

Co-funded by the



DISCO

Grant Agreement: **755443**

DELIVERABLE D1.10

1st Annual Meeting Proceedings

Author(s)/Editor(s): **L.Z. Evins, A. Valls, L. Duro (SKB & Amphos 21)**

Date of issue of this report: **08/2018**

Report number of pages: **81 p**

Start date of project: **01/06/2017**

Duration: **48 Months**

Project co-funded by the European Commission under the Euratom Research and Training Programme on Nuclear Energy within the Horizon 2020 Framework Programme		
Dissemination Level		
PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the partners of the Disco project	
CO	Confidential, only for partners of the Disco project	

Foreword

The present document is the proceedings of the First Annual Meeting of the EURATOM H2020 Collaborative Project DisCo (Modern Spent Fuel Dissolution and Chemistry in Failed Container Conditions). The electronic version of these proceedings is available on the webpage of the project (<https://disco-h2020.eu/>) The project started in June 2017 and will last for 48 months. DisCo is implemented by a consortium with 16 Beneficiaries, advised by the so-called End User Group (EUG). EUG consists of Waste Management Organisations in 7 countries (Belgium, Finland, France, Spain, Sweden, Switzerland, and the UK) as well as Regulatory Authorities in 5 countries (Belgium, Germany, Spain, Sweden, and Switzerland). The inclusion of Waste Management Organisations (WMOs) and Regulatory Authorities in this group ensures that the research conducted in the proposed project will be relevant and useful for the ultimate goal of safe radioactive waste disposal.

These proceedings document the progress of the project by means of work-package summaries and individual Scientific and Technical contributions. The key purpose is to ensure dissemination of knowledge and creating the required awareness of the project achievements.

The progress shown corresponds to the work conducted during the 1st year of the project and presented at the 1st Annual Meeting in Sheffield (May 2018). All groups have started their research and good results have already been obtained.

The main technical outcome of the meeting are the extended abstracts (brief Scientific and Technical contributions) explaining the progress of each partner. The abstracts have been reviewed by, at least, two members of the End User Group.

The proceedings give an overview of the project, its organization and planned activities. The project website provides all this information in detail. The reader could also contact the project Coordinator or its team for more information.

The editors are grateful to all consortium members and everyone involved who contributes to the smooth development of the project. We want to give special thanks to (i) work-package leaders for providing the summaries of their corresponding work-package, (ii) partners for their comprehensive and significant contributions, and to (iii) all members of the EUG for their reviews, providing constructive, relevant and interesting comments. These efforts reflect their commitment and dedication to the project and contribute to a high quality of research performed within DisCo.

Contents

Foreword	i
The Project	1
The 1st Annual Meeting	2
WP Overview	4
WP1 Overview: Management, coordination and dissemination	5
WP2 Overview: Preparation and characterization of samples and experimental systems	7
WP3 Overview: Spent fuel dissolution experiments.....	11
WP4 Overview: Model material dissolution experiments.....	13
WP5 Overview: Chemical modelling.....	16
Extended Abstracts	19
Progress on examination of UO ₂ fuel after extended storage (<i>Hambley and Goode – NNL</i>).....	20
SNF sample preparation and ⁷⁹ Se solution production (<i>Serrano-Purroy et al. – JRC-Karlsruhe</i>)	24
Description of leaching experiments with KIT’s MOX irradiated fuel (<i>González-Robles et al. – KIT-INE</i>).....	29
High-burnup spent nuclear fuel dissolution under highly alkaline conditions (<i>Iglesias et al. – CTM</i>)	33
Aqueous leaching of spent nuclear fuel under H ₂ atmosphere. A comparison between ADOPT and standard UO ₂ fuel (<i>Barreiro Fidalgo et al. – Studsvik</i>).....	37
Manufacture and characterization of CIEMAT fuel samples used for leaching tests in DisCo project (<i>Rodríguez-Villagra et al. – CIEMAT</i>).....	39
Synthesis of doped UO ₂ model materials for single effect studies to understand the long-term matrix dissolution of modern LWR fuels (<i>Brandt et al. – JUELICH</i>).....	45
Influence of iron on the oxidative dissolution of a homogeneous U _{1-x} Pu _x O ₂ MOX fuel (<i>Jégou et al. – CEA</i>).....	49
Dissolution of alpha-doped UO ₂ with and without Cr in the presence of corroding Fe, in synthetic and natural groundwater (<i>Myllykylä and Ollila – VTT</i>)	52
Synthesis and preliminary characterisation of model UO ₂ fuel doped with Al ₂ O ₃ (<i>Cordara et al. – USFD</i>)	55
Integrated spent fuel alteration model. Method and first results (<i>Riba et al. – Amphos21</i>).....	61
Modelling of the oxidative leaching of U _{1-x} Pu _x O ₂ in synthetic groundwater with metallic iron – first results (<i>De Windt et al. – Armines</i>).....	66
Preliminary thermodynamic calculations for WP5, Task 1 (<i>Curti and Kulik – PSI</i>)	70
Progress on modelling of UO ₂ fuel dissolution within storage containers (<i>Hambley et al. – NNL</i>).....	74
EUG Feedback	78

The Project

DisCo is a Collaborative Project funded by the European Commission under the Horizon 2020 Research and Training Programme of the European Atomic Energy Community (EURATOM) (H2020-NFRP-2016-2017-1), section B - Contribute to the Development of Solutions for the Management of Radioactive Waste. Topic NFRP 6: Addressing key priority R&I issues for the first-of-the-kind geological repositories.

DisCo is an acronym for “Modern Spent Fuel Dissolution and Chemistry in Failed Container Conditions.” It started on 1st June 2017 and it is planned to run for four years. The project is implemented by a consortium with 16 Beneficiaries.

The project is set up to answer the Euratom call of 2016-2017, which focused on high priority topics identified by the IGD- TP (Implementing Geological Disposal – Technology Platform: www.igdt.eu). One of these areas is the disposal of new and unconventional fuels. DisCo started as a response to the need to test the hypothesis that dopants in the UO₂ fuel matrix do not significantly affect the dissolution rate of the spent fuel in a repository environment. Dopants in the UO₂ fuel matrix here considered are Cr, or Cr+Al, and Gd. In addition, the behaviour of Mixed-Oxide fuel (MOX) which contains Pu in addition to the UO₂ matrix is also investigated, leading to the study of the effect of an analogous mixed Th-U oxide for comparison. The DisCo project uses three paths to study these issues which mainly define the objectives of the technical work-packages (WP): dissolution experiments with real spent fuel (WP3), dissolution experiments with model materials (WP4) and modelling of the chemical system expected in the failed waste container (WP5). An additional technical work-package (WP2) is devoted to the preparation and characterization of the samples to be used in the experiments planned in WP3 and WP4.

The central part of the scientific investigation in this project concerns how elements other than uranium (metal, lanthanide, actinide) in the oxide matrix affect its redox chemistry and solubility. Any impurity in a solid phase will affect the crystal lattice and atomic bonds, so that parameters such that the solubility of the solid can be affected. In addition, the electronic configuration on an atomic scale affects the average oxidation state of the uranium in the solid. Since these aspects are fundamental to the spent fuel dissolution process, it is necessary to test whether these changes affect measured dissolution rates.

This DisCo project also contributes to knowledge management, dissemination and communication, through the efforts made in WP1. The involvement of an End User Group (EUG) representing waste management organisations and national regulators, as well as an Associate Group (AG) consisting mainly but not exclusively by organisations from countries with less advanced programs (LAPs), is central to the successful knowledge transfer and management foreseen in DisCo. Efforts are focused on communication and dissemination activities such as webinars and training events.

The 1st Annual Meeting

The first annual meeting of the DisCo project was held in Sheffield (UK), 15th – 16th May 2018. The meeting was hosted by The University of Sheffield at the Halifax Hotel. There were 57 attendees including representatives of the partners, the End User Group (EUG) and some external organizations.

The meeting was scheduled in three blocks (see Figure 1): (i) work-package (WP) overviews summarizing the status of each WP and further steps; (ii) individual talks where each partner presented the work conducted during the 1st year of the project; and (iii) webinar as part of the training activities within the project.

Agenda (15 th - 16 th May 2018)	
	
Tuesday 15th May 2018	Wednesday 16th May 2018
10:00 ExCom meeting <i>(restricted to ExCom members)</i>	09:00 Individual talks (continuation)
12:30 LUNCH	09:00 CEA talk (15'+5') – WP2 + WP4
13:30 Welcome	09:20 VTT talk (15'+5') – WP2 + WP4
13:40 WP Overviews	09:40 UCAM talk (15'+5') – WP2 + WP4
13:40 WP1 Overview (15'+5')	10:00 USFD talk (15'+5') – WP2 + WP4
14:00 WP2 Overview (10'+5')	10:20 A21 talk (15'+5') – WP5
14:15 WP3 Overview (10'+5')	10.40 Coffee break
14:30 WP4 Overview (10'+5')	11:00 Individual talks (continuation)
14:45 WP5 Overview (15'+5')	11:00 Armines talk (15'+5') – WP5
15:10 Coffee break	11:20 PSI talk (15'+5') – WP5
15:30 Individual talks	11:40 NNL talk (10'+5') – WP2 + WP5
15:30 JRC talk (15'+5') – WP2 + WP3	12.00 LUNCH
15:50 KIT-INE talk (15'+5') – WP2 + WP3	12:00 EUG meeting (with Lunch)
16:10 CTM talk (15'+5') – WP2 + WP3	12:30 EUG + ExCom meeting
16:30 Studsvik talk (15'+5') – WP3	13:00 General Assembly (GA)
16:50 CIEMAT talk (15'+5') – WP2 + WP4	13:30 EUG feedback
17:10 JUELICH talk (15'+5') – WP2 + WP4	13:45 Webinar (1h), by Kastriot Spahiu
17:30 SCK-CEN talk (15'+5') – WP2 + WP4	“The influence of the fuel composition and of the content of various non-uranium cations on the oxidative fuel dissolution”
19:30 WORKSHOP DINNER	14:45 End of the 1st Annual Workshop

Figure 1: General agenda of the 1st Annual Meeting of DisCo.

In addition to the technical sessions, the meeting included the following sessions focused on the management and progress of the project.

- › ExCom meeting: the Coordination Team (CT), WP leaders and one member of the EUG discussed on the progress of the project, organizing future events (meetings, training...), identify deviations and providing/suggesting solutions.

- EUG meeting was restricted only to member of the End User Group. As Waste Management Organizations and Regulators, they ensure that the research conducted remains within the scope initially set and it is relevant and useful for the ultimate goal of safe radioactive waste disposal. At the end of each meeting they are providing their advice on the project status to all Consortium Members. Their feedback is included in the present Proceedings, Section “*Summary of Feedback from the end User Group*”.
- The General Assembly is the forum where actions that must be approved by all partners take place. All decisions taken during that Assembly are compiled in the Meeting Minutes which are available at the project website.

One important goal of this meeting was the organization of the 1st Webinar. The webinar was on “The influence of the fuel composition and of the content of various non-uranium cations on the oxidative fuel dissolution” and was given by Kastriot Spahiu (SKB). It was followed by all the DisCo attendees and by 22 persons connected online via the Webex platform. The webinar was recorded and it is available under demand (instructions at the project webpage).

The Coordination Team want to thank all DisCo participants and the host organization, the University of Sheffield, for a well-organized and productive meeting. We are looking forward the next meeting that will be held in May 2019 in Cologne (Germany), hosted by the Research Center of Juelich (FZJ).



Figure 2: Group photo of the 1st DisCo Annual Meeting attendees.

It is important to mention that the meeting was followed by the 29th Spent Fuel Workshop (SFW, 17th – 18th May). Most of DisCo participants also attended the SFW and gave presentations showing the work conducted within DisCo.

WP Overview

WP1 Overview: Management, coordination and dissemination

Lena Z Evins, SKB (SE)

The progress of the project is overseen and managed in Work Package 1, divided into two main tasks:

- 1) General management and coordination
- 2) Communication, dissemination and training

Task 1 involves maintaining all the general project management tasks including the financial and legal matters, while Task 2 involves setting up and maintaining all the communication tools used in the project, such as the webpage, meetings, webinars and other training events.

The following deliverables have been submitted during the first year of the project. All of them are available at the project website.

- D1.1 Web site open
- D1.2 Kick-off minutes
- D1.3 Newsletter #1
- D1.4 Plan for Webinars
- D1.5 LinkedIn Group Established
- D1.6 1st Mobility Grant Announcement
- D1.7 Webinar 1
- D1.8 AM1 Minutes
- D1.9 Newsletter#2
- D1.27 Plan for peer-reviewed publications in scientific journals

The project has passed the two first milestones: The Kick-off meeting, held 13 June 2017 in Brussels, and the First Annual Meeting, held 15-16 May 2018 in Sheffield. Overall, the project is following the work plan, and there are no indications that the risks identified during the project development stage will pose any problems or delays.

The next annual meeting is planned to be held in Cologne (Germany) in May 2019 (the exact date will be soon published at the project webpage). The meeting will be hosted by Juelich.

Legal and financial status

The work with the Consortium Agreement (CA) started in February 2017 and several versions have been distributed for review by project partners and their legal counsel. The CA was fully signed in April 2018.

The AG Agreements are now signed, while a small typing error in the EUG Agreement caused a delay. At the time of writing, it is in the process of being signed by the EUG members.

Connected to the CA is the Consortium Plan. In practice, this is the channel through which some minor changes in activities or budget can be documented without requiring an amendment to the Grant Agreement. There is no draft document yet to distribute but it is under development.

Preliminary reporting to the Coordinator is under way. The purpose is to make sure all participants are working according to plan and that there are no reporting difficulties. Once this is ensured, the second payment (part of the prefinancing) will be distributed.

Official reporting to the EU for the first 18 month period will take place December 2018 to January 2019.

Communication actions

During the first year, the general communication tools have been put in place. The webpage (<https://www.disco-h2020.eu/>) with a Twitter feed displaying all tweets tagged with #discoH2020 has been functional since 1 September 2017.

The LinkedIn Group, also active since September 2017, has now 31 members, representing most of the project participants and some project external members.

A first newsletter was distributed in July 2017 after the Kick-off meeting. The second newsletter has been released June 2018. It contains a summary of the project status reported during the first annual meeting, and it is available in the project website

The first Webinar, featuring Professor Kastriot Spahiu (SKB & Chalmers, Sweden) dealt with “The influence of the fuel composition and of the content of various non-uranium cations on the oxidative fuel dissolution” and it was attended by the project meeting attendants as well as followed on-line by 22 people from 10 different countries and the European Commission.

The available Mobility Grant to attend the 1st Annual Meeting was announced in December 2017. The members of the Associate Group from the countries with less advanced programs are first priority. There was no application for the grant this year, which means there will be more money available for the rest of the training events. In addition, at the Annual Meeting there was an announcement of individual training opportunity at JRC Karlsruhe. Information regarding the visits and application procedure can be found on the DisCo website.

WP2 Overview: Preparation and characterization of samples and experimental systems

Farnan, I., University of Cambridge (UK)

Preparation and characterisation of model and spent fuel materials (as of April 30th 2018)

This work package concerns the preparation and characterisation of model spent fuel samples, which includes accelerated aging with alpha-emitter doping, and actual spent fuel experimental systems before dissolution experiments are initiated. The purpose is to employ advanced micro-analytical tools on model (unirradiated, depleted or natural uranium material) that could not be deployed on spent nuclear fuel itself and to align models with higher activity experiments. The package is split into three sections for experiments involving *Hot Cells* (WP 2.1); *Alpha Glove Boxes* (WP 2.2) and *U/Th Laboratories* (WP 2.3). NB some samples for hot cell work in WP3 are already prepared and characterized and have been made available by Studsvik and CTM.

WP 2.1(a): Hot cell work at KIT-INE

Fuel	Burn-up	Forms
MOX	38 MWd·kg _{HM} ⁻¹	Three samples: two de-cladded fragments, one cladded segment.

The details of the irradiated MOX sample are as follows:

Sample is from the Obrigheim PWR (Germany) and was a 3.2% plutonium MOX fuel fabricated with the optimised co-milling method. The fuel was in the reactor for 1,157 days with an average linear power of 200 W·cm⁻¹ and an average burn-up of 38 MWd·kg_U⁻¹. It has cooled for 32 years and the fission gas release was 6%.

Four samples with zircaloy cladding have been cut from this material with a low speed saw and are being kept in a closed steel container, flushed with argon to prevent oxidation. One 4 mm segment is to be used for inventory determination and the second, 6 mm segment, for ceramography. One 10 mm cladded segment and fragments of a decladded segment will be used for dissolution experiments.

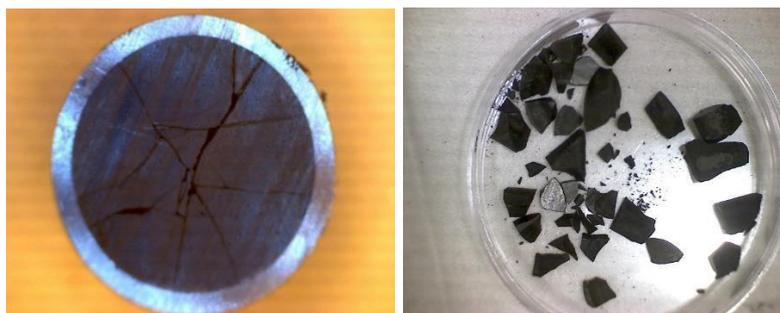


Figure 1: (a) cut pellet with zircaloy cladding (b) fragments for leaching experiments.

WP 2.1(b): Hot cell work at JRC

Fuel	Burn-up	Forms
MOX	40-60 MWd·kg _{HM} ⁻¹	Cladded segments
Cr-UOX	40-60 MWd·kg _{HM} ⁻¹	De-cladded segments

The MOX spent fuel (M502) was fabricated by the short binderless route (SBR) and had five power cycles in the Beznau PWR to give an average burn-up of 54 GWd·t_{HM}⁻¹ with an average linear power rating of 18 kW·m⁻¹. Two samples have been cut, MOX-H and MOX-L with local burn-ups estimated from gamma scans of 56 and 48 GWd·t_{HM}⁻¹, respectively. Both yielded a 2.5% fission gas release. Three cladded segments have been prepared for leaching, microscopic characterisation and chemical inventory and burn-up measurements.

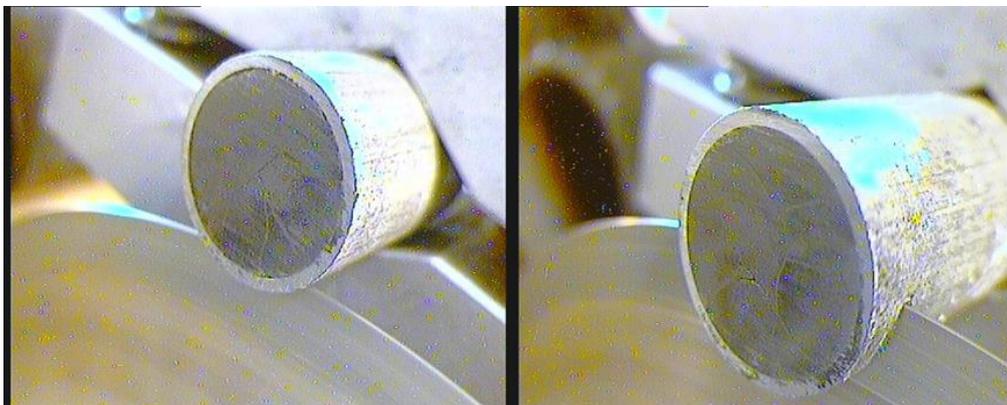


Figure 2: Cutting of MOX pellets (a) MOX-H (b) MOX-L.

Seven samples have been cut from a Cr-doped UOX fuel with an average burn-up of 58 GWd·t_{HM}⁻¹. Two will be used to prepare de-cladded fragments for leaching, one for chemical inventory and burn-up and one for microscopic characterisation. Others will be held in reserve. The leaching autoclave has been extensively tested for H₂ tightness and confirmed at less than 0.3 bar per annum at a pressure of 50 bar. Optical and ceramography characterisation for both MOX and Cr-UOX spent fuels is likely to be significantly delayed due to a failure in a hot cell where the equipment is housed. As it will exceed the deliverable (D2.1) deadline this will be addressed by a revised deadline for this characterisation to be reported as part of WP3 deliverables.

WP 2.1(c): Hot cell work at NNL

Fuel	Burn-up	Forms
UOX	21.2 GWd·t _{HM} ⁻¹	Solid pellet
UOX	7.3 GWd·t _{HM} ⁻¹	Hollow pellet

Twelve samples from intact fuel pins exposed to water in pond for > 40 years have been cut. Two of these will be used in DisCo and the exposed surfaces will be subject to examination with state-of-the-art gamma scanning optical and scanning electron microscopy and Raman spectroscopy as part of a

capability upgrade. The replacement of a shield window in the cave has delayed work thus far. This cave should be available again by June 2018.

WP 2.2(a): Alpha glovebox work at SCK·CEN/Jülich

Fuel	Doping (Laboratory)
UO ₂	Reference (Jülich)
Cr-UO ₂	Reference (Jülich)
UO ₂	²³⁸ Pu (SCK-CEN)
Cr-UO ₂	²³⁸ Pu (SCK-CEN)

Sample preparation techniques for the reference materials have been established at Jülich to optimise the production of alpha doped material. Precipitation from an ammonium diuranate solution followed by a range of heat treatments have allowed reduction and sintering temperatures to be established that produce > 95% theoretical density pellets of Cr-UO₂ and UO₂ reference materials. A wet coating followed by thermal treatment has been shown to produce an appropriate grainsize for Cr-doped reference materials (~ 19 µm) as compared with a co-precipitation production method where reference and undoped UO₂ materials exhibited a grain size of around 12 µm. Electron back scatter diffraction (EBSD) has been used to characterise the reference materials with focused ion beam (FIB) trenching of the measured area to allow post-dissolution examination of any differences in dissolution between different crystallite orientations. The sample preparation methods are ready to be deployed at SCK·CEN to produce the alpha doped versions.

WP 2.2(b): Alpha glovebox work at CEA Marcoule

Fuel	Description
24.1% U/PuO ₂ MOX	Unirradiated, homogeneous
7.3% U/PuO ₂ MOX	Unirradiated, inhomogeneous

Two materials existed for the experiment, but needed to be returned to $t = 0$ state of radiation damage and dissolution testing by thermal annealing and polishing. Pu, U and O maps were made of the materials before and after thermal annealing. These materials were also analysed for Pu, U and O content, which revealed measured Pu contents of $27 \pm 0.5\%$ Pu and a formula of $U_{0.73}Pu_{0.27}O_{1.990 \pm 0.004}$. This composition was also confirmed by the calibrated Raman shift of the principal mode of the fluorite structure. The α -activity of the pellet is $2.2 \cdot 10^9$ Bq·g⁻¹, which is similar to a MOX fuel with a burn-up of 47.5 GWd·t_{HM}⁻¹ that has been out of reactor since 1985 (22% ²³⁸Pu of total Pu). The two (homogeneous and in homogeneous) samples have been released for dissolution studies.

WP 2.3(a): U/Th lab work at USFD

Fuel	Description
UO ₂	Hot isostatically pressed (HIP)
UO ₂ +Cr	Hot isostatically pressed (HIP)
UO ₂ +Al/Cr	Hot isostatically pressed (HIP)

Two reference materials of UO_2 and $\text{UO}_2 + 1,000$ ppm Al have been prepared by dry synthesis. The aluminium does not appear to be incorporated into the fluorite structure of $\text{UO}_2 + \text{Al}$ (too low to detect by XRD). EDX shows Al agglomerating and possibly decorating grain boundaries. USFD has an approved work certificate (July 2017) to operate HIP with up to 18 g UO_2 for the production of high-density samples.

WP 2.3(b): U/Th lab work at CIEMAT

Fuel	Description
UO_2	0.02 wt%, 0.06 wt% Dry route, pressed pellet
$\text{UO}_2 + \text{Al}_2\text{O}_3$	0.02 wt%, 0.06 wt% Dry route, pressed pellet
$\text{UO}_2 - \text{Cr}_2\text{O}_3 - \text{Al}_2\text{O}_3$	0.05 wt% - 0.02 wt% Dry route pressed pellet
$\text{UO}_2 - \text{Gd}_2\text{O}_3$	4.5 wt% Dry route pressed pellet

Dry route preparation of the four samples has been completed, the sintered pellet densities have increase from ~ 80% for UO_2 to ~ 90% of theoretical densities for pellets containing additives. X-ray diffraction, and Archimedes density measurements have been made on pellets and powders. Samples have also been characterised by Raman spectroscopy in anticipation of post dissolution surface analysis.

WP 2.3(c): U/Th lab work at UCAM

Fuel	Description
U/Th MOX 75:25	Wet route, pressed pellet (homogeneous)
U/Th MOX 90:10	Dry route, pressed pellet (inhomogeneous)

Work on project began in March. Uranium and thorium nitrate have been purchased as starting materials, an homogeneous starting material $\text{U}_{0.75}\text{Th}_{0.25}\text{O}_2$ will be prepared by a wet route and used to prepare the two dry milled (inhomogeneous) samples. Some samples of thin (100 nm) films of U/Th/Ce oxides are also being sourced to support the project.

WP3 Overview: Spent fuel dissolution experiments

Ernesto González-Robles, KIT-INE (DE)

Introduction

The overall objective of WP3 is to provide results regarding the matrix dissolution of different fuel types, such as: MOX, UO₂ doped with Cr or Al/Cr and UO₂ under relevant disposal conditions. In addition, and taking into account the conditions of the different experiments performed by the institutes involved, it could be also possible to evaluate:

- Influence of the presence of dopants in the fuel: comparison with UO₂ fuels.
- Influence of different water composition.
- Influence of the H₂ content.
- Influence of the axial position of the pellets.

Finally, in those experiments performed with fresh samples it will be also possible to provide results on the Instant Release Fraction (IRF).

The experiments planned for the institutions involved in WP3 are briefly described here below:

Karlsruher Insitute für technologie (KIT) is going to perform two leaching experiments with a MOX fuel with an average burn-up of 38 GWd·t_{HM}⁻¹. The experiments will be done in autoclaves using two types of fresh samples a cladded segment (as a pellet) and decladded fuel fragments in contact with bicarbonate water (19 mM NaCl and 1 mM NaHCO₃) under anoxic/reducing conditions using an Ar/H₂ gas mixture at a pressure of 40 bar that implies a H₂ partial pressure of 3.2 bar. At the beginning of the experiments, one washing cycle will be performed with the same leachant to eliminate any pre-oxidized layer.

