Quantitative Burnup Determination: A Comparision of Different Experimental Methods

C. DEVIDA+, M. BETTI*, P. PEERANI**, E.H.TOSCANO[1]* and W. GOLL[2]

+ Comisión Nacional de Energía Atómica, Buenos Aires, Argentine
[1] European Commission, Joint Research Centre, Institute for Transuranium Elements, PO Box 2340, 75125 Karlsruhe, Germany
** European Commission, Joint Research Centre, Ispra, Italy
[2] Framatome ANP GmbH, P.O. Box 3220, 91058 Erlangen, Germany

Abstract

The burn-up of nuclear fuel is defined as the energy produced per mass of fuel and, hence, is related to the inventory of fission products formed in the matrix of the fuel. It affects both neutron-physical and material properties. Therefore, it is essential to have methods available that allow a reliable determination of this important parameter.

The burn-up is usually determined by measuring the content of an element that results from the fission process. The isotope ^{148}Nd has proven to be an ideal monitor due to its chemical and neutron physical properties. On the other hand, ^{148}Nd can only be determined by wet-chemistry methods, which means a rather costly and time consuming chemistry process. Another method using the sum of ^{145}Nd and ^{146}Nd is proposed. In case of very high burn-ups of UO_2 fuel and, especially, MOX fuel this method needs weighed yields for U and Pu to obtain a sufficient accuracy.

Among the non-destructive spectrometric methods, the burn-up determination with ^{137}Cs provides adequate results provided the gamma radiation detector is calibrated and self-attenuation effects of Cs together with measurement geometries are considered.

Introduction

The burn-up of nuclear fuel is defined as the energy produced per mass of fuel and, hence, is related to the inventory of fission products deposited in the matrix of the fuel as a result of the irradiation process. It affects both physical and material neutron properties. Therefore, it is essential to have methods available that allow a reliable burn-up determination.

The method most widely accepted is based on the chemical analysis of dissolved samples following ASTM-Norm E 321-96. Alternatively, gamma spectrometric methods are used, mainly to compare the relative burn-up between fuel rods coming from a single reactor or different positions in a single rod.

In the present paper these two widely used methods of burn-up monitoring will be discussed and the practicability of spectrometric methods in case of LWR fuel rods fuel demonstrated.

Wet chemistry

The fuel burn-up is usually determined by measuring the content of an isotope that accumulates through the fission process. Some isotopes of neodymium, in particular ^{148}Nd, have proven to be ideal monitors due to their chemical and neutron-physical properties. On the other hand, the amount of this particular isotope can only be determined by the analysis of dissolved samples, which means using rather costly and time consuming wet chemistry methods.

^{148}Nd is usually selected for the burn-up determination for the following reasons [1]:

- It is a stable fission product (no decay corrections are necessary).
- It has a well known fission yield.
- It is not volatile and has no volatile precursors.

---

toscano@itu.fzk.de
Wolfgang.goll@framatome-anp.com

- It has almost the same yield for ^{235}U and ^{239}Pu and the yield is independent of neutron energy (see below, Table I and Ref. [2]).
- The isotope ^{142}Nd can be used for natural Nd-contamination determination.
- It is formed exclusively by fission (low neutron capture cross section).
- It is not present in non-irradiated fuels.

The standard procedure normally used in the hot cells comprises:

- Sample cutting (the sample, usually considered to be representative, amounts to one fuel pellet).
- Fuel dissolution (typically in 100 ml of a 6M nitric acid heated up to about 94 °C in an appropriate vessel).
- Dilution of the liquid sample and filtering.
- Dissolution of the residues.
- Preparation and spiking of the aliquots for the mass spectrometry.
- Separation of U and Pu.
- Determination of the isotopic composition.

