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Effects of irradiation on the insolubility of sodium fast reactor $(U,Pu)O_2$ mixed oxide with a very high amount of plutonium

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HIGHLIGHTS

- Dissolution tests were carried out with irradiated and uniradiated MOX pellets containing 45% of plutonium.
- As expected, the pellets exhibit a high insolubility due to the amount of plutonium.
- Despite the lack of data at such high plutonium content, the insolubility and dissolution rates seem consistent with the literature.
- A beneficial effect of irradiation on the insolubility is observed and discussed.

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ABSTRACT

Sodium fast nuclear reactors might operate with MOX fuels containing up to 45% of plutonium, nevertheless, the reprocessability of spent nuclear fuel is sparsely investigated in the literature for plutonium contents higher than 30%. The dissolution step is a critical stage for MOX fuels since plutonium oxide exhibits a much slower dissolution kinetics as compared to uranium oxide. In particular, many authors suggested a significant change in the dissolution behavior of mixed oxides for plutonium contents between 30% and 50%. In this paper, the dissolution tests of unirradiated and irradiated CAPRA pellets with an initial plutonium content of 45% is described. Up to our knowledge, this is the first dissolution test reported in the literature with such high plutonium content in irradiated nuclear fuel. The fresh unirradiated pellets appears almost insoluble due to a very slow dissolution kinetics. Although the insolubility remains high after irradiation, a beneficial effect of irradiation on the dissolution behavior is observed with a depletion factor of five. The dissolution rates observed are very consistent with previous studies reported in the literature. The results show that complementary steps such as fuel pre-treatment or depletion steps should be considered in order to recycle spent nuclear fuel highly enriched in plutonium.

1. Introduction

The use of nuclear reactors for electricity production has led to the accumulation to several hundreds tons of plutonium through the last decades [14]. In order to stabilize the plutonium inventory, reprocessing of fuel as fresh fuel is considered not only for reducing the amount of radioactive waste, but also to overcome the use of fossil uranium ore. Reprocessing of plutonium is already partially carried out in France, for example, through the use of Mixes OXide (MOX) fuels, containing around 10%[1] of recycled plutonium, in Pressurized Water Reactors (PWR). Nevertheless, Generation-IV fast reactors, which can operate with high plutonium content fuels, are needed in order to fully close the nuclear cycle, relying on multiple recycling of plutonium [23]. Among these reactors, the sodium fast burner reactor can handle MOX fuels containing up to 45% of plutonium [3]. However, very few investigations regarding the reprocessing of such high plutonium content fuel are available in the literature, especially after irradiation due to the scarcity of such fuels and the difficulties for handling them. The aim of the European PuMMA project (https://pumma-h2020.eu/) is to extend the qualified domain of spent MOX fuel reprocessing to the highest plutonium contents, up to 45%.

The reprocessing of spent fuel by the hydrometallurgical route, as carried out in the PUREX process, starts with the dissolution of the fuel in hot nitric acid [11]. This first step can be considered as one of the limiting steps as the plutonium content increase since the dissolution

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[1] Unless specified otherwise, the plutonium content refers to the weight %Pu/(U+Pu) ratio in this paper.

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Nomenclature

c	empirical adjustment factor,
d	pellet density, g.cm^{-3}
d_{th}	theoretical pellet density, g.cm^{-3}
E	activation energy, kcal.mol^{-1}
F	surface evolution function, -
k	dissolution rate constant for Eq. (2), g.cm^{-2}.min^{-1}.(mol.L^{-1})$^{-1.74}$
m_{Pu}^{disso}	mass of dissolved plutonium, Mg
m_{Pu}^{frag}	mass of plutonium in the pellet fragments, Mg
m_{Pu}^{res}	mass of plutonium in the residues, Mg
r	dissolution rate (mass), mg.cm^{-2}.min^{-1}
r'	dissolution rate (molar), mol.cm^{-2}.min^{-1}
R	ideal gas constant, J.mol^{-1}.K^{-1}
S_0	initial geometrical surface area, cm^2
T	temperature, °C
W	mass of dissolved fuel, G
x	plutonium content in mass = Pu/(U+Pu), -

Greek letters

λ	empirical adjustment factor, -
τ_{Pu}^{res}	partial plutonium insolubility ratio, -
τ_{Pu}^{tot}	total undissolved plutonium ratio, -
τ_{U}^{tot}	total undissolved uranium ratio, -
ϕ	dissolved ratio, -

Glossary

CAPRA	unirradiated MOX fuel containing 45% of plutonium (consommation améliorée de plutonium dans les réacteurs avancés – improved consumption of plutonium in advanced reactors)
CAPRIX	CAPRA fuel irradiated on Phenix reactor (initial Pu/(U+Pu) ratio of 45%)
CEA	commissariat à l'energie atomique et aux énergies alternatives (French atomic energy commission)
FXL	X-ray fluorescence
Gen-IV	4th generation of reactors
HKED	Hybrid K-edge densitometer
ICP-AES	inductively coupled plasma atomic emission spectroscopy
ICP-MS	inductively coupled plasma mass spectrometry
MOX	Mixed OXide (U,Pu)O_2
PuMMA	plutonium management for more agility
PWR	pressurized water reactor
SEM	scanning electron microscopy
SFR	sodium cooled fast reactor
TIMS	thermal ionization mass spectroscopy

kinetics and the amount of residues are highly affected by the amount of plutonium oxide in the fuel [27]. This can be explained by the different dissolution mechanisms of UO_2 and PuO_2 in nitric acid: the dissolution of UO_2 is a self-catalytic redox reaction with gaseous NOx production involved [4,7,21], while PuO_2 is dissolved by complexation by nitrate ions [25]. It is widely known in the literature that (U,Pu)O_2 mixed oxide tends to behave like UO_2 or PuO_2 for low or high plutonium contents respectively and exhibits an intermediate behavior, typically for a Pu/(U+Pu) ratio between 30% and 50% [27]. Yet, despite the fact that SFR burners might operate with Pu/(U+Pu) ratios up to 45%, most studies reported in the literature regarding Gen-IV MOX fuels dissolutions focus on plutonium fractions under 30%. Although some studies regarding unirradiated fuels investigate mixed oxides with up to 75% of plutonium or higher [10,27,28], all studies reported with irradiated fuels involve fuels containing up to 30%[2] of plutonium at most [12,15,16,19]. The aim of this paper is to fill this gap by investigating the dissolution behavior of identical fresh and irradiated MOX fuel containing 45% of plutonium.

2. The effect of plutonium content on the dissolution behavior of fresh and spent fuel

As explained in the previous paragraph, uranium and plutonium oxides behave differently in nitric medium and the rate of dissolution drastically decreases with an increase of the plutonium fraction. Vollath et al. showed that MOX pellets are almost completely soluble for plutonium contents under 35% in 5M and 10M nitric acid, and their insolubility rises quickly to reach almost 100% for MOX containing more than 60% (at 10M) and 50% (at 5M) of plutonium [27]. Uriarte et al. carried out experiments with unirradiated (U,Pu)O_2 mixed oxides and found that, for a given acidity and pellet density, the dissolution rate decreases exponentially with an increase of the Pu/(U+Pu) ratio following Eq. (1) derived from Uriarte [26].

$$\begin{aligned} r_{UO_2} &= 480 \times [H^+]^2 \times \exp(-9.1 \times d/d_{th}) \\ r_{PuO_2} &= 5000 \times [H^+]^4 \times \exp(-27 \times d/d_{th}) \\ r_{(U_{1-x},Pu_x)O_2} &= r_{UO_2}^{1-x} \times r_{PuO_2}^{x} \end{aligned} \tag{1}$$

Where r_{UO_2}, r_{PuO_2} and $r_{(U_{1-x},Pu_x)O_2}$ correspond to the instantaneous dissolution rate of uranium, plutonium and mixes oxides, expressed in mg.cm^{-2}.min^{-1}. $[H^+]$ is the proton concentration (in mol.L^{-1}), d/d_{th} is the ratio between the actual and theoretical sintered pellet density and x is the ratio Pu/(U+Pu).

