Preparation and characterization of solid deposit samples from concentration evaporators and fission products tanks

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For the dismantling of reprocessing facilities at Marcoule, deposit solid samples coming from concentration evaporators and fission products tanks have been characterized in the laboratories and hot cells of the ATALANTE facility.
These experiments consisted in physicochemical measurements on high activity solid samples, specific dissolutions developments and characterizations of dissolution solutions and solid residues.
This work required R&D developments: technology (camera for macroscopic measurements, adapted equipment for samples recovery in hot cells, specific vials for solid analysis…), chemistry (dissolution conditions optimization) and analysis (Cs and Zr decontaminations, qualitative analyses on solid residues). Many analytical techniques have been used for these characterizations: γ and α spectrometry, isotope dilution by TIMS, L-line X-ray fluorescence, ICP/AES, ion exchange chromatography…
The dissolution process optimizations allowed to retain a dissolving protocol presenting the best dissolution yield of small actinide amounts initially present in deposit solid samples and of ^{137}Cs wich represents almost all of the initial β activity (> 99%). These developments have resulted in obtaining final dissolution residues whose dose rate does not exceed 0.1% of the initial solid aliquot dose rate (initially 1.4 Gy h^{-1} for 400 mg).
These characterizations allow determining the composition and nature of the fission products raffinates present in such reprocessing equipment. These data are essential for the definition of recovery scenarios and waste management.

KEYWORDS: characterization, decommissioning, fission products, dismantling, dissolution

Introduction

Within the framework of the dismantling projects of the CEA nuclear facilities, various investigations have been carried out in recent years on the UP1 reprocessing plant in Marcoule. These investigations concerned in particular the equipment of the fission products concentration room located in the High Activity (HA) area of UP1. An in-depth knowledge of the radiological and physico-chemical nature of the fission products raffinates present in such equipment is essential in order to apprehend the challenges involved in managing this waste: treatment processes choice, safety and radiation protection precautions, waste management and treatment...
Several samples were thus carried out on the deposits present in the concentration evaporators and fission product tanks of the UP1 plant for characterization. This paper deals in particular with the characterizations and R&D developments carried out in the laboratories and hot cells of the ATALANTE facility on solid deposit samples from the 71.26C concentration evaporator and 71.21A/B/C fission product tanks.

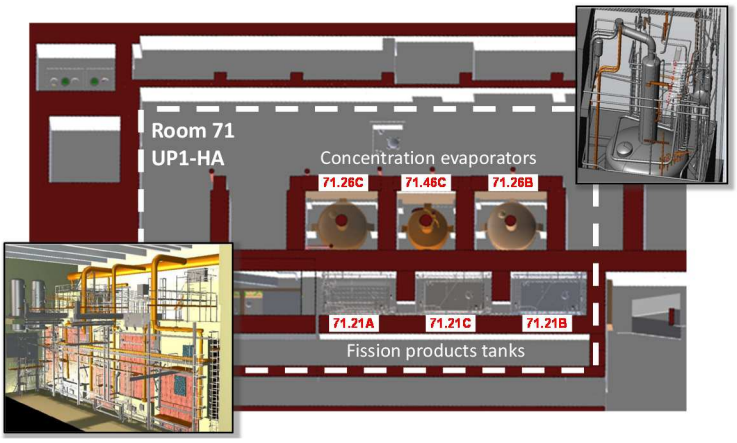

Figure 1: Room 71 - UP1 plant

1. Preliminary physico-chemical characterizations on solid deposits

Samples receipt and recovery

The samples from the tanks were taken using a mechanical device with pneumatic closure. This device is equipped with a window to visualize the sample volume taken (max. volume 20 cm^3). These samplers were then placed in crimped silicone packaging (*Fig. 2a and 2b*). The samples from the evaporators were carried out by means of a suction device and samplers were placed in screwed PVC containers (*Fig. 2c-2e*).

Figure 2: Devices and containers used for deposits from tanks (a) (b) and evaporator (c) to (e)

All the transports were carried out in PADIRAC RD-10. Each transport packaging was received on the Atalante facility and transferred to the rear area of the dedicated hot cell for connection and opening. For the opening, each sampler was positioned on a support developed specifically for this work (*Fig. 3*):

- In the case of tank samplers, the opening is made by means of a push screw. The deposit falls into a single-use wide neck glass vial (*Fig. 3c*).
- In the case of evaporator samplers, the opening is made by tipping the sample in a glass vial after having previously mechanically unscrewed the sampler on the dedicated support. (*Fig. 3e and 3f*).
- In most cases, samples are dry and easily recovered. For some wet deposits, a clean spatula was used to recover the residue.

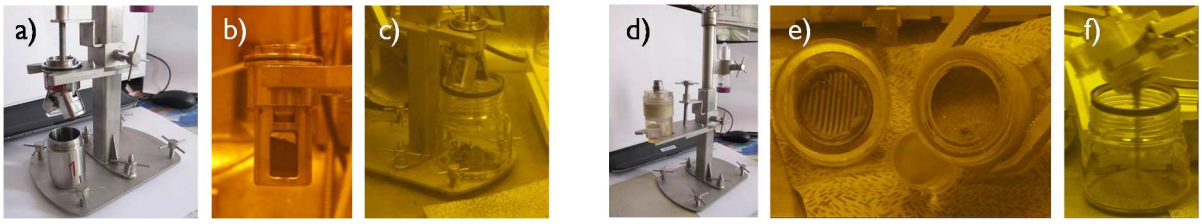

Figure 3: Opening of the tank samplers (a) to (c) and evaporator samplers (d) to (f)

Non-destructive analysis

Immediately after opening, each deposit was dried on a hot plate at 105 ℃ in its glass vial until a c onstant mass was obtained. The heating temperature was chosen on the basis of thermal drying industrial processes of sludges by conduction and limited by the use of the hot plate in the hot cell (T < 120℃). T he water content in each deposit varies between 9.1% and 40.3% (mass percentage).

