

## **Book of abstracts**

# **31<sup>th</sup> Spent Fuel Workshop**

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## FOREWORD

This document contains the abstracts of the presentations submitted to the 31<sup>st</sup> edition of the Spent Fuel Workshop (SFW), held in Barcelona between the 19<sup>th</sup> and the 21<sup>st</sup> of October 2022.

The SFW celebrated its first edition in 1981, already 41 years ago, in Studsvik, Sweden. Since then, this workshop has gathered hundreds of scientists working in the understanding of the behavior of spent nuclear fuel. From the state of the fuel at its discharge, to its behavior under repository conditions; from the dissolution under oxidic conditions to the modelling of how the fuel would behave thousands of years after its disposal. The philosophy of the SFW focuses on fostering discussions, which is one of the main reasons why it is not a multitudinary conference, but one forum where exchange of ideas is facilitated.

This is a very special edition of the SFW. 3 years have elapsed since its previous edition in Ghent. Our world has been impacted by unprecedented events. In 2020 we had a pandemic which obliged us to stay at home for an important period of time, affecting our usual way of life and impacting lives.

The pandemic also had an important impact on the scientific community. We learn to discuss through screens, and we learn to wait to get the results from the laboratories, some of them closed for long time periods...unprecedented times. The pandemic was also accompanied by an increase in the cost of energy, and this started to cause a revival of the debate of nuclear as a source of stable energy. The EC included nuclear in the green taxonomy, and several countries started to step back in their nuclear phase-out strategies. These events, together with the Russian invasion of Ukraine and the subsequent risk in energy supply, highlight the relevance of our work.

The community gathering these days in Barcelona, attending the SFW, represents those contributing to an understanding of the behavior of spent nuclear fuel, and contributing to a safe disposal of nuclear waste. Our contribution is of the highest relevance to the scientific advance and, therefore, to the advance of our society towards a safer energy framework.

36 abstracts have been submitted to this edition of the SFW. The abstracts have been reviewed by the members of the Scientific Committee, to whom I want to especially thank. We count with one short presentation per abstract. The different subjects dealt with are varied, from spent fuel characterization, through the study of its alteration under different environmental conditions to the modelling of its evolution in various media. We see abstracts presenting innovative characterization and experimental methods, and also the most advanced modelling tools.

We have the pleasure to count this year with 55 participants from 13 countries and 22 organizations; we have the pleasure to be able to hold discussions presential again, and we have the pleasure to contribute, with our research, to the present and the future of nuclear waste management.

On behalf of Amphos21, it is for me an honor to welcome you to Barcelona. I hope that you find in our organization and our cosmopolitan city an ideal site for your discussions.

Thanks for your participation. Enjoy it!



Lara Duro, *Amphos21*

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## Failed nuclear fuel characteristics relevant to geological disposal

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Prior to encapsulation and disposal in a final repository, the spent fuel characteristics need to be known to a degree required for the safety assessment. One important aspect of the spent fuel relates to the status of the cladding. At the time of encapsulation, the cladding will be intact for the vast majority of fuel rods. However, there is a small fraction of failed fuel due mainly to cladding failure during reactor operation. In this case, the uranium dioxide in the fuel will be in contact with water and oxidants during the period from the cladding failure and to a time when the fuel is dried and placed in a sealed container. For the failed fuel fraction of the spent fuel inventory, the effects of this oxidation need to be estimated. For a rod that failed in the reactor, there is an initial hot period where the fuel is in direct contact with the coolant and fission reactions are still ongoing. This is followed by a period of cooling in the reactor pool, and, in the Swedish case, drying and transport to Clab. In Clab, the fuel - if not already in a sealed container – will be in contact with ~35°C deionized water for a certain amount of time. All of these steps will affect the uranium dioxide fuel. Some results of post-irradiation experiments of failed fuel rods are found in the open literature (e.g. [1], [2], [3]) and these provide valuable insight into the fractions of oxidized matrix in the fuel rods. However, further details are required with regards to, for example, uranium phases and radionuclide content. Therefore, the detailed study presented here was initiated on a failed fuel rod after secondary failure in the reactor and subsequent cooling in the reactor pool. The failed rod, irradiated from 1974 to 1980 in a Swedish PWR reactor, was studied using various methods to provide information on how the uranium dioxide matrix was affected by a large, secondary cladding failure. Data from gamma scanning, light optical microscopy (LOM), scanning electron microscopy (SEM) including energy dispersive x-ray spectrometry (EDS) and electron back scatter diffraction (EBSD), X-ray diffraction (XRD), and laser ablation inductively coupled plasma mass spectrometry (ICP-MS) will be presented. The investigations reveal a complex structure with different mineral phases at the site of the main, secondary failure and some structural effects, much less pronounced, ca 30 cm away from the failure site.

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# In-situ characterization of a UO<sub>2</sub> surface by microRaman and synchrotron X-ray diffraction in the presence of hydrogen peroxide

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The formation of secondary phases on the surface of uranium dioxide has been the subject of numerous studies over the last thirty years by combining solution analysis and characterization of altered surfaces. The effect of hydrogen peroxide, the main water radiolysis product, has in particular been extensively studied [1] to better understand the oxidizing dissolution mechanisms of spent fuels with and without irradiation. In brief, high H<sub>2</sub>O<sub>2</sub> concentrations lead to the formation of uranium peroxide such as studtite (UO<sub>2</sub>)(O<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>·2H<sub>2</sub>O while for less oxidizing conditions, oxyhydrate phases such as schoepite [(UO<sub>2</sub>)<sub>4</sub>O(OH)<sub>6</sub>]·6H<sub>2</sub>O are usually observed.

The available studies allowing in-situ characterization and growth of these phases on the surface of UO<sub>2</sub> pellets are limited [2] and those involving crystallographically oriented surfaces are very rare. This work presents an original experimental device allowing to monitor the formation and the growth of secondary phases on a UO<sub>2</sub> single crystal surface. To do this, a leaching experiment under dynamic conditions of an oriented single crystal surface with controlled hydrogen peroxide concentrations was developed. The (111) surface was in-situ characterized by Raman spectroscopy and synchrotron X-ray diffraction in the presence of water in order to avoid possible artefacts and to limit the potential structural evolutions induced by stages of drying and change of medium.

The results show that the nature of the secondary phase formed depends well on the hydrogen peroxide concentration. It was also possible to monitor the evolution of the studtite crystal growth at the surface over time for the highest H<sub>2</sub>O<sub>2</sub> content. At the first moments, the crystals of studtite arise with an initial anisotropy in particle orientation (c\* axes parallel to the crystal surface), then a subsequent reorientation of growing particles is observed.

The evolution of the surface was also studied after draining the water from the leaching cell and air drying. The formation of schoepite was observed after the first few hours of emersion.

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# Impact of H<sub>2</sub>O<sub>2</sub> speciation and limitations in dissolution kinetics on radiation induced dissolution of UO<sub>2</sub>-based spent nuclear fuel

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The interfacial radiation chemistry of UO<sub>2</sub> is of key importance in the development of models to predict the corrosion rate of spent nuclear fuel in contact with groundwater. Here, the oxidative dissolution of UO<sub>2</sub> induced by radiolytically produced H<sub>2</sub>O<sub>2</sub> is of particular importance. The difficulty of fitting experimental data to simple first-order kinetics suggests that additional factors need to be considered when describing the surface reaction between H<sub>2</sub>O<sub>2</sub> and UO<sub>2</sub> [1]. It has been known for some time that UO<sub>2</sub><sup>2+</sup> forms stable uranyl peroxy-carbonato complexes in water containing H<sub>2</sub>O<sub>2</sub> and HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup>, yet this concept has largely been overlooked in studies where the oxidative dissolution of UO<sub>2</sub> is considered. Recently, we showed that uranyl peroxy-carbonato complexes display little to no reactivity toward the solid UO<sub>2</sub> surface in 10 mM bicarbonate solution (pH 8-10) [2]. The rate of peroxide consumption and UO<sub>2</sub><sup>2+</sup> dissolution will thus depend on the UO<sub>2</sub><sup>2+</sup> concentration and becomes limited by the free H<sub>2</sub>O<sub>2</sub> fraction. The rate of total peroxide consumption (free H<sub>2</sub>O<sub>2</sub> and peroxy ligands) can be accurately predicted based on the first order kinetics with respect to free H<sub>2</sub>O<sub>2</sub>, taking the initial UO<sub>2</sub> surface coverage by H<sub>2</sub>O<sub>2</sub> into account. This study has now been extended to cover the HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> concentration range of 1-10 mM. At lower HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> concentrations it is evident that both speciation and limitations in the kinetics of UO<sub>2</sub><sup>2+</sup> dissolution influence the overall kinetics of the system. At the lowest HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> concentration, studtite formation is observed. In this presentation we will discuss the mechanism and kinetics of H<sub>2</sub>O<sub>2</sub>-induced oxidative dissolution of UO<sub>2</sub> in view of our recent experimental findings. The peroxy ligands in uranyl peroxy-carbonato complexes also display a slightly different stability compared to free H<sub>2</sub>O<sub>2</sub> in irradiated aqueous solutions, as suggested by differences in peroxide concentrations as functions of irradiation time. This finding and its implications on radiation induced dissolution of spent nuclear fuel will also be discussed.