This exponential link between the plutonium fraction and the rate of dissolution is also observed on irradiated fuels, as suggested by Ikeuchi et al. who came up with the law given by Eq. (2) to express the dissolution rate of irradiated fuels (40 to 55 GWd/tHM) as a function of their plutonium content after irradiation (in a range of 22.4% to 24.9%) [15,16]. This model is based on the assumption that the dissolution occurs as a homogeneous chemical reaction on the solid surface.

$$r_x = c(x) \times r_{0.3} = c(x) \times [H^+]^{1.74} \times k_{0.3} \times \exp\left(-\frac{E_{0.3}}{RT}\right) \tag{2}$$

Where $r_{0.3}$ is the dissolution rate corresponding to the mixed oxide ($U_{0.7}Pu_{0.3}$)O_2 for which the empirical rate constant and the activation energy, respectively $k_{0.3} = 9600\ g.cm^{-2}.min^{-1}.(mol.L^{-1})^{-1.74}$ and $E_{0.3} = 11\ kcal.mol^{-1}$, can be found in the literature [15]. The effect of the plutonium fraction is taken into account through the adjustment factor $c(x)$ for which the authors assumed an exponential dependence as shown in Eq. (3). Finally, R corresponds to the ideal gas constant and T is the temperature.

$$c(x) = e^{\lambda \times (0.3 - x)} \tag{3}$$

Where the adjustable parameter $\lambda = 19$ is fitted to represent the experimental data and thus takes into account the irradiation effect [15,16].

By comparing the results with unirradiated pellets of the same plutonium contents (around 25%) the authors showed an improvement of the dissolution rate after irradiation by a factor 10^2 or 10^3 [15]. Conversely, all the investigations reported on irradiated fuels show that

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[2] Unless specified otherwise, the plutonium fractions of irradiated fuels correspond to their composition before irradiation.

the solubility increases significantly after irradiation. Uriarte reported an improvement by a factor five in the solubility of co-precipited mixed oxide containing 20% of plutonium in 5M nitric acid after its irradiation at a burnup level of 100 GWd/t [26]. Goode carried out dissolutions tests in boiling nitric acid at 8M with pellets prepared by classical powder metallurgy route containing 25% of PuO_2 [12]. They reported that the plutonium insolubility after 10h drops down from 16% before irradiation to 5% after irradiation at 20 GWd/tHM, 1.5%–2.7% at 61 GWd/tHM and finally 0.5%–1.5% after only 4h at 81 GWd/tHM. This substantial improvement of the solubility and dissolution rate after irradiation can be mainly attributed to the evolution of the surface area and the density of the pellet through irradiation (due to the presence of open and closed porosity and the production of gaseous fission products under irradiation). Furthermore, the depletion of fissile plutonium (by neutron capture or fission) and the catalytic effect of noble metals such as palladium in the fission products may also contribute to the evolution of the dissolution behavior from fresh to spent fuel [15].

3. Experimental

3.1. Fresh and spent fuel samples

The CAPRIX fuel was manufactured by classical powder metallurgy route, with an initial plutonium content of 45% in CEA Cadarache in 1992 [24] and irradiated in the Phenix reactor between 1995 and 2006 [2]. For this investigation, a section of 100mm length from the center of the pin, in the full flux zone, was sampled and cut in four smaller section of 25mm each. Before irradiation, the CAPRIX pellets were characterized by a density of 94.5% of the theoretical density and a diameter of 5.42mm with a central hole of 2.0mm (Blanc and et al., [2]). The maximum burnup of the central full flux zone of the pin is estimated at 103.7 GWd/tHM [2]. During the irradiation, the $Pu/(U+Pu)$ ratio has dropped from 45% to 40.6% according to a decay simulation code developed by the CEA (DARWIN code), assuming a burnup of 103.7 GWd/t and a cooling duration of 16 years.

In order to compare its solubility before and after irradiation, some fresh CAPRA pellets were manufactured in CEA Marcoule following the same fabrication protocol as for the original fresh CAPRIX fuel pellets with a $Pu/(U+Pu)$ ratio of 45%. UO_2 and PuO_2 powders were ground together in a ball mill blender for 4h and then pressed into cylindrical pellets (5.2mm diameter and 5.3mm height) using a uniaxial press at 400MPa. For technical reasons, the CAPRA pellets do not have a central hole, unlike the fresh CAPRIX fuel pellets. Finally, the green pellets were sintered at 1700°C under an Ar-H_2 atmosphere during 4h. The final density of the sintered pellets represents 94.3% of the theoretical density. The pellets homogeneity were controlled by electron probe micro-analysis, the plutonium cartography shown in Fig. 1 reveals a particularly homogeneous material with very few and small uranium or plutonium enriched spots (four different pellets were analyzed with very few dispersion, <1%). According to the histogram, 94.3% of the surface has a plutonium content, $Pu/(U+Pu+Am)$, between 36% and 52%, while 2.6% of the surface has a plutonium content strictly over 52%. The average plutonium content being 44.3%.

3.2. Fresh fuel dissolution

Two dissolution tests are carried out in a glovebox for the fresh CAPRA pellets. Both tests consist in a dissolution of four pellets (4.7g of oxides) in boiling nitric acid for 10h at a given acidity. The volume of nitric acid used is chosen for each test in order to reach a given theoretical concentration of U and Pu after a complete dissolution of the solids. The first test, called CAPRA1, is a standardized insolubility test [1] carried out at 10M for 10h with a targeted final concentration of actinides of $[U+\mathrm{Pu}] = 1\mathrm{mol}.L^{-1}=241\mathrm{g}.L^{-1}$. The second test, called CAPRA2, differs from the first one with an acidity of 8M and a targeted final actinides concentration of $[U+\mathrm{Pu}] = 0.42\mathrm{mol}.L^{-1}=100\mathrm{g}.L^{-1}$. Fig. 2 shows a schematic procedure of both tests and the analysis carried out.

To start the primary dissolution tests, the pellets are immerged in the acid solution inside a glass reactor at room temperature. Then a heating plate heats the solution until the boiling point is reached, the test begins when the acid starts boiling. The vapors are condensed by a cooling system placed on the top of the reactor. For CAPRA2 test, 0.5mL of solution is sampled every hour in order to measure the evolution of uranium and plutonium concentrations during the dissolution.

For both tests, the solution remains uncolored for several hours before turning progressively to green, which corresponds to the solubilization of plutonium at the +IV oxidation degree at high acidity. The green color appears after 1h30 and 3h for the CAPRA1 and CAPRA2 tests respectively, which denotes a particularly slow dissolution kinetics of PuO_2. This observation can be correlated to a few amount of NOx off-gas observed during both tests, which also indicates a slow dissolution kinetics of UO_2 as shown by the dissolution reactions given in Eq. (4) [22].

$$\begin{aligned} &UO_2+\frac{8}{3}HNO_3\rightarrow UO_2(NO_3)_2+\frac{2}{3}NO+\frac{4}{3}H_2O \\ &UO_2+4HNO_3\rightarrow UO_2(NO_3)_2+2NO_2+2H_2O \end{aligned} \tag{4}$$

After the primary dissolution, the solutions are filtered on a 0.30μm porosity filter in order to separate the residues. The dissolution reactor is rinsed with 0.5M nitric acid in order to get all the residues. Finally, the