Each sample was inspected using a Cyberia camera adapted to hostile environments and specially nuclearized. Before drying, the wettest deposits form sticky and dark-colored agglomerates (*Fig. 4a*), unlike the driest ones, easily friable, which form clusters of several millimeters in diameter. After drying, the grain size varies from a few dozens of microns to several millimeters. Some of deposits may be powdery and relatively homogeneous grey in color (*Fig. 4b and 4c*).

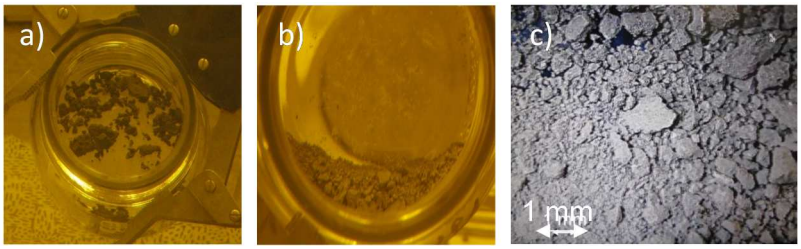

Figure 4: Deposits appearance before (a) and after (b) drying, (c) example of macroscopy on a dry deposit

Variable masses were recovered after drying, in the order of 5 to 25 g per sample. After reconditioning in stainless steel vials, the dose rate of each sample was measured using an *IF104* remote flow meter and a gamma *SHI* probe specifically calibrated with ^{137}Cs (E = 661,66 keV). The dose rate values are in the order of 0.1 - 0.2 Gy/h per gram of dry deposit for solid samples from the evaporator and vary between 0.9 and 2.7 Gy/h per gram of dry deposit for solid samples from the product fission tanks (*Fig. 6*).

Investigation of deposits heterogeneity and preparation of the average samples

In order to quantify the heterogeneity of the samples for a same equipment, qualitative analyses were carried out on a solid aliquot of each sample (400 ± 10 mg), previously dried at 105℃. These solid aliqu ots have been packaged in a new conical shaped vial model, specially developed for the analysis of small solid sample masses from A&D nuclear facilities: these are in polycarbonate, with a screw cap having a seal and equipped with a PTFE septum ensuring the tightness (*Fig. 5*). The dimensions of these small vials fit perfectly to those of the shuttles used for the analysis of liquid samples and have a square foot for self-centering in the shuttle of analysis.

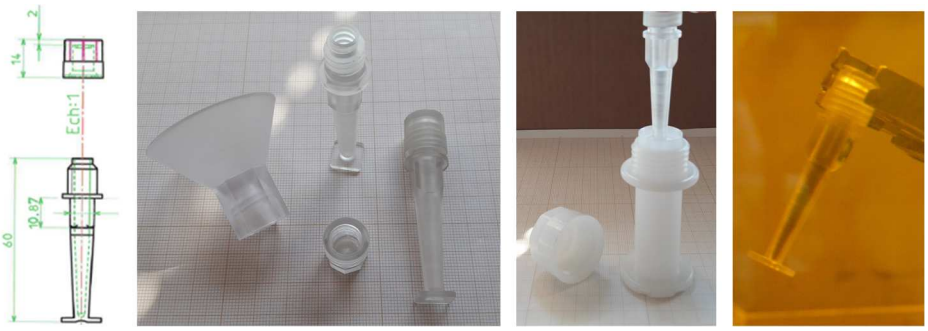

Figure 5: New conical shaped vial model for small solid samples analysis

Each solid aliquot was analyzed by gamma spectrometry and L-line X-ray Fluorescence (L-line XRF) in High Activity hot cell. The dose rate values obtained on these aliquots confirm the trend observed for measurements made on all deposits (*Fig. 6*): these aliquots are well representative of the initial samples.

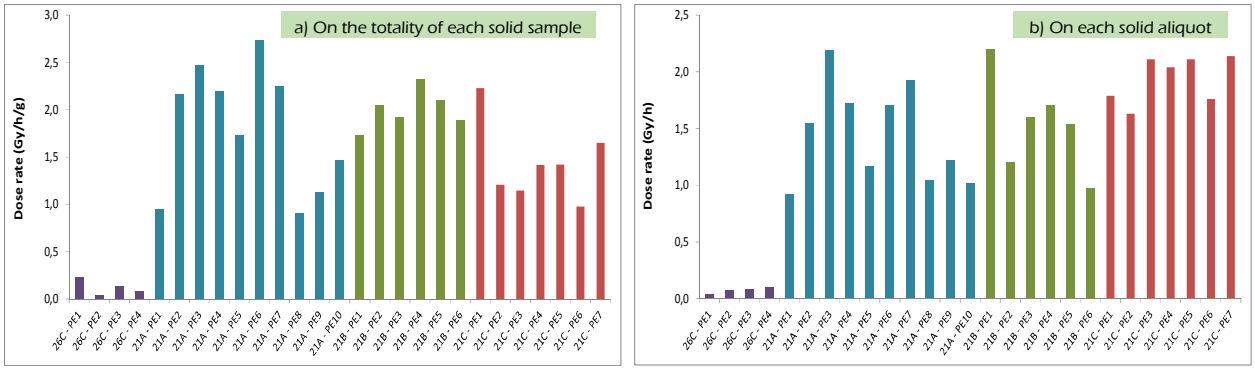

Figure 6: Comparison of measured dose rate between totality of samples (a) and solid aliquots (b)