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## Effect of hydrogen on the corrosion of pre-oxidized and naturally corroding uranium dioxide

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While there is extensive literature investigating the scavenging effect of dissolved H<sub>2</sub> on fuel corrosion inside a failed waste container, previous studies investigated either UO<sub>2</sub> samples doped with  $\alpha$ -radiation emitters [1], UO<sub>2</sub> exposed to an external  $\alpha$ -radiation source [2], SIMFUELS containing non-radioactive fission products [3], or spent fuel [4], all of which can lead to activation of H<sub>2</sub> to produce reactive •H radical species. This work explores the effect of H<sub>2</sub> on the corrosion of undoped, unirradiated UO<sub>2</sub> in the presence of H<sub>2</sub>O<sub>2</sub> when direct activation of H<sub>2</sub> has not been demonstrated.

The influence of H<sub>2</sub> on corrosion was studied in aqueous chloride solutions containing HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> anions using electrochemical and X-ray photoelectron spectroscopic techniques on discs cut from unirradiated CANDU fuel pellets. Under Ar-sparged conditions, the increase in corrosion potential indicated surface oxidation occurred when H<sub>2</sub>O<sub>2</sub> was added in the concentration range 0.1 to 50  $\mu$ M. By comparison, in Ar/H<sub>2</sub> (95%/5%)-sparged solution, the corrosion potential increased on first addition of H<sub>2</sub>O<sub>2</sub>, indicating surface oxidation but eventually decreased suggesting inhibition of oxidation and possibly reduction of the initially oxidized surface.

In additional experiments in which the UO<sub>2</sub> was pre-oxidized by applying an electrochemical potential, the presence of H<sub>2</sub> did not appear to lead to reduction of the electrochemically oxidized surface. This suggests that H<sub>2</sub> is only an effective reductant when surface •OH radicals (formed from H<sub>2</sub>O<sub>2</sub>) are present, and not directly capable of reducing the oxidized surface as previously observed on SIMFUELS containing noble metal particles [5]. Whether or not the recombination of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub> involves the oxidation (U<sup>IV</sup>  $\rightarrow$  U<sup>V</sup>)/reduction (U<sup>V</sup>  $\rightarrow$  U<sup>IV</sup>) of the UO<sub>2</sub> surface is presently under investigation.

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## Impact of Ru, Rh, Pd and Mo metallic particles on the dissolution of UO<sub>2</sub>

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Although a spent nuclear fuel (SNF) is composed of about 96 wt.% of UO<sub>2</sub>, its composition and microstructure display an extreme complexity due to the presence of more than 30 fission products. Fission products found as metallic precipitates are mainly composed of the noble metals Ru, Rh, Pd, Mo. The first step of the spent nuclear fuel reprocessing is the dissolution in a concentrated nitric acid solution. In this context, this work focuses on the impact of these elements on the kinetics of dissolution of the UO<sub>2</sub> matrix. Model samples of UO<sub>2</sub> incorporating 3 mol% of Ru, Rh, Pd or Mo were prepared using a wet chemistry route, then were sintered at high temperature under reducing atmosphere [1]. The speciation, morphology as well as the spatial distribution of the elements in the sintered samples were determined from Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy analyses. Then, the synthesized samples were submitted to various dissolution tests in order to quantify the impact of the presence of metallic particles on the dissolution rate of UO<sub>2</sub>. Dissolution experiments were carried out under conditions representative of the reprocessing of SNF (i.e. 4 M HNO<sub>3</sub>, 80°C). Additionally, specific dissolution experiments in less aggressive conditions were designed to identify the mechanisms involving each element of interest. The elemental concentrations in the dissolution media were determined by ICP-OES or ICP-MS. The dissolution rate of each model compound was then determined and compared to that of UO<sub>2</sub>. At microscopic scale, the evolution of the solid/liquid interface was monitored by Environmental-SEM. The obtained results allow to compare the behaviour of each element during dissolution and to quantify its impact on the dissolution kinetics of UO<sub>2</sub> in nitric acid. A strong acceleration of the dissolution of UO<sub>2</sub> matrix was observed in the presence of Ru [2] and Rh metallic particles. The influence of Pd was low, whereas the presence of Mo metallic particles inhibited the oxidative dissolution of UO<sub>2</sub>. These observations were supported by redox reactions taking place at both nitric acid solution/metallic particles and at metallic particles/UO<sub>2</sub> interfaces.

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## Impact of lanthanide and PGM elements on the chemical durability and surface modifications during the leaching tests of FP doped UO<sub>2</sub> pellets mimicking interim repository

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Managed by ANDRA, the European collaborative research program EURAD aims to federate research efforts and to share scientific and technical knowledge in the field on the long-term management of radioactive waste. In this context, the Laboratory of Evolving Interfaces in Materials is interested in studying the chemical durability of spent nuclear fuels under interim storage conditions (mimicking their stay in cooling pool).

Due to the complex structure and microstructure of spent nuclear fuels, the global understanding of their behavior when leaching is very difficult to analyze, although it appears as a very important task. In this study, the role of two fission products families: lanthanide elements dissolved in the structure of UO<sub>2</sub>, on the one hand, and PGM elements (Ru, Rh, Pd) forming metallic inclusions, on the other hand, has been particularly examined.

In order to discriminate the structural, microstructural and chemical impacts of these elements on the chemical durability of the prepared pellets, series of simplified model samples have been prepared by direct precipitation of hydroxide-based precursors. A calcination step of these precipitates (800°C, Ar/H<sub>2</sub> atmosphere) led to uranium based fluorite type dioxides. After shaping by uniaxial pressing, a sintering step (1600°C, 8 hours, Ar/H<sub>2</sub> atmosphere) led to dense pellets (up to 90% and 96% TD for PGM and lanthanide doped samples, respectively) based on geometrical measurements and He pycnometry. In addition, the pellets were characterized in terms of microstructure and cationic homogeneity by SEM and X-EDS analysis.

A dual approach combining microscopic and macroscopic analyses was developed to study the long-term behavior of the prepared pellets. At the macroscopic scale, leaching tests were developed on all the prepared pellets in conditions mimicking an interim storage, i.e. at pH = 5 and 7, at 50 and 70°C and in the presence (or not) of dissolved boron ( $5.0 \cdot 10^{-2}$  M). Simultaneously, the monitoring of the solid/liquid interface was performed by ESEM. The normalized dissolution rate of UO<sub>2</sub> during leaching test in  $5.0 \cdot 10^{-2}$  M boric acid, at pH = 7 and 50°C reached about  $(5.5 \pm 0.1) \cdot 10^{-4}$  g·m<sup>-2</sup>·d<sup>-1</sup> (i.e. 0.04% of dissolved material after 300 days of alteration). The presence of PGM elements induced the significant increase of the alteration rate  $(2.0 \pm 0.1) \cdot 10^{-4}$  g·m<sup>-2</sup>·d<sup>-1</sup> (i.e. 0.2% of dissolved material after 300 days of alteration). On the other hand, lanthanide elements induced a particular behavior. Indeed, after 80 days of leaching, the uranium concentration was found to be constant in the leachate, suggesting the precipitation of a secondary U-based phase onto the surface of the pellets. This phase is now under characterization.

## Dissolution of UO<sub>2</sub> in saline solutions and the role of uranyl-peroxo-halo complexes

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A deep geological repository has been considered as the most suitable strategy of permanent storage of spent nuclear fuel by several countries. To be able to assess the consequences of multiple barrier failure, it is essential to study the kinetics and mechanisms of processes that could occur when the spent nuclear fuel comes in contact with groundwater. The main component of spent nuclear fuel is UO<sub>2</sub> (95%), which has very low solubility in the slightly reducing groundwaters. However, radiolysis of groundwater adjacent to the fuel surface, caused by the inherent radioactivity of the fuel, will produce oxidizing species such as HO•, HOO•, and H<sub>2</sub>O<sub>2</sub> as well as reducing species, for example e<sub>aq</sub><sup>-</sup>, H•, and H<sub>2</sub>. For kinetic reasons, the oxidants will dominate the surface reactions initially and oxidize the UO<sub>2</sub> matrix from U(IV) to considerably more soluble U(VI) and thereby enabling the spread of the highly radiotoxic fission products and heavy actinides into the biosphere. Oxidized UO<sub>2</sub> is released as uranyl (UO<sub>2</sub><sup>2+</sup>), which is a good electron acceptor in solution, and therefore tends to coordinate with Lewis base ligands, such as water, carbonate, hydroxide, peroxide, and halides. The dissolution of UO<sub>2</sub> in saline solutions and the coordination chemistry between uranyl and halide ions are of practical importance in mainly two situations: (1) If seawater is used for emergency cooling of the core of a damaged nuclear reactor (e.g., in the Fukushima nuclear accident after which 1.25 million tonnes of seawater have been pumped through the damaged units to prevent the molten fuel debris from overheating, and pumping continues); (2) If a deep geological repository for spent nuclear fuel is placed in rock salt as a host rock. This is an option that has been considered by several countries. We recently investigated the impact of Cl<sup>-</sup>, Br<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> on the mechanism and kinetics of H<sub>2</sub>O<sub>2</sub>-induced oxidative dissolution of UO<sub>2</sub> powder in aqueous suspensions with and without added HCO<sub>3</sub><sup>-</sup> [1]. Furthermore, the stability of uranyl peroxide (studtite) in saline solution was also studied, since studtite has been found as a secondary phase on spent nuclear fuel. The species formed during the dissolution were characterized as ternary uranyl-peroxo-halo complexes. The ternary uranyl-peroxo-chloro and uranyl-peroxo-bromo complexes were identified using IR-, Raman-, and NMR-spectroscopy. Based on Raman spectra, the estimated stability constants for the identified uranyl-peroxo-chloro ((UO<sub>2</sub>)(O<sub>2</sub>)(Cl)(H<sub>2</sub>O)<sub>2</sub>)<sup>-</sup> and uranyl-peroxo-bromo ((UO<sub>2</sub>)(O<sub>2</sub>)(Br)(H<sub>2</sub>O)<sub>2</sub>)<sup>-</sup> complexes are 0.17 and 0.04, respectively, at ionic strength ≈ 5 mol·L<sup>-1</sup> [2].