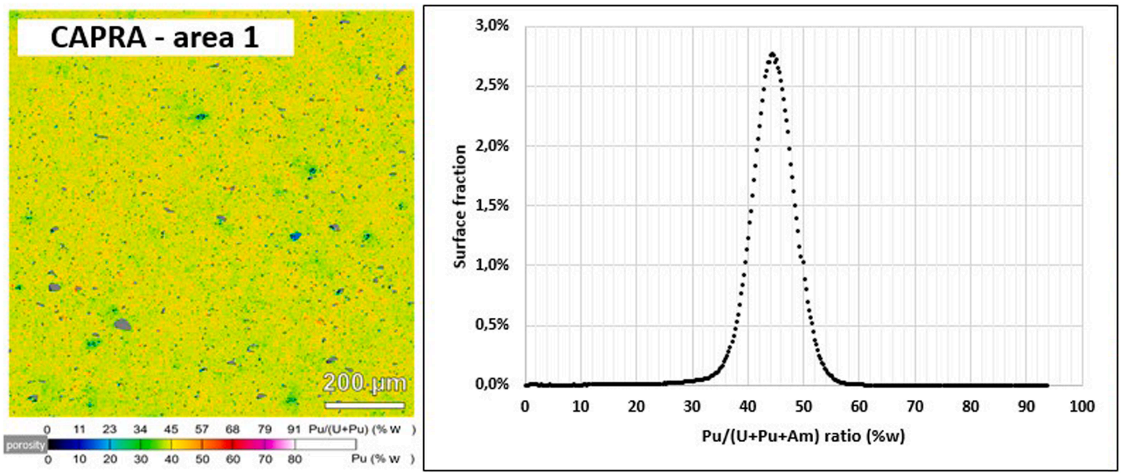

Fig. 1. Electron probe microanalysis of the plutonium distribution within the CAPRA pellets (left) and the corresponding surface fraction occupied by spots of a given Pu fraction (right). Four fields were investigated with very similar results. The sample used is representative for the ones used in CAPRA1 and CAPRA2 tests.

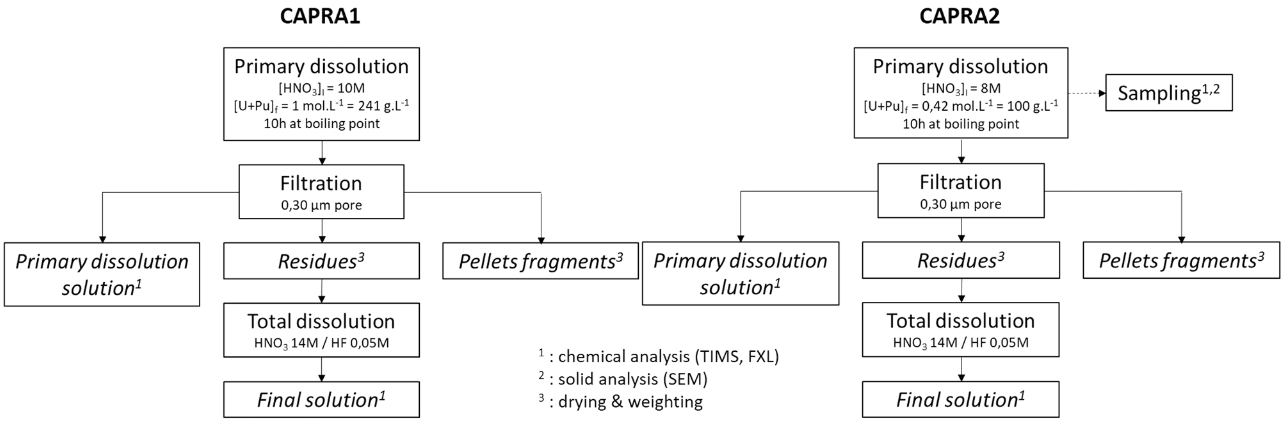

Fig. 2. Schematic protocol for CAPRA1 and CAPRA2 dissolution tests.

residues are dissolved with the filter in a nitric-hydroflouric acid solution. This last reaction occurs in a spherical vessel containing 50mL of HNO_3 14M / HF 0.05M acid mixture at boiling temperature for 2h in order to ensure a total dissolution of the residues. Both solutions of primary dissolution filtrate and secondary dissolution are then analyzed by TIMS in order to estimate the amount of insoluble and soluble plutonium and uranium.

For both tests, the four pellets are partially remaining on the filter after 10h of primary dissolution despite the severe attacking conditions (acidity of 8M to 10M at boiling temperature). Fig. 3 shows the filter at the end of the primary dissolution for the CAPRA1 test, the four pellets seem almost intact and some powder residues can be seen on the filter. The pellets were removed from the filter and only the residues were re-attacked through the secondary dissolution (even with nitric-hydroflouric acid the time needed to reach a full dissolution of these pellets fragments would be too long). The pellets fragments were washed in 0.5M nitric acid, dried and then weighted precisely.

3.3. *Spent fuel dissolution*

One dissolution test was carried out in a hot cell on the full-flux zone of the irradiated CAPRIX fuel. The mass of oxide contained in the four 25mm sections is 19.666g, which corresponds to the total mass of the sample minus the mass of the hulls. A schematic protocol of the test is represented on Fig. 4. At first, the primary dissolution conditions for the primary dissolution of spent fuel were supposed to be identical to the CAPRA2 (10h at 8M at boiling temperature with $[U{+}Pu]_{final}{=}100g.L^{-1}$). However, considering the amount of undissolved solid obtained in the CAPRA tests, and in order to avoid undissolved pellet fragments in the hot cell, an acidity of 10M was chosen instead. The targeted final actinide concentration of $[U{+}Pu] = 100g.L^{-1}$ was kept since the reactor in hot cell is designed for this concentration.

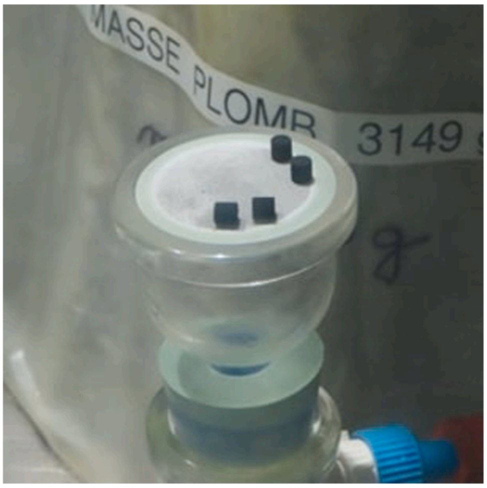

Fig. 3. Undissolved pellets fragments and residues remaining at the end of the 10h primary dissolution for the CAPRA1 test.

The experimental setup used for the CAPRIX dissolution test is similar to the device used in a glovebox for CAPRA1 and CAPRA2 tests (cylindrical batch reactor, heating plate and cooling system). The dissolution starts when the solution is boiling and the temperature is then maintained for 10h. The evolution of the dissolution is followed by the ^{85}Kr release and by sample analysis in order to measure the evolution of the uranium and plutonium concentration.

After the primary dissolution, the residues are filtered with a 0.30μm filter. The reactor and the hulls are rinsed with 3M nitric acid in order to get all the remaining residues. Four filters were needed to recover all the residues. Fig. 5 shows a picture of a filter after the CAPRIX dissolution test. From visual inspections, it seems that the amount of residues is particularly high but no pellet fragments are present on the filter, which indicates that the solubility of the pellets is higher than for CAPRA1 and CAPRA2 tests. However, it should be noted that among the four filters used, the last one is characterized by larger particles which might correspond to very small undissolved fragments. The hulls are separated from the residues and are dissolved separately in a nitric-hydroflouric solution (HNO_3 3M / HF 3M).

