

UNIVERSIDAD COMPLUTENSE DE MADRID

FACULTAD DE CIENCIAS QUÍMICAS



TESIS DOCTORAL

Oxidación de la matriz del combustible nuclear irradiado en condiciones de almacenamiento temporal

Oxidation of the spent nuclear fuel matrix under interim storage conditions

MEMORIA PARA OPTAR AL GRADO DE DOCTOR

PRESENTADA POR

Abel Milena Pérez

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*Después de haberme asegurado de la superior
cualidad del aire desflogisticado, tuve la
curiosidad de probarlo yo mismo. La sensación
en mis pulmones no era sensiblemente diferente
de la del aire común, pero creí que mi respiración
era ligera y fácil. ¿Quién puede decir que este aire
puro no se convertirá en un artículo de moda,
en un lujo para las clases altas? Hasta el momento,
solo dos ratones y yo hemos tenido el privilegio de probarlo.*

Joseph Priestley

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Llegados a este punto del camino, a este momento final, toca poner todo en perspectiva. Echar la vista atrás, hacer un balance. Y en él, todos vosotros. Gracias.

Summary

The present thesis, entitled “Oxidation of the spent nuclear fuel matrix under interim storage conditions”, deals with important aspects regarding the storage of nuclear fuel. Oxidation of spent nuclear fuel (SNF) with undetected cladding defects during dry storage might challenge its integrity if high oxygen-content uranium oxides (U_3O_8), characterised by a specific volume about 36% higher than UO_2 's, are formed. The formation of U_3O_8 could lead to failure propagation, and pulverisation of the fuel pellet. This could hinder the future retrieval of the fuel or even cause the release of radioactive material. As a consequence, an accurate characterisation of the processes involved under anticipated conditions is of utmost significance for nuclear safety, especially taking into account the foreseen lifetime extension of storage facilities of SNF.

Although the behaviour of SNF in dry interim storage scenarios is well characterised, important knowledge gaps and uncertainties of some relevant effects that control the U_3O_8 formation remain to be cleared up, in particular how lowering the oxygen partial pressure could affect the oxidation and the potential improvements that the so-called Accident-Tolerant Fuels (ATFs) could represent. Given the difficulty that working with SNF implies, the use of fresh (*i.e.* unirradiated) nuclear fuel surrogates has been a common practice. Nevertheless, often these analogues, while considered as conservative source terms when compared to real fuel (they oxidise faster than SNF), could not describe the behaviour of SNF in a realistic manner, precisely because the excess of conservativeness introduces some uncertainties. In addition, the use in the last years of new nuclear fuel designs, in particular ATFs, has considerably increased, for example in the form of doping UO_2 with different elements. The oxidation behaviour of these new fuels must be understood in order to check if an improvement in this regard is met with respect to traditional UO_2 fuels. Finally, oxidation experiments of real SNF have been commonly performed by using thermogravimetric techniques, providing an “average” degree of the advance of the reaction. Given that the formation of U_3O_8 does not need to be complete to affect the fuel safety, it is important to develop techniques that are able to detect an early formation of this phase. In order to answer these issues, this thesis addresses a thorough study of the SNF matrix oxidation by contributing to the development of new experimental methods for ensuring safe management of the SNF, with focus on the behaviour during its dry interim storage.

Several advances in the analysis of the oxidation at hardly-explored conditions with nuclear fuel surrogates, *i.e.* UO_2 and Cr-doped UO_2 fuels, are presented, including the transfer of the developed protocols and knowledge to the study of real SNF. Specifically, the main studies performed can be summarised as follows: 1) Synthesis and characterisation of a “realistically conservative” nuclear fuel surrogate; 2) Development of an *in-situ* measurement protocol to study the oxidation of the previous material in conditions of temperature and oxygen concentration of interest for dry storage; 3) Fabrication and characterisation of a set of Cr-doped UO_2 pellets for studying the improvements of using ATFs; 4) Analysis of the oxidation behaviour of the previously studied ATFs, both in air and in less oxidant atmospheres; 5) Identification of knowledge gaps regarding the experimentation with SNF, as a theoretical basis for helping the transition to irradiated fuel; and 6) Study of the oxidation behaviour of highly-irradiated UO_2 fuel applying the previously optimised measurement protocol.

The role of temperature and oxygen partial pressure on UO_2 oxidation to U_3O_8 has been investigated for natural UO_2 and Cr-doped UO_2 . Only in the experiments at 1% O_2 present, Cr starts playing a role delaying oxidation because of the presence of dopants in the matrix. A new measurement protocol has been developed by using Raman spectroscopy that allows *in-situ* determining the time at which the U_3O_8 phase is observed at each condition. This represents a significant improvement on previous experimental approaches to study the oxidation of highly-irradiated UO_2 fuel. The application of this analytical tool to real SNF shows that differences found in oxidation at different regions of the samples (centre and close to the cladding areas) must be considered in the study of the evolution of fuel stability.

Resumen

La presente tesis, titulada “Oxidación de la matriz del combustible nuclear irradiado en condiciones de almacenamiento temporal”, trata aspectos importantes sobre el almacenamiento del combustible nuclear. La oxidación del Combustible Irradiado (CI) con fallos no detectados en la vaina durante su almacenamiento en seco puede comprometer su integridad si se forman óxidos de uranio con alto contenido en oxígeno (U_3O_8), caracterizados por un volumen específico alrededor de un 36% superior al del UO_2 . La formación de U_3O_8 puede llevar a propagación del fallo, y pulverización de la pastilla de combustible. Esto podría dificultar la futura recuperación del combustible o incluso causar la liberación de material radiactivo. Como consecuencia, una caracterización precisa de los procesos implicados bajo condiciones anticipadas es de extrema importancia para la seguridad nuclear, especialmente teniendo en cuenta la extensión de vida prevista para las instalaciones de almacenamiento de CI.

Aunque el comportamiento del CI en escenarios de almacenamiento temporal en seco está bien caracterizado, permanecen importantes lagunas del conocimiento e incertidumbres sobre efectos relevantes que controlan la formación de U_3O_8 aún sin clarificar, en particular cómo disminuir la presión parcial de oxígeno podría afectar a la oxidación y las potenciales mejoras que los llamados Combustibles Tolerantes a Accidentes (ATFs) podrían representar en este sentido. Dada la dificultad que implica trabajar con CI, el uso de análogos de combustible nuclear frescos (*i.e.* no irradiados) ha sido una práctica común. Sin embargo, con frecuencia estos análogos, aunque sean considerados como un término fuente conservador cuando se comparan con el combustible real (se oxidan más rápido que el CI), podrían no describir el comportamiento del CI de una manera realista, precisamente porque el exceso de conservadurismo introduce algunas incertidumbres. Además, el uso en los últimos años de nuevos diseños de combustible nuclear, en particular ATFs, ha aumentado considerablemente, por ejemplo mediante el uso de UO_2 dopado con diferentes elementos. El comportamiento frente a la oxidación de estos nuevos combustibles debe ser entendido para comprobar si se consigue una mejora con respecto a los combustibles de UO_2 tradicionales. Finalmente, los experimentos de oxidación en CI real se han llevado a cabo comúnmente usando técnicas termogravimétricas, dando como resultado un grado de avance “promedio” de la reacción. Dado que la formación de U_3O_8 no

necesita ser completa para afectar a la seguridad del combustible, es importante desarrollar técnicas que sean capaces de detectar una formación temprana de esta fase. Para responder a estas cuestiones, esta tesis aborda un riguroso estudio de la oxidación de la matriz del CI, contribuyendo al desarrollo de nuevos métodos experimentales para asegurar la gestión segura del CI, centrándose en su comportamiento durante su periodo en el almacén temporal en seco.

Se presentan, por tanto, varios avances en el análisis de la oxidación en condiciones poco exploradas con análogos de combustible nuclear, *i.e.* UO_2 y UO_2 dopado con Cr, incluyendo la transferencia del conocimiento y de los protocolos desarrollados al estudio de CI real. Específicamente, los estudios llevados a cabo pueden ser resumidos como sigue: 1) Síntesis y caracterización de un análogo de combustible nuclear “realísticamente conservador”; 2) Desarrollo de un protocolo de medida *in-situ* para estudiar la oxidación del material anterior en condiciones de temperatura y concentración de oxígeno de interés para el almacenamiento en seco; 3) Fabricación y caracterización de un conjunto de pastillas de UO_2 dopadas con Cr para estudiar las mejoras de los ATFs; 4) Análisis del comportamiento frente a la oxidación de los ATFs previamente estudiados, tanto en aire como en atmósferas menos oxidantes; 5) Identificación de las lagunas de conocimiento sobre la experimentación del CI, como base teórica para ayudar a la transición a CI; y 6) Estudio del comportamiento frente a la oxidación de combustible UO_2 altamente irradiado aplicando el protocolo de medida previamente optimizado.

Se ha investigado el papel de la temperatura y la presión parcial de oxígeno en la oxidación de UO_2 a U_3O_8 para UO_2 natural y UO_2 dopado con Cr. Solo en los experimentos con un 1% de O_2 presente, el Cr empieza a desempeñar un papel relevante retrasando la oxidación debido a la presencia de dopantes en la matriz. Se ha desarrollado un nuevo protocolo de medida usando espectroscopía Raman, que permite determinar *in-situ* el tiempo al que la fase U_3O_8 es observada en cada condición. Esto representa una mejora significativa en aproximaciones experimentales previas para estudiar la oxidación de combustible UO_2 altamente irradiado. La aplicación de esta herramienta analítica a CI real muestra que las diferencias encontradas en la oxidación en diferentes regiones de la muestra (zonas del centro y cercanas a la vaina) deben ser consideradas en el estudio de la evolución de la estabilidad del combustible.

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Acronyms

ADU	Ammonium Di-Uranate
ADS	Accelerator Driven-Systems
An	Actinides
ATF	Accident-Tolerant Fuel
BET	Brunauer-Emmet-Teller
BSE	Back-Scattered Electrons
CIEMAT	Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas
CSN	Consejo de Seguridad Nuclear
CTSF	Centralised Temporary Storage Facility
DGR	Deep Geological Repository
DSC	Differential Scanning Calorimetry
DTSF	Decentralised Temporary Storage Facility
EC	European Commission
EBS	Ethyl Bis Stearamide
ENRESA	Empresa Nacional de Residuos Radiactivos, S.A.
FP	Fission Product
FR	Fast Reactor
GRWP	General Radioactive Waste Plan
HBS	High Burnup Structure
HWL	High-Level Waste
HWLU	High-Level Waste Unit
IAEA	International Atomic Energy Agency
IR	Instalación Radiactiva
ISF	Individual Storage Facility
ISG	Interim Staff Guidance
JRC	Joint Research Centre
LD	Laser Diffraction
Ln	Lanthanides
LWR	Light Water Reactor
MA	Minor Actinide

MOX	Mixed Oxide Fuel
NFC	Nuclear Fuel Cycle
NO_x	Nitrogen Oxides
NPP	Nuclear Power Plant
NRC	Nuclear Regulatory Commission
NZE	Net Zero Emissions
PC	Principal Component
PCA	Principal Component Analysis
PIE	Post-Irradiation Examination
PSD	Particle Size Distribution
PUREX	Plutonium Uranium Reduction Extraction
P&T	Partitioning and Transmutation
REE	Rare-Earth Elements
RQPA	Rietveld Quantitative Phase Analysis
RS	Raman Spectroscopy
RT	Room Temperature
R&D	Research and Development
SE	Secondary Electrons
SEM	Scanning Electron Microscopy
SNF	Spent Nuclear Fuel
SSA	Specific Surface Area
TGA	Thermogravimetric Analysis
WIPP	Waste Isolation Waste Plan
WNA	World Nuclear Association
XRD	X-Ray Diffraction

Chapter I

Introduction

1. INTRODUCTION

Currently, a number of parameters, resulting from the complex present socio-political worldwide situation, influence energy policies in the countries from all around the world.

- World population: By September 2022, the US Census Bureau estimated that the global population was slightly higher than 7.9 thousand million people [1], although some news assure that the 8 thousand million people were surpassed by November 2022 [2, 3]. It has taken only 11 years to pass from 7 to 8 thousand million people, which gives an idea of the extremely fast population growth rate. Nevertheless, it seems that this rate is slightly slowing down [4]. In any case, this population growth implies a significant increase in electricity demand, which rose up to 24700 TWh in 2021 (6% increase from 2020, being the largest annual increase since 2010 [5]). This demand is expected to grow year after year, not only because of the population growth, but also because of the economic development of emerging countries.
- Climate change: The evolution of the global climate change has worsened in the last century, and the threats coming from greenhouse gases emissions and global warming, among others, are now more present than ever [6-8]. In this context, important initiatives have arisen. For instance, the European Commission (EC) has gathered a set of policies and included them in the so-called European Green Deal [9]. The ultimate goal of this proposal is to turn Europe into the first continent reaching Net Zero Emissions (NZE) of greenhouse gases by 2050, which would mean climate neutrality. The way to get this goal includes a deep energetic transformation, in which the dependency on fossil-based energy sources must be overcome.
- COVID-19 pandemic: The coronavirus-derived lockdown in 2020 and its consequences during the following years have dramatically changed the energy perspective in many senses. During the months of confinement, non-essential economic activities were stopped [10]. In particular, the energy sector was impacted by a pronounced reduction on the electricity demand, mainly caused by the paralysis of large energy consumers such as commerce and industry [11]. The challenges derived from these facts have proved that not all the world's

electricity systems are equally prepared for them. In general, the trend has been the decrease of electricity production coming from non-renewable sources, while the renewable sources increased their percentage share [12]. This was the Spanish scenario during the confinement period [10].

- Russia's invasion to Ukraine: On 24th February 2022, Russia launched a military operation to occupy Ukraine, which led to a bloody war that is still ongoing nowadays. This cruel fact has provoked a dramatic worldwide crisis from many different points of view, including the energetic sector. Regions from all around the world are suffering from exorbitant prices of goods, including electricity. The situation has brought into light the volatility of the energy market, with special focus on the dependence on fossil fuel consumption [5]. Sadly, the lack of supply and thereby the high prices affect the final consumers. This scenario has pulled the trigger for an accelerated energy transition, being the low-carbon sources such as renewable and nuclear more needed than ever [5, 13].

In this complex context, the role of nuclear energy as a low-carbon, robust electricity supply and relatively low priced source, compared with other energy sources and the amount of electricity generated, is undeniable. By the end of 2021, nuclear power represented about 10% of the total global electricity production, accounting for more than one quarter of the world's low-carbon electricity production. This was possible thanks to the 437 nuclear power reactors operating in 32 different countries [14]. Nuclear energy is, in general terms, an arising energy source in the world. In fact, 26 new countries joined in 2021 as International Atomic Energy Agency (IAEA) Member States, being at different phases of the decision-making process about the construction of new nuclear facilities [14]. Most of these newcomers are developing economies, trying to give an answer to the increasing electricity demands derived not only from population increase, as pointed out before, but also because of economic and technological developments in these regions.

Regarding climate change perspective, nuclear energy is seen as a bridge built for a safe, reliable transition from the traditional carbon-emitting energy sources towards a clean energy mix that allows reaching the NZE goal. In fact, nuclear has been included in the definition of clean energy by the Global Energy and Climate Model report issued

in 2022¹ [15]. In addition, it has been added to the European Union's taxonomy for sustainable activities in 2023, labelling it as “green” energy [16, 17]. This “bridge” behaviour is clearly illustrated in Figure 1.1, where the electricity generation by energy type is displayed for different worldwide regions.

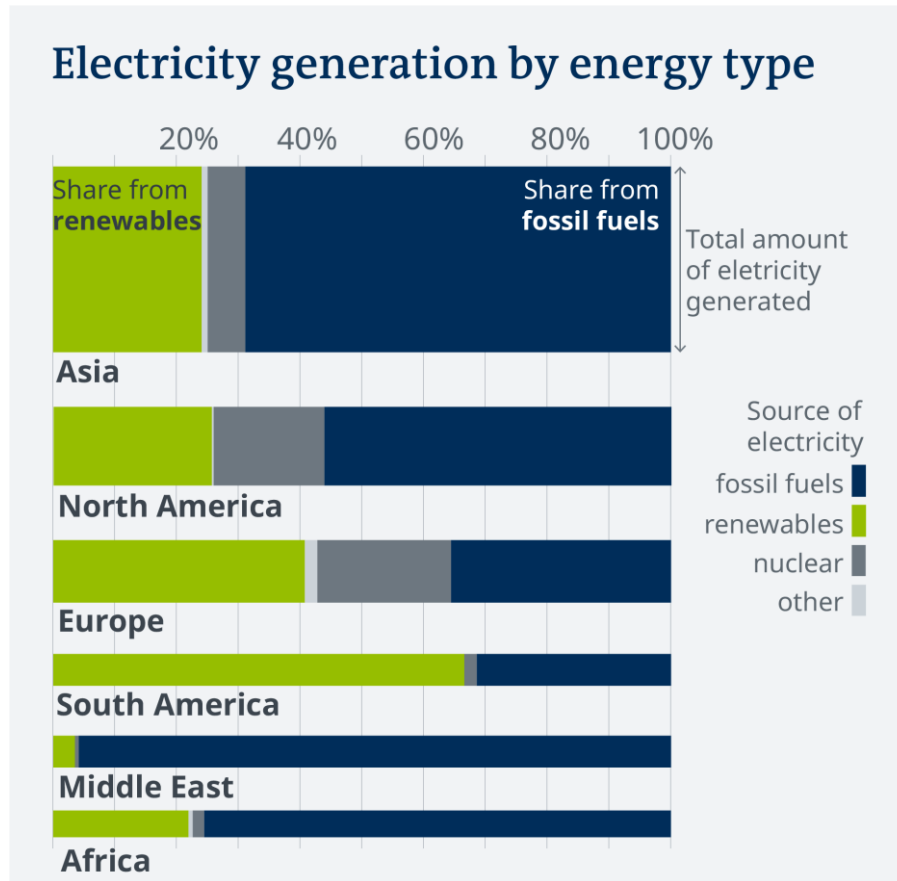


Figure 1.1. Electricity generation by energy type, for different worldwide regions. Source: BP Energy Outlook 2020 [18].

The growth of nuclear, as a supporting energy source for full-development of renewable energies, is emphasised by the fact that both types of energies are foreseen to increase their use by 2035 (see Figure 1.2). The current scenario has also pointed to this energetic mix, giving nuclear a sound answer to the needs generated by the COVID-19 pandemic (see for example Figures 22 and 23 in [10], also [19]) and the Russia-Ukraine war [20].

¹ “Clean energy: In power, clean energy includes: generation from renewable sources, nuclear and fossil fuels fitted with carbon capture, utilisation and storage; battery storage; and electricity grids”.

1.1. The Nuclear Fuel Cycle

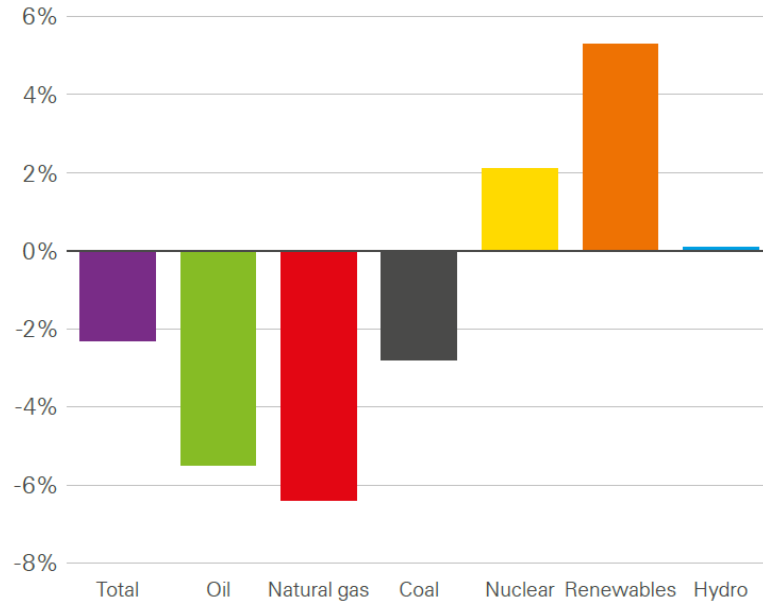


Figure 1.2. Foreseen change in primary energy sources in 2035 with respect to the end of 2022 (y axis) for several energy sources (x axis). Source: BP Energy Outlook 2023 [13].

Nevertheless, some concerns about nuclear energy are still worrying society (and thus limiting its public acceptance), mainly related to the safety of the nuclear power plants, the low-efficiency of the nuclear fuel irradiation and the radioactive waste management. The capability of the nuclear sector to give answer to these issues will be crucial for its continuity in the following decades. This PhD thesis aims to shed some light on this matter.

Nuclear energy comes from the irradiation of ^{235}U , in a process that entails several steps concerning the different stages in which the fuel can be found. These stages define the so-called “Nuclear fuel cycle” (NFC), which will be described in detail in the next sections.

1.1. The Nuclear Fuel Cycle

According to World Nuclear Association (WNA), the nuclear fuel cycle is defined as “the series of industrial processes which involve the production of electricity from uranium in nuclear power reactors” [21]. These processes involve all of the activities, from uranium mining to preparation of fresh fuel, irradiation at the nuclear power plants for electricity generation, reprocessing (in the case of closed cycles), storage and final

disposal. Figure 1.3 represents, in a schematic way, how these activities are organised throughout the cycle, and the major stages that can be inferred.

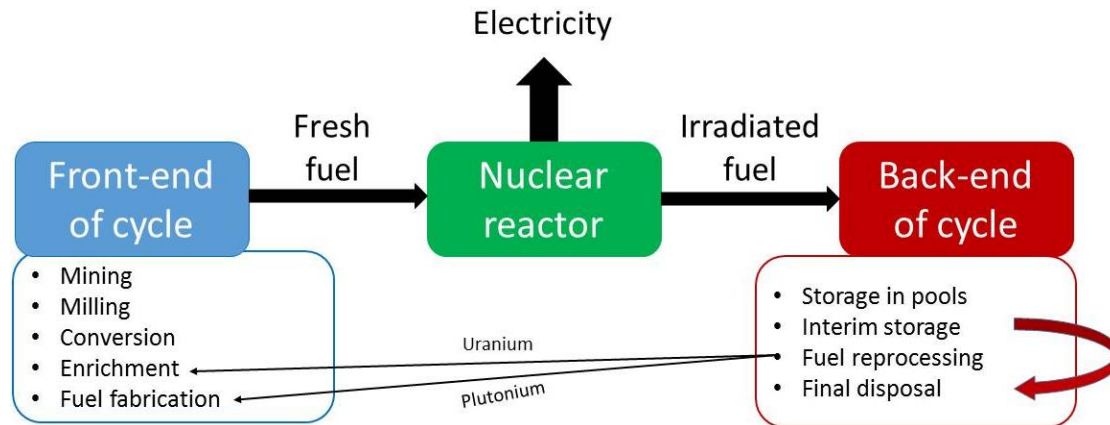


Figure 1.3. Schematic overview of the nuclear fuel cycle.

Three well-differentiated steps can be seen in Figure 1.3. The front-end of the cycle involves the steps required for turning natural uranium, extracted from mines, into the fresh nuclear fuel which arrives to the nuclear reactor. Inside the nuclear reactor, the nuclear fission of ^{235}U takes place when this fissile isotope is impacted by a neutron. In the process, more neutrons are produced, thus obtaining a controlled chain reaction. This reaction produces considerable heat, which is used to produce steam, which in turn drives a turbine and electric generator, providing electricity. As a result of irradiation, fresh fuel converts into irradiated fuel, also known as Spent Nuclear Fuel (SNF). This material is managed in the last part of the NFC. The back-end of the cycle comprises the activities devoted to prepare the fuel to be safely disposed for hundreds of thousands of years until its radiotoxicity reaches natural uranium levels [22]. In some cases, SNF is reprocessed, obtaining uranium with ^{235}U that can be enriched again and/or plutonium to fabricate other type of fuels (Figure 1.3), such as Mixed Oxide Fuels (MOX). The “mixed” term refers to a mixture of uranium and plutonium oxides, composing a fuel that has been used in nuclear reactors of some countries (*e.g.* France or Belgium) for the last 30 years, and continue nowadays [23].

In the following sections, these three parts of the fuel cycle are described in detail. Special attention is paid to those topics with particular interest within the context of this thesis.

1.2. Front-End of the Nuclear Fuel Cycle

The raw material for today's nuclear fuel is mainly uranium [24]. Uranium is a common metal that can be found throughout the Earth's crust, with an average concentration of 3 ppm [25]. In addition, it can be found in other environments, such as in seawater and groundwater. Currently, the most used process to extract uranium from Earth is uranium mining, directly from uranium ore. As an example, only in 2019, more than 53000 tons of uranium were extracted worldwide [26]. Kazakhstan, Canada and Australia are by far the largest producers of uranium ore, accounting together for 68% of the world's uranium generation [26]. Two main methods for uranium mining are currently used: *in-situ* filtration and ordinary underground or open-pit metal mining [27].

Mined uranium can be in low concentrations, mainly because in some cases it can be a by-product of other mines with different main product such as copper, phosphate or gold [24]. For this reason, uranium has to be separated and concentrated in order to obtain a purer product. This is achieved by applying the milling process, which is usually carried out in the surroundings of a uranium mine. The uranium ore is crushed, pulverized, and grounded into a fine powder. This material is leached in sulphuric acid in order to allow the separation of uranium. Then, it is recovered from the solution and precipitated, obtaining the so-called "yellowcake" [21], which is the precursor in nuclear fuel production, and basically is in the form of U_3O_8 . At this point, the concentration of uranium is raised up to approximately 80% [24, 28].

Once the yellowcake is obtained, it undergoes a number of chemical processes known as conversion. The goal is to transform the natural uranium into gaseous UF_6 , so that the concentration of ^{235}U can be later increased. For this reason, U_3O_8 is first reduced to UO_2 by using molecular hydrogen (H_2). The resulting substrate is then reacted with hydrogen fluoride (HF) to produce UF_4 , which after reaction with gaseous fluorine (F_2) forms the final product UF_6 . This compound is a gas at relatively low temperature, and it is filled into large cylinders where it is shipped to the enrichment facilities [24, 29].

Natural uranium contains only 0.7% of ^{235}U , being this the uranium isotope that is suitable for fission in the reactor (*i.e.* fissile), being the vast majority ^{238}U (99.3%) and a very little quantity of ^{234}U (less than 0.01%). In order to increase the concentration of ^{235}U up to 3-5% for use in Light Water Reactors (LWR) (enrichment) [24, 30], gaseous UF_6 is introduced into fast spinning cylinders (centrifuges). As a result of the fast

spinning of the cylinder gas, heavier ^{238}U isotopes are pushed outwards, remaining the inner gas enriched in the lighter ^{235}U . This method is well-established and tends to substitute the older, gas diffusion methodology, less energy-efficient [30]. Nevertheless, new approaches are currently under development, for example the laser enrichment [31] or even bio-enrichment, using the properties of some microorganisms [32]. Anyhow, although this process is needed for the more common LWRs, there are some reactors like CANDU, a pressurized heavy-water reactor, that do not require enriched uranium, and therefore natural uranium dioxide (*i.e.* not enriched) can be used directly as fuel [33].

Once uranium is enriched with the suitable concentration of ^{235}U (typically 3-5%, as previously mentioned), it is time to obtain the final fuel that will be used in the reactor. This is the result of the fuel fabrication process. Nuclear fuel is usually in the form of ceramic pellets, with common sizes of approximately 1 cm diameter and 1 cm long. To obtain them, enriched gaseous UF_6 is first converted into solid UO_2 powder, in a process that can be done by both dry and wet routes [34]. Then, UO_2 powder is pressed into cylindrical pellets by applying several hundred MPa of pressure. After that, these “green pellets” are subjected to a thermal treatment at high temperature (around 1700°C, although it is variable) under a reducing atmosphere to obtain the final “sintered pellets”. This type of process, with optimised parameters, is applied at the High-Level Waste Unit (HLWU) of CIEMAT, and will be explained in detail in the Methodology chapter.

UO_2 pellets are, for the most common LWR reactors, encased in a long zirconium-alloy tube, also known as the cladding, which prevents the release of fission products from the fuel and at the same time allows neutrons reaching uranium. The combination of fuel and cladding forms the so-called fuel rods. A set of fuel rods are packed together forming a fuel assembly, being ready for the introduction in the reactor. Figure 1.4a) schematically represents this set-up. The obtainment of the fuel assemblies represents the final step of the fuel fabrication, and therefore of the front-end of the NFC. The assemblies are set inside the core of the nuclear reactor, and are ready for starting the irradiation and the electricity production. As a way of example, Figure 1.4b) shows the layout of the fuel assemblies inside the reactor.

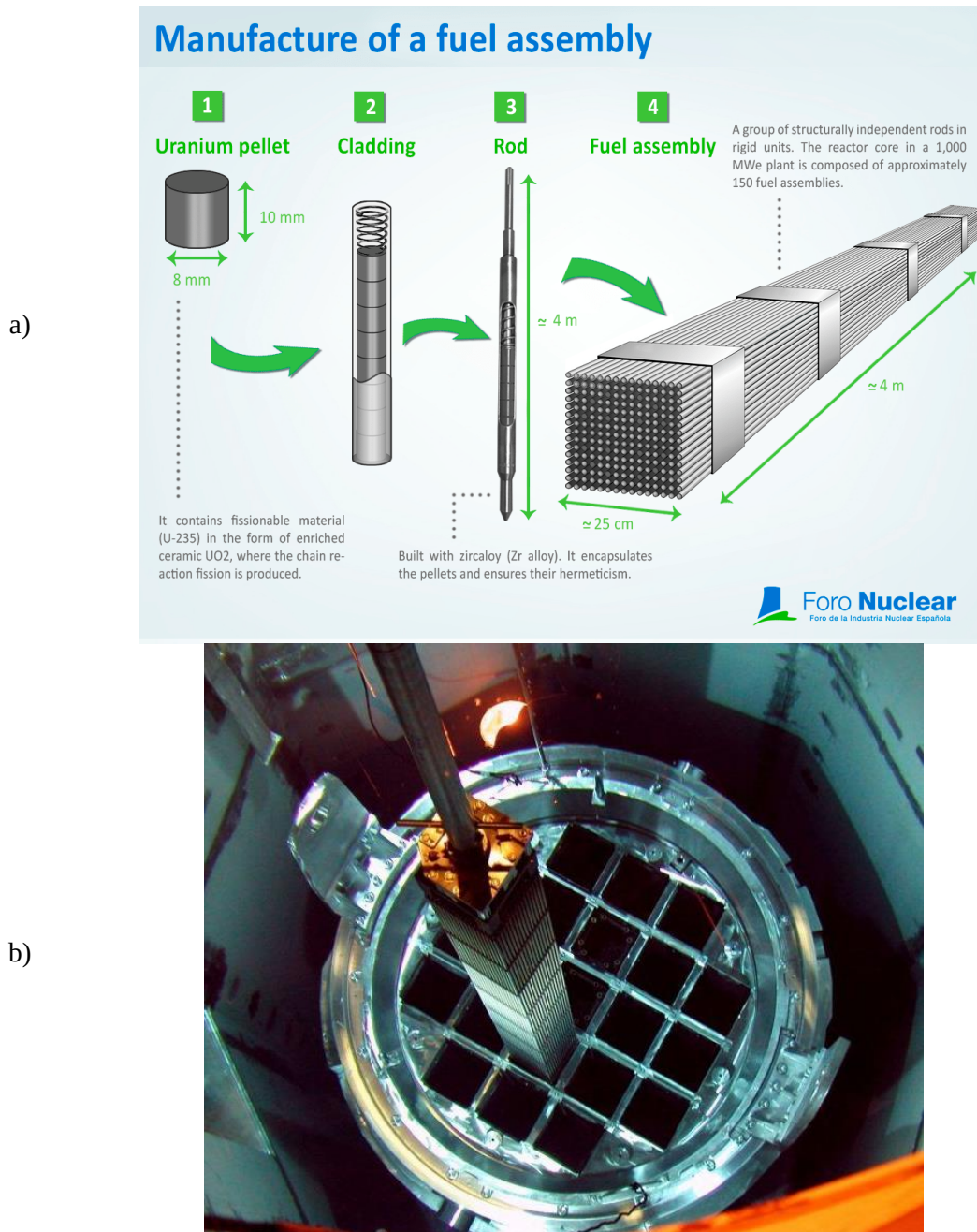


Figure 1.4. a) Scheme of the component parts of a conventional UO_2 fuel element. b) Placing a fuel assembly inside the nuclear reactor. Images taken from Foro Nuclear [35].

1.2.1. Accident Tolerant Fuels. A new nuclear fuel design

Although standard UO_2 is the most extensively used nuclear fuel worldwide, existing requirements of energy production in nuclear power plants have led to increasing the burnup in operating reactors, with the main goal of improving the economic performance of the fuel. This increased burnup could come along with some undesirable processes, such as enhanced fission gas release and pellet-cladding interaction, which

may be important under accident scenarios [36, 37]. In fact, the Fukushima Daiichi Nuclear Power Plant accident in 2011 reinforced the necessity of investigating about alternative fuel designs that would be more resistant to cladding oxidation and mechanical strength at high temperature.

In this context, in the last years there has been a growing interest in obtaining these newer fuel designs. One of the most accepted concepts developed in this regard are the so-called Accident Tolerant Fuels (ATFs) [37-39]. According to the Nuclear Regulatory Commission (NRC), ATFs are *“a set of new technologies that have the potential to enhance safety (...) at nuclear power plants by offering better performance during normal operation, transient conditions, and accident scenarios”* [40]. All in all, ATFs are meant to be improvements in the current fuels and/or claddings designs with the goal of tolerating a severe accident in the reactor core for a longer time period than the current Zircaloy-UO₂ system, while maintaining or improving fuel performance during normal operation. In general, all ATFs designs should comply with a number of requirements [39, 41]:

- Backward compatibility: Compatible with current nuclear reactor designs and handling equipment, as well as with foreseen future designs.
- Operation: Maintain or even improve plant-operating cycles, reactor power output and reactor control. ATFs must ensure reliability under normal operation and transients.
- Safety: Provide with enhanced safety margins, *i.e.* meet or exceed current fuel system performance under ab-normal conditions.
- Front-end of the NFC: Adhere to regulations and policies, for both the fuel fabrication facility and the operating plant.
- Back-end of the NFC: Ensure, at least, the same performance of standard UO₂ system, providing with delayed corrosion mechanisms, if possible.