Signal acquisition and data processing were carried out using equipment distributed by MIRION: the detectors are composed of hyper-pure Ge crystals cooled with liquid nitrogen and the acquisition electronics are controlled by a DSA-LX analyzer coupled with Genie 2000 software. The gamma spectrometer used is equipped with a controllable carousel supporting a set of interchangeable collimators, located between the detector and the sample, for high activity measurement. For the L-line XRF analyses, a graphite monochromator, located between the detector and the sample, works as a discriminatory filter. It allows to select a reduced energy band, centered on the L line of the Pu (at 14.28 keV), according to the Bragg law. The spectra are obtained using softwares specifically developed for this technique *[1].*

In order to estimate the contribution caused by these two analytical techniques to the dispersion of the measurement results, repeatability tests were carried out on the same solid aliquot by gamma spectrometry (3 replicates) and L-line XRF (8 replicates):

- the relative standard deviation (RSD) between the three γ-measurements is less than 5 % for the major γ-emitter (^{137}Cs),
- the relative standard deviation (RSD) between the eight XRF measurements is less than 1% for Zr (major element) and less than 9% for Pu (minor element).

The same operating conditions were maintained for the qualitative analysis of each solid aliquot. The gamma and L-line XRF spectra obtained for the aliquots from 71.21C fission product tank are shown in *Fig. 7* and *Fig. 8*. These qualitative analyses showed a relative homogeneity of the deposits: the RSD is 22% for the major γ-emitter (^{137}Cs), 17% for Zr (major element XRF) and 19% for Pu (minor element XRF). The same orders of magnitude were obtained on the aliquots of the other equipment.

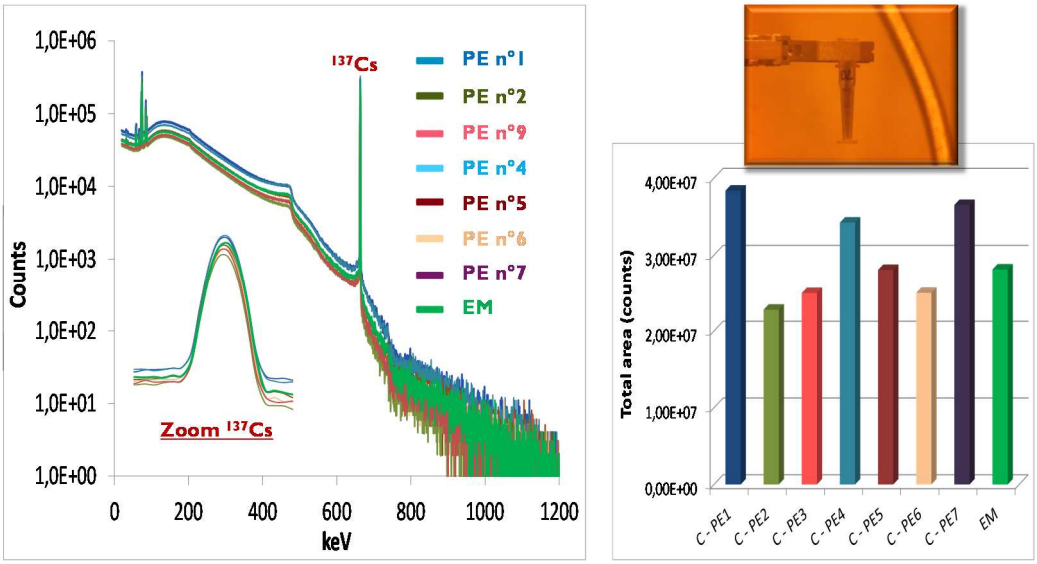

Figure 7: Gamma spectra of solid aliquots of each sample from 71.21C fission product tank