To determine the isotopic composition, two different methods are used for the U, Pu and for the Nd-vector, respectively. For U and Pu, Thermal Ionisation Mass Spectrometry (TIMS) according to the procedure of Isotopic Dilution (IDMS), is extensively used. On the other hand, for the determination of the Nd-vector the Ion

Chromatography (IC) is used on-line to separate this element from the other fission products. Subsequently, the isotopic composition of the neodymium is determined by isotopic dilution Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

The ICP is an argon plasma, at a temperature of around 8000 K and at atmospheric pressure, for direct introduction of soluted samples by a nebulisation system (see, e.g., Ref.1). The sample flows as a gas, vapour or aerosol of fine droplets or solid particles and is introduced using a pneumatic nebuliser. The plasma is formed by an electrodeless discharge in a gas (Ar) maintained by energy coupled to it from a radio-frequency generator. The discharge is initiated by a Tesla coil spark that sows the Ar-gas with free electrons. The sample is vaporised, atomised and subsequently ionised during the transit through the plasma. Afterwards, the ion beam is extracted from the plasma and focused onto the mass spectrometer,

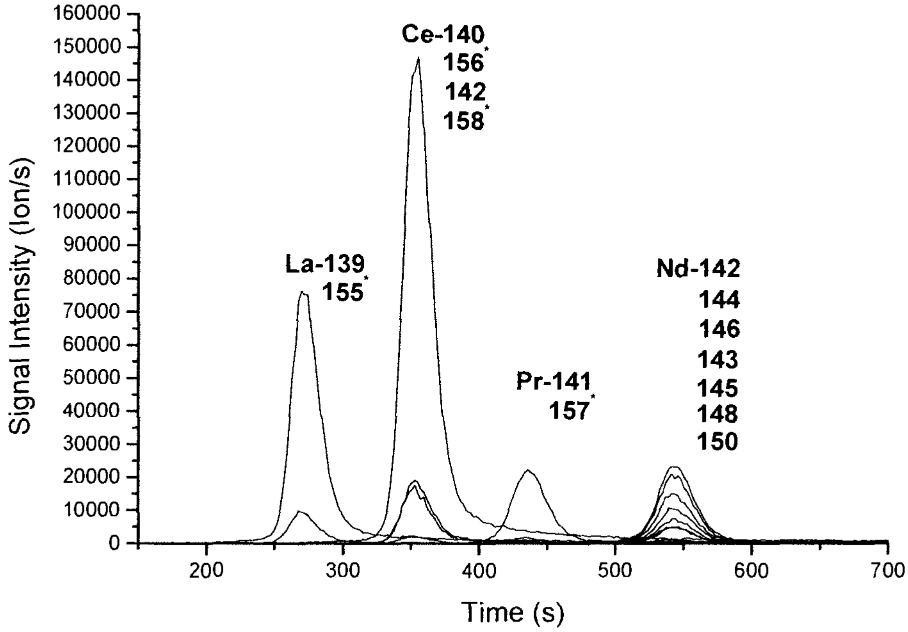

Fig. 1 Mass spectrometric determination of nuclides at different times

which consists of a sector field MS and a Faraday cup detector. Each nuclide-ion is separated according to their energy and mass. The relative amount of each nuclide is determined by specific software. In Fig. 1, an example of this type of analysis is presented.

Burnup calculation

For the burn-up calculation the following definition has been widely adopted. The definition is based on the number of fissioned atoms compared to the pre-irradiation number of heavy metal (HM) atoms in a given fuel:

$$\text{Bu [atom \%]} = \frac{\text{number of fissioned atoms}}{\text{pre-irradiation number HM of atoms}} \times 100$$

Where:

$$\text{number of fissioned atoms} = \frac{\text{number of [Bu-monitor] atoms}}{\text{yield of [Bu-monitor]}}$$

Based on this definition and considering that the yield of ^{148}Nd is about 1.7 % (see Table I below), the burn-up is calculated, specifically for this isotope, from to the following equation:

$$BU\% = \frac{\dfrac{^{148}Nd(g/g)}{0.017\times 148}}{\dfrac{^{148}Nd(g/g)}{0.017\times 148} + \dfrac{U_{total}(g/g)+Pu_{total}(g/g)}{238}} \times 100$$

Eq. 1

It should be noticed that, applying this scheme the amount of HM atoms before irradiation is consistently determined by the analytical method for the considered sample and it is not necessary to make assumptions or have the knowledge about this quantity.

