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# DISCO

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#### List of abbreviations

ADOPT	Advanced Doped Pellet Technology (by Westinghouse)
ADU	Ammonium Diuranate
AGR	Advanced Gas Reactor
BC (or BiC/BIC)	Bicarbonate Water
BET	Brunauer–Emmett–Teller (method for surface area measurements)
BU	Burn-Up
BWR	Boiling Water Reactor
Cox	Callovo-Oxfordian
CRC	Collision Reaction Cell
СТ	Coordination Team
EBSD	Electron Back Scatter Diffraction
EDS	Energy Dispersive Spectra
EPMA	Electron Probe Microanalyser
EUG	End User Group
FGR	Fission Gas Release
HAR	High-Active Raffinate solution
HBU	High Burn-Up
HIP	Hot Isostatic Pressing
HR	High Resolution
iCP	interface Comsol PhreeqC
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IRF	Instant Release Fraction
LOD	Limit of detecton
LOQ	Limit of Quantification
LSC	Liquis Scintillation Counting
MAM	Matrix Alteration Model
MOX	Mixed Oxide
MPM	Mixed Potential Model
PUREX	Plutonium Uranium Reduction Extraction
PWR	Pressurized Water Reactor
SEM	Scanning Electron Microscopy
SHE	Standard Hydrogen Electrode
ТМАН	Tetramethylammonium hydroxide
UV-Vis	Ultra-Violet Visible Spectroscopy
WDS	Wavelength Dispersive X-ray Spectroscopy
WMO	Waste Management Organisation
WP	Work package
XAFS	X-ray Absorption Fine Structure spectroscopy
XRD	X-Ray Diffraction
YCW	Young Cement Water
YCWCa	Young cement Water with Ca

#### Foreword

The results presented in this report relate to the achievements of a collaborative project that started in 2017 as a response to Euratom call NFRP-2016-2017-1 in the framework of Horizon 2020. The call was to address key priority research and innovation issues for the first-of-the-kind geological repositories. As the dissolution of spent nuclear fuel and the related release of radionuclides in a repository setting is a key element of the safety assessment of the repository, the project was financed for the original timeframe of 4 years. During this time a global pandemic hit, forcing us and the whole world to change our everyday life. Of course, this also affected our project, since laboratories closed and meetings were cancelled. However, in spite of these difficulties, there have been an impressive amount of work performed and with only a 6 months project extension, we can here summarize important results. All partners have done what they could to pursue the research plan. Since restrictions and recommendations have varied in different countries and in different organisations, some partners were affected more than others by the pandemic. One effect is the delay in data delivery from some laboratories, which of course is unfortunate. Still, an impressive amount of data has been collected and used in modelling activities that have allowed us to reach the project goals.

Spent nuclear fuel dissolution has been studied in many previous European collaborative projects and the achievements presented here build very much on the knowledge these projects have provided. In this way we have taken another step towards understanding the processes involved well enough to build reliable models to use in safety assessments. Some questions and uncertainties remain, as is always the case in research, but we are sure that with this project we have progressed towards the needs of the Waste Management Organisations in assessing the issue of doped and MOx fuels within the context of more traditional light water reactor fuels and achieving the goal of licensing and operating high level waste repositories in Europe.

## 1 Introduction

DisCo is the acronym for "Modern spent fuel dissolution and chemistry in failed container conditions". As the project title conveys, the project is concerned with research on spent nuclear fuel to be deposited in geological repositories. It is an identified important issue and part of a "Key Topic" of the European collaboration of Nuclear Waste management organisation, IGD-TP (Implementing Geological Disposal – Technology Platform). Direct disposal of spent fuel is a strategy for many European countries, and even if the main strategy is to reprocess the fuel, safety assessments of high-level waste repositories need to show sound understanding of radionuclide release and behaviour in the near field of the repository.

The main principle of most high-level waste repositories is to rely on isolation in a water tight container as a primary safety function, and retardation as a secondary safety function. It is when the isolation safety function has failed (i.e., when the container fails) that the spent fuel behaviour becomes important, since a slow dissolution is important for the retardation safety function. That is, a slow dissolution of the spent fuel matrix will aid in the retardation of the radionuclides release and dispersal in the environment. The environment inside the failed container is fundamental to both spent fuel dissolution and to the behaviour of the released radionuclides. Therefore, this project focuses on this chemical setting.

Since this important aspect was recognised early on, spent fuel dissolution and leaching behaviour has been investigated in previous projects funded by Euratom. Some examples are SFS (2001-2004), NF-PRO (2004-2007), MICADO (2006-2009), REDUPP (2011-2014) and FIRST-Nuclides (2012 -2014). All of these which focused on dissolution and radionuclide release from standard UO<sub>2</sub> spent fuels; however, FIRST-Nuclides also included experiments on Cr- & Al-doped spent fuel. In FIRST-Nuclides the focus was to determine the release of the gap inventory, the so-called "Instant Release". In the DisCo project, the focus is to further investigate the effects of dopants on the spent fuel behaviour. An important difference from the experiments performed in FIRST-Nuclides is that the central issue relates to the matrix dissolution rate.

## 1.1 Project objectives

Two overall objectives were identified:

- To test the hypothesis that there is no significant difference in dissolution behaviour between modern fuel types, such as Cr-doped and MOX fuels, and standard UO<sub>2</sub>-based fuels.
- To improve understanding of spent fuel matrix dissolution in the conditions representative of repository environments;

The expected knowledge gain is important for the Waste Management Organisations and for a wider range of potential users, for example research organisations and regulators. The aims of the project therefore included dissemination of the results through different channels.

## **1.2** Organisation of the project

Coordination was handled via a small Coordination Team (CT), led by SKB. The project was organised in five Work Packages. All Consortium members constituted the General Assembly, the decision-making body of the organisation. Two additional groups were associated with the project: the End User Group (EUG) consisting of members from the Nuclear Waste Management organisations and national regulatory bodies, and the Associate Group (AG). The Executive Committee of the project was made up of the CT, the Work package leaders and one representative of the EUG.

The five work packages were:

- WP1: Management, coordination, and dissemination
- WP2: Preparation and characterisation of samples and experimental systems
- WP3: Spent fuel dissolution experiments
- WP4: Model material dissolution experiments
- WP5: Chemical modelling

#### **1.3** The consortium

An overview of the consortium and their contributions to the project is provided in Table 1.

Short name	Role
SKB	WP1 Leader. Project Coordinator.
	WP5 Leader. Contributed to WP1 via the Coordination Team. In charge of all Communication and
	Knowledge Management activities of the project. For WP5 in charge of documenting the state-of-the-art and organizing the knowledge dissemination within the WP. Specific contribution concerning the development
A21	and implementation of the spent fuel matrix alteration model (MAM) in the reactive transport tool iCP.
LIGER	WP2 & WP4: Model material synthesis, method development and testing (WP2), and dissolution of
USFD	characterized materials (WP4).
	WP4: Dissolution of alpha-doped UO <sub>2</sub> (U-233, Pu-238) as well as dissolution of UO2 with and without
	additives (Cr, Cr+U-238). Dissolution experiments performed in presence of presence of corroding Fe in
VTT	model and natural groundwater

Table 1. 7	The DisCo	consortium
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	WP3 Leader. WP2 & WP3: For WP3 in charge of documenting the state-of-the-art and organizing the	
	knowledge dissemination within the WP. Sample preparation and characterization of MOX (WP2), and	
KIT-INE	dissolution of MOX under H <sub>2</sub> (WP3) in bicarbonate water.	
	WP2 & WP3: Synthesis and sample characterization of UO <sub>2</sub> doped with Cr. Cr/Al and Gd (WP2), dissolution	
CIEMAT	of prepared samples in young cementitious water and simplified model groundwater (WP4)	
	WP4 Leader. WP2 & WP4. For WP4 in charge of documenting the state-of-the-art and organizing the	
	knowledge dissemination within the WP. Cr-doped sample synthesis and characterization in close	
	collaboration with SCK·CEN (WP2). H2O2-promoted dissolution of non-doped and Cr -doped UO <sub>2</sub> in in	
JUELICH	degassed bicarbonate aqueous solutions.	
	WP2 Leader; WP2 & WP4: For WP2 in charge of overseeing preparation and characterisation of samples	
	before dissolution across the projectSynthesis and sample characterization of model MOX material (U,Th)	
	O2 (WP2). Dissolution of synthesized samples in bicarbonate water and synthetic Cox groundwater, using	
UCAM	hydrogen peroxide (WP4).	
Studsvik	WP3. Dissolution of Cr,Al-doped UO <sub>2</sub> fuel and standard UO <sub>2</sub> fuel under H <sub>2</sub>	
	WP3 Dissolution of High human LIO <sub>2</sub> fuel in oxic and reducing conditions (H2) using young cementitious	
	water, as well as experiments under H2 in bicarbonate water using samples from the same high-burnup. Work	
Eurecat	performed in close collaboration with JRC.	
	WP2 & WP4: Method development, synthesis and characterization of Cr-doped and alpha-doped samples in	
SCK CEN	close collaboration with JUELICH (WP2). Dissolution of non-doped, Cr-doped, alpha-doped and alpha-doped	
SCK-CEN	material with Cr m young cementitious water ad ofcarbonate water (wF4).	
	WP2 & WP4. Re-sintering and characterization of pre-existing (U, Pu)O <sub>2</sub> (WP2). Dissolution of (U,Pu)O <sub>2</sub> in	
CEA	synthetic COx water (WP4)	
	WP2 & WP5. Characterization using ceramography, gamma spectroscopy and electron microscopy of damaged	
	spent fuel stored >40 years in oxic water interaction in storage pool (WP2). Modelling of the interactions	
	between spent fuel-aqueous environment and container degradation products using a mixed-potential model of	
NNL	matrix dissolution based on previous work by Canadian and American national laboratories (WP5).	
	WP5 Assessment of the exagen potential of spent Cr deped fuel vie the development of a thermodynamic	
	model for uranium oxides with Cr2O3-UO2-U4O9 solid solution and with separate pure phases for fission	
	products. Pu and minor actinides. Modelling of chemical conditions inside the water-saturated canister under	
	repository-relevant conditions, taking into account all the materials involved and formation of secondary	
PSI	solids.	
WP5. Development of a reactive transport model describing dissolution of MOX in COx condition		
	presence of corroding Fe (in close collaboration with CEA). A former model was first extended, then the model was extrapolated to describe the long term dissolution of the homogonoous II. Du O, matrices in an	
Armines	underground spent-fuel disposal cell in France	
1 1111103		
WP2 & WP5: Preparation of samples from Cr-doped and MOX fuels (WP2), Dissolution of Cr-doped UO2		
JRC	fuel under H2, and MOX under anoxic atmosphere (WP3).	

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## 2 Background

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The existing knowledge base, up to the start of DisCo, has been achieved over decades of research, the results of which are briefly presented here.

## 2.1 Main factors influencing fuel dissolution

Most of the radionuclides are contained within the  $UO_2$ -matrix of the spent nuclear fuel pellets. Therefore the rate by which this matrix dissolves strongly impacts the release rate of radionuclide release from the spent nuclear fuel. Central to the study of matrix dissolution is the redox sensitivity of uranium, since the solubility of oxidized uranium, U(VI), is orders of magnitude higher than reduced uranium, U(IV). Since the repository environment will be reducing at the time of container failure, UO<sub>2</sub> is expected to be stable. However, due to the radiation emitted from the spent nuclear fuel, water radiolysis will influence the redox potential at the surface of UO<sub>2</sub>, where dissolution occurs. If the UO<sub>2</sub> is oxidized the rate of matrix dissolution is orders of magnitude higher than if the UO2 surface is kept reduced. An estimate of fractional dissolution rates in oxidizing environment is  $\sim 10^{-5}$  per year, while for reducing environments this rate is  $\sim 10^{-7}$ /year (SKB 2010). These very low rates have been found in experiments involving reducing agents such as hydrogen and iron under an anoxic atmosphere. If the uranium is kept reduced and dissolves very slowly, the results of experiments may still vary due to effects of sample characteristics - more precisely highenergy sites on the surface. These aspects of the matrix dissolution were further investigated in the REDUPP project (Evins et al 2014).

A fraction of the radionuclides in the spent nuclear fuel are expected to be released relatively rapidly. This is because this fraction has migrated out of the UO<sub>2</sub> matrix and is more accessible to water when the isolating contained fails in the repository. Due to the difficulty in determining exactly how this fraction is contained within the fuel (pellet-cladding gap, grain boundaries, some secondary phase) this fraction is modelled as being released instantaneously in the safety assessment models. Thus, the main question relating to this Instant Release Fraction (IRF) is the size of the fraction on how that fraction is affected by the fuel type and characteristics. These questions were the focus of the previous project First Nucldies (Kienzler and Lemmens 2015; Lemmens et al 2017).

## 2.2 Characteristics of spent nuclear fuel

## 2.2.1 Gap and grain boundary radionuclide inventory

The fraction of the radionuclides that are found in the gap between the fuel pellets and the cladding is called the gap inventory. The gap inventory is an important part of the so-called Instant Release Fraction (IRF) and it contains mainly the mobile radionuclides such as the Cs isotopes, I-129, Se-79 and Cl-36. Studies have been performed over the years to assess what

fraction of these radionuclides will be rapidly released once water enters the fuel canister in the repository. Lately the focus has been mainly on effects of higher burnups (e.g. Zwicky et al. 2011, Ekeroth et al. 2012). The results provide insight into three important aspects of how radionuclides are released from nuclear fuel upon water contact: 1) the gap inventory in spent fuel is slightly higher for high burnup fuels, but probably operating history and especially linear effect (W / cm) play a larger role than the actual burnup. The IRF for certain radionuclides, especially the I-129 and Cs isotopes, may be related to the measured or calculated fission gas release (FGR), 2) the content of fission products appears to affect the oxidative dissolution rate (slower when content is high), 3) sample preparation has an effect on the results of the experiments.

The relation between IRF and FGR in different fuel types was studied by Johnson et al (2012). This study supports the conclusions that IRF of I-129 and Cs isotopes may be related to fission gas release; for caesium, however, the IRF is slightly smaller than the fission gas release. The release of Se-79 was also studied, using a new method (Johnson et al. 2012). The results showed that less than 0.22 percent of the total Se inventory was leached. This was however based on the detection limit of the method. Johnson et al (2012) assessed that further studies were needed to determine the IRF of Se-79.

To expand the database regarding the IRF, the EU project FIRST-Nuclides (Fast / Instant Release of Safety Relevant Radionuclides from Spent Nuclear Fuel) was started in 2012. The project, which lasted for three years, examined the effect of operational history and burnup on the IRF of various radionuclides, including Se-79. Both BWR and PWR spent UO<sub>2</sub>-fuel samples, with a range of burnup from ~40 to ~65 MWd/KgU, were studied in FIRST-Nuclides; one sample was from a test rod of a PWR-MOX fuel with a burnup of ~63 (rod average; local ~73) MWd/kgHM (Lemmens et al 2017). Results from fuel leaching experiments performed in this project show that the IRF for Se-79 is small, only 0.5 to 0.8 percent of inventory. Small pieces of fuel were also examined by X-ray spectroscopy and together with thermodynamic calculations this indicates that Se-79 should be bound to the fuel matrix (Curti et al. 2015) rather than released into the gap or grain boundaries.

