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SIMS characterisation of actinide isotopes in irradiated nuclear fuel

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ABSTRACT

Numerical codes are used to calculate the inventory of plutonium and minor actinides produced during irradiation in industrial power reactors. Secondary ion mass spectrometry (SIMS) is a useful method for validating theses inventory calculations especially with regards to isotopic characterisation. Isotopic ratios measured by SIMS on the radius of an UO_2 irradiated fuel pellet are presented and compared with calculated values in this paper. The SIMS results tally well with the calculations, as both show an increase in the actinide concentration on the pellet periphery due to the rim effect.

1. Introduction

Nowadays, the nuclear industry produces most of the plutonium and actinide inventory in the world. During the irradiation of oxide ceramic pellets, uranium atoms not only undergo fission but also neutron capture, which transform them into plutonium and minor actinides. Before these materials can be handled, the quantity of plutonium and minor actinides produced during irradiation in power reactors must be accurately estimated. Some numerical codes have been developed for this purpose. The CEA computer code, APPOLO2 [1], was developed to calculate the concentration of isotopes formed during irradiation as a function of the radial position within the pellet. The isotopic analysis of dissolved nuclear fuels by inductively-coupled plasma mass spectrometry (ICP-MS) usually provides experimental data for code validation. However, the data are averaged over several pellets because of dissolution and therefore cannot be used to validate a radial profile within the pellet.

Among a few other techniques available in hot laboratories (EPMA and laser ablation), secondary ion mass spectroscopy (SIMS) is a very valuable tool for determining radial isotopic profiles in an irradiated pellet. Characterisation of real spent fuel with the high mass resolution SIMS technique has been only possible at the CEA for a few years, ever since a shielded CAMECA IMS 6f SIMS was installed in our laboratories [2]. Irradiated samples have been examined since 2002 ([3–5]).

After a short description of the nuclear reactions whereby actinides are created during irradiation, this paper will then discuss the characterisation of a UO_2 irradiated sample by SIMS before comparing the results with the isotopic ratios calculated by the APPOLO2 code.

2. Actinide formation during irradiation in a PWR

The actinide inventory in nuclear fuel results from the balance between three types of nuclear reactions:

- Fission reactions: only fission of ^{235}U occurs at the beginning of irradiation, whereas ^{239}Pu fissions can be as numerous as ^{235}U fission at high burn-up.
- Capture reactions: an actinide isotope with atomic number N can form an isotope $N + 1$ by capturing a neutron. This is the case for ^{238}U, which forms ^{239}U via neutron capture.
- Decay reactions (especially β decay): a chemical element with Z protons can form another element with $Z + 1$ protons. This is the case for ^{239}U which forms ^{239}Np and then transforms into ^{239}Pu by two subsequent β decays.

The two first reactions have cross sections that depend on the energy of the incoming neutron.

High energy neutrons produced by fissions are slowed down in water, which generates an energy spectrum ranging from fast neutrons (~MeV) to epithermal neutrons (~eV) and to thermal neutrons (~meV). Moreover, these reactions occur at different radial positions within the fuel pellet as a function of their cross sections. For example, when ^{238}U captures an epithermal neutron, it produces ^{239}Pu (after β decay) with a very high cross section. Thus, most epithermal neutrons are captured on the edge of the pellet. Consequently, plutonium is created mainly on the pellet edge, which results in a sharp increase in the ^{239}Pu concentration and a decrease in the ^{238}U concentration. The fission reaction of ^{235}U with a thermal neutron, however, has a lower cross section and so the thermal neutron flux decreases slightly when moving from the edge of the pellet to the centre. Consequently, the ^{235}U concentration increases progressively when moving from the pellet edge to the centre.

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3. Experimental details

3.1. Shielded SIMS

SIMS provides a local isotopic analysis of a solid sample. A primary beam is focused on the sample and sputters its surface. The sputtered atoms are essentially neutral but a small fraction (about 1%) is ionised and can be extracted by an electrical field. The ions are then directed into a mass spectrometer for isotopic analysis. A glove box and lead shielding were added to the commercial IMS 6f to handle radioactive material. The layout of the modified apparatus is shown in [2].