Within the set of technologies that comprise the ATF concept, including improvements in both the fuel and the cladding, different implementation timescales must be noticed. Some of these concepts have already been loaded in commercial nuclear reactors by means of lead test rods and or/assemblies, and represent the shortest-term ATFs advances. Others are currently under development, and are expected to be in operation in the following years. A schematic representation of the different ATFs available and

their evolutionary-to-revolutionary pathway is represented in Figure 1.5. A brief explanation of each one of them is given below, although there are more designs that are not included in the figure.

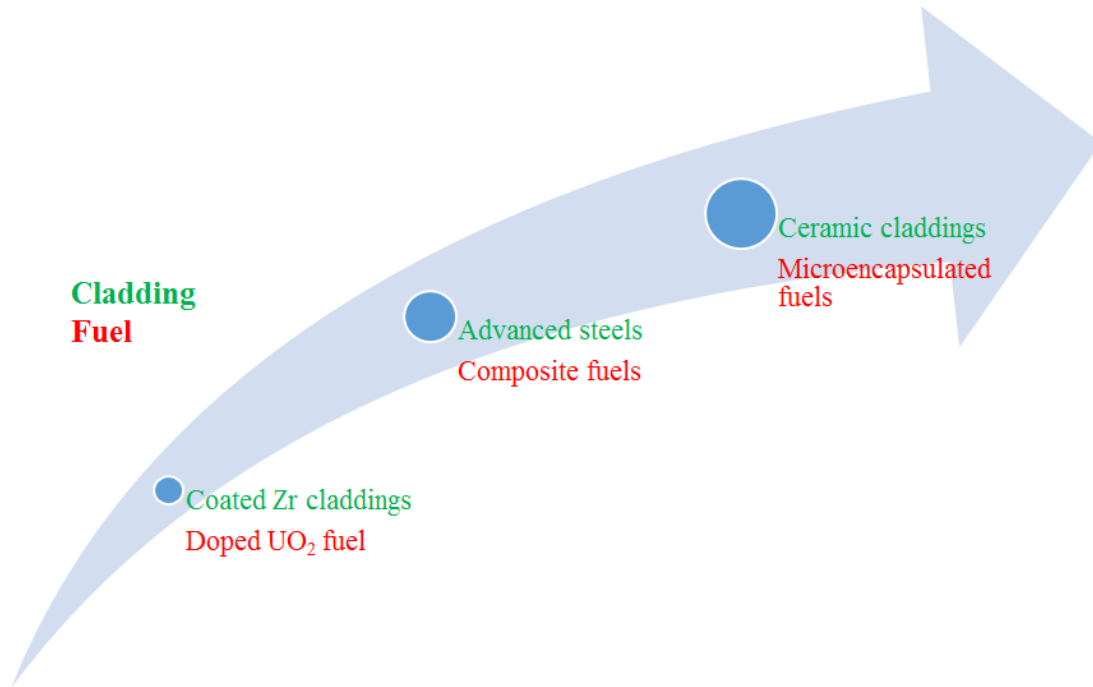


Figure 1.5. Some ATF concepts, differentiating between those applying to the fuel and the cladding. The arrow's direction represents the evolutionary-to-revolutionary pathway (left: already in operation; right: currently under development).

- Coated Zr claddings: Deposition of protective coatings on the conventional Zircaloy cladding has been considered as a short-term solution for enhanced ATF claddings, in particular after the risk of Zr of hydrogen release at high temperature pointed out by the Fukushima Daiichi accident. Among the coating elements, Cr is the most used because of its excellent chemical stability and low thermal neutrons absorption cross-section [42].
- Doped UO₂ fuel: Following the same criteria, doping UO₂ matrix with different elements have provided enhanced properties of the fuel. Due to the fact that this kind of materials has been employed during this PhD thesis, they will be detailed afterwards.
- Advanced steels: Beyond using coatings on current Zr claddings, a medium-term proposal is to use new materials for the cladding, made by different alloys. Among the most studied nowadays are the so-called FeCrAl claddings, with alloys of these elements, which are proposed to substitute Zr mainly because of

their outstanding resistance to high-temperature steam oxidation [43], in particular with quantities of Cr and Al of 12wt% and 6wt%, respectively (C26M alloy, [44]). The scarcity of irradiated data for these materials is one of the knowledge gaps to be fulfilled in the following years [43].

- Composite fuels: Some other compounds different from UO_2 are currently under study in order to improve both the characteristics and the performance of the fuel in an accidental scenario. New materials, such as uranium nitride (UN) and uranium silicide (U_3Si_2) are being developed in the last years as a medium-term ATF concept. The main improvement of these fuels is their thermal conductivity; which, unlike UO_2 , increases with increasing temperature. This would enhance safety margins by removing excess heat from the core to the rim of the pellet and, finally, to the coolant [45]. Composite fuels are made by mixing these compounds in different proportions, in order to get the maximum benefit of their improved properties [46], although it may be difficult to produce a desirable combination. Some of these fuels are already being proved under simulated accident circumstances at laboratory scale [45, 47].
- Ceramic claddings: One of the longest-term solutions for avoiding the use of Zr cladding in nuclear rods is to use ceramic materials. Probably the most promising one is silicon carbide (SiC), in particular continuous SiC fiber-reinforced SiC matrix ceramic composites. The goal is to take advantage of the general inertness that they provide (contrasting with the capability of Zr to oxidize and to release hydrogen), smaller neutron absorption cross sections, and stability in nuclear waste [48]. Nevertheless, it is first necessary to optimise the fabrication method of these materials, both in terms of quality and economics [49].
- Microencapsulated fuels: This type of fuel consists of a near-spherical fuel kernel encapsulated by multiple carbon layers, mainly containing high-strength pyrolytic carbon and SiC [50]. The kernel is commonly made of UO_2 , although new developments are also trying uranium oxycarbide (general formula UCO) [51]. These fuels have proven to be a revolutionary ATF concept, since their main improvement is to provide enhanced confinement to gaseous fission products, which are trapped inside the fuel particle. The main drawback of this ATF is that it is quite expensive to manufacture, although there are currently companies dedicated to its production at a pilot plant level [52].

Among all the possible choices to work with ATFs, in this PhD thesis we have focused on doped UO_2 , as one of the shortest-term ATF nowadays. In fact, some companies like *Framatome* are already fabricating these fuels at an industrial scale [53] and using them in commercial reactors. In particular, doping UO_2 with chromia (Cr_2O_3) has turned out to be especially effective increasing fuel resistance and plasticity, by means of increasing the average grain size in the pellet surface [54]. It is known that this change in grain size increases the diffusion length inside the pellet, and therefore, enhanced retention of gaseous products inside the ceramic is obtained [36]. Cr has proven to be particularly adequate for grain growth during sintering [55], mainly when the amount of Cr_2O_3 added is close to the solubility limit in the UO_2 matrix, which is dependent on the sintering conditions [56]. As a way of example, Figure 1.6 shows the different grain sizes that can be reached doping UO_2 with Cr_2O_3 , when compared to undoped UO_2 .

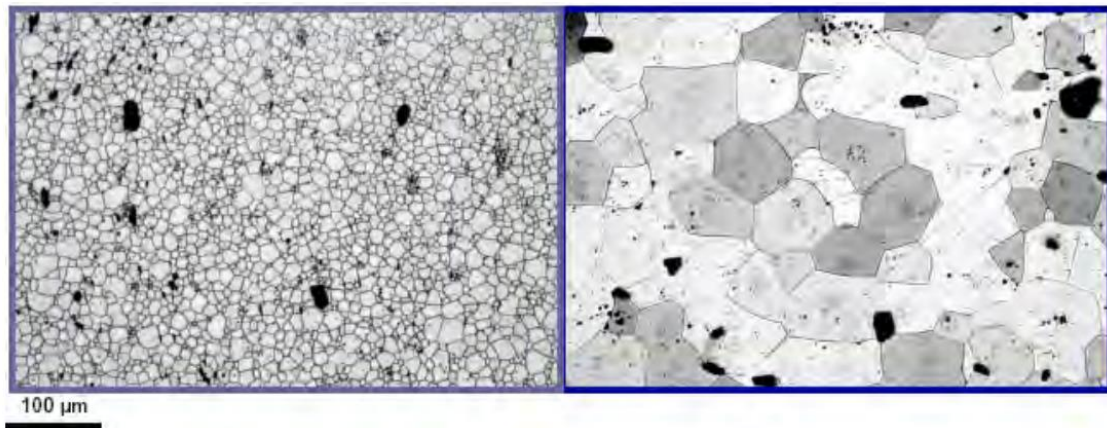


Figure 1.6. Micrographs of FRAMATOME standard UO_2 (left, grain size $8\ \mu\text{m}$) and Cr_2O_3 doped- UO_2 (right, grain size $60\ \mu\text{m}$). Figure retrieved from [53].

1.3. Nuclear Fuel in the Nuclear Reactor

When the fuel assemblies, loaded with fresh nuclear fuel, are set into the reactor core, the ^{235}U isotope undergoes fission, producing heat in a continuous process called a chain reaction, which is maintained under control in the reactor. The fission reaction starts when a neutron impacts on a ^{235}U nucleus, splitting it into lighter atoms and generating extra neutrons, which yield new fissions, producing the chain reaction. In addition, ^{238}U can experience neutron capture, producing fissile ^{239}Pu , which also undergoes fission [30]. Because of these reactions, a set of new elements besides plutonium are generated, being almost the entire periodic table present in the resulting

material. Moreover, nuclear fuel operates in a unique and harsh environment governed by high temperatures at different thermal cycles, chemical corrosion, irradiation and mechanical stresses. This fact will influence the mechanical properties of the original fuel, which suffers significant microstructural modifications, such as swelling, cracking, defects formation, etc. [57].

All in all, the resulting material from irradiation of fresh nuclear fuel is known as SNF. The composition of SNF depends on variables like reactor type, burnup and cooling time, but for LWRs the typical composition is approximately 94-95 % of U, ~1 % of Pu, ~4-5 % of Fission Products (FPs) and 0.1 % of Minor Actinides (MAs) [24, 30, 58]. Thus, uranium is still the main element present, being in the form of UO_2 . This is why UO_2 is often called as the “SNF matrix” [59]. The rest of the chemical elements are included in the aforementioned groups, in particular:

- FPs, including:
 - Volatile FPs (gases such as I, Br, Cs, Rb, Se and inert gases: Xe, Kr mainly) occur as finely dispersed bubbles in the fuel grains. They may also migrate to grain boundaries, fractures and the gap between the edge of the SNF pellet and the surrounding metal cladding.
 - Metallic FPs aggregates (Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb), would be in the form of immiscible metallic precipitates (ϵ -particles, noble metal phase) that are nanometres to micrometres in size [60]. A range of composition of these aggregates is expected to be found depending on the burnup, the diffusion rates and the oxygen potential of the fuel [61].
 - Separate oxide precipitates of FPs (Rb, Cs, Ba and Zr). Depending on the fuel temperature and, consequently, the extent of diffusion, Ba and Zr precipitate as a multi-component oxide phase of the type BaZrO_3 (termed the ‘grey’ phase). This phase has been recently identified by Raman spectroscopy in fuel surrogates [62].
 - Rare-Earth Elements (REE) dissolved as solid solutions in the UO_2 fuel matrix (Sr, Zr, Nb and Ln: La, Ce, Pr, Nd, Pm, Sm, etc.). These elements produce oxides of crystal structure close to that of the UO_2 matrix, forming extensive solid solutions with it.
- MAs (mainly Np, Am and Cm), and Pu: Most of them can be a substitute for U in the UO_2 fluorite matrix because they are, at a certain point, miscible in the

SNF matrix. In the case of Pu, it is found at higher concentrations near the pellet rim, as shown in Figure 1.7a).

This composition of elements is not homogeneously distributed within the pellet as a result of different parameters, such as location of the fuel rod within the reactor or total burnup of the fuel assembly [63]. This effect is clearly seen in Figure 1.7a) and Figure 1.7b). Isotopes of volatile elements, such as I or Cs, can migrate within the pellet due to the steep thermal gradient ($\sim 1300^{\circ}\text{C}$ at the centre of the pellet and decreasing to 400°C at its external rim) that the fuel undergoes during irradiation in the reactor. Other variations also observed in the fuel during irradiation in the reactor that are reliant on the burnup and radiation effects [64] are the microstructural changes. The study of these changes is a fundamental element in SNF characterisation, as they will determine the integrity and behaviour of the fuel rod during storage. For example, the apparition of cracks on the pellet surface is one of the main outcomes of the irradiation, as shown in Figure 1.7c).

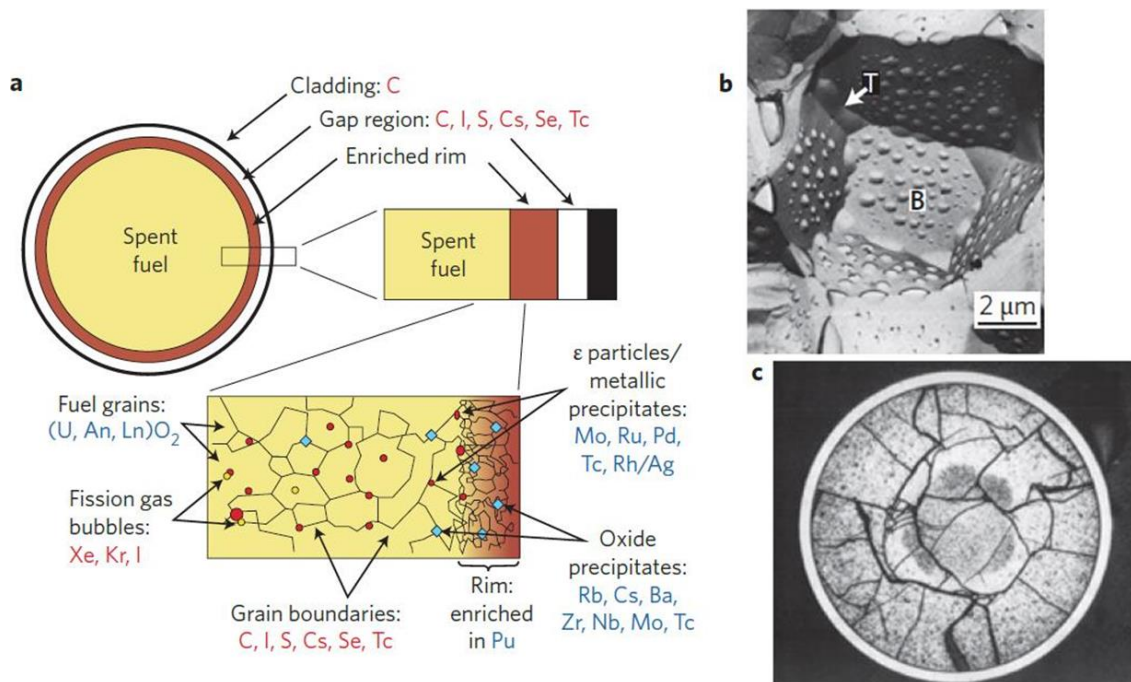


Figure 1.7. Microstructure of SNF and the distribution of FP, MAs and Pu after irradiation in a reactor. a) Schematic representation of the SNF (An = actinides and Ln = lanthanides); b) Higher-magnification image of individual grains in a fuel sample, demonstrating the segregation of FP gases into bubbles that decorate the surfaces of grains of UO₂ in the fuel (T, grain edge tunnels; B, bubbles); c) Cross-section of an irradiated fuel pellet. Figures extracted from Ewing [65] and adapted from [66-68].

1.4. Back-End of the Nuclear Fuel Cycle

The last stage of the NFC, or back-end, starts when irradiation of fresh fuel in the reactor is over and the resulting SNF is discharged. The first step is to transfer the fuel from the reactor to adjacent storage pools, where SNF will be stored for several years in order to allow radiation and decay heat levels to decrease. In the spent fuel pools, the water acts both as coolant and radiation shielding [22].

Once the temperature and radiation levels of the fuel are reduced after the initial cooling period, two management options can be considered: the open and the closed nuclear cycle. The decision is dependent on the policies of each country, having each option a number of advantages and drawbacks.

- Open cycle (once-through cycle): This is the option chosen by many countries, including Spain. Here, SNF is considered as High-Level Waste (HLW), and therefore has to be stored in a safe way. Within this fuel cycle, and after storing it in pools, SNF is dried and transferred to interim storage facilities, which can be at the Nuclear Power Plant (NPP) site or at a centralised storage facility that can receive and store HLW from more NPPs. After that, HLW will be transferred to the final disposal facilities, where it will be stored for millions of years, until the radioactivity levels of the fuel reach the ones of natural uranium [22]. The particular properties of each type of storage will be discussed in the next sections.
- Closed cycle: The main difference that this strategy provides is to consider SNF as a source of energy for fabricating fresh fuel, which can be irradiated again in the reactor in order to obtain more electricity, as well as to reduce both the volume and the radiotoxicity of the waste. With these purposes, SNF is put through a number of chemical processes known as reprocessing [69-71]. This strategy is known to take more advantage of the fuel resources than directly storing it [72]. Nevertheless, it increases the expenses of the back-end of the fuel cycle [73] and the exposure risk. Different options of the closed cycle can be found, which are currently at different levels of industrial application or still under development:
 - Partially closed cycle (twice-through cycle): With this strategy, the chemical processes applied to SNF aim to recover uranium and

plutonium from the fuel, which can be reused as fresh fuel of UO_2 or MOX. Both kinds of fuels can be directly irradiated in current LWRs. The waste from this recovery process, which mainly contains FP and MAs, is vitrified in a matrix and packaged in order to both immobilise it and reduce its volume for its eventual management. While several countries have reprocessed their SNF throughout the years (France, Japan, United Kingdom, India, etc.), currently there is one reprocessing commercial plant is available in France (La Hague) [74], several in India, such as Tarapur and Kalpakkam [75], and it is expected that another one in Japan (Rokkasho) begins commercial operation by 2024 [76], among others.

- Advanced closed cycle (full-closed cycle): Following a similar reprocessing strategy, but with the goal of reducing even more the radiotoxicity and waste volume, full-closed cycles are based on the Partitioning and Transmutation (P&T) approach [77, 78]. This alternative, currently under development, is based on the separation (partitioning) of MAs from the fuel. Then, these isotopes undergo nuclear reactions (transmutation) like nuclear fission or neutron capture that transform them into shorter-lived isotopes or even stable elements. This promising strategy cannot be achieved without the current nuclear technology, and it is foreseen to be applied in advanced nuclear reactors (Generation IV reactors), including Fast Reactors (FR) and Accelerator Driven Systems (ADS).

Regardless of the open or closed NFC decision, storage is a necessary interim step, as well as the final disposal (currently no geological disposal facilities available for HLW), that is common for all the nuclear cycles scenarios.

1.4.1. Interim storage

Interim storage is a required part of the short-term management of both SNF and HLW. Countries aimed originally for direct disposal, but the difficulties found in many of them in terms of design and site licensing led them to this approach. In fact, interim storage is aimed to provide enough timeframe (between 40-100 years [79-81], or even

considering the possibility to extend it up to 300 years [82]) to allow final disposal facilities to be built and in operation.

After cooling down of SNF in the at-reactor pools, the first step in order to prepare it for interim storage is drying. Remaining water from the pool could be the source of radiation-induced hydrolysis products that could enhance undesirable processes increasing the appearance of potential oxidants and, subsequently, this all may affect the long-term integrity of the fuel [83]. The fuel drying processes utilised today to remove such residual water from SNF that is intended for sealed dry storage designs (not for vented dry storage systems) are [80, 84, 85]:

- Vacuum drying: Consists of lowering the gas system pressure below the vapour pressure of the water at the drying temperature. The cask is considered to be satisfactorily dry when the system pressure is constant over a period of time. This option is applied by Spain, Canada, Netherlands, Germany and the USA.
- Hot-gas drying or Forced-gas dehydration: The fuel assembly is uniformly heated by a superheated non-reactive gas (e.g. N_2 or CO_2) or one of the inert gases (including He, Ar, Kr, or Xe) to evaporate the water and blow it away. The process is considered to be finished when the moisture content in the outlet and inlet atmosphere are the same. Countries like Canada, Hungary or Korea are applying this method.

Although both wet and dry are considered as options for interim storage of the fuel, dry storage is widely preferred because of the aforementioned problems associated with water. In addition, the operating costs related to dry storage were found to be lower in comparison to wet storage concepts [84, 86].

Dry storage requires minimal maintenance apart from surveillance programme, *i.e.* periodic inspection and monitoring [84]. Materials in spent fuel that must be preserved from degradation are the fuel matrix and fuel cladding [87]. For this purpose, the fuel rods, once dried, are transferred to appropriate storage casks. These casks allow the fuel to be surrounded by an inert atmosphere that reduces the potential for corrosion processes [67, 88, 89]. In fact, the NRC guidelines have allowed storage designs with cask inventories of oxidising gases less than 1.0 g/mol per cask and an inert atmosphere for storing UO_2 spent fuel in a dry environment [90]. Typically, these inert cover gas conditions are fulfilled by He or N_2 [88]. The SNF is located inside metallic containers

made of a neutron-absorbing material, such as boron-bearing stainless steel, to avoid criticality. The metallic casks are usually steel cylinders that are either welded or bolted closed, and provide a leak-tight confinement of the fuel. Each cylinder is surrounded by additional steel, concrete, or other material to provide radiation shielding. In addition, some cask designs are called dual-purpose, because they can be used both for storage and transportation. The design is based on a multi-wall concept in the following order: (1) stainless steel, (2) gamma shielding (lead), (3) stainless steel, (4) neutron shielding (absorbent polymer), and (5) stainless steel. It ensures confinement and keeps the pressure in the space between the two main lids of the cask. Inside this body there is a fuel basket with borated aluminium to assure the geometry and criticality control [91]. Multi-purpose casks decrease the risks associated with fuel handling.

1.4.2. Final disposal

Beyond the foreseen lifetime of the interim storage facilities, and whatever SNF management option is selected, there is an international consensus about the Deep Geological Repository (DGR) as the end-point of all the HLW generated throughout all the stages of the NFC. This facility will provide passive safety of the waste for several hundred thousands of years.

DGRs are planned to be underground facilities (usually around 500 m deep) located at stable geological formations, in order to provide long-term confinement of the waste and its isolation from the accessible biosphere [92]. A DGR is based on the multi-barrier concept, *i.e.* there will be a number of barriers (both natural and artificial) between the waste and the biosphere, as a way to ensure that the time required for an eventually released radionuclide to reach the biosphere is so long that its radioactivity will have decayed to natural levels [93].

To date, there are no DGRs for civilian nuclear waste in operation. The United States has a geological disposal for transuranic elements from the US defence program, the WIPP (Waste Isolation Pilot Plant) site, in a saline geological formation in New Mexico. All HLW (including SNF) coming from civilian electricity production are kept stored in different non-permanent facilities [79]. The DGR option can only happen in those countries that have an approved final repository construction or have a solid perspective of obtaining an approval for the facility in the short term. Currently, only Finland and Sweden meet these requisites. Finland is the world's first country to have a

construction license for a permanent geological repository, the DGR of Onkalo, and it is planned to start receiving SNF casks by 2024-2026 [94]. Sweden is slightly behind from Finland. Both countries share the KBS-3 concept (developed by the Swedish Nuclear Fuel and Waste Management Company, SKB). It consists in a multi-barrier concept based on the long-term stability of the SNF matrix under reducing conditions in neutral to slightly alkaline media. Reducing conditions in the repository are ensured by keeping the SNF in copper canisters with iron insets [79].

1.5. Spanish approach

In Spain, there are currently five NPPs in operation, two of which (Almaraz and Ascó) have twin units, so that there are seven operational reactors [95]. The net electrical power produced by all seven Spanish nuclear power reactors was 55984 GWh in 2022, accounting for more than 20% of the country's total net electrical production and maintaining the trend of the previous years [96]. This gives an idea of the electricity generation potential that nuclear energy offers, and how useful this resource is. The main characteristics of the seven nuclear reactors currently in operation in Spain are presented in Table 1.I. In addition:

- Vandellós I (Tarragona) was shut down in 1989. Since 2004 it is in its latency period (a 25-year waiting period until full decommissioning, programmed for 2028).
- José Cabrera-Zorita (Guadalajara) was shut down on April 2006. It is currently undergoing the last stages of the decommissioning process.
- Santa María de Garoña (Burgos) has recently passed to the decommissioning stage.

In the Spanish national programme for the SNF and HLW management, the policy is to handle radioactive waste “from cradle to grave”, *i.e.* a complete administration is proposed including the initial steps of the nuclear cycle (fuel fabrication) and going until the final disposal of the fuel is achieved. The Spanish policy for its nuclear cycle is the “open cycle” (see Figure 1.8) and, as reprocessing is not planned, all the spent fuel generated by the NPPs is directly considered radioactive waste. Likewise, the vitrified waste currently stored in France from the reprocessing of the dismantled Vandellós I reactor will eventually come back to Spain for its storage.

1.5. Spanish approach

Table 1.I. Characteristics of the Spanish nuclear reactors currently in operation [97-99].

Nuclear power plant	Owner company	Type of reactor	MWe capacity	Start of commercial operation	Foreseen end of commercial operation
Almaraz I	Iberdrola (53%) Endesa (36%) Naturgy (11%)	PWR	1049.4	September 1983	2027
Almaraz II	Iberdrola (53%) Endesa (36%) Naturgy (11%)	PWR	1044.5	July 1984	2028
Ascó I	Endesa (100%)	PWR	1032.5	December 1984	2030
Ascó II	Endesa (85%) Iberdrola (15%)	PWR	1027.2	March 1986	2032
Cofrentes	Iberdrola (100%)	BWR	1092	March 1985	2030
Trillo	Iberdrola (49%) Naturgy (34,5%) EDP (15,5%) Endesa (1%)	PWR	1066	August 1988	2035
Vandellós II	Endesa (72%) Iberdrola (28%)	PWR	1087.1	March 1988	2035



Figure 1.8. Spanish strategy followed for the SNF and HLW management policy.

ENRESA (*Empresa Nacional de Residuos Radiactivos, S.A.*) is the state-owned company responsible for managing the radioactive waste and the dismantling of nuclear facilities in Spain. The Spanish strategy and policy concerning the management of the spent nuclear fuel is announced in the General Radioactive Waste Plan (GRWP). This document, which has to be periodically renewed, includes the main course of action, the Research and Development (R&D) activities, the timeframe for implementation of the different actions and the foreseen costs of such implementation. It is compulsory by the Spanish law. Currently, its 6th version, approved in 2006, is the applicable law [100]. In this document, the “once-through” cycle is envisaged, with the HLW being stored in a DGR, when available. As this is not the case, it was foreseen to build and operate a Centralised Temporary Storage Facility (CTSF) where all the SNF coming from the NPPs would be stored. The planned lifetime of this facility was of around 100 years [80], giving enough time to find a final solution for disposal of the waste. In addition, it was planned not only as a storage facility, but also as a R&D facility, thanks to the construction of associated laboratories for SNF research. With this goal, the CTSF strategy was proposed to the Spanish Government in 2004, but it was in 2006 when a Parliamentary Committee approved a non-law proposition on the set-up of an

Interministerial Committee responsible for establishing the criteria to be met by the site to host the CTSF. The site was finally designated to be the Municipality of Villar de Cañas (Cuenca) on 30th December 2011. The licensing process in this site started in 2014, when ENRESA requested the construction authorisation (based on US reference regulation, whose guidelines are defined by NUREG-1567 [90]), according to Spanish regulation about nuclear and radioactive facilities [101]. These licenses were still under study; however, and taking into account new regional environmental regulation, recently the project has been temporarily adjourned [102].

In this scenario, the 7th GRWP is awaiting for the official approval by the Spanish Government for being published. In the current draft version [98], and given the inconveniences found with the CTSF solution, two alternatives are proposed:

- Keep the CTSF strategy as the way of storing all the waste in one single facility.
- Build and operate Decentralised Temporary Storage Facilities (DTSFs), located at the plant sites, which would provide the current Individual Storage Facilities (ISFs) (see next paragraph) with the necessary tools to ensure the correct SNF management.

The final decision to be adopted (CTSF or DTSFs) principally requires a high degree of social, political and institutional consensus. Given the delay in the selection and the urgent necessity of storing SNF, the 7th GRWP also envisages that the ISFs currently being built, or even in operation, complement the storage facilities of the nuclear power plants (pools), and need to continue their operation at least until the decision is made. ISFs constitute a facility whose goal is to house the spent fuel at the plant's site, thus releasing the saturation of the pools. They are interim, dry storage facilities, located on surface, where the HLW is prepared and stored in dedicated casks, which differ from one NPP to another. In Spain there are currently six ISFs in operation (being the ones of Almaraz and Ascó plants divided because of the two reactors), all of them in different steps of their operational life [98, 103, 104]. Table 1.II provides an overview of the situation of the Spanish ISFs at 31/12/2021, as documented in the draft version of the 7th GRWP [98]. The total amount of fuel elements stored up to that date is also presented. The continuous construction and operation of these ISFs highlights the increasing need of these facilities until the final disposal will be available.

Table 1.II. Situation of the Spanish ISFs built at 31/12/2021 [98].

Nuclear power plant	Start of ISF operation	Total capacity (casks)	Fuel elements stored at 31/12/2021 (% over the total generated)
Trillo	2002	80	800 (58%)
José Cabrera	2009	16	377 (100%)
Ascó I	2013	18	448 (28%)
Ascó II	2013	18	384 (25%)
Almaraz I	2018	10	96 (6%)
Almaraz II	2018	10	96 (6%)
Santa María de Garoña	2018	10	-
Cofrentes	2021	24	260 (5%)

1.6. Safety aspects during interim storage of SNF. The risk of a potential oxidation of the SNF matrix

In every dry storage facility for SNF, there is an agreed number of safety actions that must be ensured during the storage time [85]:

- Containment and safe enclosure of radioactive material.
- Limitation of radiation exposure.
- Sub-criticality.
- Removal of decay heat.

One process that could compromise some of these actions is SNF oxidation; in particular, oxidation of the UO_2 matrix. It is known that most of the transuranic elements formed during irradiation (which usually occur in the form of oxides), and some FPs, are embedded inside the SNF matrix [93]. Given the potential threat that they represent if they are released into the environment, the behaviour of the UO_2 matrix under these circumstances must be well-understood.

UO_2 oxidation is a reaction dependent on a number of factors. Among them, the presence of residual water after the drying process, burnup at which the fuel was irradiated (*i.e.* chemical composition of the fuel), mechanical and morphological properties of the fuel after irradiation (porosity, grain size), etc., could play a role in the reaction [105]. However, temperature and the presence of oxygen as the main feasible oxidant are the most important ones.

1.6. Safety aspects during interim storage of SNF. The risk of a potential oxidation of the SNF matrix

The upper limit temperature allowed in inert atmosphere storage conditions for LWR spent fuel is 400°C [106-108], in order to ensure the cladding integrity and prevent excessive cladding creep deformation. During normal storage conditions, there will be a range of temperatures lower than the maximum allowable of 400°C. For this reason, this threshold temperature is based upon the peak rod temperature, not the average rod temperature. That's why most of the studies regarding the oxidation of SNF have been conducted at this temperature or below [105, 109-113].

The presence of oxygen (O_2) in the atmosphere may also produce oxidation of the fuel. In this scenario, the majority of experimental studies carried out with SNF focuses on the worst case, which is the unlimited flow of oxygen due to a big hole in the cladding (*i.e.* air oxidation). However, other factors such as oxygen partial pressure should be considered for the case of failed cladding, as they could affect the oxidation rate of the fuel. In the event of tiny defects in the cladding, the access of the oxidant agent could be significantly low [114]. The literature data concerning the study of the SNF oxidation with lower oxygen partial pressures than air is scarce, and constrained to the conclusion that the oxidation rate will decrease if the oxygen content in the atmosphere is low, as pointed out by the Interim Staff Guidance 22 (ISG-22) [108]. Therefore, these issues should be evaluated when defining the operation design of a storage facility (both CTSF and DTSF) and the study of the potential fuel oxidation at these specific conditions, especially because the time-at-temperature profile of the reaction could substantially change if the oxygen availability is low. This knowledge would be helpful in managing storage facilities, especially in the safety assessment for operators, the public and the environment, and thus improving it is a goal of the present work.

In essence, in the event of exposure of high-temperature fuel to oxidant atmospheres, UO_2 oxidation may take place. This exposure can occur as a result of undetected defects in the fuel cladding, such as pinholes or hairline cracks. UO_2 oxidation has been studied through the years because of its potential implications in the safe management of SNF [105, 109-113]. The U_3O_8 phase, which is the most thermodynamically favoured product of the oxidation at the foreseen conditions of the dry storage [115], entails a 36% volume increase with respect to the initial UO_2 . In addition, this phase is formed as a fine powder at the pellet surface. In the case of a defective fuel cladding, the formation of U_3O_8 could lead to failure propagation, splitting of the sheath and finally release of

radioactive material during transport and/or storage [116-118]. Therefore, the knowledge of the kinetics that the reaction follows is of paramount importance in terms of nuclear safety.

The potential oxidation states of uranium allow the formation of a variety of oxidised compounds of uranium. UO_2 molecule is not thermodynamically stable under specific conditions, as can be seen in the phase diagram of the U-O system (Figure 1.9) [119-121]. At the expected dry storage conditions, *i.e.* temperatures below the allowable maximum of 400°C , UO_2 oxidation path, described in the phase diagram, results in a series of the mixed-valence U oxides $\text{U}_4\text{O}_9/\text{U}_3\text{O}_7$ and U_3O_8 . The characteristics of the uranium oxides involved in the oxidation reaction of the fuel are shown in Table 1.III. Besides the change in the microstructure (crystallographic system), the most remarkable feature about oxidation-caused changes is the decrease of density of the U_3O_8 phase, in contrast with the rest of intermediate oxides. In fact, the density of this phase is 23% less than that of UO_2 , which according to X-ray crystallographic densities corresponds to the aforementioned 36% net volume increase [120]. Therefore, the formation of U_3O_8 in a defective fuel element might lead to splitting of the sheath.