The fuel leaching experiments in FIRST-Nuclides, carried out in contact with air, showed that the release rate of both I and Cs decreased after a few months. Varying redox conditions were found to have an impact on the release of Sr, U and Tc (Kienzler and Lemmens 2015). An overall conclusion from the project is that linear power effect affects FGR, and thus the IRF, more than burnup. For fuels that had a high linear power (W/cm) in the reactor, the linear power could be correlated with the release of I and Cs (Lemmens et al. 2017). In addition, the results have provided insight into how fission gases are released during the course of the experiments (Kienzler et al. 2017).

#### 2.2.2 Fuel microstructure and non-oxidative dissolution

As described in the previous section, it is important to determine the IRF of the spent fuel. In the radionuclide transport calculations that are part of the safety assessment, the IRF is conceptualized as all fractions that are not contained within the fuel grains. This means there

is a connection to the fuel microstructure and thus certain characteristics of the fuel, such as grain size, grain boundaries, porosity, and crystallinity, may have an effect on the distribution of the radionuclides within the fuel.

In the REDUPP project (Evins et al 2014), carried out between 2011 and 2014, studies were focused on some aspects of the fluorite lattice, model for the  $UO_2$  crystal. The leaching experiments with CeO<sub>2</sub> and ThO<sub>2</sub> that were part of the REDUPP project show that the reactivity of the surfaces varies and that grain boundaries initially contribute to increased dissolution rate (Myllykylä et al. 2015, Corkhill et al. 2014). The results also point to a correlation between internal defects such as oxygen vacancies in ceria and dissolution rate (Corkhill et al. 2016).

A collaboration between the REDUPP project and the Delta-Min network (Mechanisms of mineral replacement reactions) yielded results that showed how crystallographic orientation of the mineral grains contained in a polycrystalline material affects the dissolution rate (Godinho et al. 2011, 2012, Corkhill et al. 2013). Combining these results with Ab Initio calculations, it could be shown that the stability of these surfaces depends on the surface structure (Maldonado et al. 2013), and that hydroxylation of the surfaces takes place for varying pressure and temperature, and this causes some modification of the structure of the surface (Maldonado et al. 2014).

## 2.3 Oxidative dissolution of spent nuclear fuel

Oxidative fuel dissolution (fuel corrosion) occurs in an oxidizing environment, that is, in water with dissolved oxygen or some other oxidant. In a common laboratory environment this oxygen comes from air. The repository environment is normally completely anoxic, but oxidative fuel dissolution can still be expected due to radiolysis. Radiolysis splits water in to both oxidants (hydrogen peroxide, and OH<sup>•</sup> and HO<sub>2</sub><sup>•</sup> radicals) and reductants (e<sup>-</sup>(aq), H<sup>•</sup> radicals and, after their recombination, H<sub>2</sub>) (Shoesmith 2000). Since the main long-lived reducing radiolysis product, H<sub>2</sub>, is volatile and more or less inert in absence of any catalyst at room temperature the overall effect of the radiolysis is that the uranium will be oxidized and be readily dissolved if there is carbonate or any other ligand to which U(VI) can complex (Ewing 2015).

Many experiments have been performed to investigate the oxidative dissolution of spent fuel and UO<sub>2</sub>, and the understanding of this process can be considered to be quite mature (Werme et al 1990, 2004, Eriksen et al 2008, Ewing 2015). However, as new developments take place, either regarding the operation of power plants or design of nuclear fuel, the experimental data base needs to be expanded and further research is needed to understand how these changes may or may not affect the processes involved in oxidative fuel dissolution.

The trend towards a higher burnup of the spent nuclear fuel means a higher content of fission products. The understanding of how oxidative dissolution of the fuel matrix is affected by the content of other metals (usually trivalent,  $M^{3+}$ ) has been significantly improved by the studies of Zwicky et al (2011), Trummer et al (2010), Pehrman et al. (2010), Nilsson and Jonsson

(2011) and Lousada (2013a). The results show that the content of trivalent elements affects to the amount of hydrogen peroxide (added to the system or produced radiolytically) that will be catalytically decomposed on the oxide surface instead of directly used to oxidize uranium. Trummer et al (2010) showed that an addition of yttrium in the UO<sub>2</sub> lattice increases the resistance to oxidation, which means that a larger part of hydrogen peroxide decomposes on the surface of the solid. Similar results are presented by Pehrman et al (2010) who showed that the ratio between dissolved uranyl species and spent hydrogen peroxide is much lower for UO<sub>2</sub> with additives.

In an experiment by Nilsson and Jonsson (2011), oxidative dissolution of Simfuel, i.e.  $UO_2$ , with a set of additives mimicking the content of fission products in spent fuel, was studied, and it was concluded that 99.8 % of the hydrogen peroxide was dissociated on the oxide surface. Only 0.2 % thus caused oxidation of uranium. A work focusing on the mechanism behind this observation, i.e. the difference between pure  $UO_2$  and  $UO_2$  material with additives (for example Simfuel), shows that it is mainly due to differences in redox reactivity (Lousada et al. 2013a). The catalytic decomposition of hydrogen peroxide that occurs at the surface has also been studied for different metal oxide surfaces (Lousada et al 2013b). The results show that in this process, OH radicals are formed at the oxide surface. Fidalgo and Jonsson (2019) also showed that the presence of gadolinium in  $UO_2$  reduces the redox reactivity of the solid when compared to pure  $UO_2$ .

These studies show that catalytic decomposition of hydrogen peroxide on the surface of spent fuel is an important process that reduces the rate of oxidative fuel dissolution in the final repository environment under certain circumstances, such as a radiation field dominated by alpha-radiation and low concentrations of halides and other radiolytic-active constituents in the groundwater. Therefore, the presence of additives, which appears to enhance the catalytic decomposition, has a "protective" effect of the fuel in front of oxidation. Fluctuations in groundwater composition and flow rates can affect the dissolution rate of spent fuel and the formation of uranium corrosion products within a failed canister (Ewing 2015). Studies have therefore been conducted to further study the surface-bound hydroxyl radicals formed during the decomposition of hydrogen peroxide. Methods to detect these surface-bound hydroxyl radicals are described by Yang and Jonsson (2014, 2015) and Maier et al (2019). The surface-bound hydroxyl radicals have been studied on both ZrO<sub>2</sub> and UO<sub>2</sub> (Fidalgo et al 2018). At considerable H<sub>2</sub>O<sub>2</sub> concentrations, elevated bromide concentrations increase both the rate of hydrogen peroxide consumption as well as the rate of uranium dissolution (El Jamal 2021).

It can be concluded that the redox reactivity of  $UO_2$ , which is central in reactions included in oxidative fuel dissolution, can be affected by additives in the material (Fidalgo and Jonsson 2019) and by the stoichiometry of the oxide (Razdan et al 2014, Kumagai et al. 2019). The studies that have been carried out show that additions of other metals, mainly trivalent, reduce the redox reactivity of the oxide, and therefore also reduce the oxidative dissolution rate.

#### 2.4 The hydrogen effect

In most concepts for final spent fuel repositories, large amounts of iron will be available. Corrosion of iron in the anoxic environment of the repository will generate divalent iron and hydrogen. Both of these have the potential to reduce the oxidants formed by radiolysis. However, molecular hydrogen is normally inert in absence of catalysts at room temperature (and also at the temperatures expected in the final repository), and iron present in solution would probably oxidize before it reaches the fuel surface, where most oxidants are formed. Despite this, fuel dissolution experiments performed with simplified groundwater simulates (diluted NaCl-NaHCO<sub>3</sub> solutions, NaCl brine or synthesized Young Cement Water type solutions) in autoclaves with a hydrogen atmosphere at room temperature have shown that the oxidation of the fuel surface decreases drastically and more or less stops after a few months (see, for example, Spahiu et al 2004, Carbol et al 2009), indicating an active effect of hydrogen in reducing or completely inhibit fuel surface oxidation, known as the "hydrogen effect". Many of the studies that have been conducted the last decade have aimed to scrutinise the hydrogen effect and also contribute to the understanding of the mechanism behind it.

One example of an experiment aimed at further our understanding of the hydrogen effect is described by Puranen et al (2017). The experiment was carried out in a steel autoclave, and iron powder as well as an iron coupon were added. Initially the atmosphere was inert (Ar), and no effect of the iron was seen. After a time when hydrogen had gradually built up in the system through anoxic corrosion of iron, the fuel dissolution decreased. After about 220 days, it seems the fuel dissolution had completely stopped, as indicated by no more release of caesium. To test the hypothesis that it is the hydrogen gas, and not Fe(II) in solution that is stopping the fuel dissolution, a new autoclave experiment was started with the same fuel but with magnetite instead of iron. Magnetite corrosion will produce Fe(II) in solution but not hydrogen. The results show that magnetite in the system does not stop the oxidative fuel solution (Puranen et al 2020). This clearly shows that, in this system, it is hydrogen and not iron in solution that is effective in suppressing oxidative fuel dissolution. Important observations in this type of experiment are how the concentration of non-redox sensitive mobile fission products, especially Cs-137, develops over time.

Studies performed to try to explain the observed hydrogen effect have shown that metallic particles, present in spent nuclear fuel, can act as catalysts for the electron transfer from hydrogen to the fuel matrix (Broczkowski et al 2007). That these metal particles can be effective catalysts for hydrogen oxidation was shown by Cui et al (2012), who studied metal particles separated from a spent fuel.

Another possible mechanism discussed by Trummer and Jonsson (2010), linked to catalytic decomposition of hydrogen peroxide and surface-bound hydroxyl radicals, is that the hydrogen gas can react with hydroxyl radicals at the oxide surface to form hydrogen atoms, which are highly reducing, and water. This mechanism is not dependent on the metallic particles. Bauhn et al (2018a, b) demonstrated the hydrogen effect in experiments with Simfuel and unirradiated MOX fuel. Since deuterium was used in the gas phase, the reactions could be monitored by isotope analysis. The results indicate that deuterium in the system has

reacted with surface-bound hydroxyl radicals. Thus, the hypothesis discussed by Trummer and Jonsson (2010) has been tested with positive results; even in a system with UO<sub>2</sub> without metal particles, the hydrogen gas reduces the oxidative effect of alpha radiation. However, it may be that the mechanism in this case is reliant on the presence of an alpha-emitting surface, i.e. the emission of the alpha particles from the surface may create reactive sites that enable the hydrogen effect. This potential effect, stemming from radiation effects in the solid near the interface, is further discussed by Pastina and LaVerne (2021). The exact mechanism is still under investigation.

Variations in spent fuel (eg radionuclide content, grain size, porosity, occurrence of secondary phases) may affect the reactions behind the hydrogen effect, as they relate to the redox reactivity of the oxide, fission product content and stoichiometry. Therefore, studies of the dissolution of fuel matrix under hydrogen are needed to study different types of fuel, for example fuels with higher or lower burnup, or fuels with different additives. Results from Puranen et al (2018) show that a Swedish PWR fuel with a burnup of about 65 MWd / kgU dissolves at the same slow rate as fuels with a lower burnup (Ekeroth et al 2020). After about a year of dissolution under hydrogen, the oxidative fuel dissolution appears to have stopped completely. This indicates that the dissolution behaviour of fuel matrix under hydrogen gas is the same for medium- and high burnup fuels.

In the DisCo project, presented in the current report, the focus of the spent fuel experiments was fuel with additives and MOX-fuels, to expand the data base and enhance the understanding of spent fuel dissolution under hydrogen atmosphere.

## 2.5 Dissolution of "old fuel"

Since the spent fuel is likely to be very old (around 100,000 years, in the Swedish case) before it eventually comes in contact with groundwater and begins to dissolve, it is relevant to study how fuel dissolution is affected by a very low alpha dose. This has been done by producing UO<sub>2</sub> with an appropriate amount of alpha-radiating nuclide added, either U-233 or Pu-238 (Ollila et al 2003, Carbol et al 2005, Muzeau et al 2009). Experiments carried out with these types of materials show that under a certain specific activity, no effect of the alpha radiation can be measured within the time frame of the experiments. This means that either there is a threshold below which the alpha radiation has no oxidizing effect, or the oxidation is so slow that it cannot be measured during the time the experiments were going on.

In the EU-project REDUPP, a test was performed with three different groundwaters with different salinity and three different  $UO_2$  samples with different contents of the alpha-emitting nuclide U-233. The first results, from experiments using the material with the highest alpha activity (10% U-233) and brackish water, indicated a slight influence of alpha radiolysis (Ollila et al. 2013). However, the results should be interpreted with some caution as these samples had a different history than the others, and a pre-oxidation of the sample may play a role. In the experiments performed for REDUPP, a higher solid to liquid ratio than in previous experiments was used (Ollila et al 2003). The final results, where an isotope exchange method was used to calculate a release of uranium from the surface of the sample, show some

variation between the three different groundwaters. However, even though all experiments indicated a slightly increased dissolution rate compared to previous experiments with synthetic groundwater, the estimated rate is still below  $10^{-6}$  per year (Evins et al. 2014). Further conclusions are that all experiments indicate that dissolution and precipitation (or sorption) occurred at the same time in the system (Evins et al. 2014).

In addition to studying synthetic samples with alpha-emitters, effects of very low alpha doses can also be elucidated by studies of natural uranium deposits. These uranium ores are usually very old, hundreds of millions or over one billion years, and have thus remained in place - and stayed more or less reduced – in spite of the unavoidable alpha radiolysis at the wet  $UO_2$  surface. With this issue as a focus, Bruno and Spahiu (2014) examined existing information about the ore in Cigar Lake. The uranium in this ore, which formed ca 1.3 billion years ago, occurs mainly in reduced form as uraninite, which indicates that the radiolytic oxidants have not caused any thorough oxidation. As an explanation, Bruno and Spahiu (2014) propose a recombination between radiolytically produced reductants and oxidants at the surface of the uraninite.

## 2.6 Fuels with additives

Fuels with additives, commonly called doped fuels, have been used since quite a while back; for example, Gd has been used as a burnable absorber since the mid 1960s (IAEA, 1995). However, relatively recently, fuels that contain an elevated amount of Cr, or Cr with Al have started to be produced and some used rods are available for study. Fuels produced today are likely to contain some Cr or other some other additive that improves fuel performance in the reactor. Considering the specifics of fuel oxidation, redox and catalytic reactions at the surface of the fuel, and the importance of determining the fate of hydrogen peroxide as an oxidant, it is clear that the effect of these additives on these processes, relevant for the back-end of the nuclear fuel cycle, need to evaluated.

