LOCAL BURNUP DETERMINATION IN UOX FUEL RODS USING SECONDARY ION MASS SPECTROMETRY

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ABSTRACT
The determination of local burn-up on irradiated fuel is a key parameter, which is directly connected to its neutronic behavior. In high burn-up UO_2 fuel, the burn-up distribution is not homogeneous, the pellet edge having the highest burn-up.
In order to measure fission products balance (like ^{137}Cs, ^{145}Nd and ^{146}Nd) several methods are available in hot labs facilities, like spectroscopy or mass spectroscopy isotopic analysis on dissolved fuel sample. Burnup values are then evaluated from neutronic codes calculations. Unfortunately, these determinations are not able to characterize any radial evolution of burnup. EPMA (Electron Probe Micro Analysis) and SIMS (Secondary Ion Mass Spectrometry) are more suitable to carried out such evaluations.
Using a shielded SIMS (CAMECA IMS6F), quantitative isotopic ratio distribution ($\frac{^{145}Nd + {}^{146}Nd}{^{238}U}$) is determined thanks to standard sample for which isotopic analyses are available after dissolution.
After to calculations performed with the CEA APOLLO2 code, SIMS Burn-up profiles are compared to those obtained from EPMA Nd w% profiles along the same radius. Radial burn up evaluations are validated on low (38 GWd/tM) and high (72 GWd/tM) burn-up PWR fuels.

KEYWORDS **Local Burn-up, Isotopic ratio, Secondary Ion Mass Spectrometry**

1. INTRODUCTION

The burnup of a nuclear fuel is related to fission products inventory resulting from irradiation process. Therefore burnup method determination are based on some specific fission products measurements using different experimental techniques : spectroscopy (^{137}Cs measurement) and mass spectroscopy on dissolved irradiated sample (^{148}Nd, ^{145}Nd and ^{146}Nd measurement) are mostly used to determine mean burnup at different fuel rod axial positions [1].

In the present paper we will detail another technique, Secondary Ion Mass Spectrometry (SIMS), based on mass spectroscopy method, and dedicated to local isotopic ratio determination. The SIMS method efficiency to determine local burnup profile will be demonstrated on low and high burnup fuel pellets :

- To verify the accuracy of radial burnup profiles, a comparison of SIMS results with both EPMA determination and neutronic computations (when available) is proposed ;
- Integration of these local measurements, to obtain mean burnup at sampling axial position are finally compared to spectroscopy results and discussed.

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2. . MATERIALS AND METHODS

2.1. SAMPLE

UO2 samples with an initial ^{235}U enrichment of 4.5 w% was taken from a French PWR (Pressure Water Reactor) fuel rod. The local burnup at the measurement position were determined from ^{137}Cs analyses using spectroscopic methods (Table I).

Fuel pellet	Low burnup "LBU"	High burnup "HBU"
Number of irradiation cycles	3	6
Axial Bu (GWd/tM) at the sampling position (^{137}Cs measurement)	37.8	72.7

Table I : LBU and HBU irradiated fuel features

2.2. SIMS PROCEDURE

Secondary Ion Mass Spectroscopy (SIMS) was performed using a shielded IMS6f (CAMECA) device [2]. $\frac{^{145}Nd}{^{238}U}$ and $\frac{^{146}Nd}{^{238}U}$ isotopic ratios were collected with a 7 nA oxygen primary beam. On each data point, the analyzed diameter was 30 µm width.

The quantitative isotopic ratio $\left(\frac{^{145}Nd}{^{238}U}\right)_{quantitative}$ is a function of the measured intensity ratio $\frac{I\left(^{145}Nd\right)}{I\left(^{238}U\right)}_{SIMS}$ using the following relation [3] :

$$\left(\frac{^{145}Nd}{^{238}U}\right)_{quantitative} = RSF_{(Nd/U)} \bullet \frac{I\left(^{145}Nd\right)}{I\left(^{238}U\right)}_{SIMS} \quad (1)$$

With :

$\frac{I\left(^{145}Nd\right)}{I\left(^{238}U\right)}_{SIMS}$: intensity ratio measured by SIMS

$RSF_{(Nd/U)}$: Relative Sensitivity Factor for (Nd/U) isotopic ratios.