After calcination for 8h at 400°C, the primary residues are weighted and then dissolved by oxidative digestion with Ag(II). The solution is then filtered once again and the secondary residues, remaining after oxidative digestion, undergo through an alkaline and acid fusion processes in order to analyze their content. All the solutions obtained after the primary dissolution, oxidative digestion, alkaline fusion and hulls dissolution steps are analyzed by FXL, FXK, ICP-MS, ICP-AES and TIMS in order to assess the amount of uranium, plutonium and fission products solubilized at each step.

4. Results

4.1. *Fresh fuel dissolution*

4.1.1. *Dissolution kinetics (CAPRA2 test)*

Each 0.5mL aliquots sampled during the CAPRA2 test were diluted in 5mL of 0.5M nitric acid and analyzed by TIMS. Due to technical difficulties during the experiment, not all the samples could be kept but the general trend is still visible on Fig. 6. It appears clearly that the dissolution plateau is not reached at the end of the test. This means that the dissolution would probably have continued at approximately the same rate after 10h. The actinide dissolution evolves very slowly (in average, approximately 4.6mg/h for uranium and 3.1mg/h for the plutonium). At

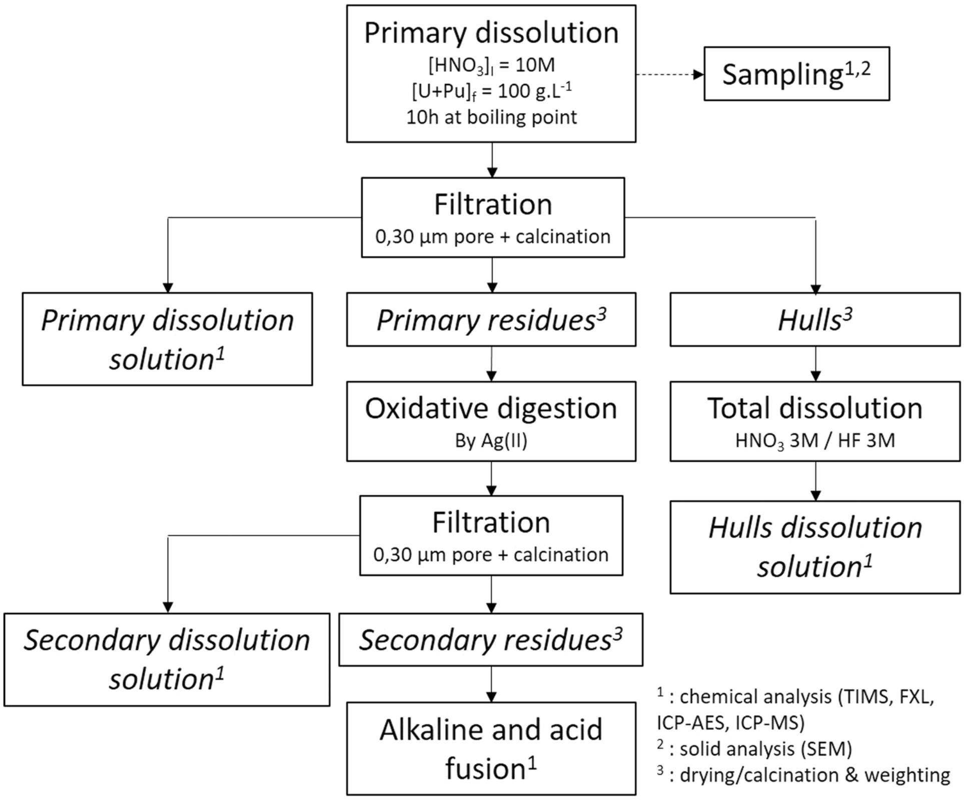

Fig. 4. Schematic protocol for CAPRIX dissolution test.

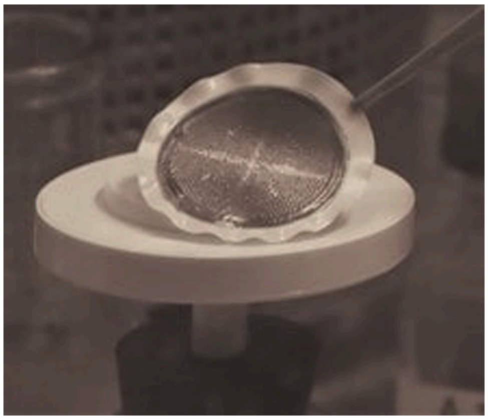

Fig. 5. One of the four filters obtained after the primary dissolution of the CAPRIX fuel.

this pace, it would take approximately 700h to reach 1% of residues assuming a linear trend. The Pu/U+Pu ratio remains constant and approximately equal to the overall plutonium content with 41±1%. This indicates a congruent dissolution of uranium and plutonium, which is consistent with the very homogeneous repartition of the plutonium within the pellets, as suggested on Fig. 1.

The dissolution rate can be computed for the CAPRA2 test from the kinetics shown on Fig. 6. Since the remaining pellets seem almost intact after the test (see Fig. 3), we considered that the geometrical surface was constant during the test and equal to the initial surface. Since four cylindrical pellets (5.2mm diameter and 5.3mm height) are dissolved, we considered a geometrical surface of 5.16 cm^2. Therefore, the dissolution rate can be estimated by a simple linear regression that gives $r_{CAPRA2} = (2.5 \pm 0.1) \times 10^{-2}\ mg.cm^{-2}.min^{-1}$.

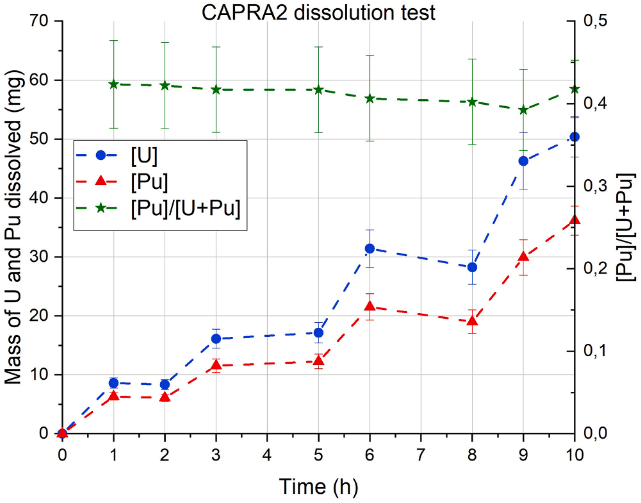

Fig. 6. Evolution of the mass of uranium and plutonium dissolved during the CAPRA2 dissolution test (TIMS analysis). The errors bars corresponds to uncertainty, taking into account the dilution factor.

4.1.2. *Insolubility ratios*

After the primary dissolution, the plutonium within the initial pellets is whether dissolved or undissolved within the powder residues or the remaining pellets fragments. The mass of dissolved plutonium, m_{Pu}^{disso}, is calculated from the plutonium concentration measured by TIMS in the dissolution filtrate. The mass of plutonium within the residues, m_{Pu}^{res}, is measured by analyzing the concentration after the secondary nitric-hydroflouric dissolution, by TIMS as well. Finally, the mass of plutonium within the pellets fragments, m_{Pu}^{frag}, can be estimated from the weight of the fragments assuming a Pu/U+Pu ratio identical to the

Table 1
Insolubility ratios and plutonium content of the undissolved solids for CAPRA1 and CAPRA2 tests.