Studsvik Nuclear AB (STUDSVIK) is going to perform two experiments with an UO₂ fuel with an average burn-up of 57.1 GWd·t_{HM}⁻¹ and an UO₂-Al/Cr doped fuel with an average burn-up of 59.1 GWd·t_{HM}⁻¹. The experiments will be performed in autoclaves using fuel decladded fragments, already leached in previous experiments, in contact with bicarbonate water (10 mM NaCl and 2 mM NaHCO₃) and with a pressure of 50 bar of H₂. Before the start of the experiments the samples will be washed five times to eliminate any pre-oxidized phases formed during humid-air storage in cell.

The Joint Research Centre-Karlsruhe is going to perform three experiments using a MOX fuel with an average burn-up of 54 GWd·t_{HM}⁻¹ and UO₂-Cr doped fuel with an average of 58 GWd·t_{HM}⁻¹. A single experiment will be carried out in an autoclave using decladded fragments of the UO₂-Cr doped fuel in contact with bicarbonate water (10 mM NaCl and 2 mM NaHCO₃) and with a pressure of 50 bar of H₂. The other two experiments will be done in autoclaves using cladded segments of the MOX fuel rod, cut at different axial positions, with a length of 2.5 mm in contact with bicarbonate water (19 mM NaCl and 1 mM NaHCO₃) and with Ar atmosphere.

The Centre Tecnològic de Manresa (CTM) is going to perform three leaching experiments with a UO_2 fuel with an average burn-up of $60 \text{ GWd} \cdot \text{t}_{\text{HM}}^{-1}$. Three clad segments with a length of 2.5 mm will be cut from the fuel rod at different axial positions. The first experiment will be performed using cementitious water under air. The other two experiments will be performed in autoclaves using bicarbonate water (19 mM NaCl and 1 mM NaHCO_3) and cementitious water under a pressure of 50 bars. The atmosphere will contain either pure H_2 or a mixture of Ar and H_2 .

Achievements

After the first year of the project all the institutions have set up the autoclaves and prepared the samples. Two of the four institutions have already started the experiments.

KIT has started both experiments. The first two samples corresponding to the wash cycle and the static leaching experiment have been taken.

STUDSVIK has set up the autoclaves and the pressure loss at 50 bar has been measured with He given as result $0.16 \text{ bar} \cdot \text{month}^{-1}$. before the start of the experiments, four wash cycles have been performed to the fuel samples using a solution of 10 mM NaCl and 2 mM NaHCO_3 . The duration of each wash cycle have been 1 day, 6 days, 2 weeks and 1 month, respectively. The last wash cycle with a duration of 2 months is ongoing.

JRC-Karlsruhe has prepared the samples. They are kept under Ar atmosphere to avoid the oxidation of the fuel surface before the start of experiments. The autoclaves have been set up and the pressure loss at 50 bar has been measured to be less than $0.3 \text{ bar} \cdot \text{year}^{-1}$ in the case of H_2 . In addition, the development of a method to measure ^{79}Se in solution has been started.

CTM has started the experiment performed with clad segments in contact with cementitious water under air atmosphere. Ten samples have been taken and analysed providing the first results. In the case of the experiments with a pressure of 50 bars, the autoclaves have been set up and the samples have been prepared. The samples are kept under Ar atmosphere to avoid the oxidation of the fuel surface before the start of experiments.

WP4 Overview: Model material dissolution experiments

Dirk Bosbach, FZJ (DE)

The main objectives of work-package 4 are: (1) Understanding matrix corrosion of modern LWR fuels under deep geological repository relevant conditions, (2) Systematic corrosion studies on Cr-doped- UO_2 -based and MOX model systems (prepared in WP2) complementary to SF corrosion studies in WP3 and (3) Special focus will be on the long-term (> 1,000 years) matrix corrosion by using alpha-doped model systems. The experimental programme is intended to overcome the inherent complexity of spent fuel corrosion and to identify the separate effects of microstructure, doping, reactive surface area in support of the spent fuel corrosion studies in WP3. The results will allow for improving the predictive capability of SF corrosion models and reduction of associated uncertainties.

The work package started formally in February 2018 and comprises contributions from FZJ, SCK·CEN, CIEMAT, CEA, VTT, UCAM as well as USFD and is organized according to the following matrix:

Samples	Bicarbonate water reducing, anoxic (H_2) (derived from WP3) (+/- additional components)	Cementitious water (YCWCa) pH ~13.5, Reducing, anoxic (H_2) (derived from WP3)	Synthetic Cox water Callovo-Oxfordian Water) (+/- Fe(0))	Natural ground water, with Fe(0)
UO_2 (reference sample)	JUELICH, SCK·CEN, USFD	JUELICH, SCK·CEN		
$\text{UO}_2 + \alpha$ dopant ($^{238}\text{Pu}/^{233}\text{U}$)	JUELICH, SCK·CEN, VTT	JUELICH, SCK·CEN		VTT
$\text{UO}_2 + \text{Cr/Al}$	JUELICH, SCK·CEN, CIEMAT, USFD	JUELICH, SCK·CEN, CIEMAT		
$\text{UO}_2 + \text{Gd}$	CIEMAT	CIEMAT		
$\text{UO}_2 + \text{Cr/Al} + \alpha$ dopant (Pu-238/U-233)	JUELICH, SCK·CEN, VTT	JUELICH, SCK·CEN		VTT
$\text{UO}_2 + \text{Gd} + \alpha$ dopant ($^{238}\text{Pu}/^{233}\text{U}$)	CIEMAT	CIEMAT		
Homogeneous unirradiated MOX ($\text{U}_x\text{Pu}_{1-x}\text{O}_2$) (high α)			CEA	
MOX ($\text{U}_x\text{Th}_{1-x}\text{O}_2$)	UCAM	UCAM		

The specific activities of each WP partner include:

FZJ – First scoping tests of accelerated dissolution experiments using H_2O_2 bearing bicarbonate solutions were performed. Additionally, these tests were used to optimize and finalize the experimental set up. The new setup allows accomplishing 11 dissolution experiments (blanks + “real” experiments) in parallel. This leads to a better control of the experimental parameters, e.g. degradation of H_2O_2 . At the moment initial blank tests are in progress.

SCK·CEN – SCK·CEN has been performing preparatory tests to optimize the experimental conditions that will be used for the planned leach tests on Cr-doped model UO_2 with and without alpha emitters (^{238}Pu). The main objective was to fix effectively reducing conditions that will keep the uranium concentration due to oxidation with airborne O_2 as low as possible, in order to better discriminate the oxidizing effect of radiolysis. Several candidate reducing agents were tested. This most promising method has been tested further with depleted UO_2 in the autoclaves that will be used for the DisCo experiments, using the two standard leach media in the DisCo project (bicarbonate water at pH 8.5 and cementitious water at pH 13.5) under argon and H_2 atmosphere. The results were presented at the annual DisCo meeting in Sheffield. Further preparatory tests are planned with addition of a Pd catalyst to the headspace of the autoclaves to remove all traces of O_2 in the atmosphere of the autoclaves by reaction with the H_2 gas. The optimization of the experimental conditions will continue in the second semester of 2018. The first DisCo experiments with Cr doped UO_2 are planned early 2019.

CIEMAT – This work is dealing with the understanding of the corrosion mechanisms of unirradiated fuel at high pH cementitious waters. The characterization of raw materials and samples to be tested are ongoing and the design and preliminary test of new experimental set-ups have already performed.

CEA – Homogeneous $(\text{U}_{0.73}\text{Pu}_{0.27})\text{O}_2$ solid solution pellets (1 cm thickness and 5.4 mm diameter) were selected for the leaching experiment. The pellets were characterized by EPMA, XRD and Raman spectroscopy to check the homogeneity of the plutonium distribution and to collect structural information. In parallel, the alpha-activities of the MOX fuel were recalculated at the date of the leaching experiment and the alpha, beta and gamma dose rates determined at the surface of a pellet and in the homogeneous solution. Iron foils were placed in the system to simulate the iron canister and to stabilize the redox conditions in the reactor. After the iron pre-corrosion phase, the reactor was opened to add two MOX pellets, which were placed on a support above the iron foil. The reactor was then closed again, purged with a mixture of Ar/CO_2 3,000 ppm for 30 min, and returned to a pressure of 3.5 bars. Samples of the leaching solution were regularly collected over time. The first results indicate a significant effect of iron on the oxidative dissolution of this homogeneous MOX fuel. Uranium concentrations are less than $1 \mu\text{g}\cdot\text{L}^{-1}$ after one month of leaching. These results are similar to those obtained on Pu-doped UO_2 or on heterogeneous MOX fuels. The experiment will continue for a long time and all the surfaces (MOX, iron foil) will be characterized at the end of the experiment.

VTT – VTT has planned to conduct the leaching test with Cr or/and alpha doped UO_2 in groundwaters from the Olkiluoto site, which is the planned site for disposal of spent nuclear fuel in Finland. The experiments will be started with old, already existing ^{233}U -doped UO_2 materials in brackish OL-KR6 groundwater under Ar glove box conditions. The OL-KR6 groundwater will be sampled and imported into the glove box in June. The UO_2 materials will be pre-leached with bicarbonate solution before starting the experiments in natural groundwater. Experiments with the new UO_2 material fabricated in DisCo project will be conducted in a saline groundwater from the disposal depth (450-500 m). This water will be sampled from Olkiluoto during autumn 2018.

UCAM – A post-doctoral fellow (Aleksiej Popel) was hired in March 2018 and is working on sample preparation (WP2). In preparation for dissolution activities in WP4, the ‘recipe’ for the preparation of the Callovo-Oxfordian clay groundwater solution has been obtained from Dr Martin (ANDRA) and a meeting has been arranged for the 18th July in Paris with Dr. Jegou (CEA) and Dr deWindt (ARMINES) to coordinate the U/Pu MOx dissolution and modeling with the U/Th MOx work at UCAM. This meeting will primarily discuss how to introduce an oxidative dissolution component into the U/Th experiments to mimic the radiolysis in the U/Pu MOx system and the detailed modeling of the compositional variation in the U/Th system.

WP5 Overview: Chemical modelling

Lara Duro, Amphos 21 (ES)

Introduction

WP5 focuses on the development and application of chemical models describing the solid and aqueous phases. The work package is divided in the following major tasks:

1. Thermodynamic equilibrium calculations, targeting (a) the effect of dopants in the dry matrix in terms of oxygen potential and (b) dissolution/precipitation reactions inside the water-saturated canister.
2. Matrix dissolution model, incorporating redox and electron transfer reactions involving matrix, separate phases (e.g. metallic fission products), radiolysis and hydrogen in the system.
3. MOX dissolution model, focusing on the interplay with Fe species released from iron-based canister materials.

Four partners are participating in this WP: Amphos 21 (ES), PSI (CH), NNL (UK) and Armines (FR). Task 1 is developed by Amphos 21, PSI and NNL; Task 2 is developed by Amphos 21 and NNL, and Task 3 is developed by Armines.

Preliminary results

After the first year of the project all the institutions have started to develop their models, which have been presented in 4 Scientific and technical contributions to the proceedings [1-4].

Amphos 21 has started to develop an integrated methodology for coupling radiolysis and chemistry in a spent fuel matrix alteration model. The methodology considers the combination of the calculation codes Chemsimul [5] and iCP [6]. The method aims at simulating the dissolution of SF inside a failed waste container. The code integration is achieved by a one-way coupling approach. First, water radiolysis is simulated with Chemsimul. Then, the concentrations of the predominant radiolytic species: H_2O_2 , O_2 , and H_2 calculated with Chemsimul at different times are introduced in iCP as source terms to calculate solute transport and SF dissolution.

The validation of the kinetic constants used in the model has been done by comparison with the experimental data described in Cera et al. [7]. The first step of the validation exercise was modelling with Chemsimul the generation rates of oxidants and reductants from the alpha and beta dose rates. The full radiolysis scheme of water radiolysis in a solution containing carbonate and chloride was considered. The generation rates of H_2O_2 , O_2 and H_2 determined in Chemsimul were implemented in PhreeqC, together with the set of kinetic reactions described above occurring at the surface of spent fuel. Once the kinetic rates have been validated, the model will be implemented in 1D reactive transport approach.

PSI work during the first project year has been focused on the selection of key thermodynamic data for exploring the effect of dopants, such as Cr and Al, on the oxygen potential of modern UO_2 fuels, and their integration in the databases and speciation codes that will be used to that purpose. In addition, the development of a model for substitution of Cr in UO_2 and its translation to a solid solution model to be implemented into the GEM-Selektor code was started.

A thorough selection of thermodynamic data for Chromium oxides was conducted by PSI from data in the literature regarding solid and gaseous species. The selected data were implemented into the GEM-Selektor code (<http://gems.web.psi.ch>) and Heracles database (<https://www.psi.ch/heracles/gems-specific-heracles-database>), and build the basis for thermodynamic calculations on Cr-doped fuels. Test calculations have been carried out to prove the consistency of the selected data with the experimental results of previously published studies. The calculations conducted by PSI on the oxygen potential of the spent fuel with and without Cr-doping, indicated that the oxygen potentials were identical or very slightly higher for undoped than for Cr-doped fuel.

We must bear in mind, however, that these results are based on an ideal model and for an ideal fuel composition, which is unrealistic considering the charge and cation size mismatch upon substitution of Cr(III) into the UO_2 lattice. Therefore, a major task in the coming project year will be to develop a realistic Cr- UO_2 solid solution model and to derive interaction parameters defining non-ideality.

Armines has continued the development of a previous reactive transport model on UOX dissolution. Implemented by HYTEC, the model considers the effect of the kinetic oxidation of Fe^{2+} by H_2O_2 on the rate of oxidation of UO_2 . The results indicate that the experimental concentrations of uranium in solution are better reproduced by considering that the interaction between Fe^{2+} and hydrogen peroxide is fast or close to equilibrium, while considering a slow reaction allows for H_2O_2 availability for UO_2 oxidation, thus overestimation of the uranium dissolved concentrations. The concentration of Fe, nevertheless, is not much affected by this reaction. The explanation is that the concentration of Fe is much higher than that of H_2O_2 , and is controlled by the solubility of iron corrosion products (chukanovite, siderite).

The preliminary HYTEC modelling of the dissolution experiment of $\text{U}_{0.73}\text{Pu}_{0.27}\text{O}_2$ under development within WP2 by CEA shows that the presence of iron foil is an important factor decreasing the dissolution of the doped material because dissolved Fe^{2+} inhibits the oxidative dissolution generated by localized alpha radiolysis of water molecules. The determination of the dissolution kinetic rate constant of $\text{U}_{0.73}\text{Pu}_{0.27}\text{O}_2$ in carbonate water under Ar atmosphere is in progress as well.

NNL is developing a hydraulic model of the pond storage system to enable appropriate boundary conditions to be modelled and allow the NNL Mixed Potential Model to be applied to model the corrosion of fuel in storage ponds. The updated model is intended to be used to provide predictions of dissolution rates, chemical equilibria and secondary phase formation under oxidic conditions relevant to NNL material characterised within WP2 and under representative repository conditions (anoxic), focusing on nominal UK granitic rock repository conditions. The development is on-going and will be updated as the project advances.

Next steps

The interaction between modellers and experimentalists have provided a document on data monitoring agreement (D5.1. “Agreement of conditions to consider in the models: discussions between modelling and experimentalists”) where experimentalists have declared the parameters that will be monitored in their experiments so that the modellers can have indications of which type of data will be of use for WP5.

Effective interactions between WP5 and experimental WPs are set and others are underway to achieve the maximum possible integration for the project.

References

- [1] Riba, O., Coene, E., Silva, O., Duro, L. (2018). Integrated spent fuel alteration model. Method and first results. *This volume*.
- [2] Curti, E. and Kulik, D. (2018). Preliminary thermodynamic calculations for WP5, task 1. *This volume*.
- [3] De Windt, L., Kerleguer, V., Jégou, C., Goblet, P., Martin, C. (2018). Modelling of the oxidative leaching of $U_{1-x}Pu_xO_2$ in synthetic groundwater with metallic iron – first results. *This volume*.
- [4] Hambley, D.H., Goode, J., Hughes, R., Maher, C. (2018). Progress on Modelling of UO_2 Fuel Dissolution within Storage Containers-Extended Abstract. *This volume*.
- [5] Kirkegaard, P., Bjergbakke, E., Olsen, J.V. (2008). CHEMSIMUL: A chemical kinetics software package. Roskilde: Danmarks Tekniske Universitet, Risø Nationallaboratoriet for Bæredygtig Energi. Denmark. Forskningscenter Risø. Risø-R-1630 EN. <http://orbit.dtu.dk/files/6278806/ris-r-1630.pdf>
- [6] Nardi, A., Idiart, A., Trincherro, P., de Vries, L.M., Molinero, J. (2014). Interface COMSOL-PHREEQC (iCP), an efficient numerical framework for the solution of coupled multiphysics and geochemistry. *Computers & Geosciences*, 69, 10-21.
- [7] Cera, E., Bruno, J., Duro, L., Eriksen, T. (2006). Experimental determination and chemical modelling of radiolytic processes at the spent fuel/water interface. SKB Technical Report, TR-06-07.

Extended Abstracts

Progress on examination of UO₂ fuel after extended storage

Hambley, D.H. and Goode, J.

National Nuclear Laboratory, Sellafield (UK)

Objectives

In preparation for emplacement of uranium dioxide fuel into long term storage there is an increased interest in the long term behaviour of ceramic fuel when exposed to water. Current understanding of the long term behaviour is based on short term experimental work (typically up to 2 years). Due to the UK's leading role in the development of civil nuclear power it is in the unique position of having small stocks of irradiated fuel that have been in contact with water for in excess of 40 years. The purpose of this work is to examine and characterise the effects of long term water exposure on irradiated uranium dioxide fuel in order to assess the extent to which observations match expectations from shorter term experiments.

Background

Experimental gas-cooled reactor fuel subjected to post-irradiation examination (PIE) was consigned for short term storage prior to reprocessing in the early 1970s. A small quantity was not sent for reprocessing and remained within an early fuel pond until recently, when it was recovered and prepared for long term storage by the National Nuclear Laboratory (NNL). The cans containing the fuel were all found to be full of water. Calculations have shown that the fuel cans would have flooded within a few months of emplacement within the ponds and therefore the fuel will have been exposed to pond water for > 40 years. Work planned in WP5 is intended to provide insights into the likely exchange of water between the cans and bulk pond water and hence the evolution of water chemistry inside the can.

The Windscale Advanced Gas-cooled Reactor (WAGR) was the forerunner or prototype of a family of low enriched, uranium dioxide fuelled power reactors, the Commercial Advanced Gas-cooled Reactors (CAGR), which were first connected to the grid between 1976 and 1988. Advanced gas-cooled reactors consisted of a graphite core containing channels into which stringers of fuel elements were loaded. The core of a CAGR is substantially larger than the prototype WAGR, with each stringer in a CAGR incorporating 8 elements of 36 pins while WAGR used stringers of 4 elements of 18 pins (Figure 1). In each case the pins are similar in size and contained uranium dioxide pellets within a stainless steel cladding.

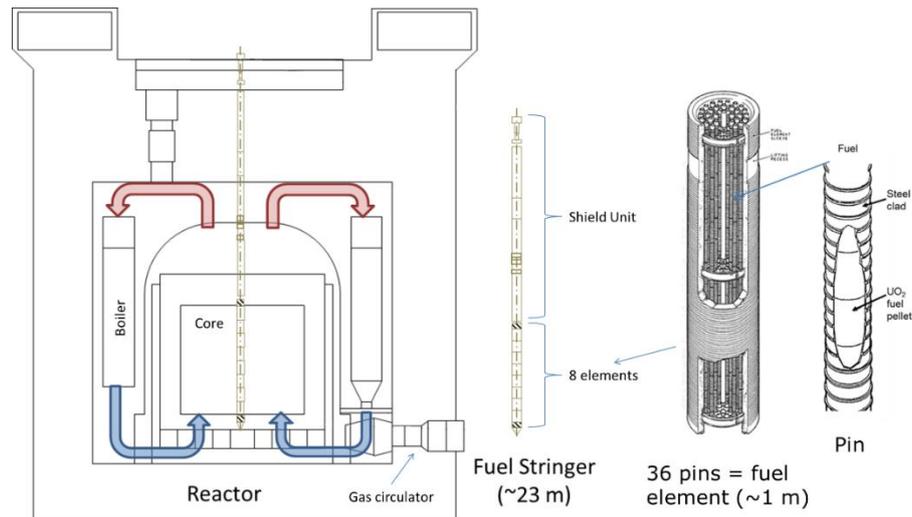


Figure 1: Schematic of a CAGR. Note: The prototype WAGR reactor was of similar design but used stringers with fewer elements and fewer pins.

Although the burnup of WAGR fuel was lower than most current CAGR fuel, the linear ratings are similar, with the main exception being element 2, which in WAGR experienced substantially higher linear ratings (Figure 2). The range of linear ratings experienced in WAGR therefore covers many current operating reactors.

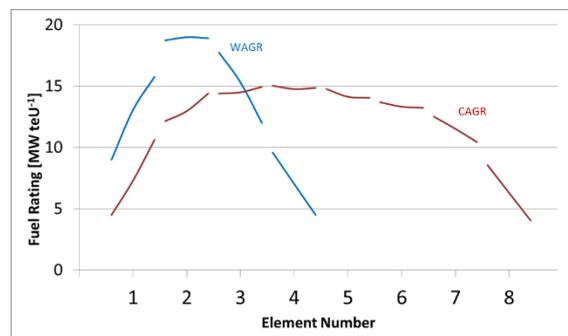


Figure 2: Comparison of typical fuel ratings in WAGR (blue line) and CAGR (red line).

Fuel Selection

Radioactive Waste Management (RWM) are undertaking a leaching programme on CAGR spent fuel as part of work to develop a geological disposal facility (GDF) for the UK. Hence the opportunity exists to compare matrix dissolution rates from these, long-exposed WAGR fuels with those gained from CAGR spent fuel. A sub-set of the available WAGR fuels were selected, in conjunction with RWM, for retention for the GDF leaching programme.

Two cans of recovered fuel were selected as the preferred source of fuel for examination because the fuel was most similar to that used in current AGRs. The fuel was selected to include:

- Cut annular fuel with the highest burn-up.
- Fuel where both cut and substantially-intact fuel pins were expected to be present, again targeting highest burn-up fuel that met these criteria.

Description of Fuel

The recovered cans contained fuel pins of three designs. The fuel pins were 1.07 m long with a Nb-stabilised stainless steel, ribbed cladding of 0.038 cm wall thickness. The fuel pellets were either 1.0 cm in diameter, 1.45 cm in diameter or 1.45 cm in diameter with a 0.3 cm hole at the centre, to provide space to accommodate fission gasses.

A total of 18 sections of fuel pin from two cans was separated during repacking operations and stored pending further examination. Details of the fuel present in the two selected cans is given in the table below.

ID	Pellet size (mm)	Enrichment (%)	Stringer Burnup (GWd tU ⁻¹)	Maximum Pin Burnup (GWd tU ⁻¹)	Mean Time Averaged Rating (MW tU ⁻¹ (kW·m ⁻¹))	Discharge Date
221B/2	10	2.9	10.8	16.4	16 (11.8)	Oct 1965
266/3	14.5	2.2	10.3	14.4	14.2 (21.0)	Oct 1966
<i>221B/4</i>	10	<i>2.9</i>	<i>21.2</i>	-	-	<i>Sep 1968</i>
<i>288/2</i>	14.5	<i>2.7</i>	<i>7.3</i>	-	<i>14.2/10.2</i> <i>(21.0, 15.0)</i>	<i>Mar 1969</i>
424/4	14.5	2.7	6.2	8.9	18 (26.6)	Jun 1969
441/1	14.5	2.7	3.2	-	-	Nov 1968

The items in italic are those that are considered of greatest interest for examination as they are the highest burn-up solid fuel and the highest burn-up hollow fuel. Examples of the current fuel condition are shown in Figure 3 and examples of the fuel structure prior to storage, from historic PIE reports, are shown in Figure 4.

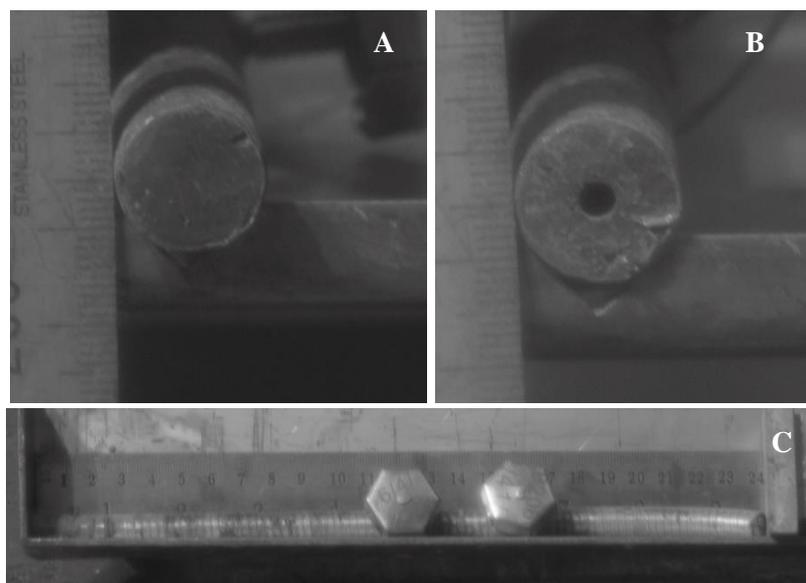


Figure 3: Current fuel condition. A) solid fuel, B) hollow fuel and C) cladding.

