 wt% ²⁴⁰Pu, 11 wt% ²⁴¹Pu, 1 wt% ²⁴²Pu.

Room temperature (20 °C) is retained.

Uranium will be neglected since its content is very low. Neglecting uranium contributes to an increase of reactivity since plutonium is more conservative than uranium in terms of criticality.

The density of the solution is calculated using formula (6).

The density of the extractant-diluent (AHA/SO₃Ph-BTP/water) is calculated using formula (7).

$$\rho_{\text{solution}} = C(\text{Pu}(\text{NO}_3)_4) + C(\text{HNO}_3) + \rho_{\text{extractant-diluent}} \times \left(1 - \frac{C(\text{U})}{\rho(\text{U})} - \frac{C(\text{Pu})}{\rho(\text{Pu})} - \frac{C(\text{Am})}{\rho(\text{Am})} - \frac{C(\text{Np})}{\rho(\text{Np})} - \frac{C(\text{Ln})}{\rho(\text{Ln})}\right) \quad (6)$$

$$\rho_{\text{extractant-diluent}} = \left(C(\text{AHA}) + C(\text{SO}_3 - \text{Ph} - \text{BTP}) + \rho_{\text{diluent}} \times \left(1 - \frac{C(\text{AHA})}{\rho(\text{AHA})} - \frac{C(\text{SO}_3 - \text{Ph} - \text{BTP})}{\rho(\text{SO}_3 - \text{Ph} - \text{BTP})}\right) \right) \quad (7)$$

With ρ_{diluent} being the density of water at the desired temperature (T).

T is the temperature in °C.

$\rho(\text{extractant} - \text{diluent})$ is the density of the solvent at 20 °C.

$V(\text{HNO}_3)$ is the molar volume of acid in cm^3/mol .

$C(\text{AHA})$ is the concentration of AHA in g/cm^3 .

$C(\text{HNO}_3)$ is the concentration of HNO_3 in g/cm^3 and H^+ is the acidity in mol/L .

$C(\text{SO}_3 - \text{Ph} - \text{BTP})$ is the concentration of $\text{SO}_3 - \text{Ph} - \text{BTP}$ in g/cm^3 .

$\rho(\text{AHA})$ is the density of AHA at 20 °C in g/cm^3 .

$\rho(\text{SO}_3 - \text{Ph} - \text{BTP})$ is the density of $\text{SO}_3 - \text{Ph} - \text{BTP}$ at 20 °C in g/cm^3 .

The density of the extractant-diluent at a temperature different from room temperature has been obtained experimentally through a linear formula (8).

$$\rho_{\text{extractant-diluent}}(T) = -0.000388678 \times T + 1.0641 \quad (8)$$

3.3. LIMITATIONS

It should be noted that actinides and fission products are involved in some of the steps of the GENIORS project. However, even if it would have been possible to do it, they have not been taken into account in the building of the volume additive laws based on the new solvents. The reason is that the quantities in these species is often low and regarding the fission products, as they absorb neutrons they contribute to a decrease of k_{eff} . Anyway, the behavior of the solvent regarding k_{eff} will not be drastically modified by their presence. If water is conservative for a solution of plutonium when compared to the GENIORS solvents, it will remain conservative with a small quantity of actinides and fission products.

3.4. DATA COLLECTED

To establish density laws, one needs to know precisely the main characteristics of the extractants/diluents that make the solvent and especially their proportions and bulk densities versus temperature. Such data were not available at IRSN. As a consequence, a request was made to the GENIORS group and the data were provided by members of the GENIORS Project under the auspices of Andrea Geist to whom IRSN is grateful.

3.4.1. DENSITY OF SOLVENTS

The majority of extractants/diluents densities were found in the literature or were provided by participants to the GENIORS project. All these data are gathered in Table 1.

Table 1: Main characteristics of solvents and behaviour versus temperature

Extractant/diluent	Reference concentration of extractant in diluent (mol/L)	Density in g/cm ³	Chemical formula	Behaviour versus temperature (°C)	Reference	
TPH		0.7551 (25 °C)	C ₁₂ H ₂₆	$0.7551 \times (1 - 0.0009826 \times (T-25))$	Data from Christian Sorel	
DEHIBA	1.151	0.8638 (25 °C)	C ₂₀ H ₄₁ NO	$-0.00066 \times (T-25) + 0.8638$	PhD works [6] and Table 2	
EXXSOL		0.798 (15 °C)	0.684	n-heptane - C ₇ H ₁₆	$-0.00068 \times (T-15) + \rho (15 \text{ °C})$	Analogy with TODGA/DMDOHEMA behaviour)
			0.7786	cyclohexane C ₆ H ₁₂		
			0.6594	n-hexane C ₆ H ₁₄		
			0.77	methylcyclohexane C ₇ H ₁₄		
TODGA	0.2	0.9054 (25 °C)	C ₃₆ H ₇₂ N ₂ O ₃	$-0.00066 \times T + 0.9219$	Data from Justine Cambe-Issaadi, Anne Lélías (CEA) (See Table 3)	
DMDOHEMA	0.5	0.914 (25 °C)	C ₂₉ H ₅₈ N ₂ O ₃	$-0.00068 \times T + 0.931$		
AHA	1	1.2837	C ₂ H ₅ O ₂ N		Recalculated	
SO3-Ph-BTP	0.055	1.842 (inferred from calculation)	C ₃₅ H ₁₉ S ₄ O ₁₂ Na ₄ N ₇	$-0.000388678 \times T + 1.0641$	Recalculated	

Density of organic solutions involved in the GANEX 1st cycle have been measured in order to estimate flowrates variations with composition and temperature in the simulation code PAREX. In addition, the knowledge of the organic density is useful to convert organic concentration from the molarity scale (mol/L) to the molality scale (mol/kg) which is retained for the modelling of extraction and complexation equilibria in our code. All the density data have been measured with an Anton-Paar density meter.

Density of TPH has been measured on the temperature range 20-60°C.

The data are gathered in Table 2.

Table 2: Density of DEHIBA solution versus temperature.

[DEHIBA] (mol/l)	T (°C)	ρ_{exp} (g/ml)
1.49	25	0.8137
1.49	35	0.8065
1.49	45	0.7991
0.99	25	0.7949
0.99	35	0.7877
0.99	45	0.7805

From these data, it is possible to establish the behavior of the density versus temperature as it is given in Table 1.

Regarding the GANEX 2nd step, acquisition of densities of the pure TODGA and DMDOHEMA was performed from 15 to 55°C, using a SVM 3000 densimeter (ANTON PAAR). Justine Cambe-Issaadi and Anne Lélías (CEA) provided the data to IRSN. Each data is the mean value of two measurements and is reported in Table 3.

From these data, it is possible to establish the behavior of the density versus temperature as it is given in Table 1.

Table 3: Measurement of TODGA and DMDOHEMA densities versus temperature.

T (°C)	Density (g/cm ³) ± 0.0002 g/cm ³	
	TODGA	DMDOHEMA
55	0.8857	0.8936
45	0.8923	0.9005
35	0.8988	0.9072
25	0.9053	0.914
15	0.9120	0.9208

Regarding the GANEX 3rd step, crystal densities of AHA and SO₃-Ph-BTP were not provided. However, measurements were performed on solutions of 1mol/L of AHA and on solutions of 1 mol/L of AHA + 0.055 mol/L of SO₃-Ph-BTP (see Figure 4 and Figure 5). From these measurements, one can derive the crystal densities of AHA and SO₃-Ph-BTP, which are respectively determined as 1.2837 g/cm³ and 1.842 g/cm³.

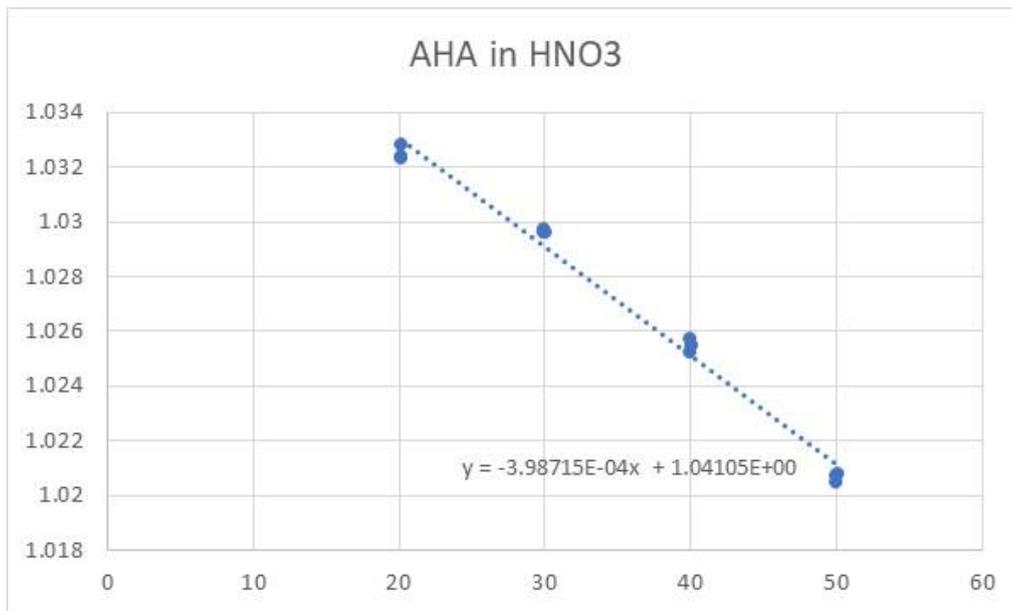


Figure 4: Measurement of a solution of 1 mol/L AHA.

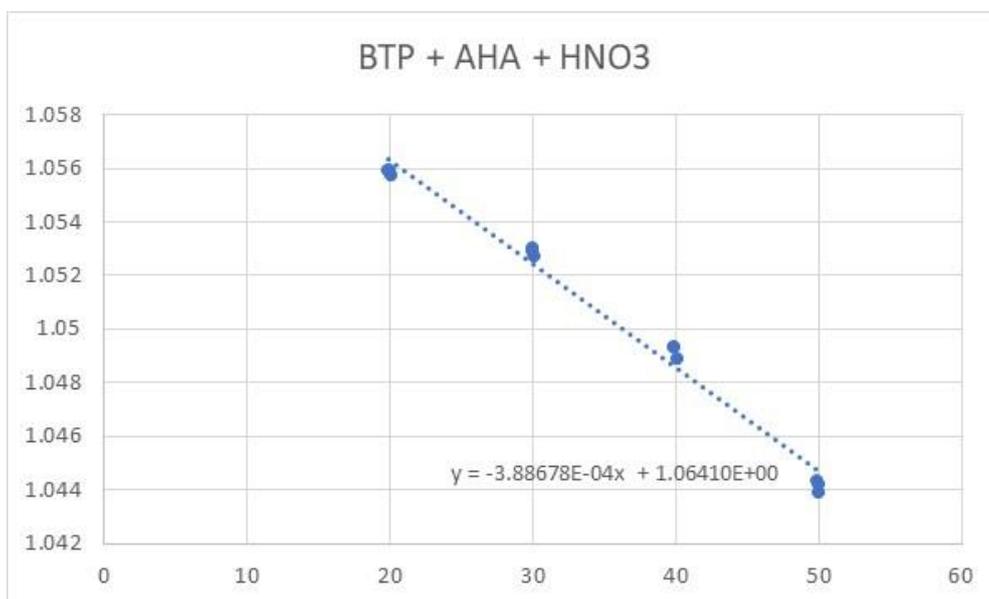


Figure 5: Measurement of a solution of 1 mol/L AHA + 0.055 mol/L SO₃-Ph-BTP.

From these data, it is possible to establish the behavior of the density versus temperature as it is given in Table 1.

3.4.2. VALIDATION OF THE SOLVENTS DENSITIES

Comparisons of densities calculated using the volume additive formula and measured densities are necessary to validate the established density laws.

3.4.2.1 VALIDATION OF THE SOLUTIONS WITH DEHIBA

Density measurements of organic solutions containing both nitric acid and uranyl nitrate have been measured at 25°C after a counter-current trial performed in mixer-settlers. These measurements were reported by Christian Sorel from CEA and are given in Table 4.

One can see that the difference of bulk density between measured densities and calculated densities is always lower than 2 %, which indicates that the volume addition law density correctly predicts the behaviour of the density trend. Moreover, except for the first sample (concentration in U(VI) equal to 0.009 g/L), the calculated density is always higher than the measured one, which is conservative from the criticality-safety point of view.

Table 4: Measurements of organic solutions with DEHIBA and an extractant.

[DEHiBA] concentration (mol/L)	[HNO ₃]org, exp (mol/L)	[U(VI)]org, exp (g/l)	Measured density (ρ exp) (g/ml)	Calculated density (ρ calc)	Difference (%)
1.151	0.2	0.009	0.8121	0.8069	-0.6403
	0.69	0.01	0.8183	0.8252	0.8432
	0.78	0.077	0.8212	0.8287	0.9133
	0.81	0.41	0.8227	0.8303	0.9238
	0.79	2.02	0.8253	0.8320	0.8118
	0.74	10.27	0.8333	0.8426	1.1160
	0.62	34.05	0.8614	0.8739	1.4511
	0.41	64.95	0.8987	0.9127	1.5578
	0.41	55.45	0.8842	0.8983	1.5947
	0.36	58.06	0.886	0.9004	1.6253
	0.31	60.56	0.8868	0.9023	1.7479
	0.27	61.39	0.8874	0.9022	1.6678
	0.23	61.2	0.8866	0.9003	1.5452
	0.2	61.72	0.8865	0.9000	1.5228
	0.18	58.77	0.8815	0.8947	1.4974
	0.16	48.88	0.8672	0.8791	1.3665
	0.026	28.48	0.8347	0.8434	1.0423
0.005	8.24	0.8055	0.8112	0.7076	

3.4.2.2 VALIDATION OF THE TODGA+DMDOHEMA DENSITY

The GANEX 2nd step solvent density (0.2 mol/L TODGA + 0.5 mol/L DMDOHEMA) was also measured by classical methods as being 0.846 ± 0.003 g/L at room temperature, by Galan Montano, Hitos from CIEMAT.

Using the bulk densities of the diluent and extractant determined previously (Table 3), one finds the value of 0.8435 g/cm³ at room temperature. This value is consistent with the measured one.

3.4.2.3 VALIDATION OF THE SOLUTIONS WITH TODGA+DMDOHEMA IN EXXSOL

Density data for TODGA + DMDOHEMA in Exxsol D80, EURO-GANEX organic phase, has been acquired by Lancaster University for the GENIORS programme (Alexander Jackson, Michael Bromley, Colin Boxall (University Lancaster)).

Density data (at the lab temperature of 14.5 ± 0.5 °C) of the pure TODGA and DMDOHEMA was used in solution preparation to accurately make up 5.5cm³ of 0.2mol/L TODGA + 0.5mol.dm⁻³ DMDOHEMA in Exxsol D80. A 5cm³ BRAND BLAUBRAND density bottle was used to measure the density of the solution and errors were calculated from the tolerance of the thermometer and the density bottle. Error in the concentration of the TODGA and DMDOHEMA in solution was calculated from the tolerance of the 2 cm³ glass pipette used in liquid transfer and volume measurement. Density as a function of temperature is shown in Table 5 and Figure 6.

Table 5: Density of 0.200 ± 0.006 mol/dm³ TODGA and 0.500 ± 0.007 mol/dm³ DMDOHEMA in Exxsol D80 from 20 to 60 °C.

T (°C) ± 0.5°C	Density (g/cm ³)
59.5	0.8141 ± 0.0016
43.0	0.8242 ± 0.0017
37.0	0.8300 ± 0.0017
30.5	0.8345 ± 0.0017
24.0	0.8387 ± 0.0017
20.0	0.8422 ± 0.0017

Density decreases linearly with temperature as shown in Figure 6.