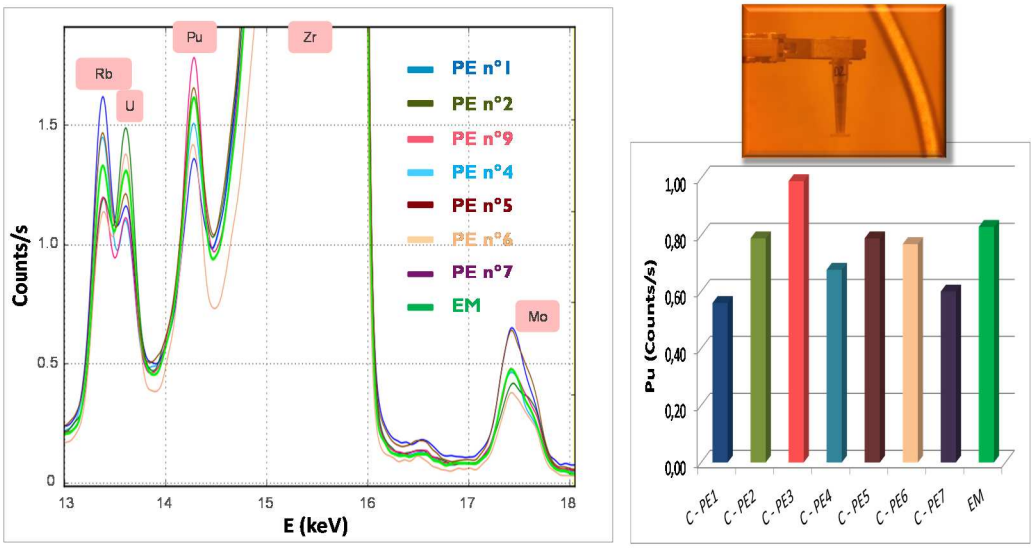

Figure 8: **L-line XRF spectra of solid aliquots of each sample from 71.21C fission product tank**

Considering the method repeatability, the observed dispersions can be mainly attributed to the heterogeneity of the samples. Theses dispersions were considered acceptable and an “average” sample representative from the whole batch was prepared from an equi-massic mixture of each sample. A solid aliquot of 400 ± 10 mg was analysed by gamma and L-line XRF spectrometry, under the same operating conditions. The results are shown in Fig. 7 and Fig. 8 for the average sample of the 71.21C tank (in green).

2. Optimization of dissolution conditions

Dissolution of solid deposits from 71.26C evaporator

For the characterization of solid deposits from the evaporator, two experimental protocols were implemented on two distinct aliquots from the same sample:

- The first dissolution protocol (*Protocol 1*) is composed of a single step: dissolution in HNO_3/HF 7M/11M medium at 70°C for 24 hours.
- The second dissolution protocol is composed of two successive stages (*Protocol 2*):
  - o primary dissolution in HNO_3/HF 3M/3M at 70°C for 24 hours,
  - o secondary dissolution of residues in HNO_3/HF 7M/11M at 70°C for 24 hours.

The dissolutions were carried out in small volume cylindrical perfluoroalkoxy reactors positioned in a container with sand to ensure good temperature homogeneity around the reactor (*Fig. 8a*). At the end of each dissolution step, the dissolution solution is filtered (*Fig. 8b*). The filter, a mixture of cellulose esters, is then dried on a hot plate at 105°C for 4 hours and then air calcined at 400°C for 4 hours in a cylindrical vertical furnace (*Fig. 8c*). The calcined residue (*Fig. 8d*) of the second dissolution undergoes an additional heat treatment: it is air calcined at 800°C for 4h in th e same cylindrical furnace.

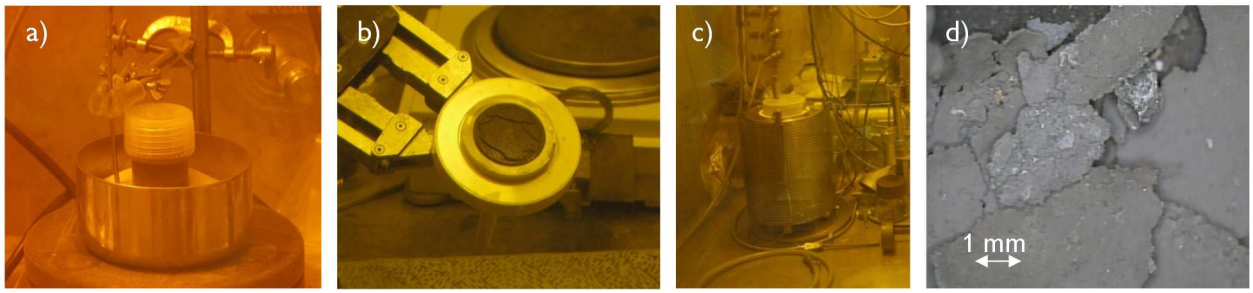

Figure 8 : Illustrations of each dissolution steps: experimental set-up (a), filter support (b), calcination furnace (c), calcined residue (d)

In order to evaluate the dissolution performance of the two protocols used, each solid residue was analyzed by gamma and XRF spectrometry. These qualitative analyses enable, by comparison with the spectral signatures of the initial solid aliquot, to assess the good recovery performance of the total gamma activity (provided essentially by ^{137}Cs) and actinides U and Pu (*Fig. 9*).

The results obtained indicate that a single step dissolution (*Protocol 1*) with high concentrations of HNO_3 and HF does not fully recover ^{137}Cs activity and actinides (U, Pu). The XRF spectral signature of the final dissolution residue (grilled at 800°C) indeed shows the significant presence of U and Pu and clearly shows a lack of actinide dissolution efficiency. *Protocol 2* presents a very good recovery efficiency of U and Pu as well as of the ^{137}Cs activity of the residues. The latter was therefore renewed for solid samples from the fission products tanks (71.21 A/B/C).