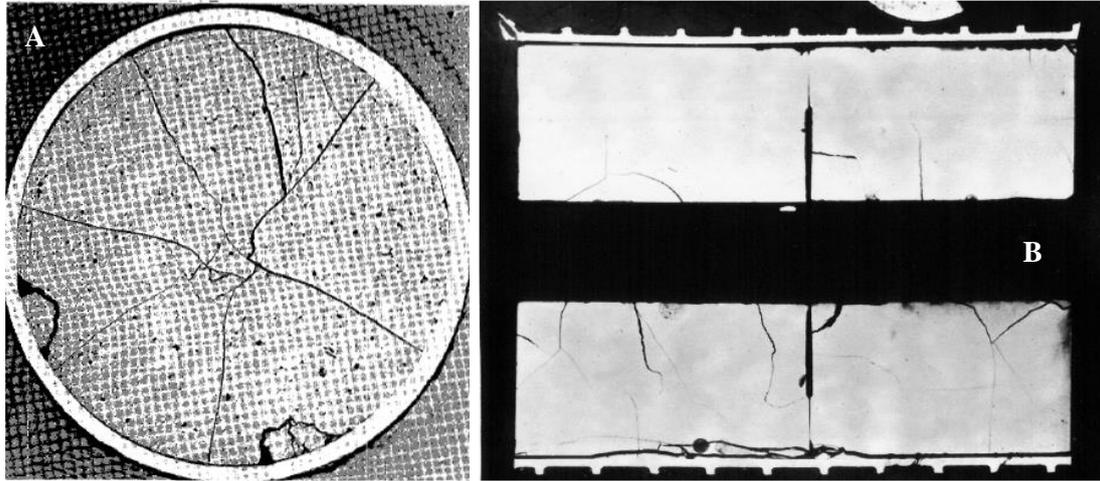


Figure 4: Micrographs from original PIE work. A) Transverse cross section from 221B/2. B) Longitudinal cross section from 228/2.

Planned Work

It is necessary to complete a gamma scan of each for the selected fuel pieces in order to distinguish the fuel of greatest interest from other lower burn-up fuel sections. Unfortunately, this work has been delayed due to a combination of an over-run of the refurbishment of the cave in which the examinations are to be conducted and delays in commissioning of new high resolution fuel gamma scanning equipment. It is currently anticipated that the gamma scanning will be started in June 2018.

Subsequently work is planned as follows:

- Ceramography to provide evidence of the extent of corrosion on cladding, fuel-cladding interface, fuel bore (inner surface of the hollow fuel) and fuel cracks, which is expected to be completed in 2018.
- Electro-optical examination (SEM + XRD) to examine for evidence of grain boundary corrosion and provide quantification of any observed degradation and to provide analyses of any observed secondary phases, which can be compared to existing data on precipitated material found in the storage cans.

Acknowledgement

NNL wishes to thank RWM for permission to use the fuel sections previously retained on their behalf.

The research leading to these results has received funding from the European Commission Horizon 2020 Research and Training Programme of the European Atomic Energy Community (EURATOM) (H2020-NFRP-2016-2017-1) under grant agreement n° 755443 (DisCo project).

SNF sample preparation and ^{79}Se solution production

Serrano-Purroy, D., Carbol, P., Aldave de las Heras, L., Millet, S., Montagnier, G., Papaioannou, D., Pell Lorente, A., Rasmussen, G., Sandow, M., Van Winckel, S., Wegen, D.H.

EC JRC, Karlsruhe (BE)

Introduction

The safe geological disposal of spent nuclear fuel (SNF) requires a robust safety assessment for which the scientific understanding of processes such as spent fuel dissolution is a prerequisite. International collaborations in the last decades have proven invaluable in improving the level of understanding of standard fuels significantly (e.g. SFS, NF-Pro, Micado, FIRST-Nuclides). In parallel, doped nuclear fuels have been developed by fuel manufacturers and utilities. These additive (e.g. Cr, Al, Gd) containing fuels have larger safety margins and are already in use in several reactors. Because of their improved irradiation properties, it can be expected that they will be widely-used in future. It has now to be proven that the corrosion behaviour under repository conditions of such fuels is similar or even better than that of standard SNF. For other fuel types in use like mixed oxide fuels (MOX) the data base is also very scarce and needs to be enhanced.

In June 2017, the project 'Modern Spent Fuel Dissolution and Chemistry in Failed Container Conditions' (DisCo) was launched with the aim to expand the database on SNF corrosion with results from dissolution studies performed under reducing conditions, with hydrogen present. Both SNF and synthetic simulant materials designed for the project will be investigated to study the effects of dopants. Chemical modelling will be performed in the frame of the project to improve the understanding and description of the dissolution process relevant to the expected chemical conditions inside a failed waste container in a deep geological repository.

JRC-Karlsruhe contributes to the project with a study on the long-term stability of advanced Cr_2O_3 -doped UO_2 -fuel in aqueous media under reducing condition. The obtained results will be compared with the well-known behaviour of standard UO_2 -fuel to verify the assumption that Cr_2O_3 -doping has none or only a minor effect on long-term radionuclide (RN)-release under H_2 -overpressure. Not only leachates and solid after leaching, but also the gas phase will be analysed in order to obtain a more complete description of the redox conditions and of the processes affecting the system evolution.

The Instant Release Fraction (IRF) and long-term stability of spent MOX fuels is tested in aqueous solution as well. Fuels with different linear power rate and known irradiation history are used to elucidate structural effects on the RN-release. Analysis of leachates and also of the solid after leaching is required to characterize the fuel alteration process.

Concerning leachate analysis, a renewed focus is on the development of analysis methods for long lived β -emitters like ^{79}Se . Analysis of ^{79}Se concentrations in the leachates of MOX and Cr_2O_3 -doped UO_2 fuel is foreseen to obtain realistic ^{79}Se release rates and thereby decrease the uncertainty of Se-release in the

performance assessment of the repository. An in-house standard solution enriched in ^{79}Se will be separated and purified from PUREX high active raffinate (HAR).

Leaching experiments

Procedure: A total of 3 experiments will be performed using a MOX fuel and a Cr_2O_3 doped UO_2 fuel. Two experiments will be carried out with cladded segments of about 2 mm thick-ness of the same MOX rod sample but with different local irradiation histories. The segments will be introduced in autoclaves containing simplified groundwater (19 mM NaCl + 1 mM NaHCO_3) and filled with Ar (anoxic conditions) mixed with a volume fraction of 0.003% CO_2 . One experiment will be carried out with fragments (without cladding) of the Cr_2O_3 doped UO_2 . The fragments will be introduced in an autoclave containing simplified groundwater (10 mM NaCl + 2 mM NaHCO_3) and pressurised with H_2 (reducing conditions) mixed with a volume fraction of 0.003% CO_2 .

Sample selection and cutting of the samples

MOX samples: the fuel selected is a Short Binderless Route (SBR) MOX (M502) irradiated in Beznau-1 (PWR) for five cycles to a rod average burnup of $\sim 54 \text{ MWd}\cdot\text{kg}_{\text{HM}}^{-1}$ [1]. At no time during the assembly's life did the average power exceed $250 \text{ W}\cdot\text{cm}^{-1}$. Two sampling sections were selected according to the rod axial gamma scan, see Figure 1, and the sample availability.

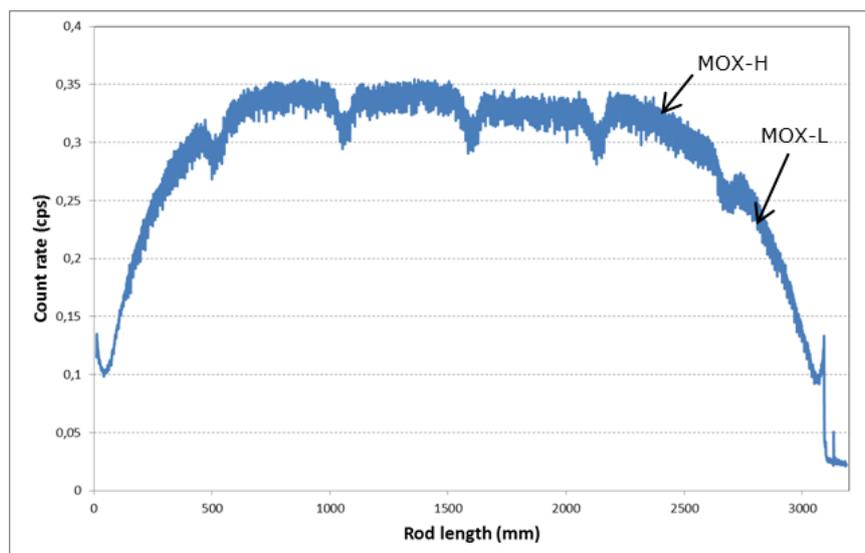


Figure 1: MOX sample rod gamma scanning. Two sections were selected for sample MOX-H and MOX-L.

At each location, three adjacent cladded segments of about 2 mm, without dishing, were cut (Figure 2). One sample from each will be used for the leaching experiment, one is reserved for scanning electron microscopy (SEM) analysis and the last one will be completely dissolved for chemical inventory determination.

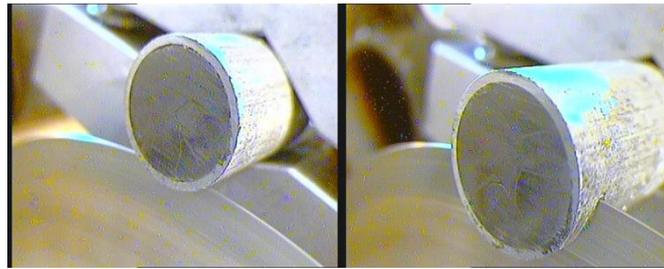


Figure 2: Cutting of MOX samples. Left: MOX-H. Right: MOX-L.

The samples were cut using a Bühler IsoMet low speed cutting machine adapted for use with manipulators and equipped with a diamond cutting blade. The samples were cut in a hot cell purged with N_2 , resulting in an atmosphere with a volume fraction of $< 2\%$ O_2 . Dry cutting was carried out using a diamond cutting blade of thickness ~ 0.20 mm yielding in a cutting loss thickness of 0.22 mm. Heating of the samples was avoided by using a slow rotation speed of less than 600 rpm and high atmosphere exchange in the cell. In addition, minimum pressure was applied to the cutting blade throughout. Measurement of the temperature of the Zircaloy surface above the cutting area showed $36^\circ C$ (the hot cell temperature was $32.5^\circ C$). One cut through the fuel rod with a diameter of 9.4 mm took approximately 45 minutes. No washing of the samples was made upon removal from the rod. The original and cut discs are stored inside an evacuated ($\sim 10^{-2}$ mbar) steel container.

The MOX samples irradiation conditions are listed in Table 1.

Table 1: Identification, enrichment, average and estimated local burn-up and fission gas release (FGR) of the two MOX samples selected.

Sample	Fabrication process	Enrichment	Rod average BU (MWd·kg _{HM} ⁻¹)	Local BU (MWd·kg _{HM} ⁻¹)*	FGR (%)
MOX-H	SBR	5.54% Pu	54	56	2.5
MOX-L				48	

*estimated from the axial gamma scan

Cr₂O₃ doped UO₂ samples: Following the same procedure as for the MOX sample several discs of the Cr₂O₃ doped UO₂ fuel were cut. The sample characteristics are shown in Figure 3.

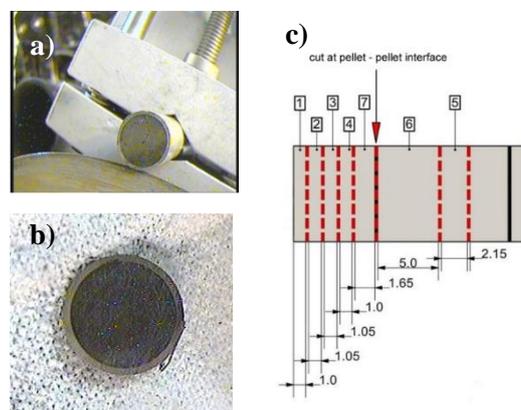


Figure 3: Samples of Cr₂O₃-doped spent nuclear UO₂ fuel: a) cutting, b) top view on one sample, c) cut position of samples.

Actual status: All samples are prepared. The autoclave design is finished and the set-up preparation well advanced. Leaching experiments will start in June 2018 after final modifications and testing of the autoclaves. SEM analysis and chemical inventory determination will be carried out in 2019.

Separation and characterisation of a ^{79}Se in-house reference solution

There is a broad consensus amongst the spent fuel and high-level vitrified waste management community concerning the importance of long-lived fission products for the safety assessment of final repositories for nuclear waste [2]. ^{79}Se , with its half-life of 327,000 years [3], is one of these long-lived fission products. Depletion calculations can provide information about the ^{79}Se inventory but the validation of such calculations is problematic due to a lack of experimental results on ^{79}Se analyses in spent nuclear fuel. In contrast, the focus is also on the analysis of spent fuel leachates. Due to the heterogeneity of spent fuel a congruent dissolution of ^{79}Se and fuel cannot be presumed a priori.

There are two main types of sensitive and selective analytical techniques for ^{79}Se determination, i.e. by radiometric techniques or by mass spectrometric techniques. The fact that ^{79}Se is a pure beta-emitter limits a radiometric determination of ^{79}Se to liquid scintillation counting (LSC) for which a very pure Se sample is needed, separated from all other radio-active fission products of the spent nuclear fuel. This is a challenging and very time consuming task. For a mass spectrometric analysis of ^{79}Se in spent nuclear fuel, the difficulties (besides its low concentration) are the rather low sensitivity (due to the high ionisation potential of Se) and the possible isobaric interferences in the Se mass spectrum. Consequently, it remains a challenging task to provide reliable quantitative analysis of this radionuclide in complex matrices such as spent nuclear fuel and/or leachates of such fuel. This explains the lack of experimental data for ^{79}Se as illustrated in the SF-COMPO 2.0 database (OECD NEA, 2017): from the > 24,000 entries in this extensive spent fuel database, there are only 15 results for ^{79}Se .

For the DisCo-project, ^{79}Se will be analysed in the spent fuel samples (for the inventory data) and in the leachate samples. To our knowledge, no Standard Reference Material for ^{79}Se analyses exists. It is our aim to separate ^{79}Se from a High Active Raffinate solution (HAR), available in our hot-cells, and to purify the solution to the extent needed and characterise this solution for its ^{79}Se content. It can serve as an in-house reference solution for ^{79}Se analyses and will be made available to interested DisCo-partners.

Some experience in collecting ^{79}Se from HAR solution via reductive deposition on metallic copper has been gained [3]. The challenges for the further mass spectrometric analysis are manifold (e.g. isobaric interference by ^{79}Br , $^{40}\text{Ar}^{39}\text{K}$, $^{40}\text{Ar}^{38}\text{Ar}^1\text{H}$, $^{63}\text{Cu}^{16}\text{O}$, ...). Different methodologies in sample preparation (e.g. column separations) and different technologies for analysis (e.g. Sector Field ICP-MS, Collision Reaction Cell ICP-MS) will be tested and optimised for the characterisation of the recovered ^{79}Se solution. The results of preliminary tests will be reported, both for the recuperation of ^{79}Se out of HAR solution as for the characterisation of the resulting solution by ICP-MS.

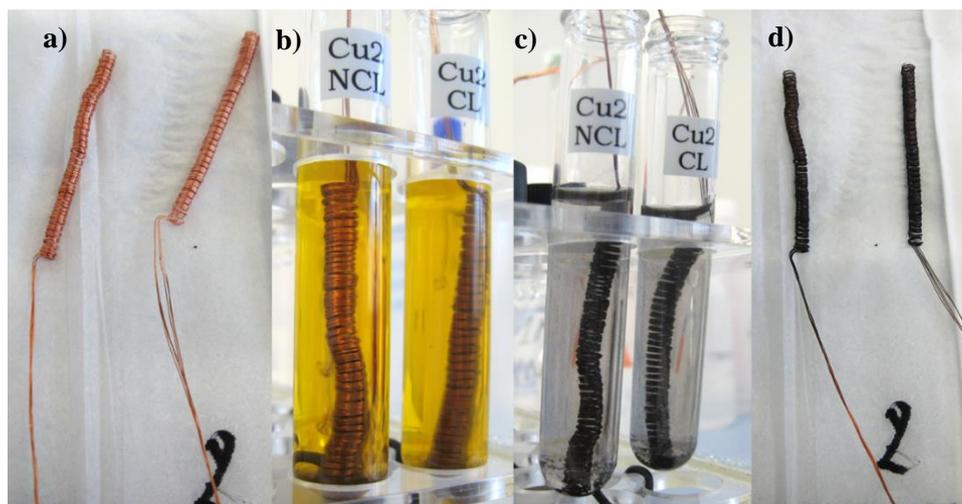


Figure 4: Cold test for the reductive deposition of Se on metallic copper out of simulated diluted HAR at room temperature a) Cu coil before electrodeposition, b) coils in simulated HAR, c) coils in simulated HAR after electrodeposition, d) Cu-coils with deposit).

Acknowledgement

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 755443 - DisCo - NFRP-2016-2017/NFRP-2016-2017-1.

References

- [1] Barker, M.A., Matthews, E., Stephenson, K., Bremier, S., Papaioannou, D., Walker, C., Parmar, Y. (2006). Post-irradiation examination of high burnup SBR MOX fuel. Top Fuel 2006, 2006 International Meeting on LWR Fuel Performance, 22-26 October 2006. Salamanca (Spain), European Nuclear Society (ENS).
- [2] OECD NEA (2011). Spent nuclear fuel assay data for isotopic validation. NEA/NSC/WPNC/DOC(2011)5.
- [3] Jörg, G., Bühnemann, R., Hollas, S., Kivel, N., Kossert, K., Van Winckel, S., Lierse, V., Gostomski, C. (2010). Preparation of radiochemically pure ^{79}Se and highly precise determination of its half-life. Applied Radiation and Isotopes, 68, 2339-2351.

Description of leaching experiments with KIT's MOX irradiated fuel

González-Robles, E., Herm, M., Müller, N., Bohnert, E., Metz, V.

KIT-INE, Karlsruhe (DE)

Abstract

This work focuses on the explanation of the methodology that will be used to perform the leaching experiments with a MOX fuel of $38 \text{ GWd} \cdot \text{t}_{\text{HM}}^{-1}$ within the DisCo project. A complete description of the materials, conditions and analytical methods that will be used during the leaching experiment is given.

Introduction

The disposal in deep bedrock repositories is considered as the preferred option for the management of Spent Nuclear Fuel (SNF) in many countries [1-3]. The aim is to permanently and safely dispose of the radioactive material so that it is isolated from the biosphere for an appropriate length of time. A multi-barrier system is interposed between the SNF and the environment considering the SNF itself as the first technical barrier. In safety assessments for disposal of SNF in deep underground repository, failure of canisters and loss of the integrity of fuel rods is considered in the long term. Some of the radionuclides within the SNF material will be directly exposed to water contact after the barrier failure. Assessing the performance of SNF in a potential future geological disposal system requires the understanding and quantification of the radionuclide release.

Up to now, many studies have been performed on UO_2 irradiated fuels under oxidizing conditions and, in a lesser extent, under reducing conditions, providing information about the matrix dissolution. On the other hand, regarding the matrix dissolution of MOX fuel there is a lack of studies specially under reducing conditions.

The work that will be carried out at KIT-INE will provide data concerning the matrix dissolution of MOX fuel under reducing conditions. In this communication an explanation of the methodology that will be used to perform the leaching experiments with a MOX fuel of $38 \text{ GWd} \cdot \text{t}_{\text{HM}}^{-1}$ is given.

Materials and methods

MOX fuel

The fuel rod segment was irradiated in a pressure water reactor placed at Obbrigheim (KKO) nuclear power plant in Germany. The irradiation was carried out in 4 cycles for a period of time of 1,157 days with an average linear power of $200 \text{ W} \cdot \text{cm}^{-1}$ and achieving an average burn-up of $38 \text{ GWd} \cdot \text{t}_{\text{HM}}^{-1}$. The fuel rod segment was discharged in 1984 that implies a cooling time of 33 years before characterisation and cutting of the segment.

Initially the fuel consisted of natural UO_2 enriched by 3.2% Pu and was fabricated following the optimised co-milling (OCOM) process.

Leachant

Bicarbonate water containing 19 mM NaCl and 1 mM NaHCO_3 , as a simplified matrix of a granitic groundwater, will be employed during leaching experiments. It will be prepared, in a glove-box under Ar atmosphere, with ultrapure water purified with a Milli-Q academic apparatus (Millipore, 18.2 M Ω ·cm, $22 \pm 2^\circ\text{C}$, pore size 0.22 μm) and suprapure grade chemicals (Merck GmbH, Germany).

Autoclave

The leaching experiments will be conducted in 250 mL Ti-lined stainless VA steel autoclaves (Berghof Company, Eningen, Germany) equipped with two valves in the lid to allow sampling of gaseous and liquid aliquots.

Prior to start the experiments, the autoclaves will be firstly modified to enable remote handling by manipulators in the shielded box-line of KIT-INE, and secondly cleaned to remove potentially wall-adhering impurities of the fabrication process. The cleaning process will be carried out in an ultrasonic bath and using three different solutions: i) RBS-solution (Roth chemicals, Karlsruhe), which is a cleaning solution for non-corrosive materials, containing mainly NaOH as well as hypochloride and tenside; ii) 1 M HNO_3 ; iii) Milli-Q-water.

Thereafter, the autoclaves will be submitted to a leak tightness test to ensure a constant pressure during the leaching experiments.

Leaching experiments

Two leaching experiments with samples of the 38 $\text{GWd} \cdot \text{t}_{\text{HM}}^{-1}$ MOX fuel rod segment are foreseen to be conducted under anoxic conditions.

The samples will be a cladded segment (as a pellet) and decladded SNF fragments. The samples will be placed inside of the autoclaves and will be in contact with bicarbonate water, as previously described. Finally, the anoxic/reducing conditions will be established using an Ar/ H_2 gas mixture (92 vol% Ar, 8 vol% H_2 ; provided by Basi and Schöberl GmbH, Rastatt, Germany). The autoclaves will be filled with this gas mixture and the total pressure will be set to 40 ± 1 bar that implies a H_2 partial pressure of 3.2 ± 0.1 bar.

At the beginning of the experiments, one washing cycle will be performed with the same leachant and the first gaseous and liquid samples will be further analysed and the solution will be completely renewed. This wash cycle will be performed to reduce the amount of Cs in solution, which will help with the handle of liquid samples outside the hot cell, as well as to remove any potential U(VI) likely present as a pre-oxidized layer on the SNF surface. In the following static phase of the leaching experiments, small solution aliquots will be sampled at different time intervals to determine the kinetics of the IRF release. The leachant will not be replenished during this static phase.

Gas sampling

In parallel to the sampling of solution aliquots, the gas phase of the autoclaves will be as well sampled. The main interest is in the release of the fission gases, Kr and Xe, as well as the radiolytic gases, H₂ and O₂.

Each autoclave of the leaching experiments will be connected by stainless steel tubing to a pump with an Ar supply within the shielded box line. The steel tubing continues to a stainless steel sampling cylinder that will be placed outside the shielded box. At first, the connections will be purged with Ar. Afterwards the overpressure from the autoclave will be reduced to approximately 1 bar in a controlled way. Once the overpressure has been reduced, the gas sampling will start by opening the valve of the autoclave and, at the same time, the valve of the sampling cylinder. The gas sample will be released from the autoclave to the sampling cylinder within two minutes.

Later on, the gas samples will be measured by means of a gas mass spectrometer (GAM400, In Process Instruments, Bremen, Germany) equipped with a Faraday and SEV detector and a batch inlet system.

Aqueous sampling

The aqueous solution will be analysed to determine the specific activity of ⁹⁰Sr, ⁹⁹Tc, ¹²⁹I, ¹³⁴Cs, ¹³⁵Cs, ¹³⁷Cs, ²³⁷Np, ²³⁸U, ²³⁹Pu, ²⁴⁰Pu, ²⁴¹Am. Following analysis techniques will be applied:

- γ -spectrometry for concentration measurements of ¹²⁹I, ¹³⁴Cs, ¹³⁷Cs and ²⁴¹Am. The separation of these radionuclides from the original solution is described in Grambow et al. [4]. Afterwards the analysis is performed by means of Ge-detectors (EGC-15-185-R and GX3018, Canberra Industries Inc, Meriden, USA).
- Liquid scintillation counting (LSC) using a Packard Tri-Carb 3110TR Low activity scintillation analyser (Perkin Elmer INC, Waltham, USA) to quantify: ⁹⁰Sr. Solution aliquots will be homogenised with a LSC-Cocktail (Ultima Gold XR, Packard) before measurement.
- High resolution inductively coupled plasma mass spectrometer (ELAN 6100, Perkin Elmer Inc, Waltham, USA) to measure the concentrations of ⁹⁹Tc, ¹³⁵Cs, ²³⁸U, ²³⁷Np, ²³⁹Pu and ²⁴⁰Pu.

Summary and future work

KIT-INE provided a 38 GWd·t_{HM}⁻¹ MOX fuel rod segment in the ownership of KIT-INE, where all data and findings can be published without restrictions.

KIT-INE will perform two static leaching experiments with a clad segment and fragments of SNF. These experiments will be conducted under reducing conditions in autoclaves performing regular sampling of gases and solution. The methodology that will be followed during the performance of the leaching experiment has been explained in the present communication. In the following month the leaching experiments will be started.

Acknowledgement

The research leading to these results has received funding from the European Commission Horizon 2020 Research and Training Programme of the European Atomic Energy Community (EURATOM) (H2020-NFRP-2016-2017-1) under grant agreement n° 755443 (DisCo project).

References

- [1] Johnson, L. and Shoesmith, D.W. (1988). Spent fuel in radioactive waste forms for the future. Lutze, W. and Ewing, R.C., Eds. (North-Holland, Amsterdam), 635-698.
- [2] Shoesmith, D.W. (2000). Fuel corrosion process under waste disposals. *Journal of Nuclear Materials*, 282, 1-31.
- [3] Bruno, J. and Ewing, R.C. (2006). Spent nuclear fuel. *Elements*, 2, 343-349.
- [4] Grambow, B., Loida, A., Dressler, P., Geckeis, H., Gago, J., Casas, I., de Pablo, J., Gimenez, J., Torrero, M.E. (1996). Long-term safety of radioactive waste disposal: Chemical reaction of fabricates and high burn-up spent UO₂ fuel with saline brines. Final Report FZKA, 5702.