Table 1.III. Characteristics of the main uranium oxides involved in the oxidation reaction of the fuel [61].

Phase	O/U ratio	Crystallographic system	Lattice parameter (Å)	Density ($\text{g}\cdot\text{cm}^{-3}$)
UO_2	2.00	Cubic	$a=5.47$	10.96
U_4O_9	2.25	Cubic	$a=5.44$	11.30
U_3O_7	2.33	Tetragonal	$a=5.47$; $c=5.39$	11.40
U_3O_8	2.67	Orthorhombic	$a=4.15$; $b=11.97$; $c=6.72$	8.35

1.6. Safety aspects during interim storage of SNF. The risk of a potential oxidation of the SNF matrix

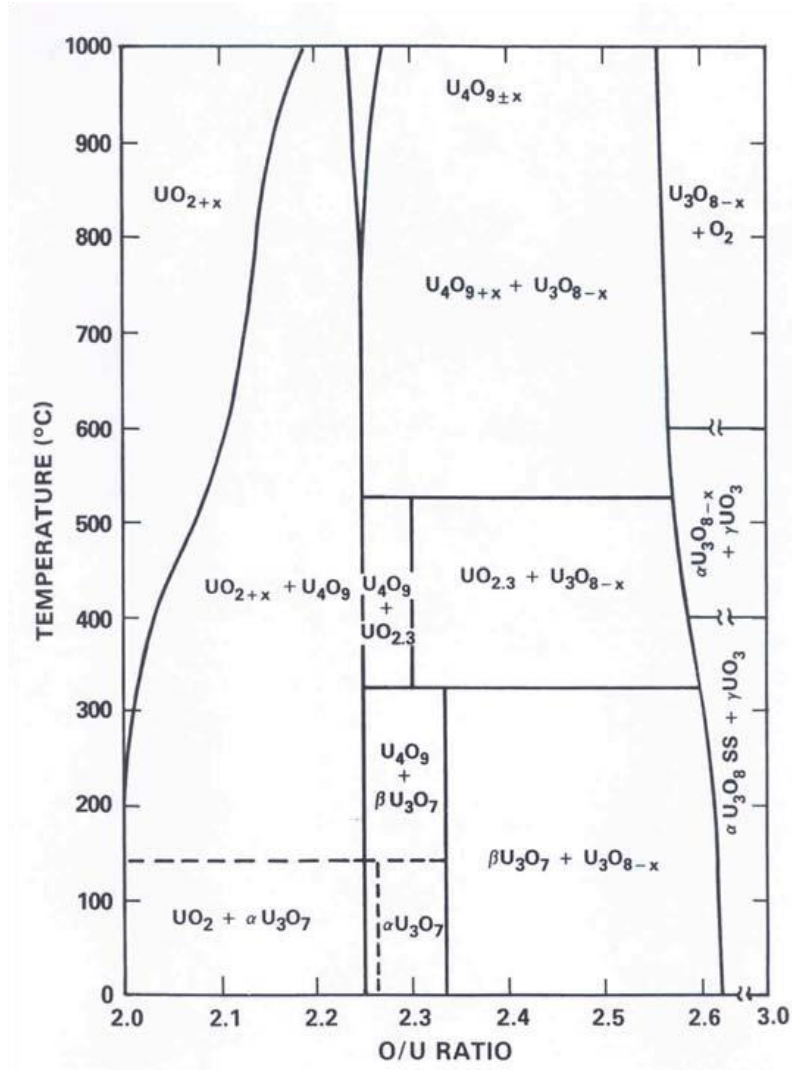
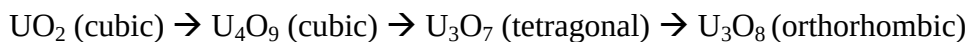


Figure 1.9. Temperature vs composition O/U phase diagram. In this PhD thesis, the focus lies on the temperature range below 400°C. Taken from [122].

The reaction of UO_2 to form U_3O_8 , as the reaction of interest in the SNF matrix oxidation, proceeds according to the following transformations:



The existence of these four domains was proposed by Rousseau *et al.* [123], who went deeper in the study of the traditional, two-step reaction [124, 125]. According to their study, the first domain would correspond to the change from UO_2 to U_4O_9 ; the second one would involve two simultaneous reactions, *i.e.* $\text{UO}_2 \rightarrow \text{U}_4\text{O}_9$ and $\text{U}_4\text{O}_9 \rightarrow \text{U}_3\text{O}_7$; and the third and the fourth would be related to the transformation of U_3O_7 into U_3O_8 . From a phenomenological point of view, the increase of oxygen content in the UO_2 structure provokes first the formation of the non-stoichiometric UO_{2+x} phase. At the

temperature range of interest, the extent of this phase is quite limited (up to $x=0.04-0.07$) [126], beyond which UO_2 and U_4O_9 would coexist [127]. U_4O_9 is the last phase retaining the cubic structure of fluorite. In fact, this oxide is actually considered a cluster of structures of UO_2 with unit cell equal to four times the unit cell of UO_2 [128].

Extra oxygen incorporation involves a change in the crystallographic system, thus resulting in the tetragonal U_3O_7 phase, with similar unit cell parameters to those of U_4O_9 . Among these oxides, there are extra phases with different stoichiometric ranges, due to the reorganisation of the structure [129-131]. Finally, higher oxygen content results in a new set of phases based on the orthorhombic structure of U_3O_8 , which spallates from the pellet [123, 132]. The latter oxide $\alpha\text{-U}_3\text{O}_8$ is consensually associated with the final oxidised phase of the U-O system in absence of moisture and at air pressure [115].

The handling and Post-Irradiation Examination (PIE) of nuclear fuel specimens is extremely difficult and challenging. Due to the large operational requirements for working with SNF (hot-cell facilities with radiation shielding) and the limited access to this material to only a few laboratories around the world, experiments carried out with surrogate materials are often found in literature. These materials are easier to handle and can reproduce the SNF behaviour [133]. The most used surrogate is unirradiated UO_2 , precisely the SNF matrix itself [123, 134-137]. Although there are differences between the oxidation mechanisms of fresh and irradiated fuel [105], unirradiated UO_2 meets an important criterion that allows using it as an adequate spent fuel analogue: its overall oxidation behaviour is conservative with respect to SNF. In other words, this means that the time to attain U_3O_8 for irradiated fuel is longer than that for fresh UO_2 . In fact, in spite of reaching the U_4O_9 phase faster, the burnup-related presence of FPs and other elements in SNF stabilises this phase, thus delaying the formation of U_3O_8 [138, 139].

Takin all of this into account, in this work both unirradiated and irradiated nuclear fuels have been used with the aim of fill some of the knowledge gaps previously analysed. This will be explained throughout the set of chapters that compose this PhD thesis, which are hereinafter presented.

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Chapter II

Objectives

2. OBJECTIVES

From the considerations made in the previous Chapter, the SNF matrix oxidation could have a direct impact on the safety of dry storage facilities, in particular if the U_3O_8 phase is formed. The aim of this PhD thesis is to study this reaction under conditions prevailing in dry storage in case of a fuel matrix exposure to an oxidising agent. To meet this purpose, surrogate fuel materials have been used, and the gained knowledge has been employed to study real (*i.e.* irradiated) nuclear fuel. The way to achieve such an aim will be pursued by following the next objectives and addressing specific tasks:

- Objective 1: To study UO_2 oxidation at hardly explored conditions. From the analysed database, there is a clear knowledge gap in the effect that lowering the oxygen concentration would have on the oxidation rate, as few studies have addressed conditions other than air-oxidation (21% O_2). Two tasks are proposed in this regard:
 - Task 1.1. To obtain a fuel surrogate that more closely resembles the SNF sensitivity to oxygen presence than those used in previous studies. In this regard, higher reactivity than SNF is preferred for conservatism reasons (Chapter IV, Result 1).
 - Task 1.2. To develop a protocol to follow the fuel matrix oxidation along time in the aforementioned conditions of interest for dry storage facilities. Hence, the measurement protocol must be able to be applied at *in-situ* conditions (Chapter IV, Result 2).
- Objective 2: To analyse the potential interest of Accident Tolerant Fuels (ATFs) matrixes as a new nuclear technology, in particular doped UO_2 pellets, providing new insights on how these fuels oxidise to U_3O_8 and verifying whether they represent an improvement in this regard or not. For doing so:
 - Task 2.1. To manufacture a set of Cr-doped UO_2 monoliths, as the selected ATF technology, and to characterise them in detail (Chapter IV, Result 3).
 - Task 2.2. To determine how the previously fabricated and characterised ATF samples behave in their transformation to U_3O_8 . The most favourable experimental conditions to attain this phase are selected,

keeping the *in-situ* criterion considered in Task 1.2. (Chapter IV, Result 4).

- **Objective 3:** To put together the outcomes from Objectives 1 and 2 and to apply them to the study of real (*i.e.* irradiated) nuclear fuel. The “bridge” between the oxidation behaviour of fresh and irradiated fuel will be built by doing the following:
 - Task 3.1. To identify similarities and discrepancies of the surrogate database built in this work and the data available for SNF oxidation experiments. Knowledge gaps in the most-affecting parameters are identified and experimentation to fulfil them is proposed (Chapter IV, Result 5).
 - Task 3.2. To combine the developed protocol in Objective 1 with the interest of ATFs for the nuclear community highlighted in Objective 2 to perform oxidation experiments with irradiated ATF samples. Firstly, a set-up step employing irradiated conventional fuel becomes necessary (Chapter IV, Result 6).

2.1. List of publications

The results achieved in this work have been published as original papers in different scientific journals. They are hereunder detailed, in order of appearance, and correspond to the Results 1-6 shown in Chapter IV.

- A. Milena-Pérez; N. Rodríguez-Villagra; S. Fernández-Carretero; A. Núñez. “Thermal air oxidation of UO₂: Joint effect of precursor's nature and particle size distribution”. *Progress in Nuclear Energy*, 2023, 159, 104629. DOI: 10.1016/j.pnucene.2023.104629.
- A. Milena-Pérez; L.J. Bonales; N. Rodríguez-Villagra; H. Galán. “Exploring the impact of temperature and oxygen partial pressure on the spent nuclear fuel oxidation during its dry management”. *Scientific Reports*, 2023, 13:1966. DOI: 10.1038/s41598-023-29265-w.
- A. Milena-Pérez; L.J. Bonales; N. Rodríguez-Villagra; S. Fernández; V.G. Baonza; J. Cobos. “Raman spectroscopy coupled to principal component analysis for studying UO₂ nuclear fuels with different grain sizes due to the

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- A. Milena-Pérez; L.J. Bonales; N. Rodríguez-Villagra; M.B. Gómez-Mancebo; H. Galán. “Oxidation of accident tolerant fuels models based on Cr-doped UO_2 for the safety of nuclear storage facilities”. *Journal of Nuclear Materials*, 2023, 582, 154502. DOI: 10.1016/j.jnucmat.2023.154502.
 - A. Milena-Pérez; N. Rodríguez-Villagra; F. Fera; C. Aguado; L.E. Herranz. “Critical review of fuel oxidation database under dry storage conditions”. *In press in Progress in Nuclear Energy*, 2023.
 - A. Milena-Pérez; L.J. Bonales; L. Emblico; D. Serrano-Purroy; N. Rodríguez-Villagra. “Spent Nuclear Fuel oxidation under dry storage controlled conditions for studying its radial oxidation behaviour”. *Submitted to Journal of Nuclear Materials*.

Other related publications, issued during the development of this work, are:

- N. Rodríguez-Villagra; O. Riba; A. Milena-Pérez; J. Cobos; L.J. Bonales; S. Fernández-Carretero; E. Coene; O. Silva; L. Duro. “Dopant effect on the spent fuel matrix dissolution of new advanced fuels: Cr-doped UO_2 and Cr/Al-doped UO_2 ”. *Journal of Nuclear Materials*. 2022, 568, 153880. DOI: 10.1016/j.jnucmat.2022.153880.
- J.M. Elorrieta; A. Milena-Pérez; J.F. Vigier; L.J. Bonales; N. Rodríguez-Villagra. “New insights into the structural transition from UO_{2+x} to U_3O_7 by quantitative Raman spectroscopy”. *Physical Chemistry Chemical Physics*. 2022, 24, 28394. DOI: 10.1039/d2cp03573a.
- N. Rodríguez-Villagra; L.J. Bonales; S. Fernández-Carretero; A. Milena-Pérez; L. Gutiérrez, H. Galán. “Exploring a surrogate of Pellet-Cladding interaction: Characterization and oxidation behaviour”. *MRS Advances*. 2023. DOI: 10.1557/s43580-022-00475-0.
- A. Milena-Pérez; L.J. Bonales; N. Rodríguez-Villagra; H. Galán. “Development of a reliable and simple method for the quantification of U_3O_8 by Raman Spectroscopy complying with nuclear safety requirements”. *To be submitted*.

Chapter III

Methodology

3. METHODOLOGY

3.1. Materials Preparation

The work performed in this thesis has been mainly carried out by using different nuclear fuel surrogates, prepared to cover a range of model materials suitable to study the oxidation of spent nuclear fuel in a potential dry storage scenario.

With the aim of obtaining the most suitable surrogate in each case, a variety of materials has been obtained and studied, controlling different physicochemical parameters such as particle size distribution, specific surface area, grain size or dopant concentration. In this regard, two main categories can be identified and used as a basis to synthesize the fuel analogues. They are described in the next paragraphs, together with their preparation route.

3.1.1. UO_2 powdered substrates

As stated by many authors and explained in the Introduction section, Chapter I, it is generally accepted that the oxidation, in the same experimental conditions, of UO_2 powders and UO_2 pellets is faster in the former case. The reason for using powdered substrates lies precisely in its faster reaction with oxygen, as the main goal of this thesis is to study the oxidation of UO_2 and the subsequent formation of U_3O_8 . Using powder represents, in fact, the most conservative case. This property allows using the powdered materials as “conservative” surrogates with respect to real SNF.

As a basis to obtain different powdered substrates, two routes have been employed:

- a) UO_2 purification. This method is based on the selective extraction of uranium coming from other processes and materials, such as defective fuel pellets, samples from finished experiments, or uranium waste generated during a specific experimental work. The main difference between this material and the powder coming from sintered pellets (see next section) is that, in purified UO_2 , the stress induced by the sintering process is broken and, thus, it does not have a “memory effect” that may affect the oxidation [1]. In short, the procedure consists in obtaining UO_2 via Ammonium Di-Uranate (ADU), following a precipitation process that involves several major steps. First of all, the mixture of uranium compounds is dissolved in highly concentrated HNO_3 , followed by

3.1. Materials Preparation

filtration of the resultant solution to eliminate possible solid impurities. After that, purification of uranium is carried out by applying a selective solvent extraction process with tributyl phosphate (TBP), which is a selective compound used at industrial scale in the Plutonium Uranium Reduction Extraction (PUREX) process [2-4]. Once a pure uranium solution is obtained, it is precipitated by using NH_4OH (30%), obtaining the aforementioned ADU compound [5, 6]. The solid is then separated by using HA 0.45 μm (Millipore) filters. Finally, this powder is subjected to a thermal treatment for denitration/dehydrating, oxidation and reduction to its final UO_2 form. This method has been optimised at the facilities of the HLWU at CIEMAT. A schematic overview of the process is presented in Figure 3.1. As a result of applying this methodology, a pure, stoichiometric UO_2 has been obtained.

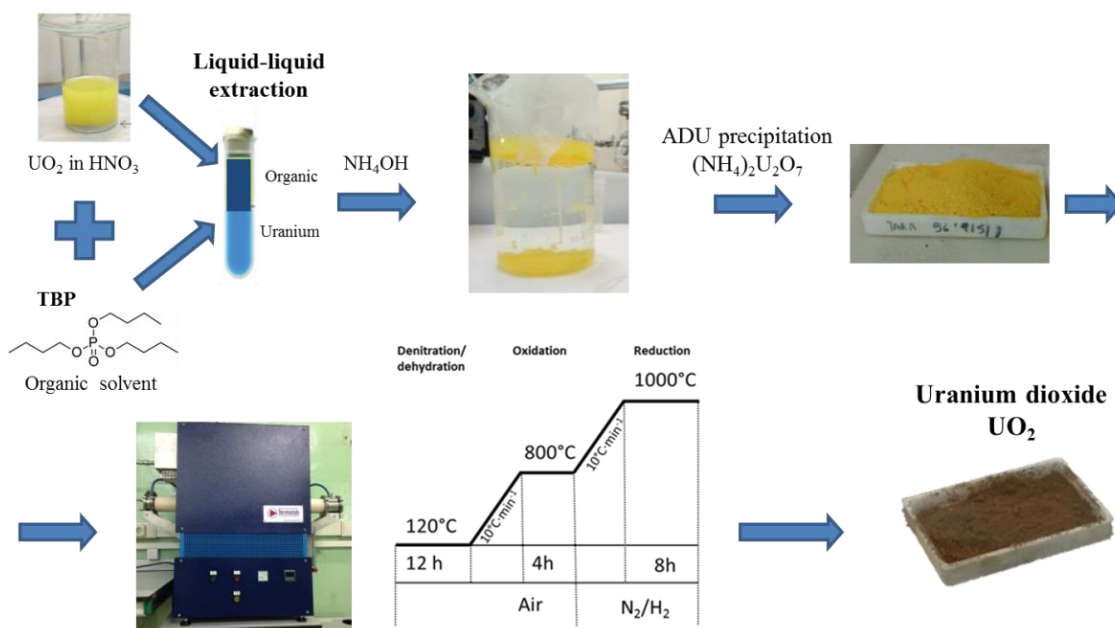


Figure 3.1. Schematic representation of the chemical process applied to obtain a purified UO_2 powdered substrate.

- b) UO_2 pellets: Conversely, other powdered substrates used in this PhD work have been obtained from monoliths of unirradiated sintered UO_2 pellets supplied by ENUSA, which were crushed into powder in a Mixer Mill MM 400 (Retsch). From this point, two different treatments were applied. Firstly, a portion of this powder was further milled and sieved to get a particle size ranging from 100 to 315 μm . After that, the sieved fraction was milled again to obtain a homogeneous distribution of the particle size lower than 5 μm . Secondly, the

other fraction coming from the crushed pellets was milled directly, *i.e.* no sieving applied, to the desired particle size range. This series of processes gave as a result two different sets of powdered UO_2 substrates, being differentiated mainly in their Particle Size Distribution (PSD), what is expected taking into account the sieving and milling steps. For illustrative purposes, Figure 3.2a) shows the original look of the used pellets, and Figure 3.2b) the changes that these pellets suffer during the process followed to obtain the powdered material.

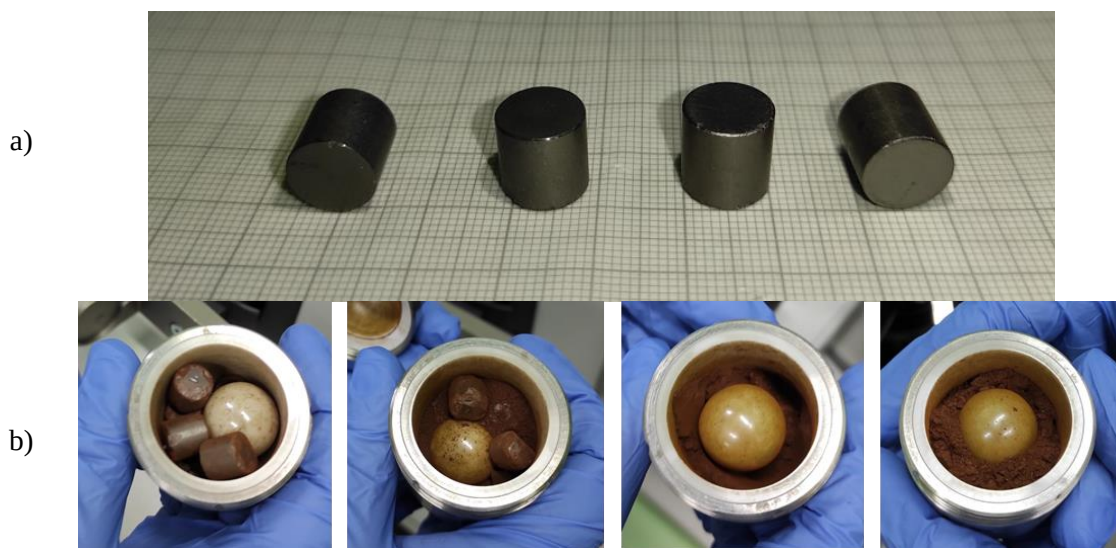


Figure 3.2. a) Appearance of fresh UO_2 pellets used in this work and b) visual changes suffered by the monoliths when subjected to the milling process.

3.1.2. UO_2 sintered pellets

In addition to powders, the work developed has required to synthesize and study a different type of nuclear fuel surrogates, in particular fabricating sintered pellets that replicate the physical properties of real fuel. Special importance deserves the aforementioned ATFs, in which different dopants are added to the UO_2 matrix prior to the sintering stage in order to improve the properties of the fuel. In this thesis, the focus is put on Cr-doped UO_2 pellets, as one of the most-effective elements enlarging grain size of the fuel. At the HLWU of CIEMAT, the fabrication process mimicking the industrial manufacture of nuclear fuel is applied, following a conventional metallurgical procedure based on classical powder pressing and sintering [7]. The first step of the process was to mix weighted amounts of the starting powders, in our case UO_2 and Cr_2O_3 , together with 1% of EBS (Ethyl Bis Stearamide, $\text{C}_{38}\text{H}_{76}\text{N}_2\text{O}_2$, supplied by Tokyo Chemical Industry) as binder and lubricant [8], using low-energy ball milling.

3.1. Materials Preparation

The batches of mixed powders were then blended for 1 minute at 15 Hz in the mixer mill. Then, the mixtures obtained were subjected to uniaxial pressing with an applied pressure of 700 MPa in a press of 25 tons C256C (Power team, Johannesburg, South Africa). After that, a heating process under a 4.7% H₂-N₂ flow –in order to avoid UO₂ oxidation– was conducted on all the “green” pellets. All discs were then calcined in three stages (100, 300 and 500°C) at 10°C·min⁻¹ and held up to 4 hours to remove the incorporated EBS, followed by the sintering process at 1675°C for 4 hours (5°C·min⁻¹). Finally, polishing and thermal annealing (10 minutes at 1590°C under a 4.7% H₂-N₂ atmosphere) were carried out to reveal grains, and therefore confirm the effect of adding Cr in the material. All of these thermal treatments have been performed in a tubular horizontal furnace TH1700 provided by Termolab (Figure 3.3), placed inside the IR-30 radioactive facility (see section 3.3.1 for further details).



Figure 3.3. Tubular horizontal furnace TH1700 used in this thesis for sintering ATF pellets.

3.2. Instrumentation

The complete set of instruments used throughout this thesis is presented in this section. It is worth mentioning that important efforts have been made with regard to the

nuclearisation of the equipment, preparing all the devices for their use with radioactive samples inside a radioactive facility.

3.2.1. Raman Spectroscopy

One of the main techniques employed in the characterisation of the uranium oxides studied is Raman Spectroscopy (RS). As other spectroscopic techniques, Raman scattering is based on the analysis of light-matter interactions [9]. In particular, the Raman effect is described as an inelastic scattering of light, a phenomenon that will change depending on the analysed molecule and its environment. This fact makes it possible to use RS as a tool to identify uranium oxides with different oxidation degrees, given that they feature distinguishable Raman bands that can be used as a fingerprint for each oxide.

At CIEMAT facilities, Raman spectra of the studied solids were obtained by using a LabRAM HR Evolution spectrometer (HORIBA, Jobin Yvon Technology, Figure 3.4). For this purpose, a HeNe laser with wavelength equal to 632.8 nm was employed, being the laser beam focused onto the sample surface through a 50x objective of an Olympus BX41 microscope. Then, the radiation scattered after the interaction of the laser with the sample was collected in backscattering geometry, dispersed by a holographic grating (600 grooved per mm) and collected by a CCD detector (256x1024 pixels). This configuration results in a spectral resolution of about 1 cm^{-1} per pixel. Acquired spectra were readjusted by using the emission lines of a Ne arc-lamp. For identification of the central position of the bands, a key parameter to study the changes in nuclear fuel due to oxidation, the second derivative method was applied [10]. This method has been previously used in the HLWU in the characterisation of uranium oxides [11, 12].



Figure 3.4. General view of the HORIBA LabRAM HR Evolution spectrometer.

3.2.2. X-Ray Diffraction

X-Ray Diffraction (XRD) is one of the most important characterisation techniques used in materials science and solid-state chemistry. It is based on the diffraction effect, which is produced when electromagnetic radiation impacts on ordered structures with geometrical variations on the length scale of the radiation wavelength. As a result of this interaction, the incident X-ray beam is scattered in all directions. Some of the scattered X-ray waves come out in phase, giving rise to constructive interferences, which are observable in the experimental diffractogram.

XRD was carried out at the HLWU by means of a Bruker D8 Advance Eco diffractometer, using Cu K α radiation ($\lambda=1.54056$ Å). The equipment can be seen in Figure 3.5. The instrument operates typically at 40 kV and 25 mA of voltage and intensity, respectively; and it is configured in a Bragg-Brentano geometry. Typical 2θ range used in the measurements taken during this thesis covers from 20° to 120° . Diffracted radiation was collected by a 1-dimensional Lynx Eye Position Sensitive Detector. All systematic sources of error, such as zero displacement, peak positions and goniometer shift, have been corrected by both a correct alignment of the instrument and measurement of a certified pattern of Al₂O₃. Lattice parameters of the crystalline structures obtained in the experimental diffractograms have been obtained by applying the unit cell refinement method implemented by the software TOPAS (Bruker Analytical X-Ray Systems).

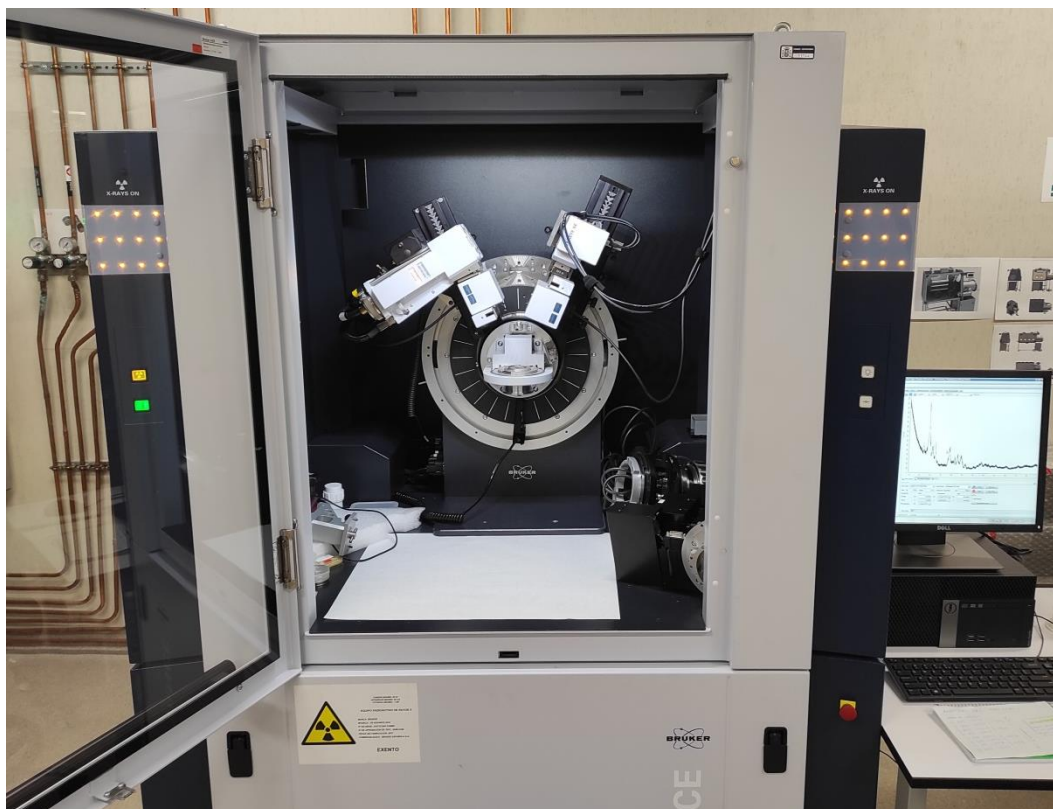


Figure 3.5. Bruker D8 Advance Eco X-Ray diffractometer.

3.2.3. Thermal analyses: TGA and DSC

Thermogravimetric Analysis (TGA) is a technique based on measuring changes in the mass of the samples as a function of temperature (or time at a given temperature). The recorded mass variations can be associated with physical and chemical phenomena induced in the samples; especially important for the purposes of this thesis is the oxidation reaction, given the capability of the technique to use different gaseous atmospheres. In fact, during this work, TGA has been used as an *in-situ* method to oxidise the as-prepared UO_2 materials, both with a temperature ramp to produce U_3O_8 in different conditions and study this reaction, and with isothermal experiments simulating a real-case dry storage scenario.

The TGA instrument used was a TGA Q50 thermobalance (TA Instruments), shown in Figure 3.6. Oxidant gas (both air and oxygen-nitrogen mixtures with lower oxygen concentrations) was flowed through the furnace chamber with a constant rate of $60 \text{ mL} \cdot \text{min}^{-1}$. In addition, a pure nitrogen flow at a rate of $40 \text{ mL} \cdot \text{min}^{-1}$ was used as a balance purge gas. The TGA calibration was performed in both, temperature of magnetic standards (Curie point, ASTM E-1582) with Alumel, Ni and $\text{Ni}_{0.63}\text{Co}_{0.37}$ alloy

standards (153, 358 and 764°C, respectively), and weight (200 mg to 1 g calibration weight range). Typical oxidations of the studied nuclear samples are performed by heating the samples from room temperature up to 700°C with a constant heating rate of 10°C·min⁻¹, using a platinum crucible as sample holder. The obtained thermogravimetric curves were analysed with the Universal Analysis software (TA Instruments). This software allows calculating a number of important parameters related to the work performed during this thesis, such as the O/U ratio, reaction rates and oxidation onset temperatures.



Figure 3.6. TA Instruments TGA Q50 thermobalance for thermogravimetric experiments.

In addition to TGA, Differential Scanning Calorimetry (DSC) has been used as a complementary characterisation technique. As TGA, it is based on measuring a physical property that changes with temperature, but in this case the signal given is the heat flux as a function of temperature (or time at a given temperature). It allows measuring both exo- and endothermal processes that occur in the samples, typically phase transitions. Sometimes these processes may not imply a mass change, being this the reason why TGA and DSC are often used combined.

DSC was performed by using a Q20 system (TA Instruments). The equipment was calibrated following the melting point and enthalpy of a pure Indium standard (28.45 J·g⁻¹; T_m = 156.6°C). Oxidant gas flow (air) in this case was set to 50 mL·min⁻¹. The DSC system installed at the HLWU is shown in Figure 3.7.



Figure 3.7. TA Instruments DSC Q20 instrument.

3.2.4. Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is a morphological characterisation technique, which is based on focusing an electron beam on the sample surface in order to create an image. The electrons of the beam interact in different ways with the sample, producing a variety of signals that can be used as a way to study the sample topography and morphology. Depending on the radiation interaction, two types of electrons can be detected:

- a) Back-Scattered Electrons (BSE): They consist of electrons of the initial beam that are dispersed backwards when reaching the sample. This kind of radiation provides clear images of surface components.
- b) Secondary Electrons (SE): Emitted by the sample itself as a result of the incident beam interaction. As they come from the sample, this radiation gives information about the relief of the surface.

At CIEMAT, the SEM technique is applied by means of a TM4000 Plus SEM (HITACHI) equipped with a tungsten filament and a turbomolecular vacuum pump, using a typical working voltage of 5-15 kV. In addition, it is a desk instrument that

presents the important advantage of not needing to metallise the samples prior to the measurement. The complete device is presented in Figure 3.8. Besides the study of the sample morphology and the changes induced by oxidation in UO_2 samples, in this thesis SEM images have also been used to observe the presence of aggregates in doped UO_2 monoliths and to calculate the average grain size of sintered pellets, by using the linear intercept method [13]. These parameters are important for the optimisation of the fabrication of the new ATFs.

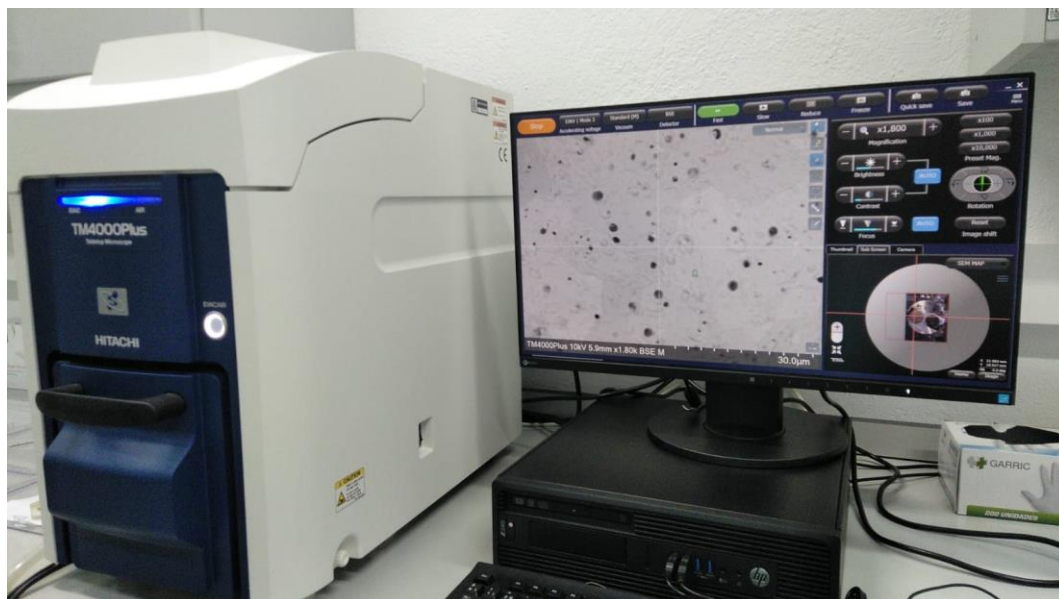


Figure 3.8. HITACHI TM4000 Plus instrument for obtaining SEM micrographs.