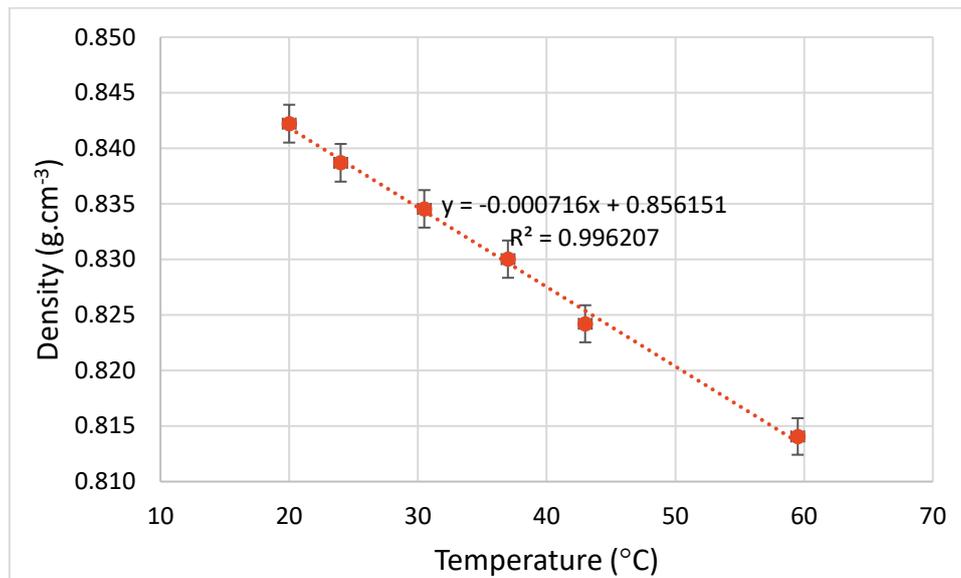


Figure 6: graph of density of $0.200 \pm 0.006 \text{ mol/dm}^3$ TODGA and $0.500 \pm 0.007 \text{ mol/dm}^3$ DMDOHEMA in Exxsol D80 from 20 to 60 °C.

4. ESTABLISHMENT OF CRITICALITY STANDARDS

4.1. DEFINITION

In criticality safety, criticality practitioners often use standards calculations to determine the critical parameters and have an idea of acceptable equipment's sizes: a mass, a diameter or a volume corresponding to a pre-determined k_{eff} . These calculations are performed with simple geometry (sphere, infinite high cylinder, infinite plan slab) with various reflectors thickness (water, concrete, steel, lead...).

The reflection conditions are representative of the interactions between the neutron and the materials surrounding fissile material(s). For instance, a reflection by 2.5 cm of water is usually considered to model the reflection by a human hand. But generally, full water reflection (20 cm of water) is taken into account to cover risk of water around equipment (water ingress or flooding).

Thus, for each fissile concentration and reflection condition, the critical parameter ($k_{\text{eff}} = 1$) is determined. It is therefore easy to use such calculations to determine which solvent/diluent, acting as a moderator, is in a first stage the most penalizing for criticality safety.

4.2. CRITICAL VALUES

For that purpose, criticality standards calculations were performed using the APOLLO2-S_n code from the CRISTAL V2.0 package [8]. The modeling and calculations were launched with LATEC 1.4.0 workbench [10]. A target k_{eff} of 1 was defined to determine critical parameters. APOLLO2-S_n code is a deterministic code, using 281-energy groups and the collision probability methodology (p_{ij}); they were then collapsed with a 20 energy groups mesh. A P3 anisotropy and 16th order of quadrature were retained for the S_n part of the calculation.

The three geometries were tested:

- sphere,
- cylinder with an infinite height,
- slab with an infinite length and width.

A reflection by 20-cm of water was retained.

The reference fissile medium is:

- Step 1: mixed uranyl nitrate and plutonium nitrate IV (step 1) with a mass ratio of 0.1806 between Pu and U+Pu moderated by water or GANEX solvents;
- Step 2 & 3: nitrate of plutonium IV moderated by water or GANEX solvents.

The isotopic vector of plutonium is: 71 wt.% ²³⁹Pu/17 wt.% ²⁴⁰Pu/11 wt.% ²⁴¹Pu/1 wt.% ²⁴²Pu; and uranium is natural uranium (0.8 wt.% ²³⁵U). This envelope composition is used specifically for the comparison of solvent/diluent and water moderators, real plutonium composition being surely more degraded (more even-numbered plutonium isotopes).

The variation of k_{inf} and B^2_m values versus moderation for the solvents corresponding with the three steps of the GANEX project are reported in Appendix and are also compared with water as solvent.

4.2.1. GANEX 1ST STEP: DEHIBA/TPH SOLVENT

The critical values (sphere radius, slab thickness and cylinder radius) are reported in Figure 7 and in Figure 8 and in Table 6¹.

In the UPu concentration range [0, 400 g/L], the critical dimensions decrease until 200-250 g/l where it reaches a minimum. Moreover, the dimensions obtained with water as a solvent being lower than the ones obtained with DEHIBA/TPH as a solvent, **water is more conservative than DEHIBA/TPH** as moderator from a criticality-safety point of view.

¹ The objective of this study is to compare the moderation by water or GANEX solvents. Consequently, the conclusions obtained for sphere diameter are also applicable to the critical mass for the same fissile concentration.

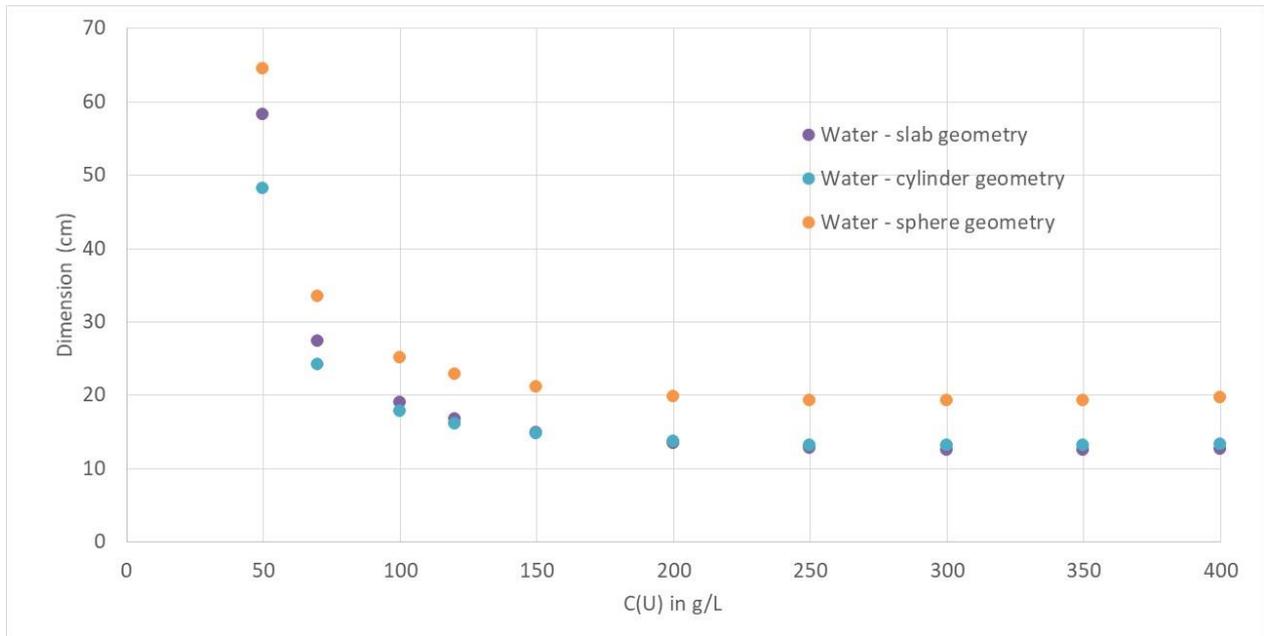


Figure 7: Critical values for water moderator

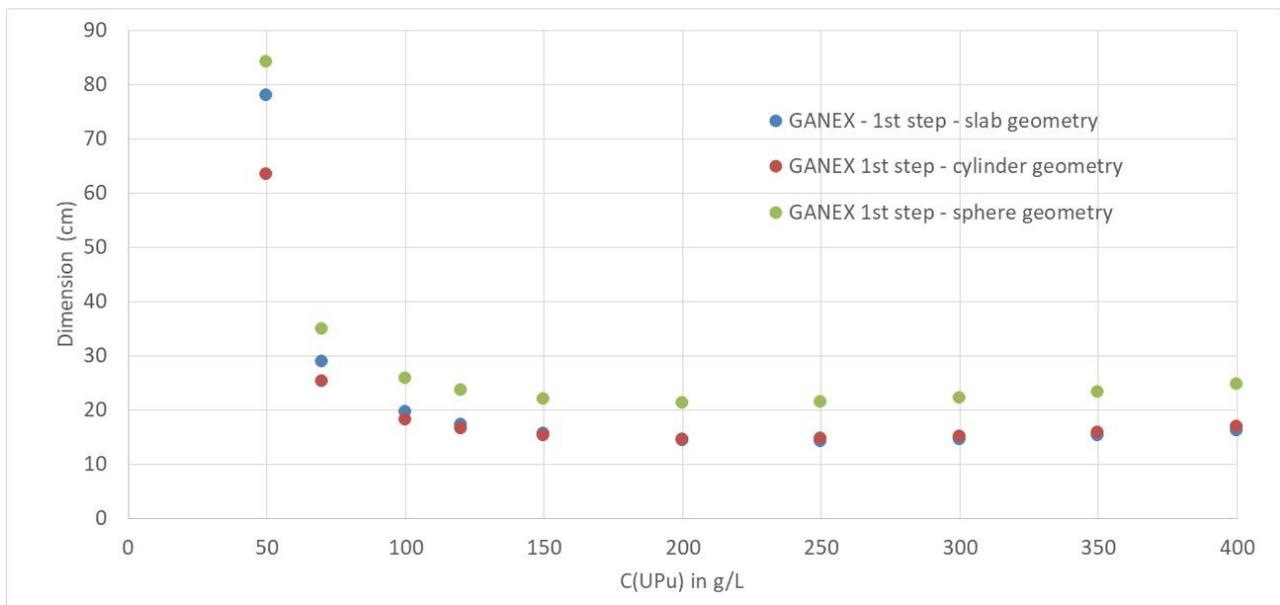


Figure 8: Critical values for organic moderator

Table 6: Comparison of critical dimensions.

Concentration in U (g/L)	Slab Critical thickness (cm)		Cylinder Critical radius (cm)		Sphere Critical radius (cm)	
	DEHIBA/TPH	Water	DEHIBA/TPH	Water	DEHIBA/TPH	Water
50	78.04	58.24	63.47	48.17	84.23	64.53
70	28.91	27.29	25.34	24.12	34.96	33.37
100	19.60	18.96	18.23	17.72	25.73	25.05
120	17.31	16.73	16.55	16.04	23.55	22.84
150	15.56	14.89	15.30	14.67	21.98	21.07
200	14.40	13.43	14.60	13.63	21.17	19.75
250	14.20	12.79	14.66	13.23	21.37	19.28
300	14.51	12.53	15.11	13.12	22.09	19.18
350	15.17	12.50	15.85	13.18	23.20	19.31
400	16.15	12.62	16.84	13.36	24.65	19.59

4.2.2. GANEX 2ND STEP

The critical values (sphere radius, slab thickness and cylinder radius) are reported in Figure 9, in Figure 10 and in Table 7.

In the Pu concentration range [0, 150 g/L], the critical dimension is always decreasing for the slab geometry with a minimum around 100 g/L. For the cylinder and sphere geometries, one can observe a small increase beyond 100 g/L.

One can see that at the optimum moderation ratio water is conservative.

However, the dimensions obtained with water as a solvent are not always bounding the ones obtained with TODGA+DMDOHEMA/EXXSOL as a solvent. This means that the curves "dimension as a function of concentration" intersect and that water moderation may not be conservative for certain concentration ranges. Water moderation is therefore not always conservative when the fissile concentration is a controlled parameter.

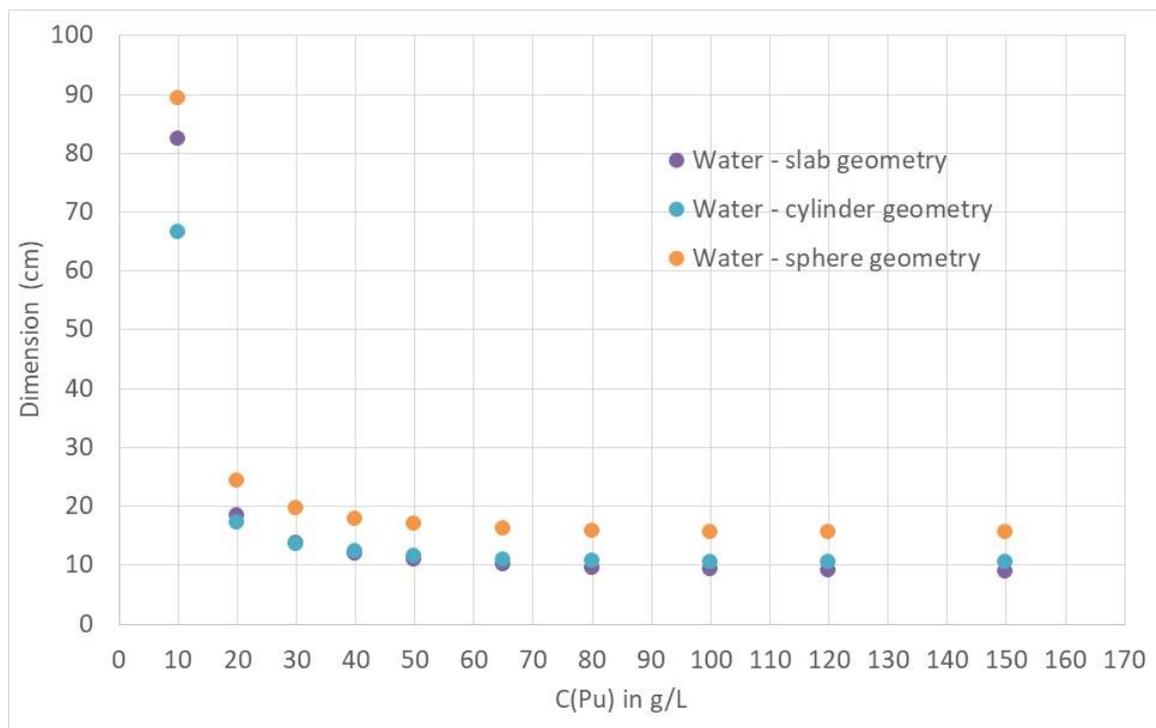


Figure 9: Critical values for water moderator

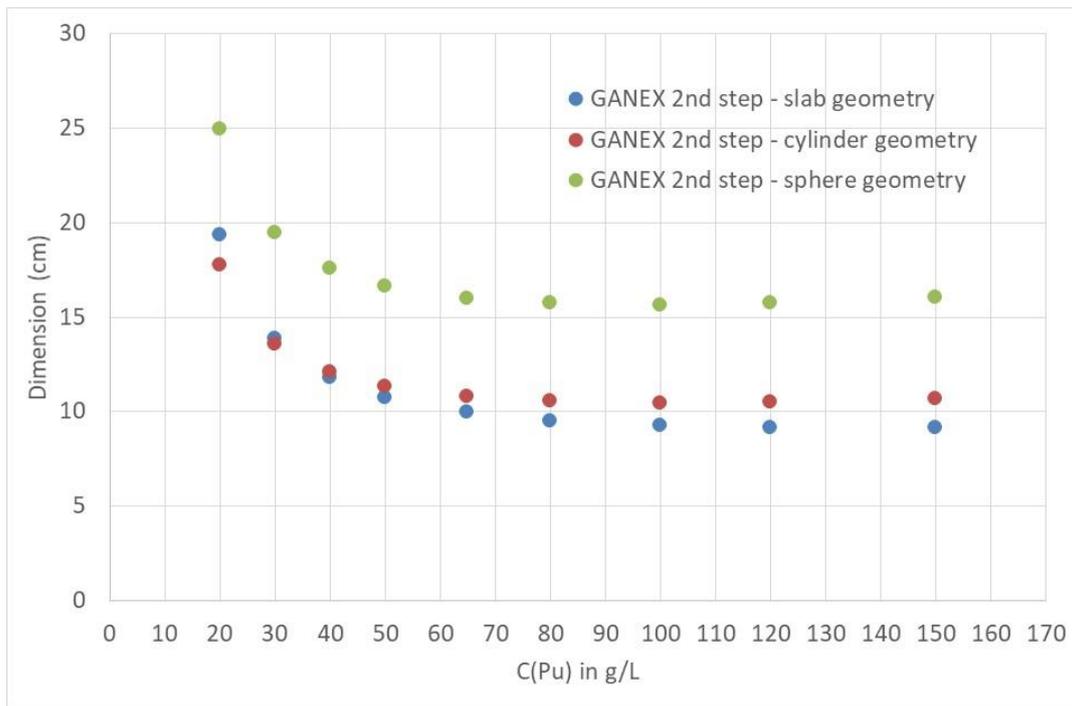


Figure 10: Critical values for organic moderator

Table 7: Comparison of critical dimensions.