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## Oxidative dissolution of uranium carbide and uranium nitride nuclear fuels under repository conditions

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Alternative materials to UO<sub>2</sub> are investigated as potential fuels for Generation IV nuclear reactors. Uranium carbide (UC) and uranium nitride (UN) are considered as potential substitutes for UO<sub>2</sub> for their better thermal conductivity and higher fissile material density [1]. Since these new materials will become part of the nuclear fuel cycle, they will be treated as spent nuclear fuel and could possibly be stored in deep geological repositories for long periods of time. As part of a safety assessment, it is essential to understand the behaviour of UC and UN under repository conditions. One commonly used scenario to study is groundwater intrusion into the fuel canister. This study will be helpful to investigate the underlying processes in radiation-induced dissolution under deep repository conditions. Previous studies have shown that the most important oxidant in radiation-induced oxidative dissolution of UO<sub>2</sub>-based spent nuclear fuel under repository conditions is H<sub>2</sub>O<sub>2</sub> [2]. The reactivity of UC and UN powder was studied and compared under the exposure to 0.2 mM H<sub>2</sub>O<sub>2</sub> in the presence and absence of HCO<sub>3</sub><sup>-</sup> at different surface area to volume ratios. It was shown that UN is 3 times more reactive towards H<sub>2</sub>O<sub>2</sub> than UC [3] while UO<sub>2</sub> [4] is the least reactive. The dissolution yield (amount of dissolved uranium per consumed H<sub>2</sub>O<sub>2</sub>) was lower for UN than UC whereas for UO<sub>2</sub> it reaches 100%. This can partly be attributed to the fact that oxidative dissolution of UN and UC is not a two-electron process like UO<sub>2</sub>. The effect of external  $\gamma$ -irradiation on suspensions of UC and UN powder are quantified and compared to UO<sub>2</sub>. The same studies have been performed on pure UN pellets and UN pellets doped with ZrN. The pellets were exposed to H<sub>2</sub>O<sub>2</sub> and  $\gamma$ -irradiation to understand the effect of fission products on the dissolution. The comparison between pure and doped UN pellets will be presented and discussed.

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## Gamma radiolysis effect on the uranyl stability in water solution

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In most countries, the long-term disposal of spent nuclear fuel (SNF) into a deep geological repository (DGR) is a radioactive waste management policy. In this scenario, oxidized U in aqueous systems will be stabilized as  $\text{UO}_2^{2+}$  (hexavalent U), as a consequence of tetravalent U oxidation, e.g. oxidising species as radiolytic  $\text{H}_2\text{O}_2$ . Uranyl cationic species in different speciation forms are expected to be found at a wide pH range. The importance of solubilized  $\text{UO}_2^{2+}$  lies in its potential incorporation of trace radioelements onto secondary uranyl phases. The complexity of U chemistry in natural groundwater, makes it necessary to improve speciation techniques in an attempt to understand chemical processes. Raman spectroscopy (RS) is a powerful tool for analysing the speciation of various actinyl forms ( $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^{2+}$  and  $\text{PuO}_2^{2+}$ ) [1] and to determine the distribution of those species which are more likely to be stable in a near-field groundwater environment. Moreover, the yield of the various radiolytic products varies with the radiation type, its energy, and time [2]. Gamma radiation emitted from the fission and neutron activation products will go across long distances from the fuel surface and even go through the cladding and the inner surface of cask [2]. In young spent fuel,  $\gamma$  radiation plays a significant role in the total dose rate under temporary or final disposal because of short-lived decay products of irradiated SNF.

Therefore, the aim of this work is to follow  $\text{UO}_2^{2+}$  changes as a consequence of  $\gamma$  radiation and aqueous media under DGR conditions, and to understand the behaviour of  $\text{UO}_2^{2+}$ , which can also help to predict the potential precipitation of the solid phases. In this work, the use of RS adapted to the empirical analysis of different nuclear applications for initial U concentrations of 0.04 M at ambient atmosphere is shown, i.e. as a monitoring tool for  $\text{UO}_2^{2+}$  precipitation influenced by pH and  $\gamma$ -radiation (dose rate:  $3.3 \text{ Gy}\cdot\text{s}^{-1}$ ), studying  $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  stability in aqueous solutions representative of groundwater, in particular at ionic strength  $I = 0.02 - 0.4 \text{ M}$ . At around  $10^{-4} - 10^{-3} \text{ M}$  of radiolytically formed  $\text{H}_2\text{O}_2$  concentration, a decreased U amount in solution was observed caused by solid precipitation due to the reaction between  $\text{UO}_2^{2+}$  and  $\text{H}_2\text{O}_2$ . The obtained results can be useful to assess the comprehensive transport of U from SNF stored in DGRs and they may also provide a partial picture of secondary phase formations, as a result of corrosion of SNF in a DGR.

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## Spent fuel leaching experiments. Where do radionuclides come from?

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Different institutions carried out spent nuclear fuel leaching experiments in order to describe the dissolution of the fuel once in contact with the groundwaters in a High-Level Nuclear Waste Repository. Such experiments have permitted to improve the knowledge of the environmental impact of the fuel dissolution and to establish potential radionuclides concentration in solution as a function of time.

However, from the results obtained in those experiments (usually given as concentration of radionuclide or FIAP as a function of time) it is much more complicated to deduce what are the localizations from where radionuclides are mainly being released to the solution. In this sense, in a recent paper [1], we developed a semi empirical model to evaluate the relative importance of the contribution of different sources on the release of a number of radionuclides from powdered spent fuel: fines or oxidized phases on the fuel surface, grain boundaries and UO<sub>2</sub> matrix.

In this work, we expand the study to leaching experiments of spent nuclear fuel pellets, where the sources should be:

- Gap between the fuel pellet and the rod
- Fines or oxidized phases on the pellet surface
- Grain boundaries
- UO<sub>2</sub> matrix
- Phases segregated from the matrix, such as metallic precipitates

The study is focused on radionuclides with expected different localizations in the pellet (U, Pu, Sr, Rb, Cs, Mo, Rh, Ru and Nd). Leaching data corresponded to irradiated fuels with different burn-up, linear power rate and fission gas release values studied during the last 10 years in JRC.

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## Database development of spent nuclear fuel dissolution under repository conditions

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DisCo European project (H2020 European Commission Program) [1] has represented for the European spent fuel research community an important step towards a deeper understanding of the chemical processes involved in the release of radionuclides from spent fuel. Being identified as a high priority topic in the Strategic Research Agenda of the IGD-TP (Implementing Geological Disposal Technology Platform), a great effort in DisCo project has been the understanding of the dissolution behaviour of modern fuel types, specifically Cr/(Cr+Al)-doped UO<sub>2</sub> fuels and Gd-doped UO<sub>2</sub> and how do they differ and compare with standard conventional nuclear fuels. With the aim to compile the great amount of experimental data obtained from spent fuel leaching experiments under different atmosphere conditions and solution compositions, Amphos 21 has updated and extended the database developed in FIRST-Nuclides project [2] to include the data generated in the framework of DisCo project on matrix dissolution [3] and additional data published in the literature since the 90's. The database is in excel format and includes both FIAP data and FGR of the different elements determined in the leaching experiments of UO<sub>x</sub>, MO<sub>x</sub> and Cr/(Cr+Al)-doped UO<sub>2</sub> irradiated fuels. The development of the described database is an added value after decades of dedicated research of many institutions and will allow to the scientific community to: i) identify correlations amount released radionuclides, ii) determine correlations with the most determining irradiation and leaching parameters and iii) identify any gap of knowledge in terms of fuel materials or relevant conditions, and, iv) it represents the stepping stone for a future development of surrogate models of spent nuclear fuel developed with machine learning techniques.

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## Effect of the aqueous composition on the dissolution of spent fuel under reducing conditions

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Dissolution experiments using two clad segments selected from a high burn-up spent UOX fuel with local burn-up of  $63 \text{ GWd} \cdot \text{t}_{\text{HM}}^{-1}$  under reducing conditions (5% H<sub>2</sub>, 0.003% CO<sub>2</sub> in argon) are presented. Two experiments using either simplified groundwater with pH 8.2 (BIC) or young cement water with pH 13.2 (YCWCa) as leaching solutions were carried out in an experimental set-up of autoclaves manufactured from non-reductive materials. Released aqueous concentrations of selected radionuclides were analysed by ICP-MS [1]. Theoretical inventory was calculated using an updated KORIGEN 2 code. The results show an initial release of uranium (up to  $10^{-7} \text{ M}$ ) attributed to unavoidable pre-oxidation during the preparation of the samples, followed by a rapid decrease in concentration in solution down to  $10^{-8}$  and  $10^{-9} \text{ mol} \cdot \text{L}^{-1}$  in BIC and YCWCa solutions, respectively. This decrease corresponds to the reduction of uranium VI to IV due to the reducing atmosphere. The lower final uranium concentration found in YCWCa solution is explained by the calcium inhibiting effect [2] compared to the BIC solution. Since H<sub>2</sub> was found to reduce the dissolution rate of the matrix, the concentration of the redox sensitive elements Am, Pu, U in solution was lower comparing with the results under oxidizing conditions [3-4]. The release of Cs in both experiments were the same, indicating that Cs dissolution is independent of pH and the water composition. On the other hand, Mo and Te release show a strong dependence on pH. The fast initial release of Cs, Mo and Te is due to segregated phases in open fuel voids.