A first evaluation has been performed in the FIRST-Nuclides project, which included leaching experiments with fuel that contains Cr and Al. These experiments were conducted in parallel with experiments with standard fuel (without additives). As expected, the results showed that the IRF for I and Cs was lower than the FGR for both types of fuel; the doped fuel showed a lower release of I and Cs than the standard fuel (Roth et al. 2013, 2014). However, other elements especially Mo and Tc, seemed to have a larger IRF than the standard fuel (Nilsson et al 2017). This was interpreted by Nilsson et al (2017) as a result of a slightly lower solubility for these substances in the Cr- and Al-doped fuel matrix.

The obvious need for further study of doped fuels was the driving force for the initiation of the DisCo project described here. Since FIRST-Nuclides provided some data for the gap inventory and IRF, the focus was turned on the fuel matrix dissolution.

### 2.7 Modelling the dissolution of spent nuclear fuel

The previous sections have focused on experiments and results that provide the data on which we must rely to build a model for the dissolution process. The development of such a model has required much effort in the past and it continues to be an important part of the process understanding. From 2005 to 2009, the EU project MICADO (Model Uncertainty for the Mechanism of Dissolution of Spent Fuel in Nuclear Waste Repository) brought together modellers to test various aspects of the models developed at that time. The results are summarized in the final report (Grambow et al, 2010) and in a scientific article (Grambow et al 2011). The models under study in the Micado project were:

- The "MAM" (Matrix Alteration Model; Martínez Esparza et al 2005). This model yielded results indicating a decrease of the dissolution rates with time, related to the dose rate decrease. It was also observed that different carbonate concentrations and/or pH of clay and granite type groundwaters produced different rates, where the matrix alteration appeared somewhat slower in clay media. This model was further developed by Duro et al (2009, 2013)
- The "Steady State" approach (Nielsen et al 2008), which considers water radiolysis, diffusion and heterogeneous kinetics at the spent fuel surface. Steady state refers here to a situation when the rate of production of the major oxidant, H<sub>2</sub>O<sub>2</sub>, is equal to the rate of consumption. The model also includes the hydrogen effect via catalytic interaction with the epsilon phases.
- The "Maksima-Traramo" model (Grambow 2008) which included coupling between radiolysis reactions and spent fuel dissolution. The coupling was based on electrochemistry, in a way that the dissolution reactions were assumed to occur on the anode and reduction of radiolysis products were considered as cathodic reactions. In this model the activation of hydrogen is included and the model appeared to explain the so-called "dose threshold".
- The French operational source term model (Poinssot et al 2005) in which, pessimistically, reducing species are neglected. In this simplified approach, only the primary radiolytic oxidants are considered. Not surprisingly this model over-predicts the alteration rate, but by limiting the effectiveness of the oxidants in the model, it appears to be able to predict the experimental yield of oxidized uranium in solution.
- A complete radiolytic model (Jegou et al 2007) taking the full radiolysis scheme, dose gradients and diffusion of species into account. This model is restricted to short-term calculations.

Some conclusions from the MICADO project were that some dispersion of the results originate not only from the uncertainties in fuel dissolution parameters but from the combination of these uncertainties with uncertainties related to properties in repository components that are included in radionuclide transport models. The suggested focus of future work, with regards to fuel dissolution, were: the hydrogen effect observed in alpha-doped materials, the effect of real groundwater compositions, the dose threshold, the effect of

surface area, increasing the database for MOX fuels, and finally, study close-to-equilibrium conditions.

## 3 Scientific Approach and Methods

## 3.1 Overall approach

In a deep geological repository, the environment will be reducing at the time of contact between water and the spent fuel (e.g. Puigdomenech et al, 2001). As described above, radiolysis implies that oxidants will be produced, but since most concepts involve anoxically corroding iron, the hydrogen produced may counteract these radiolytically produced oxidants at the fuel surface. The result is a very low oxidative dissolution rate, or indications that the concentration of uranium in solution is controlled by UO<sub>2</sub>(s) solubility (Carbol et al, 2009; Trummer and Jonsson 2010; 2008, Ollila, 2011). Therefore, to achieve the main objective of the project, the experiments aimed to collect data from anoxic and reducing conditions. However, to get a control of the effects of dopants on the oxidative dissolution, some experiments were also performed in oxic conditions, or in anoxic conditions with the controlled addition of an oxidant.

The types of fuel specifically studied in the project are MOX, regularly used since many years in some countries, and doped fuels (containing Cr or Cr and AlIn the last decade these fuel types have been increasingly used and they are now part of the solution for Accident Tolerant Fuels. Suitable irradiated doped fuels and MOX fuels were therefore available at the Hot cell facilities at the start of the project. start

The investigations carried out in this project are grouped as follows: 1) Dissolution experiments with spent nuclear fuel 2) Dissolution experiments with model materials 3) Chemical modelling. In addition, for all experiments, the systems are carefully described and where possible, mimic each other in specific ways. The aqueous solutions and solid materials were carefully prepared and characterised, in order to clearly describe the "initial state" of the experimental systems. After complete dissolution experiments, solid samples of the model materials were further analysed with various techniques. Thus, analyses before and after dissolution provide a direct link between the sample microstructure and dissolution behaviour. This is normally difficult to establish from spent fuel experiments alone.

For both types of dissolution experiments the preparatory phase is fundamentally important. For spent nuclear fuels, different sample preparation techniques may lead to systematic variations in the leaching data and even artefacts, such as surface oxidation of the sample, partial loss of Cs and I due to temperature-induced cutting of the fuel rod, and existence of fines remaining from the sample preparation procedure. In this project the aim was therefore to unify as far as possible spent fuel preparation techniques and to devise methods to control the effect of deviations in the procedures adopted by the different laboratories. For the synthesis of model materials, different techniques were used in the project to achieve a common goal. Analyses and characterisation along the synthesis procedure was utilised to optimize the sample production route. This also increased the scientific understanding of uranium oxide materials behaviour and laboratory practices in a more general way.

The spent fuel experiments focused on MOX and doped fuel in anoxic conditions with or without hydrogen overpressure. However, as a control and baseline, experiments were also performed using standard spent UO<sub>2</sub> fuel in oxic and anoxic conditions. The model materials were, with a couple of exceptions, synthesized specifically for the experiments in this project. The approach of using model materials is to work systematically with materials were the effects of individual parameters may be investigated. Thus, the different model materials studied in this project represent a systematic step-by-step move from pure UO<sub>2</sub>, to UO<sub>2</sub> with one or two additives, and finally to more complex systems doped with alpha-emitting nuclides. This enables interpretation of the effect of individual parameters. The experiments with spent nuclear fuel and model materials are in this way complementary. Finally, to complete the picture of the source term, chemical models, incorporating both solid state thermodynamics and waste form dissolution in the near field environment, were developed for the project. The focus was application of site-specific conditions, considering national differences in repository concepts, using carefully selected thermodynamic and kinetic data. In modelling conceptualisation always precedes quantification, and a close interaction between the modellers and experimentalists is needed in order to describe the modelled system as accurately as possible.

The experiments were planned for comparable conditions and/or in conditions comparable to those already existing in the literature, see Table 2. In general, 28 different systems were investigated: 12 different types of solids analysed in 4 different water types, in conditions that were either oxidizing or reducing. The four main water types used in the experiments were: Bicarbonate water (BC/BIC), Young Cement Water with Ca (YCWCa), Synthetic Callovo-Oxfordian watwer (COx) and natural ground water. WP3 (Spent fuel dissolution experiments) involved studies of 7 different systems, while for WP4 (Model material dissolution experiments) the number of systems were 21. Some systems are studied in two or more laboratories, allowing for interlaboratory comparisons. This extensive experimental program allows for comparisons between systems with and without particular parameters, and for comparisons between model materials and spent nuclear fuel. Ensuring coordination among the different experimental groups have yielded comparable data, usable for the modellers. For example, remaining uncertainties regarding the hydrogen effect and the involvement of the epsilon-particles versus the oxide surface was addressed by investigating model materials without noble metal particles but in hydrogen atmosphere, mimicking the spent fuel experiments.

Reducing (H2, Ar/N2/H2 mix, or anoxic with corroding Fe)						
Water type (reductant):	Bicarbonate Water	Young Cement	Natural Groundwater	Synth. Callovo-		
	(112)	water with ca (Hz)	(FC)			
U02	V	V	V			
UO2 w Gd	V	V				
UO2 w Cr	V	V	V			
UO2 w Cr+Al	V	V				
UO2 w 238Pu/233U	V	V	V			
UO2+Cr w 238 Pu	V	V	V			
(Pu,U)O2				V		
UO2 spent fuel	V	V				
UO2 spent fuel w Cr+Al	V					
UO2 spent fuel w Cr	V					
MOX spent fuel	V					
Oxidizing/Anoxic(Ar), H2O2,	or Air					
UO2	V					
UO2 w Cr	V					
(U,Th)O2	v			V		
UO2 spent fuel, Air		V				
MOX spent fuel, Ar	V					

#### Table 2. The experimental matrix

## 3.2 Methods

#### 3.2.1 Characterisation of solid samples

Solids have been analysed during sample preparation and pre-test characterisation for defining the initial state, and as a part of the post-mortem analyses.

For spent nuclear fuel, all sample preparation is performed in Hot Cells. Pieces of fuel rods to analyse are selected based on gamma scanning results from which local burnup is determined. To remove the pieces, normally a saw is used. For the analyses, either the full piece with cladding still attached is used, or the fuel is detached from the cladding. In this process normally the fuel is fragmented, and fragments are selected for further analyses. For this project, sample preparation of fuel has been done in three different facilities: JRC, KIT and NNL. The samples analysed at Studsvik (fuel fragments) were already available and characterised in a previous project (FIRST-Nuclides; Roth et al 2016).

Most model materials used in this project were synthesized specifically for the project. Some were however already available:

\*Un-irradiated (U,Pu)O<sub>2</sub> used by CEA, described by Talip et al (2017) . These samples were annealed to remove defects from the radiation damage, and were then characterized with Raman spectroscopy to ensure an acceptable initial state for the dissolution experiments.

\*UO<sub>2</sub> samples doped with varying amount of U-233 used by VTT, described by Ollila et al (2013). These samples had some pre-oxidized uranium and potentially some salt that had to be removed via pre-leaching (twice) with bicarbonate solution before start of the dissolution experiments.

The rest of the materials were produced using different protocols, further described in section 4.1, in order to achieve a desired microstructure and chemical composition. To characterize the materials a selection of the following analytical techniques were used:

- Archimides density measurements
- He pycnometry for density determination
- BET (Brunauer–Emmett–Teller) for surface area measurements
- Optical microscopy for microstructural analyses
- SEM (Scanning Electron Microscopy) with EDS (Energy Dispersive Spectra) and EBSD (Electron Back Scatter Diffraction),
- EPMA (Electron Probe Microanalyser) with WDS (Wavelength Dispersive X-ray Spectroscopy)
- XRD (X-Ray Diffraction)
- Raman spectroscopy,
- XAFS (X-ray Absorption Fine Structure spectroscopy

#### 3.2.2 Analyses of aqueous solutions and gases

In WP 3 and WP4, aliquots of the aqueous solutions were samples at various times during the experiments. Apart from Eh- and pH measurements of the systems, chemical and isotopic analyses of the sampled solutions were performed using a few analytical techniques:

- ICP-MS (Inductively Coupled Plasma Mass Spectrometry). This is the most commonly used techniques for determination of radionuclide concentrations. There are some varieties of this method used by the partners.
- LSC (Liquid Scintillation Counting)
- Gamma-spectroscopy
- UV-Vis (Ultra-Violet Visible Spectroscopy), for H<sub>2</sub>O<sub>2</sub> measurements
- Laser-Induced Kinetic Phosphorescence Analyser
- Luminometry
- Alpha spectrometry

In addition gases were sampled from some systems and analysed using:

• Gas Mass Spectrometry

In most cases either centrifugation or successive filtration and /ultrafiltration were used to remove and, thus, assess the contribution of colloids. In most cases the centrifugation/filtration equipment for fuel leachates is in the air atmosphere of the hot cell, hence potential oxidation of the sampled leachates should be considered. For the ICP-MS analyses, the samples were acidified for preservation, however for iodine analyses a separate

aliquot was sampled and preserved with 0.5% TMAH (Tetramethylammonium hydroxide) at Studsvik, whereas at KIT iodine was analysed radiochemically. Samples were analysed generally in duplicates and exemplary samples were analysed as triplicates.

### 3.2.3 Modelling approaches and tools

The project aims with regards to chemical modelling were to develop and apply thermodynamic and kinetic models as well as reactive transport models to provide the basis for understanding the behaviour of spent nuclear fuel in the presence of components of the near field.

The work naturally progressed from model development using already existing data, to incorporation of new data based of project results, later in the project. The following tasks were identified early on in the project:

- Task 1: Solid phase thermodynamics
- Task 2: Matrix dissolution model
- Task 3: MOX-matrix dissolution model

Task 1 focused on the effect of dopants in the dry matrix in terms of oxygen potential and the formation of secondary solids during aqueous corrosion inside an iron-based canister. For this the database HERACLES-TDB, integrated in the in-house chemical code GEM-Selektor (http://gems.web.psi.ch/) (Kulik et al.,2013) was used by PSI.

Matrix dissolution model development, performed within Task 2, incorporated redox and electron transfer reactions involving matrix, separate phases (e.g. metallic fission products), radiolysis and hydrogen in the system. The models used need to describe a range of processes such as oxidative and chemical dissolution, diffusion, reaction, radiolysis, precipitation on the fuel surface, as well as the presence of small noble metal particles on the fuel surface. Two different modelling approaches were used:

1) Radiolytical, chemical and reactive transport modelling involving thermodynamics and kinetics (by A21), using the iCP tool (interface coupling COMSOL Multiphysics and PhreeqC )

2) Electrochemical mixed-potential modelling (by NNL)

Task 3, MOX-matrix dissolution model, investigated the effect of Pu content on the alpharadiolytic dissolution kinetics of the matrix as well as the interplay with Fe(II) species released from iron-based canister in clayey groundwater under anoxic conditions. This task also involved chemical and reactive transport modelling but using the CHESS and HYTEC code (by Armines).

Within these different modelling tasks experimental data were used, when applicable, for model calibration and parametrization. Conversely, modelling is also used to check observations (e.g. formation of corrosion products in experiments) by independent thermodynamic modelling.

## 4 Results

# 4.1 Preparation and characterisation of samples and experimental systems (WP2)

There were two main aims of this work package: 1) delivery of solid samples, either via synthesis (model materials) or via preparation in hot cells (spent fuels) and 2) characterization of the initial state of the experimental systems. Obviously aim 1 is fundamental for the project and thus the achievement of this aim was considered a milestone. The samples delivered by WP2 are listed in Table 3 and 4. Characterization of the initial state of the experimental systems is important for modelling (WP5) and for interpretation of the data produced in WP3 and WP4. Details regarding the samples and experimental systems are given by Farnan et al (2021). Here, a brief summary of the sample characterization results is provided. Some of this work required method and synthesis development to produce the model systems and to provide a well-characterized experimental systems, much effort was devoted to optimization or procedures and some examples of method development connected to WP2 are given in section 4.1.1.