In this study, the primary ion beam was oxygen and positive secondary ions were detected with a 5000 V extracting voltage. Mass interferences have to be avoided in isotopic analysis, which is why a high mass resolution ($M/\Delta M > 5000$) was used to eliminate molecular interferences. However, in the case of $^{238}U^{1}H$ interference with ^{239}Pu, mass filtering was not sufficient because the $^{238}U^{1}H$ intensity was much higher than that of ^{239}Pu. This is why energy filtering was used to prevent such interference. Even with this filtering, two isotopes with the same mass number could not be distinguished. For example, ^{238}Pu could not be separated from ^{238}U. However, its concentration was low and its contribution to the ^{238}U count rate was negligible. Such an approximation was not possible for ^{241}Am–241Pu interference because the ^{241}Am intensity accounts for a non negligible part of the ^{241}Pu intensity.

Ratios between different isotopes were determined by dividing their measured intensities. Standard samples were required to achieve quantitative measurements from these intensity ratios. Multiplicative factors linking actual isotopic ratios to intensity ratios are determined in standard samples. The value of these multiplicative factors depends on the type of isotopic ratio. For isotopes of the same chemical element, the multiplicative factor only modifies the ratios by a few percent as only the mass bias effect needs correcting. For isotopes of different chemical elements, the multiplicative factor can vary by several orders of magnitude because matrix effects lead to different ionisation yields as a function of the chemical element. In our case, no standard sample was available. Due to the fact that the accuracy of the APPOLO2 calculation is ~5% on average, the isotopic ratio for isotopes of the same chemical element was used for direct comparison.

3.2. Irradiated sample

The sample was removed from a UO_2 nuclear fuel rod that had been irradiated for five cycles in a French pressurised water reactor. The local burn-up at the sampling position was calculated to be 61 GWd/tU. The fuel rod was composed of cylindrical UO_2 pellets that were ~8.17 mm in diameter and ~13 mm in length. They were initially enriched in ^{235}U by 4.5% and stacked in ~4 m long cladding made of a zirconium-based alloy. After irradiation, the fuel rod was shipped to a hot laboratory where the rod was cut up into slices. A 5 mm long slice was embedded in a metal alloy with a low melting point and polished to obtain a surface roughness of about 1 μm. SIMS was then used to analyse the polished surface.

4. Isotopic radial distribution of actinides in irradiated UO_2

SIMS was used on the irradiated UO_2 sample to measure the radial distribution of the actinide isotopes on a radius of the fuel pellet. Uranium, plutonium and various minor actinides were taken into consideration.

4.1. Uranium

Fig. 1 shows variations in the $^{235}U/^{238}U$ ratio measured with SIMS on a radius perpendicular to the pellet axis. As it can be seen, this isotopic ratio does not remain constant within the pellet. The gradual decrease in the $^{235}U/^{238}U$ ratio from the pellet centre towards its edge is a result of the decrease in the ^{235}U concentration due to fission reactions, while the ^{238}U concentration remains constant. The subsequent sharp increase in this ratio at the pellet edge results from the decrease in the ^{238}U concentration due to capture reactions, while the ^{235}U concentration changes more slowly. The calculated curve was obtained using the CEA APPOLO2 code [1].

Experimental and calculated values show in agreement within the ~5% error bars.

4.2. Plutonium

The plutonium distribution was then studied with the $^{n}Pu/^{238}U$ ratio. In order to compare the APPOLO2 calculated ratios with the experimental ratios, all the experimental ratio curves were multiplied by a single coefficient. This coefficient replaces the multiplicative factor which should have been determined with a standard sample. It was fitted to describe the $^{239}Pu/^{238}U$ ratio in the pellet centre.

Fig. 2(a) shows $^{239}Pu/^{238}U$, $^{240}Pu/^{238}U$, $^{241}Pu/^{238}U$ and $^{242}Pu/^{238}U$ ratios as a function of the pellet radius which were either obtained experimentally and multiplied by the coefficient mentioned above or calculated with the APPOLO2 computer code. Good agreement between the experimental and the calculated curves is observed. The curves evidence two different types of behaviour: (1) flat distribution in most of the pellet resulting from low capture cross sections with fast and thermal neutrons and (2) a sharp increase in the curves at the pellet edge due to an increase in the plutonium concentration and a decrease in the uranium concentration. The increase at the pellet edge is more or less pronounced depending

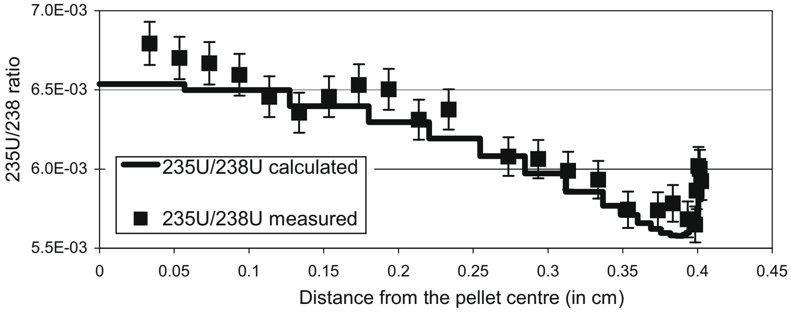

Fig. 1. Comparison of $^{235}U/^{238}U$ ratio measured with SIMS and calculated with APOLLO2 for a UO_2 fuel pellet radius (five cycles).