High-burnup spent nuclear fuel dissolution under highly alkaline conditions

Iglesias, L.^{1,2}, Serrano-Purroy, D.¹, Martínez-Torrents, A.², Clarens, F.², de Pablo, J.^{2,3}, Casas, I.³

¹ Joint Research Center Karlsruhe, Karlsruhe (EU)

² Fundació CTM Centre Tecnològic, Manresa (ES)

³ UPC-Barcelona Tech. Dept. of Chemical Engineering, Barcelona (ES)

Introduction

International research collaborations are essential to improve our understanding of the Spent Nuclear Fuel (SNF) behaviour in repository conditions. Having previous knowledge about processes such as SNF leaching is mandatory to determine which are the required safety disposal conditions. The project 'Modern Spent Fuel Dissolution and Chemistry in Failed Container Conditions' (DisCo), has the scope of boost the understanding over the processes occurring when the SNF is in contact with groundwater. Although in the last years several Instant Release Fraction (IRF) and matrix corrosion studies have been made under different redox conditions using several water compositions, there is still a lack of information regarding high burnup UO_2 samples in cementitious waters, both under oxic and reducing conditions. In this work, our aim is to study the effect of O_2 -rich water intrusion reaching High burnup UO_2 SNF deposited in a Deep Geological Repository (DGR), using Young Cement Water with Ca (YCWCa). This water considers a previous contact with cement or concrete used in the construction of the DGR, having a higher pH with dissolved elements, such as Ca and Si (silicate anion). For comparison, previous results using the same type of sample and leached in simplified bicarbonate ground water (from now onwards, BIC) are also shown.

Experimental methods

For this experiment, a cladded fuel sample from a PWR spent fuel with a local burnup of $73 \text{ GWd}\cdot\text{tU}^{-1}$ was selected, cut precisely through a pellet to obtain a segment without the interface between pellets. Further details about the sample, named 73YCWCa, are shown in Table 1. For comparison, details of a similar sample used in another project and leached in BIC water and named 73BIC are also included.

Table 1: Parameters of SNF 73YCWCa and 73BIC cladded segments used for the leaching experiment.

Sample	73YCWCa	73BIC
Length (mm)	2.9 ± 0.1	4.3 ± 0.1
Weight, only fuel (g)	2.340 ± 0.05	2.623 ± 0.05
Diameter without cladding (mm)	9.1 ± 0.1	9.1 ± 0.1
Surface area (mm^2)	460 ± 10	460 ± 10

Sample	73YCWCa	73BIC
^{235}U enrichment (weight%)	3.95	3.95
Grain size (μm)	6.4	6.4
Fission Gas Release (%)	13.6	13.6
Local burnup, estimated ($\text{GWD}\cdot\text{tU}^{-1}$)	73	73
Average Linear Power Density ($\text{W}\cdot\text{cm}^{-1}$)	255	255

Based on the theoretical composition of the YCWCa, simulated cement water was prepared, whose composition is shown in Table 2, together with BIC waters of 73BIC experiment.

Table 2: Composition of major ions present in the synthetic waters used for leaching experiments.

Solution	pH	Na^+ ($\text{mMol}\cdot\text{L}^{-1}$)	Ca^{2+} ($\text{mMol}\cdot\text{L}^{-1}$)	Cl^- ($\text{mMol}\cdot\text{L}^{-1}$)	SiO_3^{2-} ($\text{mMol}\cdot\text{L}^{-1}$)	CO_3^{2-} ($\text{mMol}\cdot\text{L}^{-1}$)	OH^- ($\text{mMol}\cdot\text{L}^{-1}$)
73YCWCa	13.4	$5.0\cdot 10^2$	$9.8\cdot 10^{-1}$	–	$2.0\cdot 10^2$	2.5	$2.5\cdot 10^2$
73BIC	7.4	$2.0\cdot 10^1$	–	$1.9\cdot 10^1$	–	1.0	$2.5\cdot 10^{-7}$

The methodology of the experiment followed a protocol reported in a previous study [1], in which the cladded segment was in contact with a leaching solution during different time intervals. Then, the cladded segment was transferred into the next bottle containing a fresh synthetic solution. After this, several aliquots were diluted in HNO_3 or tetramethylammonium hydroxide (TMAH) 1 wt.% to be analysed by ICP-MS. The emptied bottle was refilled with HNO_3 1 M and agitated during 7 days. This washing was done to remove any element that could have been adsorbed onto the plastic walls of the bottle during the first leaching step. Finally, a sample of this HNO_3 rinsing solution was taken to be analysed by ICP-MS.

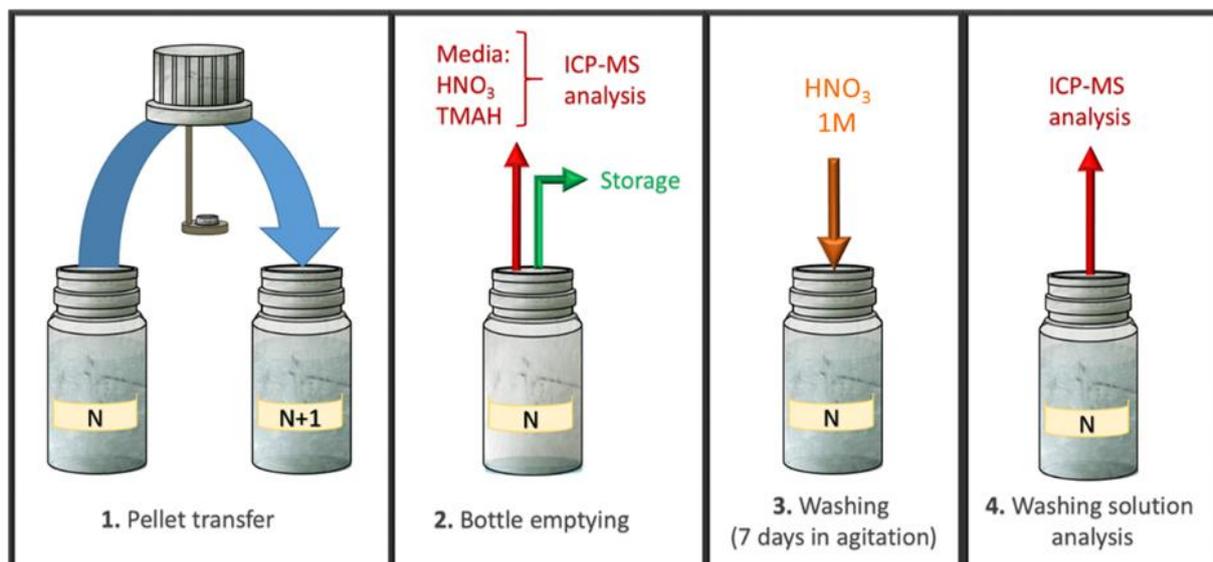


Figure 1: Solution sampling procedure.

Results and discussion

Preliminary results include 9 samples that have been partially analysed. Some relevant radionuclides (U, Rb, Sr, Mo, Tc, Cs) have been selected. Cumulative moles and Cumulative Fraction of Inventory in Aqueous Phase (CFIAP) results are shown in Figure 2 for the experiment 73YCWCa.

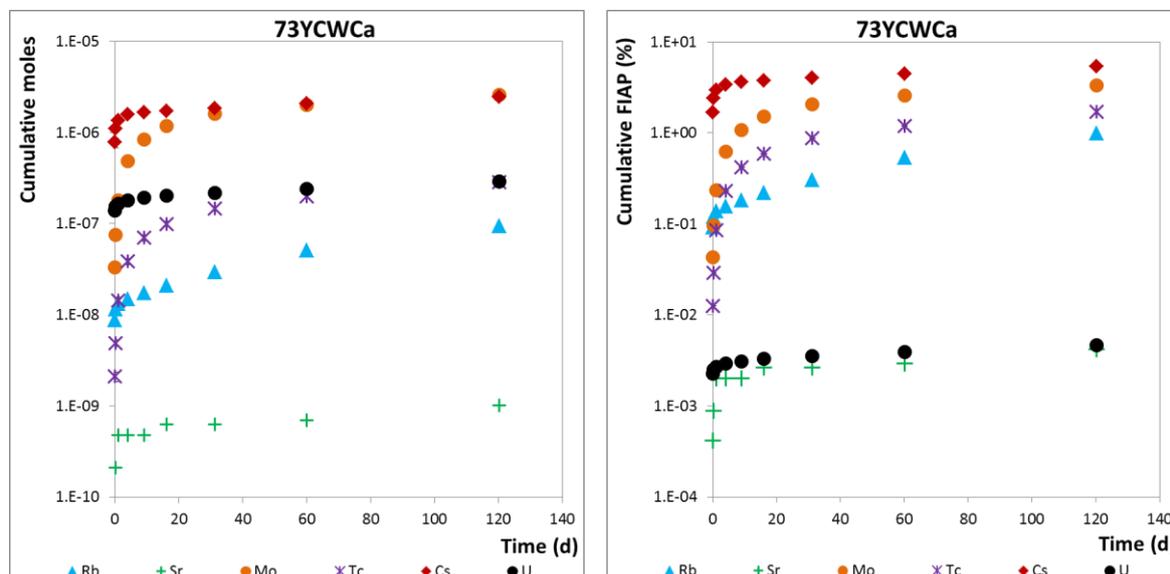


Figure 2: Cumulative moles and CFIAP (%) of the leaching experiment made with the 73YCWCa sample.

The trend is a faster dissolution at the beginning and a slower dissolution after the first week. Cs, Mo and U present the highest values of cumulative moles. This behaviour was observed for Cs and U in previous experiments, but it is important to mention that it is not observed for Mo in water with a lower pH. When comparing these results with these of the experiment 73BIC (BIC water, pH = 7.4) in Figure 3, one observes a lower amount of U released in solution for the experiment 73YCWCa (YCWCa, pH = 13.4). The lower concentration of U in the analysed solutions may indicate a lower dissolution or the formation of less soluble secondary phases by reprecipitation of uranium.

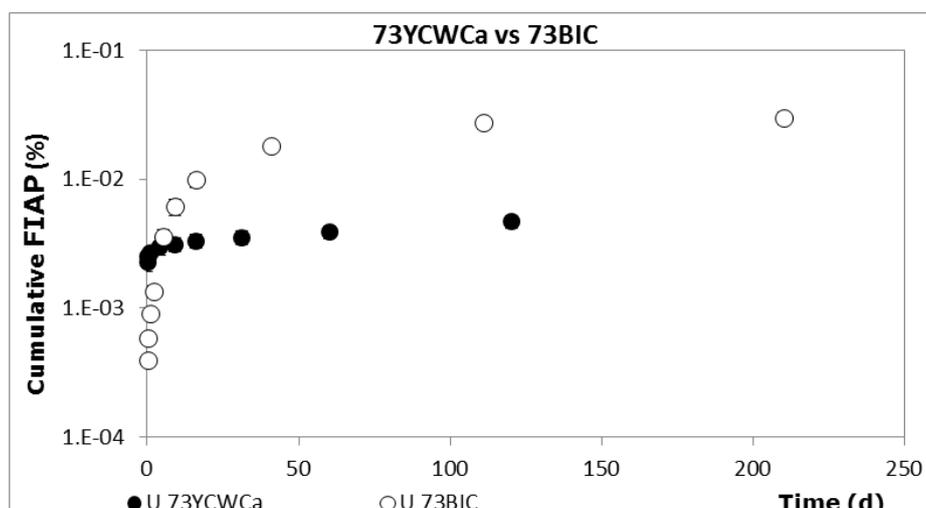


Figure 3: U CFIAP comparison of 73YCWCa and 73BIC experiments.

IRF results for the 73YCWCa experiment are shown in Figure 4. In addition, Table 3 shows the final IRF(%) results for both 73YCWCa and 73BIC.

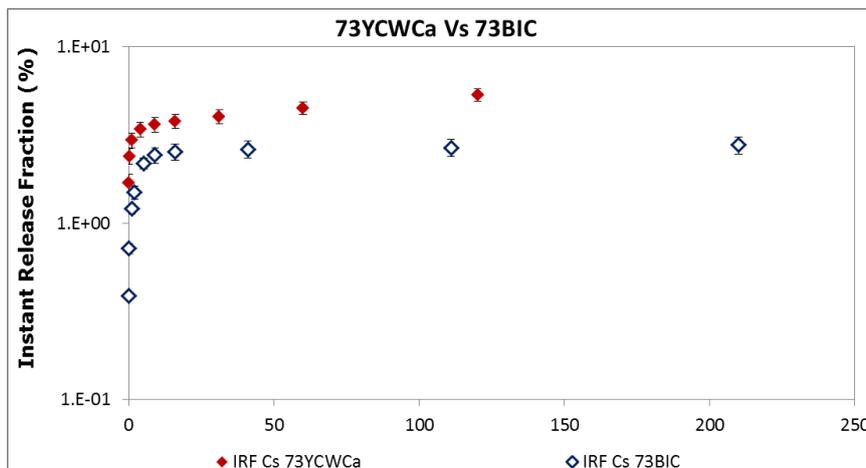


Figure 4: Instant Release Fraction (%) for Cs: comparison of 73YCWCa and 73BIC experiments.

Table 3: IRF results for 73YCWCa and 73BIC.

IRF (%)	pH	Rb	Sr	Mo	Tc	Cs
73YCWCa	13.4	1.0 ± 0.2	b.d.l.	3.3 ± 0.3	1.7 ± 0.2	5.3 ± 0.6
73BIC	7.4	0.3 ± 0.1	0.09 ± 0.01	< 0.005	0.011 ± 0.005	2.7 ± 0.3

Note: b.d.l. means Below Detection Limit.

Comparison of the IRF of Cs for these experiments shows that Cs has a higher IRF for 73YCWCa by a factor of two. The lower dissolution of U in these experiments with cementitious waters has here an effect compared to 73BIC, the difference between the elements of the IRF and the U matrix being larger. Furthermore, higher levels of Mo and Tc are also observed for the 73YCWCa. These results may indicate the formation of more soluble aqueous species of these elements.

Acknowledgement

Special thanks to Stefaan van Winckel and Gert Rasmussen for the measurements by ICP-MS and their helpful recommendations in data evaluation, and to Detlef Wegen for his interest and collaboration in this project. Daily work was supported by the Chemical Hot Cell technicians, Mariangela Cardinale, Philippe Moisei, Komlan Anika and Caroline Diebold.

The authors would like to acknowledge ENRESA for its interest in this work and also to the European Commission for financially supporting the DisCo Project H2020 EURATOM ID: 755443.

Reference

- [1] González-Robles, E., Serrano-Purroy, D., Sureda, R., Casas, I., de Pablo, J. (2015). Dissolution experiments of commercial PWR (52 MWd·kg_U⁻¹) and BWR (53 MWd·kg_U⁻¹) spent nuclear fuel cladded segments in bicarbonate water under oxidizing conditions. Experimental determination of matrix and instant release fraction. *Journal of Nuclear Materials*, 465, 63-70.

Aqueous leaching of spent nuclear fuel under H₂ atmosphere. A comparison between ADOPT and standard UO₂ fuel.

Barreiro Fidalgo, A.¹, Roth, O.¹, Puranen, A.¹, Evins, L.Z.², Spahiu, K.²

¹ Studsvik Nuclear AB, Nyköping (SE)

² SKB, Stockholm (SE)

Abstract

Within the EURATOM collaborative project ‘Modern Spent Fuel Dissolution and Chemistry in Failed Container Conditions’ (DisCo), Studsvik will contribute with a total of two experiments on different fuel types.

The main objective of these investigations is to gather data on the dissolution behavior of a new type of fuel with additives (ADOPT fuel) under reducing conditions in presence of hydrogen. The behavior of the doped fuel will be compared to the performance of standard UO₂ fuel under identical conditions. The data obtained will be used to support or refute the hypothesis that there is not major difference in leaching behavior between the two fuels. In addition, thermodynamic and kinetic models will be developed in WP5 using the experimental data.

The experiments will be performed on fuel fragments without cladding. The selected fragments are the same samples leached in a previous EURATOM project, FIRST-Nuclides, which were used to establish the instant release fraction and the matrix dissolution behavior under aerated conditions [1]. The selected fuels are listed in Table 1.

Table 1: Fuels selected for the experiments performed at Studsvik.

Sample name	Reactor type	Fuel type	FGR (%)	Calculated BU (rod average) (MWd·kg ⁻¹)
5A2	BWR	Std. UO ₂	2.4	57.1
C1	BWR	ADOPT (Al/Cr doped UO ₂)	1.4	59.1

The fuel fragments are currently being exposed to an initial leaching period under aerated conditions in 10:10 mM NaCl:NaHCO₃ solutions. The main objective of this initial step is to wash away any pre-oxidized phases formed during humid-air storage in cell by exposing them to relatively high NaHCO₃ concentrations.

After the fulfillment of the criteria for a successful washing, the fuel will be corroded in autoclaves containing simplified groundwater (10:2 mM NaCl:NaHCO₃ solution) under reducing conditions in H₂ atmosphere. The initial H₂ pressure will be up to ~ 50 bar. Tests will be performed in both autoclaves to detect potential leaks by pressurizing them with 50 bar of He and monitoring the pressure drop during an approximated period of 1 month.

Preliminary results from the washing step were presented in the 1st Annual DisCo Meeting together with all the preparations performed. The autoclaves are estimated to be loaded in June-July after fulfillment of the washing criteria.

Acknowledgement

The research leading to these results has received funding from the European Commission Horizon 2020 Research and Training Programme of the European Atomic Energy Community (EURATOM) (H2020-NFRP-2016-2017-1) under grant agreement n° 755443 (DisCo project).

References

- [1] Kienzler, B., Metz, V., Duro, L., Valls, A. (2014). Final (3rd) Annual Workshop Proceedings of the 7th EC FP CP FIRST-Nuclides project. KIT Scientific Report, 7716.

Manufacture and characterization of CIEMAT fuel samples used for leaching tests in the DisCo project.

Rodríguez-Villagra, N., Fernández, S., Bonales, L.J., Gutiérrez, L., Elorrieta, J.M., Cobos, J.

CIEMAT, Madrid (ES)

Abstract

In the framework of the DisCo project, CIEMAT is contributing in WP2 and WP4 “Model systems dissolution experiments”. This work is dealing with the understanding of corrosion mechanisms of unirradiated fuel (focused on Cr/(Cr+Al)/Gd-doped UO₂) in high pH cementitious waters. At the current stage (one year into a planned four-year project) experimental progress includes preparatory work, characterization of raw materials and samples and testing of new experimental set-ups.

WP2: Model systems dissolution experiments

Modern fuels are commonly described as UO₂-based fuels with additives such as Cr or Cr plus Al. Also, Gd is added as burnable neutron absorber with certainly good performance. An attempt to replicate Gd and Cr/(Cr+Al) doped UO₂ fuel have been made to synthesize doped novel samples in a similar way as in commercial UO₂ fuel manufacturing process.

Task 2.3: U/Th laboratory work

CIEMAT's contribution, specifically in Task 2.3: U/Th laboratory work: Model system preparation and characterization, targets the fabrication and characterization of materials to study the spent fuel matrix corrosion behaviour under repository conditions. In order to produce materials simulating the behaviour of the doped spent fuel, model materials were fabricated. Gd₂O₃ is already added to UO₂ nuclear fuel (< 10% wt Gd/U) as a burnable neutron absorber [1]. Furthermore, addition of Cr₂O₃ to UO₂ (< 1% wt. Cr/U) fuel pellets increases the grain size (above 30 microns), density and creep rate, with the main goal of making the fission gas release difficult [2]. New UO₂ doped fuels with Cr₂O₃-Al₂O₃ additives, commonly known as ADOPT fuels, have several advantages coming from a synergic effect of both dopants, such as higher densification, pellet-cladding interaction and plasticity reduction, lower fission gases release during irradiation and higher post-failure degradation. All these mentioned improvements can be achieved by enlarging the pellet grain size [3-6].

WP2.3: Ciemat-1 Fabrication by standard metallurgical route

The methodology applied for disks fabrication was classical powder pressing and sintering. Natural UO₂ was previously thermally treated in 4.7% H₂-N₂ atmosphere at 1,100°C to attain stoichiometric UO_{2.0}. The starting powders, UO₂, Cr₂O₃, Al₂O₃ and Gd₂O₃, the first one provided by ENUSA and the others by Alfa-Aesar, were previously characterized by measuring the particle size distribution, the morphology of the particles and agglomerates, the specific surface area and the crystalline structure.

These powders were mixed in the proportions indicated in Table 1 using a mechanical mixing mill to ensure suitable homogenization.

Table 1: Composition matrix for doped UO₂ samples.

Composition [X ₂ O ₃] (ppm)	Al ₂ O ₃	Cr ₂ O ₃	Gd ₂ O ₃	Cr ₂ O ₃ /Al ₂ O ₃
200	X	X		
600	X	X		
45,000			X	
500/200				X

For the Cr₂O₃, Al₂O₃, Gd₂O₃ and Cr₂O₃-Al₂O₃ doped samples 8 gram batches of UO₂ were placed in a mixing jar. The appropriate amount of ethylene bis stearamide (EBS, C₃₈H₇₆N₂O₂, Tokyo chemical industry, Japan) binder was added to powders containing no inorganic constituents. These batches of mixed powders were then blended for 1 minute at 15 Hz in the mixer mill. The samples were prepared by uniaxial pressing in a press of 25 tons C256C (Power team) with an applied pressure of 700 MPa with a 10 mm pellet punch. All disks were calcined in three stages (100, 300 and 500°C) at 10 °C·min⁻¹ and held up to 4 h to burn out organic matter under a reducing atmosphere. “Green” specimens were then sintered to 1,675°C for 4 h at 5 °C·min⁻¹ in a reducing atmosphere of 4.7% H₂-N₂ (8 ppm O₂). Table 1 includes the composition matrix for this study, chosen in accordance with literature data and Table 2 its subsequent surface characterization (XRD lattice parameters, Specific Surface Area by BET methodology and theoretical density) of ceramic starting powders. In Figure 1 a diagram of the powder metallurgical process is shown.

Table 2: Raw material characterization.

Sample	Lattice parameter (nm)	SSA (BET) (m ² ·g ⁻¹)	TD (g·cm ⁻³)
UO ₂	a = b = c = 0.546920(4)	0.95 ± 0.02	10.97
Al ₂ O ₃	a = 0.7944(6); b = 0.7980(4); c = 1.1722(6)	37.6 ± 0.4	3.95
Cr ₂ O ₃	a = b = 0.49586(7); c = 1.3592(2)	3.47 ± 0.02	5.22
Gd ₂ O ₃	a = b = c = 1.08141(4)	14.6 ± 0.1	7.41

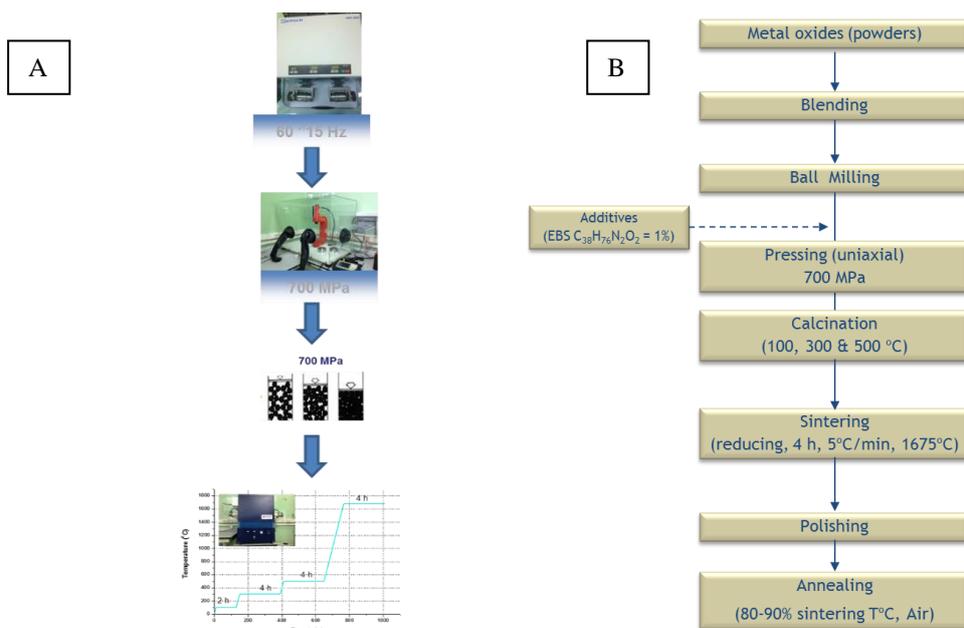


Figure 1: Fabrication process image (A) and flow diagram (B).

WP2.3: Ciemat-2 Surface characterization of the pellets to be tested

A complete group of samples from the composition matrix has been sintered. To perform the characterization of final samples, specimens obtained were polished, as well as thermally etched (95% of sintered temperature). Doped sample characterization was carried out by XRD and Raman spectroscopy in order to verify the final stoichiometry and SEM-EDX to analyse the microstructure and the grain size distribution. Specific surface area was determined by the BET method and the density was geometrically calculated. Figure 2 shows a $UO_2 + Cr_2O_3$ (500 ppm) + Al_2O_3 (200 ppm) disc with its corresponding XRD, Raman spectrometry analyses and its microstructure.

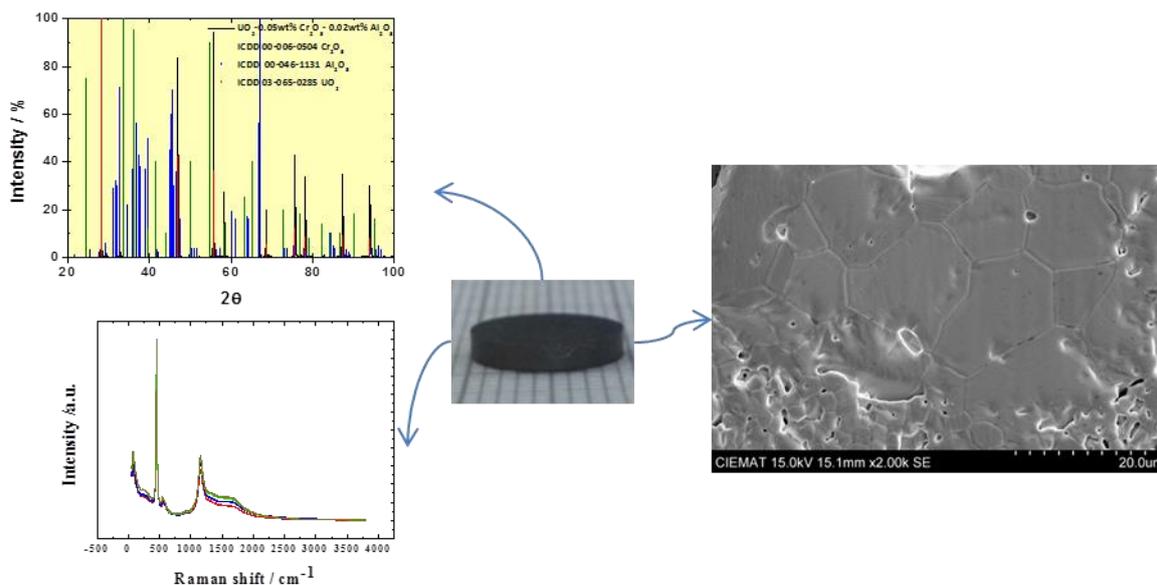


Figure 2: Characterization of $UO_2 + Cr_2O_3$ (500 ppm) + Al_2O_3 (200 ppm).