Test Conditions	CAPRA1 acidity 10M $[U+\mathrm{Pu}]_f$=1mol.L^{-1}	CAPRA2 acidity 8M $[U+\mathrm{Pu}]_f$=0.42mol.L^{-1}
Insolubility ratios		
Total undissolved Pu ratio, τ_{Pu}^{tot}	82.0±3.9%	98.0±1.9%
Partial residue insoluble Pu ratio, τ_{Pu}^{res}	0.8±0.2%	2.1±1.4%
Plutonium content		
Pu/(U+Pu) in the remaining pellet fragments	44.5±1.5%	44.2±0.5%
Pu/(U+Pu) in the powder residues	47.8±1.8%	52.2±1.9%

initial ratio. This assumption can be consolidated by the homogeneity of the pellets (Fig. 1), the congruent dissolution of uranium and plutonium (Fig. 6) and by the visual aspect of the pellets (Fig. 5) which suggests that they were attacked at the surface only and that the overall volume of the pellets remained intact. Since the plateau is not reached, two Pu insolubility ratios can be calculated from these results:

- The total undissolved plutonium ratio, τ_{Pu}^{tot}, given by Eq. (5), corresponds to the total percentage of undissolved plutonium after the tests, considering the undissolved plutonium within the powder residues and within the remaining pellets fragments. As suggested by the kinetics on Fig. 6, this ratio does not exactly correspond to the insolubility since it is also affected by the slow dissolution kinetics (longer test duration would lead to lower undissolved ratio)

$$\tau_{Pu}^{tot} = \frac{m_{Pu}^{res} + m_{Pu}^{frag}}{m_{Pu}^{disso} + m_{Pu}^{res} + m_{Pu}^{frag}} \tag{5}$$

- The partial residue insolubility ratio, τ_{Pu}^{res}, given by Eq. (6), consists in removing the remaining pellet fragments of the mass balance. This allows an estimation of the actual kinetics independent insolubility ratio, assuming a linear behavior through the dissolution process. This hypothesis is consolidated by the homogeneous microstructure of the pellets but cannot be validated with certainty since the dissolution tests only cover a few percent of the total dissolution (the kinetics shown on Fig. 6 only represents less than 2% of the solid dissolution).

$$\tau_{Pu}^{res} = \frac{m_{Pu}^{res}}{m_{Pu}^{disso} + m_{Pu}^{res}} \tag{6}$$

The results for CAPRA1 and CAPRA2 dissolution tests are given in Table 1.

As expected, the total undissolved Pu ratio is particularly high for both tests, far above the 1% limit usually considered to assess whether fresh fuels are soluble or not [1]. This is not surprising as previous investigations on fresh fuel reported in the literature suggest an insolubility threshold around 40% Pu content [27]. Despite these high undissolved ratios, a significant improvement can be observed when the acidity is increased from 8M to 10M. Actually, the mass of dissolved plutonium is improved by an order of magnitude after the CAPRA1 test ($m_{Pu}^{disso}|_{10M} = 0.328 \pm 0.010\ g$) as compared to the CAPRA2 test ($m_{Pu}^{disso}|_{8M} = 0.036 \pm 0.001\ g$).

The partial residue insolubilities are significantly lower and the CAPRA1 test even exhibits a partial insolubility under 1%. Similarly, the acidity seems to have a strong effect on the insolubility since the partial insolubility ratio at 10M is more than twice the ratio obtained at a lesser acidity of 8M. However, both partial residue insolubility ratios should be interpreted with care since they correspond to an extrapolation of the dissolution behavior observed during the first few percent of the dissolution only.

The plutonium content within the residues and the pellet fragments are given in Table 1. The pellet fragments exhibits a Pu/(U+Pu) ratio identical to the initial pellets, which is consistent with the few amount of uranium and plutonium dissolved. This confirms that the dissolution would have probably continued with the same kinetics after 10h since the solids are almost the same as the initial step.

The fraction of plutonium within the residues is slightly higher than to the overall pellet composition. This tends to confirm that these residues are the actually refractory do dissolution (whatever the duration of the test). In particular, the residues obtained after the CAPRA2 test have a plutonium content of approximately 52%. As explained in Section 3.1. (see Fig. 1), 2.6% of the surface of the pellets has a plutonium content higher than 52%, which is consistent with the insolubility ratio of $\tau_{Pu}^{res} = 2.1\%$ for this test. This comparison does not work with the CAPRA1 test for which the residues seems to exhibit a lesser plutonium content. This might come from a small pollution of the residues during the manipulation of the filter in the glovebox (which is difficult to avoid considering that the residues are constituted of a few milligrams).

Eventually, neither of the τ_{Pu}^{tot} or τ_{Pu}^{res} ratios describe exactly the real insolubility since τ_{Pu}^{tot} is affected by the kinetics effects and τ_{Pu}^{res} is an approximation based on a small part of the overall dissolution test. However, these results show that such homogeneous fuels with high plutonium contents do not necessarily lead to significantly higher insolubilities (due to the lack of very rich >50% plutonium insoluble spots) but exhibit a particularly slow dissolution kinetics. We can assume that a more heterogeneous fuel might lead to faster dissolution, due to the presence of highly reactive spots containing more uranium, but with a larger amount of insoluble rich plutonium aggregates.

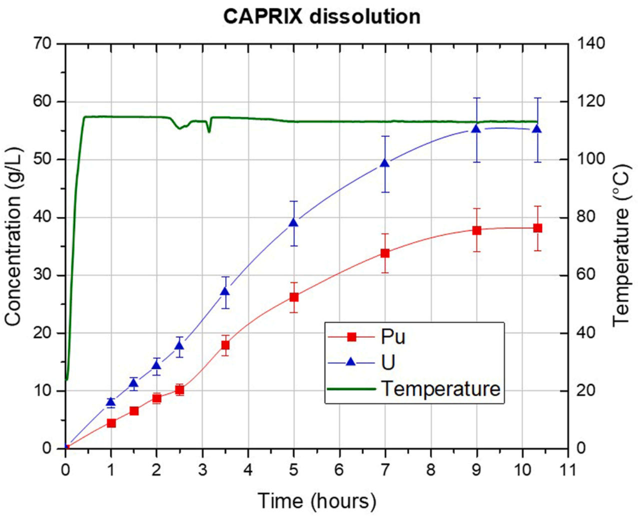

Fig. 7. Evolution of uranium (blue triangles) and plutonium (red squares) concentrations during the CAPRIX dissolution test. The temperature is represented by the green curve. The concentrations are measured by FXK and error bars corresponds to measurement uncertainties.

4.2. Spent fuel dissolution

4.2.1. Dissolution kinetics

The evolution of uranium and plutonium concentrations during the CAPRIX dissolution test are shown on Fig. 7. Both concentrations increase until reaching a plateau around 9h after the beginning of the test. Since the plateau appears at the very end of the test it is difficult to infer whether the dissolution could continue after 10h or not. At the end of the test, the final concentration reaches $[U+\mathrm{Pu}]_f$=92.4±0.4g.L^{-1} which is a bit lower than the 100g.L^{-1} expected.

It is possible to compute the empirical dissolution rate, r_{CAPRIX} (in mg. cm^{-2}.min^{-1}), for the CAPRIX test by fitting the measured data of Fig. 7 with the surface area model given by Eq. (7) [15].

$$W(t) = S_0 \times \int_0^t r_{CAPRIX} \cdot F(\phi) \cdot dt \qquad (7)$$

Where $W(t)$ corresponds to the mass of dissolved fuel (in mg), S_0 is the initial geometrical surface of the sample (in cm^{-2}) and $F(\phi)$ is a function representing the evolution of the surface area according to the dissolved ratio ϕ (no units).

The initial surface, $S_0 = 2.01\ cm^2$, was estimated by assuming that the central hole had disappeared after irradiation and then corresponds to 8 times (both ends of the 4 samples) the surface area of a disk of 5.65mm (internal diameter of the pin). It should be noted that these approximation on the initial surface have a strong impact on the computed dissolution rate (r_{CAPRIX} being inversely proportional to S_0). In particular, the presence of a central hole of 2mm diameter (corresponding to the pellet geometry before irradiation) would increase the initial surface by a factor 4.