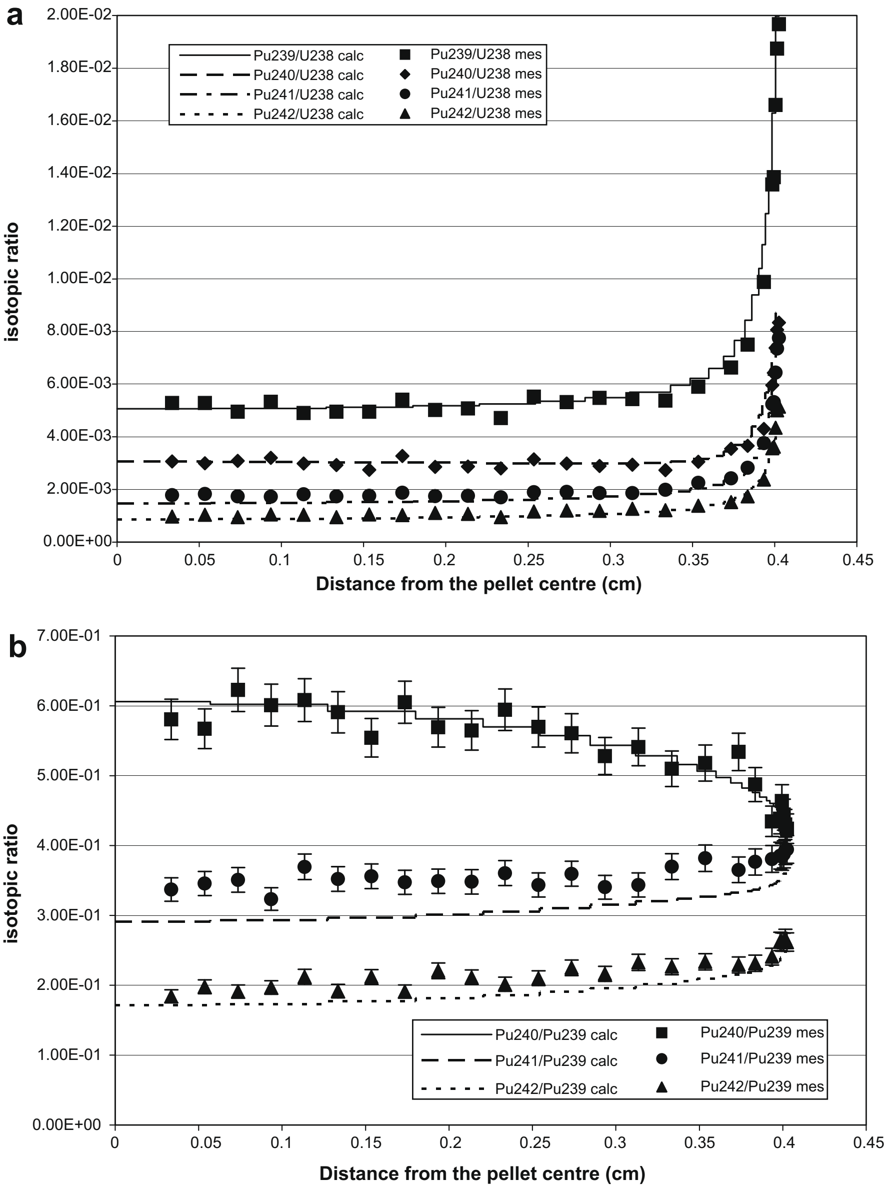

Fig. 2. (a) Comparison of experimental and calculated ^{n}Pu/^{238}U ratios along the pellet radius (error bars are of the smaller than the dot size). Experimental ratios were multiplied by a constant coefficient (see text for more information); (b) comparison of different experimental and calculated Pu isotopic ratios along the pellet radius.

on the plutonium isotope. This behaviour is better evidenced when studying ratios between various plutonium isotopes.