Partner	Fuel type (incl BU & FGR)	Samples analysed	Methods used for characterization	
KIT	MOX BU 38 (RA), PWR, FGR 6%	1 cladded segment (KWU11.38-5810) 2 as fragments (KWU11.38- 5810)	Optical microscopy	
JRC	AOX, BU 48 (L) & 56 (L) (54 RA BU),         3 cladded segments           VWR, FGR 2.5%         (MOX-H)		Optical microscopy	
JRC	Cr-UOX, BU 58 (RA), PWR, FGR not given	1 cladded segment 2 as fragments (decladded )	Optical microscopy	
Eurecat	UOX, BU 73 (L), PWR, FGR, 13.6%	4 cladded segments (73BIC/73YCWCa)	Optical microscopy, See Iglesias et al 2018	
Studsvik	UOX, BU 57 (RA), BWR, FGR 2.5%	1 as fragments (5A2)	Optical microscopy, See Roth et al 2016	
Studsvik	Cr/Al-UOX, BU 59 (RA), BWR, FGR 1.4%	1 as fragments (C1)	Optical microscopy See Roth et al 2016	
NNL	UOX BU 21.2, AGR	Solid pellet, segment	Optical microscopy.	
NNL	UOX BU 7.3, AGR	Hollow pellet, segment	Optical microscopy	

**Table 3.** Spent fuel samples. BU = Burn Up (MWd/kgHM). RA= Rod average L= Local. FGR = Fission GasRelease

Partner Materials		Sample characteristics	Methods used for characterization	
USFD	$UO_{2},$ $UO_{2} + AI$ $UO_{2} w Cr$ $UO_{2} w AI + Cr$ $UO_{2}$ $UO_{2} w Cr$	Wet and dry route pressed pellets, 0 to 150 ppm Al 5, 8 μm grainsize 0 to 2400 ppm Cr grain size 300 ppm, 5-8 μm grain size HIPed pellets 0 and 1200 ppm Cr grain sizes both 3 - 4 μm	Archimedes, SEM, Raman, EMPA, XAS	
VTT	UO2 w U-233 (5%, 10%) UO2 w Pu-238, UO2 w Cr+Pu-238 (supplied by SCK)	Pellet fragments, 1-3g ~ 6 mm pellet, 14 μm grainsize ~6 mm dia pellet, 34 μm grainsize	See Evins et al 2014 SEM, optical (by SCK CEN) SEM, optical (by SCK CEN)	
Ciemat	UO2 UO2 w Cr UO2 w Al UO2 w Cr+Al UO2 w Gd	Dry route pressed pellets 0.06wt%Cr 0.02wt%Al, 0.06wt%Al pellets 0.05 wt% - 0.02 wt% pellets 4,5wt% pellet	Optical, XRD, Raman, SEM, Archimedes	
FZJ	UO2 UO2 w Cr	Pressed pellet	XRD, SEM with EBSD and EDX, (TOF SIMS with EMPA standard?)	
UCAM	(U, Th)O2 38% Th 40%Th	~5 mm pressed pellets Homogeneous grain size 2 µm Inhomogeneous grain size 1 µm	XRD, SEM, EDX, Archimedes	
SCK CEN	UO2, UO2 w Cr, UO2 w Pu-238, UO2 w Cr+Pu-238	~6 mm dia pellets, 10μm grain size, ~6 mm dia pellet, 15 μm grain size ~ 6 mm pellet, 26 μm grain size	SEM, Optical, Archimedes	
CEA	(U,Pu)O2 MOx (22% Pu-238) 27%Pu 7%Pu	Annealed and pressed pellets, Homogeneous Inhomogeneous	Raman, Archimedes, XRD	

To identify the separate effects of variables such as microstructure, doping level, and surface area, samples were prepared and variables determined via different methods, see Table 4. The amount and type of chromate additions (100-2400 ppm) and sintering times were varied to establish a method to produce Cr-doped UO<sub>2</sub> fuels with a targeted grain-size (Cordara et al 2020 . The variation in Cr content allowed the investigation of effect of Cr on microstructure

such as grain-size (Maier et al 2020). In addition to reference UO<sub>2</sub> and Cr-doped UO<sub>2</sub>, Ciemat produced pellets with Cr and Al combined, as well as Gd-doped pellets. To remove impurities and increase crystallinity some pellets were produced using methods based on PUREX involving dissolution of solid UO<sub>2</sub> in nitric acid (Milena-Perez et al 2021). Kegler et al (submitted, in review) also describes a wet chemical route for the synthesis of Cr-doped UO<sub>2</sub> that was developed and performed in JUELICH. Characterization of the reference materials, performed using SEM, allowed imaging of grain size, crystallographic orientations (via EBSD), and evolution of the surface as a result of dissolution.

The optimization of the synthesis procedure developed by FZJ in collaboration with SCK•CEN allowed UO<sub>2</sub> and Cr-doped UO<sub>2</sub> samples to be prepared in plutonium gloveboxes at SCK•CEN. The resulting samples were doped with ca 30 ppm  $^{238}$ Pu to provide equivalent alpha-activity of ~18 MBq/g UO<sub>2</sub>, to mimic the radiation field of a 10,000 year-old spent fuel (Chachoir et al. 2021).

The homogeneous (U, Pu)O<sub>2</sub> used by CEA had a Pu content of 27  $\pm$  0.5%, confirmed by the calibrated Raman shift of the principal mode of the fluorite structure. This Pu-content corresponds to a  $\alpha$ -activity of 2.2 x  $10^9$  Bq/g, comparable to a MOX fuel with a burn-up of 47.5 MWd/kgHM and removed from the reactor 1985. The  $\alpha$  dose rate of this sample is 5 to 6 orders of magnitude higher than the  $\beta/\gamma$  dose rates (Kerleguer et al 2020. These samples were annealed to remove radiation damage before the dissolution tests. The sample were characterized with XRD, Raman and SEM.

Samples of inhomogeneous (U,Th)O<sub>2</sub> pellets with a nominal Th content of 38-40 wt.% have been prepared and analysed by SEM, electron back-scatter diffraction and X-ray diffraction. High homogeneity (U,Th)O<sub>2</sub> samples were created by extended high temperature annealing in 5%  $H_2/N_2$ .

Failed fuels recovered from a storage pond at Sellafield were investigated by gamma spectroscopy and optical microscopy. The aim was to investigate what alteration had occurred and if any secondary phases could be found. The micrographs (see examples in Fig. 1) indicate that microstructurally there is very small difference between the wetted and non-wetted ends of the fuel samples. The optical microscopy investigation did not show any sign of higher oxides or corrosion products within the fuel, nor any secondary precipitates on the surface (O'Neill et al 2019). As is discussed by Hughes et al (2021), the stainless steel cans in which these fuel samples were stored were corroded an had produced some iron containing sludge. The conditions (Eh, pH) inside the containers were strongly influenced by the iron corrosion, which would consume available oxygen that is slow to be replenished due to the quite static conditions inside the can. The modelling of the fuel corrosion inside these failed cans is further discussed in section 4.4.3.



**Figure 1**. Micrographs of the failed fuel from the pond in Sellafield. A) Non-wetted end of sample IE 424/4 B) Wetted end of sample IE 424/4 . From O'Neill et al (2019).

#### 4.1.1 Notable results in method development

The production of Pu-doped UO<sub>2</sub> with Cr as an additive required substantial efforts and collaboration between FZJ and SCK CEN. The work proceeded in stages to first optimize the production of UO<sub>2</sub> (Maier et al 2020) and Cr-doped UO<sub>2</sub> (Kegler et al 2019, 2020) during which two methods were explored: co-precipitation and wet-coating. It was found that co-precipitation had little effect on grain size, while wet-coating increases the density and grain size of the material, compared to the undoped material. An evaluation was performed regarding the influence of oxygen potential and Cr-doping level on the microstructure of pure and Cr-doped UO<sub>2</sub> pellets, in order to reach the desired result (Kegler et al, 2021). The optimized method is described by Chachoir et al (2021) in which first homogeneous  $\alpha$ -doping was obtained by co-dissolving depleted UO<sub>2</sub> and UO<sub>2</sub> powder doped with <sup>238</sup>Pu /233U achieving a specific activity of ca 18 MBq/g UO<sub>2</sub>. In a second step, the solution thus formed was precipitated as ammonium diuranate (ADU). The reduced solid was mixed with Cr powder and a lubricant. The final pellets were then formed and sintered at a set time in controlled atmosphere to reach the desired oxygen potential.

Methods based on PUREX were used to dissolve existing UO<sub>2</sub> ceramics in nitric acid to remove impurities and increase the crystallinity of the final sintered material (Rodríguez-Villagra et al 2020).

As a part of this project, Cordara et al (2020) developed a method for synthesizing  $UO_2$  pellets involving Hot Isostatic Pressing (HIP). Powders were placed in containers specialized for the HIP procedure, and vacuum-pumped at 300 °C, after which the container was crimped and welded. For this work, a special chamber for the furnace (Active Furnace Isolation Chamber) was designed and commissioned for radioactive materials at the University of Sheffield. This contained a double-filter seal containments system required to mitigate the risk for release of alpha-activity. The HIP process involved applying controlled heat and pressure for required amount of time to produce a dense sample with desired properties. The resulting Cr-doped  $UO_2$  were promising with high density, but there was no increased grain

size and Cr-content of the grains were less than the target concentration. Thus, the HIP synthesis was abandoned for the production of the pellets used in this project, but the method was successfully developed and will be available for other projects and investigations involving radioactive materials.

## 4.2 Spent fuel dissolution experiments (WP3)

Experiments under anoxic to strongly reducing conditions have been performed with irradiated standard UO<sub>x</sub> fuel, MOX fuels and UO<sub>x</sub> fuels doped with Cr+Al: Two doped BWR UO<sub>x</sub> fuels reached burnups of 57 and 59 MWd·(kg <sub>HM</sub>)<sup>-1</sup>; two PWR MOX fuels reached burnups of 38 and 54 MWd·(kg <sub>HM</sub>)<sup>-1</sup> (average burnups); one standard PWR UO<sub>x</sub> fuel reached a local burn-up of 73 MWd/kg<sub>HM</sub>. In these autoclave experiments, fragments and cladded segments of these irradiated fuel samples were exposed to diluted NaCl solution with 1 to 10 mM NaHCO<sub>3</sub> (pH ~ 8, denoted as NaCl-BIC). In two experiments, a standard PWR UO<sub>x</sub> fuel was exposed to so-called "Young Cement Water with Calcium" (denoted as YCWCa), which is a hyper-alkaline diluted NaOH, Ca(OH)<sub>2</sub> solution, containing 77 mM Na<sub>2</sub>CO<sub>3</sub> and other minor constituents. Two dissolution experiments with standard PWR UO<sub>x</sub> fuel had been conducted under oxic conditions in NaCl-BIC type solution and in YCWCa solution. All available data at the end of the project is collected in D3.3 (Metz 2021). An overview of fuel sample names and experimental conditions is given in Table 5 (see also section 4.1). Current results from the DisCo project are compared with earlier results published in the open literature (Carbol et al 2009, Kienzler et al 2016).

Sample name	Fuel type & rod average burnup	Sample type	Water type	Atmosphere	Days	Data Source
	(MWd/tHM)	, pc	, pc			
MOX-H seg	MOX, 54	Segment	BIC	Argon	623	DisCo D3.3
MOX-L seg	MOX, 54	Segment	BIC	Argon	348	DisCo D3.3
MOX-KWU-seg	MOX, 38	Segment	BIC	Hydrogen +Argon	988	DisCo D3.3
MOX-KWU-frag	MOX, 38	Fragments	BIC	Hydrogen +Argon	950	DisCo D3.3
MOX JRC-KA frag*	MOX, 50	Fragments	BIC	Hydrogen	2078	Carbol et al (2009)
UOX-C1 frag	Cr+Al doped UOX, 57	Fragments	BIC	Hydrogen	1001	DisCo D3.3
UOX-5A2 frag	UOX, 59	Fragments	BIC	Hydrogen	1001	DisCo D3.3
UOX-FIRST-Nuc seg*	UOX, 50	Segment	BIC	Hydrogen +Argon	~400	Kienzler et al (2016)
UOX FIRST Nuc frag*	UOX, 50	Fragments	BIC	Hydrogen +Argon	~500	Kienzler et al (2016)

Table 5 Samples of spent nuclear fuel plotted in the Figures 2-6. For more detail see section 4.1 and DisC	0
deliverable D3.3 (Metz et al 2021).	

UOX H2 YCWCa	UOX, 60	Segment	YCWCa	Hydrogen +Argon	172	DisCo D3.3
seg						
UOX H2 BIC seg	UOX, 60	Segment	BIC	Hydrogen +Argon	144	DisCo D3.3
UOX 73BIC seg**	UOX, 60	Segment	BIC	Air	210	DisCo D3.3
UOX 73YCWCa	UOX, 60	Segment	YCWCa	Air	457	DisCo D3.3
seg						

\* NOT DisCo, included for comparison. \*\*Experiment performed before DisCo

The available data set together with published data on dissolution of spent nuclear fuel under reducing conditions allows comparisons of various kinds, based on results of long-term experiments running for more than one year up to 5.7 years:

**Radionuclide release data of spent MOX fuel dissolution versus spent UO<sub>x</sub> fuel (nondoped) dissolution under hydrogen overpressure.** Dissolution experiments with cladded segments and fragments of irradiated MOX fuel and of irradiated  $UO_x$  fuel have been conducted in the DISCO and FIRST-Nuclides projects using similar experimental set-ups (see Table 5). A very long-term experiment with irradiated MOX fuel by Carbol et al (2009) is also considered in the comparison.

Radionuclide release data of dissolution of non-doped spent UO<sub>x</sub> fuel versus dissolution of Al+Cr doped spent UO<sub>x</sub> fuel under hydrogen overpressure. Results of dissolution experiments with fragments of Al+Cr doped spent UO<sub>x</sub> fuel, conducted in the DISCO project are compared to data of dissolution experiments with irradiated non-doped UO<sub>x</sub> fuel conducted in the DisCo and FIRST-Nuclides projects.

Radionuclide release data of spent UO<sub>x</sub> fuel dissolution under hydrogen overpressure versus spent UO<sub>x</sub> fuel dissolution under oxic conditions. Dissolution experiments with UO<sub>x</sub> fuel in BIC solution under oxic conditions, performed before the start of the DisCo project, are compared to dissolution experiments with various irradiated fuels (non-doped UO<sub>x</sub> fuel, MOX fuel, fuel doped with Al+Cr) under hydrogen overpressure, which had been conducted in the DISCO and FIRST-Nuclides project. In addition, experiments of irradiated UOx fuel in cementitious water have been performed in the DisCo project, both in oxic conditions and under  $H_2$ .

Additionally, the data set produced in this project also allows comparisons of IRF in different conditions:

**Radionuclide release from the rapidly released fraction under different conditions.** The so-called instant release fraction is expected to be released during the first year of dissolution, meaning that also short term experiments are of value for this comparison. Although the main focus of the project is long-term matrix dissolution, with these data we are able to compare release from UOx fuels in aerated conditions vs hydrogen overpressure, as well as release in BIC solution vs YCWCa aqueous solutions.