Eq. (8) was used to describe the evolution of the surface area as a function of the dissolved ratio, as suggested by Ikeuchi [15].

$$F(\Phi) = 1 - 0.6\Phi + 2.7\Phi^2 - 3.1\Phi^3 \qquad (8)$$

An empirical dissolution rate of $r_{CAPRIX} = 16\ mg.cm^{-2}.min^{-1}$ was found. As stated before, this value may be overestimated (up to a factor 4) if the central holes were still present, even partially, after irradiation.

Fig. 8 shows the dissolution progression (as a percentage of the final concentrations) as well as the evolution of the Pu/(U+Pu) ratio. It appears that the plutonium fraction evolves significantly, from 36% at the beginning of the test to 41% in the last few hours. The value of 41% at the end of the dissolution is close to the theoretical overall Pu/(U+Pu) ratio computed by the decay code (40.6%), which corroborates the hypothesis of a dissolution plateau reached around 9h. Unlike CAPRA pellets that dissolved congruently from the very beginning of the test, the CAPRIX pellets exhibits a slight preferential dissolution of uranium during the first hours of the test, highlighting the existence of possible heterogeneities caused by the irradiation.

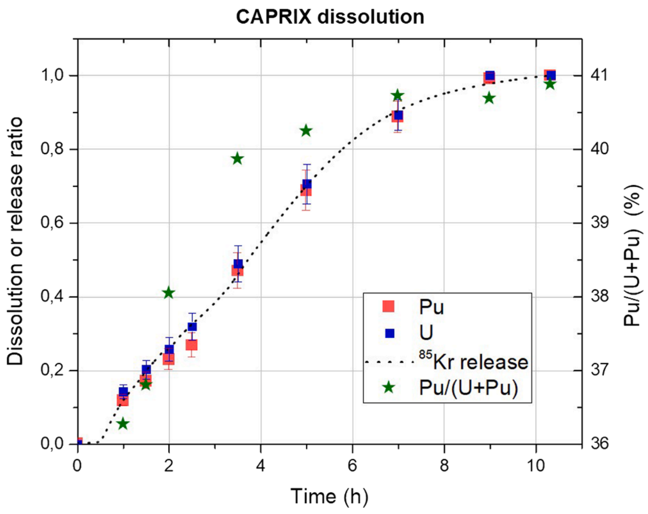

Fig. 8. Release of 85Kr (dotted line), dissolution behavior of U, Pu (blue and red squares respectively) and evolution of the Pu/(U+Pu) ratio (green stars).

The figure also shows the temporal changes on the dissolution ratios of U, Pu along with the FP nuclide ^{85}Kr release, which follows the dissolution of fuel matrix. The ^{85}Kr release phenomenon is discussed in the next section.

4.2.2. Krypton release

The irradiation conditions reached in SFR cores lead to the formation of gaseous fission products such as krypton and xenon. The gaseous krypton is released when cutting the pin (free krypton) and during the dissolution (trapped krypton). In order to follow the dissolution progress, the ^{85}Kr release was recorded in the hot cell during the CAPRIX test; the results are shown in Fig. 9. A peak of ^{85}Kr release occurs at the very beginning of the test and then decreases slowly until almost reaching the background level at the end of the test. This trend is characteristic of a slow dissolution and the fact that the background level does not seem to be reached at the end of the test (dotted blue vertical line on Fig. 9) suggests that the plateau is close but not completely reached. By comparing with the decay code simulations, the amount of ^{85}Kr released during the dissolution test represents 26.3% of the total ^{85}Kr within the irradiated pin.

4.2.3. Insolubility ratio

After calcination, the total mass of recovered residues is 2.932 ±0.07g, which corresponds to 169kg of residues per ton of fuel.

The absence of pellets fragments at the end of the CAPRIX primary dissolution test makes it impossible to distinguish the effects of chemical insolubility from the kinetics effects (as done for the CAPRA tests). Thus only the total undissolved plutonium ratio, τ_{Pu}^{tot}, can be calculated and compared with the unirradiated results. However, among the four filters used to recover the residues, the last one was characterized by the presence of much bigger particles, which could correspond to very small undissolved fragments. This suggests that the total undissolved plutonium ratio provided in Table 2 may be affected by similar but less extensive kinetics effects than from CAPRA tests.

In order to compute the insolubility ratio in Table 2, the residues are dissolved through oxidative digestion and alkaline then acid fusions in order to estimate precisely the amount of plutonium within the primary residues and at the end of the secondary dissolution step. The empty hulls were also dissolved in order to assess the plutonium contamination and it appeared that the plutonium remaining in hulls could be neglected (0.004% of the initial mass of plutonium). The plutonium insolubility after the primary dissolution of the CAPRIX fuel is still high (16.5%) but significantly lower than the unirradiated fuel. The comparison between irradiated and unirradiated insolubilities is discussed in more details in Section 5.1.

The Pu/(U+Pu) ratio within the residues is 50.0%, ten points higher than the pellets plutonium content after irradiation. This confirms the existence of a heterogeneous uranium and plutonium distribution through the pellets, as suggested in previous paragraph 4.2.1. It can be noticed that this value is also very close to the Pu/(U+Pu) ratio obtained within the residues of the CAPRA2 tests (52%). This may suggest that there is an insolubility barrier around Pu/(U+Pu) = 50%.

By comparing the mass of plutonium and uranium in the residues to the total mass of residues, assuming that the actinides are in the oxide form, we can infer that UO_2 and PuO_2 each represent 38% in mass of residues (64kg/ton). This means that the remaining 24% in mass of the residues (41kg/ton) are constituted by undissolved fission products (both metallic and oxide fission products). This highlights the importance of the role of fission products on the dissolution behavior, as they account for a quarter of the total residues mass.

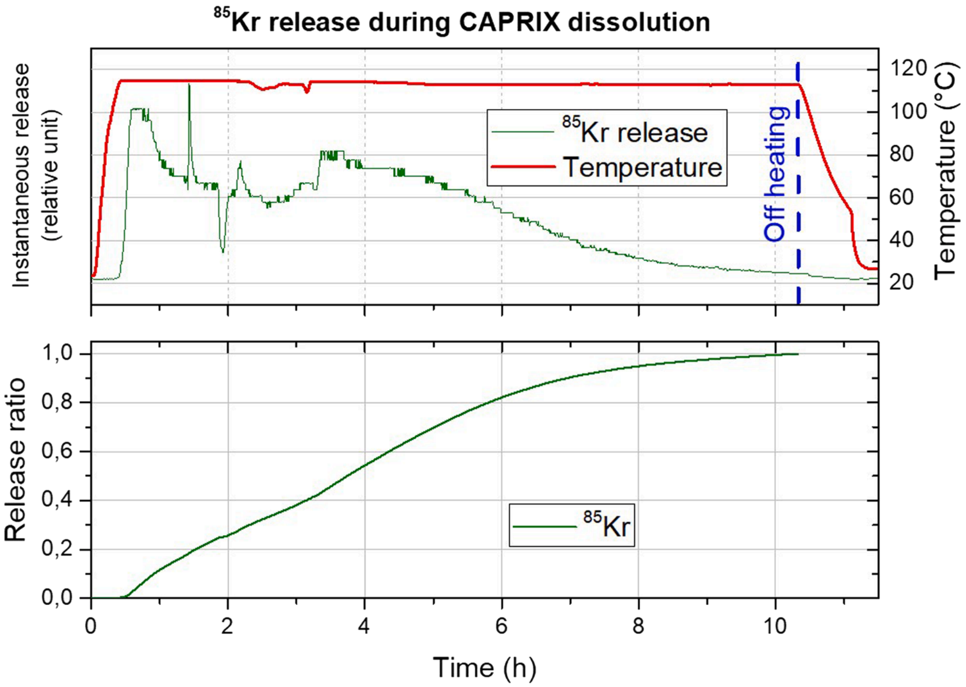

Fig. 9. Krypton release and evolution of the temperature during the CAPRIX primary dissolution test.