$\left(\frac{^{145}Nd}{^{238}U}\right)_{quantitative}$: quantitative isotopic ratio

$RSF_{(Nd/U)}$ was computed from both isotopic ratio measurement by SIMS and mass spectroscopy after dissolution, on a reference sample adjacent to the LBU one (2).

$$RSF_{(Nd/U)} = \frac{\left(\frac{^{145}Nd}{^{238}U}\right)_{Mass\ Spectr\ /\ ref\ sample}}{\left\langle \frac{I\left(^{145}Nd\right)}{I\left(^{238}U\right)}_{SIMS\ /\ ref\ sample} \right\rangle_{radius}} \quad (2)$$

With :

$\left\langle \frac{I\left(^{145}Nd\right)}{I\left(^{238}U\right)}_{SIMS\ /\ ref\ sample} \right\rangle_{radius}$: intensity ratio mean value calculated by circular integration of SIMS radial measurements on reference sample

$\left(\frac{^{145}Nd}{^{238}U}\right)_{Mass\ Spectr\ /\ ref\ sample}$: isotopic ratio measured by mass spectroscopy on reference sample.

2.3. EPMA PROCEDURE

Electron Probe Micro Analysis (EPMA) was performed using a shielded CAMEBAX model (CAMECA) [4]. Neodymium (Nd) was measured using the L□ line of the Nd X-ray spectrum with a LiF crystal. Nd radial distribution was measured at an electron potential of 15 kV and incident beam current of 250 nA, with an acquisition time of 10 s. Quantitative analysis was carried out using a reference neodymium dissolved glass sample.

2.4. BURNUP DETERMINATION

From fissions products inventory (Nd balance by EPMA and $\frac{Nd}{U}$ isotopic ratios by SIMS), burnup is computed using relationships determined with codes APOLLO2-PEPIN[5, 6]. The following equations were used :

SIMS-burnup relationship (UOX fuel 4.5% ^{235}U): $$Bu(GWd/tM) = 13642 \bullet \left(\frac{^{145}Nd + {}^{146}Nd}{^{238}U}\right)$$

EPMA-burnup relationship : $$Bu(GWd/tM) = 95.3 \bullet Nd(w\%)$$

Validity of EPMA-burnup relationship has already been demonstrated on a wide range of burnup on UO_2 fuel samples [4, 7].

Quantifications of errors on SIMS burnup determination are the consequence of :

1. counting statistic of isotopic ratios by SIMS : relative uncertainties <5%
2. error on the determination of $RSF_{(Nd/U)}$: relative uncertainties <6%
3. error on SIMS-burnup relationship : relative uncertainties <2%

The total contribution of these previous errors can be estimated to be approximately 8%.

In the same way, EPMA burnup determination are calculated taking into account the following uncertainties :

1. w% Nd measurement error : relative uncertainties <8%
2. error on EPMA-burnup relationship : relative uncertainties <2%

The propagated value is estimated to be lower than 9%.
To improve the quality of EPMA measurements, an increase of acquisition time together with analyzed area would be helpful. In these conditions w% (Nd) errors are predicted to be less than 5%.

3. RESULTS AND DISCUSSION

The location of radial burnup measurements are presented on figure 1, respectively on LBU and HBU fuel sample.

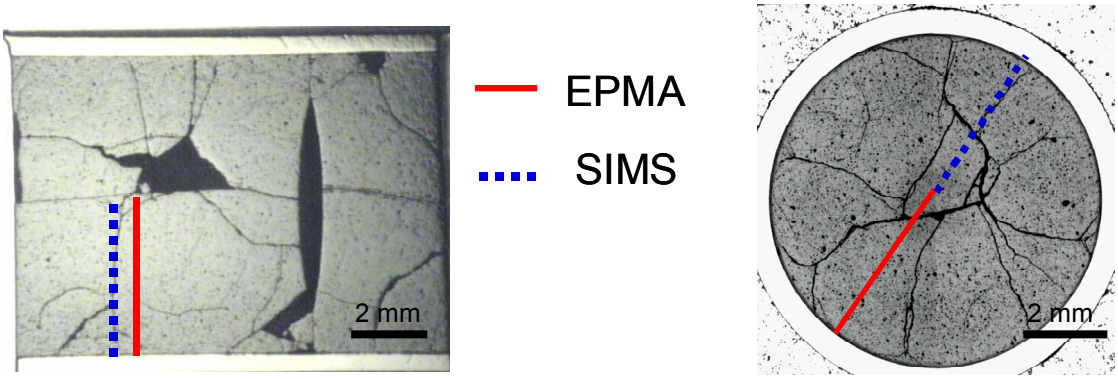

Figure 1. Location of EPMA and SIMS measurements on (a) LBU and (b) HBU fuel pellet

3.1. RADIAL BURNUP DETERMINATION

The radial evolution of burnup on respectively LBU and HBU sample from EPMA and SIMS measurement is presented on the figures 2 and 3.