Whereas ^{148}Nd is adequate when using wet chemistry analytical methods, which combine elemental separation techniques (IC) with mass spectrometric isotope determination, other methods like Secondary Ion Mass Spectrometry (SIMS) that could be used also for the determination of the burn-up of solid samples, suffer from isobaric interference problem. In this case, other isotopes - having some of the advantages cited above – can be considered. Two other isotopes appear suitable: ^{145}Nd and ^{146}Nd. They have some of the advantages previously cited but also some drawbacks which may need corrections to obtain sufficiently accurate results:

- The yields for ^{235}U and for ^{239}Pu are different (see Table I). Therefore, in cases of high burn-ups, effective yields have to be introduced accordingly.
- Since the capture cross section of the ^{145}Nd is relatively high, this isotope transmute to ^{146}Nd by neutron capture.

	^{145}Nd	^{146}Nd	^{148}Nd
^{235}U	3.932	2.982	1.675
^{238}U	3.892	3.526	2.279
^{239}Pu	3.054	2.5	1.689
^{241}Pu	3.122	2.65	1.873

Table I Cumulative Nd-isotopes yield, in percent, for U and Pu, according to JEF 2.2.

To overcome the transmutation problem, the sum of the two isotopes could be used and the equation reported above could be applied, considering the sum of both yields.

Sample	Theoretical BU [GWd/t(HM)]	^{148}Nd	^{145}Nd+^{146}Nd	Difference [%]
Th-1	60	6.22	6.31	-1,38
Th-2	65	6.73	6.78	-0.79
Th-3	70	7.24	7.3	-0.83
Th-4	75	7.74	7.75	-0.16
F-1	59	6.09	5.94	2.59
F-2	51	5.34	5.28	1.04
F-3	63	6.63	6.65	-0.33
F-4	37	3.86	3.72	3.62
F-5	78	8,1	7,7	5,0
F-6	93	9,7	9,2	5,3
MOX-1	45	4.71	4.25	10.42
MOX-2	22	2.29	2.06	10.32

Table II Burn-up calculated on the basis of experimental and theoretical results for UO_2 and MOX fuels (for the theoretical value the conversion 1% = 9.6 GWd/t(HM) was used).

In **Table II**, the burn-ups calculated applying this method are presented for theoretical calculations as well as for experimental results. As can be seen, the results obtained by using ^{148}Nd or (^{145}Nd+^{146}Nd) are in relatively good agreement for the UO_2-fuels, both in the case of theoretical (Th-1 to Th-4) as in the experimental (F-1 to F-6) results. In fact, the maximum difference determined was 3.6 % comprising burn-ups of up to 65 GWd/t(HM). This is not the case for highly burnt UO_2 fuel beyond 70 GWd/t(HM) and especially for MOX fuel, where the differences amounted unacceptably to 10 %. This is due to the substantial difference between the yield of Pu as compared to U. This problem could be overcome by using a weighted average for the two yields.

Gamma spectrometric methods

Gamma spectrometry is a non-destructive, rapid, and low cost method that serves to determine the activity of all emitting fission products still present in a fuel rod at the time of measurement. It requires the calibration of the gamma spectrometric installation in absolute values, that means, the determination of the curve of efficiency as a function of energy for given experimental conditions. In some laboratories a ^{226}Ra source, whose gamma spectrum is composed of many lines, serves to give the relative efficiency, and a standard ^{60}Co source is used for cross-checking of the absolute value. In other laboratories a ^{252}Eu source, with similar characteristics, is used for the relative efficiency and ^{137}Cs-source serves to ascertain the absolute value.

The main difficulty of this method is that the geometries of the fuels and standard sources are, in general, different. For this reason, it is necessary to determine the transmission phenomena of the gamma radiation emitted. That means that the attenuation and self-attenuation properties of the fuel and the structures surrounding the fuel have to be determined.