The relevant results obtained are found in Table 3. The grain structures were examined by SEM and grain sizes were calculated by the linear intercept method. The highest density is obtained in the sample with the greatest amount of Cr_2O_3 .

Table 3: Results obtained from the analysis of the doped UO_2 samples.

Sample (wt%)	Lattice parameter (nm)	SSA (BET) ($\text{m}^2\cdot\text{g}^{-1}$)	Density ($\text{g}\cdot\text{cm}^{-3}$)
UO_2	0.547174 (6)	0.36 ± 0.01	8.93 ± 0.07
$\text{UO}_2 - 0.02 \text{Al}_2\text{O}_3$	0.547123 (8)	0.36 ± 0.01	9.85 ± 0.14
$\text{UO}_2 - 0.06 \text{Al}_2\text{O}_3$	0.547108 (7)	0.33 ± 0.01	9.96 ± 0.17
$\text{UO}_2 - 0.02 \text{Cr}_2\text{O}_3$	0.547108 (7)	0.28 ± 0.01	9.80 ± 0.12
$\text{UO}_2 - 0.06 \text{Cr}_2\text{O}_3$	0.547113 (7)	0.63 ± 0.02	9.83 ± 0.07
$\text{UO}_2 - 4.5 \text{Gd}_2\text{O}_3$		0.63 ± 0.01	9.81 ± 0.11
$\text{UO}_2 - 0.05 \text{Cr}_2\text{O}_3 - 0.02 \text{Al}_2\text{O}_3$	0.547198 (5)	0.25 ± 0.01	9.80 ± 0.43

For all the doped discs, the sample's average grain size showed a clear increase except for the case of Gd_2O_3 doped samples, which remained unchanged. For Al_2O_3 over the solubility limit of 70 ppm at $1,700^\circ\text{C}$ and below the solubility limit of 700 ppm at $1,700^\circ\text{C}$ for Cr_2O_3 [6], the sample's average grain size showed a clear increase compared to pure UO_2 . Grain size of Cr-doped UO_2 samples are in agreement with previously published data from Bourgeois et al. [5] and Yang et al. [8] for the selected weight ratios of Cr/U, increasing with the addition of higher contents of Cr_2O_3 . Figure 3 shows the grain structure of sintered pellets. As expected, no precipitates or segregation are observed in any sample, meaning that dopants are well solubilized.

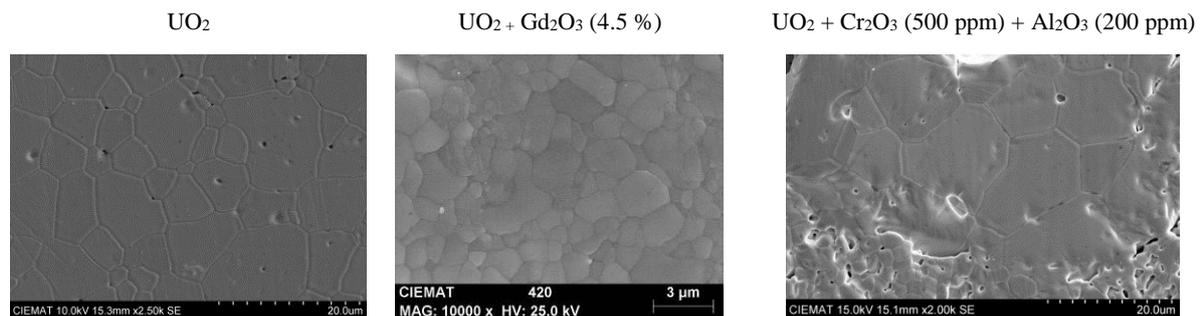


Figure 3: Microstructure images of UO_2 , $\text{UO}_2\text{-Gd}$ and $\text{UO}_2\text{-Cr-Al}$ samples and detail of grain size.

Microstructural examination of the grain growth also reveals that the U mixed oxides containing Cr and Cr-Al samples show a homogeneous distribution of dopants in solid solution. By XRD and Raman spectroscopy, no segregated phase is either found. This indicates that dopants are dissolved into UO_2 grains.

Task 2.4: Coordination of aqueous solution chemistry

Three test media were proposed as leachants: NaClO_4 0.02 M, as a blank media tests pH 7-7.6 to buffer ionic strength, bicarbonate water (0.019 M NaHCO_3 - 0.001M NaCl) pH 8-9 as highly carbonated media compared to those expected under repository conditions, and young cementitious water (YCWCa) pH ~ 13.7 to assess the stability of doped- UO_2 in the highly alkaline chemical environment. All of them have been carefully prepared by the addition of pure chemical reagents to boiled and cooled Milli-Q water and bubbling He gas to take out O_2 dissolved and minimize uptake of atmospheric CO_2 . Solutions have been stored under Ar atmosphere in a glove box (< 6 ppm O_2). Analytical results of YCW prepared are shown in Table 4.

Table 4: YCW composition prepared at CIEMAT.

YCW	Na	K	Ca	Al	Si	SO_4^{2-}	Alk ⁻	I	pH	Eh (mV)
$\text{mol}\cdot\text{L}^{-1}$	$1.5\cdot 10^{-1}$	$3.8\cdot 10^{-1}$	$4.5\cdot 10^{-4}$	$2.2\cdot 10^{-6}$	$1\cdot 10^{-4}$	$2\cdot 10^{-3}$	$4.9\cdot 10^{-1}$	> 1	13.7	-72.4

WP4: Study of the spent fuel matrix dissolution behaviour under repository conditions

WP4 CIEMAT-1 Design and installation of autoclaves by temperature and H_2 pressure

PEEK-lined 316 stainless steel thermostated autoclaves (total volume 380 mL; Figure 4) were equipped with a PEEK vessel and three valves in the lid (quick-fit type) to allow injecting/releasing gas into the reactor and sampling of solutions during the experiment. O-ring seals were made of Viton®. The pressure vessels have been designed to achieve maximum temperatures of 250°C. Sampling of the aqueous phase is carried out via a polyurethane tube.

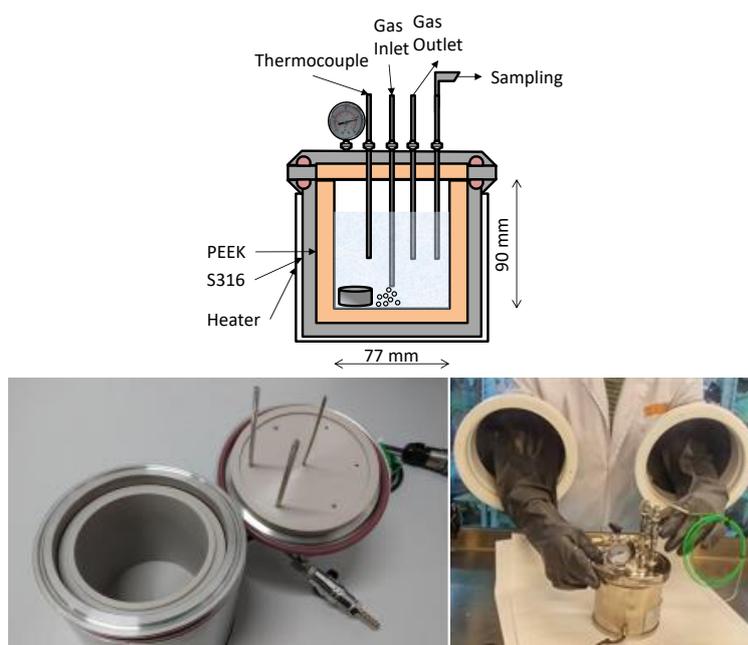


Figure 4: Image of PEEK-lined stainless steel thermostated autoclaves at CIEMAT radioactive facilities.

WP4: CIEMAT-2 Leaching experiments

Nine static leaching experiments with doped samples derived from WP2 are foreseen to be conducted under reducing conditions. The batch dissolution tests will be carried out in thermostated autoclaves. Samples of approximately 1 g (1.7 x 9.6 mm) will be placed inside the autoclaves with 300 mL of the selected leaching solution. The reducing conditions will be achieved by application of a 4.7% H₂-N₂ atmosphere within the autoclaves and run under 6-8 bar during \approx 150 days and $22 \pm 3^\circ\text{C}$. The leaching tests are at the preparation level at the present. Small aqueous aliquots will be sampled at specific intervals of time to quantify by ICP-MS the elemental release (U, Cr, Al, Gd and some other components coming from the water), without any replenishment of aqueous phase. Detailed elemental release measurements are not yet available and will be reported at a later stage. The pH, Eh and temperature values will be also measured. The ultimate aim would be to empirically determine dissolution kinetics and the effect of dopants on UO₂ dissolution rate in comparison with UO₂.

Acknowledgement

The research leading to these results has received funding from the European Commission Horizon 2020 Research and Training Programme of the European Atomic Energy Community (EURATOM) (H2020-NFRP-2016-2017-1) under grant agreement n° 755443 (DisCo project).

The authors would like to especially acknowledge ENRESA.

References

- [1] IAEA (1995). Characteristics and use of uranium-gadolinia fuels. IAEA-TECDOC-844.
- [2] Delafoy, C. and Zemek, M. (2010). Washout behaviour of chromia-doped UO₂ and gadolinia fuels in LWR environments. IAEA-TECDOC-1654 “Advanced Fuel Pellet Materials and Fuel Rod Design for Water Cooled Reactors”, 127-138.
- [3] Backman, K., Hallstadius, L., Roennberg, G. (2010). Westinghouse Advanced Doped Pellet - Characteristics and irradiation behavior. IAEA-TECDOC-1654 “Advanced Fuel Pellet Materials and Fuel Rod Design for Water Cooled Reactors”, 117-126.
- [4] Oh, J.S., Kim, K.S., Kim, D.J., Kim, J.H., Yang, J.H. (2016). Effect of sintering condition on the grain growth of Cr₂O₃ doped UO₂ pellets. Proceedings of the KNS 2016 spring meeting. Korea, Republic.
- [5] Bourgeois, L., Dehaut, Ph., Lemaignan, C., Hammou, A. (2001). Factors governing microstructure development of Cr₂O₃-doped UO₂ during sintering. Journal of Nuclear Materials, 297(3), 313-326.
- [6] OCDE/NEA (2005). Pellet-clad interaction in water reactor fuels: Seminar Proceedings. Aix-en-Provence, France, 9-11 March 2004, Nuclear Science, Éditions OCDE, Paris.
- [7] Peres, V., Bourgeois, L., Dehaut, P. (1993). Grain growth and Ostwald ripening in chromia-doped uranium dioxide. Journal de Physique IV Colloque, 03(C7), 1477-1480.
- [8] Yang, J.H., Kim, K.S., Nam, I.H., Oh, J.S., Kim, D.-J., Rhee, Y.W., Kim, J.H. (2012). Effect of step wise variation of oxygen potential during the isothermal sintering on the grain growth behavior in Cr₂O₃ doped UO₂ pellets. Journal of Nuclear Materials, 29(1-3), 25-33.

Synthesis of doped UO₂ model materials for single effect studies to understand the long-term matrix dissolution of modern LWR fuels

Brandt, F.¹, Alekseev, E.V.¹, Lange, S.¹, Bukaemskiy, A.¹, Kegler, P.¹, Finkeldei, S.C.¹, Baena, A.¹, Deissmann, G.¹, Klinkenberg, M.¹, Lemmens, K.², Cachoir, C.², Delville, R.², Leinders, G.², Mennecart, T.², Verwerft, M.², Bosbach, D.¹

¹ Forschungszentrum Jülich GmbH, Jülich (DE)

² SCK·CEN, Mol (BE)

Abstract

Complementary to dissolution experiments on spent nuclear fuels, studies on UO₂ based model materials can provide additional insights into the behaviour of modern doped LWR-fuels under disposal conditions in a deep geological repository. Here, we describe the development and optimisation of the process steps for a wet-chemical route to produce Cr-doped UO₂ pellets as well as pure UO₂ reference materials. Process optimisation was achieved by a systematic investigation of various process parameters such as calcination temperature and pelletisation pressure. The challenges met during process development and optimisation and the effects of the process parameter variations on the materials properties are discussed.

Introduction

The current efforts to improve fuel performance in nuclear power generation resulted in an increased utilisation of a variety of new types of light-water reactor (LWR) fuels such as Cr-, Al-, and Si-doped fuels [1-3]. While the improvement of in-reactor performance of these fuels has already been demonstrated, it is still not known, whether the corrosion/dissolution behaviour of such fuels in a geological repository environment is the same as for conventional spent LWR-fuels. However, due to the chemical and structural complexity of spent nuclear fuels (SNF) and its high beta- and gamma radiation field, experiments with SNF cannot unravel all of the various concurring dissolution mechanisms entirely. Thus, in order to understand how the addition of Cr- or Al-oxide into the fuel matrix affects the SNF dissolution behaviour under repository relevant conditions, within the EU-DisCo project (www.disco-h2020.eu) experiments on irradiated doped fuels are complemented with dissolution studies carried out with systematically produced and carefully characterized UO₂-based model materials in parallel. These model materials comprise Cr-/Al-doped UO₂ and UO₂ reference materials, and will be synthesized both with and without alpha-emitting nuclides such as ²³⁸Pu, to address the effects of alpha-radiolysis on the oxidative dissolution of aged SNF after recession of the beta/gamma radiation field. Single-effect studies on the dissolution behaviour of the model materials will provide complementary insights and supporting process understanding regarding the performance of modern doped fuels in the repository environment, which cannot be directly obtained from SNF studies.

In this presentation, we provide an overview on the development and optimisation of the synthesis route for the production of Cr-doped UO_2 model materials to be used in the envisioned dissolution experiments. In order to provide insights into the effects of the material's microstructure on the dissolution behaviour (e.g. regarding the larger grain size in doped fuels and contributions of grain boundaries) as well as for comparability to SNF experiments, the model materials are produced in form of sintered pellets. The following challenges had to be met during the optimisation of the synthesis process: (i) the procedures had to be robust and easily reproducible in different laboratories (i.e. in Jülich and in Mol) with slightly different equipment, (ii) in order to obtain a homogeneous distribution of Cr and, in particular, of ^{238}Pu present only in trace amounts (< 50 ppm) in the pellets, a wet chemical synthesis was favoured, (iii) milling/grinding steps should be avoided to minimise dust generation and carry-over of Pu, and (iv) no lubricants such as Zn-stearate or sintering aids should be used during pelletising and sintering. Moreover, all process steps, tested and optimised in Jülich without alpha-doping, had to be designed in a way to be accomplished also in a glove-box line at SCK·CEN in Mol, to produce ^{238}Pu -doped pellets with similar characteristics.

Development and optimization of synthesis route

The procedure followed in order to obtain UO_2 and Cr-doped UO_2 pellets with a target concentration of 1,000 ppm Cr comprised the following basic steps: (i) (co)-precipitation of ammonium-di-uranate (ADU; $(\text{NH}_4)_2\text{U}_2\text{O}_7$) with/without Cr, (ii) oxidative and reductive calcination, (iii) pelletisation by uniaxial pressing, and (iv) sintering under reducing conditions. We investigated variations of process parameters such as calcination temperatures and pelletising pressure, as well as combinations thereof in a systematic way, to obtain stable pellets with the aspired properties, such as equigranular microstructure, low porosity and high density.

For the (co)-precipitation step, a uranium nitrate solution ($c(\text{UO}_2(\text{NO}_3)_2) = 2 \text{ mol}\cdot\text{L}^{-1}$) was spiked with the desired concentration of dopant ($\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, Merck, p.a.), if needed. Quantitative precipitation of ADU was achieved by adding ammonium hydroxide ($w(\text{NH}_4\text{OH}) = 32\%$, Merck, p.a.). After washing, the material was calcined for 5 h under air atmosphere to convert the ADU into oxides and remove volatile impurities. Pure U_3O_8 was obtained at calcination temperatures above 600°C , whereas at 450°C ADU was still present with minor amounts of poorly crystalline U_3O_8 and UO_3 (Figure 1a). At calcination temperatures below 700°C mainly soft agglomerates exhibiting higher BET surface areas were obtained, whereas at 700°C pre-sintered hard agglomerates were formed. Complete reduction of U_3O_8 to UO_2 was achieved by an additional calcination step under reducing atmosphere (95% Ar / 5% H_2 -atmosphere, 5h) at temperatures between 600°C and 900°C (Figure 1b).

In Figure 2a, the dependency of the density of the green pellets on the pressure applied during pelletisation and the temperature treatment during calcination is shown. Higher green densities were generally obtained for powders treated at higher temperatures (800 to 900°C) in one of the calcination steps; the Cr-doping seemed to have no influence on this relationship.

The green pellets were generally sintered for 10h at $1,700^\circ\text{C}$ under reducing conditions (95% Ar / 5% H_2 -atmosphere). The density of the sintered pellets is depicted as function of pelletisation pressure in Figure 2b. In contrast to the green densities, the highest sinter densities were obtained for powders oxidised and reduced at 600°C during calcination; this effect was discernible in particular for materials pelletized with pressures exceeding 400 MPa. The density of the Cr-doped material calcined at 600°C was found to be distinctively higher than the one of the UO_2 reference material produced under identical

conditions. Note, however, that the final targeted density is $95 \pm 1\%$, conform with industry standard. For powders and fabrication parameters leading to higher values, a lowering of density can be easily achieved by addition of U_3O_8 , a common practice in the industry.

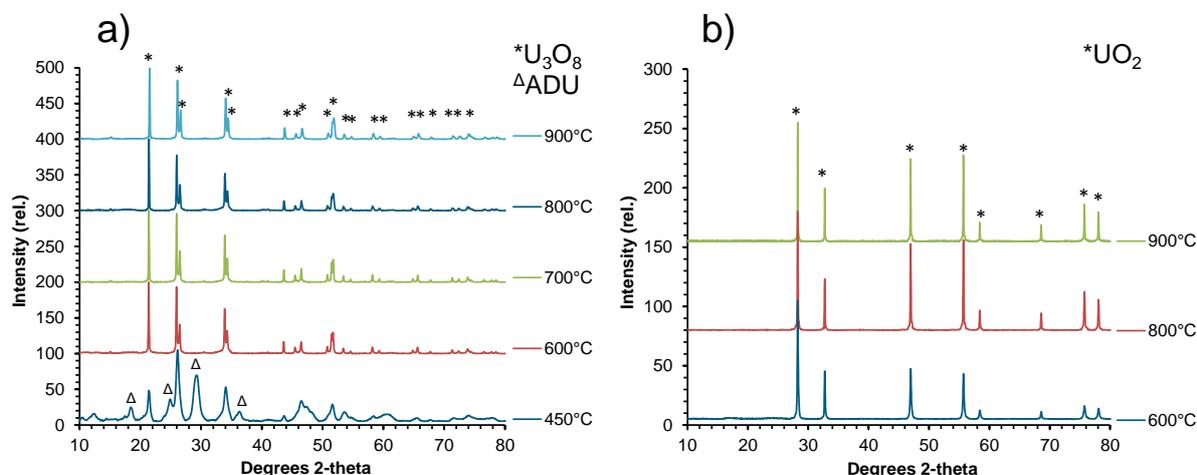


Figure 1: XRD patterns for powders obtained after oxidative (a) and reductive (b) calcination at different temperatures.

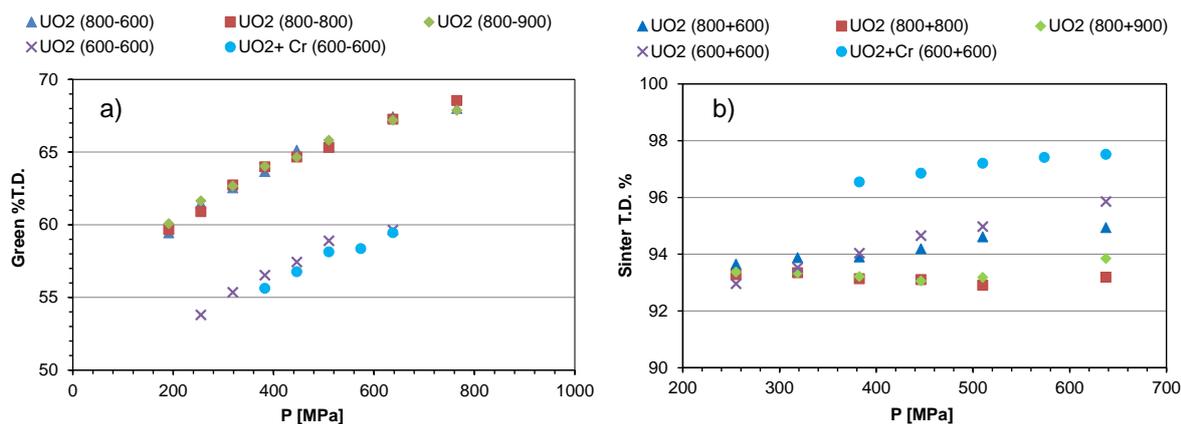
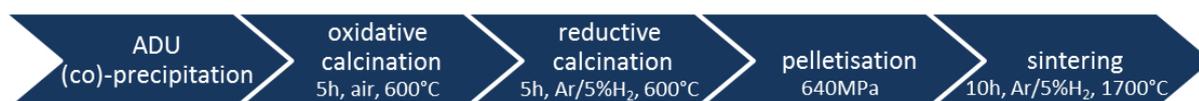


Figure 2: Density of green pellets (a) and density of sintered pellets (b) in dependence on pelletisation pressure (The numbers in brackets refer to the temperatures during the oxidative and reducing calcination steps, respectively, in °C).

Conclusions and outlook

A wet-chemical route to produce Cr-doped UO_2 pellets with and without ^{238}Pu as alpha-dopants as well as pure UO_2 reference materials has been developed and optimised. Process optimisation was achieved by systematic variation of process parameters such as calcination temperature and pelletisation pressure. Based on the results of this procedure, the following flow sheet has been developed for the pellet production:



The microstructure (grain size, grain orientation, dopant precipitation) and dopant concentration in solid solution of the UO₂-based model materials are characterised using various analytical methods (e.g. SEM, EBSD, EMPA, ToF-SIMS, XRD). Thoroughly characterised pellets will subsequently be used in single effect studies to address their dissolution behaviour in different waters (bicarbonate and artificial cement pore water), as well as in accelerated static batch experiments using H₂O₂ to induce oxidative dissolution.

Acknowledgement:

The research leading to these results has received funding from the European Union's Horizon 2020 Research and Training Programme of the European Atomic Energy Community (EURATOM) (H2020-NFRP2016/2017) under grant agreement n° 755443 (DisCo).

References

- [1] Commissariat à l'énergie atomique (CEA) (2009). Nuclear fuels. A Nuclear Energy Division Monograph. Gif-sur-Yvette, 147 pp.
- [2] Arborelius, J., Backman, K., Hallstadius, L., Limbäck, M., Nilsson, J., Rebensdorff, B., Zhou, G., Kitano, K., Löfström, R., Rönnberg, G. (2006). Advanced doped UO₂ pellets in LWR applications. *Journal of Nuclear Science and Technology*, 43, 967-976.
- [3] Massih, A.R. (2014). Effects of additives on uranium dioxide fuel behavior. SSM report, 2014:21.
- [4] Cardinaels, T., Govers, K., Van den Berghe, S., Verwerft, M., de Tollenaere, L., Maier, G., Delafoy, C. (2012). Chromia doped UO₂ fuel: Investigation of the lattice parameter. *Journal of Nuclear Materials*, 424(1-3), 252-260.

Influence of iron on the oxidative dissolution of a homogeneous $U_{1-x}Pu_xO_2$ MOX fuel

Jégou, C.¹, Kerleguer, V.^{1,2}, De Windt, L.², Broudic, V.¹, Martin, C.³

¹ CEA/DEN/DE2D/SEVT/LMPA – Marcoule, Bagnols-sur-Cèze (FR)

² ARMINES/MINES ParisTech, Centre de Géosciences, Fontainebleau (FR)

³ Andra, Chatenay-Malabry (FR)

Context

Contrary to UOX fuel, little is known on the behavior of the heterogeneous Mimas MOX fuel in the presence of environmental materials including corrosion products from the containers. The microstructure observed on this type of MOX fuel has revealed the presence of two or three zones with different plutonium contents and microstructures arising from the fabrication process (dilution of a UO_2 and PuO_2 oxide blend in UO_2 powder) and from the origin of the UO_2 powder. Although the corrosion mechanisms are likely to be close to those of UOX fuel [1], it is still necessary to study the specific features of MOX fuels to better understand their behavior, in the eventuality of direct geological disposal.

The first studies on heterogeneous fuel pellet showed preferential dissolution of the UO_2 matrix compared to the Pu-enriched agglomerates [2]. In order to fully evaluate the behavioral analogy between UOX and MOX fuels and to provide data it is still necessary to perform targeted leaching experiments on various homogeneous materials with different Pu contents. Ultimately, these data should be available for each type of phase constituting the heterogeneous material and provide information for geochemical modeling (linked to the WP5 and the Chess-Hytec modeling task). The ongoing work, which is the subject of this progress report, is to address the leaching behavior of a homogeneous $(U,Pu)O_2$ compounds with high plutonium content (about 25 wt%) in the presence of iron, a redox active species brought by the corrosion of the containers and being able to counteract the water radiolysis effects. Many data are available on UO_2 but relatively few on homogeneous compounds approaching the Pu enriched aggregates of a Mimas MOX fuel.