3.2.5. Laser Diffraction

The Laser Diffraction (LD) technique is an optical tool for analysing the Particle Size Distribution (PSD) of a material. The method is based on focusing a laser on the solid particles suspended in a liquid solution. The interaction between the incident radiation and the particles generate scattered radiation at different angles, which are directly related to the particle size. As a result, a statistical distribution is obtained, being mainly characterised by the median volume diameter of the particles, $D(v,0.5)$. Other important statistical indicators are $D(v,0.1)$ and $D(v,0.9)$, which are the sizes corresponding to percentile 10th and 90th, respectively.

The equipment used at CIEMAT for measuring PSD is shown in Figure 3.9. It is an instrument provided by Malvern, Series Mastersizer 2600, with a He-Ne laser beam ($\lambda=633$ nm) and a 63 mm lens, which allows measuring particle sizes from 1.2 to 118

μm . The samples were suspended in a solution at 10% of $\text{Na}_3\text{PO}_4 \cdot 10\text{H}_2\text{O}$, a compound which is also used to break agglomerates and calculate the real PSD.

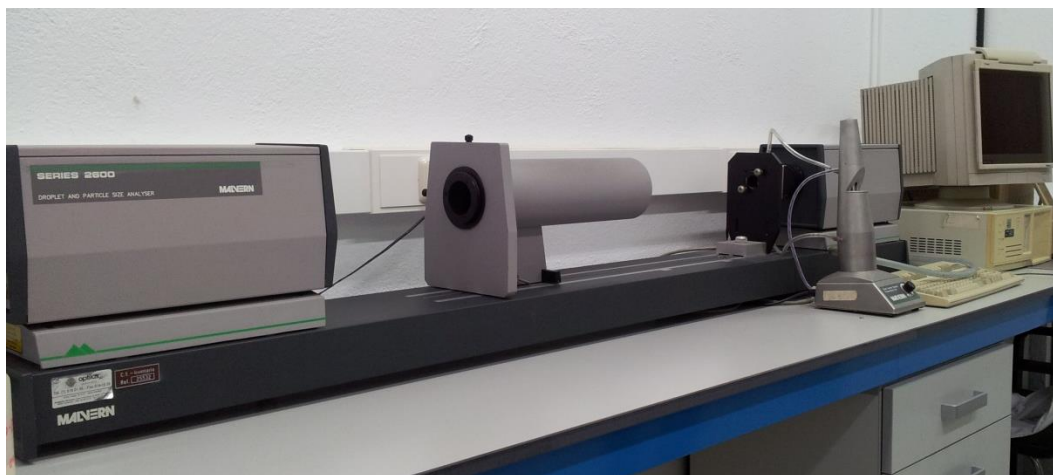


Figure 3.9. Malvern Series Mastersizer 2600 for analysing PSD.

3.2.6. Specific Surface Area

The Specific Surface Area (SSA) of a material is defined as the exposed area per mass unit, thus expressed in $\text{m}^2 \cdot \text{kg}^{-1}$. SSA of a solid plays an important role in many processes, including chemical reactivity, as it is correlated to surface roughness and porosity. Among the different methods to measure SSA, one of the most widely used is the BET method, based on the theory developed by Brunauer, Emmet and Teller [14]. This method consists in the isothermal adsorption of gaseous molecules on the surface of the sample, until a monolayer is formed.

At the HLWU, the BET method is carried out by means of an ASAP 2020 instrument (Micromeritics), employing N_2 as gaseous adsorbate and using a relative pressure (P/P_0) ranging from 0.05 to 0.35. The complete set-up is shown in Figure 3.10.

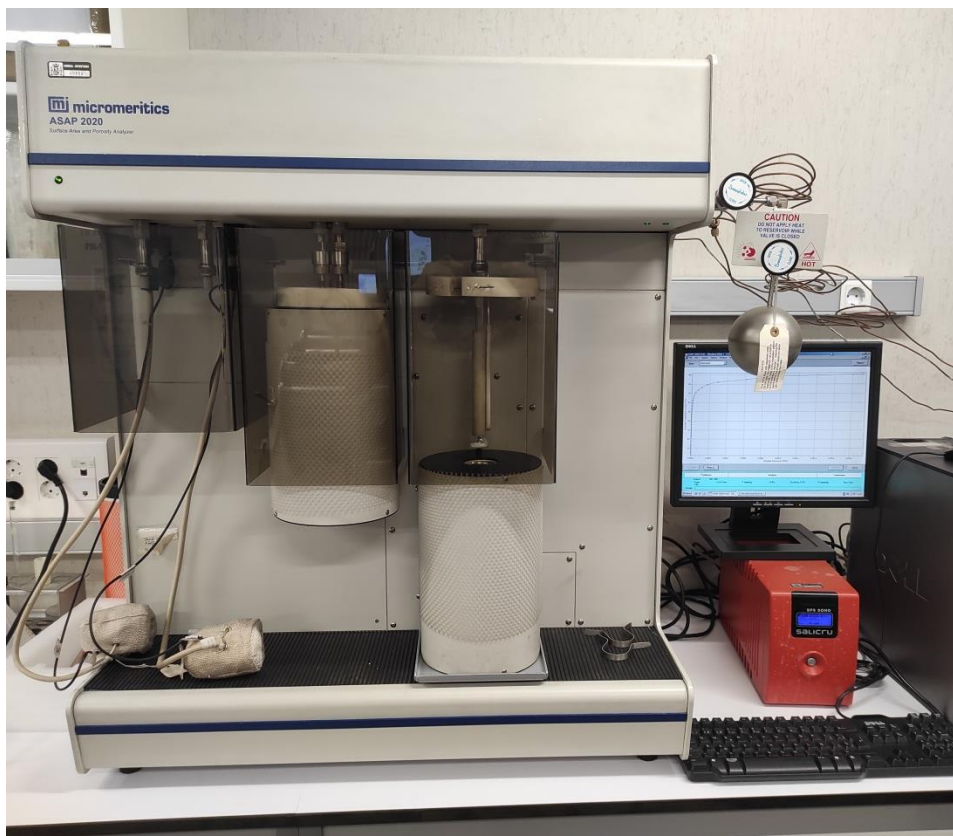


Figure 3.10. Micromeritics adsorption instrument ASAP 2020 for SSA measurements.

3.3. Facilities

3.3.1. IR-30 Radioactive Facility

Due to the nature of the samples used throughout this thesis, *i.e.* radioactive materials, the instruments and techniques employed are used in such a way that safety for the operator and environment radioprotection is guaranteed at every moment. In this regard, most of the work carried out has been developed at the CIEMAT IR-30 radioactive facility, a surveilled area located at the HLWU facilities, and licensed according to the guidelines specified by the Spanish government [15] and the instructions provided by the regulatory body (Nuclear Safety Council, in Spanish *Consejo de Seguridad Nuclear*, CSN).

This facility is fully equipped with the necessary infrastructure to work with this kind of materials, including glove boxes and fume hoods, as can be seen in Figure 3.11. Both glove boxes and hoods are prepared for any incident that may arise, including extraction

and cooling systems, electrical outlets and filters for gases. In particular, the glove boxes are filled with Ar and connected to a surveillance system in continuous operation.



Figure 3.11. IR-30 Radioactive Facility, showing the fume hoods (left) and the glove boxes (right).

The overall goal of the IR-30 radioactive facility is to provide support to the work performed in the HWLU in the frame of the different research projects in which it is involved, in particular regarding the manufacturing, characterisation and study of the nuclear fuel analogues used throughout this thesis. For this reason, the staff working in this area has taken comprehensive courses regarding radiation protection, non-encapsulated radioactive sources handling and training sessions particularly devoted to the IR-30 itself. In addition, the professionally exposed workers have exhaustive radiological controls, including the use of a personal dosimeter, urine analysis for detection of eventual contamination with radionuclides and whole-body counter examinations.

Likewise, temperature and relative humidity are monitored, and ventilation is controlled to keep depression levels inside the facility, in order to avoid eventual leakages of radioactive material outwards. Air quality is also checked by measuring filters for airborne particulates in the extraction flow of the laboratory. The maximum inventory of radioactive material allowed to work with is 10 MBq of beta-gamma emitters, 5 MBq of alpha emitters and 2 MBq of natural uranium and thorium.

3.3.2. IR-35 Laboratory

An important part of the work performed during this thesis has been carried out in the so-called IR-35 Laboratory. The nomenclature IR is given because this laboratory will

become a Radioactive Facility after the licensing process, which is currently ongoing, will finish [16, 17]. This new radioactive facility will provide the HLWU with an enhanced capacity for using radioactive materials, as it is foreseen that the maximum inventory of radioactive material allowed to work with will be 14.5 GBq of beta-gamma emitters, 40 MBq of alpha emitters and 20 MBq of natural uranium and thorium. These limits will be added to the currently used at IR-30, described in the previous section. The future facility will count with all the required safety measurements explained for IR-30, as well as two additional glove boxes for carrying out the planned experiments in the Unit.

Nevertheless, this facility is currently a cold laboratory, which means that only exempt samples (*i.e.* with a specific activity concentration below the exemption limit, which varies depending on the considered radionuclide and is associated with the radiological risks derived from its use) can be analysed. In the case of natural uranium oxides samples, as the ones used at CIEMAT, this limit corresponds to a mass lower than around 0.4 g [18, 19]. This is not an important issue from the perspective of the results reached in this thesis, as in general the characterisation techniques described in section 3.2 require small amounts of sample.

Currently at the IR-35, five extra fume hoods are in operation, as shown in Figure 3.12. In addition to them, gaseous lines with different compositions are prepared for reaching the instruments (see both sides of Figure 3.12), as well as the extraction system, already working (Figure 3.12 at the top). Nowadays, several of the techniques employed in this thesis and previously described are already located and running at the IR-35, including Raman spectroscopy, XRD, LD for measuring particle size, SEM and BET for determination of the SSA, among other instruments.



Figure 3.12. Frontal view of the fume hoods operating at the IR-35 facility.

3.3.3. Joint Research Centre (JRC) facilities

A third part of the work included in this PhD thesis has been carried out at the facilities of the Joint Research Centre (JRC) in Karlsruhe, Germany. This institution, dependent on the European Commission, is considered the core of the research on Nuclear Safety and Security across Europe.

At JRC, the work was performed at the Hot Cell Laboratory (HC-KA), a facility consisting of 24 shielded hot cells where highly radioactive materials (including full-length light water reactor pins) can be received, handled and examined with the help of external telemanipulators (Figure 3.13). The hot cells are equipped with instruments that allow performing Post-Irradiation Examination (PIE) of fuel rods, including both destructive and non-destructive techniques. At present, the research at the HC-KA is devoted to the back-end of the NFC, with special focus on the long-term chemical stability of spent nuclear fuel under different environments. The stability of damaged irradiated fuel (corium) is also being investigated.

For the purposes of the studies developed in the frame of this PhD work, oxidation experiments have been conducted on SNF by means of a temperature stage coupled to a Raman spectrometer and installed inside one of the available hot cells. The instrument and the measurement protocol are described in detail in the next section.



Figure 3.13. External view of two hot cells available at JRC facilities, with two workers holding the telemanipulators for nuclear fuel handling. Image taken from [20].

3.4. Optimised Protocols for Studying SNF Matrix Oxidation

The oxidation reaction of UO_2 , as the SNF matrix, and the associated transformation to U_3O_8 , have been studied by using a variety of techniques and approaches. As a result, a number of experimental protocols, which can be implemented and used with the corresponding analytical technique, have been obtained. As all of them have been used in different moments of the performed work, they are compiled in this section.

3.4.1. *In-situ* thermogravimetric approach

As previously mentioned, TGA has been used in this work as an *in-situ* method to oxidise the as-prepared UO_2 materials. TGA has been traditionally employed to study the oxidation behaviour of both fresh [1, 21-23] and irradiated nuclear fuel [24-27], in particular monitoring the mass changes over time at a specific temperature (*i.e.* isothermal conditions). Nevertheless, sometimes it is worthy to use temperature ramps, what stands for the experiments carried out heating the sample at a linear rate from room temperature (RT) up to a determined temperature. When carried out with the as-prepared UO_2 materials under an oxidant atmosphere, this procedure allows studying the oxidation kinetics of the nuclear fuel surrogates. With this aim, Table 3.I shows the obtained optimised protocol, which has been considered as a standard method to be systematically applied to all the samples.

Table 3.I. Optimised protocol for TGA heating ramps procedure.

Step	Temperature	Atmosphere	Description
Initial	RT	Inert	Place the mass in the TGA furnace and allow for temperature stabilisation
Gas change	RT	Inert $\rightarrow$ Oxidant	N ₂ is replaced by the desired atmosphere (1-21% O ₂), the reaction begins
Heating	RT $\rightarrow$ 700°C	Oxidant	10°C·min ⁻¹ up to 700°C under a constant oxidant flow
Gas change	700°C	Oxidant $\rightarrow$ Inert	When oxidation is finished, N ₂ is set again to prevent further change
Cooling	700°C $\rightarrow$ RT	Inert	Decrease of temperature under inert conditions to prevent further oxidation

For unirradiated, undoped UO₂, this method ensures complete oxidation to U₃O₈, so it is valid to study the oxidation kinetics. As a way of comparison when studying other materials, such as the ATFs prepared during this thesis, we have maintained the method as it was optimal to see differences in the oxidation behaviour. Therefore, this has been the procedure used and the conclusions derived from it are presented in sections 4.1 and 4.4.

3.4.2. *In-situ* Raman-Linkam approach

In addition to being used as a very suitable characterisation technique for analysing uranium oxides, Raman spectroscopy has been also employed as an *in-situ* technique in which oxidation experiments at the different conditions studied during this thesis have been carried out. This idea tries to take advantage of the special features of the Raman technique itself, and bring to light other alternatives to the traditionally used thermogravimetric methods for studying SNF alteration in dry storage conditions. In this regard, Raman spectroscopy is presented as a non-destructive technique able to measure the oxidation progress from really short times and capable of detecting the potential early appearance of U₃O₈ and follow the evolution of the reaction even if the entire sample is not yet oxidised.

3.4.2.1. Raman-Linkam at CIEMAT

In order to reach these goals, a Linkam THMS600 temperature-controlled pressure stage was used at the HLWU facilities to perform the *in-situ* measurements. A frontal view of the stage can be seen in Figure 3.14, together with the final look of the stage once coupled to the main instrument.

3.4. Optimised Protocols for Studying SNF Matrix Oxidation

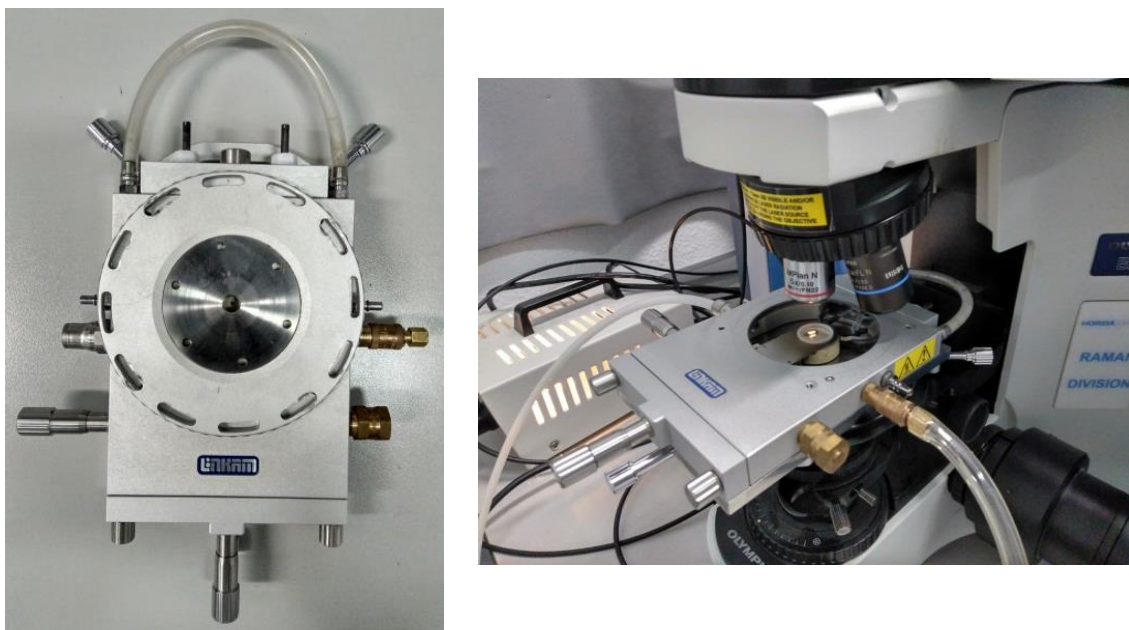


Figure 3.14. Frontal view of the Linkam stage with the lid assembly closed (left) and final look of the stage coupled to the BX41 microscope of the Raman instrument (right).

In order to perform the *in-situ* experiments, a number of extra features have been used as a way to ensure the correct design of the final set-up:

- Temperature controller T95-LinkPad (Figure 3.15).
- Water cooling system EHEIM professionnel 3 (Figure 3.16).
- Zirconia oxygen sensor EOS-1 provided by Innovative Technology (Figure 3.17).
- Gas flowmeter supplied by TecFluid (Figure 3.18).

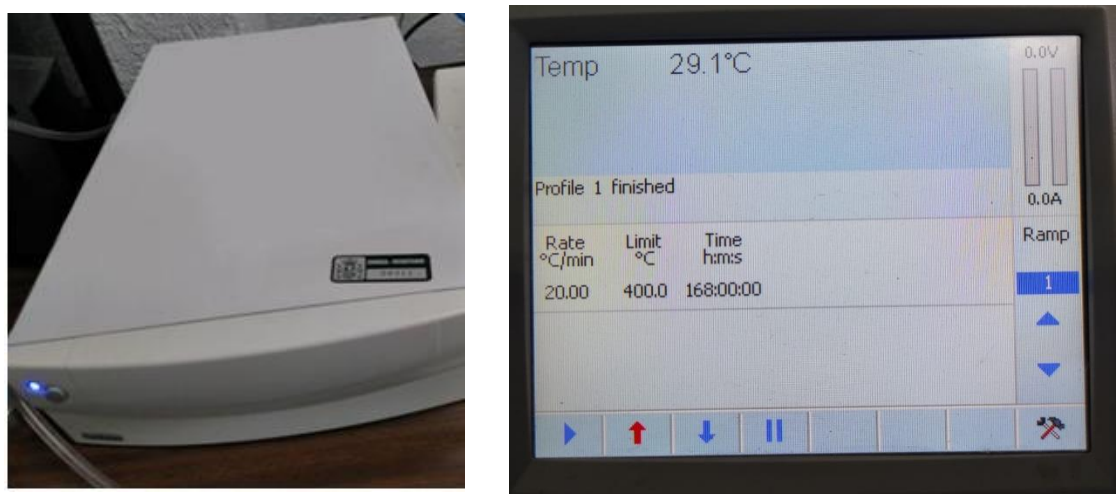


Figure 3.15. Temperature controller coupled to the Linkam stage (left) and associated temperature display (right).



Figure 3.16. Side view (left) and top view (right) of the water cooling system.



Figure 3.17. Zirconia oxygen sensor and associated instrument, where the oxygen concentration (in ppm) is displayed.

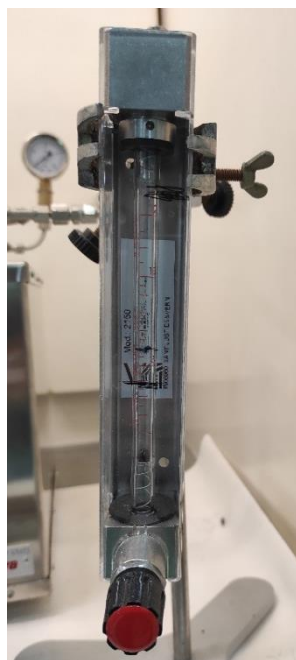


Figure 3.18. Flowmeter used to control the gas flow reaching the sample.

By setting all these devices together, a complete experimental set-up to perform the *in-situ* measurements has been built. In order to get the most accurate Raman signal of the oxidation of the UO_2 materials over the entire experiment at the different conditions, an optimised protocol has been obtained. This is summarised step by step in Table 3.II.

Table 3.II. Optimised protocol for *in-situ* Raman oxidation experiments at CIEMAT.

Step	Temperature	Atmosphere	Description
Initial	RT	-	Place the sample and close the lid assembly. Determine the measurement conditions (acquisition time and accumulations)
Inertisation	RT	Inert	Overnight low flow of Ar gas in order to remove oxygen
Heating	RT $\rightarrow$ T_{exp}	Inert	$10^\circ\text{C}\cdot\text{min}^{-1}$ up to T_{exp} (experimental temperature) still with the Ar atmosphere (to prevent early oxidation)
Stabilisation	T_{exp}	Inert	10 minutes of isotherm at the experiment temperature with Ar
Gas change	T_{exp}	Inert $\rightarrow$ Oxidant	Ar is replaced by the desired atmosphere (0.1-21% O_2), the reaction begins
Oxidation	T_{exp}	Oxidant	Spectra acquisition during the isothermal reaction
Gas change	T_{exp}	Oxidant $\rightarrow$ Inert	When the oxidation reaction is finished, Ar is set again to prevent further change
Cooling	$T_{\text{exp}} \rightarrow \text{RT}$	Inert	Decrease of temperature under inert conditions to prevent further oxidation

This optimised protocol has been systematically applied in the study of the oxidation of the UO_2 powdered surrogates, as shown in section 4.2.

3.4.2.2. Raman-Linkam at JRC

The previously described know-how on the use of Raman spectroscopy coupled to a Linkam stage for studying nuclear fuel oxidation at CIEMAT, has been exported to the facilities at JRC, where a research stay performed during the development of this PhD thesis has made it possible to apply it to the analysis of real irradiated nuclear fuel.

For doing so, at the hot cell laboratory described before (section 3.3.3), there is a Renishaw inVia Raman microscope spectrometer, equipped with a 785 nm laser. The main instrument is placed outside the hot cell, being the laser conducted to the microscope through an optic fiber that enters into the cell and reaches a nuclearised optical microscope. For the measurements, a 50x objective developed by Leica was used. The scattered radiation was collected and dispersed through an 1800 grooves per mm grating, obtaining a spectral resolution better than 1 cm^{-1} per pixel. The instrument is daily re-calibrated with a Si standard and using its emission line at 520 cm^{-1} .

In this case, also a Linkam THMS600 temperature-controlled stage was used to perform the *in-situ* measurements on SNF, but making some modifications in order to be handled with the telemanipulators inside the hot cell. The optimisation of this device has included a number of tests for checking the absence of gaseous leakages, resistance of the glass window, movement of the sample holder, etc., as previously done at CIEMAT facilities. In the same way, the gas flow during the experiment was controlled, in this case by means of a Sho-Rate flow meter (Figure 3.19). In addition, temperature was monitored by a T96-6 temperature controller, which provides temperature stability better than 0.05°C . Cooling of the system was provided by the ventilation infrastructure available inside the hot cell.

Given the particular characteristics of the samples at JRC (spent fuel) and the technical features of the hot cells, in particular the gas supply, the protocol had to be slightly modified to adapt it to the targeted experiments. It is shown in Table 3.III.

3.4. Optimised Protocols for Studying SNF Matrix Oxidation

Table 3.III. Optimised protocol for *in-situ* Raman oxidation experiments at JRC.

Step	Temperature	Atmosphere	Description
Initial	RT	-	Place the sample and close the lid assembly. Determine the measurement conditions (acquisition time and accumulations)
Heating	RT $\rightarrow$ T _{exp}	Air	50°C·min ⁻¹ up to T _{exp}
Oxidation	T _{exp}	Air	Spectra acquisition during the isothermal reaction
Cooling	T _{exp} $\rightarrow$ RT	Air	Decrease of temperature and sample removal and storage



Figure 3.19. Sho-Rate flow meter used to control the gas flow during the oxidation experiments at JRC.

The successful application of this optimised protocol to spent nuclear fuel samples has allowed attaining the results shown in section 4.6.

3.5. References

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Chapter IV

Results

Result 1

Looking for a realistically conservative UO₂ surrogate

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4. RESULTS

4.1. Result 1. Looking for a realistically conservative UO_2 surrogate

Abstract

The rate and extent of the air oxidation of UO_2 are of paramount importance due to its relevance in the management of spent nuclear fuel at dry storage facilities. In particular, the formation of U_3O_8 requires special interest because it could compromise the integrity of the fuel cladding. In an attempt to reproduce the behaviour of used fuel (in which the presence of fission products and Pu will also influence the oxidation), unirradiated UO_2 was studied in this work. UO_2 oxidation is strongly dependent on physical parameters of the starting material, although some parameters are not fully-studied. In the present study, the nature of the UO_2 starting material and the particle size distribution on thermal oxidation temperature were evaluated in detail. Since UO_2 oxidation follows a complex kinetic mechanism comprising various crystalline phases, which composition and quantity change influenced by temperature and oxidant gas phase, oxidation conditions were set to favour the formation of U_3O_8 , due to its practical importance, as well as to study the impact of the physicochemical properties of raw material in UO_2 oxidation. Various powdered sample substrates ranging from synthetic UO_2 (prepared via ADU route) to grinded and sieved fragments of fresh UO_2 pellets were oxidised in the same conditions. The average O/U atomic ratios of the samples were calculated by assuming total conversion to U_3O_8 from data of thermogravimetric analysis (TGA). Each weight variation curve was characterised and discussed in terms of the Oxidation Onset Temperature (OOT), the Maximum Reaction Temperature (MRT), and the Reaction Rate at the maximum reaction temperature (RR_{MRT}). Scanning Electron Microscopy (SEM) was employed to evaluate the surface morphology. All thermally oxidised samples exhibit the presence of oxides with spallation. Surface morphology of starting materials confirms the different nature of the samples, while the oxidised substrates present the typical pop-corn-like particles. In order to accomplish a better description of UO_2 oxidation, the results are discussed relative to the nature of different UO_2 precursors, surface area and particle size. The nature of the starting materials affects the rate of U_3O_8 formation, being faster in synthetic powders than in powder coming from milled pellets. By comparing materials with the same origin, the effect of the width of the particle size distribution is proved for the first time, being the

oxidation to U₃O₈ slower in the substrate with a wider distribution (labelled material P3). Since P3 is more similar to a real irradiated fuel pellet, from a mechanistic point of view, this work present valuable input to security studies of dry storage facilities for spent fuel.

Keywords

Air oxidation; uranium dioxide; thermogravimetric analysis; particle size distribution; nuclear fuel.

4.1.1. Introduction

It is internationally agreed that the safest solution for a definitive disposal of Spent Nuclear Fuel (SNF) is the Deep Geological Repository, including both open and closed nuclear fuel-cycles [1, 2]. Currently, while these facilities are licensed, built and commissioned in more countries, the scenario points to an interim dry storage of the fuel, in the so-called Centralised Storage Facilities (CSFs), where SNF is transported after an appropriate time cooling down in pools following the discharge of the reactor to allow temperature and radioactivity decrease [3, 4].

These facilities are subjected to strict controls and regulation, in order to ensure safety of both the public and the environment [5-7]. Various physicochemical processes may occur during dry storage (and previous handling in fuel unloading/loading cells or transportation operations), such as self-radiation damage, He build-up (due to α -decay from the actinides) or degradation/failure of the cladding that could dramatically put the UO₂ in contact with an oxidant reagent [8, 9]. Those processes are temperature dependent and lead to volume expansion of the UO₂ structure, besides the own strain from pressure due to volatile fission products accumulation in the crystal structure [10].

Generally, the oxidation of UO₂ into U₃O₈ is described as a two-step reaction UO₂ (cub.)→U₄O₉(cub.)/U₃O₇ (tetrag.)→U₃O₈ (orth.) [11, 12]. Nevertheless, in the last years there have been significant advances in the understanding of the phases involved in the reaction, as well as to better define the effect of the parameters involved in the oxidation. The current consensus is that the reaction occurs following the sequence UO₂→U₄O₉→U₃O₇→U₃O₈. The existence of these four domains was proposed by Rousseau *et al.* [8], who oxidised UO₂ powder with grain sizes ranging from 2 to 10 μ m at 250°C in air by using *in-situ* synchrotron X-ray diffraction. From their study, the first

domain would correspond to the formation of UO_2 to U_4O_9 ; the second one would involve two simultaneous reactions, *i.e.* $\text{UO}_2 \rightarrow \text{U}_4\text{O}_9$ and $\text{U}_4\text{O}_9 \rightarrow \text{U}_3\text{O}_7$ (which would explain the plateau found in most of the TGA experiments with unirradiated UO_2); and the third and the fourth would be related to the transformation of U_3O_7 into U_3O_8 . Similar findings were reported by Leinders *et al.* [13], who used very fine UO_2 powders (<200 nm) to study the low-temperature (40-250°C) oxidation by means of XRD, HR-TEM and TGA. This fine UO_2 was found to oxidise differently from coarse-grained UO_2 , as below this temperature U_3O_8 seemed to be inhibited, appearing amorphous UO_3 instead [13]. All in all, it appears to be coexistence between the U_4O_9 and U_3O_7 phases, being the former the first to be formed from UO_2 and the latter the precursor of U_3O_8 . In this regard, Quémard *et al.* [14] gave evidence about the formation of U_3O_7 as a layer covering the UO_2 substrate, which after reaching a critical thickness, would begin to crack; starting nucleation and growth of U_3O_8 at this point. The formation and extent of this layer is temperature and particle size dependent; in fact, it is not observed for nanometric powders. This observation was also reported by Leinders *et al.* [13].

In any case, U_3O_8 is consensually associated with the final oxidised phase of the U-O system in absence of moisture or at ambient pressure, as the most thermodynamically stable product of UO_2 oxidation formed in dry air [15]. Formation of U_3O_8 could lead to particle breakdown and pulverization [16], which in the case of a defective fuel cladding may produce the release of radioactive material. In the event of an accident, such as a cladding breach, the fuel may be exposed to an oxidising atmosphere and, together with an eventual high temperature coming from decay heat of the fuel itself, may lead to the oxidation of the SNF matrix (UO_2 for most of current Light Water Reactors, LWR) up to U_3O_8 , a phase which comes along with a volume increase of about 36% [11]. Thus, the knowledge of the kinetics that follows the reaction is of paramount importance in terms of nuclear safety. Unlike unirradiated UO_2 , the oxidation reaction of UO_2 to form U_3O_8 in the SNF matrix with low-medium burnup (in the range 20-50 MWd/kg U), is described as a two-step process with one intermediate phase, as follows: UO_2 (cub.) $\rightarrow$ U_4O_9 (cub.) $\rightarrow$ U_3O_8 (orth.) [17, 18]. At high temperature, the increase of the oxygen content in the UO_2 structure provoke the formation of the non-stoichiometric UO_{2+x} phase, which preserves the fluorite cubic structure up to $x=0.25$ [11]. At low temperatures, it seems that the extent of the UO_{2+x} phase is very limited; for example Smith *et al.* [19] reported that the limit of this non-stoichiometric phase would be

$x=0.04-0.07$ at room temperature, from which UO_2 and U_4O_9 would coexist [20]. For this reason, the UO_2 oxidations carried out in these conditions (as performed in this work) can be followed by calculating the O/U ratio, but has to be taken into account that this ratio represents a weighted average of the present uranium oxide phases. In any case, when UO_2 starts oxidising, the phase U_4O_9 is formed. This phase is characterised by a fluorite-related structure, in which the excess of oxygen anions is defined by the occurrence of oxygen clusters. This makes the global structure of U_4O_9 to remain cubic, but with several positions differing from the original fluorite structure. In fact, the real stoichiometry of U_4O_9 was calculated and reported as $\text{U}_{256}\text{O}_{572}$ [21], but for the sake of simplicity, usually this domain is referred as “ U_4O_9 ” or even “ U_4O_{9-y} ” [13, 22, 23]. Finally, higher oxygen content causes more structure distortions and yields the orthorhombic structure of U_3O_8 [8, 15, 16]. The extreme difficulty to handle SNF due to the large operational requirements and the limited access to this material to only a few laboratories around the world, has made common to find in literature experiments with surrogate materials, which are easier to handle and are assumed to reproduce the SNF behaviour. The most commonly used analogue of spent fuel is unirradiated UO_2 as the greatest part of the fuel currently used in nuclear power plants is based on an UO_2 matrix. Nuclear fuel of LWRs is in the form of UO_2 pellets that are typically ~ 1 cm in diameter and 1 cm long, with ~ 10 μm average grain size [24]. The oxidation of UO_2 has been extensively studied through the years [12, 13, 17, 25-28], and although it is not fully-understood, its mechanism is different according to its physical properties (besides the common features temperature and exposition time):

- The oxidation of powdered UO_2 follows a mechanism dependent on temperature, time and microstructure of the material, giving place to several domains, as previous mentioned. For simplicity, it is commonly said that the intermediate phases $\text{U}_4\text{O}_9/\text{U}_3\text{O}_7$ are obtained in a parabolic kinetics (at temperatures higher than 100°C), typical of diffusion reactions [11]. After that, and if temperature is high enough, the reaction proceeds up to U_3O_8 following a “nucleation-and-growth” mechanism, with a sigmoid with plateau curve shape behaviour [8, 11, 29].
- The oxidation of sintered UO_2 pellets presents some differences. The oxygen diffuses along grain boundaries to form the intermediate oxides, which are denser than UO_2 [4]. This densification may induce cracking that exposes fresh

UO_2 to the oxidant, accelerating the reaction. This finally leads to spallation of U_3O_8 from the grain surfaces. In this case, both steps occur simultaneously with coexistence of UO_{2+x} , $\text{U}_4\text{O}_9/\text{U}_3\text{O}_7$ and U_3O_8 in a diffusion-controlled mechanism, and as a consequence the two-step curve is not obtained. In addition, temperatures to obtain U_3O_8 in pellets are usually higher than in powders [29].

As discussed, the physical features (and likely the production method) of the materials impacts the transformation of UO_2 to U_3O_8 . Clayton and Aronson [30] published an extensive report showing the relationship between the preparation mode and the physical properties of UO_2 powders. They found some interesting conclusions, for example that the surface area of the obtained UO_2 would depend on the surface area of the precursor and confirm the dependence of UO_2 physical properties upon their preparation method. In that study, one of the materials was prepared from precipitated ammonium diuranate, and the UO_2 prepared in this mode showed the highest surface area.