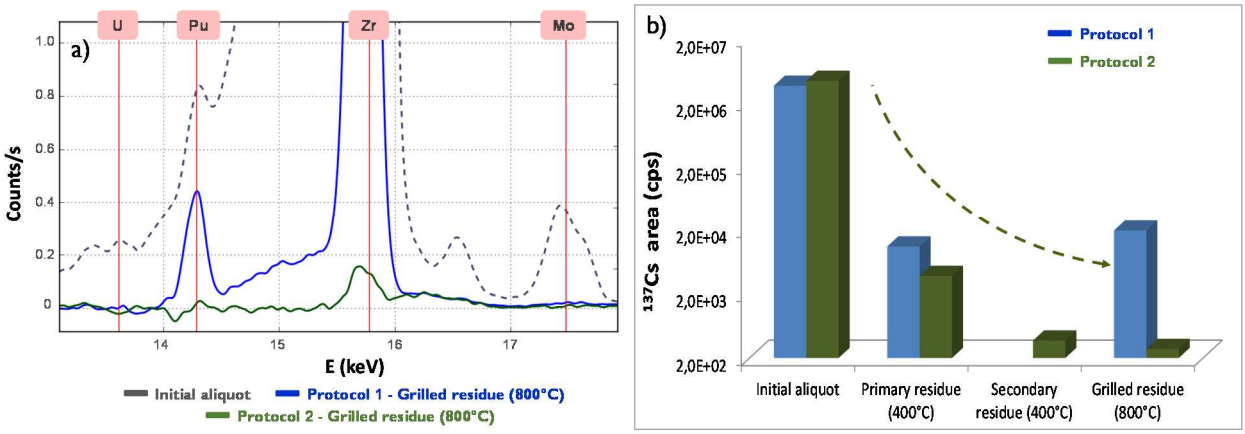

Figure 9 : Comparison of the solid residues obtained by dissolution protocols 1 and 2 used for the evaporator 71.26C: a) XRF spectra, b) ^{137}Cs peak area

Dissolution of solid deposits from fission products tank

A first test carried out on the average sample from a tank with *Protocol 2* showed that:

- gamma activity was recovered to more than 90% from the first stage of dissolution,
- the plutonium in the final residue (grilled à 800°C) is present in significant quantity (Fig. 10).

Although the dissolution conditions are identical to those carried out for the deposits from the evaporator, *Protocol 2* did not recover all the plutonium initially present in the solid aliquot of the tank. On the basis of work in the literature, several hypotheses can be put forward to explain the low recovery efficiency of plutonium with concentrated hydrofluoric acid attack solutions:

- precipitation of PuF_4 whose solubility decreases with increasing concentration of hydrofluoric acid above 0.5M *[2]*,
- the presence of Pu(III), resulting from the presence of hydrogen peroxide in solution, and the formation of PuF_3 complexes even less soluble than those of PuF_4 *[3]*,
- the creation of a passivation layer on the surface of the grains due to the high content of HF.

These hypotheses corroborate the results obtained when comparing the two experimental protocols for the dissolution of solid deposits from 71.26C evaporator.

In order to quantitatively recover the plutonium in the second dissolution step, the operating conditions had to be optimized. Laboratory studies show that plutonium recovery efficiency increases when the nitric acid concentration is high (above 10M) with a low hydrofluoric acid concentration (below 0.1M). On the basis of these studies, the second stage of the protocol was adapted: an HNO_3/HF 12.2M/0.05M solution was used (*Protocol 3*). The results obtained show very good recovery yields of actinides (*Fig. 10* in blue) and gamma activity (*Fig.11a*) after these two successive dissolutions. This very good dissolving performance has resulted in obtaining final dissolution residues whose dose rate does not exceed 0.1% of the initial solid aliquot dose rate (initially 1.4 Gy h^{-1} for 400 mg, *Fig 11b*).

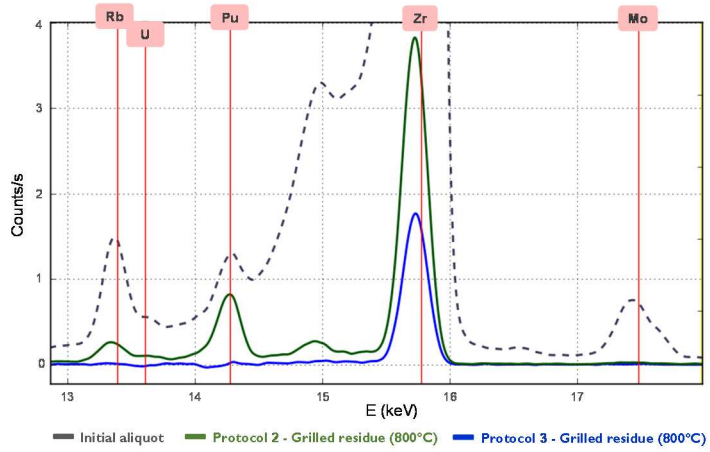

Figure 10 : Comparison of the solid residues obtained by dissolution protocols 2 and 3 used for the tanks