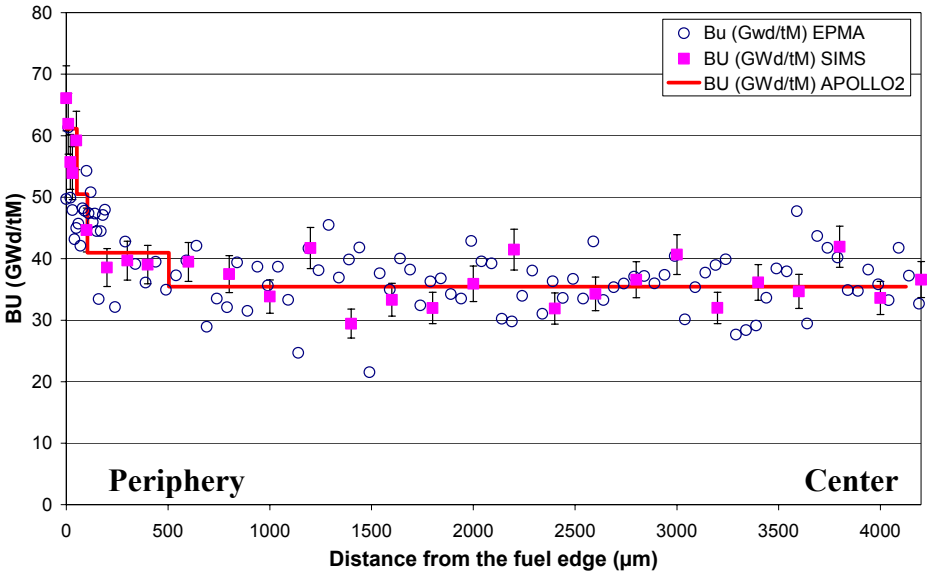

Figure 2. Radial burnup distribution collected on the LBU sample using SIMS and EPMA method

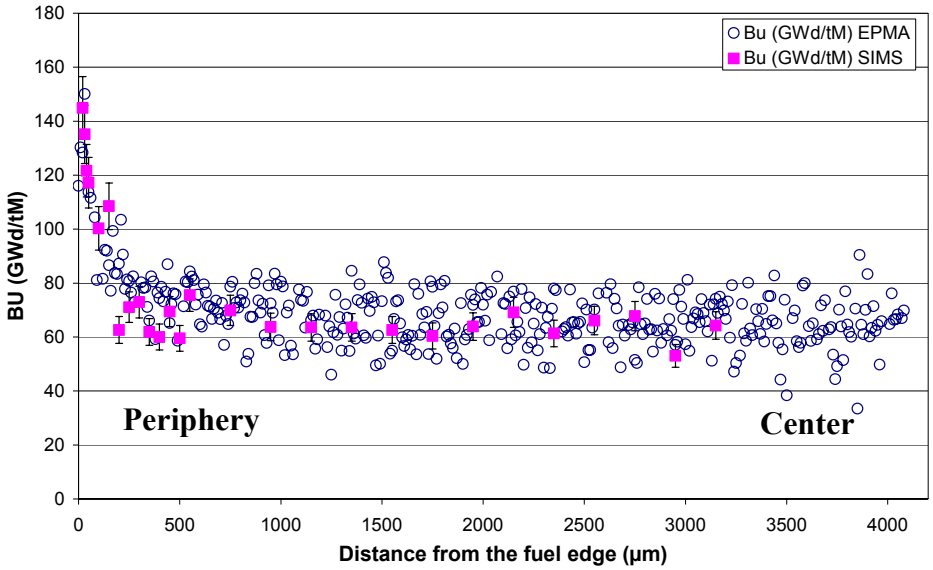

Figure 3. Radial burnup distribution collected on the HBU sample using SIMS and EPMA method