Particle size distribution (PSD) is other variable affecting the UO_2 oxidation that should be taken in consideration. As a general rule, it has been reported that smaller particles react more rapidly than larger particles [11, 13]. Previous oxidation studies have shown that, in general, very fine UO_2 powders (*i.e.* higher Specific Surface Area, SSA) will oxidise faster, even at very low temperatures, than those with a higher size [11, 31]. For example, the studies by Anderson *et al.* [26] described the pyrophoric reaction between oxygen and very fine UO_2 particles (size lower than $0.05\ \mu\text{m}$). In a similar way, Hoekstra *et al.* [32] obtained an enhanced oxidation with fine powders at room temperature. Both studies related these particle sizes with very high specific surface areas. In an attempt to improve the knowledge on the effect of particle size in fresh fuel oxidation, Quémard *et al.* [14] oxidised sieved powders ($10\ \mu\text{m}$, $5\ \mu\text{m}$ and $100\text{-}200\ \text{nm}$). They found that the effect of small particle sizes is more accentuated in the first step of the oxidation, but is contrary on the U_3O_8 formation. Nevertheless, to the best of our knowledge, no studies related to the impact of the PSD have been published up to date. This detailed study could be important in current conditions of nuclear power plants operation, *i.e.* increasing the burnup as a way to extend the fuel performance and duration in the reactor. A consequence of this increased burnup is the apparition of the so-called “rim” structure or High Burnup Structure (HBS) [33-36] at the periphery of

fuel pellets, which consists of the restructuration of the outermost region of the fuel pellet due to the enrichment of Pu in the area, and it is characterised by the subdivision of grains, cracking, and a higher porosity. This new structure makes that an irradiated fuel pellet presents a variety of grain sizes, ranging from the initial 10 μm (UO₂-based fuels) in the centre of the pellet to 0.1-0.3 μm in the new structure at the rim [24]. In this context, it is worthy to cite the recent study on the isothermal oxidation (300°C, air) of UO₂ fragments with various grain sizes (3.08, 0.478 and 0.163 μm , labelled as micro, sub-micro and nano-sized, respectively) by De Bona *et al.* [37]. They followed the oxidation by *in-situ* high-temperature synchrotron XRD and XANES. Important insights with respect to the extent of oxidation as function of grain size were made. The samples with larger grains (micro and sub- μ grain sizes) followed the same behaviour, being almost fully oxidised to U₃O₈ after about 11h of oxidative treatment. On the contrary, no U₃O₈ was detected in the nano sample. This would mean that an effectively fine microstructure (below 0.4 μm) in dense UO₂ hinders both the cracks appearance of U₃O₇ and the subsequent U₃O₈ formation. These findings prove the involvement of the microstructure in the oxidation kinetics and the development of the different uranium oxide phases, especially when considering the HBS peripheral region of SNF (characterised by 100–300 nm-sized grains, then on the order of magnitude of the nano sample), preventing the volumetric expansion of UO₂. Characterising the impact of fuel matrix with a wide PSD on the oxidation becomes important to obtain experimental data on UO₂ oxidation at different grain sizes representative of the various size distribution found in irradiated fuel, and to come up to the real situation in the case of an air intrusion.

In the present work, the oxidation of UO₂ up to U₃O₈ is addressed from a different approach. An attempt to identify and describe the morphology effects is proposed in order to study the combined impact of the physical form of the material and its PSD to adapt the extensive knowledge of this reaction to the current nuclear fuel operation. The aim is thus to obtain a representative material that, maintaining a conservative criteria against used fuel (where fission products and other elements should be taken into account), behaves in a possibly more realistic scenario. This study not only presents new data and protocols on the oxidation of UO₂, it could be also important to the fabrication methods to obtain UO₂, in particular in the calcination in air of recycled UO₂, one of the main process to manufacture nuclear fuel [29, 38, 39].

Thereby, the work is structured as follows: in Section 4.1.2, the manufacture of each material is described in detail, as they will be the studied samples. Analytical techniques employees are also described. In Section 4.1.3, the characterisation of the materials is presented, and the impact of each parameter in the oxidation is explained. Also in this section, the complete oxidation of the materials up to U_3O_8 is presented and described, in terms of both the weight gain curves and kinetic data obtained. The comparison of effects that is presented in this paper is explained here. Finally, the conclusions of this work are presented in Section 4.1.4.

4.1.2. Materials and methods

4.1.2.1. UO_2 preparation

In this work, different UO_2 substrates have been prepared by several methods, taking into account the effects intended to be studied here (nature of the UO_2 precursor and PSD). With this aim, three different powdered UO_2 samples (labelled as P1, P2 and P3, see the explanation later on) have been prepared with similar mean particle size. For comparison purposes with the real case, a sintered pellet of fresh UO_2 has been cut into fragments for oxidation (labelled as F).

UO_2 via Ammonium Di-Uranate (ADU) (referred to as P1) was obtained following a precipitation process that involves several major steps. First of all, UO_2 is dissolved in highly concentrated HNO_3 , followed by filtration of the resultant solution to eliminate possible solid impurities. After that, purification of uranium is carried out by applying a selective solvent extraction process with tributyl phosphate (TBP), a compound widely used on an industrial scale [40, 41]. Once a pure uranium solution was obtained, it was precipitated by using NH_4OH (30 wt. %). The precipitated powder was then separated by using HA 0.45 μm (Millipore) filters, and identified as ADU [42, 43]. Finally, this powder was subjected to a thermal treatment for denitration/dehydrating, calcine and reduce it to its final form of UO_2 . The conditions of such a treatment are presented in the flowchart of Figure 4.1.1.

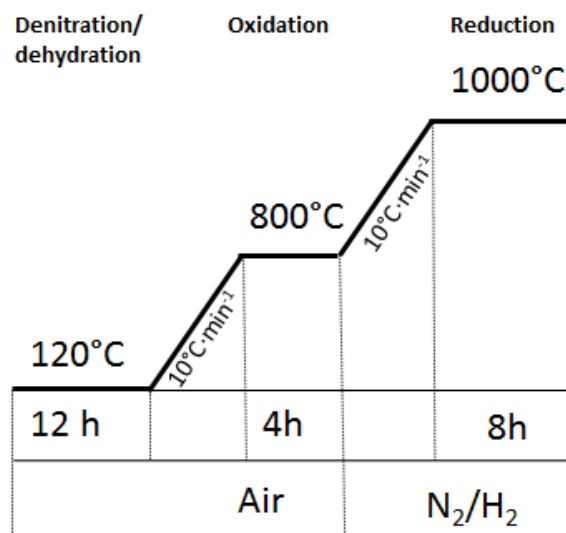


Figure 4.1.1. Thermal treatment cycle (temperature, ramp and atmosphere) applied to obtain the substrate P1.

UO_2 powdered samples P2 and P3 were obtained from monoliths of unirradiated sintered UO_2 pellets supplied by ENUSA that were crushed into powder in a Mixer Mill MM 400 (Retsch), using ZrO_2 milling jars. From this point, two different treatments were applied. Firstly, a portion of this powder was milled (2 minutes, 30 Hz) and sieved to get a particle size ranging from 100 to 315 μm . After that, the sieved fraction was milled again (5 minutes, 30 Hz) to obtain a homogeneous distribution of the particle size lower than 5 μm . This gave as a result the labelled material P2. Secondly, the other fraction coming from the crushed pellets was milled directly (7 minutes at 30 Hz), *i.e.* no sieving applied, to the desired particle size range. As a result, a broader PSD was obtained on P3 than in the previous case.

Finally, for the sake of comparison, a dense sintered pellet of UO_2 was prepared for TGA analysis by cutting it into fragments, representative of a sintered material, using a low-speed diamond saw (Micromet M, Remet; Bologna, Italy). The obtained sample is labelled as “F” in the results section.

4.1.2.2. Characterisation

4.1.2.2.1. Raman spectroscopy

Raman spectra of samples were acquired by means of a Horiba LabRAM HR Evolution spectrometer (Jobin Yvon Technology). A He-Ne laser ($\lambda=633\text{ nm}$) was focused onto

the samples through an Olympus BX41 microscope, using a 50x objective which led to a spot diameter of around 1 μm . The scattered radiation was collected in back-scattering geometry, dispersed through a 600 grooves per mm grating and recorded by a CCD detector, obtaining a spectral resolution better than 2 cm^{-1} . Spectra were acquired during 300 seconds and 3 accumulations in the range 200-1250 cm^{-1} , where the Raman features of UO_2 appear [44]. Acquired spectra were recalibrated by using the emission lines of a Ne arc-lamp. In order to ensure the homogeneity of the samples, 10 spectra were acquired at different locations for each sample under the same acquisition conditions.

4.1.2.2.2. Physical properties

The PSD of the powdered materials was measured by using the laser diffraction technique. With this purpose a Malvern, Series 2600 instrument was used. In the measurement, the powdered particles were suspended in a dispersant liquid (Na_3PO_4 , 10%) in order to avoid the agglomerated particles. The suspension was left to fill the instrument lens, through which a He-Ne laser ($\lambda=633 \text{ nm}$) was diffracted. Scattered radiation was collected by the detector in the angle range 0.015 to 144°. Several parameters have been chosen to properly describe PSD. The median volume diameter $D(v,0.5)$ is commonly used. In this work, and in order to have a better understanding of PSDs of the different oxides, $D(v,0.5)$ is shown together with the SPAN, as a measurement of the “width” of the distribution. It is defined according to the expression:

$$\text{SPAN} = \frac{D(v, 0.9) - D(v, 0.1)}{D(v, 0.5)}$$

Where $D(v,0.9)$ and $D(v,0.1)$ are the sizes corresponding to percentile 90th and 10th, respectively; and $D(v,0.5)$ the value corresponding to percentile 50th, *i.e.* the median.

Specific Surface Area (SSA) of the samples was measured following the Brunauer–Emmett–Teller (BET) method [45] by using nitrogen adsorption/desorption tests at 77K in a Micromeritics ASAP 2020 instrument.

4.1.2.2.3. Morphology

Sample surface morphology has been studied by means of a SEM microscope TM4000 Plus SEM by HITACHI, using an accelerating voltage of 15 kV. The microscope is

equipped with a Back-Scattering Electrons (BSE) detector. The photographs have been acquired with an optimised magnification of $\times 2.0\text{k}$, which has proved to be good enough to observe the powder morphology with the particle size of study. In addition, SEM micrographs of the UO_2 pellets have allowed us to estimate the grain size of the fragments by applying the linear intercept method [46].

4.1.2.3. Oxidation experiments

In order to study the oxidation behaviour of the prepared materials, TGA was carried out by using a TGA Q50 thermobalance (TA Instruments) under a synthetic air flow at a constant rate of $60 \text{ mL} \cdot \text{min}^{-1}$. In addition, a pure nitrogen flow at a rate of $40 \text{ mL} \cdot \text{min}^{-1}$ was used as a balance purge gas. The TGA calibration was performed in both, temperature of magnetic standards (Curie point, ASTM E-1582) with Alumel and Ni standards (153 and 358°C , respectively), and weight (200 mg to 1 g calibration weight range). Oxidations were conducted by heating the samples in an open platinum crucible from room temperature up to 700°C with a linear rate of $10^\circ\text{C} \cdot \text{min}^{-1}$, to obtain the complete conversion to U_3O_8 and study the overall reaction. Thermogravimetric curves have been analysed by using the software Universal Analysis, by TA Instrument. The average O/U atomic ratios of the samples have been calculated by assuming total conversion to U_3O_8 . This assumption has been checked measuring the oxidised samples by Raman spectroscopy (data not shown), and this procedure has been previously applied in our laboratory [47]. The exhaustive characterisation of the weight gain curves is based on the following parameters:

- Δm (%): Weight variation of each substrate, in percentage, divided into steps 1 and 2 of the oxidation, as previously described.
- Average $\text{O/U}_{\text{plateau}}$: Derived O/U ratio at the end of the first step of the oxidation, calculated from the theoretical mass gains associated to the transitions $\text{UO}_2 \rightarrow \text{U}_4\text{O}_9$ (mass gain 1.48%); $\text{UO}_2 \rightarrow \text{U}_3\text{O}_7$ (mass gain 1.98%); and $\text{UO}_2 \rightarrow \text{U}_3\text{O}_8$ (mass gain 3.95%).
- OOT ($^\circ\text{C}$): Oxidation Onset Temperature. It is defined as the extrapolated beginning point of a determined transition, obtained from data analysis. Here, it is defined as the temperature at which 5% of the weight change at each transition is reached [48].

- MRT (°C): Maximum Reaction Temperature. It is defined as the temperature at which the maximum rate of weight gain as each step is reached. It is obtained from the first derivative of the weight change curve.
- RR_{MRT} (%·min⁻¹): Reaction Rate at the Maximum Reaction Temperature.
- Total weight change (%): The sum of Δm of each oxidation step.
- Average O/U₀: Initial O/U ratio of the substrates, calculated from weight change data assuming total conversion to U₃O₈.

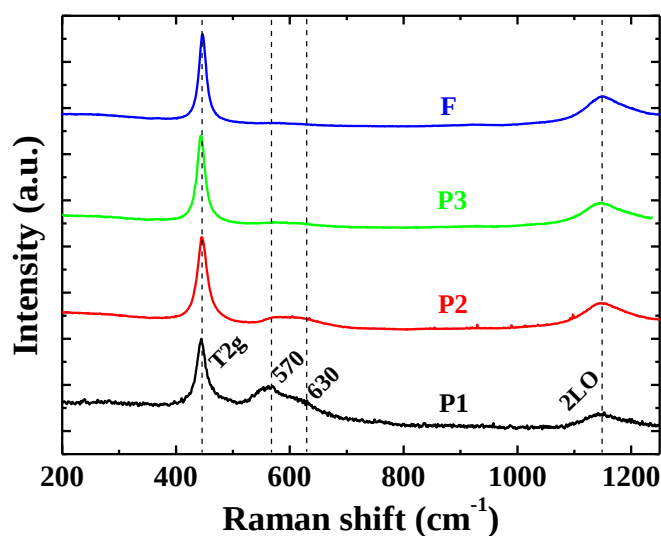
Differential Scanning Calorimetry (DSC) was performed using a Q20 system (TA Instruments). The DSC calibration was performed using the melting point reference temperature and enthalpy reference of a pure Indium standard (28.45 J·g⁻¹; T_m = 156.6°C). The oxidation procedure was analogous to the one followed in TGA in an open platinum crucible, *i.e.* heating the samples at 10°C·min⁻¹ up to 700°C with an air flow of 50 ml·min⁻¹. The enthalpy of the oxidation for each material in J·g⁻¹ was calculated by integration of the DSC signal peak area, taking a linear baseline (with an estimated uncertainty of about 2%).

4.1.3. Results and discussion

4.1.3.1. Characterisation

4.1.3.1.1. Pre-oxidation of the substrates

Raman spectroscopy was used to determine the initial stoichiometry of the samples, that could have an impact on their oxidation behaviour [47], as well as to check the phase purity and homogeneity of the materials. Previous studies have confirmed the suitability of this technique to characterise uranium compounds [44, 49-51], in particular to quantify the oxidation degree of UO_{2+x} solid-solutions [47]. Raman spectra of the materials, represented by the sum of 10 spectra acquired at different points of the samples, are shown in Figure 4.1.2.

Figure 4.1.2. Raman spectra of raw UO_2 materials.

It can be noticed that in Figure 4.1.2, characteristic Raman features of UO_2 are obtained in all cases. These bands have been described elsewhere [47] and correspond to: T_{2g} mode at 445 cm^{-1} , assigned to the stretching of the U-O bond; the LO phonon centred at 570 cm^{-1} ; a band at 630 cm^{-1} indicating the presence of hyperstoichiometric UO_{2+x} species [52]; and finally the 2LO phonon at 1140 cm^{-1} . From Figure 4.1.2, the presence of the band at 630 cm^{-1} , clearly in P1 and slightly in P2, might thus indicate a minor surface pre-oxidation of the two first materials, being more evident in the case of P1. Quantitatively, this tendency is confirmed by using the second derivative method and the equation proposed by Elorrieta *et al.* [47] for the position of the 630 cm^{-1} band. Thus, the oxidation degree of such average solid solutions of the form UO_{2+x} would roughly correspond to $x = 0.09 \pm 0.01$ for P1; 0.04 ± 0.01 for P2; and 0.002 ± 0.001 for both P3 and F.

4.1.3.1.2. Physical properties

The main parameters affecting UO_2 oxidation [11] of the as-prepared materials were characterised by BET area (SSA) and Laser Diffraction (PSD). The results are presented in Table 4.1.I.

Table 4.1.I. Physical properties of the as-prepared materials, including SSA and parameters related to the PSD.

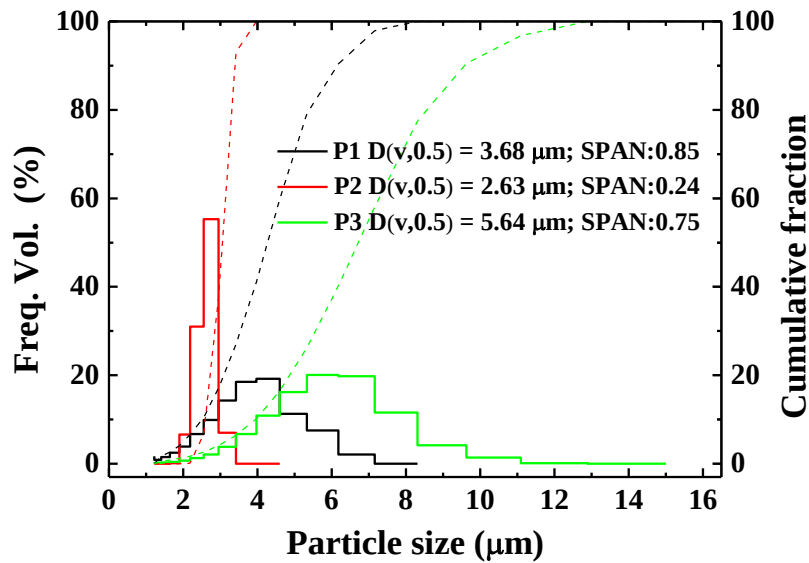
Material	P1	P2	P3	F
SSA (BET) ($\text{m}^2 \cdot \text{g}^{-1}$)	4.67±0.04	0.87±0.02	0.18±0.01	0.12±0.01
Particle size D(v,0.5) (μm)	3.68±0.06	2.63±0.01	5.64±0.07	6.55±1.03*
Particle size D(v,0.1) (μm)	2.16±0.04	2.27±0.01	3.51±0.04	-
Particle size D(v,0.9) (μm)	5.30±0.07	2.90±0.01	7.73±0.08	-
SPAN (μm)	0.85±0.01	0.24±0.01	0.75±0.02	-

*Average grain size value

Table 4.1.I data show different nature of the UO_2 materials studied. This can be seen in SSA data. In particular, the highest P1 value compared with those from P2, P3 and the pellet fragment, reveal the sintering effects of the latter materials, showing their likeness with a real fuel pellet [53]. Regarding powdered materials coming from sintered pellets, SSA values of P2 and P3 are in the same order of magnitude of those reported by Forsyth for SNF with the same particle size (*e.g.* $0.2770 \text{ m}^2 \cdot \text{g}^{-1}$) [54].

One of the key parameters showed in Table 4.1.I is the mean particle size of the powdered material. This factor is of special relevance in the study of the UO_2 oxidation [11, 13, 55], because of the oxidation mechanism itself. Since, at high temperature, the formation of the first oxidation product is a diffusion-controlled process [12, 56-61], it is expected that starting materials with lower particle size will react faster than those with a higher size [31].

Figure 4.1.3 shows the PSDs obtained in this work. The results allow comparing the materials in terms of the width of this distribution, as all the values are of the same order of magnitude. This broad range has been selected trying to simulate an average behaviour of a highly-irradiated fuel pellet, where the grain size ranges from the typical $10 \mu\text{m}$ value from UO_2 fuel to the reduction to tenths of microns in the rim zone [62], appeared as a consequence of the tend to increase burnup in current reactors [63, 64].

Figure 4.1.3. PSD of the powdered UO_2 materials.

4.1.3.1.3. Morphology

Finally, the studied materials have also been characterised by SEM to study their initial morphology. Figure 4.1.4 shows a representative image from each material. For the sake of comparison, the photographs corresponding to powdered materials are shown with the same magnification. Figure 4.1.4a, corresponding to P1, shows that the morphology of this UO_2 corresponds to small, dendritically shaped crystallites arranged in larger agglomerates. The PSD values measured will likely relate to the agglomerate size whereas the crystallite size could be smaller. On the contrary, Figure 4.1.4b and c, corresponding to P2 and P3, respectively, shows heterogeneous-sized coarse particles, with a sharper shape, as they correspond to a range of fractured grains of the original sintered pellet. The observed PSD values relate to the grain sizes, which correspond to the crystallite sizes. The very fine material (less than 1 %) in the region of 1-2 μm , is dust attached to the larger particles in P3. In addition, it is remarkable the lack of interconnection regions between adjacent particles or grain boundaries after pellet milling. Lastly, a photograph of the sintered surface of a pellet fragment is shown in Figure 4.1.4d, where individual grains of pellets can be distinguished. From this kind of pictures, the average grain size of the pellet by the linear intercept method was calculated, leading to the value of $6.55 \pm 1.03 \mu\text{m}$ presented in Table 4.1.I.

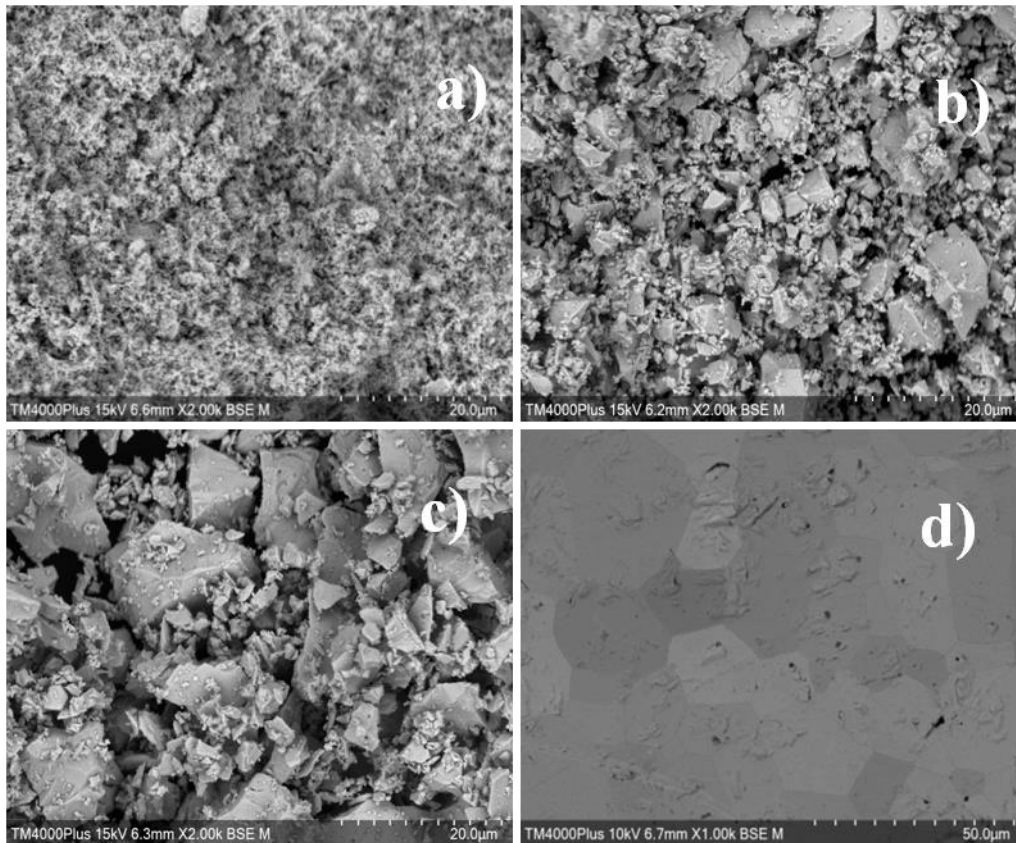


Figure 4.1.4. Representative SEM images and particle/grain size of each material: a) P1; b) P2; c) P3; d) Pellet fragment (F).

4.1.3.2. Oxidation behaviour

As already discussed in the introductory part of this paper, the aim of this work is the examination of singular oxidation behaviour as a function of different kinds of fresh UO_2 systems, useable for single effect studies representing the microstructure of a real irradiated fuel. As a result of this first part of the paper, we have obtained and characterised in detail different UO_2 materials that allow studying the oxidation of fresh fuel as a comparison of effects, as discussed below:

- On the one hand, the effect of the material nature on UO_2 oxidation can be studied comparing purified (*i.e.* breaking the stress that produced a "memory effect" of the sintered material) powders and sintered (*i.e.* "tensioned") crushed powders. It is known that sintered materials oxidise slower than those which do not have these tensions in their structure [29], because the tridimensional packaging of the structure results in a less material surface exposed to the oxidant atmosphere. Sometimes this assumption has been used as a conservative

criterion to justify the use of purified powders, although the difference with a real fuel pellet may be so high that the oxidation behaviour in real fuel may be distorted [32, 65]. In order to study this effect, and eliminating the effect of the particle size (*i.e.* surface area), the behaviour of the oxidation of P1 and P3, with a similar PSD, will be studied and compared.

- The effect of particle size itself, on the other hand, plays an important role on the oxidation of UO_2 . This effect has been investigated by comparing the oxidation mechanism of different sized materials [13, 14, 31] performed over the same temperature range and under the same oxidation conditions (*i.e.* dry-air flow). It was found that the first oxidation step, which involves the reactions observed during the first two domains of the reaction (*i.e.* $\text{UO}_2 \rightarrow \text{U}_4\text{O}_9$ and $\text{U}_4\text{O}_9 \rightarrow \text{U}_3\text{O}_7$), as a diffusion-controlled kinetics under our experimental conditions, will be faster with lower particle size, *i.e.*, higher exposed surface. On the contrary, the rate of the conversion $\text{U}_3\text{O}_7 \rightarrow \text{U}_3\text{O}_8$ (domains three and four of the reaction, for simplicity named as the second oxidation step) decreases with the particle size, due to spallation of U_3O_8 . Here, we compare the oxidation behaviour of similar-sized UO_2 , but with a different PSD (narrow vs wide) in P2 vs P3, respectively. The same origin of both materials (crushed and milled pellets) removes the impact of other effects.

Thus, with the aim to study the behaviour of the different materials prepared and characterised in the previous section, all of them have been subjected to oxidation in air, heating at $10^\circ\text{C}\cdot\text{min}^{-1}$ up to 700°C . These conditions have proved to be enough to oxidise the samples to the final state U_3O_8 .

Figure 4.1.5 shows the air oxidation curves of the different materials analysed in this work. All the powdered materials present the representative oxidation behaviour of pure uranium dioxide, *i.e.* the first step at temperatures in the range of $140\text{--}350^\circ\text{C}$; and the second step above 330°C . As previously mentioned, the overall reaction theoretical weight gain is 3.95% [11, 12, 26].

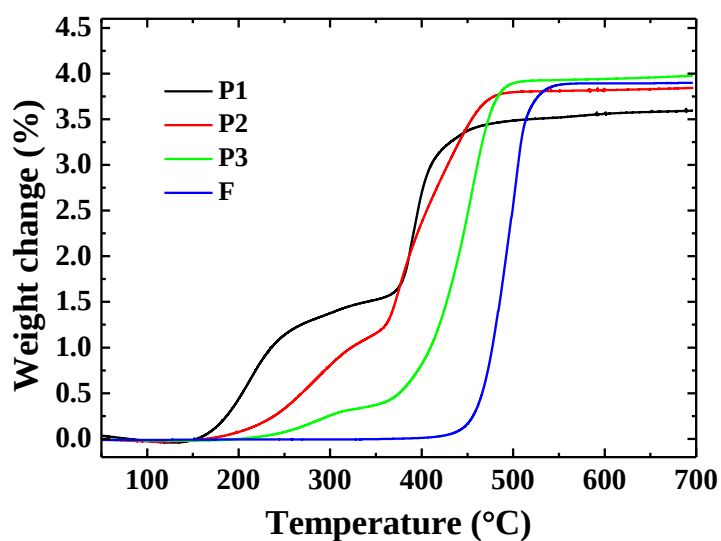


Figure 4.1.5. *In-situ* oxidation in air of the different UO_2 starting materials studied in this work: P1 ($\text{SSA}=4.7 \text{ m}^2\cdot\text{g}^{-1}$; $D(v,0.5)=3.7 \text{ }\mu\text{m}$), P2 ($\text{SSA}=0.9 \text{ m}^2\cdot\text{g}^{-1}$; $D(v,0.5)=2.2 \text{ }\mu\text{m}$), P3 ($\text{SSA}=0.2 \text{ m}^2\cdot\text{g}^{-1}$; $D(v,0.5)=5.6 \text{ }\mu\text{m}$), and F ($\text{SSA}=0.1 \text{ m}^2\cdot\text{g}^{-1}$; average grain size= $6.5 \text{ }\mu\text{m}$).

The shape of the curves shown in Figure 4.1.5 varies slightly depending on the nature and physical form of UO_2 and it provides important numerical data that, together with the graphical variation of the weight change, can help to understand the behaviour of each material. These data are presented in Table 4.1.II and Figure 4.1.6.

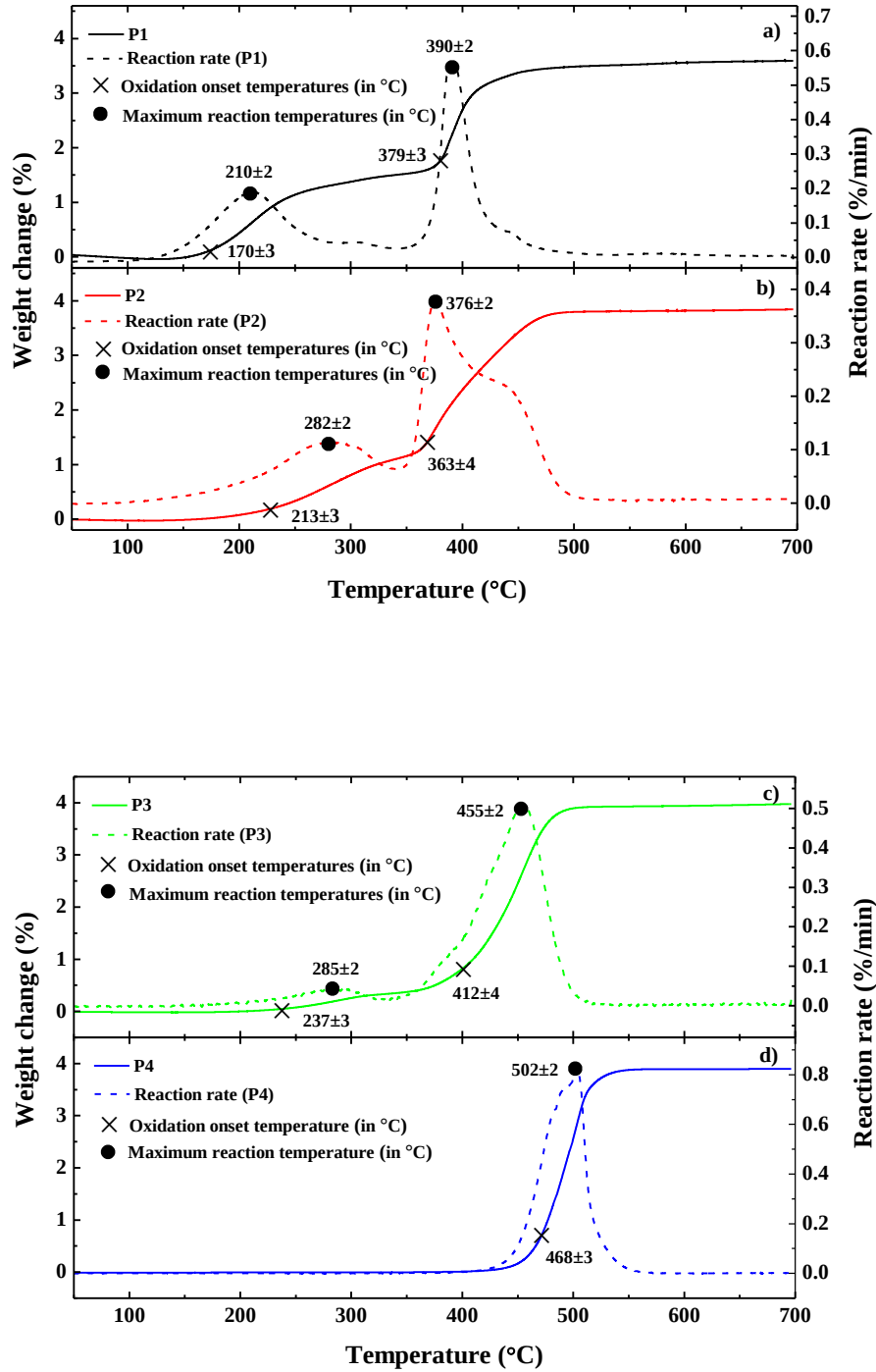


Figure 4.1.6. Weight changes curves (solid lines) and reaction rates (dashed lines) of a) P1 ($\text{SSA}=4.7 \text{ m}^2 \cdot \text{g}^{-1}$; $D(v,0.5)=3.7 \text{ }\mu\text{m}$), b) P2 ($\text{SSA}=0.9 \text{ m}^2 \cdot \text{g}^{-1}$; $D(v,0.5)=2.2 \text{ }\mu\text{m}$), c) P3 ($\text{SSA}=0.2 \text{ m}^2 \cdot \text{g}^{-1}$; $D(v,0.5)=5.6 \text{ }\mu\text{m}$) and d) F ($\text{SSA}=0.1 \text{ m}^2 \cdot \text{g}^{-1}$; average grain size= $6.5 \text{ }\mu\text{m}$). Oxidation onset temperatures and Maximum reaction temperatures are also displayed.

Table 4.1.II. Kinetic data for the oxidation of each material. Uncertainty for each parameter lies around 1%, taking into account the precision of the instrument in mass and temperature. See text for further details.