Table 2
Insolubility ratios of plutonium and uranium for the CAPRIX dissolution test.

Test	CAPRIX
Total undissolved Pu ratio, τ_{Pu}^{tot}	16.5±2.5%
Total undissolved U ratio, τ_{U}^{tot}	11.1±1.8%
Pu/(U+Pu) in the powder residues	50.0% ± 5,5%

Table 3
Insolubility ratios measured for different tests before and after irradiation.

Total undissolved Pu ratio τ_{Pu}^{tot}	
CAPRA1 (unirradiated fuel, 10M – 1mol/L)	82.0±3.9%
CAPRA2 (unirradiated fuel, 8M – 100g/L)	98.0±1.9%
CAPRIX (irradiated fuel, 10M – 100g/L)	16.5±0.5%
Deletion factor (CAPRA1 vs CAPRIX)	~ 5.0

5. Discussions and comparison with the literature

5.1. Insolubility ratios

The insolubility ratios measured for the irradiated and unirradiated fuels are summarized in Table 3. These ratios correspond to the total undissolved ratios as defined by Eq. (5). By comparing CAPRIX and CAPRA1 experiments, we can notice that the irradiation significantly improves the solubility of the fuel with a deletion factor of approximatively 5 in similar dissolution conditions.[3] This beneficial effect of irradiation on the dissolution behavior has been reported previously un the literature [12,16,26].

The total undissolved plutonium ratio of 82.0% obtained for CAPRA1 can be compared to the experiments reported by Vollath [27] carried out at in very similar conditions: $[U+\mathrm{Pu}]_f$=1mol.L^{-1} with boiling nitric acid at 10M, the only difference being a shorter dissolution duration of 6h (instead of 10h in our investigation). Despite similar dissolution conditions, the authors found a lower insolubility of 18.7% for Pu/(U+Pu) = 44.0% and 46.7% for Pu/(U+Pu) = 48.6% [27]. By interpolation of Vollath's data, an insolubility of 82.0% is obtained for mixed oxides containing approximately 54% of plutonium instead of 45% found in this paper. Such difference is not surprising since the dissolution behavior of MOX pellets prepared by metallurgical route is known to depend on the blending, compaction and sintering parameters that affect the pellets properties [9,12]. In particular, the better solubility obtained in Vollath studies may be explained by the lower density (near 89% of the theoretical density in average, compared to 94.3% in this paper). Indeed, a higher density after sintering was shown to increase drastically the amount of undissolved plutonium, as suggested for example in Eq. (1) [20,26]. Other parameters such as the porosity size distribution, surface roughness, local degree of oxidation, crystallization state and of course, the homogeneity may also affect the dissolution kinetics and the final insolubility. All these properties depends on the fabrication parameters and are closely linked to the notion of reactive surface [8,18] which is particularly relevant for nuclear mixed oxide dissolution behavior [5]. With these considerations in mind, the undissolved and insolubility ratios reported in this paper seem consistent with the sparse literature on 45% Pu/(U+Pu) mixed oxide dissolution. It also shows that, for a given plutonium content, the dissolution behavior can be significantly improved through the fabrication process.

To our knowledge, this paper is the only investigation reported in the literature dealing with the dissolution of irradiated MOX fuel containing more than 30% of plutonium. Some irradiated MOX fuel insolubilities found in the literature are summarized in Table 4. The results are hardly comparable with this study since the Pu/(U+Pu) ratios previously studied are much lower.

5.2. Dissolution kinetics

The dissolution rate computed for the unirradiated CAPRA2 test could not be compared with any relevant value in the literature. How-

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[3] To be precise, one can argue that the solid/liquid ratio was 2.4 times higher for the CAPRA1 test. However, we can consider that the initial solid/liquid ratio has a negligible influence on the dissolution tests considering the very small amount of solid dissolved through CAPRA1 test. CAPRA1 and CAPRIX tests conditions can thus be considered as similar.

Table 4
Some irradiated fuel insolubilities reported in the literature. The “*” character means that the information has not been found.

Reference	Pu/(U+Pu) (initial / final)	Burnup (GWd/tHM)	Dissolution conditions	Pu insol. or {(U+Pu) insol.}
[12]	25% / *	20	8M; boiling point; 8 h	5%
		61	8M; boiling point; 8 h	1.5% to 2.7%
		81	8M; boiling point; 4 h	0.5% to 1.5%
[19][4]	25% / *	26	12M; boiling point; 12 h	0.07%
[16]	18% / 17.6%	40.1	*	{0.5%}
	23.7% / 22.3%	53.3	*	{0.8%}
	26.4% / 24.9%	54.7	*	{0.9%}
	29.0% / 28.1%	31.7	*	{1.3%}
This paper	45.0% / 40.6%	103.7	10M; boiling point; 10 h	16.5%

[4] The author reports the insolubility of 11 other irradiated samples with burnups from 4.2 to 137.0 GWd/t, the plutonium insolubility varies from <0.01% to 0.78% with a strong dependence on the manufacturing conditions. We chose to highlight only the most similar samples in terms of fabrication process in Table 3.

Table 5
Summary of the empirical and predicted values for the dissolution rates for irradiated and inurradiated tests.

Test	Dissolution rate ($mg.cm^{-2}.min^{-1}$)		Model and reference
	Empirical value	Predicted value	
CAPRA2 (unirradiated)	0.025±0.001	0.054±0.013	(1) [26]
CAPRIX (irradiated)	16	45	(2) [15]

ever, the CAPRA2 empirical dissolution rate can be compared with the value predicted from Uriarte’s law given by Eq. (1) with $x = 0.45$, $[H^+] = 8\ mol/L$ and $d/d_{th} = 0.943$. The model gives a predicted value of $r_{0.45} = 0.054 \pm 0.013\ mg.cm^{-2}.min^{-1}$ which is near the actual measured dissolution rate ($r_{CAPRA2} = 0.025 \pm 0.001\ mg.cm^{-2}.min^{-1}$, see Section 4.1.1.). The empirical and predicted values are reported in Table 5. The difference of a factor 2 between experimental and theoretical data could be expected considering the fact that Uriarte’s law was mainly derived from experiments carried out with plutonium contents around 20% and pellets densities between 75% and 90% [26]. Further experimental data would be needed in order to confirm the relevance of this law for high plutonium contents. However, the fact that the model predicts the dissolution rate with the right order of magnitude suggests that the high plutonium content of the CAPRA fuel and its relatively high density can explain the particularly slow dissolution kinetics at 8M.

Regarding the CAPRIX irradiated fuel, the closest experiment reported in the literature is Ikeuchi’s dissolution test referenced as DM-29, which was carried out on spent fuel with a plutonium content of 26.5% after irradiation (it is the highest plutonium content reported in the literature for spend fuel) [16]. The authors found a molar dissolution rate of $r'_{DM-29} = 0.45 \times 10^{-3}\ mol.cm^{-2}.min^{-1}$ which roughly corresponds to $r_{DM-29} = 110\ mg.cm^{-2}.min^{-1}$. This is one order of magnitude higher than the empirical dissolution rate of $r_{CAPRIX} = 16\ mg.cm^{-2}.min^{-1}$ computed for the CAPRIX test, which is consistent with a lower amount of plutonium after irradiation.