Concentration in Pu (g/L)	Slab Critical thickness (cm)		Cylinder Critical radius (cm)		Sphere Critical radius (cm)	
	DMDOHEMA + TODGA/EXXSOL	Water	DMDOHEMA + TODGA/EXXSOL	Water	DMDOHEMA+ TODGA/EXXSOL	Water
20	19.31	18.47	17.75	17.26	24.91	24.37
30	13.83	13.71	13.58	13.62	19.48	19.62
40	11.80	11.84	12.08	12.23	17.55	17.83
50	10.76	10.84	11.34	11.51	16.63	16.91
65	9.94	10.01	10.80	10.93	15.97	16.20
80	9.51	9.56	10.56	10.65	15.71	15.85
100	9.24	9.22	10.46	10.46	15.64	15.64
120	9.14	9.05	10.49	10.39	15.74	15.58
150	9.17	8.95	10.65	10.38	16.04	15.61
250		9.20		10.44		15.63

4.2.3. GANEX 3RD STEP

The critical values (sphere radius, slab thickness and cylinder radius) are reported in Figure 11 and in Table 8.

The dimensions obtained with water as a solvent are always lower than the ones obtained with AHA+SO₃-Ph-BTP as a solvent; water is therefore more conservative than AHA+SO₃-Ph-BTP from a criticality-safety point of view. However, the critical dimensions calculated for water avec GANEX step 3 solvent are very close for all geometries.

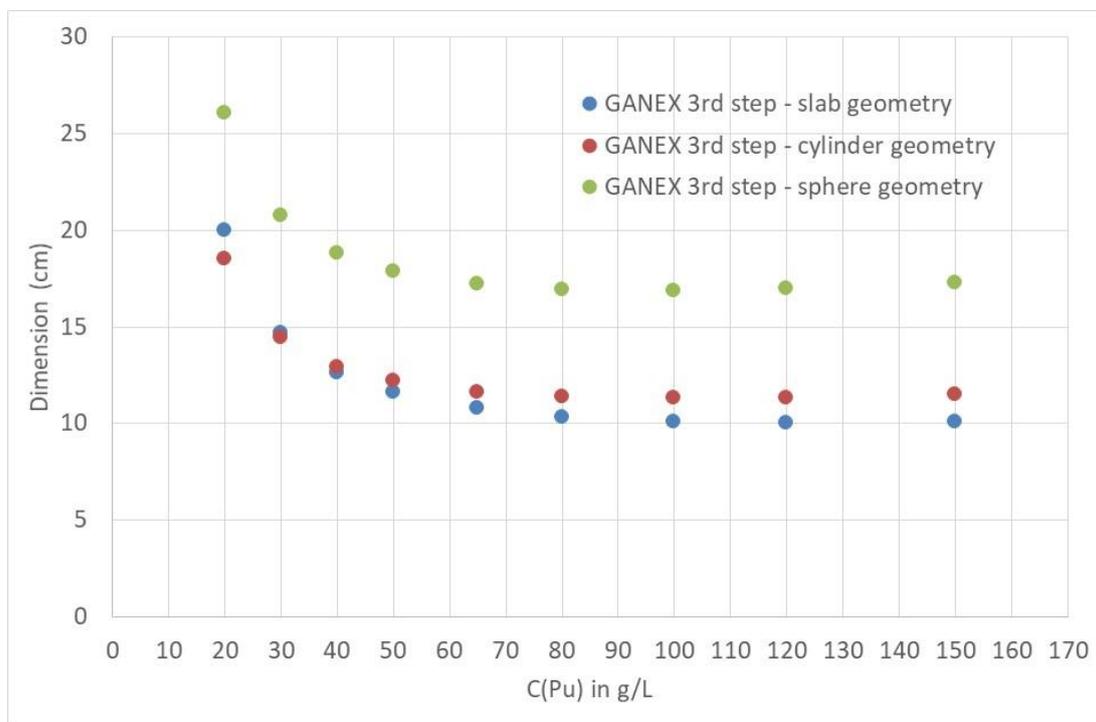


Figure 11: Critical values for organic moderator

Table 8: Comparison of critical dimensions.

Concentration in Pu (g/L)	Slab Critical thickness (cm)		Cylinder Critical radius (cm)		Sphere Critical radius (cm)	
	AHA + SO ₃ -Ph-BTP + HNO ₃	Water	AHA + SO ₃ -Ph-BTP + HNO ₃	Water	AHA + SO ₃ -Ph-BTP + HNO ₃	Water
20	20.01	18.47	18.50	17.26	26.03	24.37
30	14.65	13.71	14.43	13.62	20.72	19.62
40	12.63	11.84	12.93	12.23	18.80	17.83
50	11.59	10.84	12.19	11.51	17.87	16.91
65	10.76	10.01	11.64	10.93	17.20	16.20
80	10.34	9.56	11.40	10.65	16.94	15.85
100	10.08	9.22	11.31	10.46	16.87	15.64
120	10.01	9.05	11.34	10.39	16.97	15.58
150	10.06	8.95	11.51	10.38	17.26	15.61
250		9.20		10.44		15.63

4.3. COMPARISON OF MODERATORS

4.3.1. COMPARISON BETWEEN MODERATORS

In order to compare the reactivity worth induced by the change of solvent/diluent, a continuous Monte Carlo calculation using the MORET 5.D.1 code [9] associated with the JEFF-3.1.1 evaluation of nuclear data is performed. Calculations are performed for slab, cylinder and sphere geometries. For each geometry, the critical dimensions obtained previously for a water moderation are used to evaluate the reactivity variation. It is a good way to translate in terms of reactivity worth the penalizing effect of the solvent/diluent.

The results are reported for the three geometries in Figure 12 through Figure 14.

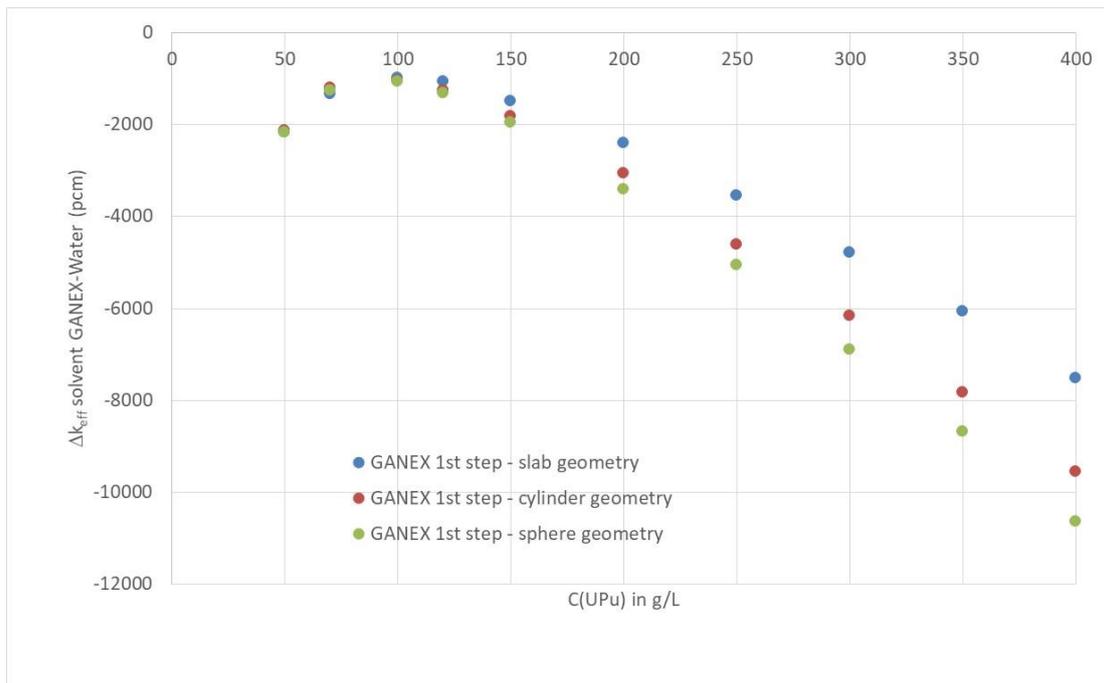


Figure 12 : k_{eff} discrepancy versus solvent/diluent nature – GANEX 1st step

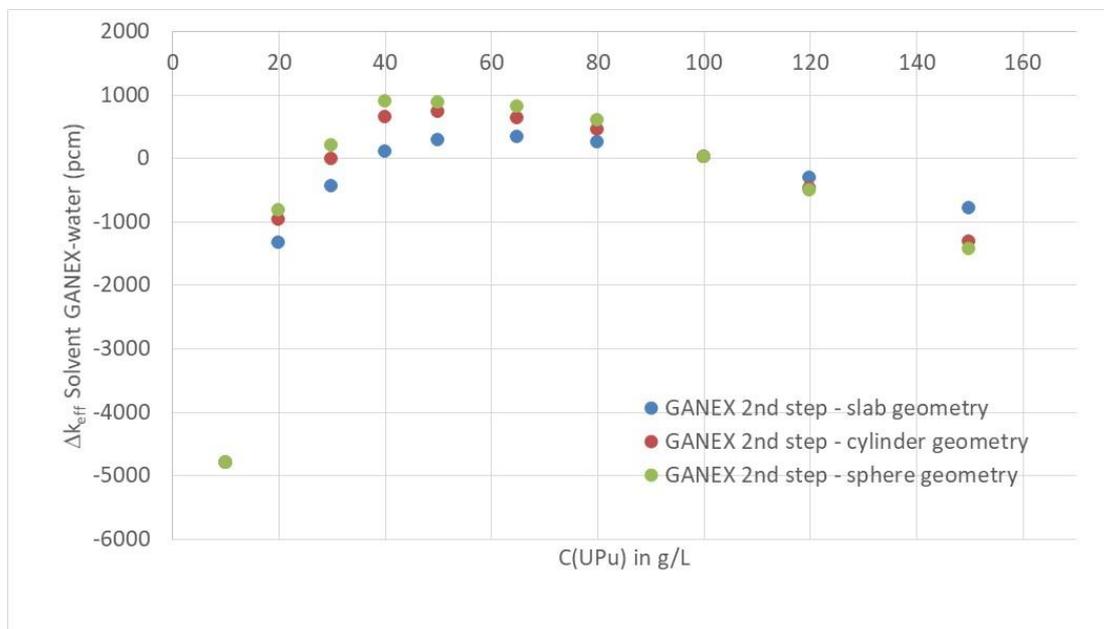


Figure 13: k_{eff} discrepancy versus solvent/diluent nature – GANEX 2nd step

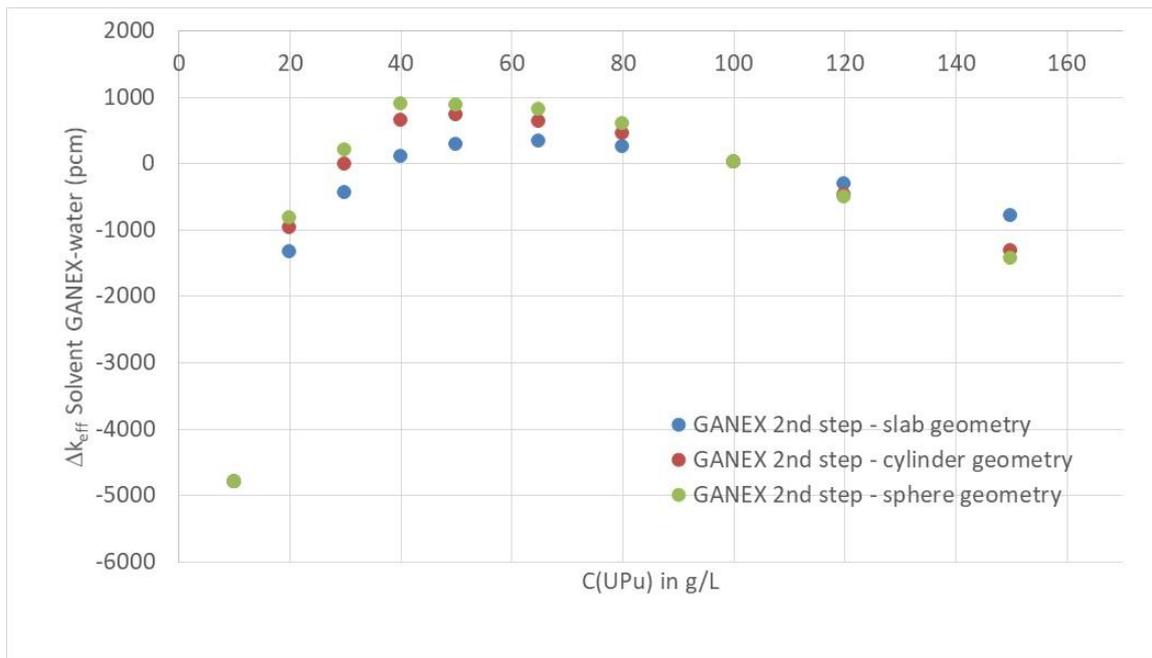


Figure 14: k_{eff} discrepancy versus solvent/diluent nature – GANEX 3rd step

Figure 12 shows that water moderation is conservative compare to DEHIBA/TPH (solvent/diluent of GANEX 1st step) moderation, whatever the concentration.

Figure 13 shows that water moderation is not conservative compare to DMDOHEMA+TODGA /EXXSOL (solvent/diluent of GANEX 2nd STEP) moderation between around 30 and 100 g/L (exact data range depending on the geometry considered). The maximum underprediction ($\Delta k_{\text{eff}} \geq 0$) with water moderator is 1000 pcm.

Figure 14 shows also that water moderation is not conservative compare to AHA + SO₃-Ph-BTP + HNO₃ (solvent/diluent of GANEX 3rd STEP) moderation between around 30 and 100 g/L (exact data range depending on the geometry considered). The maximum underprediction ($\Delta k_{\text{eff}} \geq 0$) with water moderator is also 1000 pcm.

Special attention should be taken if the concentration control mode is used with solvent/diluent of GANEX 2nd STEP and 3rd STEP. Nevertheless, this underprediction disappears as soon as acidity is taken into account as it will be shown in the following paragraphs.

4.3.2. VARIATION OF PROPORTIONS OF EXTRACTANT/DILUENT

In this section, it is postulated that the proportion extractant/diluent can vary. A $\pm 20\%$ variation of the extractant concentration is considered and the same calculations as in the previous sections are redone.

The results are reported for the three geometries in Figure 15 through Figure 20.

4.3.2.1 GANEX 1ST STEP

For the three geometries of the first step of the GANEX process, the decrease of the concentration of DEHIBA in TPH leads to an increase of reactivity worth (decrease of critical dimensions). It can be explained by the fact that TPH is conservative in terms of molar volume (smaller molar volume than DEHIBA) and also does not contain nitrogen in its chemical formula, which is a neutron absorber.