Material		P1	P2	P3	F
STEP 1	Δm (%)	1.52	1.12	0.38	-
	OOT (°C)	170	213	237	-
	MRT (°C)	210	282	285	-
	RR _{MRT} (%·min ⁻¹)	0.1742	0.1025	0.0407	-
	Average O/U _{plateau}	2.35	2.25	2.06	-
STEP 2	Δm (%)	2.01	2.65	3.56	3.95
	OOT (°C)	379	363	412	468
	MRT (°C)	390	376	455	502
	RR _{MRT} (%·min ⁻¹)	0.5342	0.3492	0.5084	0.8196
Total weight change (%)		3.53	3.77	3.94	3.95
Average O/U ₀		2.09	2.05	2.00	2.00

Figure 4.1.6 (a-d) represents the weight change curves in air up to 700°C, together with the first derivative curves for each material. OOT and MRT are also included. As can be seen in both Figure 4.1.5 and Figure 4.1.6, the three powdered materials (P1, P2, P3) show the same qualitative behaviour and the two aforementioned oxidation steps, behaving all of them in a similar way: a weight gain starts to be observed in the 150-200°C range, when samples begin to oxidise. Above this temperature, a plateau is reached at temperatures between 300-350°C, depending on the material. This plateau is associated with partial transformation of UO₂ into intermediate oxides U₄O₉/U₃O₇, with coexistence of the three phases [12]. Finally, oxidation continues with a second weight gain at the interval 350-450°C, until a stabilisation of the mass is reached, linked to the total conversion to U₃O₈ [12]. All of the powdered samples showed a nearly identical sigmoid profile of weight gain; however, the different “origin” of each material resulted in markedly different reaction rates of the first oxidation step, that occurs in the sequence P1 > P2 > P3 (0.1742, 0.1025 and 0.0407 %·min⁻¹, respectively, Table 4.1.II). This variation will now be discussed in detail, following the comparison of effects explained in the previous section. In the fragment from a sintered UO₂ pellet, one-step oxidation is noticed, typical of pure UO₂ in the form of pellets [66, 67].

To examine if the oxidation process of the UO₂ powers changed with its preparation procedure, we first compared data from P1 and P3. The effect of the pressed ceramics and sintering residual stress that remains in the material structure is seen in Figure 4.1.6c, where the P3 curve (green) is much more similar to the fragment (F) used as a reference (blue curve, Figure 4.1.6d) than the P1 weight gain (black curve, Figure

4.1.6a). With both materials prepared with a comparably broad PSD (Figure 4.1.3), the influence of the preparation mode, *i.e.* the specific surface area, is clear. In this instance, the thermal oxidation behaviour of P1, which presents a much higher surface area ($4.67 \pm 0.04 \text{ m}^2 \cdot \text{g}^{-1}$) compared to P3 ($0.18 \pm 0.01 \text{ m}^2 \cdot \text{g}^{-1}$), shows the fast kinetic of this kind of UO_2 . This effects is specially emphasised by Hoekstra *et al.*, who oxidised UO_2 of $30 \text{ m}^2 \cdot \text{g}^{-1}$ at 25°C reaching to O/M ratios of near 2.5 [32]. The behaviour of high surface area UO_2 is confirmed by Wadsten *et al.* [65] and Leinders *et al.* [13]. The latter authors reported an O/U value of 2.35 at 160°C in air even for their sample with the lowest area ($4.0 \text{ m}^2 \cdot \text{g}^{-1}$, similar to P1). The tendency is to increase O/U with SSA under the same isothermal conditions. Even more, in spite of reacting like a pure powder (from the sense of particle size reached after milling), P3 behaves somewhat more like a pellet. This difference in thermal oxidation resistance is supported not only based on the substantially different morphology exhibited by both samples in the SEM micrographs (Figure 4a and c) but also, owing to structural differences between the agglomerates of P1 with lower expected defects and the fractured grains of P3, which still maintains an internal stress, as a consequence of the sintering process. In fact, OOT value for P3 is 237°C for the step 1, compared to 170°C of P1, thus providing evidence that P1 begins to oxidise earlier compared to P3. Actually, the first step of the oxidation of P3 is almost negligible, with a mass gain of only 0.38% in this stage. This small value is related to the $\text{O/U}_{\text{plateau}}$ ratio of P3, of only 2.06. Given that $\text{O/U}_{\text{plateau}}$ will probably represent a mixture in different proportions of UO_2 , U_4O_9 and U_3O_7 , it is clear that almost the entire sample P3 remains as UO_2 . The opposite is found for P1, where $\text{O/U}_{\text{plateau}}=2.35$. After this first step, the reaction rate of P3 becomes faster and comparable to that of P1 (0.5084 and $0.5342 \text{ \%} \cdot \text{min}^{-1}$ at their MRTs of the second step, respectively). The formation of intermediate oxidised phase (first stage) starting from UO_2 powder is a “diffusion-controlled” reaction in our particular experimental conditions (*i.e.* at high temperature, since $\text{OOT} > 170^\circ\text{C}$), [12, 56-61] controlled by the diffusion of oxygen atoms through the surface, and the second stage of the oxidation of UO_2 is described as “nucleation-and-growth” mechanism [12]. In contrast, the mechanism of the oxidation in pellets (*i.e.* nucleation and spallation of U_3O_8 from the particles surface) [11, 29, 68, 69] seems to fit better to the results of P3, which would indicate a surface reaction [70, 71]. The heterogeneity and wide range of the P3 PSD, with larger particles than P1 and P2, may be responsible of an intermediate behaviour between isolated particles and a sintered pellet. Also, Valdivieso *et al.* [29] reported this

behaviour, but not with such a big difference because in their comparison of UO_2 pellets and powders, they used a powder with large agglomerates and lower specific surface area ($0.031 \text{ m}^2 \cdot \text{g}^{-1}$) than P1. The reference for this behaviour is the fragment curve (Figure 4.1.6d), where the first step of the oxidation is not present, occurring both at the same time, and resulting in a higher RR_{MRT} value ($0.8196 \% \cdot \text{min}^{-1}$, Table 4.1.II). The effect of the delay in oxidation is obvious, as the fragment begins to oxidise later than any of the powdered materials (OOT of 468°C).

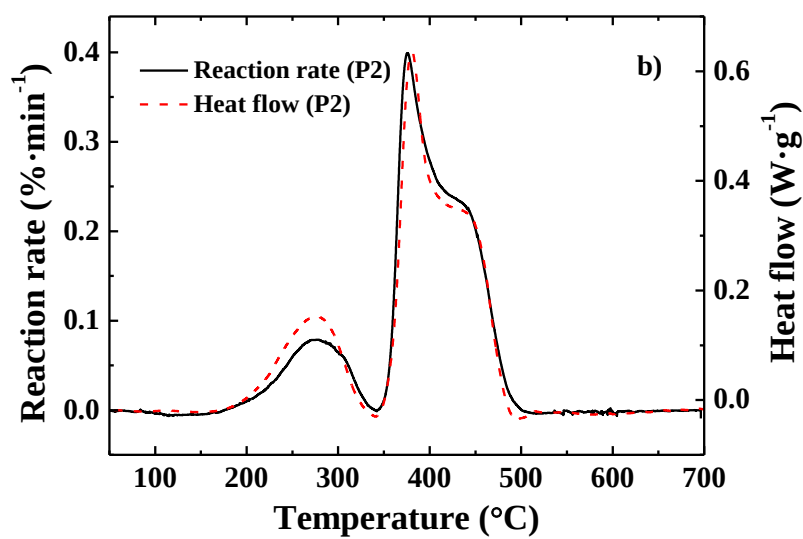
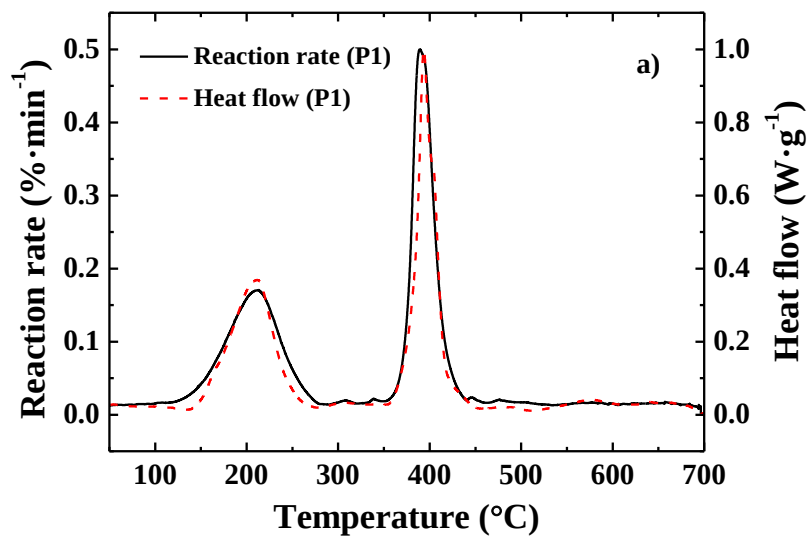
The comparison between P2 and P3 goes deep in the influence of PSD on the oxidation of UO_2 , having both of them the very same origin and morphology, and a comparable order of magnitude in the mean particle size, but a different distribution (see Table 4.1.I and Figure 4.1.3). The same origin of both materials makes the comparison possible. Walker [72] was one of the first studying UO_2 powder coming from sintered pellets with a surface area comparable to the materials used in this study ($0.135 \text{ m}^2 \cdot \text{g}^{-1}$ measured with Kr). He observed that at a high enough temperature (420°C), the oxidation proceeded via “nucleation and growth” sigmoid mechanism, *i.e.* the formation of U_3O_8 occurs simultaneously to the formation of U_3O_7 , as expected from a surface reaction. The same behaviour is found here with P2 and P3, especially the latter, with a reduced first step of the oxidation (mass gains of 1.12% and 0.38%, respectively, which are much lower than the theoretical value of 1.95% of the transformation $\text{UO}_2 \rightarrow \text{U}_3\text{O}_7$). In this regard, the $\text{O}/\text{U}_{\text{plateau}}$ ratio could be related with the particle size of each material. While the grains of P2 are smaller and with a similar size ($\text{O}/\text{U}_{\text{plateau}}=2.25$), the difference in sizes of the P3 particles provoke the different behaviour of this material, as P3 larger grains would oxidise superficially until a certain U_3O_7 layer thickness is reached, delaying the oxidation ($\text{O}/\text{U}_{\text{plateau}}=2.06$). In this sense, the values of Quémard *et al.* [14] with $5 \mu\text{m}$ powder obtained from broken pellets followed a very similar oxidation trend in air in the $250\text{--}330^\circ\text{C}$ temperature range as the new data presented here, indicating these authors the presence of multiple cracks and pulverization of oxidised samples [14]. Similar results were also obtained by De Bona *et al.* [37], who observed firstly the appearance of U_4O_9 and U_3O_7 and later the formation of U_3O_8 after 15 minutes of the oxidative treatment (300°C , air) for their $3 \mu\text{m}$ grinded pellet, while no U_3O_8 was reported for the nano-sized sample. Between P2 and P3, Figure 4.1.5 and Figure 4.1.6b and 6c show that the U_3O_8 formation (*i.e.* overall reaction) from a wider PSD (P3) proceeds at a higher temperature than that of a narrower PSD (P2), comparing

MRTs of the second step for both materials (Table 4.1.II). This delayed kinetics in the case of P3 is observed in the RR_{MRT} value ($0.0407\% \cdot \text{min}^{-1}$ compared to $0.1025\% \cdot \text{min}^{-1}$ of P2), which is especially remarkable since both materials have the same oxidation onset temperature. Thus, we can say that the presence of heterogeneous particles, especially the large ones, tends to slower kinetics. This leads us to think that these bigger grains are still mechanically together, an effect that is not so clear in P2, where most of the particles have a similar size. The oxidation mechanism of sintered fragment (F) causes that the reaction does not yield pure U₄O₉/U₃O₇ because U₃O₈ usually begins to form when the oxidised layer is only a few micrometers thick [14, 71, 73]. In light of recent studies, this seems to happen only if the grain size is larger than a certain threshold level, for example in the case of De Bona *et al.*, this threshold is around 0.4 μm [37]. When compared this data with irradiated or simulated spent fuels, it is observed in general a delayed oxidation kinetic as the burnup increases [67]. It is generally accepted that oxidation of unirradiated UO₂ fragments is slower in the first stage than that of used fuel while oxidation to U₃O₈ is faster for some types of used fuel ([11] and its references), possibly due to oxidation delayed by the presence of trivalent fission products, among others [74].

Finally, the major similarity of P3 with the fragment gain curve, used as a reference, is the indicator that this material could be the most appropriate to be used as a powdered SNF surrogate, given the difficulty to work with and handle this radioactive material. The previously cited work by De Bona *et al.* [37] has also dealt with the fabrication of representatives SNF surrogates, by trying to replicate the different grain sizes that can be found in an irradiated UO₂ pellet, but in different samples. P3 accomplishes with the requirements of the analogue to be used as starting materials for further corrosion experiments, especially to be conservative respect to the real case, but not in such an extreme that the conclusions reached may not be directly applicable to reality.

In addition to the previous discussion, Table 4.1.II also shows the total weight change of all the materials, calculated as the sum of the first and the second steps of the oxidation. From this value, the initial, average O/U ratio has been calculated, in order to know the initial stoichiometry of each sample. The values, as reported in Table 4.1.II, have been 2.09 for P1; 2.05 for P2; and 2.00 for P3 and F and in agreement with those calculated from Raman analysis (Figure 4.1.2). This confirms the pre-oxidation of P1 (and gives an idea of the fast oxidation kinetics of this material, not subjected to any thermal

treatment before this oxidation experiment), as seen by Raman spectroscopy, as pointed out before.



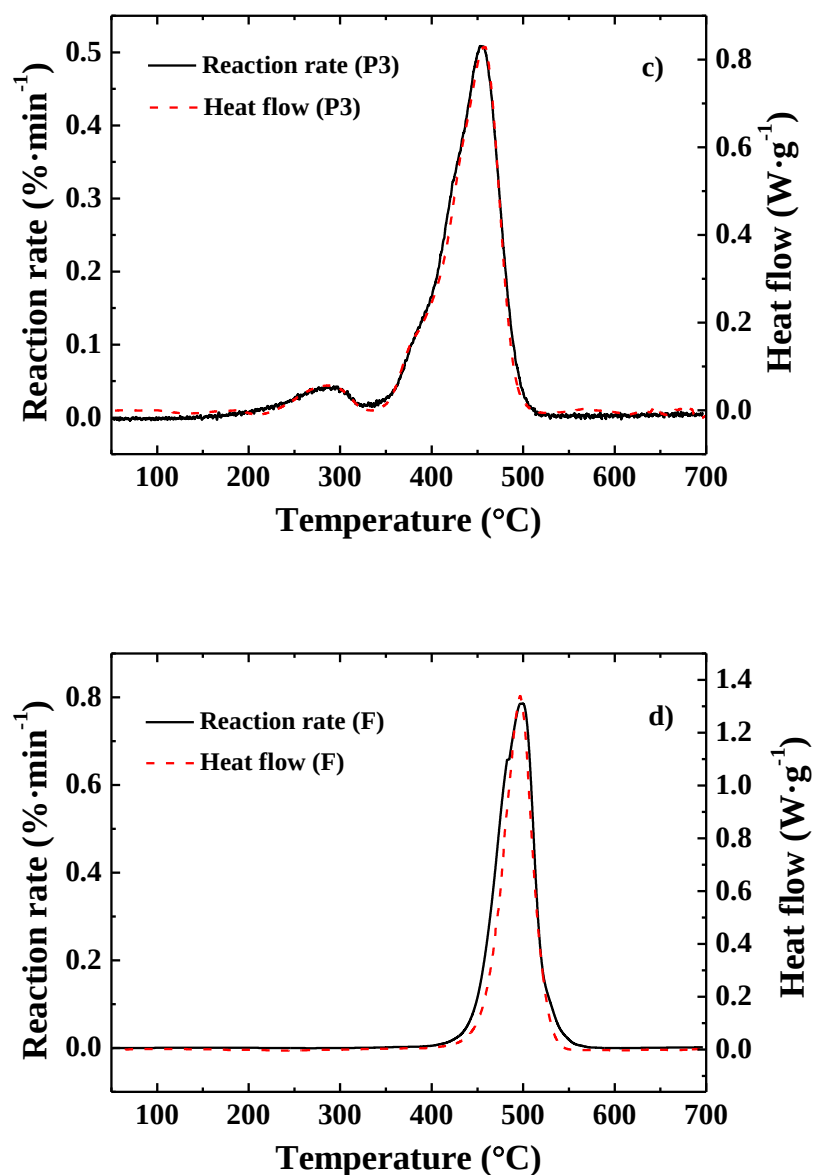


Figure 4.1.7. Reaction rate (%·min⁻¹) and heat flow (W·g⁻¹) vs temperature for the different materials studied: a) P1 (SSA=4.7 m²·g⁻¹; D(v,0.5)=3.7 μm), b) P2 (SSA=0.9 m²·g⁻¹; D(v,0.5)=2.2 μm), c) P3 (SSA=0.2 m²·g⁻¹; D(v,0.5)=5.6 μm) and d) F (SSA=0.1 m²·g⁻¹; average grain size=6.5 μm).

In general, in solid-state reactions with gaseous species as the one studied in this work, the kinetic analysis relies on various assumptions in terms of analysis conditions, characterisation of the solid phase and validity of the starting hypothesis/ mathematical equation [75]. Two of them are of paramount importance: the steady-state and the rate-limiting step approximations. For the first one, it is necessary to measure the kinetic rate by two methods, being calorimetry and thermogravimetry commonly used. The second

one is based on quick changes during an experiment, changing a variable affecting the reaction kinetics.

According to our experimental dynamics, here we prove the first assumption, *i.e.* the existence of a pseudo steady-state in the oxidation of the studied materials. In this regard, the two rates measured by both TGA and DSC techniques should remain proportional during the whole experiment [29, 75]. To confirm this hypothesis, both the reaction rate and the heat flow are plotted together in Figure 4.1.7 for each substrate. For comparison purposes, the DSC data is plotted as positive values; in spite of corresponding to exothermal reactions. Accordingly, enthalpy values given in Table 4.1.III are negative. As can be seen in the Figure, the curves can be well superposed during all the temperature range, thus demonstrating that the system is in a pseudo steady-state throughout the main steps of the reaction. Valdivieso *et al.* [29] proved this effect by oxidising unirradiated pellets at 370°C, while Rousseau *et al.* [8] did it by oxidising UO_2 powder from 2 to 10 μm at 250°C in air. Both authors carried out isothermal experiments to support this hypothesis, being also valid when a temperature ramp from ambient conditions is applied, as demonstrated here. It should be highlighted that the pseudo steady-state behaviour for the transformation of UO_2 to U_3O_8 is valid regardless of the origin of the materials. Moreover, it does not depend on the reaction pathway, as it is obtained when the reaction undergoes via a plateau at intermediate oxides $\text{U}_4\text{O}_9/\text{U}_3\text{O}_7$ (P1), when the two steps of the oxidation overlap as a consequence of a “pellet-like” behaviour (P2 and P3) and when only one single step is observed (F).

The DSC data plotted in Figure 4.1.7 reveals the exothermal character of the reaction, as expected. Two exothermic phenomena are recorded in DSC for powdered samples. DSC curve profiles and the onset temperatures for the two reaction steps are consistent with other author’s results [76, 77]. From the analysis of the temperatures onset and the reaction enthalpy, some interesting conclusions can be extracted. These data are presented in Table 4.1.III. The tendency in DSC, OOTs, and MRT is the same than data from TGA: the values are higher for purified UO_2 (P1) than those for powder coming from sintered pellets (P2 and P3). P2 displays a longer heat flow tail from UO_2 to $\text{U}_4\text{O}_9/\text{U}_3\text{O}_7$ than P3. The reaction enthalpies are presented as a single-reaction step for each peak of the curve, being the total enthalpy the sum of the values of both the first and the second steps of the oxidation.

Table 4.1.III. DSC oxidation onset temperature (DSC OOT), maximum reaction temperature (DSC MRT), and calculated enthalpies for air oxidation of the studied materials. Uncertainty for each parameter lies around 1%, taking into account the precision of the instrument.

Material		P1	P2	P3	F
STEP 1	DSC OOT (°C)	155	198	228	-
	DSC MRT (°C)	212	272	283	-
	Enthalpy (J·g ⁻¹)	-114±2	-60±1	-9.2±0.3	-
STEP 2	DSC OOT (°C)	382	353	388	448
	DSC MRT (°C)	394	376	454	482
	Enthalpy (J·g ⁻¹)	-124±2	-211±4	-324±6	-317±7
Total enthalpy (J·g ⁻¹)		-238±5	-271±5	-333±7	-317±7

The tendency found here for the powdered substrates confirms the previous discussion about the oxidation kinetics for each one. In the first step of the oxidation, the values of the net enthalpy decrease in the sequence $P1 > P2 > P3$, thus being P1 the highest absolute value with $-114 \text{ J}\cdot\text{g}^{-1}$. This value is remarkably lower than other reported in literature, for example the one given by Leinders *et al.* [28] for the transformation of $\text{UO}_2 \rightarrow \text{UO}_{2.33}$ ($-198 \text{ J}\cdot\text{g}^{-1}$). This is probably due to the detected pre-oxidation of P1, which makes the mass gain not reaching the theoretical value of 1.95% in the first step of the oxidation ($\Delta m = 1.52\%$ for P1, Table 4.1.II). In P2 and P3, the small transformation obtained in the first step is the cause of the low enthalpies. In these two substrates, it seems that the different origin of the material is the cause for the lower enthalpies in the first step of the reaction with respect to the value given by Leinders *et al.* Different experimental conditions could also influence the enthalpy (Leinders use a heating ramp of $5^\circ\text{C}\cdot\text{min}^{-1}$ up to 450°C ; here we use $10^\circ\text{C}\cdot\text{min}^{-1}$ to 700°C).

In the second step of the oxidation, the opposite tendency is found for the reaction net enthalpies, being in this case $P3 > P2 > P1$, as corresponds to the progressive likeness to the “pellet behaviour”. In fact, in the case of the fragment used as a reference, one intense exothermal effect related was observed at high temperature, indicating that the U_3O_8 phase is transformed directly from UO_2 without any intermediate phases [29]. In this case, the enthalpy is close to the value from Leinders *et al.* [76] of $-315\pm7 \text{ J}\cdot\text{g}^{-1}$.

For the sake of comparison, in Figure 4.1.8 a visual check on the U_3O_8 conversion from UO_2 under these conditions is presented by means of SEM morphologies of the pre and post-oxidised samples in air.

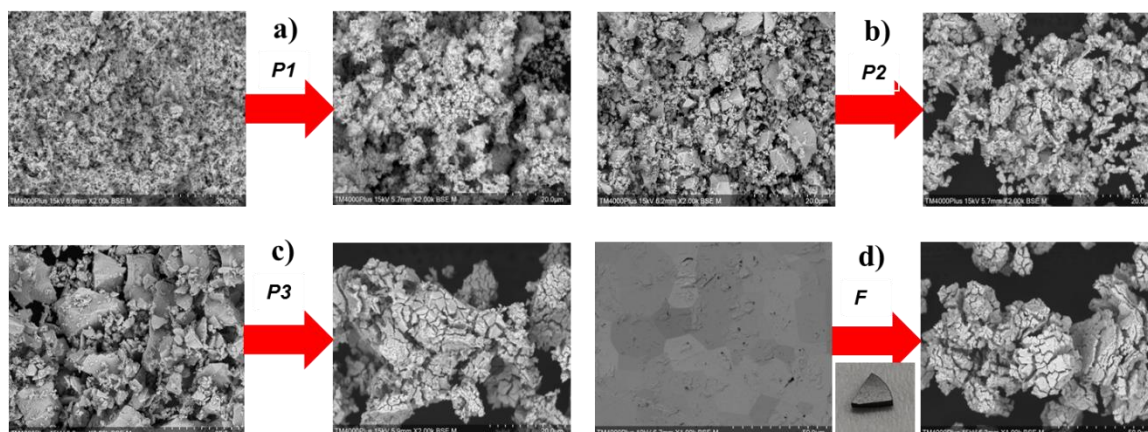


Figure 4.1.8. SEM morphological changes of the as-prepared and oxidised (a) P1, b) P2, c) P3 and d) F) to U_3O_8 . The inset in the “F” image corresponds to the initial, pre-oxidised fragment cut from a UO_2 pellet. Cracking and spalling were observed in the samples.

Morphological changes in the samples are appreciated, mainly the apparition of cracks and the previously described “popcorn”-like shape particles [14, 38, 78]. During the oxidation, the UO_2 fragment (Figure 4.1.8d) was pulverized to U_3O_8 powder as a result of the lattice volume increase of about 36% from UO_2 to U_3O_8 . In the four studied materials, the surface morphology of the oxidised U_3O_8 looks like a fine detached powder; and indeed voluminous due to this volume change [11, 29]. The spallation of U_3O_8 pellets was assigned to the formation of intermediate phases, distortions in the structure and to the volume change which infers the development of intergranular cracks, causing these cracks the spallation [8, 16, 79].

4.1.4. Conclusions

In the current work, the effect of different UO_2 unirradiated powders on the thermal air oxidation kinetics to U_3O_8 has been investigated. As the basis of the conclusion, which applies to safety studies of SNF alteration under dry storage conditions and the manufacture precursor for nuclear fuel pellet, several remarks can be made.

The powdered substrates were prepared to cover a comparison of effects in the mentioned oxidation. On the one hand, the obtention route was investigated by comparing the materials obtained via ADU precipitation and milling a sintered pellet (P1 and P3, respectively). On the other hand, the effect of the width in the PSD has been studied by comparing the substrates obtained milling sintered pellets, and applying different sieving treatments to reach the aimed particle size in each sample (P2 vs P3).

As a first remark, it has been shown that TGA curves are primarily affected by the UO₂ nature over particle size factor, as P1 is the material that oxidises faster. This is also the material with the highest specific surface area (in spite of not being the one with the lowest particle size), and even starts to oxidise at ambient temperature, revealing the impact of this parameter. This behaviour could distance this material for studying SNF oxidation, which is not expected to oxidise at low temperatures.

Regarding the substrates with the same origin (P2 and P3) the influence of the PSD width has been studied here for the first time. The oxidation in this case proceeds faster in P2 than P3 during the transformation UO₂ → U₄O₉/U₃O₇. In fact, this first step in P3 is almost negligible. However, in the second step of the oxidation the reaction rate at the maximum temperature for P3 is notably higher than P2, behaving somehow like a pellet, rather than a powder. This higher oxidation resistance highlights the “intermediate” behaviour of this material, supported by the fact that the fractured grains of P3 still keep the typical properties of ceramic such as the internal stress, as a consequence of the sintering process. This tendency is confirmed by DSC, as P3 is the substrate with the highest reaction enthalpy ($333 \pm 7 \text{ J} \cdot \text{g}^{-1}$). As a matter of fact, a comparison of TGA data and DSC data shows that the studied materials satisfy a pseudo-steady state kinetics in all the temperature range.

This study provides new insights into the size-dependence of UO₂ oxidation and the nature of different UO₂ precursors and might be helpful to further understanding the SNF behaviour at dry storage conditions. Fresh (*i.e.* unirradiated) UO₂ powder coming from the recycling of other materials is frequently used as a nuclear fuel analogue. In this work, it is proved that this analogue may be too far from the reality that tries to model. On the contrary, unirradiated UO₂ powder coming from milling sintered pellets, with a wide PSD (analogue to the one found in irradiated fuel, with larger particles corresponding to the pellet centre and finer particles matching the high burnup structure formed at the pellet rim), is much closer to the oxidation of a pellet fragment (used here as a reference), and therefore can be used maintaining the conservative criterion but with more applicable conclusions related to air-oxidation studies. Further studies regarding the behaviour of these materials in dry storage scenarios (*i.e.* isothermal oxidations) are required in order to support these conclusions.

Acknowledgements

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4.1.5. References

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Result 2

Studying UO_2 oxidation at upgraded conditions

Published as “Exploring the impact of temperature and oxygen partial pressure on the spent nuclear fuel oxidation during its dry management”, **A. Milena-Pérez, L.J. Bonales, N. Rodríguez-Villagra, and H. Galán.** *Scientific Reports* (2023) 13:1966

4.2. Result 2. Studying the UO_2 oxidation at upgraded conditions

Abstract

The management of Spent Nuclear Fuel (SNF) comprises different stages in which security is demonstrated. Nevertheless, fundamental research can lead to other design options that must be considered. Currently, one of the focuses is the dry interim storage option, as the shortest-term solution until final repositories are available. During this stage, one concern is the oxidation of the fuel. If UO_2 (SNF matrix) is exposed to air at high-enough temperature, formation of U_3O_8 takes place. The larger volume of this phase could entail stresses on the SNF clad, which is the first barrier to prevent radioactive material release.

It is known that this oxidation is a temperature-dependent reaction and ensuring an inert atmosphere discards any effect during SNF dry management. However, at what extent temperature and oxygen concentration would have an impact on the U_3O_8 formation is not established, being the available experimental data very scarce.

We follow this oxidation in representative ranges of temperature and oxygen concentration of dry storage facilities by using *in-situ* Raman spectroscopy. The results show that temperature is a more-affecting factor than the oxygen concentration at the studied conditions. Therefore, efforts to limit temperatures would yield more benefits in preserving fuel matrix integrity.

4.2.1. Introduction

There is an international and increased concern on the Spent Nuclear Fuel (SNF) integrity during SNF management for pre-disposal activities, being the interim dry storage the intermediate step before the final disposal. At present, dry storage is one of the shortest-term solutions for SNF accumulation difficulties in the near future because of the limited space in water-pool, used as a passive heat-removal system for cooling, and the uncertainty of the deep disposal operation schedule, which is the last stage planned. In dry storage conditions, the safety of the fuel must be ensured mainly in front of oxidation, which can occur at high-enough temperature in presence of oxygen, and may possibly lead to a potential mechanism affecting the clad integrity driven by the formation of U_3O_8 .

Therefore, the formation of U_3O_8 and other intermediate oxides from the oxidation of UO_2 , the main constituent of most of the nuclear fuels (thus being often called “Spent Nuclear Fuel matrix”), has received considerable attention through the past decades [1-7]. The study of the different parameters that can affect this reaction, such as temperature and oxygen partial pressure, is of interest for irradiated fuel under operational and accidental scenarios during handling and transport. This has been the origin of regulation limiting the exposure of fuel matrix to temperature and oxidant species [8-12].

The oxidation of UO_2 is a well-understood process, which involves a number of intermediate oxides with different characteristics. In the case of unirradiated fuel, these oxides include the generally labelled UO_{2+x} , where cubic lattice from the original UO_2 is still maintained; U_3O_7 , that implies a change in the structure, obtaining a phase with a tetragonal lattice; and U_3O_8 , in which lattice changes are again observed, obtaining an orthorhombic oxide. This phase is the final product of the oxidation at the range of temperatures and pressures expected during the fuel storage [4, 5]. Compared to UO_2 , U_3O_8 entails an increase in volume of around 36%, and comes along with spallation and pulverization of the initial UO_2 sample [5]. Therefore, the formation of U_3O_8 could lead, depending on the condition of a pre-existent failure in the clad, to failure propagation, splitting the clad and even allowing certain release of radioactive material [13-16].

Due to its practical importance from the nuclear safety point of view, the boundary conditions in current nuclear storage facilities at which U_3O_8 does not form are widely studied (*i.e.* low temperature and lack of oxygen). Other conditions impacting on the formation of U_3O_8 have been studied under the circumstances expected during dry storage of the fuel, especially focused on temperature. At the interim storage facilities, the upper limit temperature allowed in inert atmosphere for LWR fuel is 400°C [9, 11, 17], to protect the fuel rod cladding [18]. During normal conditions of storage, there will be a range of temperatures lower than the maximum allowable of 400°C. That’s why most of the studies regarding the formation of U_3O_8 during oxidation of SNF have been conducted at this temperature or below [5, 15, 19-22]. The huge majority of these experiments have been carried out by using thermogravimetric analysis and flowing air as the oxidant phase.

About the reaction atmosphere, the fuel has been mainly studied after being exposed to air. Investigating the potential oxidation of the fuel matrix at lower oxygen partial pressures, *i.e.*, with specific loading cells being partially inert, might bring to other alternatives to air that might delay or even prevent this oxidation. However, the literature regarding the effect of lower oxygen partial pressures than air on UO_2 oxidation is scarce. With SNF, Nakamura *et al.* [23] oxidised prepared defective fuel rods with burnups ranging from 14 to 30.6 GWd/tU at 200-240°C in different atmosphere (1%, 5% and 21% O_2). At 200°C, they found a decrease of the oxidation rate with the oxygen content and a stabilisation of the U_4O_9 phase [5, 24]. In addition, Kolyadin *et al.* [25] studied the oxidation of irradiated samples (burnups between 10.07 and 19.7 GWd/tU) with very low oxygen atmospheres (0.08%, 0.48% and 1.3% O_2) at temperatures in the range of 100-300°C. They concluded that the lower the oxygen concentration, the slower the oxidation reaction.

Unirradiated fuel has been studied only by a few authors at different temperatures and atmospheres [2, 26-28]. In addition, most of the studies published up to date were conducted by using traditional techniques, mainly thermogravimetry. This technique gives information about the kinetic behaviour of UO_2 oxidation under the specified conditions, as well as the different mechanisms that take place during this reaction by studying the shape of the weight gain curves [5]. This technique measures the “bulk” oxidation of the sample, giving as a result an average O/M value reached by UO_2 after the experiment. Taking into account the possible security controls at storage facilities, it could be interesting to detect the potential early apparition of U_3O_8 and follow the progress of the reaction even if the entire sample is not yet oxidised. Only Olsen *et al.* [28] recently studied the oxidation of purified UO_2 in a wider range of temperatures (100-400°C) and oxygen partial pressures (0-21% O_2). They aged the samples in a furnace with controlled atmosphere at different times (2, 25 and 48h) and characterised *ex-situ* the final product at each condition by XRD. Nevertheless, more studies covering a complete range of temperatures and oxygen concentrations under the same experimental conditions are needed to support and validate the singular conclusions from each study.