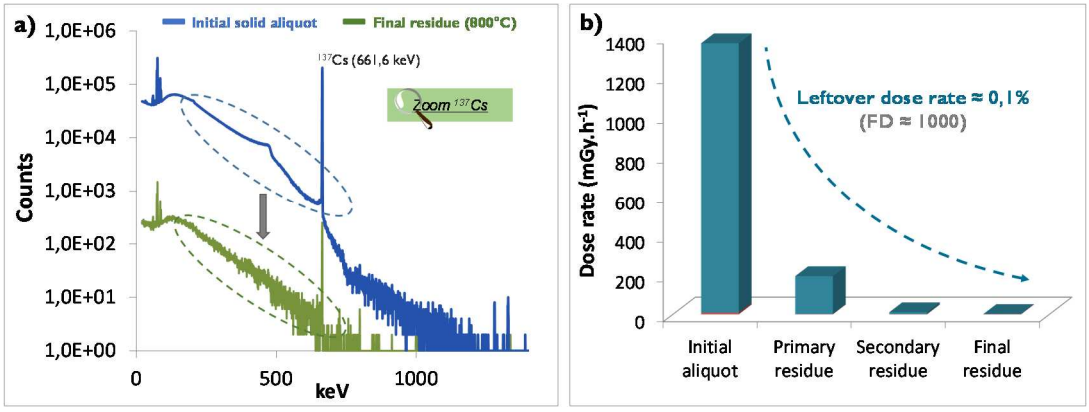

Figure 11: Example of dissolution performance: a) comparison of qualitative gamma analyzes on solid, b) leftover dose rate and decontamination factor

3. Characterization of dissolution solutions

For the characterization of dissolution solutions, different analytical techniques have been implemented in hot cells and glove box laboratories dedicated to MA/FA activities: α and γ spectrometry, isotope dilution by TIMS (*Thermal Ionization Mass Spectrometry*), L-line X-ray fluorescence, ICP/AES (*Inductively Coupled Plasma Atomic Emission Spectroscopy*), ion exchange chromatography… All these analytical operations are illustrated *Fig. 12*. This synoptic has been established in order to optimize:

- the required volumes of solution for each analytical technique used,
- the sequence of analytical operations,
- the chemical dilutions and/or separations to be carried out, according to the detections limits (*LD*) to be achieved.

Since dissolution solutions are mainly composed of fission products, they present strong gamma activities. In order to minimize the impact on the detection limits of analyses performed in MA/FA laboratories, it was necessary to treat each solution of dissolution. Since ^{137}Cs represents the major of the gamma activity of the sample (> 99% of the total γ activity), a Cs decontamination by extraction chromatography has been specially developed for this type of solution.

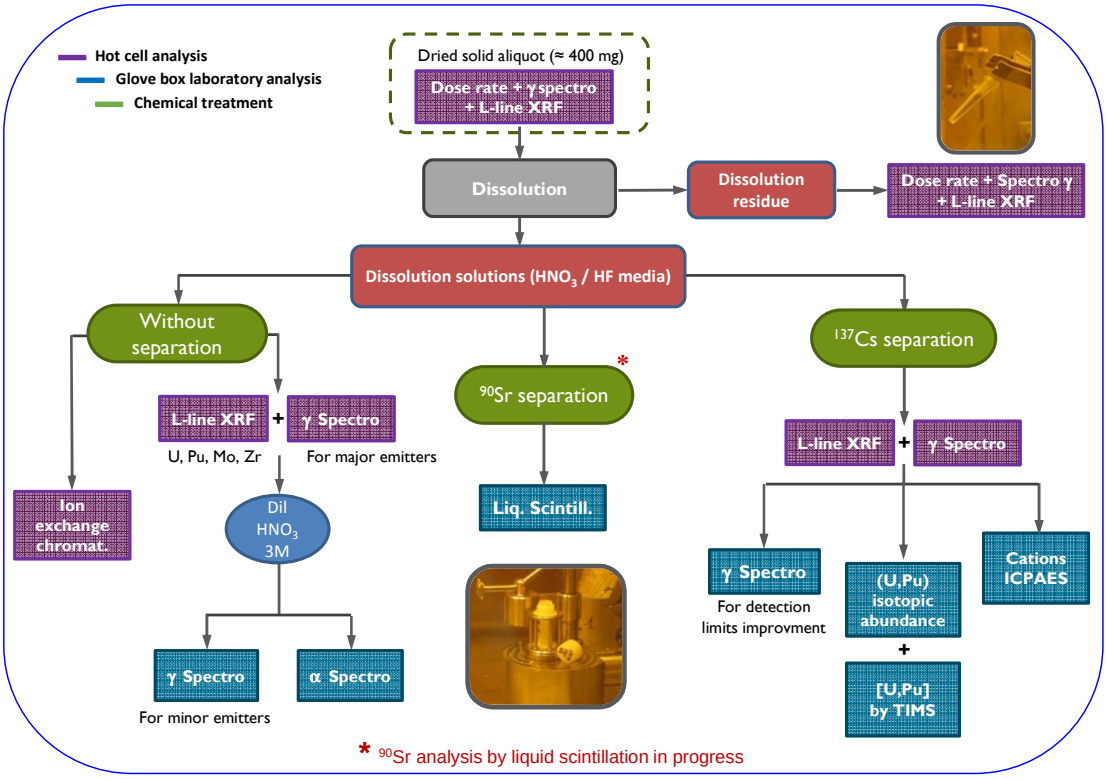

Figure 12: Analytical synopsis for the characterization of dissolution solutions

The column used is a Triskem AMP-PAN column, chosen for its separating properties [4-6]. The R&D work carried out for this study led to the following performances [7]:

- recovery yield of cations other than Cs greater than 98%, except for Ag, Pd and Mo (molybdophosphonate resin),
- decontamination factor greater than 50 000 and drastic reduction of dose rate,
- volumes involved inducing a dilution factor of 4 (compared to the usual factors 500 to 1000 for this type of sample), in order to be able to analyse dissolution solutions in glove box laboratories.

