



Oxidative dissolution of unirradiated Mimas MOX fuel (U/Pu oxides) in carbonated water under oxic and anoxic conditions



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H I G H L I G H T S

- Heterogeneous MOX fuels were leached in carbonated water.
- The oxidative dissolution was controlled by alpha radiolysis.
- The UO₂ matrix was preferentially dissolved.
- The Pu-agglomerates were slightly oxidized but less sensitive to dissolution.

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Few studies exist concerning the alteration of Mimas Mixed-Oxide (MOX) fuel, a mixed plutonium and uranium oxide, and data is needed to better understand its behavior under leaching, especially for radioactive waste disposal. In this study, two leaching experiments were conducted on unirradiated MOX fuel with a strong alpha activity ($1.3 \times 10^9 \text{ Bq.g}_{\text{MOX}}^{-1}$) reproducing the alpha activity of spent MOX fuel with a burnup of 47 GWd $\cdot \text{t}_{\text{HM}}^{-1}$ after 60 years of decay, one under air (oxic conditions) for 5 months and the other under argon (anoxic conditions with $[\text{O}_2] < 1 \text{ ppm}$) for one year in carbonated water ($10^{-2} \text{ mol L}^{-1}$). For each experiment, solution samples were taken over time and Eh and pH were monitored. The uranium in solution was assayed using a kinetic phosphorescence analyzer (KPA), plutonium and americium were analyzed by a radiochemical route, and H₂O₂ generated by the water radiolysis was quantified by chemiluminescence. Surface characterizations were performed before and after leaching using Scanning Electron Microscopy (SEM), Electron Probe Microanalyzer (EPMA) and Raman spectroscopy. Solubility diagrams were calculated to support data discussion. The uranium releases from MOX pellets under both oxic and anoxic conditions were similar, demonstrating the predominant effect of alpha radiolysis on the oxidative dissolution of the pellets. The uranium released was found to be mostly in solution as carbonate species according to modeling, whereas the Am and Pu released were significantly sorbed or precipitated onto the TiO₂ reactor. An intermediate fraction of Am (12%) was also present as colloids. SEM and EPMA results indicated a preferential dissolution of the UO₂ matrix compared to the Pu-enriched agglomerates, and Raman spectroscopy showed the Pu-enriched agglomerates were slightly oxidized during leaching. Unlike Pu-enriched zones, the UO₂ grains were much more sensitive to oxidative dissolution, but the presence of carbonates did not enable observation of an oxidized layer by Raman spectroscopy with the exception of a few areas revealing the presence of U₄O₉. This data shows the heterogeneous nature of the alteration and the need to combine information from different techniques to determine the origin of releases.

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1. Introduction

The safe underground disposal of radioactive waste requires fuel degradation processes to be characterized, in particular to model

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the so-called source term leading to potential mobility of radionuclides in the geosphere [1]. A key issue is therefore the reactivity of the fuel matrix with respect to water. A substantial effort has been devoted to studying spent UOX fuel dissolution and radionuclide release under a wide range of waste repository conditions [2–5]. The redox conditions are by far the most important factor influencing the dissolution of UO₂ based fuel. Studies conducted in reducing and oxic environments show that the dissolution kinetic rates are lowered by three orders of magnitude in reducing media compared to oxic conditions. UOX fuels basically consist of homogeneous uranium dioxide, natural or enriched with ²³⁵U, but other kinds of fuels exist, such as mixed plutonium and uranium dioxides (called MOX fuels). Contrary to UOX fuel, little is known on the behavior of the MOX fuels and especially on the behavior of the heterogeneous Mimas MOX fuel in contact with water [5,6]. The microstructure observed on this type of MOX fuel has revealed the presence of two or three zones with different plutonium contents and microstructures arising from the fabrication process (dilution of a UO₂ and PuO₂ oxide blend in UO₂ powder) and from the origin of the UO₂ powder [7,8]. Although the mechanisms are likely to be close to those of UOX fuel [5], it is still necessary to study the specific features of MOX fuels to better understand their behavior, in the eventuality of either interim wet storage in a pool or geological disposal. Data is also needed for a better understanding of the chemistry of all Pu–U oxides as solid solutions in contact with water.

In particular, the preferential dissolution of the UO₂ matrix compared to the Pu-enriched agglomerates has been suspected [7,9,10]. The dissolution kinetic rate of the UO₂ matrix could also be impacted by the microstructural heterogeneity of Mimas MOX compared to homogeneous UOX. The Pu content of Mimas MOX leads to a higher activity, especially in the Pu-agglomerates. This could impact the dissolution of the UO₂ matrix in particular locally around these Pu-agglomerates and, subsequently, the relative release of Am (due to ²⁴¹Pu beta decay, americium is also present in minor amounts in the oxides) and Pu that could occur congruently or incongruently with U release. Moreover, it is worth noting that water radiolysis is a major difference between unirradiated UOX and MOX fuels. The Am/Pu-content of MOX corresponds to an inherent radiolytic activity on the aqueous solution in contact with the fuel pellets.

