

**Open 3-years PhD thesis at  
Institut de Chimie Séparative de Marcoule (ICSM), Bagnols-sur-Cèze, France  
Ecole doctorale 459 Sciences Chimiques Balard (University of Montpellier)**

**SIM-MOX dissolution mechanisms and kinetics:  
Study of the specific behavior of Rh**

**Starting date: October 2023**

The French nuclear power industry is one of the largest in the world, with 56 reactors deployed throughout the country, representing up to 70% of annual electricity production. These reactors are of the PWR (Pressurized Water Reactor) type. They can contain uranium dioxide  $\text{UO}_2$ , slightly enriched in  $^{235}\text{U}$ , called UOx fuel (for Uranium Oxide), which currently constitutes the majority of nuclear fuel used in the world. In France, reprocessing of spent fuel has been carried out at the Orano plant in La Hague since 1976 using the PUREX process (Plutonium Uranium Reduction Extraction). The fuel is dissolved at the head of the process in hot nitric acid, then the uranium and plutonium are extracted separately from the solution, while the fission products and minor actinides are vitrified and stored. The uranium and plutonium extracted during reprocessing operations are used to manufacture MOx fuel (for Mixture of Oxides) of the general formula  $(\text{U,Pu})\text{O}_2$ , for which some French reactors are compatible. The most widely used MOx fabrication process is the MIMAS (Micronized MASTer blend)<sup>1</sup> process. MIMAS MOx has a heterogeneous microstructure, inherited of its preparation process<sup>2</sup>.

During its irradiation in the reactor core, the MOx fuel undergoes significant physico-chemical modifications. The heterogeneous microstructure favors in particular the appearance of hot spots during irradiation in the reactor in the zones with high fission density (= Pu-rich clusters). As a consequence of the numerous nuclear reactions taking place within the MOx fuel, an important restructuring as well as modifications of its chemical composition are observed<sup>3</sup>. Six main groups of chemical elements composing the fuel at the end of the reactor can be identified<sup>4</sup>; the nominal mass contents (excluding oxygen) of each group are given for a spent MOx fuel cooled for 50 years and an average burnup of  $60 \text{ GWj.t}^{-1}$ :

- actinides (93.9%*m*): Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf;
- lanthanides (1.9%*m*): La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho;
- oxide precipitates (1.4%*m*): Zr, Nb, Rb, Cs, Sr, Ba;
- metallic precipitates (2.1%*m*): Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te;
- gases and volatile elements (1%*m*): Br, Kr, I, Xe, Cs;
- metalloids (<0.01%*m*): Ge, As, Se.

As previously explained, the local burn-up rates are significantly higher in the restructured Pu-rich clusters and the local fission product (FP) inventories are therefore larger. These elements are ultimately heterogeneously distributed in the spent fuel and distributed between the  $(\text{U,Pu})\text{O}_2$  ceramic grains and the free volumes of a rod. The grains of the  $(\text{U,Pu})\text{O}_2$  matrix contain actinides and fission products such as rare earths, while the free volumes (cracks, gaps, occluded porosity, etc.) contain fission gases (Kr, Xe) and some volatile elements (Cs, I). The metallic precipitates are often located at the grain boundaries.

<sup>1</sup> Konings, R. J. M. et al. Comprehensive nuclear materials. (Elsevier, 2012).

<sup>2</sup> Oudinet, G. et al. Characterization of plutonium distribution in MIMAS MOX by image analysis. *Journal of Nuclear Materials* **375**, 86-94 (2008). doi: [10.1016/j.jnucmat.2007.10.013](https://doi.org/10.1016/j.jnucmat.2007.10.013)

<sup>3</sup> Dehaut, P. Le combustible nucléaire et son état physicochimique à la sortie des réacteurs. CEA, France, Rapport CEA-R-5923 (1999).

<sup>4</sup> Ferry, C. et al. Synthesis on the spent fuel long term evolution. CEA Technical Report, 257 (2005).

The multi-recycling of nuclear fuel in PWRs is the preferred way of managing irradiated fuel in France. This strategy of nuclear material management implies in particular the reprocessing of spent MOX fuel and, consequently, the development of an optimized dissolution process for irradiated MOX. On the other hand, among the PF contained in irradiated MOX, platinum elements, such as ruthenium and rhodium, are today considered as critical raw materials. Thus, spent MOX nuclear fuel could be considered as a potential unconventional mine for these strategic metals. However, these elements are difficult to dissolve quantitatively at the top of the current reprocessing process and may have an influence on the dissolution kinetics of the fuel matrix<sup>5,6</sup>.

**The main objectives of this thesis work are therefore:**

- **to evaluate the impact of the heterogeneous microstructure of irradiated MOX fuel on the dissolution kinetics in nitric acid medium, on the quantity and the nature of the dissolution residues**
- **to identify dissolution conditions favorable to the selective recovery of Rh**

Given the major difficulties related to the handling of highly irradiating materials, the study of the dissolution of spent fuel, although essential, remains mainly empirical. The use of model compounds is generally a necessary step in order to decouple, or even exacerbate, the effects of the many factors likely to influence the dissolution kinetics of spent fuel. The experimental approach developed in the framework of this thesis is therefore based on the preparation of model fuels or "Sim-MOX", reproducing as closely as possible the distribution and chemical form of the fission products observed in irradiated MOX fuels, and then proceeding to the in-depth study of the dissolution mechanisms of these Sim-MOX. In the course of previous work, the host laboratory of the thesis has acquired a long experience in the preparation of such model fuels in order to study the dissolution mechanisms<sup>7,8,9,10,11,12</sup>. In addition, the representativeness of the Sim-MOX prepared could be evaluated through collaboration with several teams of CEA Marcoule confronted with the characterization and the study of the dissolution of real irradiated MOX.