This summary focuses on the first three stages defined for the first year of the Disco project: the initial characterization of the MOX fuel pellets, the precorrosion of an iron foil in a synthetic Callovo-Oxfordian (COx) water and the beginning of the leaching experiment of the MOX pellets at 25°C.

Initial characterizations of the pellets before leaching (From Mid-2017 to January 2018)

Homogeneous $(U_{0.73}Pu_{0.27})O_2$ solid solution pellets (1 cm thickness and 5.4 mm diameter) were fabricated in 1985 at CEA Cadarache (COCA Process) and stored over 30 years at room temperature under air in a hot-cell. The initial stoichiometry was O/M: 1.983 and the density was 10.421 g·cm⁻³.

Table 1 shows the initial isotopic composition of the sample. The damage level of the sample due to the accumulation of alpha decays during the 30 years of storage was calculated as 0.58 dpa by considering each alpha decay event produces 1,750 atomic displacements in UO₂ due to the recoil nucleus (~ 100 keV) and the alpha particle (5-6 MeV). After 30 years of storage period, one of the pellets was cut into ~ 2 mm thickness disks, which were then annealed at 1,373 K for 6 h (heating and cooling rate 5 °C/min) under Ar/H₂ 4% atmosphere to recover the radiation damage and to adjust the stoichiometry of the sample. The pellets were characterized by EPMA, XRD and Raman spectroscopy to check the homogeneity of the plutonium distribution and to collect structural information.

In parallel, the α and $\beta\gamma$ activities of the MOX fuel were recalculated at the date of the leaching experiment and the alpha, beta and gamma dose rate profiles determined from the surface of a pellet to the homogeneous solution.

Pre-corrosion step of the iron foil (From November 2017 to January 2018)

Iron foils were placed in the autoclave to simulate container corrosion products and to move towards realistic reducing conditions in the absence of the fuel pellet [3]. Such reducing conditions are expected in deep geological disposal. Rolled 99.99% pure iron foils were purchased from Goodfellow. Their size was 2.5 cm by 2.5 cm for a thickness of 125 μm and a weight of around 0.64 g. One iron foil was used for the leaching experiment. Before being set up in the reactor, the foil was rinsed in ethanol and ultrasound-cleaned for 2 minutes.

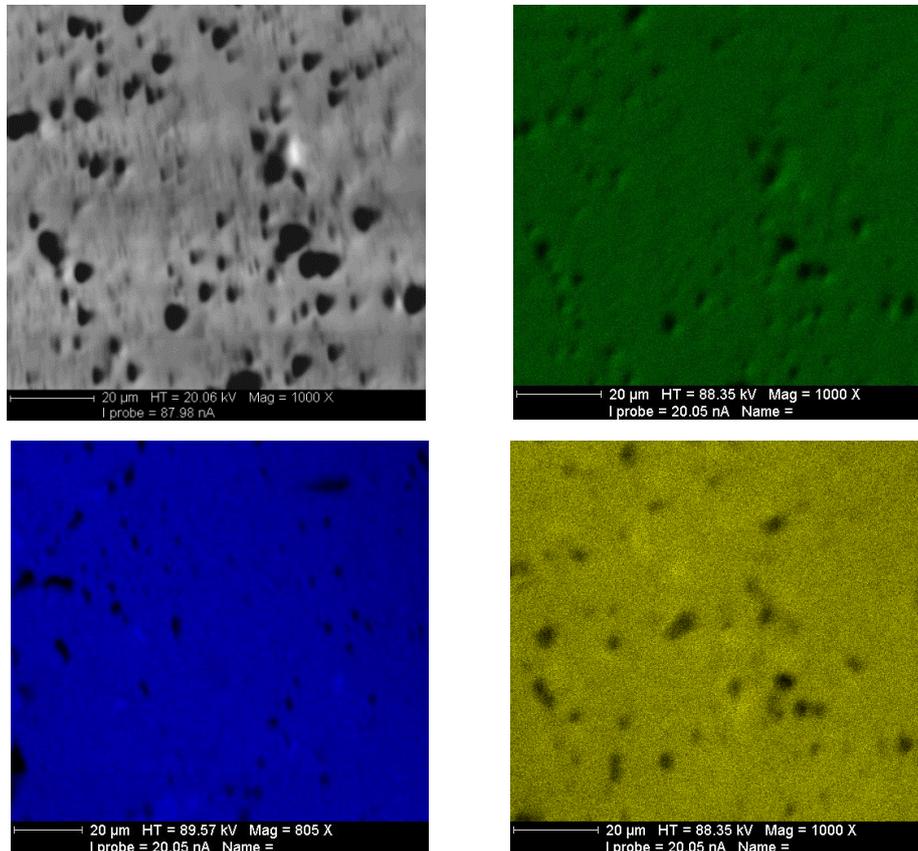
The iron foil was first pre-corroded in 180 mL of synthetic CO_x water for around 80-90 days in the absence of the MOX pellets. This first step was intended to ensure the presence of corrosion products on the iron foil surface, to obtain a solution chemistry containing Fe²⁺ ions not initially present in the synthetic CO_x water, and to have reducing conditions when the MOX pellets were introduced at a later date. The iron foil was slightly curved to enable maximum contact with water, and placed on the platform immediately under the pellet support. Once the leaching reactor had been closed, it was purged with a mixture Ar/CO₂ 3,000 ppm for 2 h 30 min and then put under a pressure of 3.5 bars. The leaching solution was regularly sampled over time.

Long term leaching experiment with the MOX fuel pellet (From January 2018 to 2019)

After the iron pre-corrosion phase, the reactor was opened to add two MOX pellets, which were placed on a support above the iron foil. The reactor was then closed again, purged with a mixture of Ar/CO₂ 3,000 ppm for 30 min, and returned to a pressure of 3.5 bars with the same gas mixture. Samples of the leaching solution were regularly collected over time. The first results indicate a significant effect of iron on the oxidative dissolution of this homogeneous MOX fuel. Uranium concentrations are less than 1 $\mu\text{g}\cdot\text{L}^{-1}$ after one month of leaching. These results are similar to those obtained on Pu-doped UO₂ [3] or on heterogeneous MOX fuels. The experiment will continue for about a year and all the surfaces (MOX, iron foil) will be characterized at the end of the experiment.

Table 1: Initial isotopic composition of the sample (November 1985) in weight.

Isotopic Pu composition (%)					Isotopic U composition (%)	
Pu-238/Pu	Pu-239/Pu	Pu-240/Pu	Pu-241/Pu	Pu-242/Pu	U-235/U	U-238/U
0.22	70.09	24.51	4.095	1.085	0.73	99.27

**Figure 1:** BSE picture and X mapping of O, U and Pu of a homogeneous MOX sample after heat treatment.**Acknowledgement:**

The research leading to these results has received funding from the European Union's Horizon 2020 Research and Training Programme of the European Atomic Energy Community (EURATOM) (H2020-NFRP2016/2017) under grant agreement n° 755443 (DisCo).

References

- [1] Ewing, R.C. (2015). Long-term storage of spent nuclear fuel. *Nature Materials*, 14, 252-257.
- [2] Odorowski, M., Jegou, C., De Windt, L., Broudic, V., Peugeot, S., Magnin, M., Tribet, M., Martin, C. (2016). Oxidative dissolution of unirradiated Mimas MOX fuel (U/Pu oxides) in carbonated water under oxic and anoxic conditions. *Journal of Nuclear Materials*, 468, 17-25.
- [3] Odorowski, M., Jegou, C., De Windt, L., Broudic, V., Jouan, G., Peugeot, S., Martin, C. (2017). Effect of metallic iron on the oxidative dissolution of UO₂ doped with a radioactive alpha emitter. *Geochimica et Cosmochimica Acta*, 219, 1-21.

Dissolution of alpha-doped UO₂ with and without Cr in the presence of corroding Fe, in synthetic and natural groundwater

Myllykylä, E. and Ollila, K.

VTT Technical Research Centre of Finland Ltd,
Espoo (FI)

Abstract

The objective of this study is to investigate effect of Cr-doping on the dissolution of α -doped UO₂ in conditions relevant to final disposal. The idea is to compare the results of these dissolution experiments to the ones conducted with real spent nuclear fuel in DisCo project and also the ones conducted previously with similar simulant materials but in different reaction media and without Cr-doping. The aim is to understand the matrix dissolution of novel Cr-doped spent fuel.

In the previous EU project, REDUPP [1], 3 different groundwaters selected from the Olkiluoto site, which is the planned site for disposal of spent nuclear fuel in Finland, were used (see Table 1). The materials leached in those waters were the same ²³³U alpha doped UO₂ fragments [2] referred as “old” material herein. In the DisCo project, the experiments with ²³³U-doped UO₂ are conducted in brackish OL-KR6. The composition of natural water (OL-KR6) has shown slight temporal variation depending on the sampling year. The composition of OL-KR6 water will be analysed in context of the sampling (June 2018). A saline groundwater from the disposal depth, close to composition of OL-KR5 (457-476 m), will be selected for experiments conducted with the new UO₂ material fabricated in DisCo project. As a reference and to allow for comparability of results of other working groups within the DisCo project, the selected experimental series are also conducted in bicarbonate water (0.01 M NaCl + 2 mM NaHCO₃).

The experiments are conducted under anaerobic conditions in Ar atmosphere of the glove box. The new pellet materials (UO₂, Cr-doped UO₂, ²³⁸Pu-doped UO₂ and Cr/²³⁸Pu-doped UO₂) will be prepared by SCK·CEN. The first experiments will be conducted with old UO₂ material with 5% or 10% ²³³U alpha doping, simulating the alpha dose of 10,000 years old and 1,000 years old spent nuclear fuel, respectively. The doping level of ²³⁸Pu-doped UO₂ pellets, to be fabricated, will correspond to the alpha dose of 10,000 years old nuclear fuel.

Table 1: Compositions for natural groundwaters used in REDUPP dissolution experiments [1]. Units are given in mmol·L⁻¹ if not otherwise indicated.

	Brackish water OL-KR6	Saline water OL-KR5	Fresh water ONK-PVA1
pH	7.7	8.1	7.9
Ammonium, NH ₄	0.018	< 0.001	0.026
Bicarbonate, HCO ₃	2.29	0.26	5.29
Bromide, Br	0.15	0.69	0.01
Calcium, Ca	12.73	43.66	1.32
Chloride, Cl	97.03	224.24	5.92
Dissolved Inorganic Carbon	2.00	< 0.25	5.08
Fluoride, F	-	0.063	0.021
Iron, Fe (total)	0.0063	0.0036	0.0007
Iron, Fe ²⁺	-	-	0.0007
Magnesium, Mg	6.17	2.80	0.74
Nitrate, NO ₃	< 0.00032	0.00048	< 0.0065
Nitrite, NO ₂	< 0.00022	< 0.00022	< 0.0043
Nitrogen, N (total)	0.03	0.086	0.041
Non Purgeable Organic Carbon	0.47	1.58	0.66
Phosphate, PO ₄	-	-	0.0032
Potassium, K	0.49	0.46	0.18
Silicate, SiO ₂	0.183	0.10	0.23
Sodium, Na	67.86	130.06	9.57
Strontium, Sr	0.068	0.19	0.0068
Sulphate, SO ₄	4.36	0.031	1.38
Sulphide, S ²⁻	-	0.062	0.004
Sulphur, S (total)	4.37	0.053	1.40
Total dissolved solids (mg·L ⁻¹)	6,268	12,880	981
Carbonate alkalinity, HCl uptake	< 0.05	< 0.05	< 0.05
Total acidity, NaOH uptake	1.15	< 0.05	0.08
Total alkalinity, HCl uptake	2.3	0.27	5.3

The experimental system is described in Figure 1, showing the test vessel with an iron strip leaning to vessel wall, and UO₂ fragments placed into the saucer to avoid any influence from dissolved Si on the results. On the other hand, zircaloy is more relevant as it will also be present in final disposal system. In DisCo experiments the UO₂ is planned to be placed in zircaloy saucers instead of glass ones used before. The initial composition of the groundwaters are analysed and the concentration of essential elements; U, Cr, Fe and Zr followed by double focusing sector field ICP-MS during the dissolution experiment. Solution pH and Eh are also measured few times during the experiments. Duplicate experiments with Fe and UO₂ will be conducted to extract H₂(g), formed due to anoxic metal corrosion, via a septum. In the end of the experiments the metallic surfaces are going to be studied with microscopic methods (SEM, TEM) for identification of the formation of secondary minerals.



Figure 1: Schematic view of closed plastic vessel ($V = 60$ mL) (left) in which the experiments will be conducted in the anaerobic glove box (right). UO_2 fragments are placed in the zircaloy saucer and the iron strip is leaning on the vessel wall in experimental media.

New laboratory facilities are now ready for dissolution experiments and the first experimental series with ^{233}U -doped UO_2 are launched as soon as possible after receiving the groundwater from Olkiluoto site and equilibrating it with Ar atmosphere of the glove box. According to the plan, pre-leaching with carbonate solution will be started in July and actual experiments in September. Before start of the uranium analyses the sensitivity of SF-ICP-MS is to be enhanced with APEX IR sample desolvation system, which is known to increase the sensitivity 3 to 10 fold depending on flow rate of the sample solution [3, 4]. Hence, the sample desolvation system improves the detection limit of U in the analyses of groundwaters. This is essential as relatively saline groundwaters have to be diluted and thus measured concentrations are close to the analytical detection limit.

References

- [1] Evins, L.Z., Juhola, P., Vähänen, M. (2014). REDUPP Final Report (FP7, agreement no. 269903). Posiva Working Report, 2014-12.
- [2] Ollila, K., Myllykylä, E., Tanhua-Tyrkkö, M., Lavonen, T. (2013). Dissolution rate of alpha-doped UO_2 in natural groundwater. *Journal of Nuclear Materials*, 442(1-3), 320-325.
- [3] Santos, J.S., Teixeira, L.S.G., dos Santos, W.N.L., Lemos, V.A., Godoy, J.M., Ferreira, S.L.C. (2010). Uranium determination using atomic spectrometric techniques: An overview. *Analytica Chimica Acta*, 674(2), 143-156.
- [4] Esaka, F., Magara, M., Lee, C.G., Sakurai, S., Usuda, S., Shinohara, N. (2009). Comparison of ICP-MS and SIMS techniques for determining uranium isotope ratios in individual particles. *Talanta*, 78(1), 290-294.

Synthesis and preliminary characterisation of model UO₂ fuel doped with Al₂O₃

Cordara, T., Smith, H., Stennett, M., Hyatt, N., Corkhill, C.

NucleUS Immobilisation Science Laboratory,
Department of Materials Science and Engineering,
University of Sheffield, Sheffield (UK)

Abstract

The addition of Cr₂O₃ and Al₂O₃ to modern UO₂ fuel modifies the microstructure so that, through the generation of larger grains during fission, a higher proportion of fission gases can be accommodated. This reduces the pellet-cladding mechanical interaction of the fuel rods, allowing the fuels to be “burned” for longer than traditional UO₂ fuel, thus maximising the energy obtained. Despite being common practise across Europe, the influence of Cr- and Al-oxide additions on the U coordination and local structure is not well understood. Elucidation of the chemistry is required to support understanding of fuel behaviour during storage and disposal. The objective of this study is to investigate effect of Al₂O₃/Cr₂O₃-doping on the microstructure and dissolution kinetics of UO₂. In this contribution, we describe the rationale for the use of these fuels, and the development and preliminary characterisation of model UO₂ materials doped with Al₂O₃.

Introduction

One of the main limitations for how long UO₂ fuel can remain in the reactor is the accumulation of fission products, especially fission gases like Kr, Xe, He, etc. The build-up of these gases at grain boundaries of the UO₂, and in the gap between the cladding and the fuel when the grain boundaries have become saturated, results in swelling of the fuel. If the volume of the fuel exceeds that of the cladding, or the cladding experiences excessive strain from the swollen fuel, the cladding may rupture, resulting in downtime of the reactor. The solution to this issue is to improve the UO₂ fuel by promoting the growth of larger grains and increasing the rate of diffusion of fission products to the grain boundaries during fission [1]. This is achieved by doping UO₂ with additives; the most extensively applied are Cr₂O₃ [2-8], Al₂O₃ [3, 9, 10] and a mixture of Cr₂O₃ - Al₂O₃ [7, 11].

The influence of Cr- and Al-oxide additions on the U coordination and local structure is not well understood; preliminary studies show that even small additions of these elements may significantly alter the defect chemistry and uranium stoichiometry [e.g. 12]. Recent studies [13, 14] have shown that small alterations in defect chemistry and uranium stoichiometry can strongly influence the rate at which UO₂ corrodes; this is an important consideration for the disposal of spent nuclear fuel, which will be disposed of in a geological facility where interactions of the fuel with groundwater will eventually lead to corrosion. In the meantime, the fuel will be stored in a dry-cask store, where the local coordination may influence any accidental corrosion of the fuel should the dry cask containment fail. In comparison to UO₂ fuel these new fuels are poorly understood, which may prove problematic for storage and disposal regulators.

As such, we aim to synthesise simplified UO_2 materials with additions of Al_2O_3 and Cr_2O_3 dopants to understand how the addition of dopants influences: i) the defect structure and grain size of the fuel; and ii) the kinetics and mechanisms of oxidative dissolution. In this contribution, we describe our preliminary studies on the synthesis and characterisation of Al_2O_3 -doped UO_2 material and plans for synthesis of $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ mixed dopant model UO_2 materials.

Methodology

Materials and synthesis

Uranium dioxide materials doped with Al_2O_3 were prepared using a dry synthesis route where UO_2 was mixed with 500, 1,000 or 1,500 ppm Al_2O_3 . A sample of UO_2 powder was also prepared as a reference material. The oxide powders were milled for 5 minutes at 30 Hz and pelletized using a die of 6 mm diameter. Pellets thus obtained were sintered at 1,700°C for 8 hours under a reducing atmosphere (N_2 - 5% H_2).

Characterisation

The morphology of UO_2 oxides doped with additives were characterised by Scanning Electron Microscopy (SEM). Back Scattered Electron (BSE) images were recorded using a Hitachi TM3030 SEM operating with an accelerating voltage of 15 kV. Furthermore, Energy Dispersive Spectroscopy (EDS) was used to verify the composition of the oxide powders. EDS analysis was performed using a Quantax 70 software and elemental maps were collected for 10 min. X-ray Diffraction (XRD) analyses were performed using a Bruker D2 Phase diffractometer utilizing a $\text{Cu K}\alpha$ source. Measurements were taken from 10° to $100^\circ 2\theta$ with a step size of 0.02° and 2 s counting time per step. The densification rate and porosities developed by the pellets were determined by geometric measurements.

Results

The grain size of UO_2 and Al_2O_3 -doped UO_2 samples prepared by dry synthesis were investigated by SEM, as shown in Figure 1. The observed porosity was low, confirming that high density pellets were successfully synthesised. The grain size was determined as a function of Al_2O_3 dopant concentration, using the FiJi software (image treatment software) to obtain the diameter of each grain. The grain size results presented in Figure 1 are an average value based on the measurement of ~ 650 grains. In comparison with UO_2 , the grain size of Al_2O_3 -doped samples was larger, confirming previous observations in the literature [3, 10]. Moreover, it was observed that the grain size increased when the Al_2O_3 content decreased from 1,500 to 500 ppm. This result is in accordance with that of Backman et al. [11].

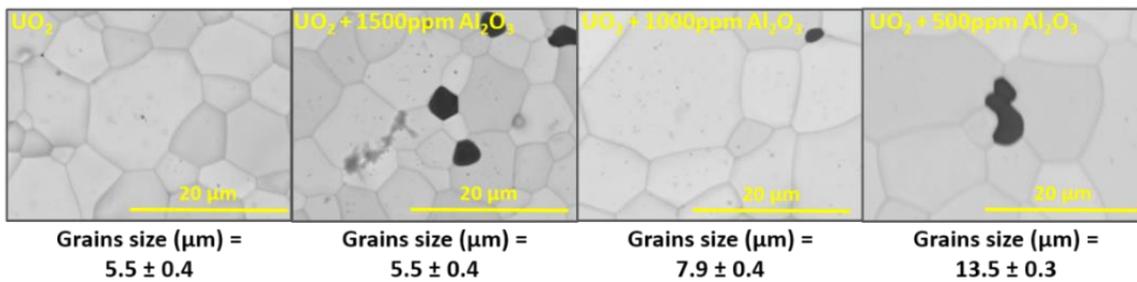


Figure 1: Evolution of grain size in UO_2 and Al_2O_3 doped UO_2 pellets, as function of dopant concentration.

Using a calliper, geometric measurements of the pellets was performed to determine the density of UO_2 and Al_2O_3 -doped UO_2 . Results are presented in Table 1. These preliminary results suggest that the densification of UO_2 is increased in presence of additives. More accurate analysis will be performed by He pycnometry in the near future.

Table 1: Densification rates (%) determined by geometric measurements for each Al_2O_3 contents of Al_2O_3 doped UO_2 pellets.

UO_2	$\text{UO}_2 + 1,500 \text{ ppm Al}_2\text{O}_3$	$\text{UO}_2 + 1,000 \text{ ppm Al}_2\text{O}_3$	$\text{UO}_2 + 500 \text{ ppm Al}_2\text{O}_3$
91 ± 1	94 ± 1	94 ± 1	93 ± 1

EDS analyses, shown in Figure 2, indicated that aluminium was incorporated in the UO_2 matrix. However, agglomerates of Al_2O_3 observed at the surface of prepared pellets for all the different samples highlights that the Al_2O_3 contents used are higher than the limit of solubility of Al_2O_3 in UO_2 .

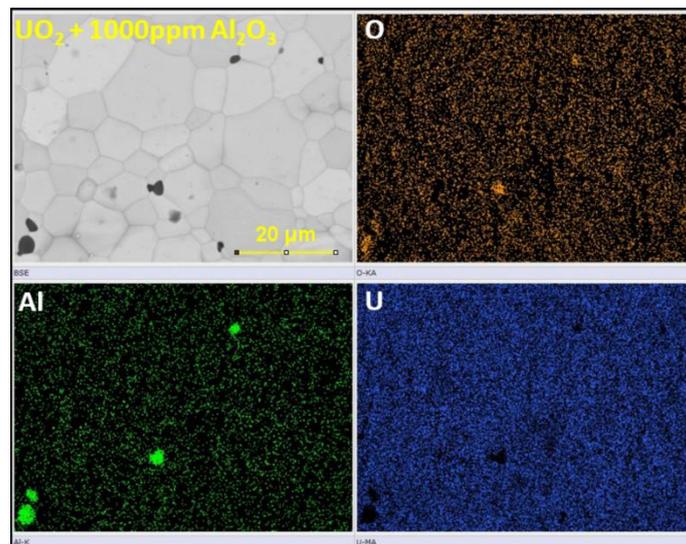


Figure 2: Elemental distribution in UO_2 pellets doped with 1,000 ppm Al_2O_3 .

XRD analyses were performed on each pellet, and Rietveld refinements were conducted, to determine the lattice parameter. XRD patterns are presented in Figure 3 with the lattice parameter cited for each sample.

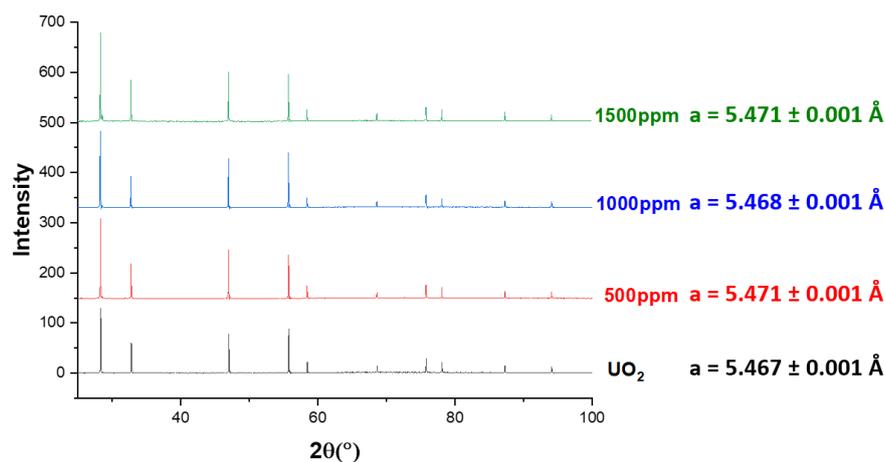


Figure 3: XRD patterns for UO_2 and Al_2O_3 -doped UO_2 and lattice parameters determined by Rietveld refinements.

XRD patterns confirmed that the fluorite structure (space group Fm-3m), the characteristic crystalline structure of UO_2 , was retained when the samples were doped with Al_2O_3 . Despite the presence of micro-precipitates of Al_2O_3 as observed in the EDS analysis (Figure 2), no additional reflections for Al_2O_3 were observed; this is likely because the concentration of these precipitates are below the detection limit of the XRD. Concerning the lattice parameter, values obtained in presence or absence of Al_2O_3 were close to the theoretical value for UO_2 found in the literature, $a = 5.468 \pm 0.001 \text{ \AA}$ [15]. This indicates that either: i) aluminium incorporated in the UO_2 crystalline structure is located in one of the many defect positions in the UO_2 lattice and thus does not change the cell volume; or ii) Al is not incorporated into the lattice. The latter, however, is in contrast with EDS analysis (Figure 2).

Conclusions and Future work

In conclusion, this preliminary study investigated the preparation and characterisation of UO_2 and Al_2O_3 -doped UO_2 pellets. SEM and geometric measurements have highlighted the increase of the grain size and of the densification rate in presence of Al_2O_3 . This result is in accordance with the literature. However, it was not possible to elucidate the mechanism of Al_2O_3 incorporation into UO_2 ; EDS and XRD results are opposed in this respect. Further characterisations (e.g. HR-XRD and EXAFS) will be performed to further determine the solubility limit, the lattice parameter and Al coordination in these materials.

In addition to the preparation of Al_2O_3 -doped UO_2 materials, we will prepare samples doped with Cr_2O_3 , and with both Al_2O_3 and Cr_2O_3 . Dry, and a series of wet synthesis routes, will be investigated. The preparation of high density samples will also be performed using hot-isostatic pressing (HIP), which is a sintering method where the pellet is heated at the same time as the application of gas pressure.