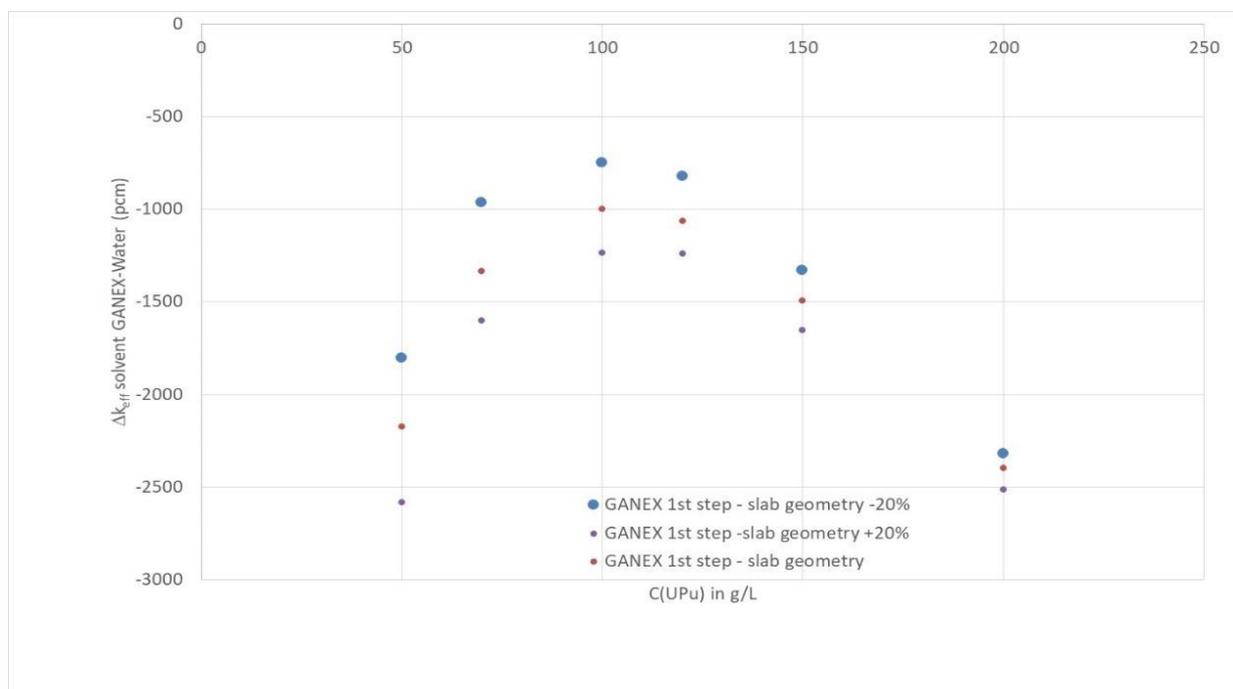


Figure 15 : k_{eff} discrepancy versus solvent/diluent proportions – GANEX 1st step – slab geometry

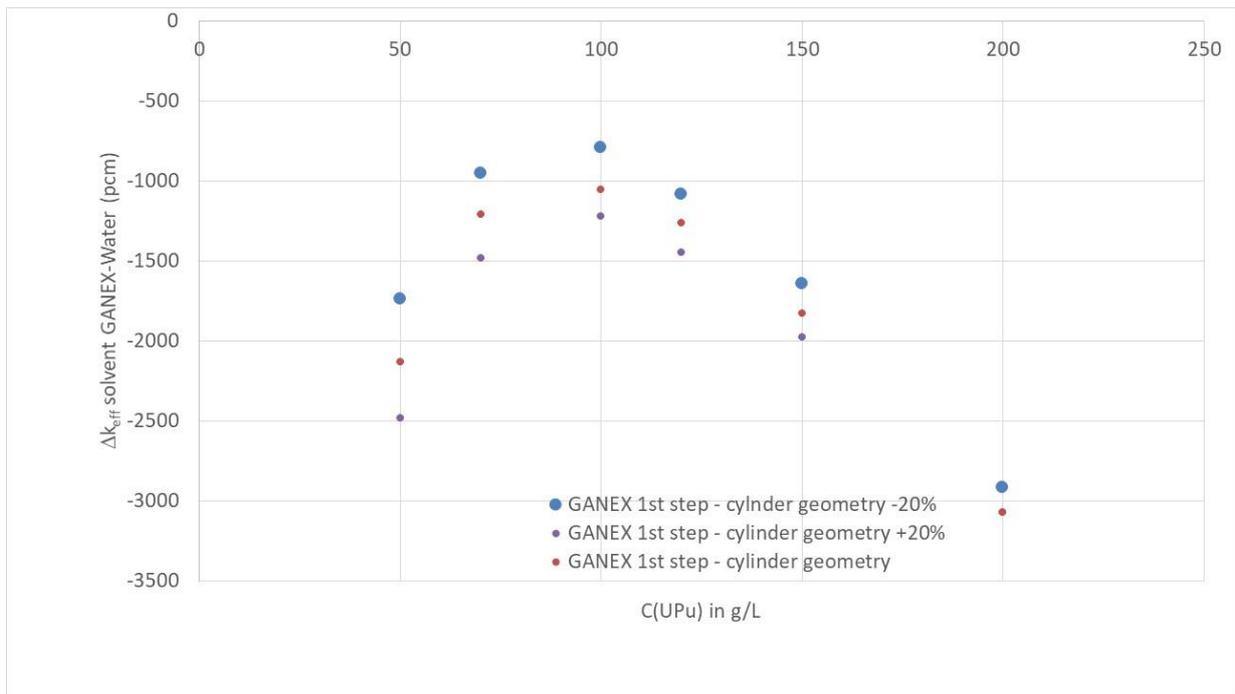


Figure 16 : k_{eff} discrepancy versus solvent/diluent proportions – GANEX 1st step – cylinder geometry

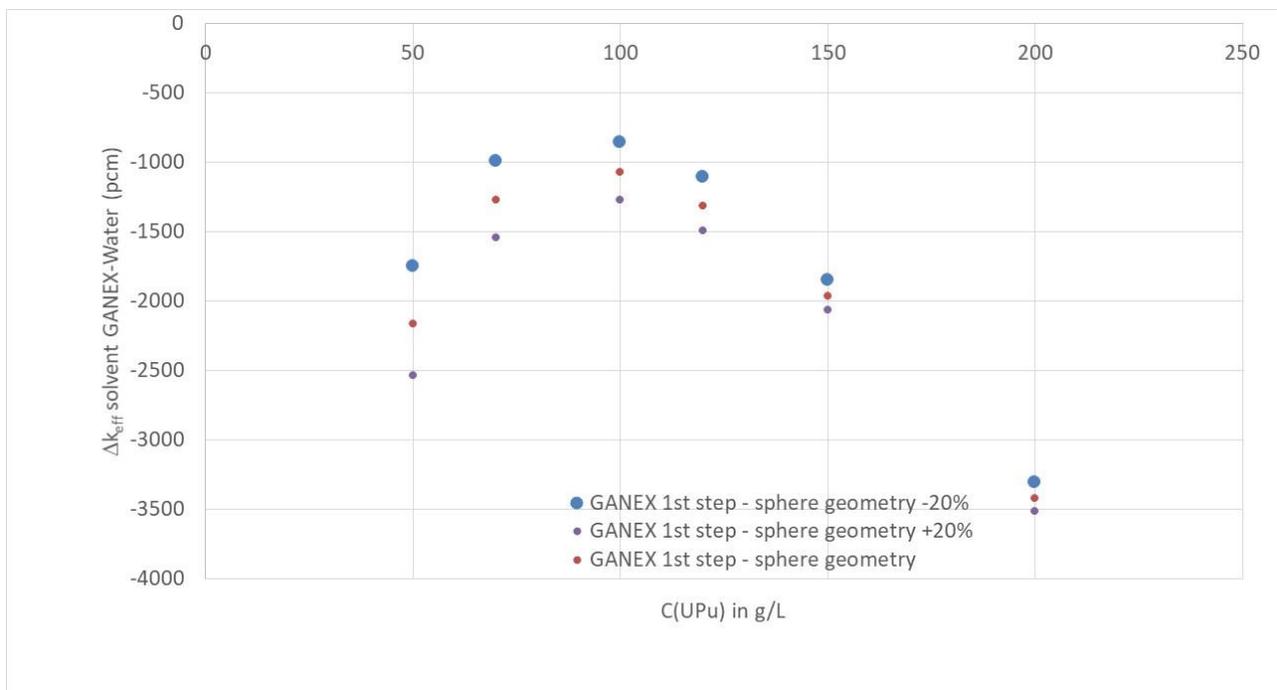


Figure 17 : k_{eff} discrepancy versus solvent/diluent proportions – GANEX 1st step – sphere geometry

4.3.2.2 GANEX 2nd STEP

For the three geometries of the second step of the GANEX process, the decrease of the concentration of TODGA+DMDOHEMA in EXXSOL leads to an increase of reactivity worth (decrease of critical dimensions). It can be explained by the fact that EXXSOL is conservative in terms of molar volume (smaller molar volume than TODGA+DMDOHEMA) and also does not contain nitrogen in its chemical formula, which is a neutron absorber.

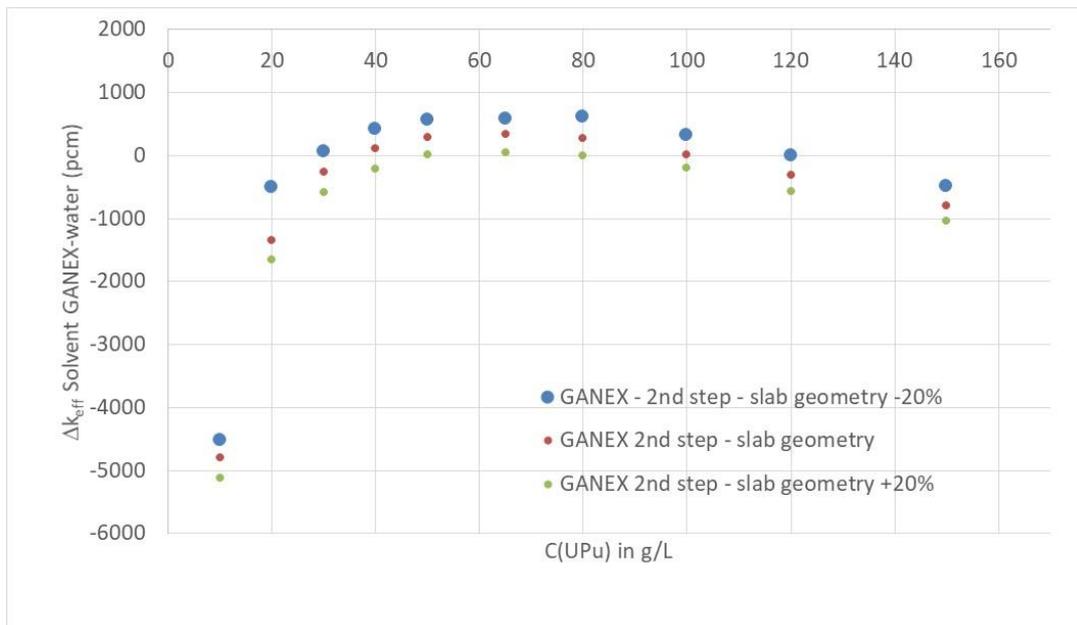


Figure 18 : k_{eff} discrepancy versus solvent/diluent proportions – GANEX 2nd step – slab geometry

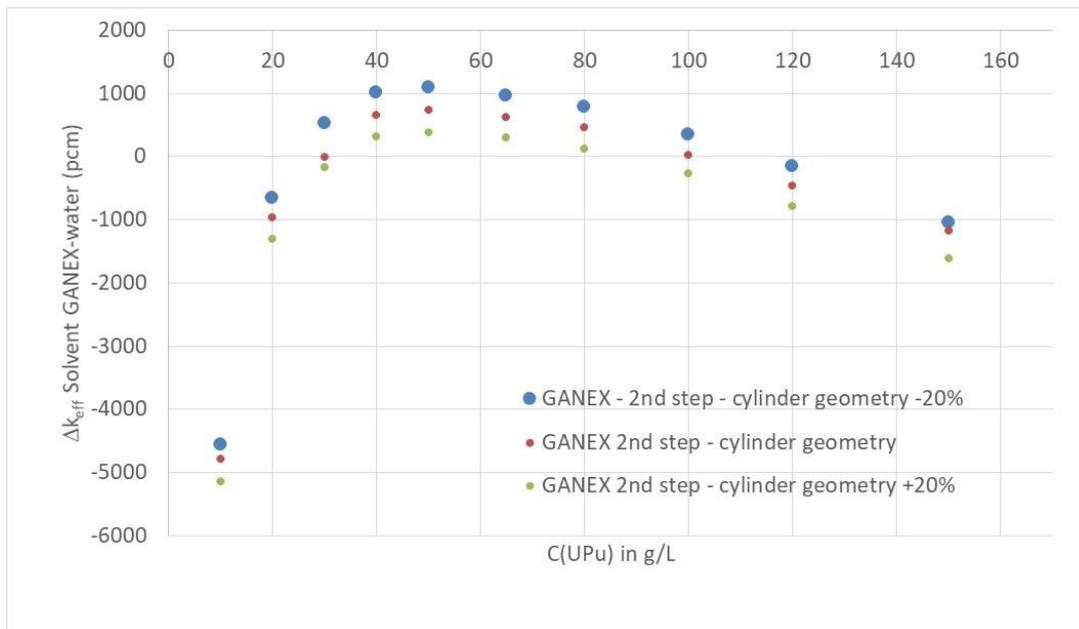


Figure 19 : k_{eff} discrepancy versus solvent/diluent proportions – GANEX 2nd step – cylinder geometry

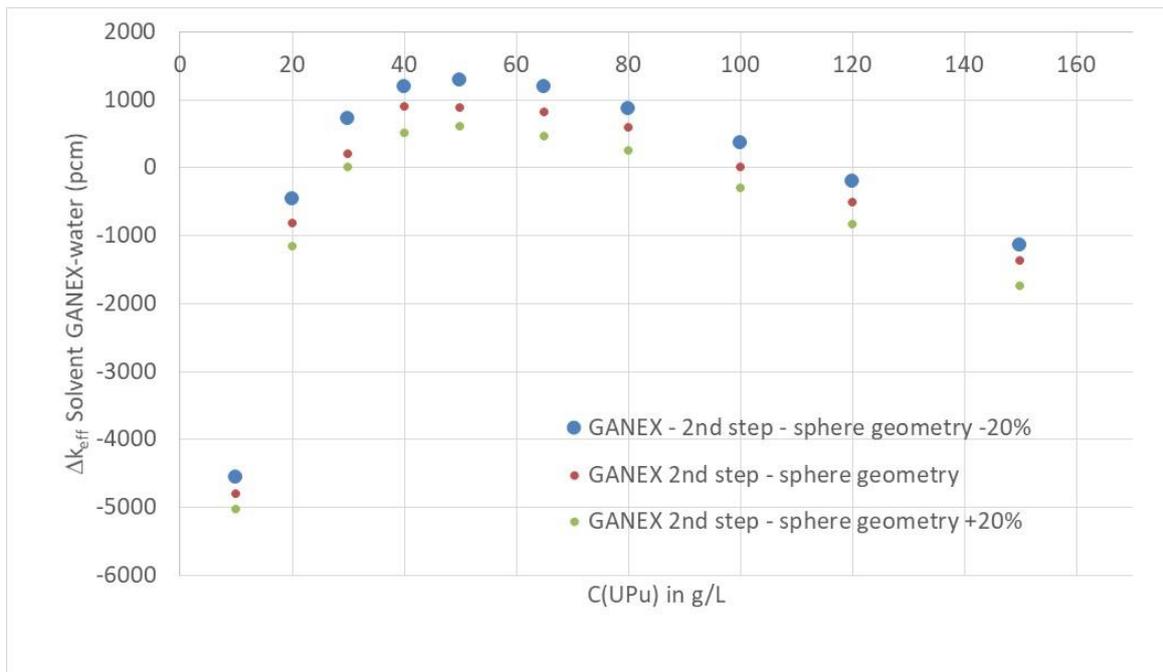


Figure 20 : k_{eff} discrepancy versus solvent/diluent proportions – GANEX 2nd step – sphere geometry

4.3.2.3 GANEX 3RD STEP

For the three geometries of the third step of the GANEX process, the decrease of the concentration of AHA+SO₃-Ph-BTP in water leads to an increase of reactivity worth (decrease of critical dimensions).