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## Spent UOX fuel leaching in repository relevant conditions: Influence of H<sub>2</sub> concentration and high pH on fission product release

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Spent nuclear UOX fuel leaching experiments are conducted both by SCK CEN and KIT in a joint project financed by ONDRAF/NIRAS in order to investigate the (fast) release of radionuclides under conditions representative for a near field influenced by the presence of high pH concrete (e.g. the supercontainer design, which is the current reference design for the geological disposal of spent nuclear fuel in Belgium). Clad samples originating from the PWR reactors Tihange 1 in Belgium (54 MWd·kg<sub>HM</sub><sup>-1</sup>) and Gösgen in Switzerland (50 MWd·kg<sub>HM</sub><sup>-1</sup>) are leached in a highly alkaline synthetic cement water (pH<sub>25°C</sub> 13.5). The expected presence of hydrogen in the repository, coming from the anaerobic corrosion of the metallic components in the supercontainer, is investigated using pressurized autoclaves at maximum 40 bar with various mixture of H<sub>2</sub> in Ar to impose reducing conditions and in pure Ar for the comparison with anoxic conditions. A parallel test is performed with the Tihange 1 fuel in a bicarbonate solution (pH<sub>25°C</sub> 7.4) to verify the pH effect and to compare the results with those of the previous EU program "FIRST-Nuclides" [1]. For about 3.5 years, samples of gas and solution were taken to determine the amount of fission gas, actinides and fission products released. Divided in two consecutive periods, the first one (about 733 days) aimed at investigating the easily leachable fraction, while the second period is foreseen to study the matrix dissolution. In all experiments, the results show a fast release of several fission products to the aqueous and gaseous phase in the first days. Focussing on the first period, differences appeared between the two fuels in the release of Xe and Kr, which are attributed to the irradiation history rather than to the redox conditions or the leachate composition. In case of the Tihange 1 fuel, the iodine release follows the fission gas release and levels off at a value lower than the fraction determined upon the puncture tests (14%). A clear effect of hydrogen and/or leachate composition was observed for fission products such as Sr and Tc. Also, despite relatively close burnups of the two fuels, Sr release was two times higher from the Tihange 1 fuel than the Gösgen fuel likely due to a higher linear power rate of the Belgian fuel. The results for the actinide release from these tests are presented at this workshop by KIT.

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## Release of actinides from spent nuclear UOX fuel under anoxic/reducing atmosphere and alkaline pH

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Disposal in deep geological repositories is considered as the preferred option for the management of spent nuclear fuel (SNF) in many countries to permanently and safely isolate the radionuclide inventory from the biosphere for an appropriate length of time. In post-closure safety assessments of deep underground repositories for SNF, water access, consecutive failure of canisters and loss of fuel cladding integrity is considered. In this context, it is indispensable to evaluate the release of actinides under repository relevant geochemical conditions.

In the present study, the release of radionuclides from spent UO<sub>2</sub> fuel under conditions representative of the Belgian “supercontainer concept” were investigated. Six leaching experiments with high burn-up SNF clad pellets were performed in highly alkaline (cementitious) solution and anoxic/reducing atmosphere to analyse the impact of hydrogen and hydrogen partial pressure on the mobilisation of actinides, fission products and fission gases. These experiments were carried out in parallel by SCK CEN in Belgium and KIT-INE in Germany with a duration of up to 1399 days.

The SNF were sampled from fuel rods irradiated in the Gösgen pressurized water reactor (PWR) in Switzerland (KIT-INE) and the Tihange-1 PWR in Belgium (SCK CEN). A synthetic high pH Ca-bearing cementitious water (pH ~13.5) was prepared and used in five of the experiments and a bicarbonate solution was used in one experiment also to compare with those of the previous EU program "FIRST-Nuclides".

The experimental results show scattering in aqueous concentrations of actinides during the first 300 days. In the long-term the concentrations of U-238 are lower in experiments with H<sub>2</sub> than in experiment under anoxic conditions, indicating that hydrogen inhibits the matrix dissolution. In the experiment under anoxic conditions, the <sup>238</sup>U concentration approaches the solubility limit of UO<sub>2</sub>(am,hyd), while the presence of hydrogen inhibits the dissolution kinetics of spent nuclear fuel. The relatively low Am, Cm, Np and Pu concentrations in the current experiments are close to or below calculated solubility limits of respectively Np(IV), Pu(IV), Am(III) and Cm(III) oxyhydroxide solid phases. Although Np and Pu are redox sensitive elements, the difference in redox conditions between the anoxic dissolution experiments and the two experiments under hydrogen overpressure was too small to result in major differences in aqueous concentrations.

The results for the fission products from these tests are presented at this workshop by SCK CEN.

## Effects of environmental conditions on radionuclide leaching from irradiated mixed oxide (MOX) fuels

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In the context of spent nuclear fuel (SNF) disposition, a deep geological repository (DGR) based on a multi barrier concept is considered as the safest disposal option in many countries. The assessment of the long-term safety of a DGR requires a profound understanding of the corrosion behaviour of SNF in groundwater, which will occur when the waste canisters are eventually breached. Various studies addressed this topic in the past, leading to a good phenomenological understanding of the long-term behaviour of SNF in a DGR. However, these studies considered mainly uranium dioxide-based fuels, and some processes contributing to the (radiolytic) matrix corrosion of SNF in the generally reducing repository environment are still not fully understood.

In this study, performed within the SF-ALE project (Spent Fuel Autoclave Leaching Experiments), the corrosion of irradiated MOX fuels under reducing conditions was investigated, since respective data are scarce to date. MOX fuel with an initial Pu/U ratio of 14.3% and a well-known irradiation history was characterised by optical microscopy, SEM and EPMA before leaching experiments with a duration of 3.5 years were started. The latter aim at elucidating the impact of environmental conditions on SNF corrosion, addressing the instant release of radionuclides as well as the (long-term) matrix corrosion. Three clad fuel rod segments with burnups between 29 GWd·t<sub>HM</sub><sup>-1</sup> and 52 GWd·t<sub>HM</sub><sup>-1</sup> were exposed to bicarbonate water as reference groundwater at neutral pH, and a synthetic young cementitious water (pH 13.5). Considering that the anoxic corrosion of metallic waste canisters leads to H<sub>2</sub> generation in a repository, the autoclave leaching experiments were performed under reducing conditions (Ar/H<sub>2</sub> atmosphere at a pressure of 40 bar,  $p(\text{H}_2) = 1.6$  bar). The leachates and the gas phases were regularly sampled in order to determine the release of more than 30 radionuclides from the irradiated MOX by various analytical techniques.

Results regarding the instant release fractions of the fission products caesium and iodine observed within the first two years of leaching were published recently [1]. In this contribution, we report the release behaviour of further selected radionuclides throughout the whole duration of SF-ALE.

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## Matrix dissolution of irradiated MOX fuels. Effect of the axial location

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Dissolution experiments under anoxic conditions on two spent MOX fuel samples taken from two different axial positions of the same fuel rod were performed. Uranium, Plutonium, Molybdenum, Technetium and Caesium results have been analysed and reported.

Uranium and Plutonium concentration levels at the end of both experiments were similar and close to those expected under anoxic conditions [1]. However, differences of up to one order of magnitude were found for the Instant Release Fraction (IRF) values of both samples, see Table 1.

**Table 1:** Instant Release Fraction (%)

Element	IRF (%)	
	MOX-H	MOX-L
Mo	0.073 ± 0.004	0.278 ± 0.006
Tc	0.052 ± 0.004	0.869 ± 0.006
Cs	0.856 ± 0.007	6.83 ± 0.02

Typically, the interpretation of leaching experiments correlates the instant release fraction with the irradiation history of the selected rods, but does not take into account axial variations within the same rod. These experimental results indicate that although the irradiation history is the main factor affecting the IRF, also local differences in the irradiation experienced by the fuel along the rod axis play an important role, which should be taken into account to estimate IRF values for the safety assessment of radioactive waste repositories.

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## Leaching experiments with spent MOX fuel under hydrogen overpressure in bicarbonate water

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Disposal of spent nuclear fuel (SNF) in deep geological repositories is considered as preferential option for the management of such wastes in many countries with nuclear power plants. In safety assessments of such facilities, water access, consecutive failure of canisters and interaction of groundwater with the emplaced waste is considered in the long-term. Hence, the performance of SNF under these deep geological repository conditions has to be evaluated. So far, studies have been performed on dissolution of initially <sup>235</sup>U enriched UO<sub>2</sub> and CANDU fuels under oxidizing conditions and, in a lesser extent, on SNF dissolution under reducing conditions. The number of studies on dissolution of irradiated mixed Pu/U oxide (MOX) fuels is very limited, especially, under reducing conditions. In the present study, the contribution of fission products and gases to the instant release fraction as well as the matrix dissolution of irradiated MOX fuel was studied in a simplified groundwater simulate under strongly reducing conditions.

A clad pellet and fragments of a pellet without cladding were sampled from a fuel rod segment with an average burn-up of 38.0 MWd·kg<sub>HM</sub><sup>-1</sup> to perform the experiments. The fuel was initially enriched with 3.2% Pu. Two static leaching experiments under 40 bar Ar/H<sub>2</sub> overpressure ( $p(\text{H}_2) = 3.2$  bar) were performed with the samples in bicarbonate water (19 mM NaCl + 1 mM NaHCO<sub>3</sub>, pH 7.9). The experiments were periodically sampled and solution aliquots and gas phases were analysed. The cumulative release of the fission gases (Kr + Xe) as well as the release of <sup>90</sup>Sr, <sup>137</sup>Cs, <sup>129</sup>I, <sup>99</sup>Tc and actinides were determined over a period of > 1000 days of leaching under strongly reducing conditions.