Fig. 2(b) shows ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu, and ^{242}Pu/^{239}Pu experimental and calculated ratios. This time, the experimental ratios are only affected by a mass bias effect with approximately 5% accuracy since all isotopes belong to the same chemical element. Agreement between experimental and calculated values depends on the ratio; this is assumed to be due to interference which cannot be neglected. Based on an accuracy of a few percent between the experimental results and the APPOLO2 calculations, agreement between experimental and calculated ^{240}Pu/^{239}Pu and ^{242}Pu/^{239}Pu ratios can be considered satisfactory in Fig. 2(b). This was not the case for the ^{241}Pu/^{239}Pu ratio. Though the ^{241}Pu and ^{241}Am isotopes were measured together, the experimental ratio actually corresponds to the (^{241}Pu + 241Am)/^{239}Pu ratio and cannot be compared directly to the calculated ^{241}Pu/^{239}Pu ratio. ^{241}Am forms after irradiation by decay during the cooling period and the ^{241}Am intensity depends on the cooling time after the irradiation has been stopped.

4.3. Other minor actinides

Due to mass interferences, only two minor actinide isotopes showed sufficient intensity permitting them to be measured. Fig. 3 shows both the ^{243}Am/^{238}U and ^{237}Np/^{238}U experimental and calculated ratios. As mentioned previously, the experimental and calculated ratios differ because the experimental data did not take into account the different ionisation yields of uranium and minor actinides. Comparison can only be made in terms of the curve shapes; in this respect the results tally well with the calculations.

^{243}Am and ^{237}Np have different radial distributions along the pellet radius because they are produced in a different manner. ^{243}Am results from a neutron capture on ^{242}Pu; its radial distribution reflects the concentration increase at the pellet edge as observed for ^{242}Pu. However, ^{237}Np mainly results when ^{235}U captures two neutrons; its radial distribution reflects the flat profile of uranium at the beginning of irradiation.

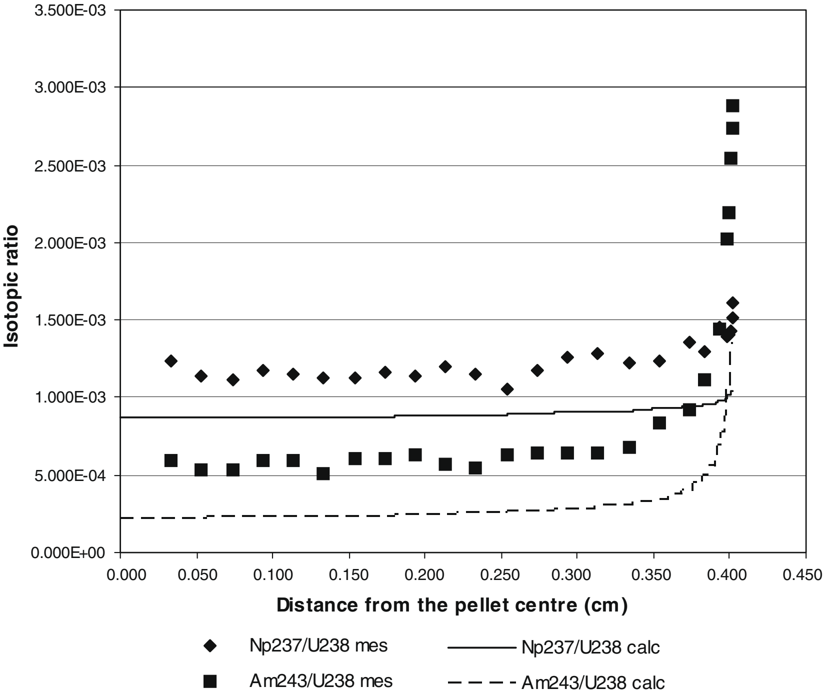

Fig. 3. Comparison of ^{243}Am/^{238}U and ^{237}Np/^{238}U experimental and calculated ratios.

5. Conclusion

The shielded SIMS made it possible to obtain the radial distribution of actinide isotopic ratios on a sample of irradiated nuclear fuel. These experimental results were compared with calculations obtained using the APPOLO2 code: the results showed good agreement. This comparison provided a cross-validation of SIMS and APPOLO2 code calculations for the description of the actinide content in irradiated UO_2 fuel. However, the number of isotopes that can be used for this validation remains limited because of (1) the low abundance of minor actinides, (2) the existence of numerous atomic interferences and (3) the lack of suitable standard samples. Some improvements may be gained when studying other nuclear fuels with higher contents in plutonium and minor actinides, as this would improve the abundance of minor actinides (point 1).

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