In the first step, the study will consist of the preparation of Sim-MOX model fuels, based on UO<sub>2</sub>, containing thorium and/or cerium (as simulants of plutonium) as well as several FPs among which lanthanide elements and the 5 elements present in the metallic precipitates (i.e., Mo, Ru, Rh and Pd and Tc simulated by Re). These model sintered materials will be prepared by wet process, followed by a shaping step and then sintering at high temperature. Advanced characterization of the materials will be performed in order to analyze the speciation of the different FPs prior to their dissolution. In addition, several materials with degraded homogeneities in terms of composition (agglomerates enriched with ThO<sub>2</sub> or CeO<sub>2</sub>, representative of PuO<sub>2</sub>), will also be prepared in order to analyze their impact on the dissolution operation.

In a second step, all sintered samples will be submitted to dissolution tests under conditions representative of the current reprocessing process. A multiparametric study will be conducted through a

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<sup>5</sup> Cordara, T. et al. Impact of platinum group metals (Ru, Pd, Rh) on the dissolution of UO<sub>2</sub>. *Journal of Nuclear Materials* **528**, 151836 (2020). doi: [10.1016/j.jnucmat.2019.151836](https://doi.org/10.1016/j.jnucmat.2019.151836)

<sup>6</sup> Cordara, T. et al. Microstructural evolution of UO<sub>2</sub> pellets containing metallic particles of Ru, Rh and Pd during dissolution in nitric acid solution: 3D-ESEM monitoring. *Hydrometallurgy* **188**, 182-193 (2019). doi: [10.1016/j.hydromet.2019.07.001](https://doi.org/10.1016/j.hydromet.2019.07.001)

<sup>7</sup> Claparede, L. et al. Impact of the cationic homogeneity on Th<sub>0.5</sub>U<sub>0.5</sub>O<sub>2</sub> densification and chemical durability. *Journal of Nuclear Materials* **514**, 368-379 (2019). doi: [10.1016/j.jnucmat.2018.12.009](https://doi.org/10.1016/j.jnucmat.2018.12.009)

<sup>8</sup> Claparede, L. et al. Dissolution of Th<sub>1-x</sub>U<sub>x</sub>O<sub>2</sub>: Effects of chemical composition and microstructure. *Journal of Nuclear Materials* **457**, 304-316 (2015). doi: [10.1016/j.jnucmat.2014.11.094](https://doi.org/10.1016/j.jnucmat.2014.11.094)

<sup>9</sup> Dalger, T. et al. Kinetics of dissolution of Th<sub>0.25</sub>U<sub>0.75</sub>O<sub>2</sub> sintered pellets in various acidic conditions. *Journal of Nuclear Materials* **510**, 109-122 (2018). doi: [10.1016/j.jnucmat.2018.07.050](https://doi.org/10.1016/j.jnucmat.2018.07.050)

<sup>10</sup> Montaigne, T. et al. Oxidative dissolution of (U,Ce)O<sub>2</sub> materials in aqueous solutions containing H<sub>2</sub>O<sub>2</sub>: a suitable analogue to (U,Pu)O<sub>2</sub> MOX fuel submitted to *Npj Materials Degradation* (2022).

<sup>11</sup> Tocino, F. et al. Dissolution of uranium mixed oxides: The role of oxygen vacancies vs the redox reactions. *Progress in Nuclear Energy* **72**, 101-106 (2014). doi: [10.1016/j.pnuene.2013.09.014](https://doi.org/10.1016/j.pnuene.2013.09.014)

<sup>12</sup> Kaczmarek, T. et al. Impact of ruthenium metallic particles on the dissolution of UO<sub>2</sub> in nitric acid. *Npj Materials Degradation* **6** (2022). doi: [10.1038/s41529-022-00246-0](https://doi.org/10.1038/s41529-022-00246-0)



multi-scale approach to understand the dissolution mechanisms and to identify the various obstacles associated with the quantitative recovery of the elements of interest. The macroscopic approach will be based on the analysis of the elemental releases in solution while the microscopic approach will include the *operando* monitoring of the solid/solution interface during dissolution by different techniques (MEBE, Raman, AFM, ...). At this stage, a precise analysis of the speciation of the 5 metallic elements will be carried out, as well on the soluble fraction, at the solid/solution interface as within the dissolution residues whose chemical and physicochemical characteristics will be specified (granulometry, composition, morphology, reactive surface, ...).

The third axis of the study will be focused on the optimization of the dissolution of the metallic inclusions themselves, from the elemental balance realized in the solution and on the dissolution residues. This optimization can be done during the initial dissolution step of the fuel but also on the insoluble fraction after the separation of the liquid and solid phases. In this last case, several alternative conditions will be examined.

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**Further information:** The successful candidate will join the LIME group of ICSM and will be enrolled at the doctoral school ED459 Sciences Chimiques Balard of the University of Montpellier (France).

**Education and skills required:** Applicants must have completed a MSc's Degree (or equivalent qualification) in Chemistry, Radiochemistry, or Materials Chemistry

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