A relatively fast release of volatile radionuclides such as <sup>137</sup>Cs and <sup>129</sup>I, compared to predominately matrix bound elements such as <sup>90</sup>Sr and <sup>99</sup>Tc is seen. However, the release rates of <sup>137</sup>Cs and <sup>129</sup>I decrease with time and converge to the release rate of <sup>90</sup>Sr in the long run. Also, a fast, initial release of fission gases is seen, reaching its maximum at around 200 days of leaching. The release rates of Kr and Xe are constantly decreasing with time in both experiments. Solubility of actinides approaches towards the solubility limits of the respective An(IV) (U, Np, Pu) and An(III) (Am) solid phases in the long-term in all experiments. The retardation of the matrix dissolution is attributed to the presence of hydrogen.

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## MOX fuel alteration mechanisms under deep geological repository conditions

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Although spent fuel reprocessing remains the reference scenario in France, direct disposal in a deep geological repository is also studied as an option within the framework of the French national plan for the management of radioactive waste. Even though  $\text{UO}_2$  spent fuel alteration mechanisms are associated to an extensive literature, it is not the case when considering  $\text{U}_{1-x}\text{Pu}_x\text{O}_2$  fuels and especially, Mimas® MOx fuels. This work is focused on the alteration of heterogeneous Mimas® MOx fuel and surrogate materials  $\text{U}_{1-x}\text{Ce}_x\text{O}_2$  with various Ce contents and microstructures in oxidizing conditions. The objective is to reach a better understanding of the mechanisms associated to MOx fuel alteration under oxidizing conditions. More specifically, the influence of oxidizing species produced by water radiolysis such as  $\text{H}_2\text{O}_2$  is considered. Homogeneous and heterogeneous  $\text{U}_{1-x}\text{Ce}_x\text{O}_2$  dense pellets with x ranging from 0 to 0.25 were prepared via wet and dry chemistry routes, respectively. These materials were submitted to dynamic leaching experiments for two weeks at 25°C and pH = 7.2 to investigate oxidizing conditions effects induced by radiolytically produced  $\text{H}_2\text{O}_2$ . The feeding solution containing  $0.2 \text{ mmol}\cdot\text{L}^{-1} \text{H}_2\text{O}_2$  was kept under air and renewed every 48 to 72 h to guarantee the stability of  $\text{H}_2\text{O}_2$  during the experiments. When considering homogeneous  $(\text{U,Ce})\text{O}_2$  materials, the normalized alteration rate decreased by a factor of 3 when increasing the Ce molar content from 0.08 to 0.25. Surfaces characterizations of the altered pellets revealed that studtite precipitated all over  $\text{UO}_2$  surface. Similar results were obtained with heterogeneous  $\text{U}_{0.92}\text{Ce}_{0.08}\text{O}_2$ , with the exception that studtite was found to precipitate on  $\text{UO}_2$  grains only. This result is in very good agreement with that observed for heterogeneous  $(\text{U,Pu})\text{O}_2$  in comparable conditions [1], which ascertains the reliability of cerium as a valuable plutonium analogue.

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## Modelling of $\alpha$ -doped $\text{UO}_2$ dissolution in claystone water in presence of iron at 70°C

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The present study brought insights into the modelling of the dissolution of spent fuel matrix under conditions representative of failed containers (carbon steel) under reducing repository environments with a focus on the effect of temperature. The model was developed and applied to two experiments of  $\text{UO}_2$  leaching performed in synthetic  $\text{CO}_x$  claystone groundwater representative of the French disposal site in the presence of an iron foil simulating the steel container. Plutonium-doped  $\text{UO}_2$  pellets were used to simulate the activity of an aged spent fuel after 50 years of alpha radioactive decay. The first experiment was carried at ambient temperature [1] and the second one at 70°C, which was representative of the long-term temperature induced by spent nuclear fuels in underground disposal cells.

The reactive transport model (HYTEC code) took into account the kinetics of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) radiolytic production and disproportionation on the  $\alpha$ -doped  $\text{UO}_2$  pellet surface, the kinetics of the oxidative dissolution of the  $\text{UO}_2$  matrix by  $\text{H}_2\text{O}_2$ , the kinetics of reducing dissolution of the  $\text{UO}_2$  matrix, and the kinetics of anoxic corrosion of the iron foil. A large set of reactions at thermodynamic equilibrium were considered by using the ThermoChimie database. Temperature dependency was implemented for the diffusion coefficient, all the thermodynamic and kinetic rate constants, with parameters either selected from the literature or fitted on the experimental data. Sensitivity analysis was performed on the Fe(II)-phases precipitation and the corresponding dissolved concentration of Fe(II) that reacted with  $\text{H}_2\text{O}_2$ .

The increase of temperature did not globally change the release of uranium into the solution characterized by a low release of U(IV) controlled by amorphous  $\text{UO}_2 \cdot n\text{H}_2\text{O}$ . Dissolved Fe(II) species inhibited the oxidizing dissolution by consuming  $\text{H}_2\text{O}_2$  and precipitating magnetite at the extreme surface of the pellet. On the contrary, the increase of temperature significantly affected the water chemistry and the amount of iron corrosion products (chukanovite and siderite).

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## Long term leaching of spent nuclear fuel and characterization of secondary phases

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For a future deep repository for spent nuclear fuel, the rate and mechanism for dissolution of fission products and actinides from the fuel is a key parameter for the safety assessment of the disposal concept. At the time of encapsulation, the cladding is expected to be intact for the vast majority of the fuel rods. There is however a small fraction of rods where the cladding has failed and the fuel has been exposed to water and/or air prior to encapsulation. In these rods an alteration of the fuel matrix can be expected. In order to predict the mechanism and dissolution rate of radionuclides from failed fuel, the effects of this matrix alteration need to be investigated. Although the leaching behaviour of spent nuclear fuel under deep repository conditions has been studied extensively [1-2], studies of failed fuel under these conditions are relatively scarce. However, at the Studsvik laboratory, aerated leaching tests of spent fuel started in the 1980s and two of these were finalized only recently [3]. This provides an opportunity to investigate the effects of long-term contact with water under aerated conditions similar to wet interim storage conditions. In this study, the leaching of two spent nuclear fuel samples, in deionized water and simulated ground water respectively, has been followed for 37 years. After finalizing the leaching studies, the fuel samples were subject to visual inspection as well as scanning electron microscopy and X-ray diffraction investigations in order to study the formation of secondary phases. Furthermore, the fuel samples have been exposed to carbonate solutions in an effort to dissolve the secondary phases formed during the extended leaching time. Investigation of the fuel sample leached in deionized water showed significant formation of secondary phases, mainly consisting of studtite, whereas the sample leached in simulated groundwater had a much lower amount of secondary phases. Leaching in carbonate solution significantly increased the release rate of radionuclides for the sample initially leached in deionized water. For the sample leached in simulated groundwater the increase in release rate was marginal. It was observed that after 119 days of leaching in carbonate solution there was remnants of secondary phases left on the surfaces and in cracks on both fuel samples.

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## The dissolution of UO<sub>2</sub>-based spent nuclear fuel under storage and disposal conditions: Insights from SIMFUEL studies

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Historically, UO<sub>2</sub>-based spent nuclear fuel (SNF) in the UK was reprocessed at Sellafield's Thermal Oxide Reprocessing Plant (THORP). THORP closed in 2018 and current UK policy is that SNF will be sent to a GDF due to open ~2075. Until then fuel will be kept in storage ponds at Sellafield.

Internationally, the vast majority of UO<sub>2</sub>-based SNF is from LWRs and a significant amount of research has been carried out to support both the wet storage and direct disposal concepts in terms of the physical and aqueous durability of cladding and irradiated UO<sub>2</sub>. However, in the UK, the vast proportion of SNF is from indigenous Advanced Gas-cooled Reactors (AGRs). AGRs, whilst also using UO<sub>2</sub>-based fuel, employ CO<sub>2</sub> as coolant and are graphite moderated. Further, the fuel assembly cladding is comprised of 20/25/Nb steel (20% Cr, 20% Ni) rather than zircalloy as is the case in PWRs. Consequently, AGR fuel has unique characteristics that need to be evaluated in order to satisfy safety case requirements for both extended pond storage and geological disposal.

In the UK, the very high radiation fields arising from real SNF prohibits their study in all but a few specialised "hot cells" operated by Sellafield or NNL, a resource that is necessarily constrained. One way to obviate this problem is to work on simulated SNF (SIMFUELS).

Thus, we have been studying a series of novel SIMFUELS designed to replicate SNF discharged from a UK AGR at a range of simulated burnups. AGR SNF destined for long term wet-storage could face pond water ingress through the fuel cladding as a result of damage to that cladding. Similarly, in a GDF, at some point after repository closure, it is expected that the canisters within which the SNF is sealed will fail, allowing the ingress of groundwater. In either scenario, the pond/groundwater may come into contact with the UO<sub>2</sub> fuel pellets initiating their corrosion and dissolution. Consequently, our studies have focussed on understanding both the materials properties of these SIMFUELS and their corrosion behaviour as a function of electrolyte compositions and conditions relevant to pond storage and geological disposal. This presentation will present the key findings from those studies, with an emphasis on those conducted electrolyte systems designed to simulate storage pond waters and granitic and evaporite groundwaters. Features to be presented include: the role of each of the main classes of additives to the SIMFUEL (the trivalent lanthanides, the so-called grey phases, the  $\epsilon$ -particles) play in determining the behaviour of the fuel matrix; the effect of galvanic coupling of the SIMFUEL to the stainless steel cladding on their corrosion behaviours (inc. the sacrificial protection afforded to the fuel in some groundwaters); and a comparison of SIMFUEL corrosion data with similar data recently obtained from real AGR SNF at NNL's "hot cell" facility.