#### 4.2.1 Overview of results in WP3

This overview of results follows the presentation by Metz (2021), focusing on five different elements: U, Pu, Am, Sr and Cs. These represent actinides and fission products with different chemical characteristics and therefore release behaviour.

Based on release behaviour of uranium (Fig. 2), plutonium (Fig. 3), americium (Fig. 4) and other minor actinides it is clear that all experiments are characterized by a considerable scatter in measured concentrations of these radioelements within the first year. In some experiments, release data of some fission products show less pronounced fluctuations in the initial stage of the experiments. Such a scatter of radionuclide release data and a significant decrease of uranium concentrations in an initial stage is a common observation in spent nuclear fuel dissolution experiments under disposal conditions (reducing conditions, near neutral pH to (weakly) alkaline conditions). Often, the initial scatter of uranium concentration and concentrations of other matrix bound elements is related to dissolution of pre-oxidized layers of the used spent nuclear fuel samples. Thus, it is concluded to focus on results of long-term dissolution experiments, running for at least one year.

In the studied dissolution experiments under hydrogen overpressure, aqueous uranium concentrations tend to approach a steady state level after one year (Fig. 2): uranium concentration are progressing to approach to a so-called "concentration plateau" between 1 to  $5 \cdot 10^{-8}$  mol/L in the long run. Uranium concentration are more than two orders of magnitude higher in the experiments under oxic conditions (Fig 2). Clearly, the hydrogen overpressure inhibits the U release. However, since the uranium "concentration plateau" is distinctly above the solubility of UO<sub>2</sub>(am, hyd) (defined by the reaction UO<sub>2</sub>(am, hyd) + 2H<sub>2</sub>O (l)  $\leftrightarrow$  U(OH)<sub>4</sub>(aq)). After one year of dissolution, the U release rate is very slow, and close to zero for a few experiments. Since it cannot be concluded that the rate is zero and, combined with the concentration levels that are above the solubility for U(IV), it appears that for these experiments the dissolution of the UO<sub>2</sub> matrix continues even under hydrogen overpressure. However, the dissolution rate slows down with time, indicating that is approaching zero.

Notable is also that the effect of hydrogen appears to be stronger than any effect of leachant composition. Comparison of short-term experiments (less than one year) performed with the high pH YCWCa solution vs experiments with BIC solution indicates that the inhibition of uranium release by hydrogen also in experiments with YCWCa.



MOX-JRC-KA frag. under hydrogen overpressure



As shown in Fig. 3 and Fig. 4, aqueous concentrations of plutonium and americium (as well as for other minor actinides) are, for experiments performed with hydrogen, relatively low, i.e. below  $1 \cdot 10^{-8}$  mol/L, at the initial stages of the experiments. For the Studsvik experiments with standard UOx ("UOx-5A2 frag.") and Al+Cr doped UO<sub>x</sub> fuels ("UOx-C1 frag."), Pu and Am release continues during the experiments to reach comparatively high concentrations. For all other experiments under H<sub>2</sub>, long-term release data indicate that aqueous concentrations tend towards concentration plateaus at levels of Pu(OH)<sub>4</sub>(am) and Am(OH)<sub>3</sub>(am) solubility levels (log [Pu]<sub>tot</sub> =  $-(9 \pm 1)$  and log [Am]<sub>tot</sub> =  $-(9 \pm 1)$ , respectively). Whereas the relatively high Pu concentration in the experiments under higher Eh conditions is explained by formation of soluble Pu(V) species, the continuous increase in Am and Pu concentrations in the Studsvik experiments with standard UOx and Al+Cr doped UO<sub>x</sub> fuels is related to particular sample characteristics and a potential colloid formation in the experimental set-up. This hypothesis was tested via ultrafiltration for the final samples (at 1001 days), which resulted in lower Pu and Am concentrations. Thus, the presence of colloids or small particles could be confirmed.

In all experiments, the temporal evolution of concentrations of fission products differs significantly from the respective evolution of the actinides concentrations. For an overview on the release patterns of the fission products, cesium and strontium are selected (see Fig. 5 and Fig. 6).



Figure 3. Concentration of plutonium released into solution versus time in long-term dissolution experiments with irradiated  $UO_x$  and MOX fuels (From Metz 2021).



**Figure 4**. Concentration of americium released into solution versus time in long-term dissolution experiments with irradiated  $UO_x$  and MOX fuels (From Metz 2021).

Aqueous concentrations of cesium increase throughout all dissolution experiments until ca 400 days and display fast release rates in the initial stage; a slowdown of the release rate is observed in the long term of the experiments under reducing conditions. Cesium concentrations measured in experiments "MOX-KWU seg" and "MOX-KWU frag" show a steady increase up to 721 and 988 days, respectively, whereas Cs concentrations in experiments "UOx-5A2 frag" and "UOx-C1 frag" after 421 and 642 days are at the same level. In the longest dissolution experiment under hydrogen overpressure ("MOX JRC KA frag"), a steady increase in Cs concentration is observed until ca 700 days. Then the Cs concentration reaches a plateau which lasts until ca 1500 days. The Cs data in the final part of the experiment is scattered, due to experimental problems and air intrusion in the autoclave, as explained by Carbol et al (2009).

The release pattern looks a bit different for Sr, where the concentration continues to increase for the duration of the experiments, though the release rate slows down in the long run. Both aqueous concentrations and release rates of Cs are significantly higher than those values of Sr. The relatively fast Cs release is related to the so-called "instant release fraction" of cesium. This may not be true for the samples UOx-5A2 and UOx-C1 since these samples apparently were strongly affected by aerated conditions, and probably the released Cs then originates from a pre-oxidized phase. Towards the end of some experiments (UOx-5A2 frag., UOx-C1 frag. and MOX-KWU seg., Fig. 5 and Fig. 6) the release of both Sr and Cs data appear to be close to zero. The relatively slow Sr release in the long-term is related to release of strontium of the UO<sub>2</sub> matrix of the spent nuclear fuel samples. In agreement with the long-term uranium release data, the continued (slow) release of the two fission products after two years of exposure of the spent nuclear fuel samples to the aqueous solutions indicates that dissolution of the UO<sub>2</sub> matrix continues slowly even under strongly reducing conditions. This result may be related to various aspects of sample characteristics or experimental set-ups, and illustrates the need for data from very long-term experiments.



Figure 5. Concentration of cesium released into solution versus time in long-term dissolution experiments with irradiated  $UO_x$  and MOX fuels (From Metz 2021).



Figure 6. Concentration of strontium released into solution versus time in long-term dissolution experiments with irradiated  $UO_x$  and MOX fuels (From Metz 2021).

#### 4.2.2 Observations related to fuel type, chemical conditions and sample characteristics

Based on the release patterns of uranium, cesium and strontium it is concluded that Al+Cr dopants in the UO<sub>x</sub> fuel do not significantly change the release of uranium and the two major fission products under reducing conditions. In particular the Cs release in the experiments with fragments of Al+Cr doped UO<sub>x</sub> fuels (conducted in the DISCO project) and in the experiment with fragments of a non-doped UO<sub>x</sub> fuel (conducted in the DisCo and the FIRST-Nuclide projects) are quite similar.

There are no indications of a significant difference in the dissolution behaviour between MOX fuel and non-doped  $UO_x$  fuel under strongly reducing conditions in NaCl-BIC solution. Release of cesium, strontium, I-129 (not shown here) and uranium are similar in the experiments with MOX and and non-doped  $UO_x$  fuels.

The chemical conditions affect the results most. We know from many previous studied (eg Werme et al 2004) that spent nuclear fuel when in contact with air-saturated water will dissolve more rapidly due to oxidation of uranium. In agreement with published studies, the results from the two air-saturated experiments presented here demonstrate relatively high aqueous concentrations and release rates of uranium, americium, cesium, strontium and plutonium (except Pu and Am in experiment UOx-73YCWCa). Although the data set from experiments using YCWCa is limited, the indications are that this water composition lowers the concentrations of some radionuclides (Sr, U, Pu, Am) significantly. As expected, however, the Cs concentration does not appear to be much affected by leachant composition.

The character of the solid sample is another important parameter to consider. For the irradiated MOX fuel (studied in the DISCO project) and the non-doped UO<sub>x</sub> fuel (studied in the DisCo and FIRST-Nuclides project), it is possible to directly compare radionuclide release from fragments versus radionuclide release segment. The actinides seem to be released similarly irrespective of sample type, while a difference is seen in the Cs and Sr data. A certain amount of Cs can be expected to be part of the gap inventory, and this can be expected to be released more slowly from the cladded segment. In spite of this, both Cs and Sr concentrations in the cladded MOX experiment ("MOX-KWU-seg") increase to a higher concentration relative to the experiment with the MOX fragments ("MOX-KWU-frag"). The reason for this release pattern is not clear, at present. Finally, the data of experiments "UOx-5A2 frag." and "UOx-C1 frag." provides a strong argument against re-using fuel fragments that have been exposed to air or air saturated water for an extended period of time. Even if a pre-leaching campaign indicates most U(VI) has been removed from the sample surface, it appears the oxidation has affected the sample on a deeper level.

#### 4.2.3 Notable results in method development (WP3)

As an outcome from the FIRST-Nuclides project it was noted that the analysis of Se-79 from aqueous solutions resulting from leaching experiments needed some attention. It is a difficult radionuclide to analyse, but an important one from a safety assessment point of view. Therefore, as a part of the DisCo project, JRC initiated work to develop a Se-79 reference solution to improve this situation (see details in Carbol et al 2019). They prepared two High-

Active Raffinate solution (HAR) for Se-79 extraction. The separation of Se from the HAR were done by reductive precipitation and the precipitated Se was recovered through dissolution from a Cu-wire. The solution was then purified and then content of Se-79 determined using a Collision/Reaction Cell ICP-MS. This is used with high-purity CH<sub>4</sub> and CO<sub>2</sub> gases in order to analyse the full Se isotopic spectrum in one run (Carbol et al 2019). The intention is that the produced Se-79 reference solutions will be made available to project partners, thus providing the possibility to improve and increase the data set for Se-79.

## 4.3 Model materials dissolution experiments (WP4)

The WP4 work was designed to test effects of dopants, repository chemistry (eg Eh, pH, complexants, cations, etc) and alfa-radiolysis. The intention was to see if any of the parameters affect [U] in solution – either the rate at which stable concentrations are reached, or final solubility level.

The experimental programme was intended to overcome the inherent complexity of spent fuel corrosion and to identify the separate effects of microstructure, doping level, surface area in support of the spent fuel corrosion studies in WP3. The results clearly allow for improving the predictive capability of SF corrosion models and reduction of associated uncertainties.

For that a broad range of samples was studied in a range of experimental conditions. In general, a set of experimental conditions was defined in close communication with WP3 in order to allow for an easier comparison between the dissolution experiments performed in WP3 and WP4. Five different chemical compositions for the aqueous solution had been defined: (1) a bi-carbonate solution with H<sub>2</sub> (reducing, anoxic), (2) cementitious water with H<sub>2</sub> (YCWCa, reducing, anoxic), (3) synthetic COX water, (4) natural ground water (with (Fe(0)) and (5) a H<sub>2</sub>O<sub>2</sub> solution (for accelerated dissolution experiments).

The dissolution behaviour of the model systems has been studied on respective pellets, which were prepared (and characterized) in WP2. One focus was on Cr-doped  $UO_2$  pellets. The preparation of these materials in different groups provided a range of samples which cover a range in dopant level and particle size. Since these parameters are not known for irradiated fuel pellets, the approach followed here ensured that the envelope of these parameters covers most likely those in "real" SNF.

## 4.3.1 Doped model systems

Dissolution data, produced in oxidizing conditions at USFD, indicate an increased durability with increasing Cr-content. By relating dissolution results to studied of grain size, defect concentration and Cr oxidation state, it is possible to infer an influence of oxygen vacancy formation on the observed changes (Smith et al 2020). Further studies showed that Cr oxidation state switches from +2 for a Cr content of 5-300 ppm, to +3 for samples with 600-2400 ppm Cr. During dissolution three rate regimes were observed; in general, the initial dissolution rate appears to be reduced when Cr is increased. In the third regime, where steady state was achieved, no clear effect of Cr was observed.

Experimental work at CIEMAT focused on the dopants effect on UO<sub>2</sub> matrix leaching resistance through experiments in different representative aqueous systems. For this work three types of solids were studied in three different waters (BC, YCWCa and as a control, water with perchlorate). The static autoclave dissolution experiments were set up in a glove box with inert atmosphere and a hydrogen/nitrogen atmosphere in the autoclaves under anoxic/reducing conditions of 7-8 bar 4.7%H<sub>2</sub>-N<sub>2</sub> gas. In experiments with bicarbonate and young cement water a Pt wire was used to suspend the samples in the solutions.

For the tests in bicarbonate water, a trend was observed for the U concentration levels in relation to additive:  $\sim 10^{-6}$  M for Cr-doped UO<sub>2</sub>,  $\sim 10^{-7}$  M for Cr/Al-doped UO<sub>2</sub> and  $10^{-8}$  M for Gd-doped UO<sub>2</sub> (Fig 7). For the Cr-doped UO<sub>2</sub>, the concentration in bicarbonate water seem to increase slightly with time. In young cement water, the effect of dopant is less pronounced and [U] is between  $10^{-7}$  and  $10^{-8}$  M for all Gd- and Ctr+Al-doped UO<sub>2</sub>; for UO<sub>2</sub> with only Cr [U] is slightly higher, just above  $10^{-7}$  M. Using Al with Cr seem therefore to lower [U] compared to using Cr only. It seems from these data that the chemical environment has a strong effect -when the dopant is only Cr. In bicarbonate water, Gd protects better against oxidative dissolution – but it should be noted it was also a much higher concentration of dopant. However, the smaller grain size would have counteracted the beneficial effect of the high dopant concentration – as it is, it seems the doping effect is stronger than grain size effect.