An example of Cs decontamination is shown *Fig. 13.* The gamma spectrum before Cs separation presents an important Compton front, due to the phenomenon of inelastic diffusion of photons in the detector. Gamma emitters with lower activity and energy than ^{137}Cs are therefore masked by the Compton front, which causes detection limits degradation. On the contrary, the gamma spectrum after Cs separation shows a significant signal-to-noise (S/N) ratio, allowing the determination of the weak activities of the γ emitters present in solution.

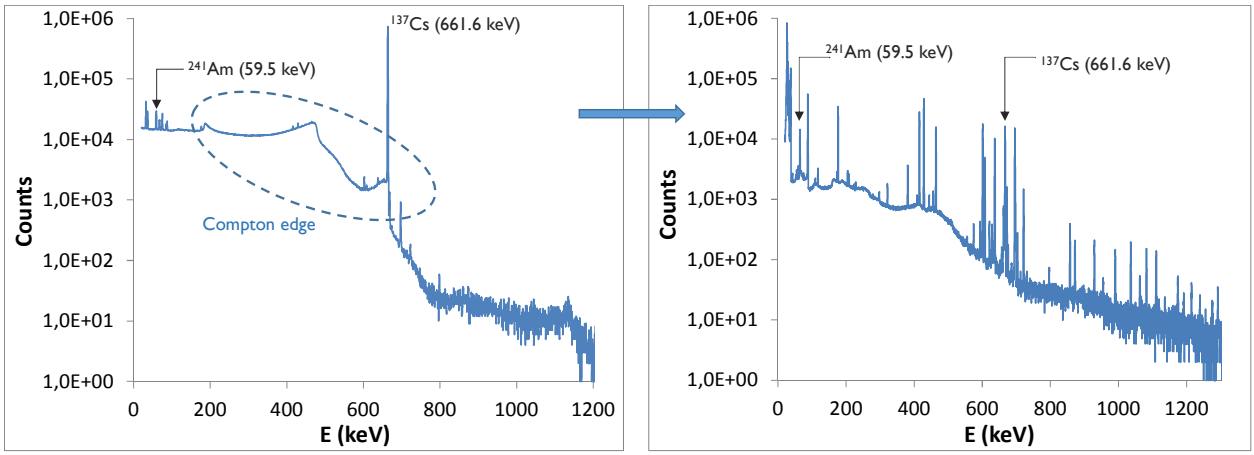

Figure 13: Comparison of gamma spectral signatures before and after Cs decontamination

Thanks to these chemical separations, analyses by alpha and gamma spectrometry, ICP/AES and TIMS were carried out in laboratories. This has drastically reduced detection limits, by a factor of 10 to 100 depending on analytical techniques. The most significant analytical results are presented below (*Tables 1 to 5).* They are expressed in milligrams and becquerels per gram of dry solid aliquot used for dissolutions.

		^{137}Cs	^{241}Am	^{125}Sb	Tot. act.	[(^{137}Cs)/Tot. act.] ratio
Evapo 71.26C	activity (Bq/g)	**5.18×10^{8}**	8.2×10^{5}	2.08×10^{6}	**5.22×10^{8}**	**99.30 %**
	unc. (k=2)	0.46×10^{8}	1.4×10^{5}	0.34×10^{6}	0.46×10^{8}	-
Tank 71.21A	activity (Bq/g)	**9.39×10^{9}**	2.82×10^{6}	1.50×10^{6}	**9.40×10^{9}**	**99.94 %**
	unc. (k=2)	0.89×10^{9}	0.35×10^{6}	0.15×10^{6}	0.89×10^{9}	-

Table 1: Major gamma emitters

		Tot. act.	[(^{241}Am)/Tot. act.] ratio
Evapo 71.26C	activity (Bq/g)	4.50×10^{6}	18.22 %
	unc. (k=2)	0.45×10^{6}	-
Tank 71.21A	activity (Bq/g)	6.52×10^{6}	43.25 %
	unc. (k=2)	0.68×10^{6}	-

Table 2: Alpha emitters

		U	Pu
Evapo 71.26C	Concentration (mg/g)	**1.23**	**0.334**
	unc. (k=2)	0.21	0.033
Tank 71.21A	Concentration (mg/g)	**0.464**	**0.743**
	unc. (k=2)	0.054	0.074

Table 3: (U, Pu) actinides

		Al	Ca	Cr	Fe	Mo	Na	Ni	Pd	Zr	PO_4^{3-}
Evapo 71.26C	Concentration (mg/g)	2.18	0.909	15.7	40.0	30.4	16.7	15.7	16.2	203	233
	unc. (k=2)	0.42	0.086	1.5	4.0	9.0	2.9	1.4	1.6	20	24
Tank 71.21A	Concentration (mg/g)	3.49	3.13	1.88	11.3	58	2.28	3.67	< 0.51	198	272
	unc. (k=2)	0.44	0.33	0.17	1.1	17	0.20	0.99	-	20	27

Table 4: Major anions and cations

Note: Silicon is a chemical element commonly found in this type of deposits, it has been analyzed by ICP-AES. However, part of the material of this instrument (torch, nebulizer and nebulization chamber) is made of quartz. The risk of Si pollution during analysis is high because of the high HF content (glass attack): consequently, the silicon value obtained was not been returned.