## Aqueous leaching of ADOPT and standard UO<sub>2</sub> spent nuclear fuel under H<sub>2</sub> atmosphere

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Over the last decades, new types of nuclear fuel are developed by fuel vendors and introduced in commercial reactors to improve fuel cycle economics and accident tolerance. One example of these novel fuels is the ADOPT fuel (Advanced Doped Pellet Technology), a UO<sub>2</sub>-based fuel doped with small amounts of Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>. In order to safely dispose these new fuels, it must be shown that the dopants do not cause unacceptable changes in the dissolution behaviour. Such fuel additives introduce minor modifications in the UO<sub>2</sub> matrix which could potentially affect the release rate of radionuclides under relevant repository conditions. The objective of this study is to gather new data that will be used to support or refute the hypothesis that there is no significant difference in the leaching behaviour between ADOPT and standard UO<sub>2</sub> fuels under hydrogen atmosphere. This project is part of the DisCo Project, a Collaborative Project funded by the European Commission under the Horizon 2020 Research and Training Programme.

The experiments are performed on irradiated fuel fragments without cladding. Prior the experiments, the fragments were exposed to an initial leaching period under aerated conditions in relatively high NaHCO<sub>3</sub> concentrations (10 mM) as an attempt to wash away any pre-oxidized phases presumably formed during air storage in cell. Thereafter, the samples were introduced into their respective autoclave containing simplified groundwater (10:2 mM NaCl:NaHCO<sub>3</sub>) and pressurized to a target pressure of 55 bar of H<sub>2</sub>. The concentration of radionuclides of interest released into the aqueous phase as well as the composition of the gas phase have been monitored for more than 2 years.

In this study, radionuclide concentrations have remained low throughout the experiment but are relatively high compared to previous leaching studies under similar experimental conditions [1-2]. The results are probably affected by the presence of a pre-oxidized phase on the surface of the fragments and the presence of very small particles in solution. Additional examinations of the solid phase are being considered to corroborate this hypothesis. The results of the experiment support that there is no significant difference in leaching behaviour between ADOPT and standard UO<sub>2</sub> fuels.

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## The oxidative dissolution of Cr<sup>2+</sup> doped UO<sub>2</sub> fuel

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Advanced Cr-doped UO<sub>2</sub> fuels are essential for driving safe and efficient generation of nuclear energy. Although widely deployed, little is known about their fundamental chemistry, which is a critical gap for development of new fuel materials and radioactive waste management strategies. Utilising an original approach, we directly evidence the chemistry of Cr<sub>2</sub>O<sub>3</sub>-doped UO<sub>2</sub>. Advanced high-flux, high-spectral purity X-ray absorption spectroscopy (XAS), corroborated by diffraction and high energy resolved fluorescence detection-XAS, is used to establish that Cr<sup>2+</sup> directly substitutes for U<sup>4+</sup>, accompanied by U<sup>5+</sup> and oxygen vacancy charge compensation. Extension of the analysis to heat-treated simulant nuclear fuel reveals a mixed Cr<sup>2+/3+</sup> oxidation state, with Cr in more than one physical form, explaining the substantial discrepancies that exist in the literature.

Sintered pellets of Cr-doped UO<sub>2</sub> were subject to dissolution in simulated groundwater (FIN) solution at 25°C, 40°C and 60°C, under oxic conditions. The normalised mass loss, dissolution rate and activation energy were determined as a function of Cr content allowing insight into the mechanisms and kinetics of Cr-doped UO<sub>2</sub> dissolution. At 25°C and 40°C, U dissolution rates were systematically lower than undoped UO<sub>2</sub>, suggesting a link between Cr content and durability, postulated to be the result galvanic coupling of Cr<sup>2+</sup> in the UO<sub>2</sub> matrix with oxidised U species at the surface. However, at 60°C, the effect of bicarbonate solution-driven oxidative dissolution was greater than at the other temperatures, effectively negating the galvanic effect of Cr<sup>2+</sup> on the dissolution rate, although activation energy analysis indicates that it still contributes to the dissolution mechanism. With continued dissolution, saturation of U in solution was observed and, at this stage of dissolution, there was no apparent effect of Cr on the dissolution rate of U. Assessment of microstructural effects on the dissolution rates suggested that an increased grain size also reduces the dissolution rate of U. This work shows that Cr-doped UO<sub>2</sub> is possibly more durable than undoped UO<sub>2</sub> owing to both Cr content and increased grain size, but further work is required to determine which of these two factors is the most important in terms of the long-term durability of doped nuclear fuel.

## Influence of iron strips on dissolution of Pu- (Cr)-doped UO<sub>2</sub> in cementitious water (pH 13.5) and carbonated solution (pH 9)

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In the framework of the European DisCo project, studies on the leaching behaviour of Gd/Cr/Al-doped model materials have been performed to investigate whether these fuels will behave similarly to standard fuels in geological repository conditions [1]. At SCK CEN, two 'inactive' model materials (UO<sub>2</sub> and Cr-UO<sub>2</sub>) and two 'active' ones (Pu-UO<sub>2</sub> and Pu-Cr-UO<sub>2</sub> with an  $\alpha$ -activity of ~18 MBq/g UO<sub>2</sub> representative for 10,000 years old spent fuel) were prepared and leached in reducing conditions. To achieve the reducing conditions, experiments with both inactive and active model materials were conducted in autoclaves with 10 bar H<sub>2</sub> pressure in presence of Pd/Pt catalyst. Experiments were carried out in two reference solutions: Young Cementitious Water at pH 13.5 (YCW) and a reference bicarbonate water at pH 9 ('FIN solution'). After a first period of 150 days (Phase I), the measured U concentrations in the active experiments were significantly higher ( $10^{-7}$  to  $5 \cdot 10^{-7}$  mol·L<sup>-1</sup>) than the reported UO<sub>2</sub> solubility range of  $10^{-8.5 \pm 1}$  mol·L<sup>-1</sup> in reducing conditions [2] for both solutions, while they were close to this solubility range in the inactive systems. This demonstrated that the effect of dissolved H<sub>2</sub> was not sufficient to prevent the short-term radiolytical oxidation/dissolution, or to reduce oxidised U(VI) in solution. Iron foil strips were then added to the autoclaves with the 'active' model materials to verify if this would further decrease the uranium concentrations, as observed by VTT in similar experiments with the same materials [1]. The influence of iron was studied in two subsequent steps. In the first step, iron foil was added without solution replacement. The leach test was continued like this for a period of about 130 days (Phase II). In a second step, fresh iron foil was added and the leaching solution was replaced, keeping the leached pellets from phase I + phase II. The leach test was again continued like this for 232 days (Phase III). As a result of the iron addition, stable U concentrations of ~ $10^{-8}$  mol·L<sup>-1</sup> were reported at pH 9 for phase II and phase III while at pH 13.5 the iron effect on U concentration is only visible after 30 days in phase III. To complete the mass balance, the U sorption on iron foils and vessels was measured. Surface analysis showed some uranium rich spots on the iron foils, but no secondary uranium phases on the UO<sub>2</sub> surface were observed.

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## Gd-doped UO<sub>2</sub> corrosion in the presence of silicate and calcium under alkaline conditions

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The incorporation of Gd<sub>2</sub>O<sub>3</sub> into the UO<sub>2</sub> matrix as a burnable neutron absorber in some PWR and BWR fuels is of great importance in order to determine its influence on the oxidation/dissolution processes of UO<sub>2</sub>, which are relevant in case of a canister failure in a deep geological repository. In addition, cement has been recently considered a possible material present in such repositories [1], therefore it is necessary to determine the effect of cementitious water in the near field of these doped spent fuel. For this reason, a series of electrochemical experiments were performed in presence of calcium and silicate to approach the composition of this type of water.

Three working electrodes were prepared. One using unirradiated UO<sub>2</sub> and two UO<sub>2</sub> doped pellets with 5% and 10% wt. of Gd<sub>2</sub>O<sub>3</sub>. Ag/AgCl (3 M KCl) and a Pt wire were used as a reference and counter electrodes, respectively. Test solutions were prepared at pH 10 with NaCl 0.1 mol·dm<sup>-3</sup> in the presence of NaHCO<sub>3</sub>, Na<sub>2</sub>SiO<sub>3</sub> and/or CaCl<sub>2</sub>. The corrosion process was studied by performing cyclo-voltammograms from -1.6 mV to 0.8 mV at 10 mV·s<sup>-1</sup>, potentiostatic experiments at 0.4 mV for 1 hour and corrosion potential experiments for 24 hours.

Preliminary results for the three working electrodes show that the presence of silicate and calcium decreases the oxidation of UO<sub>2</sub>, considering the small anodic oxidation current measured, as previously observed in SIMFUEL [2]. In contrast, when only bicarbonate is added to the solution the oxidation process is enhanced. Considering the composition of the working electrode, a decrease in reactivity is observed for the Gd-doped UO<sub>2</sub> electrodes. According to the literature, the formation of Gd-oxygen vacancy clusters could reduce interstitial sites available for the accommodation of O<sub>2</sub><sup>-</sup> ions, which grants stability to the cubic structure [3] and protects the matrix during anodic oxidation [4].