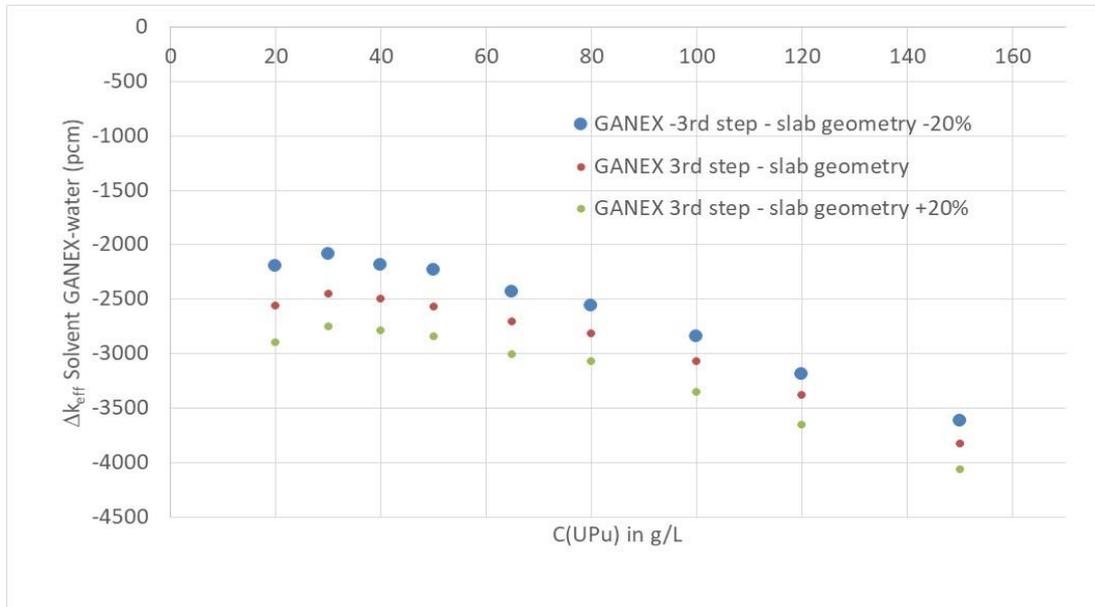


Figure 21 : k_{eff} discrepancy versus solvent/diluent proportions – GANEX 3rd step – slab geometry

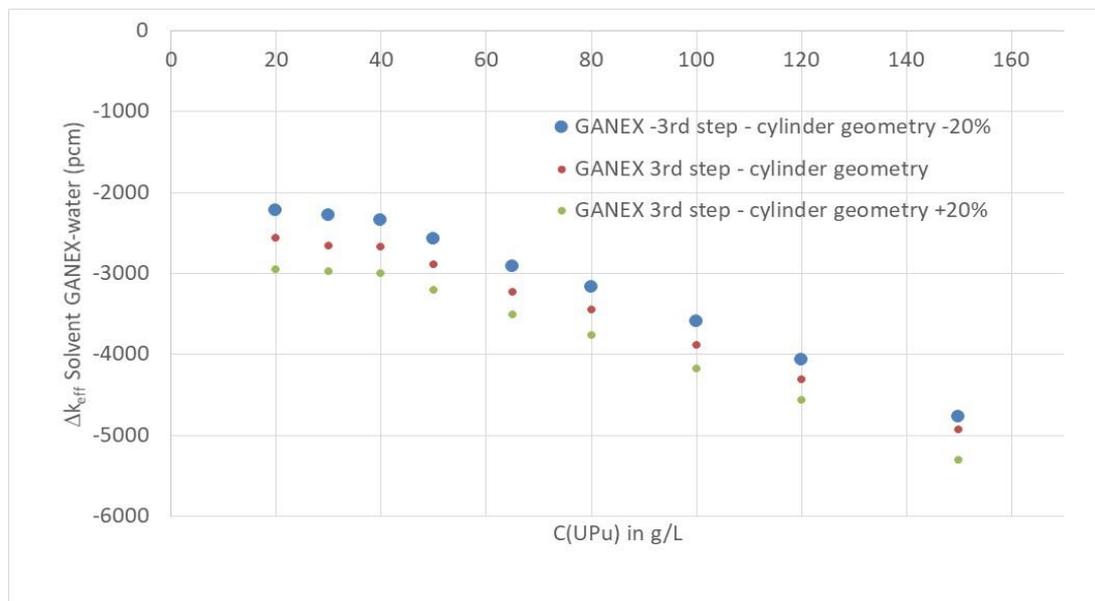


Figure 22 : k_{eff} discrepancy versus solvent/diluent proportions – GANEX 3rd step – cylinder geometry

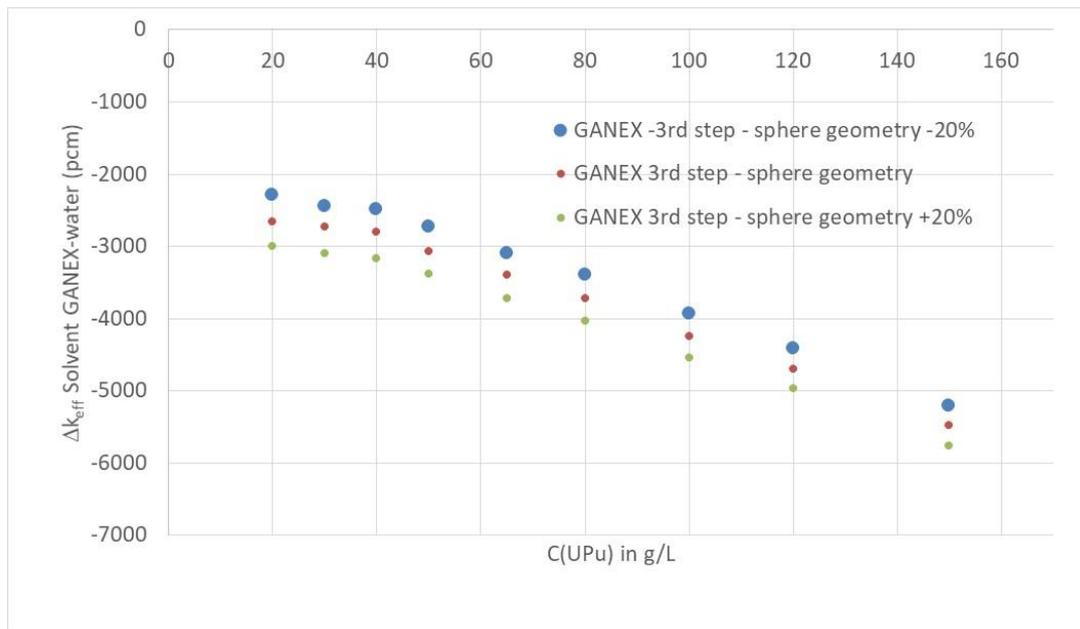


Figure 23 : k_{eff} discrepancy versus solvent/diluent proportions – GANEX 3rd step – sphere geometry

4.3.3. VARIATION OF PROPORTIONS BETWEEN SOLVENTS (GANEX 2ND AND 3RD STEP)

4.3.3.1 GANEX 2ND STEP

In this section, it is postulated that the proportion between the solvents DMDOHEMA and TODGA varies. A variation of the TODGA concentration corresponding with $\pm 20\%$ of the DMDOHEMA concentration (0.5 mol/L) is considered and is applied on the TODGA concentration. The DMDOHEMA concentration remains constant, whereas the TODGA concentration takes the 0.1 mol/L and 0.3 mol/L values. The TODGA/DMDOHEMA ratio takes therefore the 20% and 60% values (reference value 40%), respectively for the negative and positive variations. Then, the same calculations as in the previous section are redone.

The results are reported for the three geometries in Figure 24 through Figure 26.

The increase of TODGA part leads to decrease the reactivity. However, the impact of this ratio is low and do not change the conclusions regarding the comparison of this solvent with water.

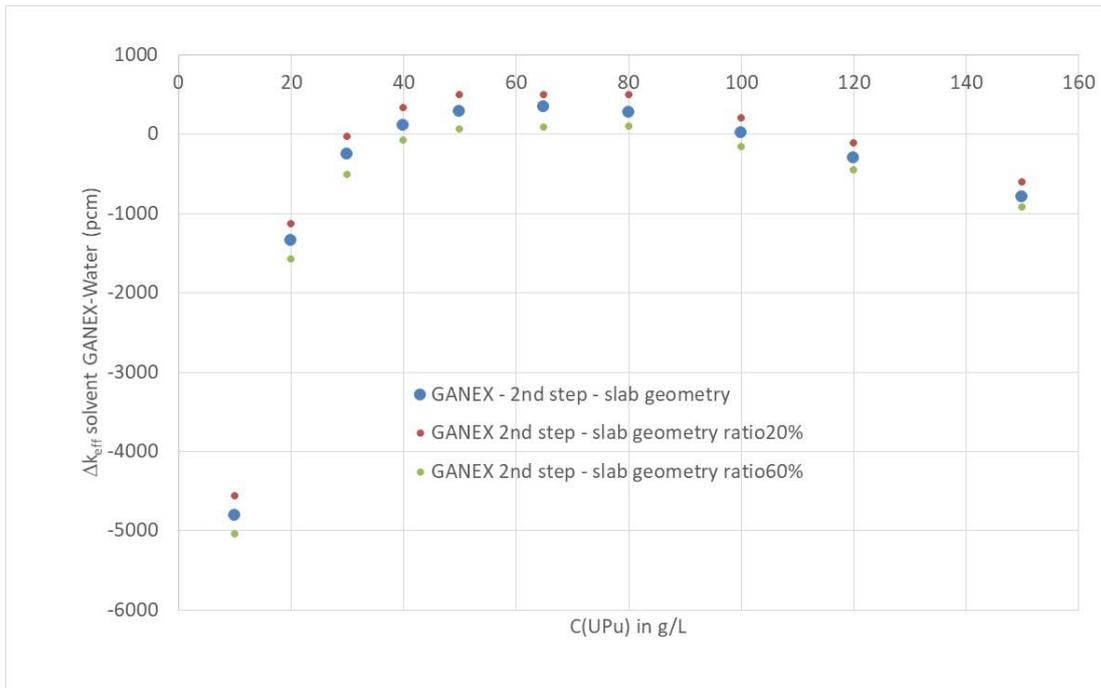


Figure 24 : k_{eff} discrepancy versus solvent/diluent nature – GANEX 2nd step – slab geometry

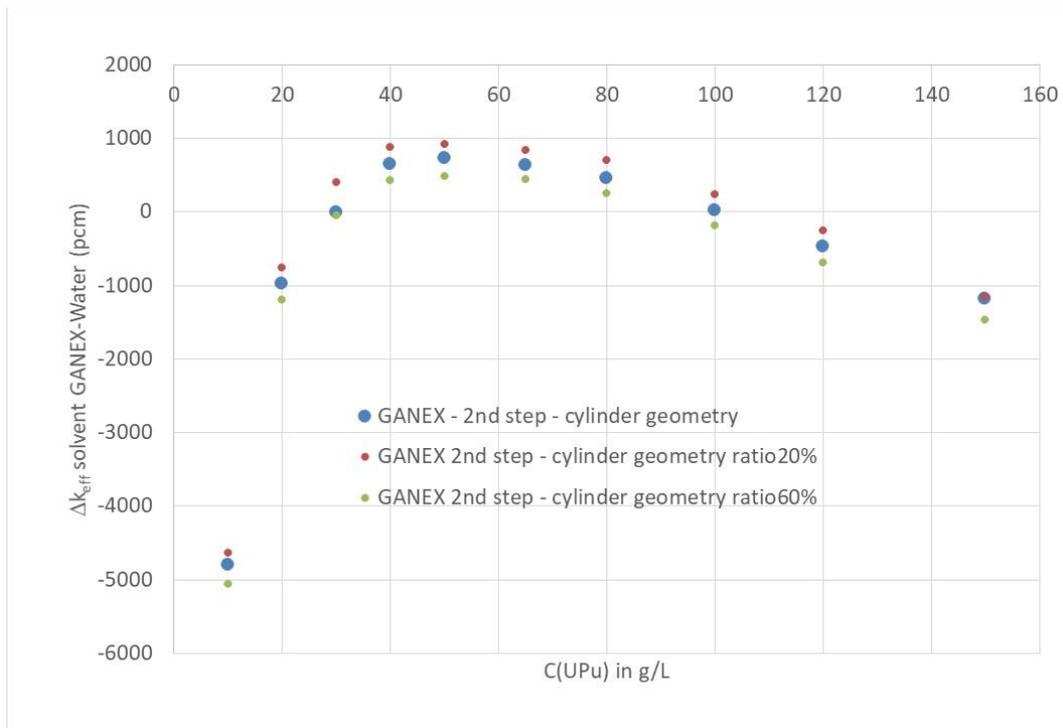


Figure 25: k_{eff} discrepancy versus solvent/diluent nature – GANEX 2nd step – cylinder geometry

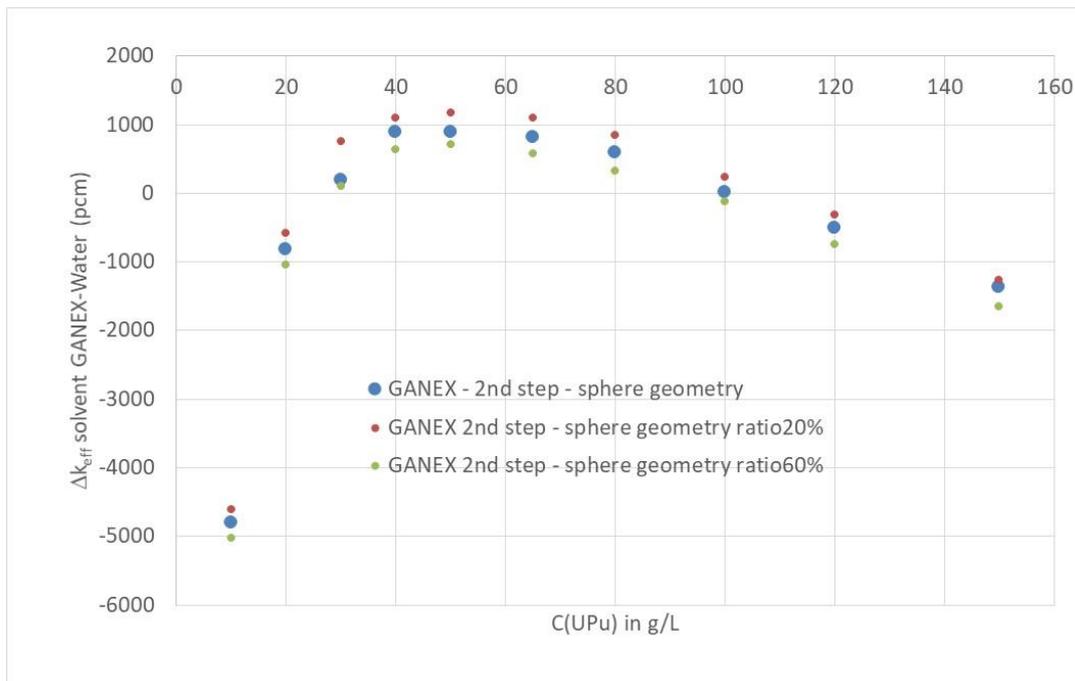


Figure 26: k_{eff} discrepancy versus solvent/diluent nature – GANEX 2nd step – sphere geometry

4.3.3.2 GANEX 3RD STEP

In this section, it is postulated that the proportions between the solvents AHA and SO₃-Ph-BTP varies. The initial ratio SO₃-Ph-BTP/AHA was equal to 0.055. In this section, it takes arbitrarily the values of 0.028 and 0.11. The AHA concentration remains constant, whereas the SO₃-Ph-BTP concentration varies. Then, the same calculations as in the previous section are redone.

The decrease of SO₃-Ph-BTP concentration leads to increase the reactivity.

The results are reported for the three geometries in Figure 27 through Figure 29.

The increasing of the ratio leads to decrease the reactivity.