In order to consolidate the results, internal verifications by "cross-checking" of different analytical methods were carried out on certain elements: this is notably the case for U, Pu and Zr. The values obtained are comparable, taking into account the measurement uncertainties (*Table 6*):

		XRF	α spectro	TIMS	ICPAES
Tank 71.21A	Concentration U (mg/g)	**0.510**	-	**0.464**	**-**
	unc. (k=2)	0.097	-	0.054	-
	Concentration Pu (mg/g)	**0.77**	**0.743**	**0.74**	**-**
	unc. (k=2)	0.18	0.074	0.10	-
	Concentration Zr (mg/g)	**198**	-	-	**207**
	unc. (k=2)	20	-	-	20

Table 5: Comparison of U / Pu / Zr concentrations obtained par XRF, α spectrometry, TIMS and/or ICPAES

To quantify by XRF the minor elements U and Pu relative to the major element Zr present in solution (concentration factor > 250), *chemical separations of the Zr* had to be performed. These separations by extraction chromatography on a UTEVA resin were carried out according to different chemical steps [8] summarized below:

- oxidation of U and Pu to valence VI by addition of Ce(IV),
- neutralization of fluoride ions by addition of $Al(NO_3)_3$,
- selective fixation of U(VI) and Pu(VI) with concentrated nitric acid (8M),
- elution of U(VI) and Pu(VI) with a mixture HNO_3/HF 0.05M/0.05M.

After separation, each dissolution solution was sufficiently decontaminated to allow quantitative measurement of U and Pu by XRF (*Table 4*). An example of L-line XRF spectra obtained before and after Zr separation is shown in *Fig. 14*.

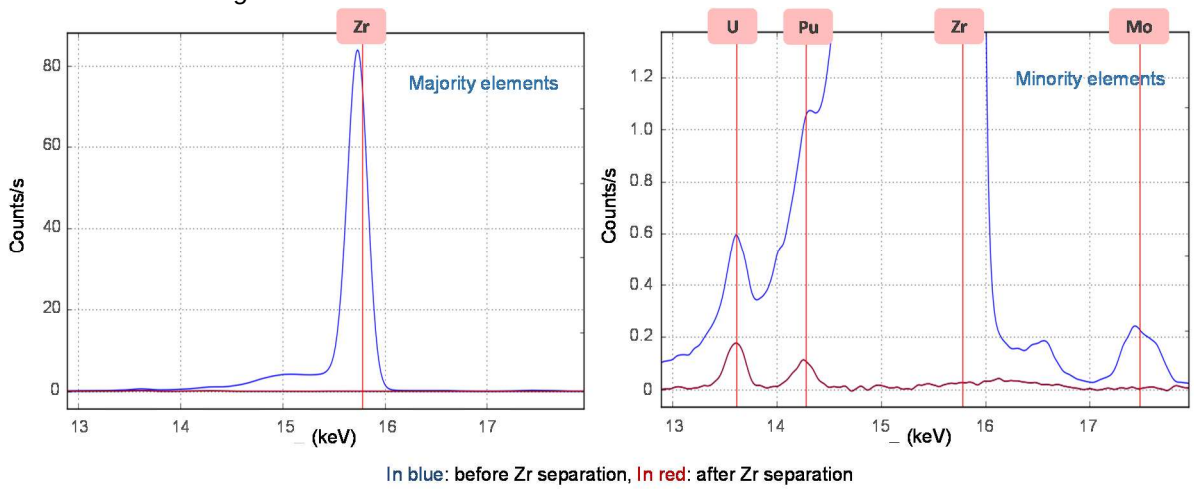

Figure 14: Example of L-line XRF spectra obtained before and after Zr decontamination

Conclusion

For the dismantling of reprocessing facilities at Marcoule, deposit solid samples coming from concentration evaporators and fission products tanks have been characterized in the laboratories and hot cells of the ATALANTE facility. These experiments consisted in physicochemical measurements on HA solid samples, specific dissolutions developments and characterizations of dissolution solutions and solid residues.

The results obtained during the optimization of the dissolution conditions have shown that:

- the recovery of the activity of the deposits is governed by an equimolar mixture of nitric acid and hydrofluoric acid not exceeding 3M,
- the plutonium recovery is favored by a high concentration of nitric acid (> 10 M) and a low concentration of hydrofluoric acid (<0,01 M).

Complementary tests are underway to reduce the number of dissolution stages of this type of deposit.

After optimization of the dissolution conditions, a complete analysis of the dissolution solutions and associated solid residues was carried out in hot cells and glove box laboratories. Many analytical techniques have been used for these characterizations: γ and α spectrometry, isotope dilution by TIMS, L-line X-ray fluorescence, ICP/AES, ion exchange chromatography… In order to minimize the impact on the detection limits of analyses performed in glove box laboratories, it was necessary to realize a Cs decontamination on each solution of dissolution, specially developed for this type of solution. This has drastically reduced detection limits, by a factor of 10 to 100 depending on analytical techniques.

The dissolution process optimizations allowed to retain a dissolving protocol presenting the best dissolution yield of small actinide amounts initially present in deposit solid samples and of ^{137}Cs wich represents almost all of the initial β activity (> 99%). These developments have resulted in obtaining final dissolution residues whose dose rate does not exceed 0.1% of the initial solid aliquot dose rate.

These characterizations allow determining the composition and nature of the fission products raffinates present in such reprocessing equipment. These data are essential for the definition of recovery scenarios and waste management.

Acknowledgment

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