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## Dissolution of (U,Th)O<sub>2</sub> under deep geological repository conditions with continuous H<sub>2</sub>O<sub>2</sub> additions.

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This presentation will outline recent experimental work toward improving the simulation of radiolytic oxidant production in batch dissolution studies with lower activity model fuels. To plan for mixed-oxide (MOx) spent fuel disposal, it is important to understand how its dissolution may differ from uranium-based spent nuclear fuels. MOx is more radioactive so will have a higher radiolytic production rate than uranium-based spent nuclear fuels. There are concerns that this will cause an accelerated dissolution, but these concerns are countered by evidence that the chemistry of plutonium mitigates these effects. This mitigation depends on enhanced autocatalytic decomposition of the peroxide (the most dominant radiolytic oxidant [1]) and the formation of a 'protective', less soluble plutonium-rich surface on the altered MOx as uranium is released.

Experiments with plutonium are limited in number so complementary experiments on lower activity model fuels are required. In this work, (U,Th)O<sub>2</sub> has been selected to model Pu(IV) homogeneously distributed in the UO<sub>2</sub> fluorite structure. Typically, H<sub>2</sub>O<sub>2</sub> is added initially and the consumption of H<sub>2</sub>O<sub>2</sub> is observed over time [2]. This consumption is due to the autocatalytic decomposition, the oxidative dissolution and peroxide decomposition processes unrelated to the pellet. The background consumption can be subtracted to calculate dissolution yield, but it does limit the timescales of the experiments. In our own batch experiments, accelerated decomposition has been observed to occur due to groundwater ions the presence of a Si (100) wafer and certain container materials.

Groundwater doped with 0.6 mM H<sub>2</sub>O<sub>2</sub> was added through a microfluidic tube to the fuel pellet surface at a flow rate of 6.5 nL·s<sup>-1</sup> by a syringe pump to simulate the production rate of unirradiated MOX MIMAS fuel pellets with a dose rate of 5640 Gy·h<sup>-1</sup> [3]. The solutions were added to three groundwater solutions without pellets and into three containing U<sub>0.72</sub>Th<sub>0.28</sub>O<sub>2</sub> pellets. The leachant volume was returned to 50 mL by sampling every 5 days. Sedimentary rock groundwater has been simulated by synthetic Callovo-Oxfordian groundwater. Ion concentrations were followed through the study by ICP-MS and H<sub>2</sub>O<sub>2</sub> concentrations by UV/vis spectroscopy. The experiment ran for 60 days. This method was intended to be more comparable to experiments with uranium-plutonium dioxide fuels because H<sub>2</sub>O<sub>2</sub> concentrations do not become the rate-limiting step in uranium release.

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## Experimental AGR fuel-groundwater interactions as an analogue for geological repository leaching

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The UK's current planning assumption for disposal of spent nuclear fuel is within a geological disposal facility (GDF), whereby spent fuel will be encapsulated within canisters and entombed below ground in bedrock. A substantial body of research on Light Water Reactor (LWR) fuel behavior on eventual exposure to groundwater in such a GDF has been completed. In the UK, however, the main inventory of fuel requiring disposal is from Advanced Gas-cooled Reactors (AGRs), which is UO<sub>2</sub> but clad in stainless steel. Therefore, separate research must be conducted to understand whether LWR fuel leaching behavior is applicable to that of AGRs.

Funded by the UK's Nuclear Waste Services (NWS; formerly RWM), NNL has undertaken a set of oxic leach tests within the Windscale Active Handling Facility. These tests complement an initial set of leach tests on AGR fuel undertaken by Studsvik [1] from 2012-2015. The material tested by NNL consists of stainless steel-clad, uranium dioxide fuels that were irradiated during fuel development programs in the Windscale Advanced Gas-cooled Reactor (WAGR), subjected to post irradiation examination (PIE) in the 1960s and subsequently stored in pond for over 40 years, where they were exposed to water. This is the longest wet-stored fuel known and is accordingly an invaluable source of information for understanding leaching behavior on timescales longer than those permitted by practical experiments.

Three types of WAGR fuel were used: low burnup; relatively high burnup, which is believed to have been exposed to water; and relatively high burnup fuel that is believed to have stayed dry. Fuel samples were loaded into porous glass baskets and periodically moved into fresh liquid with the used liquid then analyzed for radionuclide content. The test solutions were weak carbonate-chloride solution as a basic simulation of groundwater. The campaign was successful: ten samples were obtained at lengthening intervals for each of the three experiments, alongside an identical blank. All experiments show clear, almost exponential decreases in leach rate through time, with commensurate decreases in sample activity and concentration. This is consistent with the behavior of LWR fuel as well as the AGR fuel experiments of Studsvik [1].

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## Passive gamma and neutron measurements for characterization of spent nuclear fuel

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In Sweden, the spent nuclear fuel (SNF) assemblies are planned to be encapsulated in copper canisters and placed in a geological repository. In January 2022, the Swedish government approved SKBs (the Swedish Nuclear Fuel and Waste Management company) application for such a repository. Before the encapsulation, the SNF must be characterized to determine important safety and safeguards parameters. Depletion calculations are used to predict the values of these parameters and measurements are planned to verify and update the calculated values. Gamma-ray measurements have been performed on 50 Swedish SNF assemblies selected by SKB (the so-called SKB-50 assemblies). As part of the EURAD project (<https://www.ejp-eurad.eu/>), different techniques to analyse neutron and gamma-ray data are presented here. Ratios of radionuclides such as  $^{134}\text{Cs}/^{137}\text{Cs}$  and  $^{154}\text{Eu}/^{137}\text{Cs}$  are derived from recorded HPGe gamma-ray spectra [1] using an intrinsic self-calibration technique [2]. The results are discussed in terms of reproducibility and sensitivity to experimental conditions. The SKB50 data have also been examined by the Differential Die-Away Self Interrogation (DDSI) prototype instrument [3], which is a passive neutron measurement technique. Here we present results from an analysis of DDSI data by fitting the extracted time-coincidence distribution, the so-called Rossi-Alpha distribution, with a double exponential function. Both synthetic and experimental data are studied and potential benefits of using a double exponential to extract information about the SNF are presented. Finally, we present how the analyzed neutron and gamma-ray data can be used to infer SNF parameters of safety and safeguards concern such as initial enrichment and burnup.

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## UO<sub>2</sub> based model systems for spent nuclear fuel: microstructure and oxidative dissolution

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In safety assessments, the possibility and results of direct contact between SNF and water must be considered. In contact with SNF, oxidative species are continuously produced due to the radiation induced hydrolysis of water, which then corrode the SNF, releasing radionuclides [1-2]. For many ceramics, grain boundary dissolution is the dominant dissolution mechanism. However, a detailed mechanistic understanding of the role of microstructure in SNF corrosion is still largely absent. For UO<sub>2</sub> and SNF even the details of the grain boundary structures have been the subject of just a handful of studies [3]. UO<sub>2</sub>-based SNF is a complex multi-component ceramic containing several oxide solid phases as well as decay and fission products. UO<sub>2</sub> based model systems are commonly utilized to gain a deeper understanding of the effects of individual components on the dissolution kinetics of the complex SNF, an approach that has also been taken for this work. Pure UO<sub>2</sub> samples as well as Nd and Gd doped samples are synthesised using a co-precipitation method [4]. In this work the microstructure of these samples is evaluated by an automated SEM examination process in order to create quantitative and representative data to compare the doped with pure reference samples. A method based on EBSD measurements is developed in order to determine suitably oriented grain boundaries (GB) e.g. coincidence site lattice (CSL) boundaries, which can be prepared by focused ion beam (FIB) for high-resolution transmission electron microscopy (TEM) examinations. The high-resolution TEM measurements and orientation measurements will be used to adapt atomistic simulations to be closer to the real data. Thus, an atomistic model for the grain boundary structures and especially the oxygen sublattice will be created to be used as first step in the theoretical study of oxidative UO<sub>2</sub> and SNF corrosion.

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## Spent nuclear fuel decay heat uncertainty implementation into a fuel loading optimization program

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Spent nuclear fuel (SNF) disposal is a process lasting decades and entailing substantial investments. This requires careful investigation e.g. of scheduling and storage capacities as well as disposal strategy. In addition, each disposal canister (DC) loaded with SNF should meet the safety criteria related to e.g. decay heat power, radiation dose rate, and criticality safety. It is known that uncertainties especially related to the decay heat play significant role in the disposal optimisation and have a significant impact on the disposal costs. For example, a reduction of uncertainties related to decay heat would lead to an optimised spacing of the DC thereby reducing excavation and backfilling of the deposition tunnels and preventing too high temperatures in bentonite buffer surrounding DCs. By applying an optimised fuel loading it is possible to fulfil the safety criteria as well as to achieve increased levels of safety. In addition, by applying an efficient canister disposal strategy, including robust decay heat uncertainty handling, sustainability of disposal can be achieved as well. In this study, SNF decay heat uncertainty was analysed for DCs containing two PWRs (EPR and VVER) and one BWR fuel type. The purpose was to combine measurements and coding estimates to provide a conservative determination of the components driving the uncertainty in the decay heat. In addition, it was investigated how FAs' uncertainty components are mutually related. Finally, these determinations can be applied in fuel loading optimization calculations.