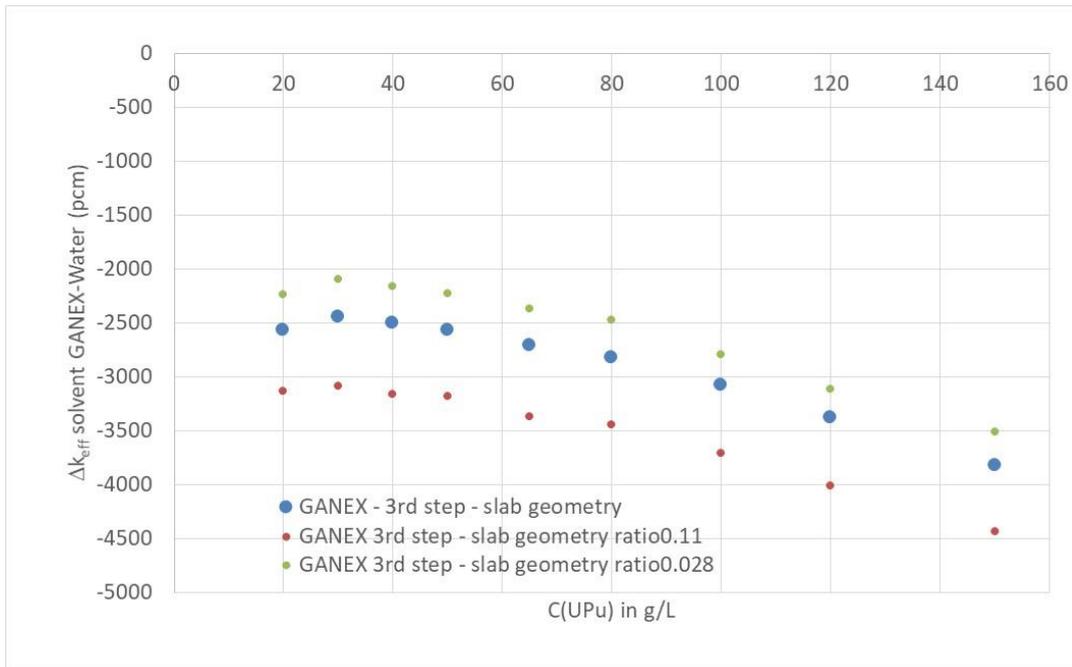


Figure 27 : k_{eff} discrepancy versus solvent/diluent nature – GANEX 3rd step – slab geometry

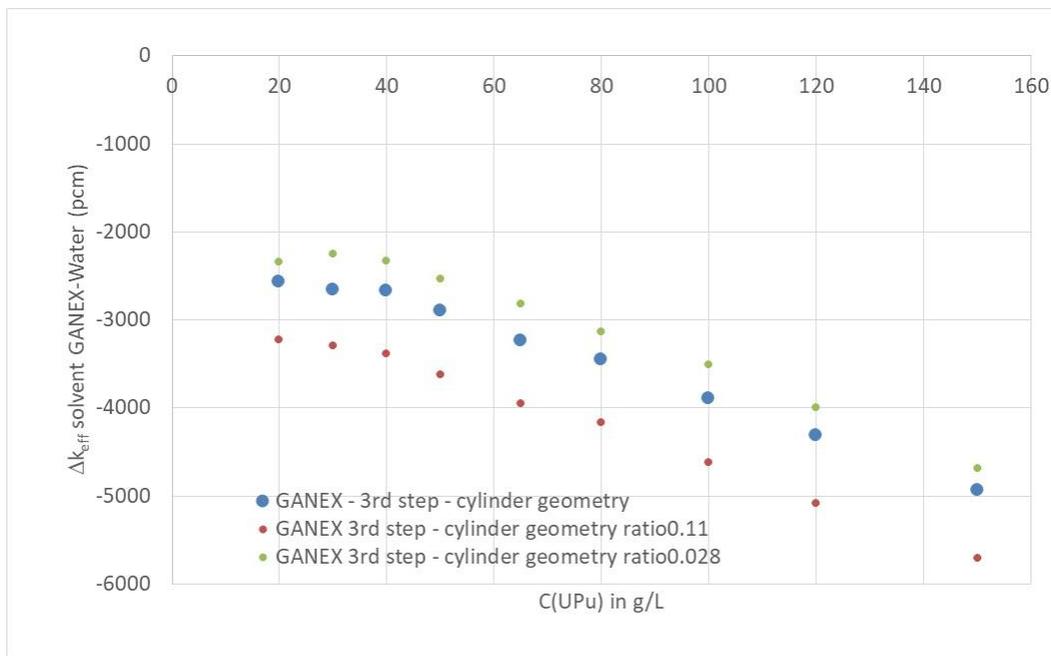


Figure 28 : k_{eff} discrepancy versus solvent/diluent nature – GANEX 3rd step – cylinder geometry

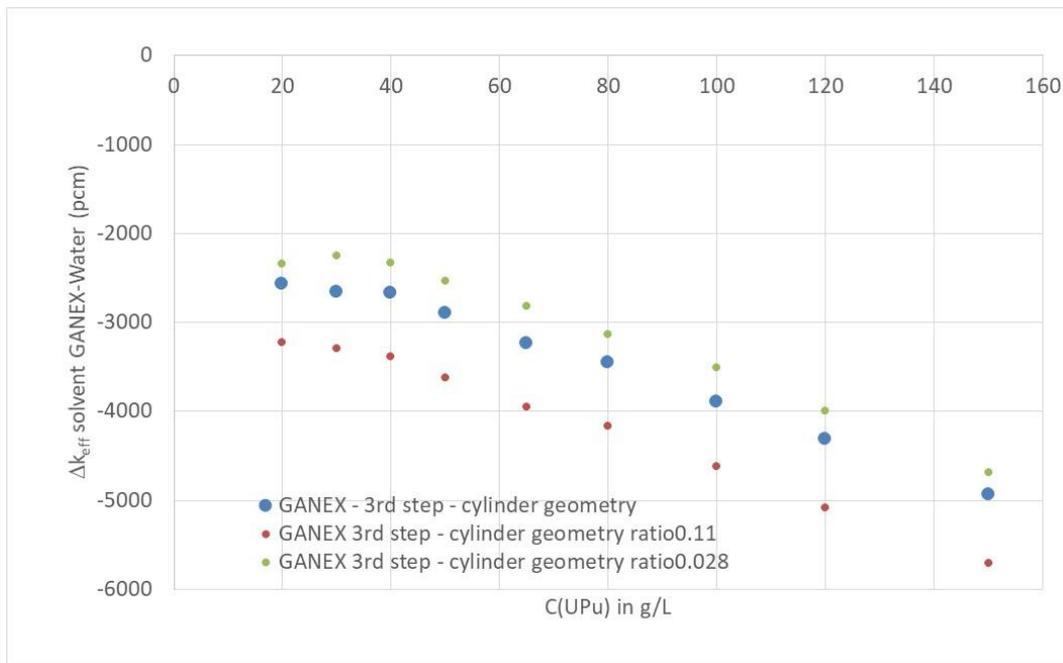


Figure 29 : k_{eff} discrepancy versus solvent/diluent nature – GANEX 3rd step – sphere geometry

4.3.4. ACID TAKEN INTO ACCOUNT IN SOLVENT/DILUENT

One of the margins of conservatism in the calculation is to assume no acidity in the solution (all calculations presented until now). Indeed, nitrogen atom (N) is a neutron absorber.

For the 2nd step of the GENIORS process, for which water is not conservative with respect to the organic solvent for a concentration range of Pu between 30 and 100 g/L, it is proposed to consider 1 mol/L of acidity far below the realistic 6 mol/L acidity. The same calculations as in the previous sections are then redone.

The results are reported in Figure 30 (acid) and Figure 31 (without acid). It can be seen that in that case water remains conservative when compared with TODGA+DMDOHEMA/EXXSOL + 1N.

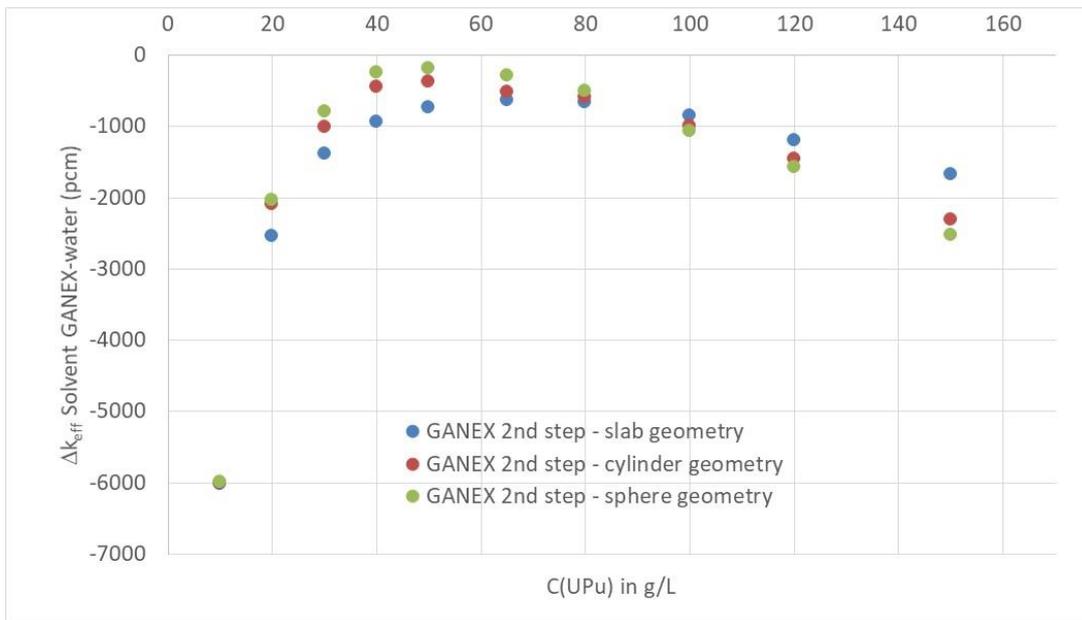


Figure 30: k_{eff} discrepancy versus solvent/diluent nature – GANEX 2nd step – three geometries – 1 mol of acid (HNO_3)

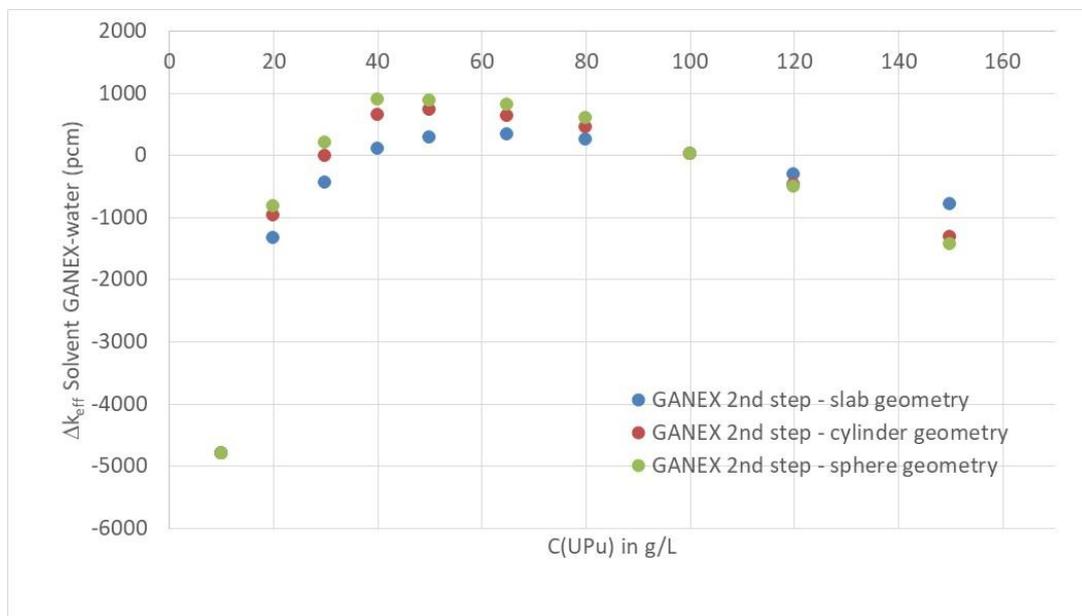


Figure 31: k_{eff} discrepancy versus solvent/diluent nature – GANEX 2nd step – three geometries – no acidity

4.3.5. COMPARISON WITH TBP/TPH

The former fuel reprocessing process involved TBP as an extractant and TPH as a diluent. It is therefore also interesting to compare TBP/TPH with water and the new extractant/diluent of the GENIORS project. As previously performed², critical dimensions obtained with water are considered.

The density of TPH is assumed to be 0.7448 g/cm³.

The density of TBP is taken equal to 0.9722 g/cm³.

The proportion of extractant in the solvent is assumed to be 0.3587 % in weight.

A volume additive law is built as previously at room temperature as can be seen on formula (9 and (10).

$$\rho_{solution} = C(UO_2(NO_3)_2) + C(Pu(NO_3)_4) + \rho_{TBP-TPH} \times \left(1 - \frac{C(U)}{\rho(U)} - \frac{C(Pu)}{\rho(Pu)}\right) \quad (9)$$

$$\rho_{TBP-TPH} = \frac{1}{\frac{wt\% TBP}{\rho_{TBP}} + \frac{wt\% TPH}{\rho_{TPH}}} \quad (10)$$

It should be noted that acid has not been considered in the solvent.

The two EURO-GANEX steps are investigated replacing the dedicated solvents by TBP/TPH. The discrepancies between k_{eff} for the two solvents³ are displayed on Figure 33 and Figure 37.

² Calculations are performed with the continuous energy code MORET 5, the JEFF-3.1.1 nuclear data library, these dimensions and compositions corresponding with the various solvents.

³ In that case, the critical dimensions of the case with water solvent are also used for the case with the GANEX solvents/diluents.

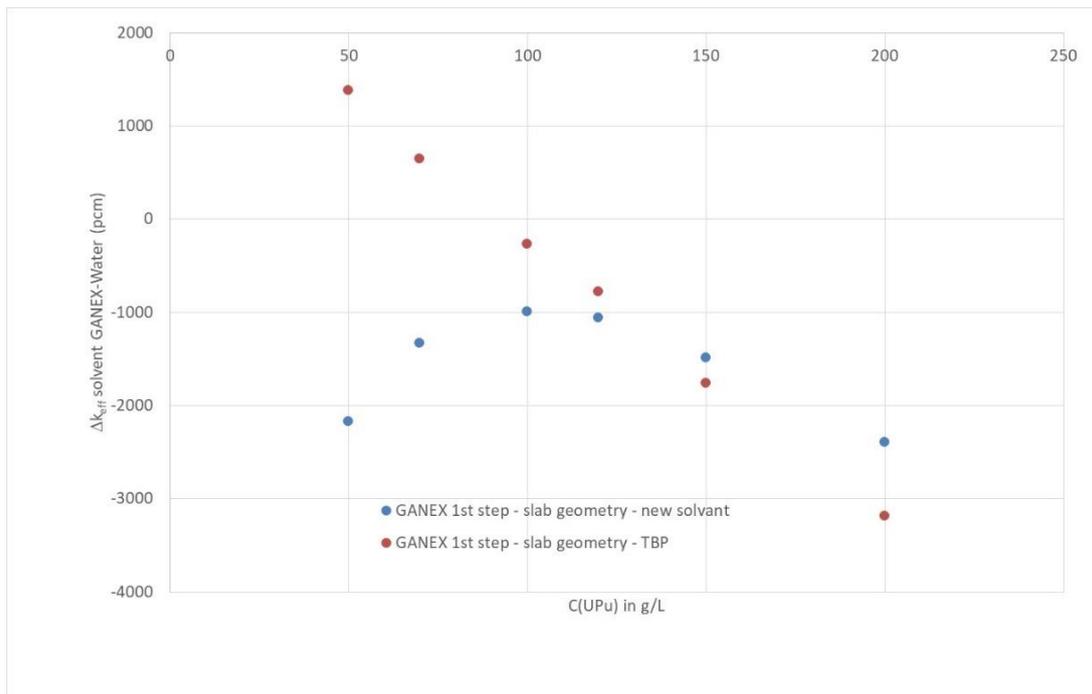


Figure 32: comparison of k_{eff} between water, new solvent and TBP/TPH for GANEX 1st step – slab geometry.