In this work, we study the effect of three temperatures at and below the aforementioned maximum allowable of 400°C [9, 11] (*i.e.* 200, 300 and 400°C) each of one at four different atmospheres (0.1, 1, 10, and 21% O_2) on the formation of U_3O_8 , which is the

terminal thermodynamic state at these conditions [29], from a fresh UO₂ surrogate, whose representativeness is proved in terms of its conservatism in relation to actual spent fuel [30]. In addition, in this study the oxidation at *in-situ* conditions is measured from really short times (2 min) up to longer times (three days), depending on the oxidation products obtained at every specific condition.

In this regard, Raman spectroscopy is presented in this work as a non-destructive technique able to meet this purpose. This technique provides a fingerprint to distinguish between chemically similar compounds, as it is the case of uranium oxides. Besides, it gives the possibility to perform *in-situ* measurements, allowing studying the materials in the real conditions at which they will be in a real storage facility. Raman spectroscopy has been previously used in the characterisation of uranium oxides [31-40]. In our laboratory, several identification studies have been carried out [41-44], and some initial tests have been performed *in-situ* [41, 45]. However, to the best of our knowledge, this is the first time that this technique is employed to study the oxidation of UO₂ at *in-situ* conditions, including lower oxygen partial pressures than air. Also, the measurement protocols developed here can be directly applied in the study of irradiated fuel.

Thus, the main goal of this work is to analyse in detail and clarify the impact of changing, in a broad range of conditions, both the temperature and the oxygen concentration in the atmosphere in contact with SNF on the oxidation of the spent fuel matrix.

4.2.2. Results

The aim of this work is to evaluate the combined effect of the decrease in the O₂ content and the temperature on formation of the oxidised phases of UO₂. The method used to study this reaction is based in the analysis of the Raman spectra obtained at *in-situ* conditions (0.1, 1, 10 and 21 % O₂ and temperatures of 200, 300 and 400°C). These conditions are obtained by using a Linkam stage which has been slightly modified in order to house it to a Raman spectrometer (see method section).

The Raman spectra of each oxidised UO₂ phase (*i.e.* UO_{2+x}, U₃O₇, U₃O₈) is well known [31, 32, 34, 35, 38, 46-48] and, as it was confirmed in our previous works [41-45], this spectroscopy can unequivocally identify each phase at room temperature. At higher temperatures, we already demonstrated that the main features of the spectra

corresponding to UO_2 [42] and UO_{2+x} [45] do not suffer any drastic change, but as expected, all Raman bands downshift in wavenumber and increases its bandwidth with increasing temperature. Raman spectra of U_3O_7 and U_3O_8 at higher temperatures are evaluated here.

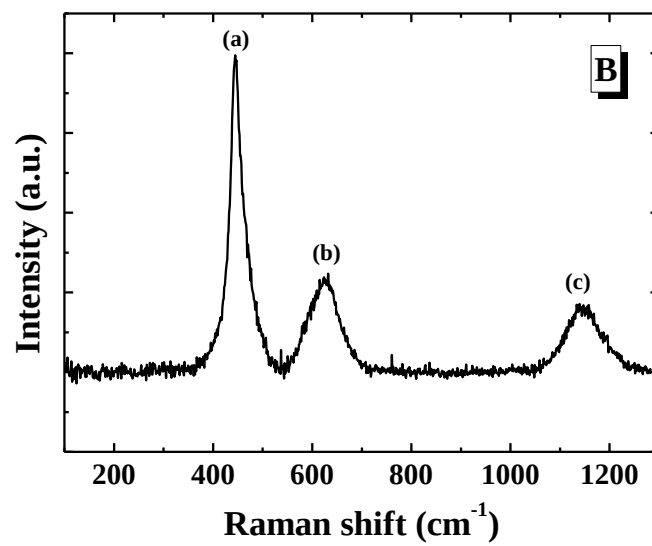
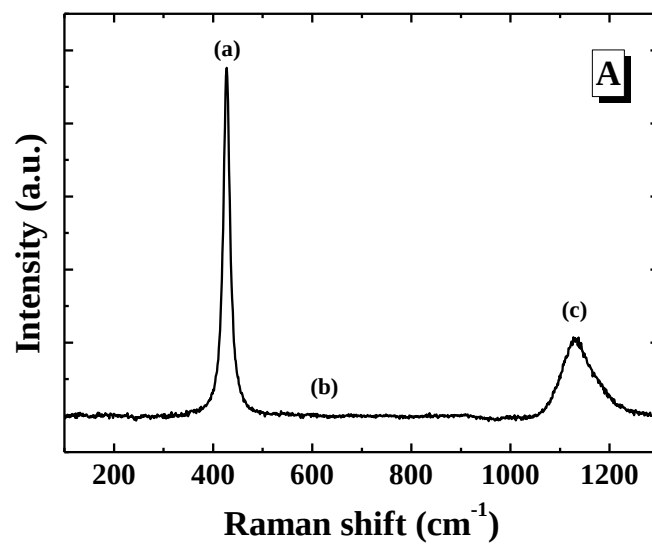
The analysis was carried out as follows: we first establish the criteria to identify the different phases *i.e.* determine the Raman fingerprint or Raman signature of each phase. After verifying that the characteristics corresponding to the U_3O_7 and U_3O_8 phases are not modified due to temperature, these Raman signatures are used to analyse the spectra acquired *in-situ* in the different experiments, *i.e.* the Raman spectra acquired at each time (up to 3000 s, *i.e.* around two days), temperature and O_2 concentration.

4.2.2.1. UO_2 , UO_{2+x} U_3O_7 and U_3O_8 Raman signatures

The characteristic UO_2 spectrum shows (see Figure 4.2.1A) the triply degenerate T_{2g} mode at 445 cm^{-1} (a), the LO mode at about 570 cm^{-1} (b), and the first overtone of the LO mode (2LO) centred about 1140 cm^{-1} (c) [31]. Figure 4.2.1B shows the spectrum corresponding to UO_{2+x} with $x = 0.1$. This x value represents the average composition of the sample, probably formed by a mixture of UO_2 and U_3O_7 in the conditions studied here [29]. As is clearly shown in the figure, with the increase in the oxidation the spectrum suffers a broadening and upshifting of the 445 cm^{-1} band (a), an increase in the intensity of the 570 cm^{-1} (b) and a decrease in the intensity of the 2LO band (c) compared with the initial UO_2 ($x=0$). Moreover, the spectrum shows the apparition of a new band near 630 cm^{-1} associated to the oxidation [31, 41]. It should be noted that these two bands (570 cm^{-1} and 630 cm^{-1} bands) overlap, giving a broad band centred above 600 cm^{-1} , which will be referred in this work as defects band (b) [41].

The characteristic Raman spectrum of the next oxidised phase U_3O_7 is presented in Figure 4.2.1C. It is identified by the two bands corresponding to the T_{2g} mode (a), the band associated to the defects above 600 cm^{-1} (b) and the fading of the 2LO band originally at $\sim 1140\text{ cm}^{-1}$ [31, 41, 49]. In this phase, an extra Raman feature located at about 120 cm^{-1} (c) becomes visible, which has been assigned to tetragonal distortions of the cubic lattice of UO_2 , therefore confirming that the spectrum corresponds to U_3O_7 [31, 50].

Finally, the Raman spectrum of U_3O_8 is presented in Figure 4.2.1D. Compared to previous oxidised phases, it is characterised by a completely different pattern. The main Raman feature is the broad triplet in the $300\text{-}500\text{ cm}^{-1}$ region (a), associated with the different modes of the U-O stretching in the orthorhombic lattice [46, 47]. This mode has been used as a fingerprint for identification of this compound [33]. The Raman spectrum of U_3O_8 also presents a quartet of modes between 90 and 150 cm^{-1} (b), an intense peak at 240 cm^{-1} (c), and a broad band around 750 cm^{-1} together with a narrower peak at around 810 cm^{-1} (d). The assignment of these bands is more or less known, although some details are still missing [33, 47, 51].



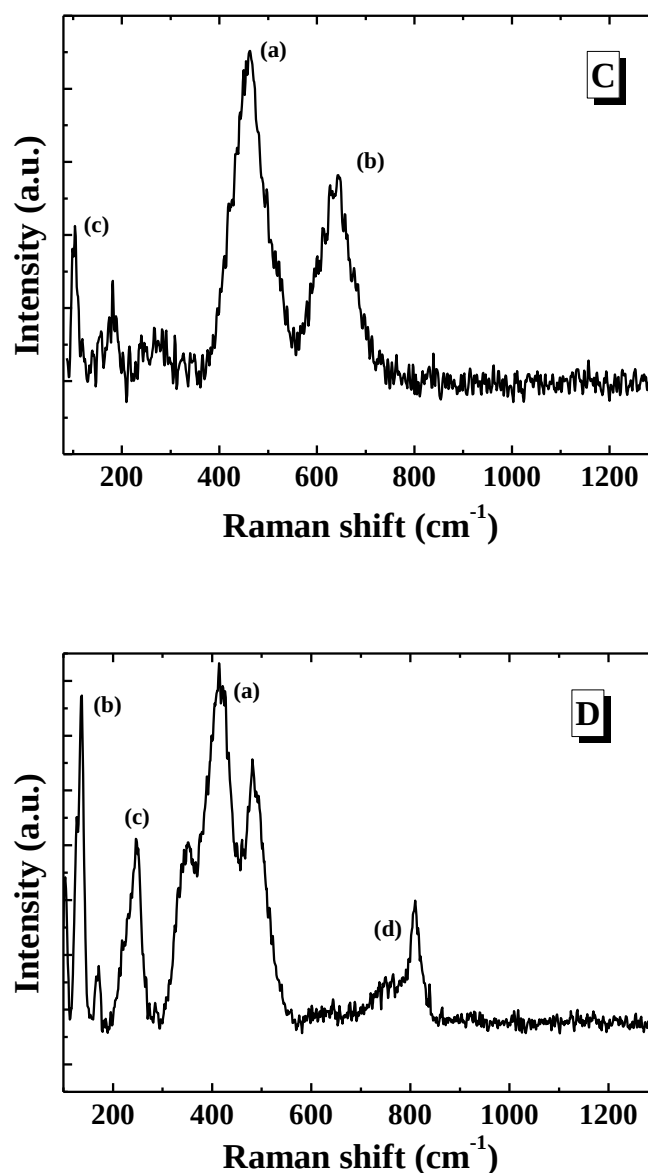


Figure 4.2.1. Raman signatures of the different uranium oxides characterised in this work, being A) UO_2 B) UO_{2+x} ($\text{UO}_{2.10}$) C), U_3O_7 and D) U_3O_8 .

As seen in Figure 4.2.1, the evolution of the Raman spectra with the oxidation can be described as follows: the initial UO_2 spectrum varies by increasing the intensity of the band located above 600 cm^{-1} and decreasing the intensity of the band at 1140 cm^{-1} (2LO band) when oxidised to UO_{2+x} . Thereafter, when U_3O_7 is formed, the 2LO band disappears and therefore the spectrum has two intense features at 445 cm^{-1} and above 600 cm^{-1} . The change that occurs when the oxidation proceeds up to U_3O_8 is evidenced by the triplet of bands in the $300\text{--}500\text{ cm}^{-1}$ region.

Once we have stabilised the Raman signature of each phase, let us to check that the effect of the temperature do not modify the Raman fingerprint of the U_3O_7 and U_3O_8 phases described above. In order to reach this goal, we have measured the U_3O_7 as U_3O_8 phases as a function of temperature at inert conditions (Ar) (Figure 4.2.2A and Figure 4.2.2B). According to the results, the main Raman modes suffer a slight broadening and shift to lower wavenumbers. Nevertheless, the main spectral features remain constant for the working temperatures, allowing us using them to identify the different oxides not only at room temperature but also at high temperature up to 400°C. On the one hand, for U_3O_7 (Figure 4.2.2A), the disappearance of the 2LO band with respect to the UO_{2+x} spectrum is used. On the other hand, for U_3O_8 (Figure 4.2.2B), the presence of the broad signal in the 300-500 cm^{-1} region, although the triplet is not as evident as at room temperature, can still be used for a quick identification of this phase.

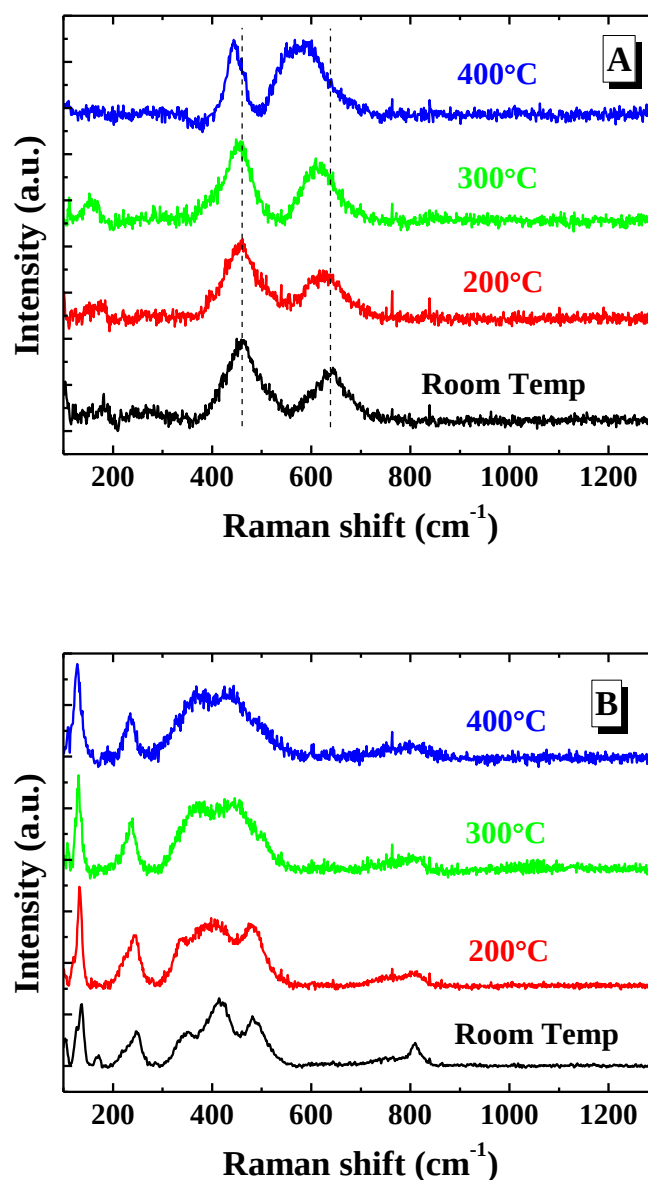


Figure 4.2.2. Raman spectra of A) U_3O_7 and B) U_3O_8 under inert conditions (Ar) as a function of temperature in the region studied in this work.

4.2.2.2. *In-situ* Raman study of the UO_2 oxidation at different atmospheres and temperatures

By using the Raman signatures described above we have identified the formation of each phase formed at each time (up to 3000 s, *i.e.* around two days) at the testing conditions (0.1, 1, 10 and 21 % O_2 and temperatures of 200, 300 and 400°C). Next paragraphs show some representative results obtained at different conditions studied in this work. They have been selected in order to present an illustrative picture of the

possible scenarios that could be considered in new design options of dry storage facilities. The rest of the results, covering the complete range of experiments, can be found at the supplementary information.

Figure 4.2.3 shows the spectra as a function of time obtained at the lowest temperature and O_2 concentration studied (200°C and 0.1%). In the Figure, the typical features of the hyperstoichiometric UO_{2+x} phase are obtained in the whole time period experimented *i.e.* three main bands at around 445 , above 600 and 1140 cm^{-1} corresponding to the aforementioned T_{2g} , “defects band” and $2LO$ modes. It should be noted that the evolution of the spectra as a function of the oxidation time is demonstrated by the continuous increase in the intensity of the band above 600 cm^{-1} and the decrease in the intensity of the $2LO$ band.

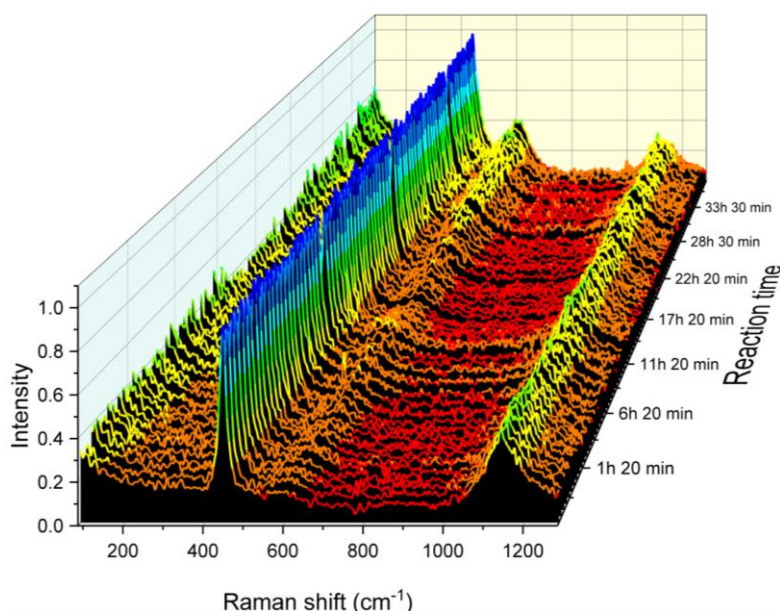
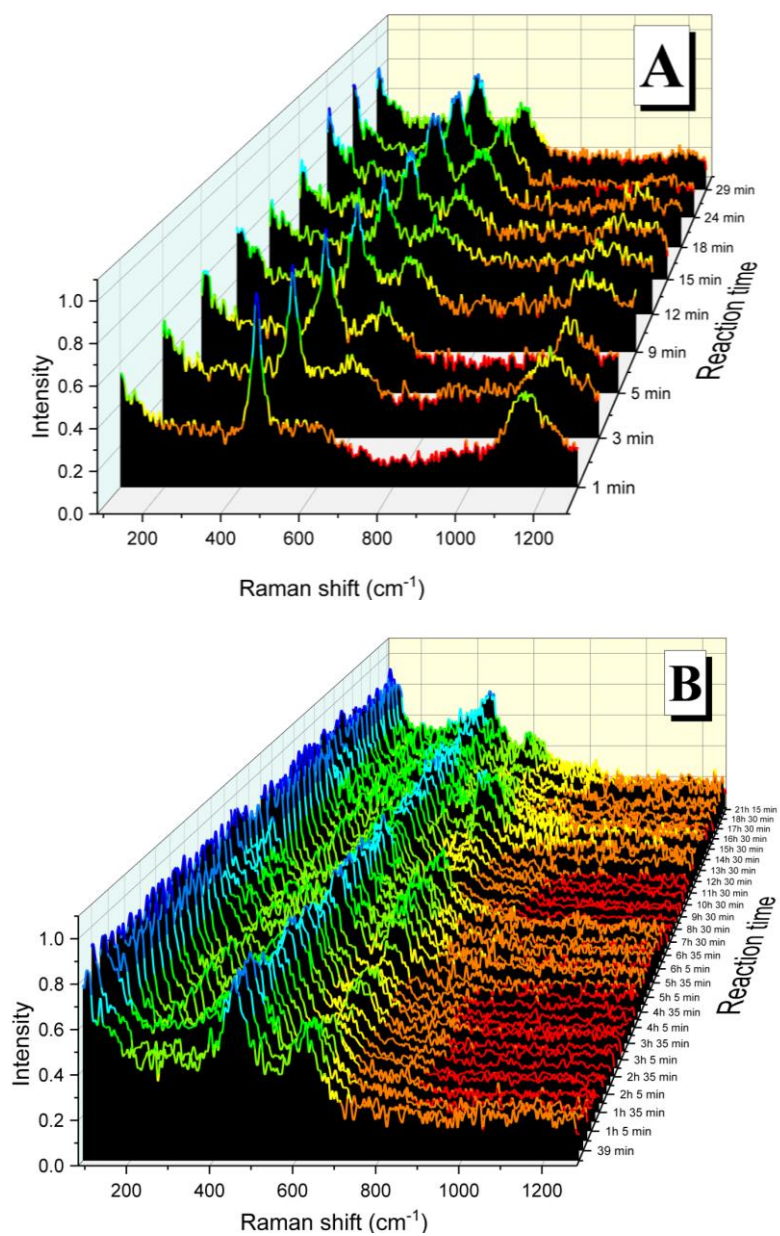


Figure 4.2.3. Raman spectra acquired during the experiment at 200°C and $0.1\% O_2$.

At same O_2 concentration (0.1%) and higher temperature (300°C) the spectra show the formation of UO_{2+x} up to 18 min (Figure 4.2.4A), note the three bands at around 445 , 600 and 1140 cm^{-1} . At times close to 24 min the disappearance of the $2LO$ band (1140 cm^{-1}) becomes evident, indicating the formation of U_3O_7 (Figure 4.2.2B). This phase prevails up to times of 21h, after this (at times ranging from 22h to 45h) the apparition of the trident evidences the formation of U_3O_8 (Figure 4.2.2C).



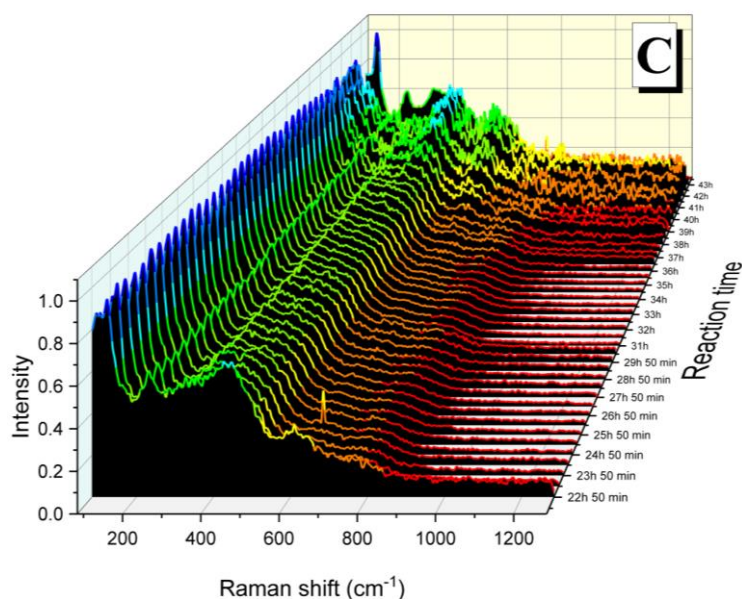


Figure 4.2.4. Raman spectra acquired during the experiment at 300°C and 0.1% O₂ showing the formation of different oxidised phases from the initial UO₂: A) UO_{2+x} up to 18 min, B) U₃O₇ from 24 min to 21h and C) U₃O₈ from 22 h to the end of the experiment.

Same three phases (UO_{2+x}, U₃O₇ and U₃O₈) have been detected at 21% O₂ and 300°C (Figure 4.2.5). At short times (up to 23 min) the spectra have the three main bands corresponding to the UO_{2+x} phase, then the disappearance of the 2LO band (1140 cm⁻¹) evidence the formation of U₃O₇ (Figure 4.2.5A), and finally from around 5h the spectra correspond to the U₃O₈ phase (Figure 4.2.5B).

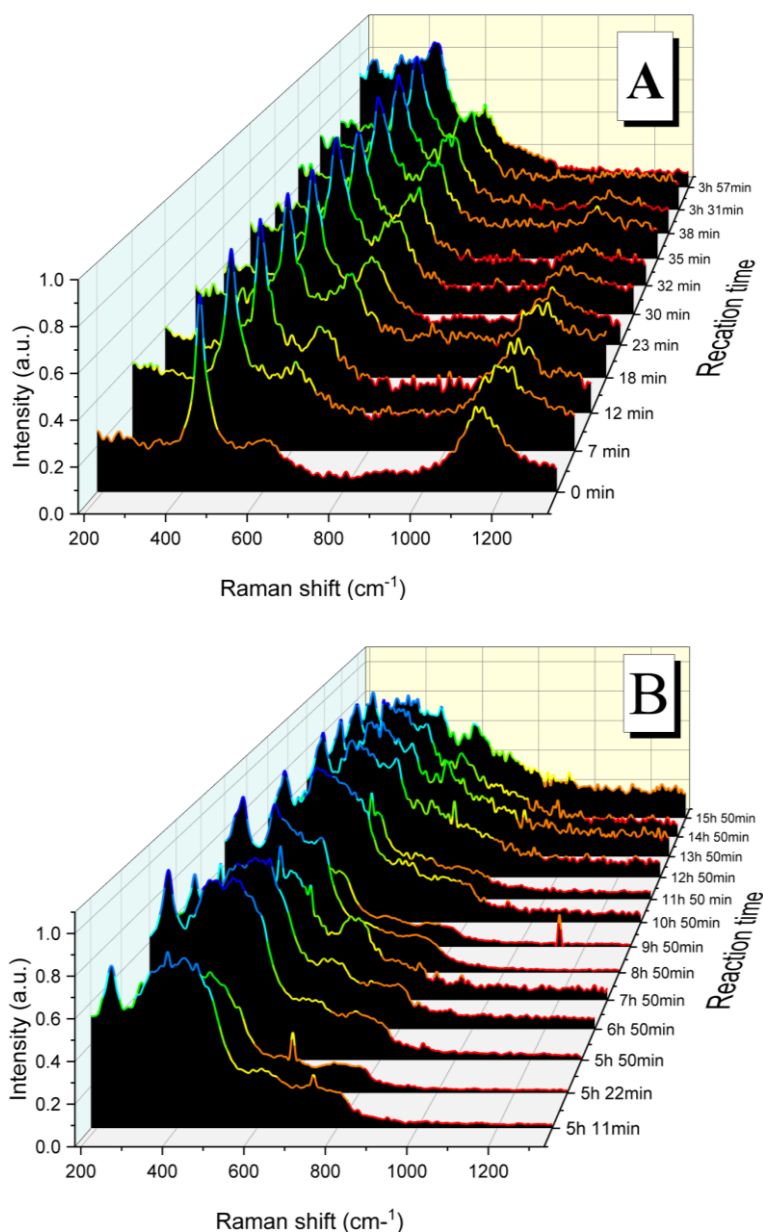


Figure 4.2.5. Raman spectra acquired during the experiment at 300°C and 21% O_2 showing the formation of different oxidised phases: A) UO_{2+x} and U_3O_7 during the first 5 h and B) U_3O_8 from 5 h on.

From the spectra acquired at the different experimental conditions, and previously presented, valuable information can be extracted. The spectral differences aforementioned have been associated to the structural changes that occur in UO_2 when starts to oxidise first to UO_{2+x} , maintaining the cubic lattice; then proceeding via U_3O_7 with such a distortion that the lattice goes to a tetragonal intermediate; and finally oxidising up to U_3O_8 , which is orthorhombic and present completely different Raman bands.

4.2.3. Discussion

The spectra acquired at the different experimental conditions, and previously presented, have been interpreted in terms of the oxidation degree of UO_2 . The O/U ratio has been estimated according to the evolution of the Raman spectra with time. This assessment has allowed us characterising the overall reaction and to divide it into three different phases UO_{2+x} , U_3O_7 and U_3O_8 . First of all, the initial step of the reaction has been evaluated by determination of “ x ” in the structure UO_{2+x} , to confirm the increasing oxygen incorporation to the lattice with time, but not observing a substantial structural change reflected in the spectra. With this purpose, we have used a previous analysis of the Raman spectra as a function of x [41], taking also into account the temperature correction factor [45], as shown in Equations 1 and 2.

$$\Delta\nu_{630}(\text{cm}^{-1}) = -(610 \pm 60)x - (0.049 \pm 0.003)T(\text{K}), (I_{630}/I_{445} < 0.24) \quad (\text{Eq. 1})$$

$$\Delta\nu_{630}(\text{cm}^{-1}) = -(90 \pm 20)x - (0.049 \pm 0.003)T(\text{K}), (0.27 < I_{630}/I_{445} < 0.24) \quad (\text{Eq. 2})$$

In Equations 1 and 2, $\Delta\nu_{630}$ is defined as $\Delta\nu_{630} = \nu_{630} - \nu_{\text{int}}$, being ν_{630} the Raman shift of the band associated to the increase in the oxidation degree [31, 35, 41, 51, 52], and ν_{int} the Raman shift of the linear fit intercept. To obtain both Raman shifts, a detailed profile analysis has been carried out in every single spectrum. Central position of the spectral bands was obtained by the second derivative method [53]. The use of two equations to calculate x responds to the distinct regions observed in this transition, as reported by Elorrieta *et al.* [41].

Secondly, a second step in the oxidation reaction is defined, where the intermediate U_3O_7 phase is mainly obtained and interpreted as a stabilisation phase of the reaction before reaching the final oxidation product. This phase has been associated with an O/U between 2.25 and 2.40, according to different values reported in literature [7, 31, 54, 55]. The Raman spectrum of this phase shows two strong bands (the T_{2g} mode at $\sim 445 \text{ cm}^{-1}$ and the oxygen-clusters-related $\sim$ above 600 cm^{-1} band), and the lack of the 2LO mode, which makes it distinct from the UO_2 and the UO_{2+x} spectrum [31, 38, 41, 56]. Finally, a third step in the reaction is defined by the presence of acquired spectra corresponding to the U_3O_8 phase, which is associated with the final of the oxidation process (O/U=2.67).

By following these guidelines, the overall progress of the oxidation in the different conditions studied is presented in Figure 4.2.6, in terms of the O/U ratio vs reaction time. The results have been plotted distinguishing temperatures (200, 300 and 400°C) and oxygen partial pressures at which the oxidation has been carried out (0.1%, 1%, 10% and 21% O_2).

At 200°C, only the UO_{2+x} phase is observed, regardless of the oxygen concentration, in the whole duration of the experiments (approximately 2 days per temperature and oxygen concentration). The effect of the limited availability of oxygen in this low temperature is the extent of the UO_{2+x} phase, *i.e.* the O/U value. From Equations 1 and 2, we have calculated the O/U, obtaining that with 0.1% O_2 is $\text{O/U}=2.07\pm0.03$. This value grows with oxygen concentration, resulting in $\text{O/U}=2.17\pm0.05$ with 1% O_2 ; $\text{O/U}=2.18\pm0.05$ with 10% O_2 ; and $\text{O/U}=2.24\pm0.06$ with air (21% O_2) (Figure 4.2.6A to D, respectively). Thus, no formation of higher oxides has been detected in any case. In addition, it should be highlighted that the effect of a higher presence of the oxidant is to accelerate the first step of the reaction with time. This effect has been previously reported as a consequence of the diffusion mechanism in the first part of the oxidation of UO_2 [1, 4, 7, 57]. In fact, Blackburn *et al.* [2] measured the oxidation of unirradiated UO_2 at 200°C covering a range of oxygen concentrations from 0.07 to 100% O_2 . They reported a lack of effect on the oxidation degree between 20 and 100% O_2 , but stated that a decrease of the oxidation occurred in the 0.07-20% O_2 range when the oxygen concentration was low, being consistent with the results of this work.

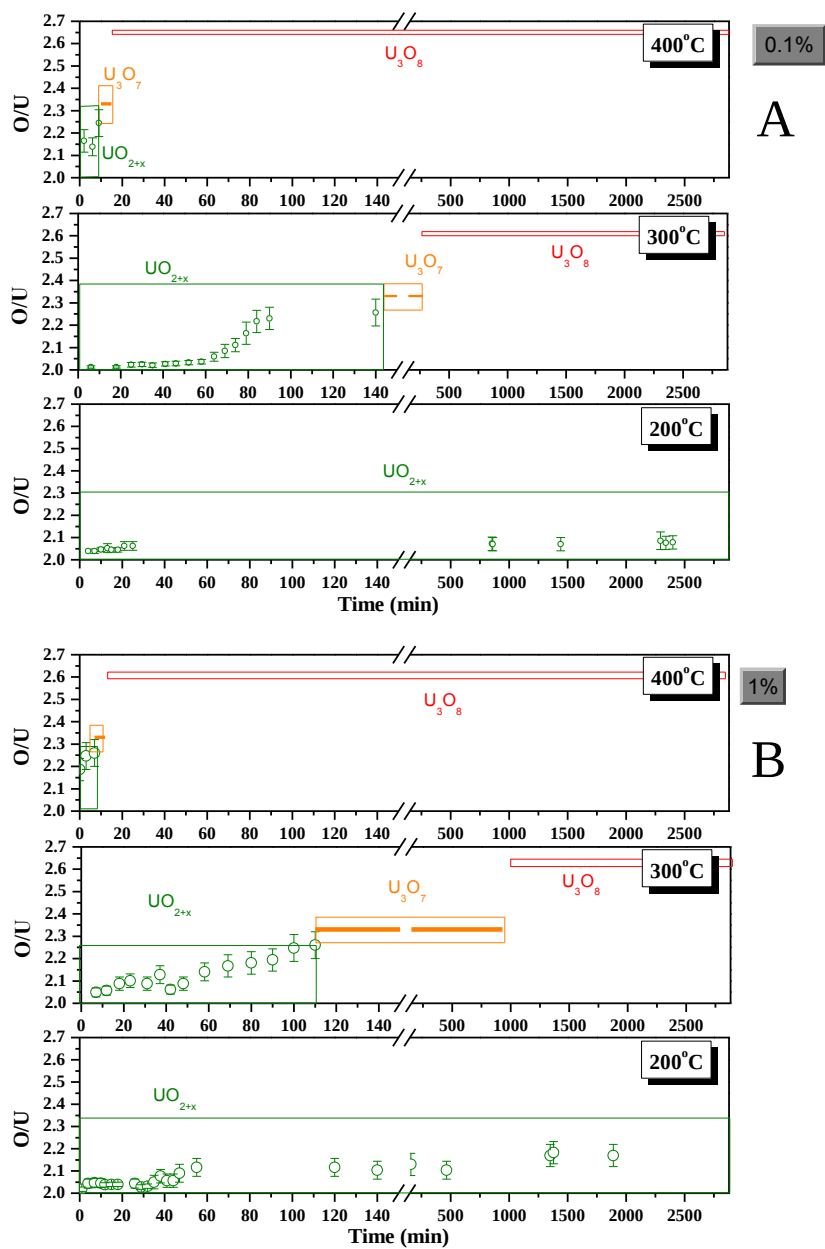
On the other hand, at 400°C the U_3O_8 phase is prevalent, independently of the oxygen concentration. In the most extreme case, *i.e.* 21% O_2 , only U_3O_8 is observed even at the very beginning of the experiment, giving an idea of the quickness of the oxidation at these conditions. These data could be taken into account in new designs for nuclear fuel storage facilities given the risk of fuel exposure to air at this temperature. With lower oxygen partial pressures, it is possible to observe the lesser oxidised phases UO_{2+x} and U_3O_7 . However, the temporal frame of the reaction is very short, being U_3O_8 the only oxide observed from 20 min even with the lowest oxygen concentration, 0.1%. Earlier in this case, UO_{2+x} spectra, with the x value continuously increasing, are acquired during approximately 10 min. At this point, the transformation to U_3O_7 seems to happen, obtaining a couple of spectra corresponding to this phase during the period 10-20 min (Figure 4.2.6A). The increase of the oxygen presence results in a shortening of the time

where the lower oxides are observed, obtaining U_3O_8 spectra from around 15 min with 1% O_2 and from around 10 min with 10% O_2 (Figure 4.2.6B and C, respectively).