Accelerated dissolution experiments were performed at FZJ using hydrogen peroxide to simulate the effect of oxidative radiolysis on the dissolution of UO<sub>2</sub> and UO<sub>2</sub> +Cr in bicarbonate water (Kegler et al 2019, 2020). Additionally, to the pure and Cr-doped UO<sub>2</sub> pellets produced in the framework of WP2, commercially available fresh Cr-doped UO<sub>2</sub> pellets were used in the dissolution experiments. A focus was set on the influence of microstructure of the used pellets (e.g. porosity, grainsize) on the dissolution rates. A special characteristic of the accelerated experiments is that the dissolution is driven by the concentration of H<sub>2</sub>O<sub>2</sub> in the solution. The experiments were ended after complete consumption of H<sub>2</sub>O<sub>2</sub> in the solution which results in a plateau of the uranium concentration in the solution. In the context of this work, the experiments with Cr<sub>2</sub>O<sub>3</sub> doped UO<sub>2</sub> show no

significant difference in the dissolution behaviour of uranium to the experiments conducted with pure UO<sub>2</sub> pellets. The comprehensible changes in the microstructure caused by Cr<sub>2</sub>O<sub>3</sub> doping do not seem to have any significant influence on the dissolution behaviour of the  $UO_2$ matrix. The surface normalised uranium concentration after accomplishment of the plateau is between 0.08 and 0.26  $\mu$ mol/L/mm<sup>2</sup>. The initial dissolution rates for the experiments performed with pellets with and without  $Cr_2O_3$  doping are between  $5.55*10^{-7}$  and  $1.83*10^{-6}$ mol/sec·m<sup>2</sup>. The mean of the initial dissolution rate of these experiments is  $1.24*10^{-6} \pm$  $4.1*10^{-7}$  mol/sec·m<sup>2</sup>. Initial dissolution rates determined for the commercially available pellets are in good accordance with the values determined for pellets produced within WP2. Another important observation is that the density of the samples appears to influence the result more than changes in dopant concentration. This is likely due to the fact that a less dense sample will have a higher surface area. Additionally, the studies on pure UO<sub>2</sub> pellets reported by Maier et al (2020) indicate that the surface is affected by repeated exposures to hydrogen peroxide leading to a surface passivation effect. XRD and Raman measurements suggest that this apparent surface passivation may be due to the formation of a thin layer of a secondary phase or hyperstoichiometric uraniumoxide on the surface of the pellets.

At SCK CEN, four types of solids (UO<sub>2</sub>, UO<sub>2</sub>+Cr, UO<sub>2</sub>+Pu, UO<sub>2</sub>+Pu+Cr) were investigated using both bicarbonate and young cement water. The experiments were performed in autoclaves with 10 bar hydrogen and a Pd/Pt catalyst. The Eh potential for both systems were reducing, and over the duration of the experiment decreased to -350 mV/SHE in carbonate water and -440 MV/SHE in young cement water. A high initial U release was observed in both water types, but after this initial release U concentration developed differently (Fig 8). In young cement water, the concentration slowly decreases over time, while the reduction is much faster in bicarbonate water, implying that the high pH seems to stabilise U(VI) in solution, perhaps due to OH complexes. The Cr-doping had a large effect on the U concentrations in the young cement water, as opposed to the bicarbonate water where none or very small effects were observed (Cachoir et al 2021). The effect of alpha-doping is very pronounced in bicarbonate water, where the concentration of U in alpha-doped systems appear to be constant at levels significantly above the solubility for  $UO_2$  (am). The data from young cement water also show an effect of the alpha-doping, however the final, relatively stable U concentrations in all alpha-doped systems are similar (between ca  $1 \times 10^{-7}$  and  $5 \times 10^{-7}$ <sup>7</sup>). The results from these systems show that the dissolved hydrogen did not prevent the effect of radiolysis in the alpha-doped systems (Cachoir et al 2021). The data from the initial U release indicates that Cr-doped UO<sub>2</sub> could be less sensitive to pre-oxidation or the exposure to traces of oxygen at the start of the leach test.



**Figure 8.** Results from SCK CEN presented in final proceedings (D1.25) Left: YCWCa, right: BC

The bicarbonate waters used in the experiments described above are expected to mimic groundwaters from granite repository sites such as those in Finland and Sweden. To test if the more complex, natural groundwater will influence the results, groundwaters the Finnish Olkiluoto site were used in dissolution experiments by VTT. The experiments were set up in a glove box with Ar atmosphere, and reducing conditions were imposed by introducing a Festrip in the leaching vessel. At first, experiments were performed on U-233-doped material already available, and the water used was OL-KR6 with a carbonate content of 2.5 mM HCO<sub>3</sub><sup>-</sup>, comparable to the 2 mM bicarbonate used in synthetic groundwaters. A U-235-rich solution spike was added at the start. This elevated the initial U concentration to concentration of  $3.4 \times 10^{-9}$  mol/L. After 200 days, the concentration of 238U decreased to between  $2 \times 10^{-11}$  and  $5 \times 10^{-11}$  mol/L in these experiments. For these systems there is no observed effect of the alpha-doping, which is in line with previous observations with synthetic waters (eg Ollila and Oversby 2005), and with natural groundwaters (Ollila et al 2013; Evins et al 2014).

Additionally, VTT conducted 200 days leaching experiments with Cr-doped UO<sub>2</sub> materials fabricated by SCK-CEN during the DisCo project. These materials included Cr-doped UO<sub>2</sub> pellets with and without  $\alpha$ -doping with <sup>238</sup>Pu, and similar UO<sub>2</sub> materials without Cr as reference materials. The  $\alpha$ -doping of <sup>238</sup>Pu in pellets correspond to an  $\alpha$ -dose of approximately 10 000 years old SNF. These materials were leached under reducing conditions (with Fe as a reducing agent) in reference FIN water and in natural groundwater, ONK-KR15, sampled at disposal level in ONKALO at the Olkiluoto site. Another notable difference is that these experiments were performed using pellets, not fragments, for an easier comparison with results from SCK CEN. The U-235 spike solution was used in the bicarbonate solution only, since some uncertainties regarding the interpretation of the results from the isotope dilution (see section 4.3.4 below). The main observations are that the U concentration goes down to similar levels as seem in previous projects (eg Evins et al 2014), to ca 10<sup>-11</sup> M after 288 days. There is also no observed effect of either Cr-doping nor alpha-doping. The Eh in systems the natural groundwater system was -650 mV while in the synthetic bicarbonate water, it was ca -550 mV.

Finally, in light of potential effects of U isotope fractionation during the initial rapid reduction (see section 4.3.4), the isotope analysis also included U-233 for the samples with U-233 doping. The results show that a small amount of U-233 is measured at 12 days (2% of all U in solution) but that decreased rapidly and U-233 is unmeasurable at 288 days. It means at the start there is some release of uranium from the sample, even though precipitation is happening. This uranium release seems to diminish to insignificance quite quickly.

#### 4.3.2 MOX-related model systems

At CEA, the experiments were focused to study how homogenous MOX, with a high Pucontent, dissolves in Cox water in the presence of a pre-corroded iron foil. The two-staged experiment consists of a first stage of corrosion of the iron foil in a synthetic COX groundwater (84 days) followed by a leaching experiment of two MOX pellets in the study environment (468 days) in an autoclave. The experiments were conducted under Ar, the pH was 8,2 and Eh around -100mV/SHE. The main elements in the Cox water were Ca, K, Mg, Na, Si, Sr, and Fe. The evolution of these elements was followed over the duration of the experiment (552 days) and the concentrations of Ca, Sr, Si and Fe indicate the precipitation and equilibrium with secondary phases. The hydrogen peroxide was below detection limit ( $10^{-7}$  M) and the U concentration was at or below the solubility level for UO<sub>2</sub> (am).

The sample was studied with SEM/EDS after the experiments, and this reveals massive precipitation of secondary phases on the MOX pellet. These phases contain mainly Fe, but also small amounts of Si and sometimes U/Pu. Using Raman the phase was determined to be magnetite. These data show that Fe(II) is reacting with oxidants (H<sub>2</sub>O<sub>2</sub>) directly at the MOX surface. Previous studies using UO<sub>2</sub>, precipitation of a Fe-phase on the UO<sub>2</sub> surface was also observed. In that UO<sub>2</sub> case the phase was akageneite (Odorowski et al 2017).

Secondary phases were also found on the Fe foil, determined to be aragonite and chukanovite based on shape, SEM/EDS and Raman analyses. Both of these are likely metastable and would in time be expected to transform to calcite and siderite. However, in previous work (Odorowski et al 2017), magnetite had not been observed on the surface of the fuel pellets but rather iron hydroxides like akaganeite. The slightly more basic pH measured for the MOX experiment seems able to explain these differences in the iron-based phases formed.

In close collaboration with CEA and Armines, UCAM investigated the dissolution of  $(U,Th)O_2$  mixed oxide pellets in aqueous solutions mimicking those used by CEA, i.e. the synthetic Cox water. Hydrogen peroxide was added to simulate the oxidative effects of radiolysis. During the preparation stage it was found imperative to establish the stability of the hydrogen peroxide in this experimental system. This required a method development (see section 4.3.4). Results show that contacting (U,Th)O<sub>2</sub> with synthetic COx water and 0.13 mM hydrogen peroxide and Ar in the gas phase for 2 weeks, cause U to dissolve with a rate of  $4.0 \times 10^{-9}$  mol/s.m<sup>2</sup>. To this point, the data on U release and H<sub>2</sub>O<sub>2</sub> consumption in homogeneous U<sub>0.75</sub>Th<sub>0.25</sub>O<sub>2</sub> can be compared with the early stages of the homogeneous U<sub>0.73</sub>Pu<sub>0.27</sub>O<sub>2</sub> dissolution experiments in this project (Kerleguer et al 2020; Table 6). No thorium release could be detected during the dissolution experiment above the LOQ (LOQ =

 $LOD \pm 3\sigma$ : 280  $\pm$  360 = 640 ppt Th). No precipitation of U phases was observed; however, some Ca rich deposits were found on the pellet surface after dissolution. The majority (95%) of the hydrogen peroxide in this system was consumed via disproportionation.

(mol.m <sup>-2</sup> .day <sup>-1</sup> )	$H_2O_2$ consumption (mol.m <sup>-2</sup> .day <sup>-1</sup> )	Oxidative dissolution (mol.m <sup>-2</sup> .day <sup>-1</sup> )	Yield
Homogeneous (U,Th)O	$7.1 \times 10^{-3}$	$3.1  imes 10^{-4}$	4.4 %
Heterogenous MIMAS (U,Pu)O <sub>2</sub> MOx (Odorowski et al 2016)	$3.4 \times 10^{-3}$	9.4 × 10 <sup>-4</sup>	28 %
Homogeneous (U,Pu)O (Kerleguer et al 2020)	$^{2}$ 1.1 × 10 <sup>-3</sup>	$1.2  imes 10^{-4}$	11 %

**Table 6.** Comparison of hydrogen peroxide consumption and uranium release (mol.m<sup>-2</sup>.day<sup>-1</sup>) in the presence of mixed actinide oxides and the derived dissolution yield (fraction of peroxide yielding soluble uranium rather than decomposing).

#### 4.3.3 General observations regarding WP4 results

The microstructure and Cr content of Cr-doped UO<sub>2</sub> pellets is controlled by the preparation method. Systematic studies unraveled contributions of various parameters. Cr plays a key role as a sinter agent that promotes UO<sub>2</sub> grain growth while present along grain boundaries during sintering. However, some of the Cr will be dissolved in the UO<sub>2</sub> matrix. Its solubility is limited in the order of up to 1000 ppm though. Both aspects also highly depend on the oxygen potential during sintering - in fact the H<sub>2</sub>/O<sub>2</sub> ratio of the sintering atmosphere – there is an interplay between Cr concentration and oxygen potential.

A range of preparation routes were used by the project partners. As a consequence, a large envelope of different microstructures and Cr content were studied in dissolution experiments on simple model systems. It seems reasonable, that these simplified compounds mimic some aspects of "real" Cr-doped spent fuel.

Oxidative dissolution (e.g. in the presence of excess  $H_2O_2$ ): The microstructure (grain size) and the presence of Cr affect the rate of oxidative dissolution. Grain size effects seem to be larger than chemistry effects (e.g. Cr concentration). However, the observed dissolution rates are in the same order of magnitude as for Cr-free UO<sub>2</sub> pellets. Dissolution under conditions of an accelerated dissolution experiment using  $H_2O_2$  leads to the formation thin layer of a secondary phase or of hyperstoichiometric uranium oxide on the surface of the pellets that seems to reduce the surface reactivity towards  $H_2O_2$ .

Dissolution under reduced conditions: In reducing conditions (H<sub>2</sub>, iron strips) and in anoxic conditions (low  $O_2$  pressure), an effect of fuel doping with Cr, Cr+Al or Gd was observed only in some particular cases, leading to lower uranium concentrations, and thus indicative of a mitigation of the U oxidation. This was the case for inactive Cr doped UO<sub>2</sub> in high pH cement water, and for inactive UO<sub>2</sub> doped with Cr+Al or Gd in bicarbonate water (and to a lesser extent in cement water). For Pu-Cr doped UO<sub>2</sub>, the effect in cement water was less clear, suggesting that the anti-oxidation effect of the Cr is visible only when the conditions are weakly oxidizing (by traces of oxygen). In the other studied cases, an effect of the Cr was not observed. Other important results are the observation that the addition of H<sub>2</sub> gas did not lead to low U concentrations in equilibrium with the low redox potential. Iron strips as reducing agent in bicarbonate water were more effective in keeping the U concentrations low.

In conclusion, the studies performed on Cr-doped model systems gave experimental evidence that those compounds do not dissolve / corrode very differently compared to Cr-free compounds. Because a potential anti-oxidation effect is observed only in conditions with low amounts of oxidizing species, it is not expected to have an effect on real spent fuel with high  $\alpha$ ,  $\beta$ ,  $\gamma$ -activity. In effectively reducing conditions (e.g. by the action of iron), UO<sub>2</sub> oxidation is prevented anyway, with or without dopants.

However, some questions could not be resolved during these studies: What is the redox state of the Cr dissolved in the UO<sub>2</sub> matrix? How is the Cr incorporated in the UO<sub>2</sub> structure and what is the charge compensation mechanism? How much Cr has been dissolved in the UO<sub>2</sub> matrix – it was not determined for all samples. The microstructure and the Cr content of "real" Cr-doped spent fuel is not known. The grain size at the surface of the Cr-doped pellets is not affected much by the Cr doping (SCK CEN data), so how could we explain the effect observed in particular cases? Therefore, answering those questions would further substantiate our view on Cr-doped spent fuel

The presence of Pu in an unirradiated mixed oxide fuel is 'protective' against oxidative dissolution (caused by radiolysis) in an anoxic aqueous environment when compared with UO<sub>2</sub>. This is evidenced in the normalised U releases measured for both Th and Pu MOx and so will be related to the stability of the oxidation state of added actinide. Dissolution yields (fraction of peroxide yielding soluble uranium rather than decomposing) in Pu and Th MOx experiments were of the order of 1-10%. This is an order of magnitude more than conventional spent fuel dissolution experiments where tri-valent fission products and epsilon phases appear to efficiently catalyse peroxide decomposition. Homogeneous Pu MOx, at 24%,Pu, produces a lower normalised release of uranium than a much lower Pu containing (Pu 7%) inhomogeneous Pu MOX.