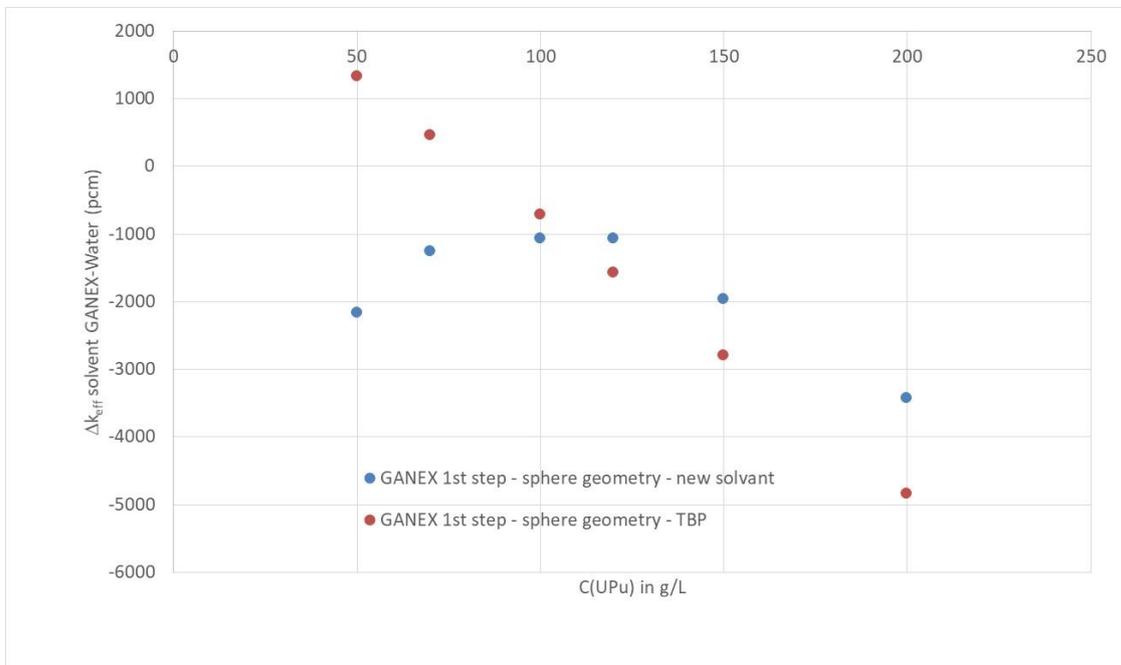


Figure 33: comparison of k_{eff} between water, new solvent and TBP/TPH for GANEX 1st step – spherical geometry.

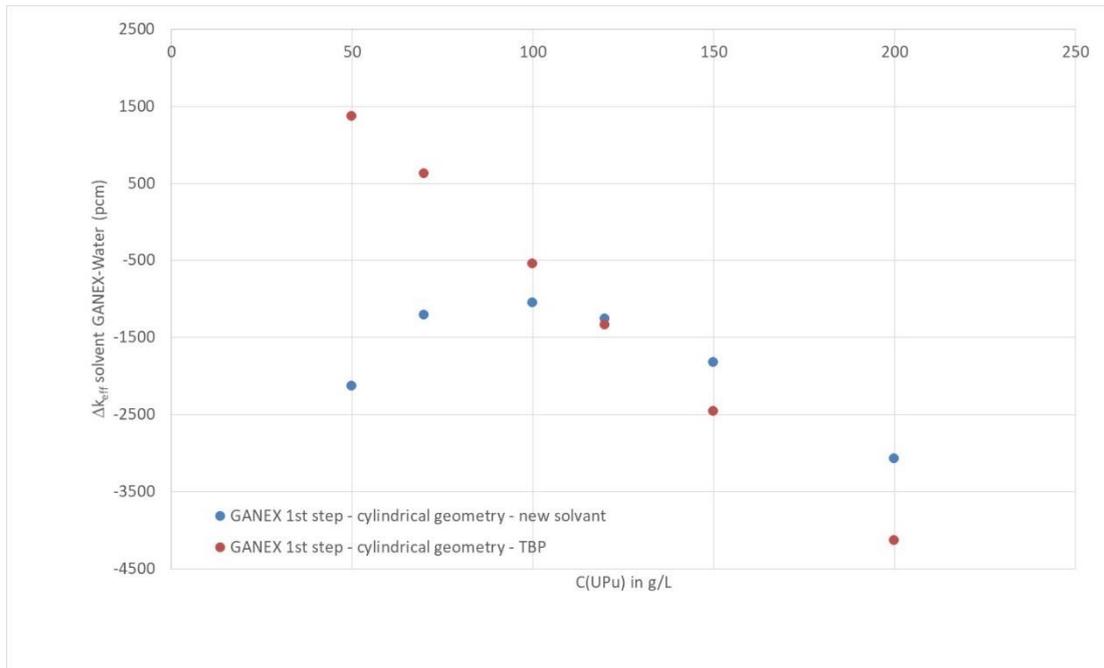


Figure 34: comparison of k_{eff} between water, new solvent and TBP/TPH for GANEX 1st step – cylindrical geometry

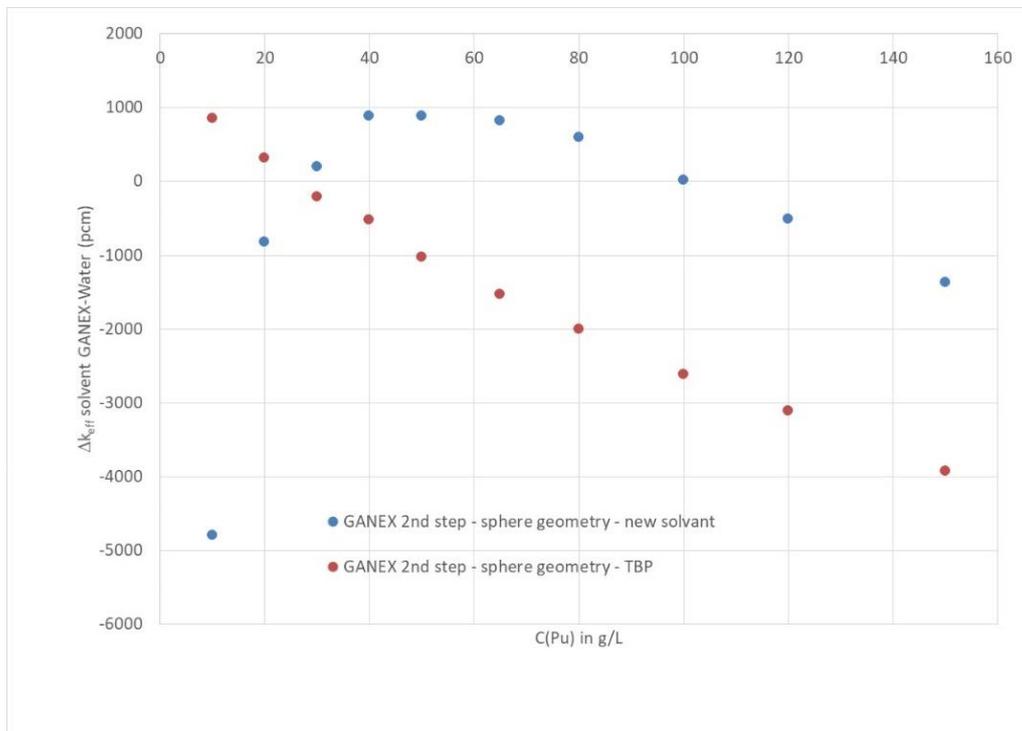


Figure 35: comparison of k_{eff} between water, new solvent and TBP/TPH for GANEX 2nd step – spherical geometry.

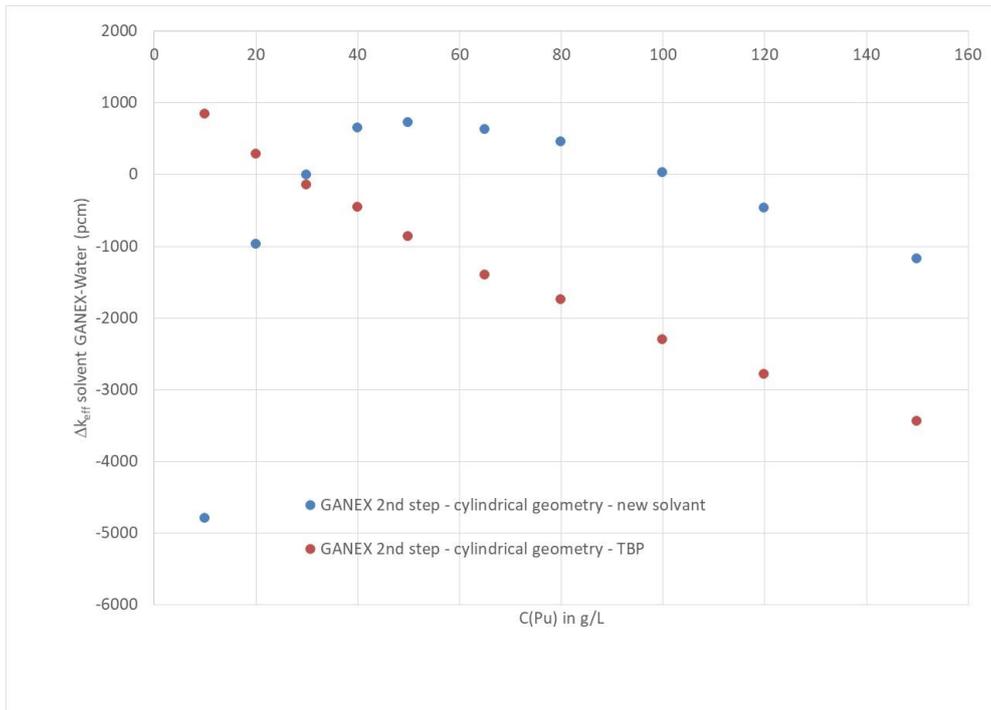


Figure 36: comparison of k_{eff} between water, new solvent and TBP/TPH for GANEX 2nd step – cylindrical geometry.

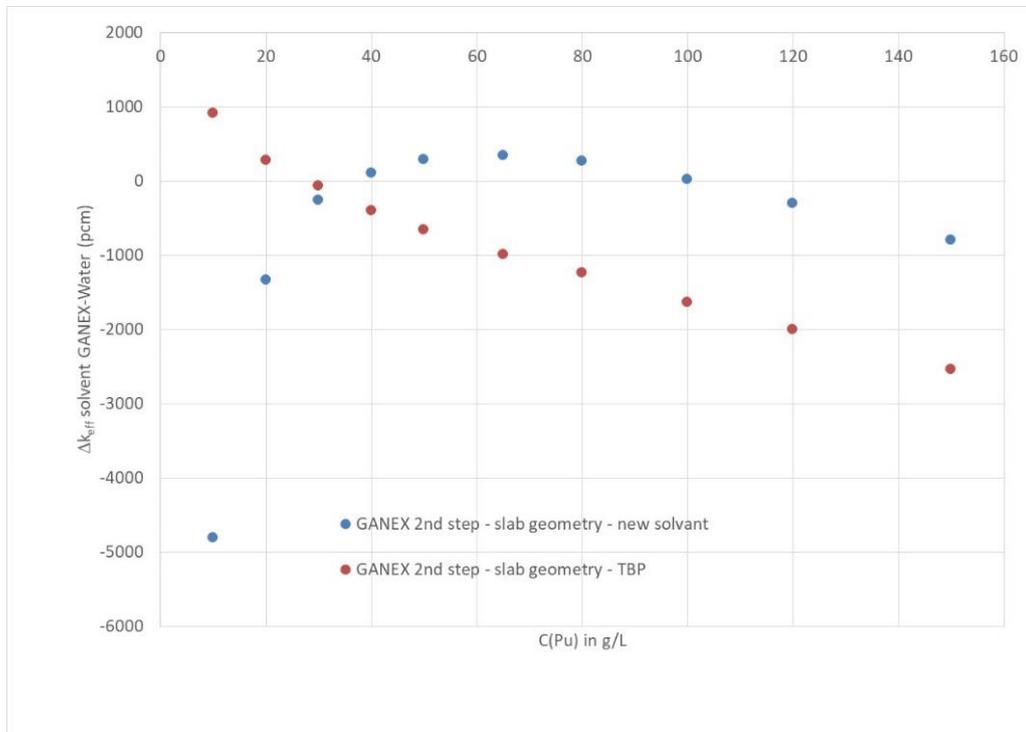


Figure 37: comparison of k_{eff} between water, new solvent and TBP/TPH for GANEX 2nd step – slab geometry.

One can see that for concentrations in UPu lower than ~ 70 g/L in the 1st step of the process, water is not conservative when compared with TBP/TPH. TBP/TPH is more conservative than the new solvent for concentrations lower than 100 g/L, then it is bounded by the new solvent.

In the 2nd step of the process, TBP/TPH is more conservative than water and the new solvent for concentrations in Pu lower than 25-30 g/L. For concentrations higher than 30 g/L, it is bounded by the new solvent and also by water.

However, as soon as at least 1 mol/L of nitric acid is taken into account in the solvent TBP/TPH, water becomes more conservative than TBP/TPH as a solvent from the viewpoint of criticality safety, as can be seen for the sphere geometry in Figure 38 and Figure 39.

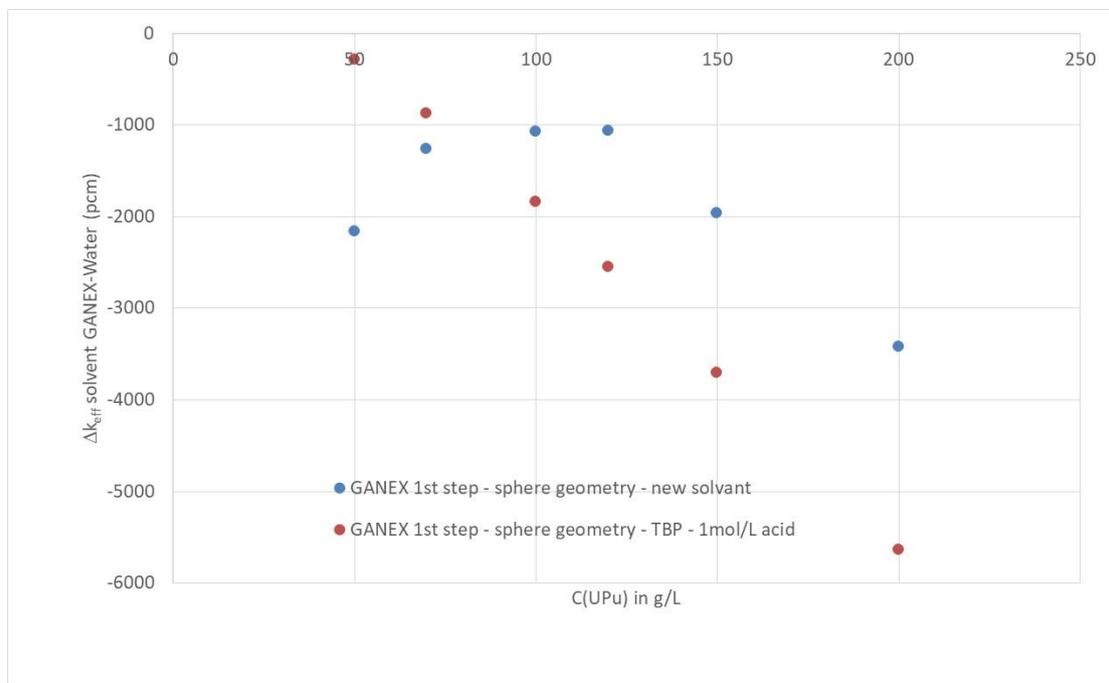


Figure 38: comparison of k_{eff} between water, new solvent and TBP/TPH (1 mol/L of acidity) for GANEX 1st step – sphere geometry.

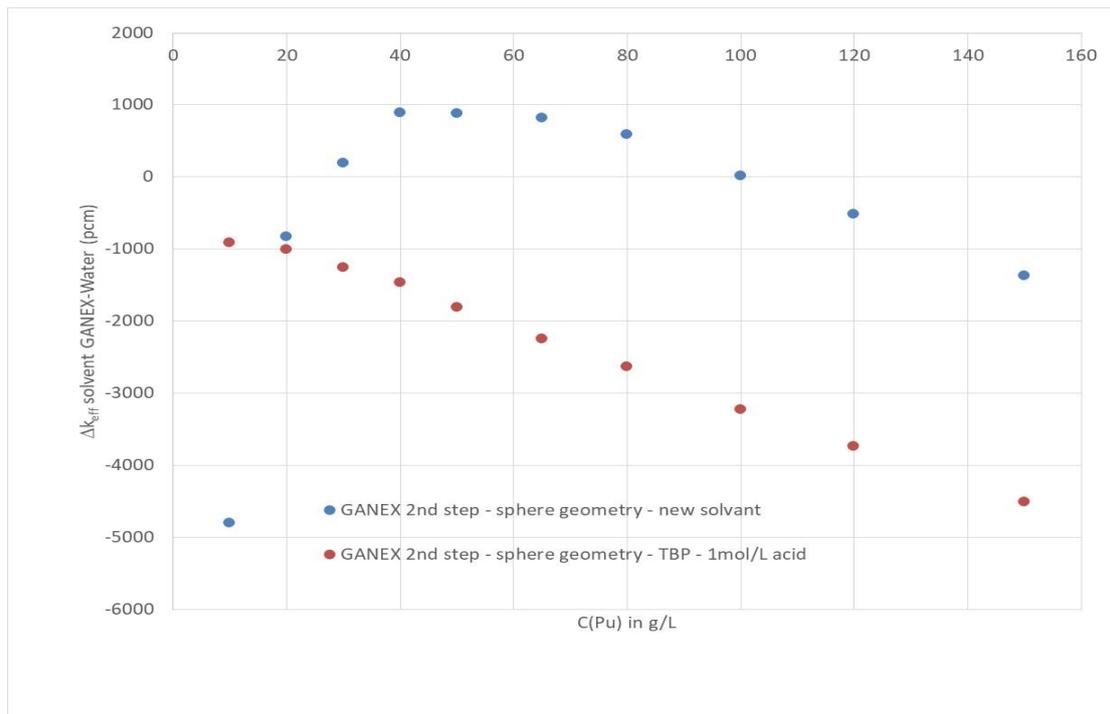


Figure 39: comparison of k_{eff} between water, new solvent and TBP/TPH (1 mol/L of acidity) for GANEX 2nd step – sphere geometry.