Once samples have been synthesised, multi-parametric dissolution experiments will be performed to realise the dissolution rate as a function of dopant concentration. Previous work conducted at the University of Sheffield [13, 16, 17] showed that microstructural features including grain boundaries and surface defects can significantly enhance the dissolution rate of spent fuel analogue materials. The change in grain size of the doped UO_2 samples is therefore expected to influence the dissolution rate. We propose to use a surface-based approach to resolve these effects, using vertical scanning interferometry and atomic force microscopy.

Acknowledgements

The authors wish to acknowledge funding for this research from the Modern Spent Fuel Dissolution and Chemistry in Failed Container Conditions (DisCo project). This is a Collaborative Project funded by the European Commission under the Horizon 2020 Research and Training Programme of the European Atomic Energy Community (EURATOM) (H2020-NFRP-2016-2017-1). This research was performed at the MIDAS Facility, at the University of Sheffield, which was established with support from the Department of Energy and Climate Change

References

- [1] Lindback, J.E. (2003). Westinghouse doped pellet technology. IAEA-TECDOC-1416: “Advanced fuel pellet materials and designs for water cooled reactors”, 101-110.
- [2] Bourgeois, L., Dehaut, Ph., Lemaignan, C., Hammou, A. (2003). Factors governing microstructure development of Cr₂O₃-doped UO₂ during sintering. *Journal of Nuclear Materials*, 297(3), 313-326.
- [3] Kashibe, S. and Une, K. (1998). Effect of additives (Cr₂O₃, Al₂O₃, SiO₂, MgO) on diffusional release of ¹³³Xe from UO₂ fuels. *Journal of Nuclear Materials*, 254(2-3), 234-242.
- [4] Killeen, J.C. (1980). Fission gas release and swelling in UO₂ doped with Cr₂O₃. *Journal of Nuclear Materials*, 88(2-3), 177-184.
- [5] Leenaers, A., de Tollenaere, L., Delafoy, Ch., Van den Berghe, S. (2003). On the solubility of chromium sesquioxide in uranium dioxide fuel. *Journal of Nuclear Materials*, 317(1), 62-68.
- [6] Cardinaels, T., Govers, K., Vos, B., Van den Berghe, S., Verwerft, M., de Tollenaere, L., Maier, G., Delafoy, C. (2012). Chromia doped UO₂ fuel: Investigation of the lattice parameter. *Journal of Nuclear Materials*, 424(1-3), 252-260.
- [7] Arborelius, J., Backman, K., Hallstadius, L., Limbäck, M., Nilsson, J., Rebensdorff, B., Zhou, G., Kitano, K., Löfström, R., Rönnerberg, G. (2006). Advanced doped UO₂ pellets in LWR applications. *Journal of Nuclear Science and Technology*, 43(9), 967-976.
- [8] Delafoy, C. and Zemek, M. (2010). Washout behaviour of chromia-doped UO₂ and gadolinia fuels in LWR environments. IAEA-TECDOC-1654: “Advanced Fuel Pellet Materials and Fuel Rod Design for Water Cooled Reactors”, 127-138.
- [9] Costa, D.R. and Freitas, A.C. (2017). Thermal stability test of UO₂-doped pellet manufactured at INB. INAC 2017, Belo Horizonte, MG, Brazil.
- [10] Kim, D.-J., Rhee, Y.-W., Yang, J.-H., Kim, J.-H., Kang, K.-W., Kim, K.-S. (2007). Effect of sintering conditions on the grain growth of an Al-doped UO₂ pellet. *Transactions of the Korean Nuclear Society Spring Meeting*, Jeju, Korea, May 10-11, 2007.
- [11] Backman, K., Hallstadius, L., Rönnerberg, G. (2010). Westinghouse advanced doped pellet - Characteristics and irradiation behaviour. IAEA-TECDOC-1654: “Advanced Fuel Pellet Materials and Fuel Rod Design for Water Cooled Reactors”, 117-126.
- [12] He, H., Qin, Z., Shoesmith, D.W. (2010). Characterizing the relationship between hyperstoichiometry, defect structure and local corrosion kinetics of uranium dioxide. *Electrochimica Acta*, 56(1), 53-60.
- [13] Corkhill, C.L., Bailey, D.J., Tocino, F.Y., Stennett, M.C., Miller, J.A., Provis, J.L., Travis, K.P., Hyatt, N.C. (2016). Role of microstructure and surface defects on the dissolution kinetics of CeO₂, a UO₂ fuel analogue. *ACS Applied Materials & Interfaces*, 8(16), 10562-10571.

-
- [14] Cordara, T. (2017). Effect of fission products on uranium dioxide dissolution. PhD Thesis, University of Montpellier.
- [15] Desgranges, L., Baldinozzi, G., Rousseau, G., Nièpceand, J.-Cl., Calvarin, G. (2009). Neutron diffraction study of the in-situ oxidation of UO_2 . *Inorganic Chemistry*, 48(16), 7585-7592.
- [16] Corkhill, C.L., Myllykylä, E., Bailey, D.J., Thornber, S.M., Qi, J., Maldonado, P., Stennett, M.C., Hamilton, A., Hyatt, N.C. (2014). contribution of energetically reactive surface features to the dissolution of CeO_2 and ThO_2 analogues for spent nuclear fuel microstructures. *ACS Applied Materials & Interfaces*, 6(15), 12279-12289.
- [17] Myllykylä, E., Lavonen, T., Stennett, M., Corkhill, C., Ollila, K., Hyatt, N. (2015). Solution composition and particle size effects on the dissolution and solubility of a ThO_2 microstructural analogue for UO_2 matrix of nuclear fuel. *Radiochimica Acta*, 103(8), 565-576.

Integrated spent fuel alteration model. Method and first results

Riba, O., Coene, E., Silva, O., Duro, L.

Amphos 21, Barcelona (ES)

Introduction and objectives

In the last years, existing models that account for the postulated oxidative dissolution of spent nuclear fuel have been extended by incorporating new processes that were not considered in classical quantitative approaches. Examples of later advances are those of Wu et al. [1-3] and the models by Jerden et al. [4], who developed the Fuel Matrix Dissolution Model (FMDM) based on the calculation of the corrosion potential at the surface of the fuel.

Improved numerical resolution methods implemented in modelling software such as COMSOL [1-3] or MATLAB [4] and model simplifications have allowed to include the most relevant processes of the system in the models. So far, simplifications were mainly applied to the radiolytic scheme and to the chemistry of the system. Radiolysis and chemical complexation/dissolution reactions have very different kinetics, often differing by more than 6 orders of magnitude. Also, uranium (the most abundant component of the fuel) and iron of the container have a complex chemistry. This complexity and the difference in time scales represent an important modelling challenge and the main reasons for adopting simplifications.

The objectives of Amphos 21 in the DisCo European project are:

- Task 1. To develop a conceptual geochemical model that accounts for the impact of metal alloy particles (epsilon metals) on spent fuel (SF) dissolution under highly reducing conditions and in presence of hydrogen.
- Task 2. To implement a reactive transport model in iCP [8] (interface coupling COMSOL Multiphysics [9] and PhreeqC [10]) for simulating the dissolution of spent nuclear fuel matrix inside a failed waste container.

During the first year of the project the focus has been in Task 2, to set up a method for coupling radiolysis and chemistry in a spent fuel matrix alteration model. This scientific and technical contribution presents the modelling approach and results of preliminary simulations.

Modelling approach

A practical method to couple radiolysis, the water system chemistry and the solute transport through the combination of Chemsimul [7] and iCP [8] is developed in DisCo. The method aims at simulating the dissolution of SF inside a failed waste container.

The code integration is achieved by a one-way coupling approach. First, water radiolysis is simulated with Chemsimul. Then, the concentrations of the predominant radiolytic species: H_2O_2 , O_2 , and H_2 calculated with Chemsimul at different times are introduced in iCP as source terms to calculate solute transport and SF dissolution.

In a first approach, a 1D reactive transport model will be implemented considering a homogeneous SF solid surface (UO_2 containing 1% of Pd, as representative of epsilon particles). A sketch of the system domain is shown in Figure 1.

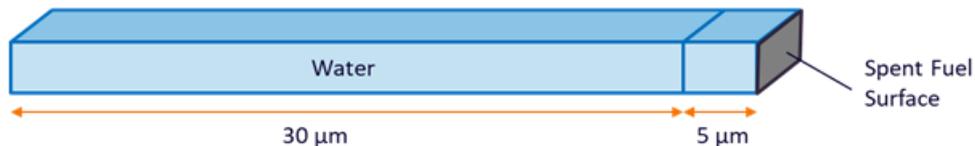


Figure 1: Sketch of the system considered in the preliminary calculations. The model considers two domains: a $30\ \mu\text{m}$ domain of water and a $5\ \mu\text{m}$ domain of water in contact with the spent fuel surface. The water domain considers aqueous speciation only, while the second domain also considers reactions with the solid surface.

The detailed developed method is described below:

- Determination of oxidants and reductants produced by water radiolysis with α radiation

The complete radiolytic scheme of generation of oxidants and reductants by water radiolysis and the recombination reactions of radiolysis products included in Matrix Alteration Model (MAM) [7] is considered in the present work.

The spatial alpha dose rate profiles have been calculated using the method and equations described in [1] and considering an alpha range of 35 microns.

The temporal evolution of the concentrations of oxidants and reductants are determined with Chemsimul for each specific dose rate calculated at a given distance from the SF surface.

- Transport of dissolved species

The reactive transport model considers transport by diffusion through groundwater according to the following equation:

$$\phi \frac{\partial c_i}{\partial t} + \nabla(-D_e \nabla c_i) = S_i + \sum_j R_{ij} \quad (1)$$

ϕ [-] is the porosity, c_i [$\text{mol}\cdot\text{kg}_w^{-1}$] is the aqueous concentration of species i , D_e [$\text{m}^2\cdot\text{s}^{-1}$] the effective diffusion coefficient, S_i [$\text{mol}\cdot\text{kg}_w^{-1}\cdot\text{s}^{-1}$] the source term of species i and R_{ij} the reaction term between species i and j . In the model presented here, spent fuel is considered only as a surface, not as a porous medium. Therefore, the porosity is 1 and the effective diffusion coefficient is $10^{-9}\ \text{m}^2\cdot\text{s}^{-1}$ in the whole 1D geometry.

The production of the main oxidants and reductants altering the spent fuel matrix calculated with Chemsimul are introduced in iCP with their respective source terms (S_i) as described in the transport equation. Note that these production rates have been calculated for different dose rates and are a function

of the distance to the spent fuel surface. The chemical reaction terms of the transport equation, on the other hand, are calculated with the PhreeqC model presented in the next section.

- Corrosion of the SF surface

The solid phase considered as SF matrix is the amorphous UO_2 with the formulation: $\text{UO}_2 \cdot 2\text{H}_2\text{O}$, doped with certain amounts of Pd representing epsilon particles for hydrogen activation. The following kinetic reactions are implemented in PhreeqC:

- Generation of $\text{OH}\cdot$ by decomposition reaction of H_2O_2 on the $\text{UO}_2 \cdot 2\text{H}_2\text{O}$ surface
- Oxidation of $\text{UO}_2 \cdot 2\text{H}_2\text{O}$ to $\text{UO}_3(\text{s})$ by $\text{OH}\cdot$ and O_2
- Dissolution of $\text{UO}_3(\text{s})$ by H_2O and CO_3^{2-}
- Non-oxidative dissolution of $\text{UO}_2 \cdot 2\text{H}_2\text{O}$
- Activation of H_2 by Pd surface
- Reduction of $\text{UO}_3(\text{s})$ to $\text{UO}_2 \cdot 2\text{H}_2\text{O}$

These reactions only take place in the 5 μm model domain that includes the SF surface. The thermodynamic database used in the modelling is ThermoChimie version 9b0 [11].

Preliminary results

First of all, validation of kinetic constants has been done by comparison with the experimental data described in Cera et al. [12].

The dissolution experiments of spent fuel fragments from a PWR rod with a burn-up of $40 \text{ MWd} \cdot \text{kgU}^{-1}$ reported in Cera et al. [12], also used in the MICADO project [13] were set up at long reaction time (> 350 days) in closed ampoules to keep the gases produced by radiolysis (O_2 and H_2). The generated experimental data in Cera et al. [12] have great value for our validation exercises as:

- It provides the concentration of uranium in 2 mM NaCl solution and in 10 mM $\text{NaHCO}_3 + 2 \text{ mM NaCl}$, so the effect of carbonate and chloride in the water radiolysis and in uranium dissolution can be validated, allowing to adjust the dissolution kinetic constants of $\text{UO}_3(\text{s})$ in water and also in the presence of carbonate.
- It provides the concentration of generated O_2 , H_2 and H_2O_2 at long reaction times, allowing to adjust the following rate constants of the model:
 - o oxidation of $\text{UO}_2 \cdot 2\text{H}_2\text{O}$ by O_2
 - o activation of H_2 by Pd
 - o decomposition of H_2O_2 on $\text{UO}_2 \cdot 2\text{H}_2\text{O}$ surface, respectively

The first step of the validation exercise was modelling with Chemsimul the generation rates of oxidants and reductants from the alpha and beta dose rates determined in Cera et al. [12]. The full radiolysis scheme of water radiolysis in a solution containing carbonate and chloride was considered.

The generation rates of H_2O_2 , O_2 and H_2 determined in Chemsimul were implemented in PhreeqC, together with the set of kinetic reactions described above occurring at the surface of spent fuel.

Finally, the adjustment of the kinetic reactions occurring in the spent fuel surface was performed by comparison with the experimental data. The modelling results together with the experimental concentration of O_2 , H_2 , H_2O_2 and U obtained in 2 mM NaCl solutions are shown in Figure 2.

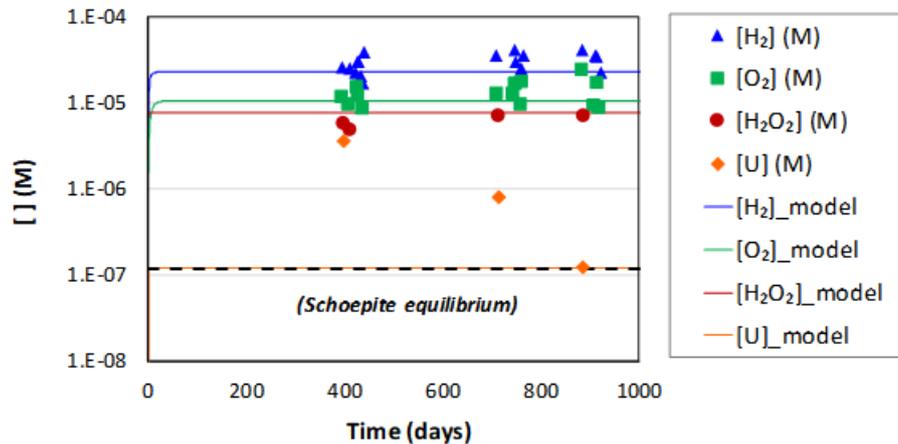


Figure 2: Concentration of H_2 , O_2 , H_2O_2 and U as function of time. Symbols represent experimental data from Cera et al. [12] solid lines represent the modelling results and the dashed line represent the uranium concentration in equilibrium with schoepite ($\text{UO}_2(\text{OH})_2(\text{beta})$).

As it is shown in Figure 1, uranium in equilibrium with schoepite has been considered in the model and it has been possible to model the experimental concentrations obtained in NaCl solutions for all the species.

The validated kinetic rates will be implemented in 1D reactive transport model as described in the modelling approach section.

Future work

The second year of the project will be devoted to extent the model by including:

- Heterogeneity of the SF matrix to account for different concentrations of epsilon particles (Pd).
- Including the SF as a porous medium. In this case, the concentrations of H_2O_2 , O_2 , $\text{OH}\cdot$, H_2 and H calculated with Chemsimul will also be introduced as source terms within the fuel matrix.
- Porosity changes of the SF by precipitation of secondary phases within the SF and on the SF surface.
- Inclusion of Fe surface simulating the effect of the corroding canister.

Acknowledgement

The research leading to these results has received funding from the European Union's Horizon 2020 Research and Training Programme of the European Atomic Energy Community (EURATOM) (H2020-NFRP2016/2017) under grant agreement n° 755443 (DisCo).

References

- [1] Wu, L., Beaugard, Y., Qin, Z., Rohani, S., Shoesmith, D.W. (2012). A model for the influence of steel corrosion products on nuclear fuel corrosion under permanent disposal conditions. *Corrosion Science*, 61, 83-91.
- [2] Wu, L., Liu, N., Qin, Z., Shoesmith, D.W. (2014). Modeling the radiolytic corrosion of fractured nuclear fuel under permanent disposal conditions. *Journal of the Electrochemical Society*, 161(8), E3259-E3266.
- [3] Wu, L., Qin, Z., Shoesmith, D.W. (2014). An improved model for the corrosion of used nuclear fuel inside a failed waste container under permanent disposal conditions. *Corrosion Science*, 84, 85-95.
- [4] Jerden, J.L., Frey, K., Ebert, W. (2015). A multiphase interfacial model for the dissolution of spent nuclear fuel. *Journal of Nuclear Materials*, 462, 135-146.
- [5] Odorowski, M. (2015). Etude de l'altération de la matrice (U,Pu)O₂ du combustible irradié en conditions de stockage géologique: Approche expérimentale et modélisation géochimique. Doctoral Thesis.
- [6] Duro, L., Riba, O., Martínez-Esparza, A., Bruno, J. (2013). Modelling the activation of H₂ on spent fuel surface and inhibiting effect of UO₂ dissolution. *MRS Proceedings*, 1518, 133.
- [7] Kirkegaard, P., Bjergbakke, E., Olsen, J.V. (2008). CHEMSIMUL: A chemical kinetics software package. Roskilde: Danmarks Tekniske Universitet, Risø Nationallaboratoriet for Bæredygtig Energi. Denmark. Forskningscenter Risø. Risø-R-1630 EN. <http://orbit.dtu.dk/files/6278806/ris-r-1630.pdf>
- [8] Nardi, A., Idiart, A., Trinchero, P., de Vries, L.M., Molinero, J. (2014). Interface COMSOL-PHREEQC (iCP), an efficient numerical framework for the solution of coupled multiphysics and geochemistry. *Computers & Geosciences*, 69, 10-21.
- [9] COMSOL Multiphysics. <https://www.comsol.com/>
- [10] Parkhurst, D.L. and Appelo, C.A.J. (2013). Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497 p.

Modelling of the oxidative leaching of $U_{1-x}Pu_xO_2$ in synthetic groundwater with metallic iron – first results

De Windt, L.¹, Kerleguer, V.^{1,2}, Jégou, C.², Goblet, P.¹, Martin, C.³

¹ ARMINES/MINES ParisTech, Centre de Géosciences, Fontainebleau (FR)

² CEA/DEN/DE2D/SEVT/LMPA – Marcoule, Bagnol sur Cèze (FR)

³ Andra – Châtenay-Malabry (FR)

Context

The dissolution rate of the oxide matrix of spent nuclear fuels is a key factor controlling the long-term release of radionuclides in deep geological disposals. Whether the knowledge acquired for UOX (uranium oxide) fuels [1, 2] can be transferred to MOX (mixed plutonium and uranium oxide) fuels is still a debated issue, especially due to the expected resistance of Pu-enriched agglomerates specifically found in MOX fuels [3]. The microstructure of industrial MIMAS MOX fuels is indeed heterogeneous with three different phases: an UO_2 matrix containing circa 3 wt.% of Pu, agglomerates with 20 wt.% of Pu, and a coating zone with an intermediate composition. The modelling of a simpler material ($U_{0.73}Pu_{0.27}O_2$) with a high but homogeneous Pu distribution is, therefore, a necessary step towards the modelling of the leaching of heterogeneous MOX matrices.

Modelling approach

In a previous study [2], a geochemical model (CHESS code) and a reactive transport model (HYTEC code) were validated (at 25°C) on leaching experiments of UO_2 matrices with low-Pu content in contact with a synthetic Callovo-Oxfordian (COx) groundwater (representing groundwater at the proposed French waste disposal site) and metallic iron foils (simulating the fuels proximity to steel disposal canisters). These models, which are under further developments for the DisCo project, currently take into account the:

- kinetics of H_2O_2 production and disproportionation at the pellet surface,
- kinetics of $U_{0.73}Pu_{0.27}O_2$ and UO_2 dissolution vs. both H_2O_2 and O_2 ,
- kinetics of the generalized corrosion of metallic iron,
- thermodynamic equilibrium for aqueous reactions and precipitation of secondary phases,
- diffusion of dissolved species (HYTEC only).

The geometric configuration of the experimental set-up can be modelled with HYTEC, in particular the several centimetres distance between the pellet and the iron foil. Only time-related results can be calculated with CHESS.

Secondary plutonium phases

Based on the literature, a subset of plutonium solids that may precipitate as secondary phases has been taken from the ThermoChimie thermodynamic database [4]: $\text{PuO}_2(\text{coll-hyd})$, $\text{Pu}(\text{OH})_4(\text{am})$, $\text{PuO}_2(\text{OH})(\text{s})$, $\text{PuO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}(\text{s})$, $\text{PuO}_2(\text{CO}_3)(\text{s})$. The formation constant of $\text{U}_{0.73}\text{Pu}_{0.27}\text{O}_2$ was roughly estimated from an ideal solid solution between UO_2 and PuO_2 . However, this phase is only under kinetic control in the modelling. Speciation diagrams of plutonium have been calculated with CHESS for experimental conditions as well as expected geological disposal facility conditions.

Kinetics of Fe(II)/ H_2O_2 reaction in solution

The experimental and modelling study of the effect of metallic iron on the oxidative dissolution of UO_2 doped with a radioactive alpha emitter [2] demonstrated that the redox reaction between dissolved ferrous iron (produced by iron corrosion) and hydrogen peroxide (produced by water radiolysis and enhancing UO_2 dissolution)



was a key reaction in the present system. This reaction has now been implemented under kinetic controls (instead of thermodynamic equilibrium in [2]) to refine the modelling. A literature review has led to a combination of two first-order reactions,

$$R(\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}) = \frac{d[\text{H}_2\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{Fe}^{2+}]}{dt} = -k a_{\text{Fe}^{2+}} a_{\text{H}_2\text{O}_2} \quad (2)$$

where a stands for the activity of the dissolved species, and k for the rate constant. The value of k varies over several orders of magnitude, from $5 \cdot 10^1$ (in acidic pure water) to more than $10^4 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ (in moderately saline and alkaline water, like the COx groundwater).

The HYTEC results of Figure 1a show that the calculated concentration of uranium is in good agreement with the experimental data at thermodynamic equilibrium or fast kinetics, whereas modelling with the lower kinetic rate overestimates uranium release. Figure 1b indicates that iron concentration is not sensitive to kinetics in the present system, due to the relatively higher concentration of Fe(II) with respect to H_2O_2 and the solubility control by siderite.

The mass transport over space plays an important role. The H_2O_2 generated within the alpha-track is initially very close to the fuel surface (tens of μm), while the Fe^{2+} generated through corrosion of metal iron in either inserts or overpacks of the fuel containers, lies usually much longer from the fuel surface (cm to dm scales). This coupling process has been preliminary assessed in [3] and will be further developed in the DisCo project.

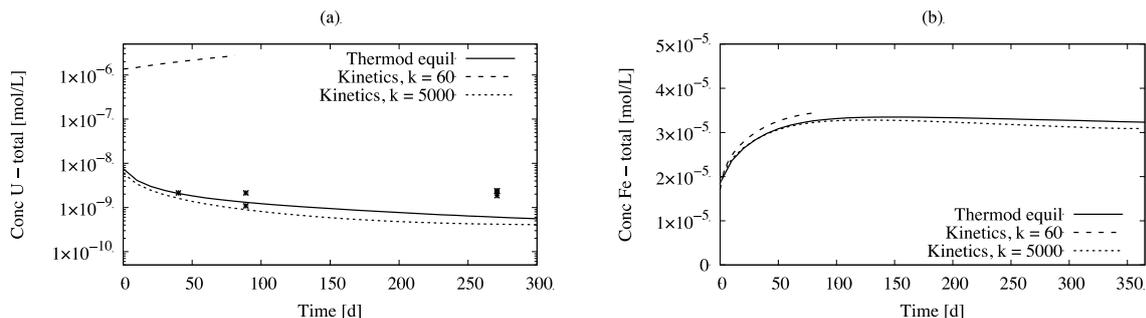


Figure 1: Modelling of Pu-doped UO₂ pellets in synthetic CO_x groundwater in presence of a pristine iron foil: sensitivity of the calculated concentrations of dissolved uranium and iron with respect to kinetics, Eq. (2).

Leaching of homogeneous (25% Pu) MOX pellets

CHESS modelling has been first applied to the leaching of homogeneous U_{0.73}Pu_{0.27}O₂ pellets in carbonate water under Ar atmosphere. This experiment is required to determine the dissolution kinetic rate constant. Figure 2a shows that dissolution of the pellets in carbonate water is relatively high and progressively decreases over time, as well as the concentration of H₂O₂. Not shown in this abstract, the release of plutonium in solution is several orders of magnitude lower than uranium release during the whole experiment. This could indicate either a congruent dissolution, with a surface precipitation of Pu, or an incongruent dissolution of U at the very surface of the pellet. For now, the preliminary model only considers the first hypothesis that is the easiest to be implemented.

A second leaching experiment (still in progress and closely linked to WP2) has been modelled with CHESS/HYTEC. Figure 2b shows that the release of uranium becomes significantly lower in synthetic CO_x groundwater in the presence of a metallic iron foil. In the modelling, iron corrosion is the most important factor since Fe(II) plays a key role in inhibiting the oxidative dissolution generated by localized alpha radiolysis of water molecules.