Efficiency calibration of the gamma scanning system based on ^{137}Cs:

Cesium-137 is a primary fission product with high yield per fission, relatively long half-life and the gamma spectrum shows a good resolution peak. In fact, it is the decay product Ba with a very short half-live compared to ^{137}Cs that is measured. The inventory of Cs along the fuel rod is proportional to the local burn-up. In this context, the accurate efficiency calibration of the gamma scanning system is essential to determine the exact ^{137}Cs activity within the fuel rod.

A certified ^{137}Cs source having similar geometry and characteristics as the fuel rod, has been used to calibrate the efficiency of the spectrometry system. The width of the collimator was selected according to the activity of the fuel rod to be measured and the maximum acceptable count rate of the spectrometry chain. The axial homogeneity and the central position of the source were determined by performing a scan with an analogue rate meter. In this central position of the source, a spectrum was taken and the source count rate (**R_{Cs}**) normalised to length according to the following equation:

$$\mathbf{R_{Cs} = N_{Cs}\,.\,l_{Cs}\,/\,t\,.\,w_s \quad [\,counts\,.\,sec^{-1}]}$$

Where	N_{Cs}	net counts 137Cs peak (661,6 Kev)
	T	acquisition life-time (sec)
	l_{Cs}	source length (mm)
	w_s	collimator width (mm)

From this equation, the efficiency of the gamma scanning system (**E**) is given by the following equation:

$$\mathbf{E = R_{Cs}\,/\,(\,D_{Cs}.\,P_e.\,T.\,A_{Cs}\,) \quad [\,counts.\,sec^{-1}.\,Bq^{-1}]}$$

Where	D_{Cs}	source decay, $e^{-0,693.\,\tau\,/\,30,25}$
	τ	decay time
	P_e	137Cs gamma emission probability
	T	transparency factor of the source.
	A_{Cs}	certified source activity (Bq)

^{137}Cs activity of the fuel rod at end of irradiation

From each spectrum of the axial gamma scanning the net counts of ^{137}Cs peak are taken (N_i), where the "i" represents each measured fuel rod interval number. N_i is the integral counts along the continuous scan in each interval (i). The count rate (**R_i**), normalised to length fuel rod for each interval, is given by the follow equation:

$$\mathbf{R_i = N_i\,.\,l\,/\,t_i\,.\,w_s \qquad [counts.\,sec^{-1}]}$$

Where	N_i:	net counts ^{137}Cs peak in each interval (661,6 Kev)
	t_i	acquisition life-time (sec)
	l	fuel stack interval length (mm)
	w_s	collimator width (mm)

The small stack length not measured between spectra acquisition, while the software save data and reset the system, is considered as systematic error.

Then the activity of each interval (**A_i**) is given by the follow equation:

$$\mathbf{A_i = R_i\,/\,(\,D_{fr}.\,P_e.\,T.\,E\,) \quad [Bq]}$$

Where	D_{fr}	fuel rod decay factor, $e^{-0,693.\,\tau\,/\,30,25}$,
	τ	fuel cooling time
	P_e	137Cs gamma emission probability
	T	transparency factor of the fuel rod.
	E	efficiency (counts. Sec^{-1}. Bq^{-1})

And the total 137Cs activity of the fuel rod at end of irradiation (A_{fr}) is given by:

$$\mathbf{A_{fr} = \Sigma\, A_i \quad [Bq]}$$

Total ^{137}Cs activity including the fuel irradiation time

The total ^{137}Cs activity has to take into consideration the decay occurred during the irradiation periods. The following formula gives a reasonable good precision value for the ^{137}Cs equivalent activity (**A_{eq}**), taking into consideration the irradiation history data:

$$\mathbf{A_{eq} = A_{fr} .\ \{\lambda.\ \Sigma\ P_j.\ t_j\ \}\ /\ \{\Sigma\ P_j.\ (1\text{-}\ e^{-\lambda.\ tj}\ ).\ e^{-\lambda.\ tk}\ \}} \qquad \mathbf{\{1\}}$$

where	λ	decay constant for ^{137}Cs (year^{-1})
	P_j :	average relative reactor power at a considered irradiation interval
	t_j .	irradiation interval (year); reasonably short comparing with the ^{137}Cs half life
	t_k :	elapsed time from end of t_j to EOI (year).