## Incorporation and use of detailed mechanisms for surface reactions in numerical models for spent fuel dissolution

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Numerical models to predict the dynamics of radiation induced spent nuclear fuel dissolution under geological repository conditions are not always based on the most recently confirmed reaction mechanisms for the relevant surface reactions involved. This is a major drawback as it could be argued that the models are not accounting for state-of-the-art knowledge and also because the models cannot be used when planning new experiments. The general understanding of the mechanism for the reaction between H<sub>2</sub>O<sub>2</sub> and UO<sub>2</sub> has changed quite a lot during the last decade as experiments have confirmed that a surface-bound hydroxyl radical is the common intermediate for both oxidation of UO<sub>2</sub> and for catalytic decomposition of H<sub>2</sub>O<sub>2</sub>. [1] This mechanism also opens up for new possible reactions involving the surface-bound hydroxyl radical and other solutes. The most obvious candidate is the possible reaction between the surface-bound hydroxyl radical and H<sub>2</sub> which could inhibit oxidative dissolution. The previously well-established epsilon-particle catalyzed reduction of oxidized uranium by H<sub>2</sub> is also a reaction that is often not included in the models. [2,3] In this work we have incorporated the mechanisms mentioned above in a numerical model which also accounts for the spatial and temporal heterogeneity of the system. The rate constants of the reactions involved are discussed in view of literature data and the impact of the various possible H<sub>2</sub>-effects are evaluated on the basis of simulations performed using the updated model. Finally, simulation results are compared to results from different types of experiments.

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## Burnup-dependence of the fuel composition uncertainty

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Fuel composition characterisation is crucial both for fuel in-core evolution and for spent nuclear fuel (SNF). Its relevance refers to criticality, safety, radiation protection, and impacts the ecological and the economic aspects of fuel handling and disposal. Uncertainty quantification complementing the information on fuel composition is needed as it determines the uncertainty on the many observables considered in the mentioned fields (such as radiation emission, decay heat, contribution to criticality etc.). Among the sources of fuel uncertainty computed through simulations, nuclear data (ND) are relevant ones. In this regard, the uncertainty of the cross sections of the actinides and of the fission products was propagated to the fuel composition and analysed in sample D047-MKP109-P irradiated in the Calvert Cliffs Unit 1 reactor (sample burnup 44.13 GWd·t<sub>HM</sub><sup>-1</sup>, initial enrichment 3.038 wt.% in <sup>235</sup>U) [1].

The statistical sampling-based uncertainty propagation procedure implying SANDY code was extended to fuel sample SF95-4 irradiated in the Takahama reactor (sample burnup 36.69 GWd·t<sub>HM</sub><sup>-1</sup>, initial enrichment 4.1 wt.% in <sup>235</sup>U). The comparison among the ND propagated uncertainty estimated in these two case studies indicates the dependency of fuel concentration uncertainty on burnup. It appears that the mechanisms of uncertainty propagation themselves vary with burnup as well, resulting not only in changing uncertainty, but also in varying sensitivity to the different production paths of the nuclides.

In this work, the uncertainty propagation scheme developed for Calvert Cliffs sample P is extended to Takahama sample SF95-4 using models validated against the experimental benchmark results. Then, a comparison of the fuel composition uncertainty evolution during the irradiation time is reported and analysed with focus on the uncertainty generating mechanisms and on their relation with burnup and initial enrichment. Coherently to what reported in [1], the comparison involves three major nuclear data libraries (ENDF/B-VIII.0, JEFF-3.3 and JENDL-4.0u), highlighting the effect of both the cross sections and the covariance matrices in different evaluations.

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## Characterisation of spent nuclear fuel for a typical PWR

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Characterisation of spent nuclear fuel (SNF) is vital for safe, secure, ecological and economical operations during transport, interim storage, (possible) reprocessing and final disposal. Apart from integral observables, e.g. decay heat, neutron and gamma-ray emission, the inventory of fissile nuclides and of strong neutron absorber nuclides is also needed. Full characterisation requires computational effort in addition to experimental methods, both destructive and non-destructive (NDA). In order to pursue this goal, an informal collaboration between the three institutions (JRC Geel, SCK CEN and JSI) was formed, majorly within the framework of the project EURAD. Some of the activities, conducted within this collaboration, are listed below:

- Main contributors to decay heat, neutron and gamma-ray emission were identified [1] for a typical PWR UO<sub>2</sub> and MOX fuel, for cooling time within the interval [1,1000] years.
- In addition to the participation within the Blind Test exercise on decay heat [2], a systematic comparison between different neutron transport and fuel depletion codes was performed [3].
- A SNF sample from Tihange NPP (PWR) was characterised for neutron emission with a combination of experimental NDA and computational methods [4] using a novel approach.
- A sensitivity study of relevant SNF observables to operational conditions was performed [5,6].
- Production paths of some important nuclides in SNF were studied in more detail [7].

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## Burnup credit application in CONSTOR SNF cask criticality analysis for RBMK-1500 fuel

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Almost 200 of CONSTOR RBMK-1500/M2 type casks for storage and transportation were designed and made for SNF storage in the dry type storage facility in the vicinity of the Ignalina NPP in Lithuania. Safety analysis and design justification were performed for interim dry type SNF storage facility [1]. Additionally, we applied burn-up credit approach for criticality analysis taking into account reduction of the fissile material and production of the neutron absorbing nuclides. These dry storage and transportation casks were not studied in the light of burn-up credit, while the safety analysis showed that only particular loading schemes of these casks might be used due to sufficient heat removal and criticality safety issues [1]. SCALE 6.1 code package was used for calculations [2]. The impact of RBMK-1500 burn-up of different enrichment fuel on the effective neutron multiplication factor was studied. Conditions for the storage in the SNF cask for modelling were assumed to be unfavourable regarding fuel enrichment, water density, temperature and burn-up and possible radionuclide leakage due to aging or radiolysis occurred in water and gamma flux during operation/storage in the pools. Modelling shows, that  $K_{eff}$  did not exceed the value of 0.95. Different burn-up credit approaches were studied. It was found that a decrease of  $K_{eff}$  in high burn-up fuel is caused by the increasing concentration of fission products, but not due to burnable absorber erbium. This type of analysis might be applied to evaluate safety of RBMK reactor SNF storage (for any type of casks) as well as may help to optimize the SNF storage volume inside the existing CONSTOR R RBMK-1500/M2 cask without compromising criticality safety.

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## Impact of some 3-D modelling effects on the spent fuel characterization

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Accurate characterization of the spent fuel is vital for many nuclear facilities, such as: fuel storage pools in nuclear power plants, spent fuel transportation systems, interim storage facilities, reprocessing plants and final disposal sites. The main observables typically considered are decay heat, activity, neutron and photon emission rate. Full characterisation process requires significant computational efforts in addition to experimental methods. Accuracy plays an important role, as compliance with safety and design requirements for the specific storage solution should be demonstrated. Moreover, significant cost savings can be achieved, if the uncertainties can be reduced. For example, it was shown in [1] that several million dollars can be saved by developing optimal loading strategies for disposal canisters.

Various computational tools can be used for the spent fuel characterization. Roughly speaking we can divide them into two categories:

1. reactor core simulators such as VERA-CS and CASMO5/SIMULATE/SNF, where detail observables distributions are obtained directly from the 3-D reactor core depletion,
2. codes capable of specific 2-D or 3-D depletion on the fuel assembly level, such as TRITON/NEWT from the SCALE package or the Monte Carlo code Serpent2.

The first approach is more straightforward, but requires significant computer resources. For industrial applications, the second approach is more commonly used. In this approach, the fuel assemblies are divided into several independent regions, which leads to additional uncertainties resulting from this process. Namely, in these regions the average fuel input parameters such as the fuel temperature, moderator density, etc. are used. However, it was shown in [2] and [3] that the observables do not depend linearly on the input parameters. Therefore, the segmentation of the fuel has a noticeable effect on the accuracy of the whole process. In this paper, the effect of the fuel segmentation is evaluated for the real variations of input parameters of the NPP Krško fuel. In addition, impact of specific spectral axial end effects is investigated by comparing Serpent2 results of the 3-D and 2-D models. The work was carried out within the framework of the EURAD project.

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## Recent spent fuel research at VTT

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Safe and economic spent fuel management and final disposal requires knowledge of spent fuel properties such as e.g. decay heat, reactivity, neutron and photon emissions and concentration of mobile nuclides. For example, decay heat determines how densely spent fuel canisters can be placed in the final disposal repository. Large uncertainty of decay heat during the first 100 years after disposal demands large safety margins which increases expenses. Safety justification requires among other things knowledge of dose estimates to biosphere which are partly based on the amount of mobile nuclides in spent fuel. In order to plan safe and economic spent fuel management, spent fuel properties and related uncertainties must be estimated by suitable calculation codes. However, calculation of spent fuel properties involves various uncertainty sources. These uncertainty sources include manufacturing tolerances such as e.g. fuel density and pin radius, operating history such as e.g. burnup, water density and fuel temperature and burnup induced changes such as e.g. fuel swelling. At VTT in recent years, computational uncertainties have been examined in a project called KÄRÄHDE funded by Finnish Research Programme on Nuclear Waste Management [1] and in EU project EURAD [2]. The goal of the projects in VTT's perspective has been to identify the most significant uncertainty components and their impact on spent fuel properties important in spent fuel management and final disposal in a geologic repository. Some emphasis has been given to uncertainties related to decay heat determination due to its importance in repository spacing. The work has included e.g. studies on effect of impurities, fuel type, choice of calculation parameters, operating history and manufacturing tolerances on spent fuel properties. The studied properties include decay heat, activity, photon emission rate, spontaneous fission rate and nuclide concentrations of some mobile and fissile nuclides. Current work is concentrated mainly on propagating nuclear data uncertainties through burnup calculation with Serpent [3] using Total Monte Carlo method [4]. We propose to present an overview of the activities carried out at VTT on uncertainties related to computational spent fuel characterization and the results achieved so far.

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