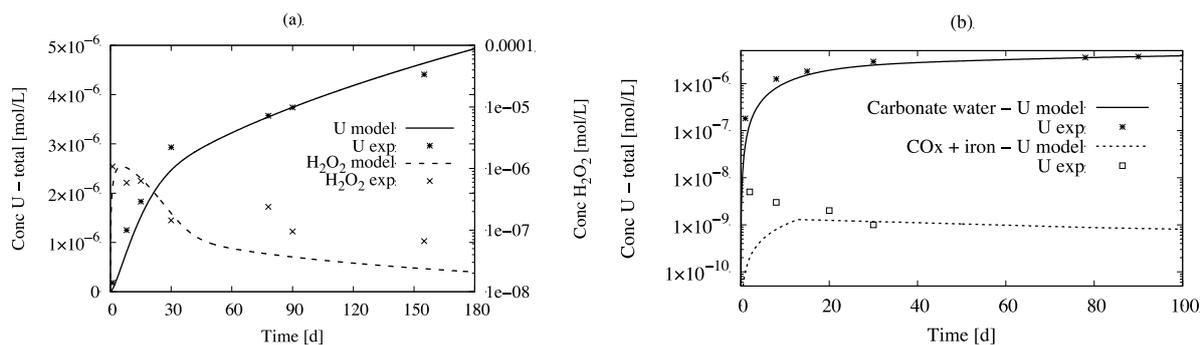


Figure 2: Experimental and modelling results of leaching of homogeneous (25% Pu) MOX pellets in carbonate water (a) and in synthetic CO_x groundwater in presence of a pre-corroded iron foil (b).

Acknowledgement



The research leading to these results has received funding from the European Union's Horizon 2020 Research and Training Programme of the European Atomic Energy Community (EURATOM) (H2020-NFRP2016/2017) under grant agreement n° 755443 (DisCo). The comments of two reviewers are gratefully acknowledged.

References

- [1] Ewing, R.C. (2015). Long-term storage of spent nuclear fuel. *Nature Materials*, 14, 252-257.
- [2] Odorowski, M., Jegou, C., De Windt, L., Broudic, V., Jouan, G., Peugeot, S., Martin, C. (2017). Effect of metallic iron on the oxidative dissolution of UO₂ doped with a radioactive alpha emitter. *Geochimica & Cosmochimica Acta*, 219, 1-21.
- [3] Odorowski, M., Jégou, C., De Windt, L., Broudic, V., Peugeot, S., Magnin, M., Tribet, M., Martin, C. (2016). Oxidative dissolution of unirradiated Mimas MOX fuel (U/Pu oxides) in carbonated water under oxic and anoxic conditions. *Journal of Nuclear Materials*, 468, 17-25.
- [4] Giffaut, E., Grive, M., Blanc, P., Vieillard, P., Colas, E., Gailhanou, H., Gaboreau, S., Marty, N., Made, B., Duro, L. (2014). Andra thermodynamic database for performance assessment: ThermoChimie. *Applied Geochemistry*, 49, 225-236.

Preliminary thermodynamic calculations for WP5, Task 1

Curti, E. and Kulik, D.

Paul Scherrer Institut (PSI), Villigen (CH)

Background and Introduction

Thermodynamic calculations are foreseen in WP5, Task 1 for a double purpose:

1. Explore the effect of dopants, such as Cr and Al, on the oxygen potential of modern UO₂ fuels (Subtask 1).
2. Define thermodynamic equilibrium conditions during spent fuel dissolution inside a corroding metallic canister (Subtask 2).

During the first project year, the major effort was put on the selection of key thermodynamic data for Subtask 1 and their integration in the databases and speciation codes that will be used to that purpose. In addition, the development of a model for substitution of Cr in UO₂ and its translation to a solid solution model to be implemented into the GEM-Selektor code was started. This work will be finalized during the next project year.

Subtask 1: Effect of Cr-doping on UO₂ fuels

For this subtask, an entire set of Cr data had to be selected and integrated into the in-house Heracles database (<https://www.psi.ch/heracles/gems-specific-heracles-database>) and GEM-Selektor code (<http://gems.web.psi.ch>). We started by reviewing the source data reported by Jeannin et al. [1] and Toker et al. [2]. The focus was on the key equilibrium between eskolaite (Cr₂O₃) and metallic Cr, since this reaction would buffer oxygen partial pressures if both phases would coexist in the fuel. Moreover, thermodynamic properties of these phases are required for the definition of Cr solid solution end-members.

Unfortunately, the cited references do not include temperature dependent heat capacity data, which are necessary to carry out thermodynamic calculations at any given temperature of interest. Heat capacities are however available in the comprehensive compilation of Barin [3]. After verifying that the latter data are consistent with the experimental data of references [1] and [2] it was decided to use Barin's compilation as the main source of Cr thermodynamic data. The reported heat capacity values were interpolated to obtain appropriate coefficients for the equation built-in in the GEM-Selektor code.

The selected data for chromium solids and gaseous species (standard molar Gibbs free energy, entropy and heat capacity at 298.15 K, 1 bar) are listed in Table 1 and Table 2. They were implemented into the GEM-Selektor code and Heracles database, and build the basis for thermodynamic calculations on Cr-doped fuels presented here and in future reports.

Table 1: Selected thermodynamic data for chromium solids.

Property	Cr ₂ O ₃	Cr	CrO ₂	CrO ₃	CrI ₂	CrI ₃
ΔfG^0 (kJ·mol ⁻¹)	-1,057.9	0.147	-544.84	-512.51	-165.56	-205.47
S^0 (J·mol ⁻¹ ·K ⁻¹)	81.20	23.35	51.05	73.22	169.03	199.58
c_p^0 (J·mol ⁻¹ ·K ⁻¹)	117.56	23.24	99.67	69.33	73.68	111.68

Table 2: Selected thermodynamic data for chromium gas species.

Property	Cr(g)	CrO(g)	CrO ₂ (g)	CrO ₃ (g)
ΔfG^0 (kJ·mol ⁻¹)	352.62	154.63	-87.31	-273.39
S^0 (J·mol ⁻¹ ·K ⁻¹)	174.31	239.27	269.22	266.17
c_p^0 (J·mol ⁻¹ ·K ⁻¹)	20.79	31.33	43.33	55.76

Test calculations have been carried out to prove the consistency of the selected data with the experimental results of previously published studies. Moreover, we implemented a first ideal solid solution model using Cr(III)O_{3/2}, U(IV)O₂ and U(V)O_{2.5} as end-members. These end-members represent the charged-balanced coupled substitution $2U^{4+} \rightleftharpoons Cr^{3+} + U^{5+}$, which has been identified as one of several possible incorporation mechanisms of Cr(III) in UO₂. This solid solution allows for compositions on the hyperstoichiometric side, i.e. (U⁴⁺,U⁵⁺,Cr³⁺)O_{2+x}, but not for hypostoichiometry, since reduced species of other actinides (e.g. Am³⁺, Cm³⁺, Pu³⁺) and trivalent lanthanides are not taken into account in this model. Moreover, this formulation does not yet include the presumably strong non-ideality effects of substituting Cr(III) for U(IV). More realistic formulations will be worked out soon, based on the solubility data of Cr in UO₂ available from the literature.

Figure 1 shows the results of the preliminary calculations in the form of an Ellingham diagram, where the oxygen potential is plotted as a function of temperature. The thick orange line shows, for a simple system composed of UO₂ with 1% total Cr (= 0.5 mol% Cr₂O₃), the calculated oxygen potentials in equilibrium with the aforementioned ternary ideal (U⁴⁺,U⁵⁺,Cr³⁺)O_{2+x} solid solution. The thick violet line is the corresponding calculation for a model spent fuel composition, now containing (besides 0.5 mol% Cr₂O₃) all the major fission products. The inventories correspond to about 60 GWd·t_{IHM}⁻¹ burn-up, 100 years after irradiation. Finally, the thick red curve is obtained for equilibrium between pure Cr(s) and pure Cr₂O₃(s). These GEMS calculations are compared with oxygen potential measurements on LWR fuels taken from the literature [4, 5] (shown as grey-shaded field) and the equilibrium oxygen potentials for redox couples of selected fission products (taken from Figure 2 in [6]). If the equilibrium line of a given redox pair lies below the fuel oxygen potential, the oxidized form is predicted to be thermodynamically stable in the fuel. In contrast, if it lies above the fuel oxygen potential, the reduced (metallic) form is predicted to be stable.

Several important pieces of information can be drawn from Figure 1:

- I. If minor amounts of chromium are added in any form to the UO₂ fuel, the expected final oxidation state is definitely Cr(III). The predominance of Cr(III) in UO₂-Cr solid solutions has also been verified spectroscopically, see e.g. [7].

- II. The calculated difference in oxygen potential between the simple $\text{UO}_2 + \text{Cr}_2\text{O}_3$ system and spent fuel is considerable. Fission reactions liberate oxygen which is only partially bound to fission products, thus increasing ΔGO_2 (compare orange and violet lines).
- III. Ideal solid solution calculations for the Cr-doped spent fuel predict oxygen potentials falling within the range measured for non-doped LWR fuels, which encompasses a widely range of burn-ups (from 28 to 200 $\text{GWD}\cdot\text{t}_{\text{HM}}^{-1}$, see [4, 5]).

The calculated spent fuel curve has a sigmoidal shape with three segments: at low temperatures (up to about 600°C , before entering the measurements field) the oxygen potential of the Cr-doped fuel is buffered by the Mo-MoO₂ equilibrium. At about 670°C MoO₂ is destabilized, so the aforementioned pO₂ buffer is no longer active. As temperature increases the oxygen potential decreases down to a minimum at 820°C and then increases again as the solid species Cs₂Te appears.

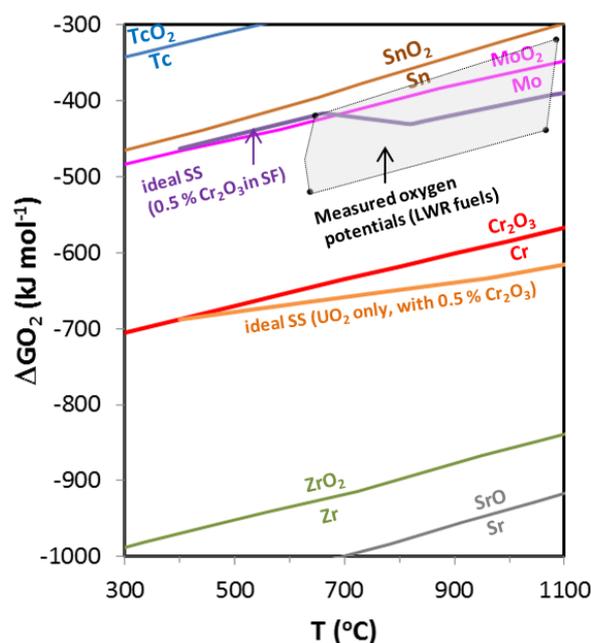


Figure 1: Ellingham diagram showing calculated oxygen potential curves for various systems and redox pairs compared with measured oxygen potentials of non-doped UO_2 fuels.

The formation of solid solutions between UO_2 and Cr_2O_3 is ascertained since experiments have shown that Cr has a small (< 1 mol%) but measurable solubility [7]. By analogy with other dopants dissolving in UO_2 in small quantities (e.g. Gd, see [8]), incorporation of Cr in the UO_2 lattice might affect considerably the oxygen potential of the fuel. With reference to Figure 1, this means that the oxygen potential of Cr-doped fuel could conceivably reach values exceeding the equilibrium lines of the Sn-SnO₂ and Tc-TcO₂ couples, implying that long-lived safety-relevant fission products such as ^{126}Sn and ^{99}Tc , which are stabilized as metals in ϵ -particles of non-doped UO_2 fuels, would become oxidized and thus potentially more water-soluble in Cr-doped fuels. This could happen if significant fractions of these nuclides substitute for U(IV) and Zr(IV) in the grey phase along the $\text{BaZrO}_2 - \text{BaUO}_2$ join (see Figure 23 in [6]).

When the calculation shown in Figure 1 for Cr-doped spent fuel is repeated for the same fuel composition, but without Cr_2O_3 added, the resulting oxygen potentials are either identical (in the

Mo-MoO₂ buffered region) or unnoticeably higher than for Cr-doped fuel. This result is in line with experimental data of UO₂ doped with other trivalent dopants (Nd, Gd), which show the oxygen potential to increase with dopant concentration, but only as the dopant concentration exceeds several moles% (see e.g. Figure 5 in [8]). The comparison of calculations with and without Cr-doping thus suggests a negligible effect of Cr on the oxygen potential of the fuel.

The calculations in Figure 1 however are based on a model fuel composition and on the assumption of ideality, which is unrealistic considering the charge and cation size mismatch upon substitution of Cr(III) into the UO₂ lattice. Therefore, a major task in the coming project year will be to develop a realistic Cr-UO₂ solid solution model and to derive interaction parameters defining non-ideality. Moreover, the fuel compositions of samples used by the WP2 DisCo partners will be used.

Acknowledgement

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 755443 - DisCo - NFRP-2016-2017/NFRP-2016-2017-1.

References

- [1] Jeannin, Y., Mannerskantz, C., Richardson, F.D. (1963). Activities in iron-chromium alloys. Transactions of the Metallurgical Society of AIME, 227, 300-305.
- [2] Toker, N.Y., Darken, L.S., Muan, A. (1991). Equilibrium phase relations and thermodynamics of the Cr-O system in the temperature range of 1500°C to 1825°C. Metallurgical and Materials Transactions B, 22B, 225-232.
- [3] Barin, I.B. (1989). Thermodynamic data of pure substances, VCH Verlagsgesellschaft mbH, 0-6940 Weinheim (Vol. 1, pp. 418).
- [4] Matzke, H. (1994). Oxygen potential in the rim region of high burnup UO₂ fuel. Journal of Nuclear Materials, 208, 18-26.
- [5] Matzke, H. (1995). Oxygen potential measurements in high burnup UO₂ fuel. Journal of Nuclear Materials, 223, 1-5.
- [6] Kleykamp, H. (1985). The chemical state of the fission products in oxide fuels. Journal of Nuclear Materials, 131, 221-246.
- [7] Riglet-Martial, Ch., Martin, Ph., Testemale, D., Sabathier-Devals, C., Carlot, G., Matheron, P., Iltis, X., Pasquet, U., Valot, C., Delafoy, C., Largenton, R. (2014). Thermodynamics of chromium in UO₂ fuel: A solubility model. Journal of Nuclear Materials, 447, 63-72.
- [8] Une, K. and Oguma, M. (1982). Thermodynamic properties of nonstoichiometric urania-gadolinia solid solutions in the temperature range 700-1100°C. Journal of Nuclear Materials, 110, 215-222.

Progress on modelling of UO₂ fuel dissolution within storage containers

Hambley, D.H., Goode, J., Hughes, R., Maher, C.

National Nuclear Laboratory, Sellafield (UK)

Introduction

NNL is undertaking development of chemical models for the interaction between incoming groundwater, spent fuel, waste container corrosion products and corrosion products from the spent fuel, suitable for incorporation in a mixed-potential model (MPM) which uses a number of one-dimensional reaction-diffusion equations, each referencing a different species within the system and is derived from the original Canadian MPM model [1]. The purpose is to:

- provide a reliable prediction of the interaction of dissolved species in ground waters, with and without iron from the canisters.
- determine dissolution rates under representative pond (oxic) and repository conditions (anoxic), chemical equilibria and secondary phase formation in surrounding aqueous phase.

The objectives of the model development work are to:

- identify relevant data on aqueous phase reactions from previous work on historic long-term pond stored fuel at Sellafield.
- review options for, and benefits of, integration of PHREEQC for aqueous phase equilibrium modelling.
- adapt the NNL mixed potential model developed for advanced gas reactor (AGR) fuel using the results of these activities in order to optimise the modelling of complex solution chemistries.

The updated model is intended be used to provide predictions of dissolution rates, chemical equilibria and secondary phase formation under oxic conditions relevant to NNL material characterised in WP2 and under representative repository conditions (anoxic), focusing on nominal UK granitic rock repository conditions.

Sensitivity and uncertainty analyses will also be undertaken to understand the sensitivity of predictions to key parameters, particularly those whose value are known to be poorly characterised or highly variable.

Progress on Model Development

A hydraulic model of the pond storage system has been developed to enable appropriate boundary conditions to be modelled and allow the NNL MPM to be applied to model the corrosion of fuel in

storage ponds (Figure 1). The model has been tested using data for AGR fuel storage conditions as part of ongoing work for a customer [2].

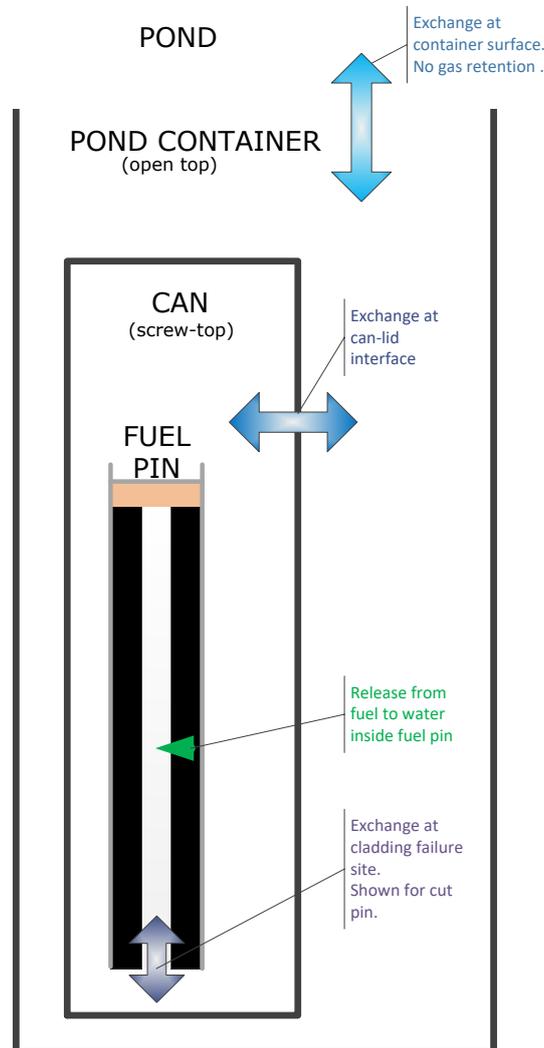


Figure 1: Conceptual model for pond storage system.

Initial work under this project has evaluated the coupling of the MDM model to PHREEQC. This has indicated that coupling is feasible and hence is a possible approach to modelling increased liquid phase complexity. However, it is clear that there is a significant run-time penalty associated with repeated calls to PHREEQC. Therefore, we are currently exploring the possibility of translating the core algorithms within PHREEQC directly into the MDM code to determine whether this can provide a more effective modelling approach.

The characteristics of the steel storage cans (Figure 2) have been defined and an assessment undertaken to calculate the time taken for the cans to become flooded. This has shown that the cans would have been substantially flooded within 1 year of loading to the pond and the hydraulic behaviour can be modelled dynamically. The fuel types and irradiation histories have been identified as described in the WP2 report.

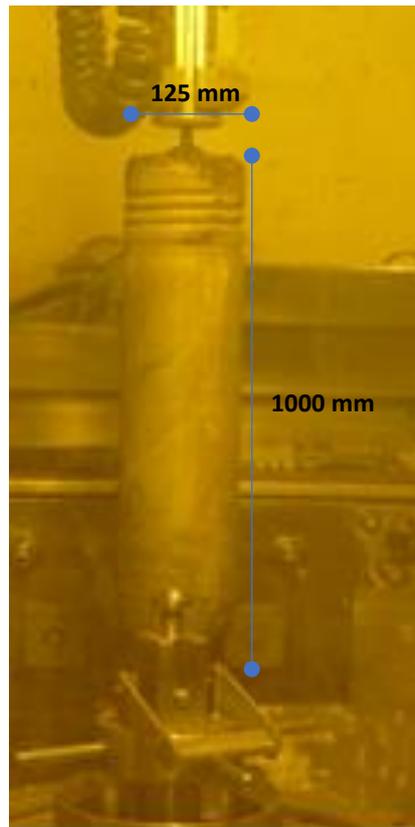


Figure 2: Stainless Steel storage can for historic fuel following post irradiation examination fuel.

Electrochemical studies of AGR fuel cladding corrosion in repository-relevant and pond-relevant conditions have been undertaken [3, 4]. Data from these experiments are being analysed to provide information on stainless steel cladding corrosion for use in the modelling of the stored legacy fuels and support modelling of the effects of iron species on the chemical processes in fuel storage cans. An example of electrochemical testing on as manufactured AGR fuel cladding is shown in Figure 3, which indicates the effect of NaOH ions on the corrosion susceptibility of the cladding: an increase in open circuit potential and a decrease in corrosion rate in the passive region.

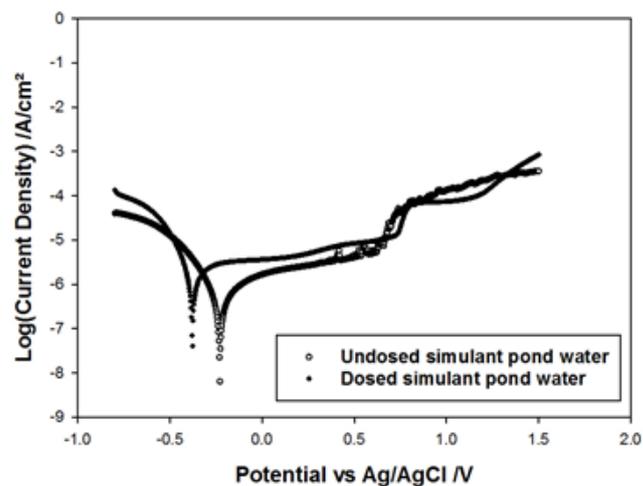


Figure 3: Linear scanning voltammetry results for unsensitised 20/25/Nb electrodes in pH 11.4 NaOH-dosed and undosed (pH 7) pond water simulants at 24°C.

Many of the UK fuel storage ponds operate at high pH and therefore there are relevant data available on the behaviour of uranium and fission product species under these conditions. These will also be relevant to the higher pH conditions associated with some repository designs. It is therefore proposed that NNL focusses on the development of chemical models at higher pHs within this project to complement existing work at near-neutral conditions [5, 6].

Acknowledgement

NNL wishes to acknowledge Sellafield Limited for funding the development of the NNL MDM model and for use of relevant fuel and pond characteristics to enable future modelling work.

The research leading to these results has received funding from the European Commission Horizon 2020 Research and Training Programme of the European Atomic Energy Community (EURATOM) (H2020-NFRP-2016-2017-1) under grant agreement n° 755443 (DisCo project).

References:

- [1] Shoesmith, D., Kolar, M., King, F. (2003). A mixed-potential model to predict fuel (uranium dioxide) corrosion within a failed nuclear waste container. *Corrosion*, 59(9), 802-816.
- [2] Hambley, D. and Hughes, R. (2018). Mechanistic modelling of irradiated fuel exposed to pond water. *In: Proceedings of the International Nuclear Engineering Conference 2018, Manchester (to be published)*.
- [3] Anwyl, C., Boxall, C., Wilbraham, R., Hambley, D., Padovani, C. (2016). Corrosion of AGR fuel pin steel under conditions relevant to permanent disposal. *Procedia Chemistry*, 21, 247-254.
- [4] Howett, E., Boxall, C., Hambley, D. (2017). AGR cladding corrosion: Investigation of the effect of temperature on unsensitized stainless steel. *MRS Advances*, 2(11), 615-620.
- [5] King, F. and Kolar, M. (1999). Mathematical implementation of the mixed-potential model of fuel dissolution, model version MPM-V1.0. Ontario Hydro, 06819-REP-01200-10005 R00.
- [6] Jerden, J., Frey, K., Ebert, W. (2015). A multiphase interfacial model for the dissolution of spent fuel. *Journal of Nuclear Materials*, 462, 135-146.

EUG Feedback

Summary of Feedback from the End User Group

During the second day of the DisCo workshop, the members of the End User Group (EUG) had their first meeting. Present at the EUG meeting were representatives of the following WMO's: Andra (Christelle Martin), Enresa (Miguel Cunado Peralta), Nagra (Veerle Cloet), Ondraf/Niras (Roberto Gaggiano), RWM (Robert Winsley), Posiva (represented by Jani Huttunen from TVO) and SKB (Kastriot Spahiu). Furthermore, representatives of the following 5 regulators were also present at the EUG meeting: BfE (Christoph Borkel), CSN (Carlos Javier Diez), ENSI (Eduard Feldbaumer), FANC (Pierre De Cannière), and SSM (Jinsong Liu). The meeting was led by Veerle Cloet (Nagra), who is the EUG representative and was also present at the ExCom meeting on the first day of the workshop.

The tasks of the EUG are to review the ongoing scientific work within the project and to make sure that the work remains within the initially set scope of the project. The review of the scientific work entails on the one hand reviewing the Scientific & Technical (S&T) contributions that are written by the beneficiaries and on the other hand attending the annual workshops. Only the EUG representative (Veerle Cloet, Nagra) is present at the ExCom meeting, and reports on the ExCom meeting to the other members of the EUG at the EUG meeting. The EUG members do not participate at the General Assembly, which is restricted to project beneficiaries only.

The S&T contributions were sent to the EUG members in advance of the workshop and the consensus among the EUG members was that the S&T contributions were all within the scope of the project, of high quality and focused on the work ahead. Given the early stage of the project, very few comments could be made to the current S&T contributions. This will probably be different in future S&T contributions. The format of commenting directly into the S&T Word document was greatly appreciated by all EUG members and should not be changed for future S&T contributions. In the future review process, a reply from the authors to any comments made by the EUG members would be highly appreciated but is not needed for the 1st year contributions (as there are very few comments). During the annual meeting, all participants presented their work in an understandable manner, although some presentations were difficult to read due to the small font size on the slides and in the graphs.

The annual meeting itself was well-organised, communication excellent and the time table followed. Sufficient time was foreseen for the EUG discussion (lunch meeting and additional time during the General Assembly). For future annual meetings, it was noted that there should be sufficient time in the programme to allow for interaction between the work packages, as this interaction is what makes an EU-project unique. Thus, the next meeting should be longer than this meeting (presently only 2 half days). Furthermore, the agenda for the annual meeting should be sent well in advance to the meeting (the agenda came slightly late this year).

For the work in DisCo to receive an even higher visibility and to ensure its data longevity, it was suggested to also upload the main deliverables of the project onto the IGD-TP website. The suggestion was passed on to the ExCom and they will get in touch with IGD-TP, via Robert Winsley (RWM), who made the suggestion.

The entire EUG looks forward to the next annual meeting in Cologne (May 2019) and wishes to thank the ExCom and all the beneficiaries for their excellent work done so far.