Fresh fuel (before irradiation in a nuclear reactor) can be used as a first step in a progressive approach to the final research target that is the behavior of spent MOX fuel. The absence of all the elements (fission products and some minor actinides) appearing during irradiation in reactors means a simpler system and facilitates the study, in particular for the solution chemistry and the understanding of the processes involved. The lower βγ activity of fresh fuel compared to spent fuel also permits its manipulation in glove boxes instead of hot cells, and a focus on the impact of a strong alpha irradiation field alone. Nevertheless, it is important to mention that the alpha activity of this fresh fuel remains high compared to the expected values under geological disposal conditions. The objective here is to better understand the oxidative dissolution of MOX fuel under alpha radiolysis and, in the future, the influence of the environment on this dissolution. Moreover, studies using fresh fuel do not take into account the complex composition and the damaged/re-organized structure of spent fuel after exposure to a neutron flux in a reactor.

In this context, the behavior of fresh Mimas MOX fuel in carbonated water was studied in order to determine the effect of its particular microstructure on the alteration and the fate of the released elements (U, Pu and Am). Carbonates present a strong complexing ability with respect to uranyl ions that prevents secondary precipitation of uranium onto the fuel pellets and sorption

on the TiO₂ leaching reactor. Uranium can therefore be considered as a tracer of MOX dissolution. Two leaching tests were conducted, one under air (oxic conditions) for 5 months and one under argon (anoxic conditions) for one year in carbonate water. Samples of solution were collected at different times. Uranium, radioelements (americium, plutonium), and H₂O₂ were analyzed. Eh and pH were also monitored. Quantity balances of Am, Pu and U between the aqueous, colloidal, precipitated and sorbed fractions were realized at the end of the experiments. Surface characterizations were performed before and after leaching using scanning electron microscopy (SEM), electron probe microanalyzer (EPMA) and Raman spectroscopy. To support data discussion, solubility diagrams were calculated with CHESSE [11] and the ThermoChimie database [12]. A large set of high quality thermodynamic data on U, but also Pu and Am speciation, is now available thanks to the successive NEA efforts [13,14] compiled in the database used.

2. Materials and methods

2.1. MOX pellets

Unirradiated MOX MIMAS fuel pellets enriched at 7.48 wt.% PuO₂ from the MELOX factory were used. These samples have a special microstructure due to the Mimas fabrication process. This microstructure is heterogeneous and has three different phases:

- a zone called the UO₂ matrix containing 2.7 wt.% of plutonium (corresponding to 15 wt.% of total Pu),
- Pu-enriched agglomerates with 20.2% of Pu (40 wt.% of total Pu),
- a coating zone with an intermediate composition of 7.3% of Pu (45 wt.% of total Pu).

Moreover, equal quantities of these three phases are not present in the fuel. This leads to surface fractions of 46.7% for the UO₂ matrix, 42.2% for the coating zone, and 11.1% for the Pu-enriched agglomerates [8]. The composition of the MOX pellets is given in Table 1, and the characteristics of all the pellets used for the experiments are listed in Table 2. The average alpha activity of a pellet is 1.3×10^9 Bq.g⁻¹MOX reproducing the alpha activity of spent MOX fuel with a burnup of 47 GWd·t_{HM}⁻¹ after 60 years of alpha decay. All the pellets were polished on one face and annealed at 1000 °C for 16 h under an atmosphere of Ar/H₂ 5% and 20,000 ppm H₂O (oxygen potential of -375 kJ mol⁻¹) to restore the material stoichiometry. Before each experiment, the pellets were subjected to 11 one hour pre-leaching cycles (with one night for the sixth pre-leaching) in carbonated water (NaHCO₃ 10⁻³ M). The purpose of the pre-leaching was also to avoid a U(VI) release peak due to surface oxidation that could skew the estimated total quantity of uranium oxidized during the leaching experiments.

2.2. Solution chemistry

The pre-leachings and the leachings were carried out using carbonated waters respectively at concentrations of 10⁻³ M and 10⁻² M HCO₃. The concentration of 10⁻³ M is an average value of deep groundwater carbonate concentrations (like the Callovian–Oxfordian groundwater from the Andra Underground Research Laboratory [15]), but the concentration was increased to 10⁻² M during leaching in order to prevent any U(VI) secondary precipitation. The solutions were prepared by dissolution of NaHCO₃ powder (VWR AnalaR NORMAPUR) in ultrapure water.

2.3. Leaching tests

Two experiments were conducted: one in an oxic glove box (O₂

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