#### 4.3.4 Notable results in method development

A careful preparation of the isotope dilution experiments at VTT, involving a U-235-rich spike solution (see for example Ollila 2013), included analysing blank solutions with only spike and no UO<sub>2</sub>. The results strongly suggest that there an issue with U isotopic

fractionation in these systems (Bosbach et al 2021). A rapid change in U isotopic ratio in the absence of dissolving UO<sub>2</sub> was observed, which means that during the initial phase dominated by precipitation from an oversaturated solution, precipitation and/or sorption appears to favour the lighter isotope. Such a fractionation would have the effect of lowering the U-235/U-238 ratio in the aqueous solution - an effect also expected if a solid with a U-235/U-238 ratio lower than the aqueous solution was dissolving. Since the rapid change of the ratio is observed without any uranium dissolving, in the systems with alpha-doped UO<sub>2</sub>, the solution was therefore analysed for U-233 as a sign of dissolution of the UO<sub>2</sub> solid. Thanks to the high resolution instrumentation (sector field ICP-MS with APEX IR sample introduction system) U-233 could be measured even at U concentrations less than 10<sup>-10</sup> M, and was found to be ca 2% of all U in solution after 12 days, but this fraction decreased to 0,7% at 41 days. At 288 days, it was no longer measurable<sup>1</sup>. Another preliminary observation is that the presence of an Fe strip affects these results. These analyses are important for both adding to the current scientific investigations concerning biotic and abiotic U fractionation (Stylo et al 2015, Brown et al 2018, Basu et al 2020) and for a re-interpretation of datasets produced with isotope dilution method (eg Ollila and Oversby 2005).

To improve the possibility to evaluate the stability of hydrogen peroxide in the experimental system used, UCAM developed a method using UV/vis spectroscopy of hydrogen peroxide connected to direct spectroscopic tests using nuclear magnetic resonance (NMR). Since the hydroperoxide measurement needed to be performed in a glovebox setting, the method involved a portable spectrometer and fibre optic feedthroughs. A micro-fluidic pump system was employed to simulate the constant production of peroxide induced radiolysis (in non-Pu samples or real spent fuel). Comparisons with batch peroxide dissolution experiments will provide useful information on optimization of experimental set-ups involving hydrogen peroxide.

## 4.4 Modelling (WP5)

WP5 was devoted to the development of models to better understand the alteration of spent nuclear fuel. The models were built upon data and observations already existing in the literature before the onset of DISCO, but some of the new data gathered in this project were also used to test the predictive abilities of the models and/or as experimental evidences upon which new developments were based. Different type of models were developed in WP5. PSI specifically addressed the solubility of Cr in Cr-doped fuels and how it could affect the oxygen potential in the fuels. PSI also developed reactive transport simulations of the fuel dissolution when the canister is failed. Armines used the experimental data produced by CEA in WP4 to further develop a reactive transport model under repository conditions. NNL tested mixed potential models to simulate the behaviour of an old fuel, what allowed to identify that the efforts needed to further develop MPM are too large and concluded that other type of models are more adequate to understand fuel alteration. Amphos21 was able to further develop a matrix alteration model by coupling radiolytic, chemical and transport processes

<sup>&</sup>lt;sup>1</sup> Data was presented at the DisCo project Pre-final meeting, April 2021

through the implementation of a coupled PhreeqC-Comsol model (iCP). Data generated by Ciemat, by Juelich and by Studsvik in WP3 and WP4 was very useful to test the performance of the model. In the sections below, the work is described in more detail and references are given to the documents where the specific models are described.

#### 4.4.1 Thermodynamic modelling

Thermodynamics was used to describe the in-pile chemical evolution of Cr-doped spent fuel. The model development and its application are described in Deliverable D5.2 and Curti and Kulik (2020). From this model the oxygen potential of irradiated Cr-doped fuels was calculated as a function of fuel temperature and burnup, taking into account equilibrium with complex solid solutions for the major UO<sub>2</sub> phase and noble metal (epsilon particle) inclusions, as well as separate stoichiometric phases for fission products. The model is calibrated against experimental data from the literature to consider defect chemistry and substitution mechanisms of Cr(III), REE(III) and U(V) in UO<sub>2</sub> (Curti and Kulik, 2019). For this work, key thermodynamic data for Cr were collected and used along with experimental data (Riglet-Martial et al., 2014) to define the mixing properties of  $Cr_2O_3$  in stoichiometric UO<sub>2</sub>.

#### Cr-solubility in UO2

The solubility of Cr (III) in UO<sub>2</sub> predicted by the model is about 0.6 mol% for a typical fuel sintered temperature of 1800°C, which is consistent with the upper limit of ca 0.52 mol % Cr (1000 ppm) in the commercial production of some Cr-doped pellets by the ADOPT process (Arborelius et al., 2006). According to the available experimental data, the Cr solubility in stoichiometric UO<sub>2</sub> decreases with temperature. This behaviour is well reproduced by the model of Curti and Kulik (2019), which predicts exsolution of Cr under reactor operation temperatures. The actual solubility will however be also influenced by the deviation from the ideal stoichiometry of the fuel as well as by the thermal diffusion kinetics of Cr dissolved in  $UO_2$ .

#### Oxygen potential in conventional and Cr-doped fuels

In standard fuels, it is well known that molybdenum, a major fission product, controls the oxygen potential via the Mo(0)/Mo(IV) redox system (Matzke, 1995). Curti and Kulik (2019) calculated the oxygen potential developed with and without Cr doping of the fuel, taking into account the incorporation of Mo(0) in the noble metal inclusions. The results show that the oxygen potential increases with increasing dilution and non-ideality of Mo(0) mixing in the noble metal solid solution. Three model variants were calculated: pure Mo, ideal mixing and non-ideal mixing following the state-of-the-art model of Thompson et al.(2012). The oxygen potential differences among the three variants are small but significant, implying that a realistic calculation of the MoO<sub>2</sub>/Mo buffer can only be obtained using the state-of-the-art mixing model (Thompson et al 2012). In contrast to the effect of Mo, the model calculations indicate that Cr-doping has a negligible effect on the oxygen potentials, as they are calculated to be almost identical for non-doped and Cr-doped UO<sub>2</sub> fuels at burnups > 20 MWd/kgHM. Finally, a dedicated calculation showed that including zirconium alloy oxidation may locally reduce the oxygen potential of the fuel at the pellet-cladding interface.

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#### Thermodynamic modelling of spent fuel dissolution in a failed canister

Curti (2021) uses thermodynamic modelling to describe the chemical system and expected reactions inside a failed spent fuel canister surrounded by bentonite clay. The model has been applied both to a closed system and to an open system, in which solute transport along a crack in the canister is allowed. In the closed system, batch equilibrium is assumed and limited amounts of spent fuel and other materials react with bentonite pore waters. In the batch equilibrium model, non-oxidative dissolution of spent fuel is assumed based on ample evidence for a strong effect of the molecular hydrogen expected in the system. In the reactive transport model, oxidative dissolution is assumed, allowing an assessment of the effect of the Fe-based canister on the oxidizing front propagating from the spent fuel.

Results from the batch equilibrium modelling show that the chemical environment in the failed canister is controlled by redox reactions involving S, C and Fe. In all calculation cases the equilibrated water is predicted to be more alkaline and more reducing than the initial input bentonite pore water. If sulphate reduction is included in the calculations, there is a large impact on pH and Eh. However, for both S and C redox reactions to occur in the system, H<sub>2</sub> needs to be chemically reactive, and away from the spent fuel surface this is expected to occur only via microbial mediation. However, various lines of evidence point towards a low likelihood of microbiological activity in the near-field.

Assuming oxidative spent fuel dissolution means that there is a redox front propagating in the system. The reactive transport model shows that assuming sulphate reduction has an important effect on how the radiolytic oxidation front propagates through the fissure. In this case, even if Fe(0) in the fissure is no longer available, the oxidizing front would move very slowly through the fissure.

#### 4.4.2 Matrix dissolution model

Based on the considerable knowledge on spent fuel dissolution that has become available over the years due to collaborative efforts in the research field, a model called "Matrix Alteration Model", or MAM-model, was developed (Martínez-Esparza et al., 2005; Duro et al., 2009; 2013)). In the current project, this model has been implemented in the iCP tool which couples COMSOL Multiphysics and PhreeqC as described by Riba et al (2020, 2021). The model has been calibrated with experimental data, both from available literature and from experimental results from project participants. Using the iCP tool has allowed a connection between the radiolysis reaction scheme with solubility and speciation-related reactions, including the complex chemistry of both U and Fe. One difficult issue solved in the modelling is the connection of the very rapid radiolysis reactions with the slower dissolution and precipitation reactions.

The model describes the system in one dimension. Generation of radiolysis products (oxidants and reductants) is calculated using COMSOL. In addition, two important reactions describing the fate of hydrogen and hydrogen peroxide are included: the catalytic decomposition of hydrogen peroxide, which results in generation of  $\cdot$ OH, and the activation of H<sub>2</sub> on the Pd surface, generating H. $\cdot$  COMSOL is also used to calculate solute transport. The calculations

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carried out by PhreeqC describe both the thermodynamics of the aqueous solution and the kinetics of the reactions involving U and Fe.

The model was used to simulate some of the data produced in the DisCo project. One data set came from Fidalgo et al. (2020) in WP3 (spent fuel) while two data sets came from the model systems investigated in WP4: Rodríguez-Villagra et al. (2020) and Kegler et al. (2020).

The simulation of the spent fuel data of Fidalgo et al (2020) indicated 1) a stabilization of the Eh at a value of -0.3 V, in agreement with an oxygen buffer effect exerted by the  $MoO_2/MoO_4^{2-}$  redox pair and in agreement with the experimental measurements. At this Eh the modelled total U is equal to the U(IV) and only a very small fraction of U(VI) is expected in solution. However, the experimentally measured U concentration is higher than what the model predicts. As is described in section 4.2.1, this is likely due to the history of the fuel samples which includes years of leaching and storage in aerated conditions, causing oxidation, and the influence of colloids originating from an initial dissolution of a pre-oxidized fraction of the fuel matrix. The modelled concentrations of Tc, Mo, and Pu in the long-term (over 300 days) are in agreement with the experimental observations, and in line with the calculated solubilities of the solid phases expected to control their concentration (TcO<sub>2</sub>·1.6H<sub>2</sub>O); colloidal PuO<sub>2</sub>; MoO<sub>2</sub>(s) and NpO<sub>2</sub>·2H<sub>2</sub>O.

Simulations of dissolution data from unirradiated model systems produced by Rodríguez-Villagra et al. (2020) (see section 4.3.1) were performed in two ways: with and without hydrogen activation. The simulations indicate that hydrogen activation can occur when Cr is combined with Al, but not when Cr is used as sole dopant. Although not sufficient data are yet available to support definitively these conclusions, this outcome agrees with the results on the different catalytic activity of Cr in the oxidative deshydrogenation used in the production of alkenes, that shows that Cr activity is improved when it is supported by other metal oxides such as Al<sub>2</sub>O<sub>3</sub> (e.g. Józwiak and Dalla Lana. 1997, Cherian et al. 2002).

The effects of oxidation by hydrogen peroxide on the dissolution of  $UO_2$  studied by Kegler et al (2020) (se section 4.3.1) were also simulated with the model. The dissolution observed was higher than the one simulated with the model. The concentration of  $H_2O_2$  was well reproduced by the model although to account for the experimental observation of the concentration of uranium in solution the calculations had to assumed that only a 4% of the  $H_2O_2$  present was involved in the dissolution of uranium. Previous results in the literature already indicated low yields of uranium oxidation vs. hydrogen peroxide in uranium oxide pellets (e.g. Pehrman et al. 2012, Trummer et al., 2008) what supports the results of the model adjustment to the data.

The matrix dissolution model developed here was shown to reproduce dissolution rates used in various safety assessments. It was also able to reproduce the results from dissolution experiments performed in the project, suggesting that the main processes controlling the uranium chemistry in these systems have been captured by the model. In particular, simulating the data from this project has revealed that hydrogen activation on the oxide surface appears to be more efficient for systems with Al and Cr compared with Cr as sole dopant. A fundamental advance of the model was the ability to couple very different kinetic processes, such as radiolysis and chemical kinetics with equilibrium processes.

## 4.4.3 Mixed potential model

Another approach to model spent fuel dissolution is to focus on electrochemistry, considering the importance of electron transfer reactions at the surface of the fuel to promote U dissolution. In this approach the dissolution is modelled as a corrosion process with anode and cathode reactions. In this project, an electrochemical mixed-potential model, based on earlier models (King and Kolar, 1999) was developed, complemented with some modifications on the effect of noble metal particles, as explained in detail in Hughes et al. (2020). The aim was to be able to use this model for a range of conditions and scenarios. A specific environment of interest for the UK is the high pH pond systems used at Sellafield.

The work performed to improve and develop a mixed-potential model (MPM) (see Deliverable D5.4; Hughes et al 2021) included a dose model based on alpha radiolysis, a radiolysis model, bulk chemical reactions, surface reactions, and 1D diffusion. The model was compared with experimental data and with other similar models in the literature. A wide range of uncertainties in the approach, parameters and implementation of the model were identified. Even though the model was shown to agree somewhat with observations made on real pond-stored fuel pins (see section 4.1), there were some indication of omissions in the mechanisms include within the model. The final recommendation of the work is that the effort needed to address the existing uncertainties would be too large and that further development work on the mixed-potential model should be paused in favour for simpler approaches. Hughes et al (2021) present a thorough discussion of the different MPM in the literature and constitutes a very detailed literature review of this type of models, addressing advantages and disadvantages as well as raising concerns over some aspects of the existing modelling approach.

## 4.4.4 MOX dissolution in a repository setting

The modelling work focused on the dissolution of a non-irradiated homogenous MOX pellet  $(U_{0.73}Pu_{0.27}O_2)$ . It has been performed in close cooperation with the experiments performed by CEA in WP 4 (see section 4.3.2). Some preliminary results have been presented in the progress report (D5.3) and by Kerleguer et al (2020). The final detailed results, which can be found in De Windt et al (2021), are summarised below.

The approach involved chemical modelling using the CHESS code and coupling this to the reactive transport code HYTEC. The models took into account the kinetics of hydrogen peroxide ( $H_2O_2$ ) radiolytic production and disproportionation at the MOX pellet surface, the kinetics of the oxidative dissolution of the MOX matrix by  $H_2O_2$ , the kinetics of reducing dissolution of the MOX matrix, and the kinetics of anoxic corrosion of the iron foil. A large set of reactions at thermodynamic equilibrium (among others for U, Pu and Fe species) were considered by using the ThermoChimie database.

The model was first based on the experimental data gathered by Kerleguer et al (2020) in carbonated water to get the intrinsic kinetics of dissolution. The model was further developed to include the effect of the near-field repository environment, by specifically addressing the effect of metallic iron in synthetic COx claystone groundwater, which was experimentally tested by CEA in DISCO. An upscale of the model to a simplified configuration of a generic disposal cell of spent MOX fuel assemblies in clay rock was finally applied. The purpose of this last modelling was to perform mass-balance simulations at the scale of a disposal cell between the diffusive flux of radiolytic  $H_2O_2$  and Fe(II) and its effect on MOX dissolution with a sensitivity analysis on the iron corrosion products.