Ikeuchi et al. suggested the model (Eq. (2)) predicting the dissolution rate for irradiated fuel as a function of its plutonium content, assuming an exponential decrease with the plutonium content [15]. Applied to the CAPRIX dissolution conditions ($[H^+] = 10 mol.L^{-1}$, $T = 115°C$, $x = 0.406$) with an empirical factor value of $\lambda = 19$ as suggested by the authors, a predicted dissolution rate of $r_{0.406} = 45\ mg.cm^{-2}.min^{-1}$ was found. This overestimates the empirical dissolution rate by a factor 3 approximately. The recalculated factor of $\lambda' = 29$ was found to better fit the CAPRIX dissolution results. Several explanations can be found to explain the difference between predicted and empirical values (reported in Table 5):

- Ikeuchi’s Eq. (2), with the adjustable parameter $\lambda = 19$, have been suggested based on empirical results obtained with plutonium contents in a range of 17.6% to 26.5% after irradiation. Thus, the extrapolation to higher plutonium contents (40.6% for CAPRIX fuel) cannot be guaranteed.
- The effects of burnup level and fabrication process are not taken into account in the model, meaning that they are probably contained in the adjustable parameter λ. It is then not surprising to find a different value of $\lambda' = 29$ in this investigation.
- As explained in Section 4.2.1, the initial geometrical surface of the irradiated fuel was assessed assuming a flat disk at both edges of the hulls. This hypothesis probably leads to an overestimation, up to a factor 4, of the empirical dissolution rate for the CAPRIX fuel.
- Other uncertainties may come from the evaluation of the plutonium content after irradiation from the decay code. Indeed, one should keep in mind that the predicted kinetics evolves exponentially with the plutonium content according to Eqs. (2) and (3).

Overall, it is difficult to assess a precise uncertainty on experimental and predicted CAPRIX dissolution kinetics, but it seems reasonable to consider that these values may vary within an order of magnitude.

Despite the uncertainties, the measured and predicted dissolution rates are of the same order of magnitude for both irradiated and unirradiated fuels (see Table 5), which tends to confirm the exponential dependence of the dissolution kinetics according to the plutonium content, as suggested by Uriarte and Ikeuchi’s model.

It should be noted that the dissolution rates given in Table 5 before (CAPRA2 test) and after (CAPRIX test) irradiation cannot be compared directly because both tests were carried out at different acidities (8M for the CAPRA2 test and 10M for the CAPRIX test). However, since Uriarte’s model seems to predict quite well the dissolution rate of the CAPRA pellets at 8M, it was used to predict the dissolution rate of these pellets at an acidity of 10M and a value of $r_{0.45-10M} = 0.104\ mg.cm^{-2}.min^{-1}$ was found. It appears that the irradiation improves significantly the dissolution rate by more than two orders of magnitude (for a similar material and at the same acidity of 10M), which is perfectly consistent with the results reported by Ikeuchi other fuels [16]. This significant improvement of the dissolution behavior after irradiation can be attributed to various known effects such as the depletion of fissile plutonium (by neutron capture or fission), changes in oxygen potential, presence of catalytic fission products such as platinoids [17] or light trivalent lanthanides which may replace the cations in MO_2 fluorite structures, enhancing the dissolution kinetics [13], redistribution of the actinides, crystallographic defects produced by irradiation, swelling or formation of cracks, presence of smaller grains (and thus of more grains boundaries) after irradiation which has been demonstrated and denoted as high burnup structure (HBS) [2].

6. Conclusions and perspectives

This paper describes the dissolution tests carried out in similar conditions on SFR MOX fuels before and after irradiation. The CAPRA and CAPRIX fuels used for this investigation both share the same initial properties such as an initial Pu/(U+Pu) ratio of 45%. The CAPRIX fuel samples were irradiated at 103.7 GWd/t in the Phenix reactor while CAPRA samples remained unirradiated.

The unirradiated CAPRA samples exhibits a very high amount of undissolved plutonium despite a significant improvement when the initial acidity was increased from 8M (98.0% of undissolved plutonium) to 10M (82.0% of undissolved plutonium). The presence of remaining pellets fragments after both tests may be attributed to kinetics effects rather than actual insolubility. This is confirmed by the absence of kinetic plateau during the test, the particularly homogeneous plutonium distribution of the pellets and the differences in Pu/(U+Pu) ratios between the pellets fragments (identical to the initial samples) and the powder residues (richer in plutonium). The dissolution rate was calculated and occurs to be very consistent with Uriarte's law [26], which takes into account the plutonium content and the density of the pellets. Thus, these two parameters combined might explain the dissolution behavior of the CAPRA pellets. A partial undissolved plutonium ratio was defined in order to estimate the actual insolubility of the pellets cleared of any kinetic effects. The values obtained of 0.8% and 2.1% at 10M and 8M respectively, suggest that the insolubility could be acceptable if the kinetics were accelerated in a way or another. A brief comparison with the literature showed that some kinetics improvements could be achieved by mastering the pellets fabrication parameters in a way that increases the available reactive surface area [27]. However, the possibility to adjust the manufacturing parameters to improve dissolution is limited at industrial scale since a good behavior of the fuel under irradiation remains a prime and necessary criterion. Since it is well known that the dissolution kinetics highly depends on the available reactive surface [5,8,18,28], a pre-treatment of the irradiated pellets, such as mechanical crushing or thermal treatment, could be considered in order to improve their dissolution behavior. Therefore, it could be interesting to compare the CAPRA insolubility ratios after grinding the pellets for example.

The amount of undissolved plutonium after irradiation is still high with a total undissolved plutonium ratio of 16.5% after the CAPRIX dissolution test. Even if no pellet fragments are remaining after the primary dissolution, we can still assume that kinetics effects have contributed to the amount of undissolved plutonium and that the dissolution was not completely finished after 10h. Indeed, the presence of bigger particles on the last filter, the late plateau observed at the end of the dissolution test and the fact that a few ^{85}Kr continues to be released after the dissolution corroborate this hypothesis. Anyway, a significant improvement is observed after irradiation were a deletion factor of 5 is found. Unlike unirradiated pellets, the spent fuel was shown to dissolve non-congruently in the first few hours, this might be linked to the formation of fission products through irradiation which affects locally the dissolution behavior in various ways [6,17]. In addition to the formation of catalytic fission products, various factors may explain the improvement of the dissolution behavior after irradiation, such as the depletion of fissile plutonium (by neutron capture or fission), changes in oxygen potential, redistribution of the actinides, swelling or formation of cracks… The results provided in this paper show that these chemical and physical modifications that occur through irradiation still have a great beneficial impact on the dissolution behavior for SFR burner fuels with plutonium contents as high as 45%. The amount of plutonium and uranium oxides within the residues only accounts for 76% in mass of the residues meaning that the remaining 24% is constituted of metallic or oxide fission products. This clearly show the importance of the fission product dissolution behavior for MOX reprocessing. Finally, the comparison between the rate of dissolution of the CAPRIX fuel with those of other MOX fuels reported in the literature tends to confirm that the dissolution rate decreases exponentially with the amount of plutonium.

It should also be noted that the CAPRIX dissolution test was carried out on a sample from the full-flux zone of the pin. A dissolution in similar conditions of a less irradiated zone with a smaller local burnup, such as the upper end of the pin, would allow a more complete assessment of the CAPRIX fuel solubility in nitric acid.

This paper shows that, despite a larger amount of residues after nitric acid dissolution, the reprocessing of high plutonium content SFR MOX fuels can still be considered at industrial scale provided that the dissolution kinetics is significantly improved. This might be achieved by means of mastering some MOX fabrication parameters in a way that promotes its dissolution and mechanical or thermal pre-treatment of the spent fuel prior to dissolution. In addition to the primary dissolution step, an additional depletion process, such as oxidative digestion, may be needed in order to achieve a satisfactory recovery of the fissile elements.

CRediT authorship contribution statement

Martin Giraud: Conceptualization, Investigation, Formal analysis, Writing – original draft. **Nathalie Reynier-Tronche:** Conceptualization, Investigation, Formal analysis, Writing – review & editing. **Emilie Buravand:** Conceptualization, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no competing financial interests

Data availability

The data will be made available on request, provided that it is not confidential.

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