Burnup profiles determined by the two methods are very close whatever the level of irradiation. Data dispersion observed on EPMA diagram (± 5 GWd/tM on LBU sample, and ± 10 GWd/tM on HBU sample) is associated to measurements uncertainties (consequence of counting time statistic) and the ceramic microstructure (i.e. porosity, cracks, grain boundaries…).
SIMS diagram do not exhibit such amplitude in data dispersion (± 5 GWd/tM on both LBU and HBU sample) due to a larger analyzed area (30 µm by SIMS compared to 1µm by EPMA).
On both LBU and HBU samples, radial profiles exhibit a specific behavior at the pellet periphery. From 0 to 200 µm for LBU, and from 0 to 500 µm for HBU a steep increase of burnup is evidenced. This specific shape at the pellet periphery is partly a consequence of Pu production caused by neutron resonance absorption of ^{238}U.
On LBU fuel pellet, available radial neutronic simulations carried out on the same type of fuel are shown. The specific behavior previously discussed is well predicted that demonstrates its accuracy.

3.2. INTEGRAL BURNUP EXTRAPOLATION

From radial EPMA and SIMS burnup profiles, average values were obtained by a circular integration of radial data. The calculated integral burnup values are then compared to those determined on the same sample, either by gamma spectrometry or from neutronic calculation (Table 2).

Table 2. Comparison of EPMA and SIMS Burnup determination together with spectroscopy results

Fuel pellet		Low burnup "LBU"	High burnup "HBU"
Number of irradiation cycles		3	6
Sampling position (mm/rod bottom)		1764	2984
Mean BU At the sampling position (GWd/tM)	EPMA measurement	37.2	71.7
	SIMS measurement	37.6	68.8
	spectroscopy	37,6	72,7
SIMS-EPMA difference (%)		+ 1 %	- 4.0 %
SIMS- difference (%)		< 0.1 %	- 5.0 %
EPMA- difference (%)		-1 %	- 1.4 %

Integral burnup determinations exhibit similar values with a relative difference that does not exceed 5%. It has to be noticed that mean burnup determination by SIMS on HBU is slightly different from EPMA and ones. Several hypothesis are proposed to explain this difference :

- Measurement radius are different by SIMS and EPMA that could modify local fission products distribution and consequently the burnup evaluation.
- On HBU sample the rim region is Pu rich and local burnups are very high. As a consequence SIMS-burnup relationship is maybe used out of its validity range.
- On HBU fuel there was a lack of measurement points close to the cladding-pellet interface (i.e. where high burnup are determined). It could explain the lower value observed by SIMS.

4. CONCLUSIONS

The accuracy of local burnup determination on low and high irradiated fuel has been demonstrated.
The comparison of SIMS and EPMA profiles with radial burnup distribution from neutronic code calculation allows the validation of these simulations.
Mean burnups determined from integrations of radial profiles are well connected to gamma spectroscopy measurements.
The efficiency of the "w%(Nd)-burnup" and "isotopic ratio-burnup" relationships have been demonstrated on a wide range of burn-up values for a 4.5% ^{235}U enrichment, from SIMS and EPMA data collection.
Using the same quantification procedure, radial burnup determinations are carried out on irradiated MOX fuel.

5. REFERENCES

[1] C. Devida, M. Betti, P. Peerani, E.H. Toscano, W. Goll, Hotlabs 2004 meeting proceedings (2004) 106-113.

[2] B. Rasser, L. Desgranges, B. Pasquet, Applied Surface Science 203-204 (2003) 673-678.

[3] Microcaractérisation des solides, Méthodes d'observation et d'analyse, CRAM-CNRS ed. (1989).

[4] J. Noirot, L. Noirot, L. Desgranges, J. Lamontagne, Th. Blay, B. Pasquet, E. Muller, Proceedings of the 2004 International Meeting on LWR Fuel Performance. (2004) 329-338.

[5] R. Sanchez, J. Mondo, Z. Stankovski, A. Cossic, I. Zmijarevic, Nuclear Science and Engineering 100 (1988) 352-362.

[6] P. Cousinou, C. Lavarenne, D. Biron, M. Doucet, J.P. Grouiller, N. Thiollay, E. Guillou, Nuclear Engineering and Design, 208 (2001) 205-214.

[7] M. Verwerft, Journal of Nuclear Materials 282 (2000) 97-111.