The effects of Pu in the  $U_{0.73}Pu_{0.27}O_2$  matrix could be argued to be both detrimental, due to a higher alpha activity, and beneficial, due to an observed stabilizing chemical effect on the matrix. The incongruent release of U and Pu controlled by the precipitation of an amorphous Pu hydroxide layer, and the high disproportionation of  $H_2O_2$  by the  $U_{0.73}Pu_{0.27}O_2$  surface, were correctly modelled. The results shown that the release of uranium in synthetic groundwater in the presence of metallic iron was very significantly lowered compared to carbonated water conditions. The Fe(II) released in solution by the iron foil anoxic corrosion consumed  $H_2O_2$  produced by alpha-radiolysis of water. This redox reaction front occurred where radiolytic  $H_2O_2$  was produced, i.e. on the surface of the MOX pellets. The oxidative dissolution was strongly inhibited despite a high alpha activity due to plutonium. The predicted iron secondary phases formed (chukanovite and magnetite) were also in agreement with the experimental results.

In comparison with previous similar experiments on  $\alpha$ -doped UO<sub>2</sub> pellets, the plutonium content made the solid solution U<sub>0.73</sub>Pu<sub>0.27</sub>O<sub>2</sub> more resistant towards leaching whereas no significant difference was found with the synthetic claystone water and metallic iron. Eventually, De Windt et al. (2021) discussed on the advantages and limitations of the model developed and concluded that the model would benefit from more detailed mechanism of Pu surface enrichment and a solid solution model of the mixed U-Pu oxide matrix.

## 5 Summary and discussion of main outcomes

The results presented above constitute an important contribution to the spent fuel data base. They provide a deeper insight into crystal chemistry of unirradiated uranium oxides, with and without additives, as well as a better understanding of what controls the results from spent fuel leaching experiments. Besides our overall objective to improve understanding of spent fuel matrix dissolution in the conditions of repository environments, the initial aim of the project was to test the hypothesis that the dissolution behaviour of modern fuel types, doped or MOX, does not differ significantly from that of standard fuel. It seems clear that both experimental and modelling results presented here support this hypothesis, and that mechanisms and rates of radionuclide release from the modern fuel types studied in this project can be considered very similar to those of standard fuels. This result is advantageous for assessing properties of  $UO_2$  based fuels with respect to both front end and back end of the nuclear fuel cycle. However, one of many lessons learned is that there are many aspects of the

fuel that may affect the dissolution behaviour, such as density, stoichiometry, heterogeneity and microstructure. Therefore, caution is warranted due to the still fairly limited data set that this project has produced. As fuel vendors are developing new fuel types, this must be done in close collaboration with back-end studies such as this. It is essential that, as we are progressing towards licensed facilities for geological disposal, new fuel types are in line with acceptance criteria and do not affect the safety assessments in unacceptable way.

## 5.1 Scientific advances

Complementary and coordinated dissolution studies on spent fuel and simplified model systems have been carried out on a large scale for the first time. The use of systematically produced, and carefully characterized model materials in parallel with spent fuel dissolution experiments has uncovered new aspects of the dissolution process not clearly visible in previous studies. The connection to the modelling work has also advanced our understanding of model systems and of spent fuel dissolution in various repository conditions.

## 5.1.1 Characteristics of spent nuclear fuel

Through the efforts of synthesising the solid materials needed to perform this systematic study, several new insights have been gained. The concern mainly the characteristics of the  $UO_2$  solid state and what effects additives have one the crystal structure and U valence. Important steps have been taken towards a better understanding of how the additives are incorporated in the oxide. The systematic studies of effects of additives have advanced the knowledge concerning uranium oxide lattice defects and microstructure.

The spent fuel dissolution experiments performed in this project have not only added to the data base, but also provided a unique opportunity to compare many different aspects that may vary between fuel types as well as experimental set-ups. Somewhat unexpectedly it also provided important information concerning the effects of prolonged contact with air-saturated water. This has proven to be useful for studies regarding the effects of failed cladding in fuels that have been stored a long time in pools.

Combined results from across the work packages show that although synthesis procedures and doping with Cr (or Cr+Al) affect grain size and microstructure in the unirradiated material, the effect on irradiated fuel is insignificant with regards to oxygen potential and radionuclide release patterns.

## 5.1.2 Oxidative dissolution of spent nuclear fuel and the hydrogen effect

The results have clearly illustrated the importance of the chemical environment. Clearly, if the system is in contact with air, U(VI) will be stable and this will have a major effect on U release from the samples. However, different water types, as has been seen in both spent fuel experiments and model systems, will also have important effects on the results. If the initial U release is related to dissolution of a pre-oxidized phase - which may be less for Cr-doped UO<sub>2</sub>

- the aqueous speciation is fundamental for the development of the system, on an experimental timescale. In reducing environments, complexing agents may slow down reduction of this initially released U – as may be the case in the young cement water - or if there is a significant release of oxidized U, this may form colloidal material when reduced – as may have been the case in one spent fuel experiment. Another aspect is that a system with enough Fe(II), the dissolution process is clearly affected by precipitates on the dissolving surface. Important advances have been made with regards to the effects of the chemical environment, due to the comparison of spent fuel dissolution in bicarbonate and young cement water.

Results from spent fuel experiments performed in this project support the hypothesis that hydrogen can strongly reduce the oxidative spent fuel dissolution rate. They do however not provide support the hypothesis that hydrogen can fully stop the spent fuel dissolution: a very slow release of radionuclides predominantly bound in the spent fuel matrix (such as U and Sr) during the full experimental time frames show that the spent fuel matrix is still reacting, even in the presence of hydrogen. The U release rates in these experiments are estimated to about  $10^{-11}$  mol/(L·d), indicating a release of ca  $10^{-9}$  mol/(L·year) (Metz et al 2021). Other experiments performed under similar conditions (Carbol et al 2009, Puranen et al 2018, Ekeroth et al 2020) resulted in very low U concentrations (~ $10^{-11}$  to ~ $10^{-9}$  M) indicating that a fully reduced system was achieved, in which no oxidative dissolution could be observed. Why the DisCo experiments did not reach this state is unclear but it may be related to differences in sample characteristics and experimental set-up.

In light of these results and the recent suggestion by Pastina and Laverne (2021), that an excess of radiolytically produced reducing species may maintain the spent fuel surface in a reduced state, it is clear also that there still are some unresolved issues regarding the hydrogen effect.

Results from across the work packages have thus provided us with new insights on the effect of the chemical environment on the oxidative dissolution of uranium and evolution of uranium chemistry in aerated and reduced systems. With regards to the hydrogen effect, both spent nuclear fuel and model systems show that hydrogen will have a reducing effect but there are still remaining unresolved issues – for example, concentrations required to suppress radionuclide release from spent fuel, or mechanisms involved when there are no metallic particles. Can a combined doping (Cr+Al) activate hydrogen but not when Cr is the sole additive?

#### 5.1.3 Dissolution of "old fuel"

This question has been addressed via the dissolution studies performed on alpha-doped model materials. The materials were designed to be mimicking ca 10 000 years old fuel, which have previously been considered to be close to the limit of where any effects of the alpha radiation on the dissolution can be observed experimentally (Grambow 2010).

Insight has been gained with regards to the so-called "threshold" by the observations made by SCK CEN (see section 4.3.1) and it appears at the doping level chosen, there is a clear

oxidative effect of the alpha dose. However, in the experimental system used by VTT, where reducing conditions were achieved using corroding iron, the alpha doping made no difference. There is obviously a strong effect of the chemical environment and it appears the presence of iron lowers the U concentrations significantly. This is seen also in the CEA experiments using MOX – even though the alpha doping was much higher in that system, it seems the chemical environment provided by the COx water reduces the U release and keeps the concentration close to the solubility of U(IV). Some further investigation of the "threshold", ie at which alpha-dose there is no observable dissolution of U(VI) in anoxic conditions, is probably needed, using simple aqueous solutions to avoid risk of precipitates and secondary phase formation.

#### 5.1.4 Fuels with additives

Thanks to major efforts in sample preparation, the carefully set up dissolution experiments have furthered our understanding of how the reactivity of the oxide is changed depending on type and amounts of additives with different valence. Experimental data from both spent nuclear fuel and model systems used in modelling has further enhanced the understanding of the systems. By using alpha-doped material as well as hydrogen peroxide, the potential effect of additives on the oxidative dissolution of uranium has been clarified. From the thermodynamic calculations, the solubility of Cr(III) in UO<sub>2</sub> is found to be ca 1000 ppm. Based on this work it would seem that only octahedrical coordination would be possible for Cr(III), according to the calculations on the basis of Cr/O radius ratio. The results from this project indicates that a three-valent additive may protect the uranium dioxide from oxidation. This effect is less pronounced for Cr than for Gd, however combining Cr with Al, which is done in some commercial fuels, appear to decrease the reactivity towards oxidants, at least in the presence of hydrogen (see section 4.3.1). This supports the hypothesis that additives do not negatively affect the dissolution of spent fuel. If anything, it seems to have some protective effects. Since Gd exists in the UO2 matrix as Gd(III), the observed effect of Gd corroborates previous results (eg Fidalgo and Jonsson 2019) that indicate that three-valent elements will reduce the oxidative dissolution rate of U. Why Cr has less effect is not yet clear, however, even if Cr is expected to exist as Cr(III), depending on sample synthesis conditions, the valence of Cr in the UO2 solid can be an uncertainty.

The outcome of the systematic studies performed in all work packages is that even if microstructures of the unirradiated material may change due to the additives, the addition of Pu (or Th), Cr, Gd, or combined Cr and Al, is not expected to have a negative effect on the dissolution rate of the irradiated fuel.

#### 5.1.5 Modelling the dissolution of spent nuclear fuel

Thanks to state-of-the art chemical modelling, employing thermodynamics, kinetics and reactive transport, our understanding of both solid state characteristics of spent fuel and mechanisms of dissolution have been advanced. Existing models have been improved and developed to be used in computational tools that are readily available to be used in safety assessments. New conceptual advances and observations, such as the hydrogen effect, have

been successfully incorporated in the models (see section 4.4.2). The models have been used to provide basic insights and understanding of the mechanisms governing fuel dissolution under repository conditions. Specifically concerning the modern fuels under study, the modelling performed has effectively been a test on the adequacy and adaptability of the existing models to the behaviour of these fuels. Importantly, experimental data from both model systems and spent nuclear fuel dissolution have been successfully simulated using the updated models.

## 5.2 Remaining knowledge gaps

In the previous section, overall outcomes and scientific achievements of the project have been presented and discussed. In connection to this, some unresolved issues and knowledge gaps that will require further attention are identified. These are:

- What are the relations between H<sub>2</sub> concentration in the aqueous solution and oxidative dissolution rate, and how does this change as the radiation field changes over time? At what alpha activity is the so-called "threshold" passed, where no effect of radiolysis can be observed experimentally?
- The complete picture of how hydrogen acts on the system: Does molecular hydrogen react with hydroxyl radicals at the surface of the fuel and to what extent other radiolytically active groundwater constituents, such as chloride and bromide, counteract the hydrogen inhibition effect?
- What is the relevance of the dissolution rate of U(IV), ie non-oxidative dissolution, in a system where the solubility of U(IV) is reached very rapidly? May recrystallization of the spent fuel surface cause radionuclide release, even when at the solubility level of U(IV)? If so is this a short, transient period involving a very small fraction of the radionuclide inventory, or is something that can proceed for a significant time?
- What Fe (II)-concentrations are required for the effect seen in the MOX studies, and how can we expect this concentration to evolve over time in different repository settings?
- To fully understand the effects of Cr-doping on the redox reactivity of UO2 and connected catalytic properties of the surface, the valence of Cr in the uranium oxide needs to clarified. The expected valence based on a "classical" view is that Cr exists in the oxide matrix as +3. There are however results that indicate that it may be +2 or even +1.
- For irradiated fuel, there is an observed beneficial "doping effect" caused by fission products where the valence mostly is +3. This is commonly explained as due to charge compensation and partial change of valence of U in the lattice from U(IV) to U(V). It is however also observed that Th (IV) may also protect U against oxidation, so that

oxidative dissolution is slowed down. This should not affect the U valence, and the protective effect of four-valent additives is therefore yet to be explained.

- There are other additives suggested for UOX fuel, for example aluminosilicate (SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) or beryllium oxide (BeO) (Khatib-Rahbar et al 2020). The effects of these other additives need to be addressed and clarified before these fuel types are commercialized.
- Grain boundaries: How do the grain boundaries participate in the dissolution process? What fraction of various radionuclides segregate to grain boundaries?
- Effects of additives on segregation of mobile radionuclides (IRF nuclides) some results from the ADOPT studies indicate that the Cr-Al doping will affect the IRF of certain radionuclides.

The above list of identified knowledge gaps should guide future research to help strengthen the safety case for deep geological facilities developed for direct disposal of spent nuclear fuel.

## 6 Concluding remarks and highlights

The ambition of this project was to advance understanding of the underlying mechanisms controlling spent nuclear fuel dissolution in repository environments. In particular the aim was to fill in knowledge gaps associated with modern types of LWR fuel currently in use. This aim has been fulfilled. The hypothesis that doped fuels and MOX fuel can be considered to behave like standard  $UO_2$  fuel in a repository environment has been tested. The results provide strong support for this hypothesis, at least for MOX and Cr+Al-doped fuels, and therefore the dissolution rate of these modern fuels is not expected to be significantly different from that of standard fuels. This is an important conclusion for the whole nuclear fuel cycle. By testing this hypothesis direct support to safety assessments has been provided. Some caution is however warranted due to the limited data set; more data from long-term experiments and different fuel samples would enhance the confidence in the overall conclusion.

Another project aim was to expand the data base needed to analyse how spent fuel will dissolve in repository environments. Different concepts involve different chemical environments and an expanded data base allows us to deepen our understanding for the effects of repository components and varying groundwater compositions. This aim has also been achieved by means of state-of-the-art modelling and experimentation performed as a systematic study of behaviours under repository conditions.

Some highlights from the project achievements are:

• Similar matrix dissolution behaviour is observed for MOX, doped fuels and standard fuel types.

- Systematic studies, both experimental and theoretical, of effects of additives on the UO<sub>2</sub> solid state have enhanced understanding of uranium oxide lattice this new knowledge can be transferred to future studies involving other additives and more complex compositions.
- The importance of the chemical environment in the repository is confirmed: low Eh and the presence of corroding iron and/or hydrogen is especially efficient in suppressing the dissolution rate. This is shown both via experiments and models.
- Models that take the chemical environment into account have been developed for potential use in safety assessments
- Methods to synthesise model systems that can be used in further work have been optimized
- Failed spent fuels that have experienced over 40 years in water contact show very little change in structure and appearance compared to pristine fuel.

In DisCo the focus was on doped fuels that are already in use in nuclear reactors. It is clear, however that similar studies may have to be performed for other types of fuels that are being developed as a response to the need for more accident-tolerant fuels (ATF). There is an array of suggested compositions, but there is hardly any data available for these that can be used to assess their performance in a geological repository. In the licensing process, there is a need to define waste acceptance criteria. In other words, we need to show that the waste generated – be it the actual spent fuel or some other high-level waste form generated by the use of newly developed "ATF"-fuels– can be deposited without negatively affecting the long-term safety of the repository. In light of this, one can recommend and foresee that the whole nuclear chain, from front-end to back-end, need to communicate and work closely together.

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