In this correction factor, the numerator represents the perfect production of ^{137}Cs without decay and the denominator represents the formation/decay of ^{137}Cs during irradiation.

The formation/decay of ^{137}Cs during irradiation (denominator) can be taken into consideration by:

$$d\ N_{Cs} / dt = \text{production rate} - \text{decay} \quad = \sigma_{fis}\ \ \phi\ \ y\ -\ \lambda\ \ N_{Cs} \quad [\text{atoms.sec}^{-1}]$$

$$= R\ -\ \lambda\ \ N_{Cs}$$

$$\text{and for each period} \quad = k.\ P_j\ -\ \lambda\ \ N_{Cs}$$

where	$d\ N_{Cs} / dt$:	temporal variation of ^{137}Cs atoms
	λ	decay constant for ^{137}Cs (sec^{-1})
	y ·	^{137}Cs atoms yield per fission.
	ϕ	neutron flux (n. cm^{-2} sec^{-1})
	σ_{fis}	fission cross section (cm^2)
	R	production rate = k. P_j
	P_j .	average relative reactor power at a considered irradiation interval
	k	conversion units factor

the general solution for this equation is:

$$N_{Cs} = k1\ \ e^{-\lambda.\ t}\ +\ k2 \qquad \{2\}$$

With the following limits condition:

t = 0 (initial condition) is $N_{Cs} = 0 \rightarrow k1 = -k2$

t = ∞ (saturation condition) is $R = \lambda\ \ N_{Cs} \rightarrow N_{Cs} = R / \lambda = k2$

and substituting in {2} $\quad N_{Cs} = R\ .\ (1\text{-}\ e^{-\lambda.\ t}) / \lambda$

then the ^{137}Cs activity produced for each interval

where $A_{Cs} = N_{Cs}\ .\ \lambda$ [atoms. sec^{-1}]

$$A_{Cs} = R\ \ (1\text{-}\ e^{-\lambda.\ tj}\ )$$

represents the formation/decay of ^{137}Cs in each period and the remained activity of the ^{137}Cs of this interval. Hence, at EOI, the activity is:

$$\mathbf{A_{Cs} = R\ .\ (1\text{-}\ e^{-\lambda.\ tj}\ )\ .\ e^{-\lambda.\ tk}}$$

The theoretical production of ^{137}Cs without decay (numerator) is:

$d\, N_{Cs} / dt$ = production rate = R [atoms.sec^{-1}]

the solution is: $N_{Cs} = R \quad t$

then the ^{137}Cs activity produced for each interval:

where $A_{Cs} = N_{Cs} \quad \lambda$ [atoms. sec^{-1}]

$$\mathbf{A_{Cs} = \lambda \,.\, R \,.\, tj}$$

Finally the ratio between perfect production of ^{137}Cs without decay and the formation/decay of ^{137}Cs during irradiation is given by equation **{1}**.

Burn-up calculation

In order to calculate the burn-up from ^{137}Cs equivalent activity is necessary to calculate the weighed average for both: ^{137}Cs atoms yield and energy release per fission, considering all contributing fissile isotopes present in the fuel composition. For UO_2 fuel the contribution of ^{235}U can be considered as a first approximation.

Finally, the average burn-up of the U enriched stack fuel rod (**Bu**), is given by the follow:

$$\mathbf{Bu = (A_{eq}.\, f_c.\, E_f\,)\; /\; (\lambda\, .\, y.\, w\,) \qquad [\,MW.\, day.\, tonU^{-1}\,]}$$

Where A_{eq} .	^{137}Cs equivalent activity (Bq).
λ .	decay constant for ^{137}Cs (sec^{-1}).
f_c	unit conversion factor (1,854e-24 MW. day Mev^{-1}).
E_f:	energy release per fission (profitable Mev fission^{-1}).
y ·	^{137}Cs atoms yield per fission.
w	metallic U mass in the U enriched stack fuel rod (ton).