5. CONCLUSION

Density data of diluents and extractants acting as solvents for the various steps of the GENIORS process were gathered with the help of the GENIORS partners. In a previous report, IRSN defined the methodology for determining density laws for the new solvent [11]. In this deliverable, IRSN has compared standard critical values for different moderators: water, TBP/TPH and the new solvents of the GANEX process.

For a geometry criticality control mode, water moderator is conservative compare to the new solvent/diluent used in GANEX. It means that minimum critical values obtained with water moderator are always the lowest compare to the new solvent/diluent.

On the other hand, it appears that water does not systematically bound other moderators when the control mode is concentration, unless a certain level of acidity is considered. Special attention should be taken if the concentration control mode is used with solvent/diluent of GANEX 2nd STEP and 3rd STEP.

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7. APPENDIX

Derivation of the density of solutions

The aim of this appendix is to show how to determine numerically the density of the solution with the formulas given in the report and the data collected. This exercise is done with solutions of the first step of the GENIORS process.

In the first step of the process, the extractant is DEHIBA and the diluent TPH.

The below formulas, given in the report, are used for the calculation.

$$\rho_{\text{solution}} = C(\text{UO}_2(\text{NO}_3)_2) + C(\text{Pu}(\text{NO}_3)_4) + \rho_{\text{extractant-diluent}} \times \left(1 - \frac{C(\text{U})}{\rho(\text{U})} - \frac{C(\text{Pu})}{\rho(\text{Pu})}\right) \quad (11)$$

$$\rho_{\text{extractant-diluent}} = \left(C(\text{extractant}) + \rho_{\text{diluent}} \times \left(1 - \frac{C(\text{extractant})}{\rho(\text{extractant})}\right)\right) - 0.00072 \times (T - 25) \quad (12)$$

- **Data available (see Table 1):**

At 25 °C, the density of TPH is 0.7551 g/cm³ so $\rho_{\text{diluent}} = 0.7551 \text{ g/cm}^3$. $M_{\text{TPH}} = 170.337 \text{ g/mol}$.

At 25 °C, the density of DEHIBA is 0.8638 g/cm³, so $\rho(\text{extractant}) = 0.8638 \text{ g/cm}^3$. $M_{\text{DEHIBA}} = 311.55 \text{ g/mol}$.

The concentration of extractant in the solvent is 1.151 mol/L, so $C(\text{extractant}) = 1.151 \text{ mol/L} = 0.35859 \text{ g/cm}^3$ with $M_{\text{DEHIBA}} = 311.55 \text{ g/mol}$.

- **Calculation of density of solution:**

Using the previous data and formula (12), we obtain $\rho_{\text{extractant-diluent}} = 0.80022 \text{ g/cm}^3$.

- **Calculation of density of solution:**

The ratio in weight of plutonium (Pu/UPu) in the first step of the process is 18.05887 %, since the concentration in Pu is assumed to be 22.7 g/L and that in uranium 103 g/L (see flowsheet Figure 1).

If we assume a concentration in uranium of 103 g/L, the concentration in plutonium is 22.7 g/L. The isotopic vector of plutonium in wt. % is assumed to be 71/17/11/1 % for the exercise.

$\rho(U) = 1.3306 \text{ g/cm}^3$ since the density of U in $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$ crystal is 2.8 g/cm^3 [7]. Indeed,
 $(\rho(U) = d_{crystal} \times \frac{M_u}{M_{crystal}})$

$\rho(\text{Pu}) = 1.2024 \text{ g/cm}^3$ since the density of $\text{Pu}(\text{NO}_3)_4 \cdot 5 \text{ H}_2\text{O}$ crystal is 2.9 g/cm^3 [7].

⇓

$$C(\text{UO}_2(\text{NO}_3)_2) = C(U) \times M(\text{UO}_2(\text{NO}_3)_2)$$

$$C(\text{Pu}(\text{NO}_3)_4) = C(\text{Pu}) \times M(\text{Pu}(\text{NO}_3)_4)$$

With $M_{\text{UO}_2(\text{NO}_3)_2} = 394.0350 \text{ g/mol}$ and $M_{\text{Pu}(\text{NO}_3)_4} = 487.49045 \text{ g/mol}$.

As a result, $\rho_{solution} = 0.93989 \text{ g/cm}^3$.

This last density solution allows, with the other calculated values and data, to determine all species concentrations in solution need for criticality calculation.

Variation of k_{inf} and B^2_m versus concentration in U or Pu

In this section, one shows the variation of K_{inf} and B^2_m values versus moderation (Figure 40 through

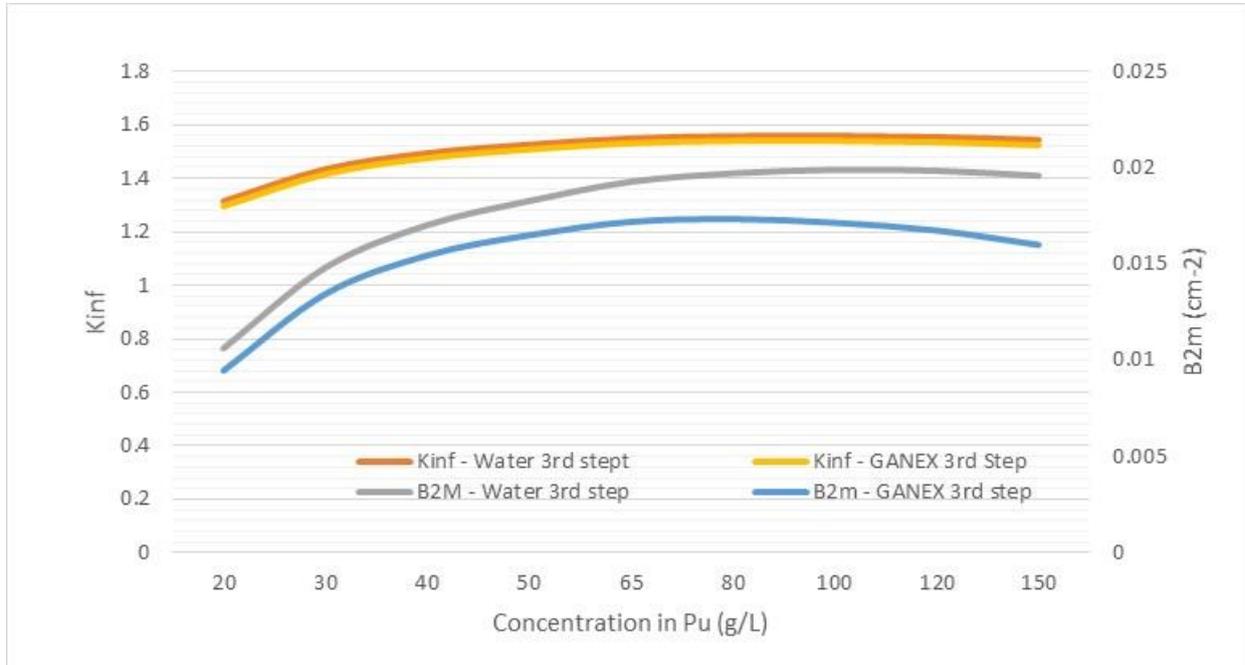


Figure 42).

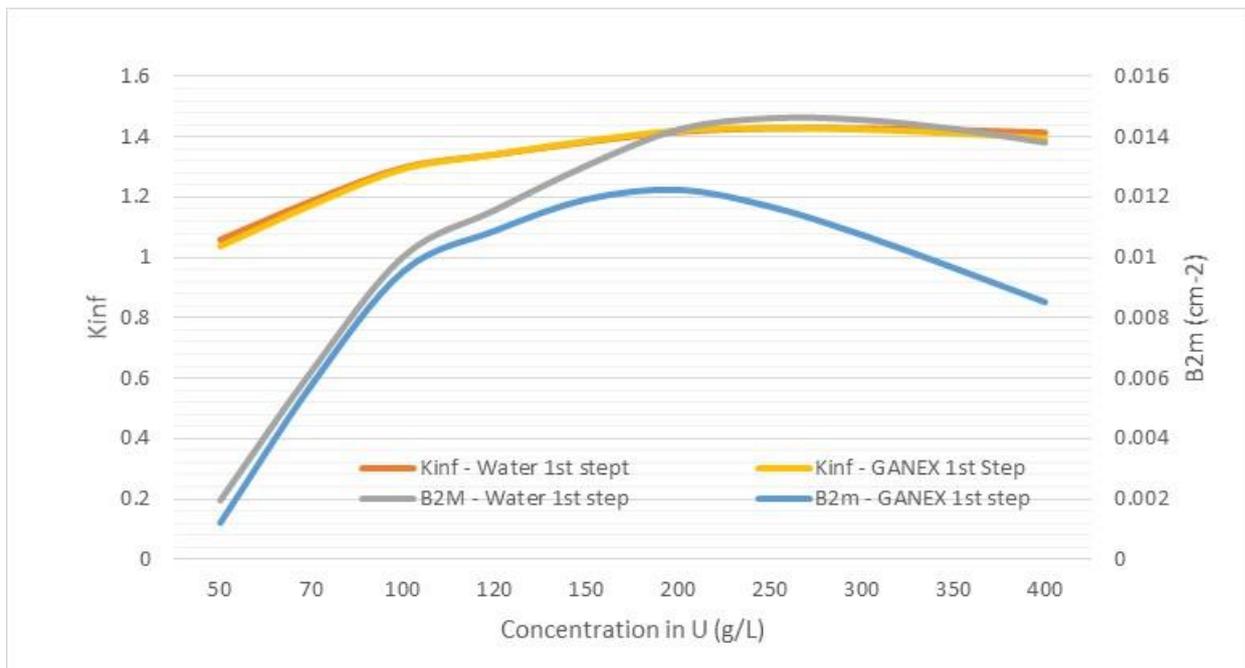


Figure 40: k_{inf} and B^2_m vs U concentration for GANEX 1st step.

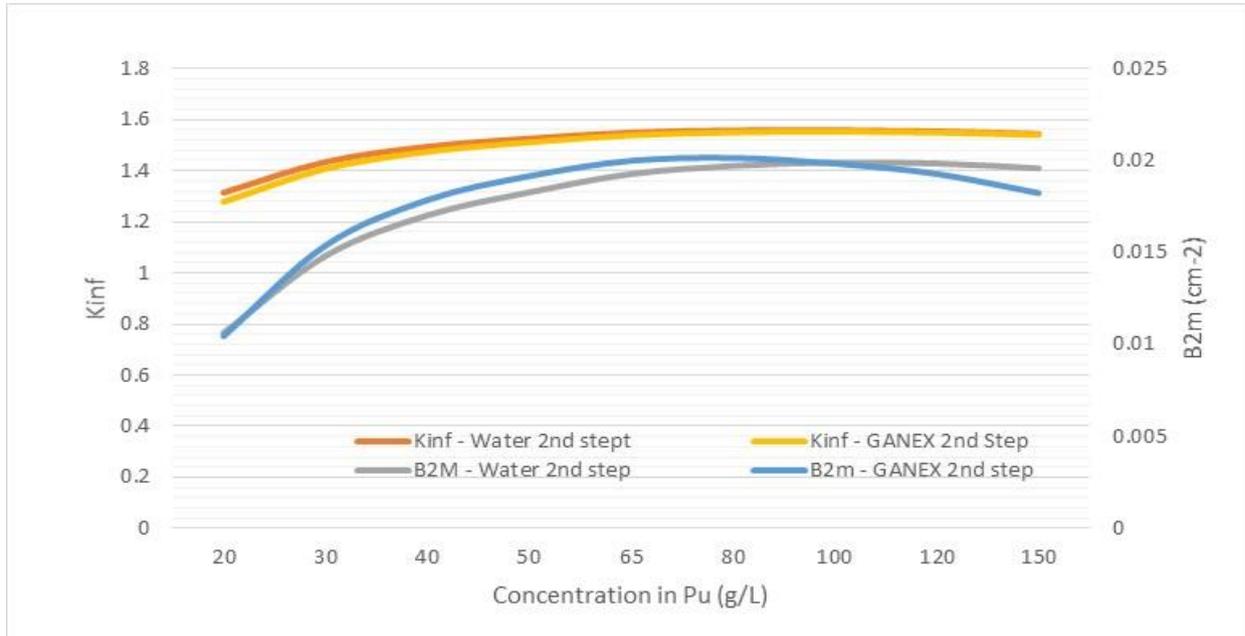


Figure 41: k_{inf} and B^2_m vs Pu concentration for GANEX 2nd step.

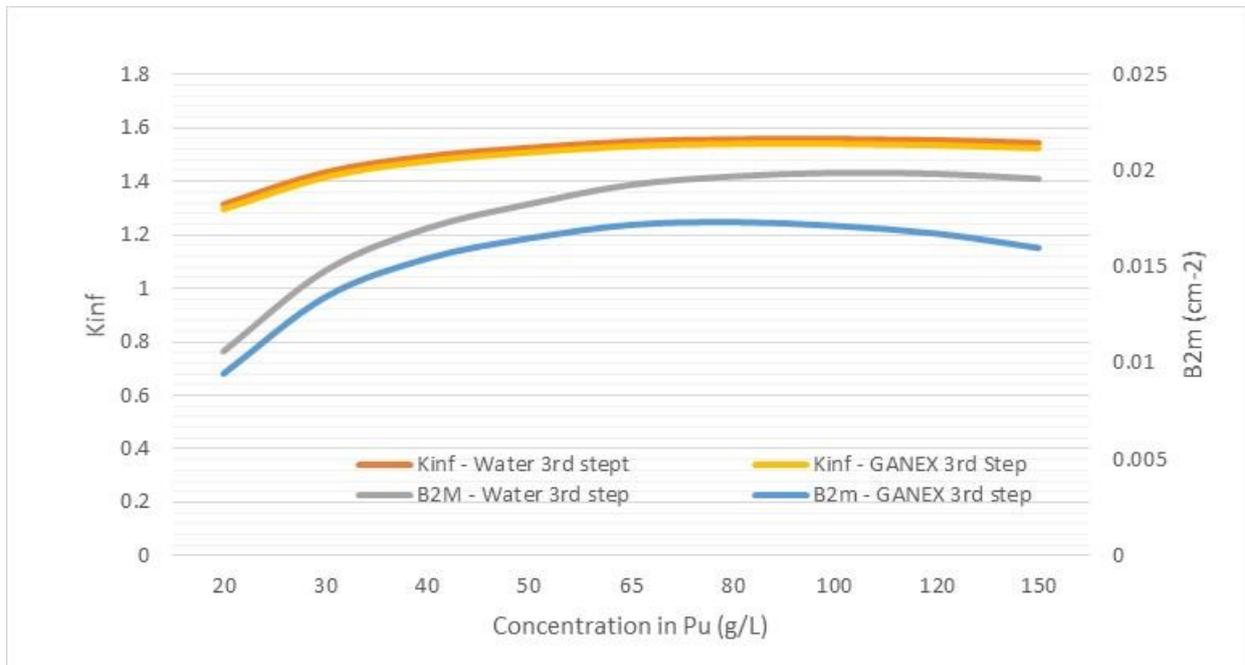


Figure 42: k_{inf} and B^2_m vs Pu concentration for GANEX 3rd step.