The axial profile burn-up of the fuel rod is obtained by the local Bu calculated in each measured interval from the local (Ai) to average (ΣAi /n) ^{137}Cs activity ratio.

The previous described method has been applied to several fuel rods irradiated in commercial reactors. The differences between the calculated burn-up and the burn-up determined by wet chemistry were around 30%. This deviation is obviously attributed to the different gamma absorption coefficient between the fuel rod and the standard.

Additional work is on way to improve the calibration of the gamma measuring system using a standard performed on the basis of a well-characterised fuel rod segment.

The last equation indicates a linear relationship between the burn-up and the concentration of the isotope ^{137}Cs. In fact, experimental data coming from a single reactor, plotted in Fig. 2, reveals a basically linear relationship between the measured ^{137}Cs and the average burn-up of fuel rods. The linear relationship holds for a wide range of burn-ups, from 15 to more than 80 GWd/tU.

The last equation indicates a linear relationship between the burn-up and the concentration of the isotope ^{137}Cs. In fact, experimental data coming from a single reactor, plotted in Fig. 2, reveals a basically linear relationship between the measured ^{137}Cs and the average burn-up of fuel rods. The linear relationship holds for a wide range of burn-ups, from 15 to more than 80 GWd/tU.

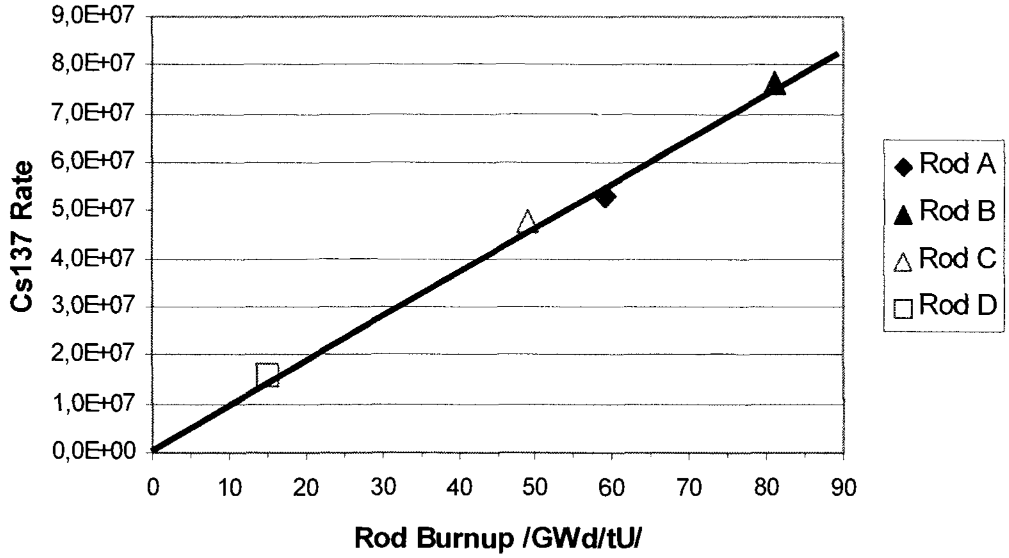

Fig. 2 The integral ^{137}Cs-rate as a function of burn-up for fuel rods from a single reactor and measured under constant calibration conditions

Conclusion

In conclusion, two methods for the burn-up determination of irradiated fuel rods have been described. Methods, built on wet chemistry and based on the quantitative determination of Nd-isotopes, provide reference values of high quality but are costly and time consuming. On the other hand, gamma spectrometry provides a simple and accurate methodology for the comparison of the burn-up values for a single series of fuel rods. The linear relationship between the ^{137}Cs-rate and the burn-up has been demonstrated for a wide range of burn-up values.

References

[1] M. Betti, Journal of Chromatography A 789 (1997) 369-379