This tendency, maintained through all the oxygen concentrations studied, emphasises the importance of the fuel temperature, and points out to put efforts on limit the fuel temperature rather than partially inertise (above 0.1% O_2), which would yield more benefits in preserving fuel matrix integrity. These results, agreeing with published studies using other techniques, such as those reported by Olsen *et al.* [28], who by using XRD observed the formation of a 100% of U_3O_8 at 400°C within 2h when any oxygen is present (the lack of a measurement at shorter times in the referenced study makes a deep comparison of the early apparition of U_3O_8 impossible). This behaviour is comparable to the oxidation of irradiated fuel, as demonstrated in the study by Hastings *et al.* [22]. They studied the oxidation of CANDU fragments irradiated at low burnup levels (8 GWd/tU) in air, in the same temperature range than this work (200-400°C). At 200°C, they did not observe any weight change during 24 h of experiments. However, at 400°C, they reported a severe sheath splitting due to the formation of U_3O_8 in less than 24 h.

At intermediate temperatures, *i.e.* 300°C, the formation of U_3O_8 is not as fast as in the previous case, but this phase is still clearly observed from a time around 24 h in all the cases. At 300°C, the effect of decreasing the oxygen concentration is to delay the formation of U_3O_8 , extending the temporal frame when UO_{2+x} and U_3O_7 are present. Thus, at the lowest oxygen concentration, 0.1% O_2 , UO_{2+x} spectra are acquired during the first 140 min approximately, with increasing x . From that moment, U_3O_7 becomes visible and appears until around 10 h of experiment, when U_3O_8 becomes principal. When increasing the oxygen partial pressure, the observed results indicate that the time range where UO_{2+x} is observed is increasingly shorter, and U_3O_7 phase appears earlier. However, the final result of every experiment at this temperature is the formation of U_3O_8 at a time around 16 h for the lowest oxygen concentrations, and even earlier when the amount of oxygen present is higher. This would suggest that the temperature dependence over oxygen content on the oxidation of UO_2 is therefore more evident at relatively high temperature, especially from 300°C. In fact, it seems that once that a certain threshold temperature for the formation of U_3O_8 is exceeded, this phase will be formed even with low oxygen availability (as low as 0.1%). Therefore, the effect of this oxygen decrease will be to delay the presence of U_3O_8 .

Result 2. Studying UO_2 oxidation at upgraded conditions



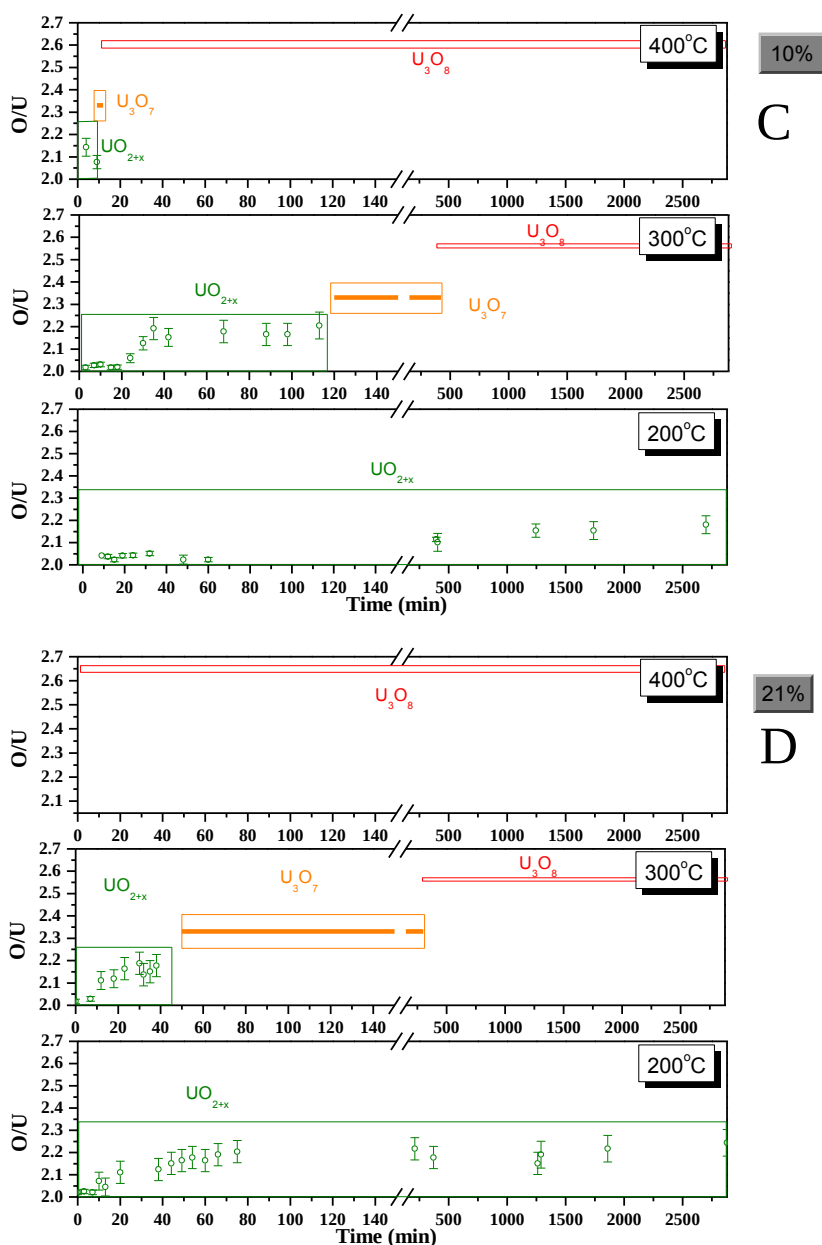


Figure 4.2.6. O/U ratio vs reaction time in the different temperatures and oxygen partial pressures studied.

From the analysis of Figure 4.2.6D, one may note that the observed change in the O/U ratio resembles the typical sigmoidal behaviour characteristic of the oxidation. In a similar time scale, this pattern has been found in thermogravimetric analysis of UO_2 oxidation [7]. This fact reinforces the use of Raman as a suitable technique for studying this reaction, and validates the conclusions obtained here.

4.2.4. Conclusions

In this work, representative oxidation experiments with the aim to determine the combined effect of partial inertisation and temperature on the formation of U_3O_8 are performed in order to be considered in new design options of fuel storage facilities. Specifically, we study the impact of the oxygen partial pressure (0.1 to 21% O_2) and temperature (200-400°C) in the oxidation of fresh UO_2 (labelled as P3 in the reference [30]). With this purpose, Raman spectroscopy has been selected as a suitable technique, given first its capacity to analyse the oxidised compounds of UO_2 , second its application at *in-situ* conditions to follow the formation of the oxidation products in a very long time frame (from min up to days), and third this protocol could be implemented in the analysis of irradiated nuclear fuel.

At 200°C, no quantitative oxidation of UO_2 to higher oxides has been detected, neither U_3O_7 nor U_3O_8 , at any of the different atmospheres studied. Given the conservativeness of fresh fuel compared to irradiated fuel, this temperature ensures a low oxidation of SNF matrix that can be considered as a “first barrier” for the spent fuel dry management activities, regardless of the content of oxygen at which the fuel may be exposed.

On the other hand, at 400°C the oxidation of UO_2 is extremely fast whatever the oxygen concentration may be. In fact, although the lower oxygen slows down the reaction, even at oxygen concentrations as low as 0.1%, the formation of U_3O_8 occurs within 2 h. The larger volume of this phase could entail stresses on the SNF clad, which is the second barrier to prevent radioactive material release.

At intermediate temperatures, *i.e.* 300°C, the decrease of the formation of U_3O_8 is clearly observed, confirming the predominant effect of the temperature over the oxygen concentration at which UO_2 is exposed. However, U_3O_8 is detected within 24 h for all oxygen concentrations studied.

All in all, the results of this work indicate that temperature is the main factor of the oxidation of fuel while the oxygen concentration of the atmosphere, up to 0.1% O_2 , only affects the reaction rate without preventing it to occur. As a consequence of the present work it could be noticed that, in order to avoid the oxidation of the fuel matrix to U_3O_8 , keeping the fuel at low temperatures could be very effective. On the other hand, the

control of the oxygen-content (above 0.1% O₂) in the atmosphere where the UO₂ is exposed is less effective.

Finally, in order to extrapolate these conclusions to other conditions, further research not only studying other intermediate temperatures, but also other characteristics of the starting materials and involving other characterisation techniques will be carried out.

4.2.5. Methods

The fuel analogues studied consisted of powdered UO₂ samples coming from monoliths of unirradiated sintered UO₂ pellets that were crushed into powder in a Mixer Mill MM 400 (Retsch). The resulting powder was used with no further sieving treatment, giving place to a material with a wide particle size distribution (average particle size 5.64 ± 0.07 μm , but with particle's sizes ranging from ~ 1 μm up to ~ 10 μm). Specific surface area of the material was measured by applying the BET method (with N₂) and was found to be 0.18 ± 0.01 $\text{m}^2 \cdot \text{g}^{-1}$. Initial O/U of the substrate is 2.002 ± 0.001 . This material has been characterised in detail in our laboratory (labelled as P3 in [30]).

The gases used in this study with different oxygen concentration were supplied by Air Liquide (France). These gases comprised a mixture of oxygen and nitrogen in different proportions, giving place to three special mixtures as follows: 0.1% O₂-99.9% N₂; 1% O₂-99% N₂; 10% O₂-90% N₂. Finally, synthetic air was also provided by Air Liquide, with a licensed composition of $20 \pm 1\%$ O₂, being the rest N₂. An extra gas line of Ar is used when inert conditions are required. A certified purity higher than 99.999% is applied for all the gases.

Raman spectra were acquired by means of a Horiba LabRAM HR Evolution spectrometer (Jobin Yvon Technology). A red He-Ne laser beam ($\lambda = 632.8$ nm) was focused onto the sample through the 50x objective of an Olympus BX41 microscope. The scattered radiation was then collected with the same objective, dispersed with a 600 grooves/mm grating, and finally detected with a Peltier-cooled CCD detector (256×1024 pixels). For the *in-situ* measurements, the sample was placed inside a Linkam THMS600 temperature-controlled pressure stage. This stage allows maintaining the sample in a closed environment and focusing the incident radiation through a central aperture in order to acquire the spectra. The sample temperature is controlled by using a

T95-Linkpad temperature controller, which provides temperature stability better than 0.2°C. Atmospheric environment can be selected changing the gas tubes in a quick-fit.

The experimental work has consisted, first, of placing the sample inside the Linkam stage and closing the lid assembly. After overnight inertisation of the chamber with a low flow of Ar gas in order to remove the oxygen, the sample is heated at 10°C·min⁻¹ up to the experimental temperature (*i.e.* 200, 300 or 400°C), still with the Ar atmosphere to prevent undesirable oxidation. Once the chosen temperature is reached, it is maintained during 30 min to allow thermal stabilisation of the sample. After that, the gas is switched to the specific oxidant gas, depending on the experiment (*i.e.* 0.1, 1, 10 or 21% O₂). Raman spectra are acquired continuously at random locations of the sample surface within typically 50 seconds of acquisition and 2 accumulations in the 100-1300 cm⁻¹ range. These acquisition conditions have been confirmed as low enough to not oxidise the samples by local heating [41].

Acknowledgements

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4.2.6. References

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SUPPLEMENTARY INFORMATION

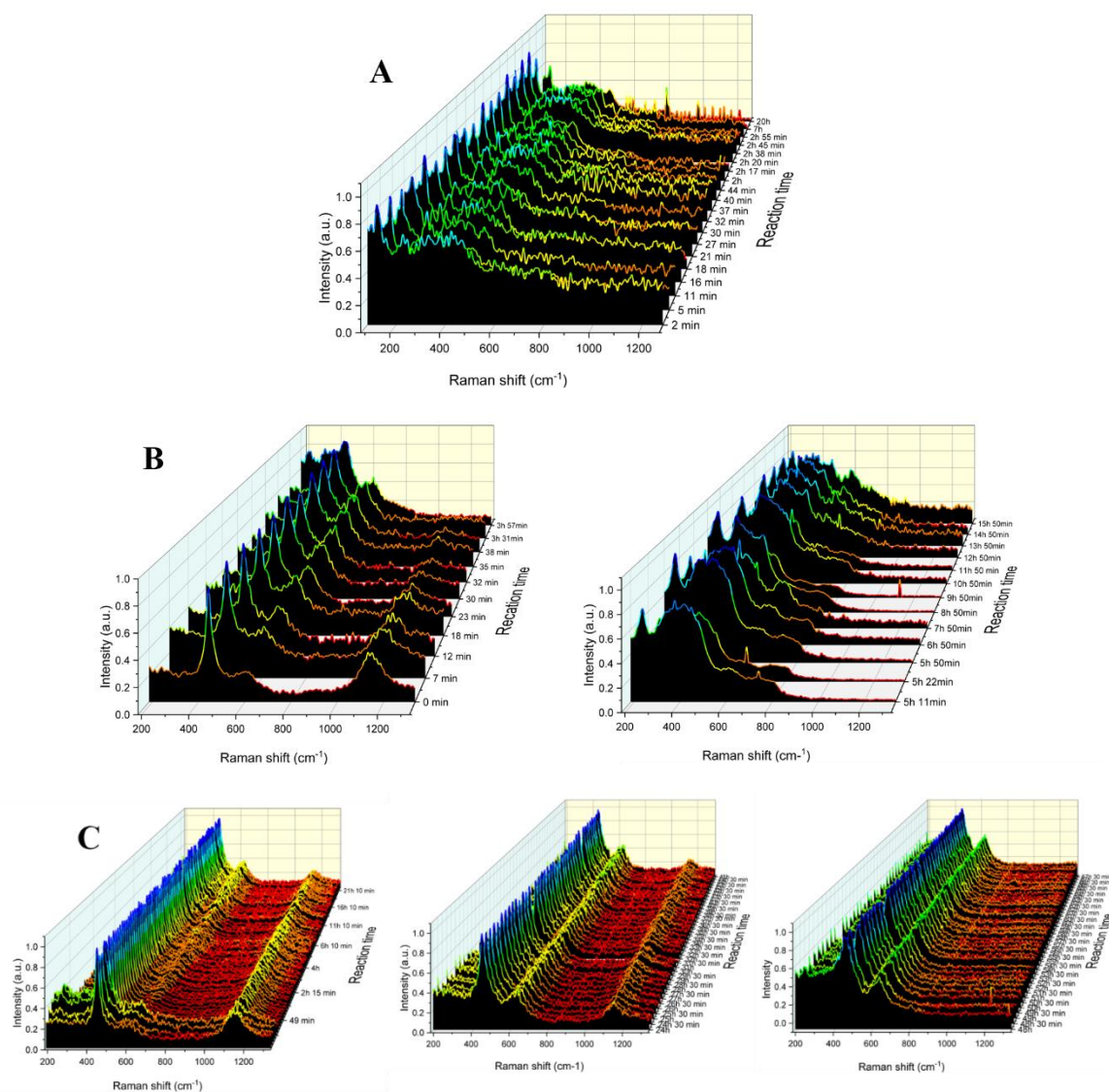


Figure 4.2.S1. Raman spectra obtained at 21% of O_2 at 400°C (A), 300°C (B) and 200°C (C).

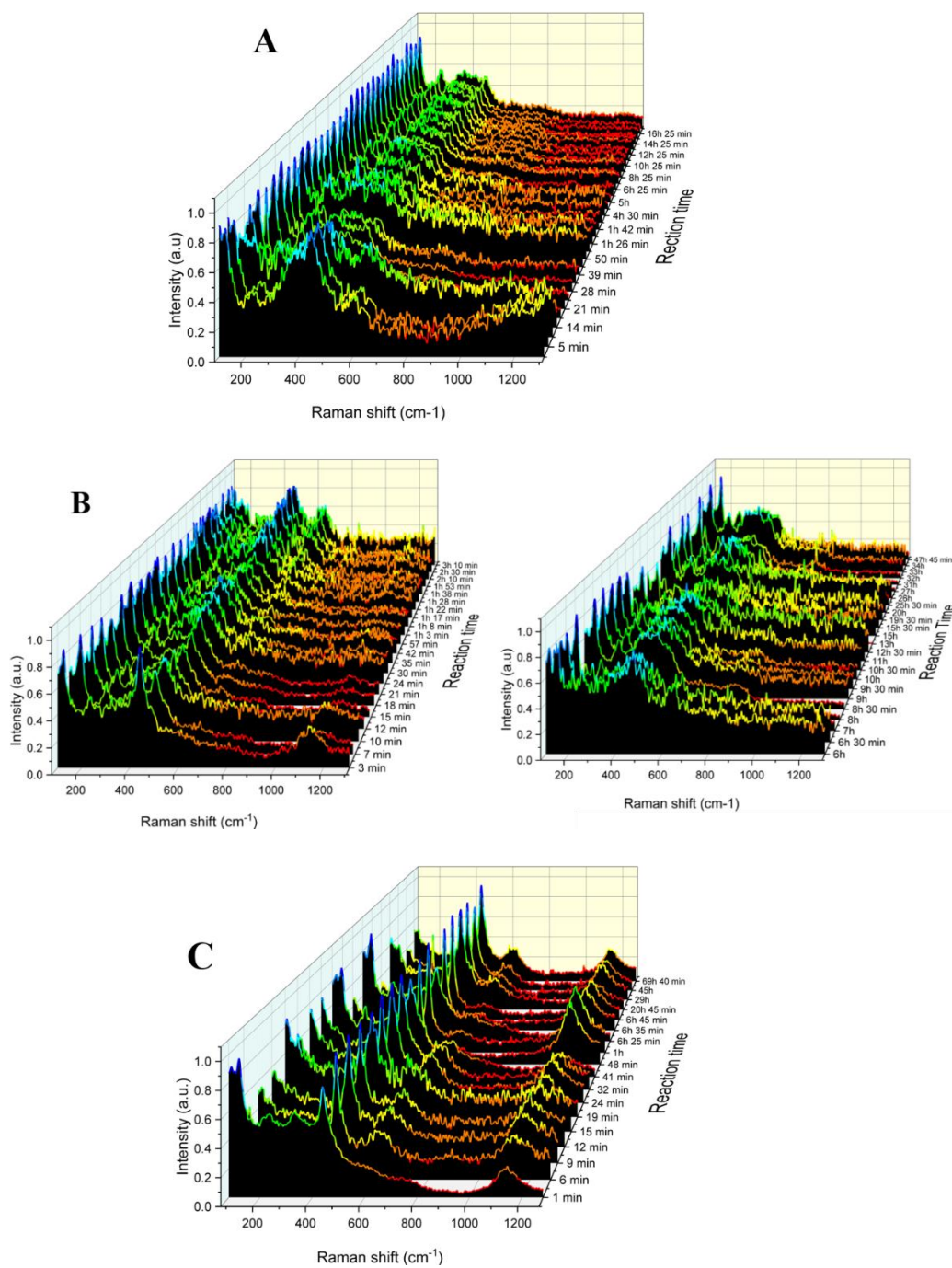


Figure 4.2.S2. Raman spectra obtained at 10% of O_2 at 400°C (A), 300°C (B) and 200°C (C).

Result 2. Studying UO_2 oxidation at upgraded conditions

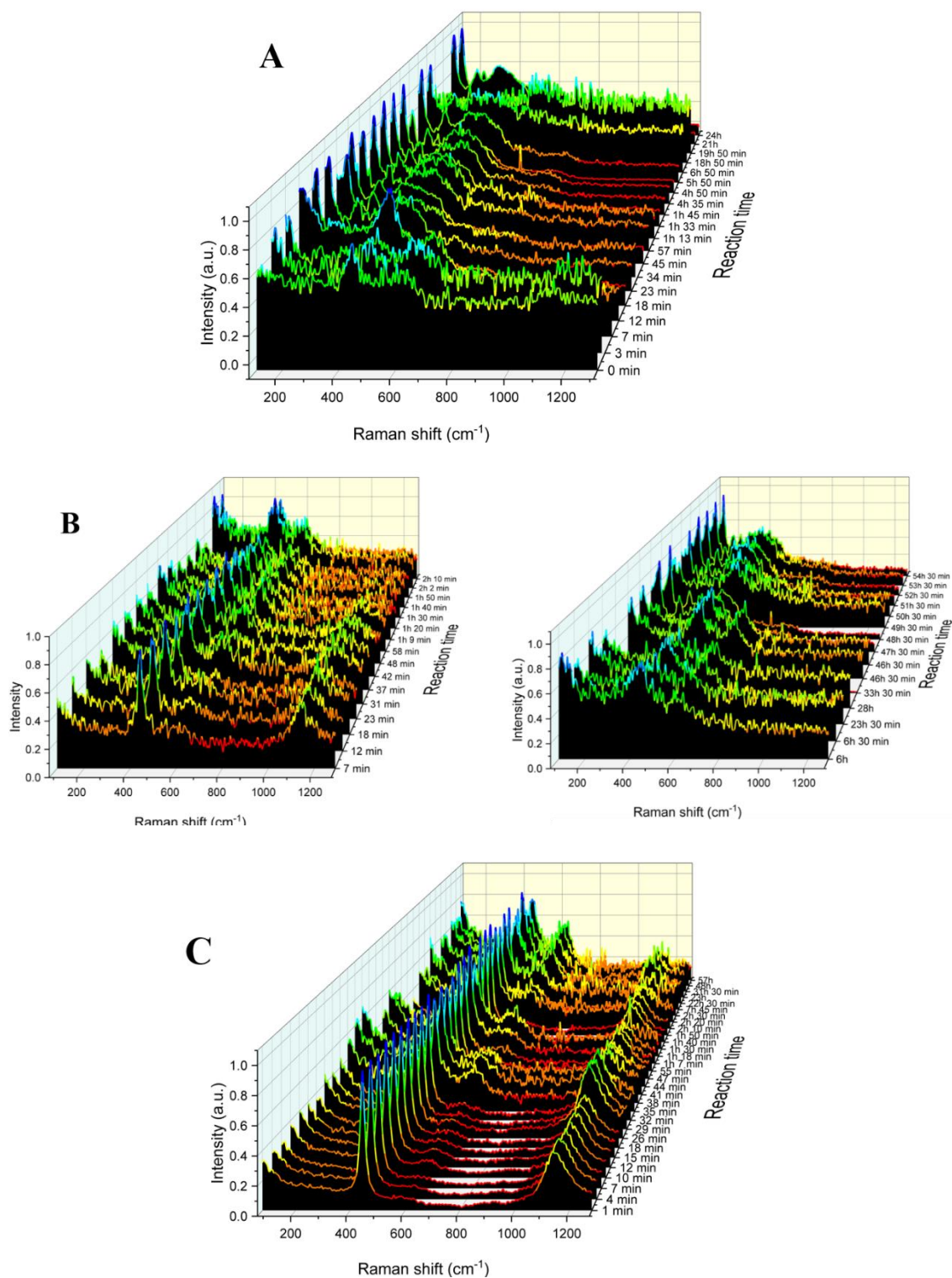


Figure 4.2.S3. Raman spectra obtained at 1% of O_2 at 400°C (A), 300°C (B) and 200°C (C).

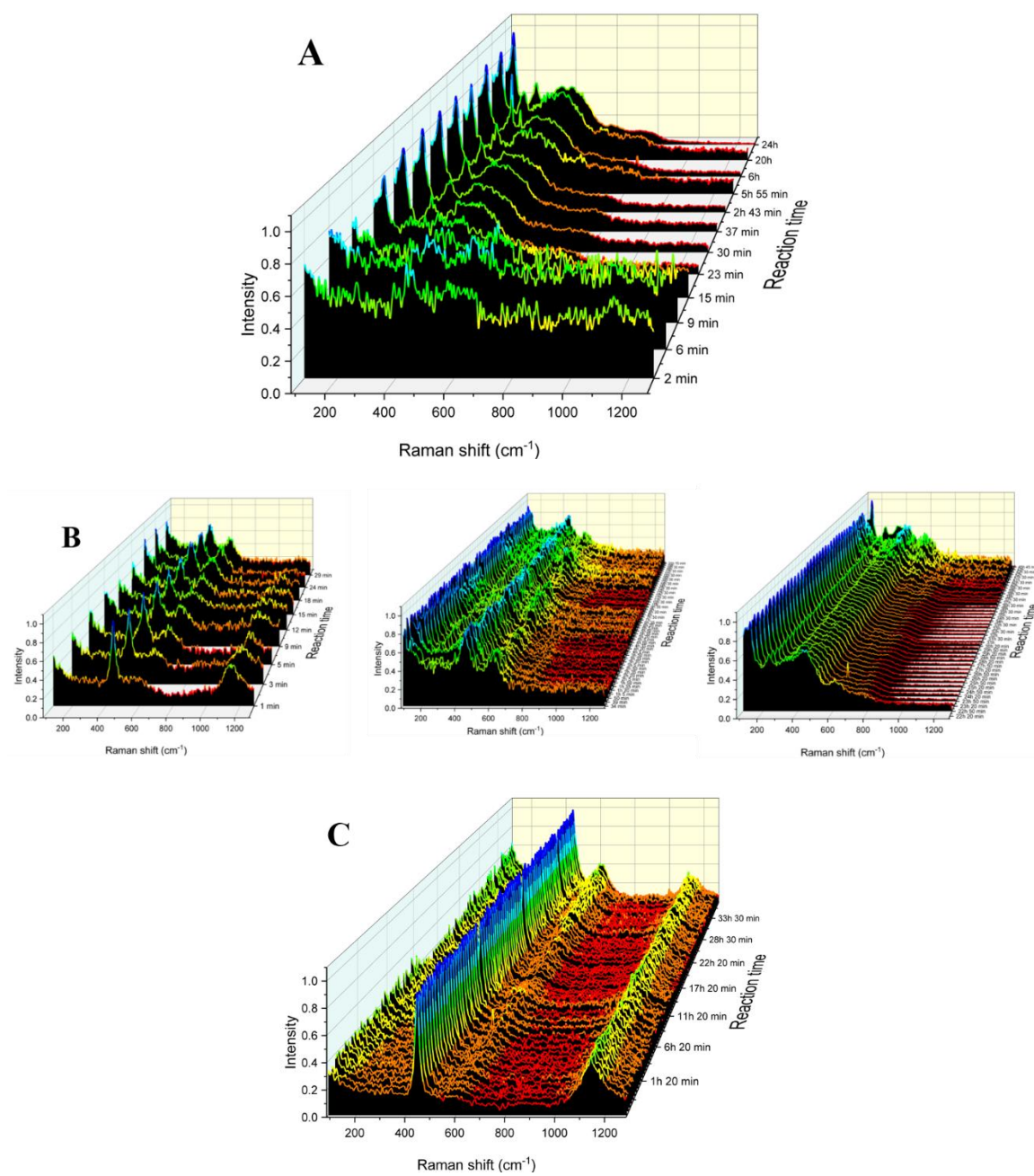


Figure 4.2.S4. Raman spectra obtained at 0.1% of O_2 at 400°C (A), 300°C (B) and 200°C (C).

Result 3

Manufacturing and characterising new nuclear fuels

Published as “Raman spectroscopy coupled to principal component analysis for studying UO_2 nuclear fuels with different grain sizes due to the chromia addition”, **A. Milena-Pérez, L.J. Bonales, N. Rodríguez-Villagra, S. Fernández, V.G. Baonza, and J. Cobos.** *Journal of Nuclear Materials* 543 (2021) 152581

4.3. Result 3. Manufacturing and characterising new nuclear fuels

Abstract

Current necessities of nuclear power plants have led to increase burnup of the fuel during operation. In this context, some undesirable processes, such as a higher release of gaseous fission products, may occur. New UO_2 -based fuels are being developed by adding doping agents. Chromia (Cr_2O_3) has proved to considerably enhance grain growth during sintering, and thus promote the retention of these fission products. The study of these Cr-doped UO_2 fuels at *in-situ* conditions would allow testing the real performance of the fuel in operating conditions. The existence of Raman portable instruments makes this scenario feasible. But first, the measurement protocols need to be developed. Therefore, in this paper, we explore the use of Raman spectroscopy as an approach for the analysis of the effect of Cr_2O_3 addition in a set of UO_2 - Cr_2O_3 sintered pellets. The validity of Raman is demonstrated by using Principal Component Analysis (PCA). Three Principal Components describe 98.8% of the total variance of the data, and they are related to the main Raman modes of the samples. In addition, SEM images have shown the presence of bigger precipitates of Cr_2O_3 not only when the solubility limit of Cr^{3+} is exceeded, but also when it is not reached. By XRD, the well-known Vegard behaviour is observed, and a solubility limit of Cr^{3+} dissolved into the UO_2 matrix is found to be (748 ± 16) ppm for the particular sintering conditions used.

4.3.1. Introduction

Nowadays, current necessities of the nuclear facilities have led to increase the burnup in operating reactors, with the aim of making the most of the fuel power in those UO_2 -based fuels. In fact, current Light Water Reactors (LWR) are typically designed to achieve a burnup about 50 GWd/tU, but with newer fuel technology (*i.e.* doped fuels), these same LWRs are now capable of achieving up to 60 or even 70 GWd/tU with the present enrichment limit (between 3-5% ^{235}U) [1-3]. However, several processes need to be taken into consideration at high burnup. Especially important are the fission gas release and the pellet-cladding interaction, which decreases the flexibility of the reactor, *i.e.*, reduces the capability of the reactor to extend the burnup in the established security requirements [4]. Both processes could compromise the safety margins in nuclear power plants, and needs to be minimised.

In view of the events that occurred at the Fukushima Daiichi nuclear power plant in March 2011, one of the most accepted concepts to this problem is the use of improved fuels referred as Accident-Tolerant Fuel (ATF) [5], made by the refinement of the fuel microstructure by using different dopants and clad designs. The purpose of these additives is to increase the fuel resistance by means of an enlargement of the average grain size of the matrix (densification) and the plasticity of the fuel. It is known that this change in grain size alters the diffusion phenomena inside the fuel pellets, causing an increased retention of the gaseous products inside the ceramic [6].

In order to address this issue, different dopants have been considered through the years, including oxides of chromium [4, 7-10], magnesium [8, 11], niobium [12-14] or titanium [15, 16], among others. In addition, several investigations have been carried out studying the performance of some of these dopants together, *e.g.* aluminosilicates [17]. Among them, chromia (Cr_2O_3) doped fuel has turned out to be an especially effective alternative to traditional UO_2 fuel (today used in LWRs) in the grain growth process during sintering, also showing a great improvement on pellet-cladding interaction and fission gas retention [4, 10, 18, 19]. In fact, adding an amount of chromia close to the solubility limit has demonstrated to improve this behaviour [10].

A wide variety of characterisation techniques has been set to study chromia doped fuels [4, 6, 7, 10]. Among them, X-Ray Diffraction (XRD) is the most frequently applied to deduce if the fluorite-type cubic structure is maintained with the increasing Cr_2O_3 concentration [4]. Scanning Electron Microscopy (SEM) has also been widely used in Cr_2O_3 doped fuels, mainly to confirm the increased grain size of the Cr-doped samples as a consequence of the chromium effect [7]. Some other techniques, such as X-Ray Photoelectron Spectrometry (XPS), Electron Microprobe Analysis (EPMA) and Differential Scanning Calorimetry (DSC) have been also used in order to characterise Cr-doped fuels [1, 10, 20].

On the other hand, as far as our knowledge, previous studies are lacking in the literature about the use of Raman spectroscopy to characterise Cr_2O_3 -doped UO_2 , in spite of have been widely used in the characterisation of spent nuclear fuels analogues, such as UO_2 doped with different fission products, including gadolinium [20-22], neodymium [23, 24], lanthanum [25], cerium [26], or SIMFUEL (SIMulated high burnup FUEL, a spent nuclear fuel surrogate based on UO_2 doped with fission products) [20, 27]. This

technique meets two relevant features: it allows focusing on a specific area of few micrometers size of the sample, and it provides a spectral fingerprint to distinguish between chemically similar compounds. However, the main advantage of this technique is the possibility to perform *in-situ* measurements with the aim to track different processes that may occur to the samples, such as oxidation, thermal decomposition, hydrolysis reactions, etc., in controlled conditions of temperature and gaseous atmosphere. This property allows studying different materials in their original conditions, due to the existence of portable Raman instruments which could accomplish these *in-situ* measurements; *i.e.* real Cr-doped fuel could be studied and its performance could be tested. Thus, in this work we take advantage of Raman spectroscopy combined with multivariate analyses. The advent of spectroscopy techniques coupled with multivariate analysis, such as Principal Components Analysis (PCA) is being increasingly used in more and different fundamental and applied fields [28-32]. Nowadays, the multivariate analysis is not only performed by sophisticated tools. In fact, due to the development of commercial statistical software, it is possible to perform a PCA in an easy and fast way [33].

In order to achieve these goals, measurements protocols need to be developed and optimised, so they can be applied at *in-situ* conditions. Therefore, in this paper our work of Raman spectroscopy combined with PCA is completely new in the field of the solid dissolution of Cr_2O_3 into the UO_2 matrix. This work is part of a broader investigation of doped fuels within the frame of the European DisCo project (EC H2020 program, grant agreement 755443), where once a complete Raman analysis is performed for this material, *in-situ* reactions will be studied to understand the behaviour of the dopant and the improvement on the fuel properties.

In this work, a series of solid-solutions of UO_2 and $\text{U}_{1-y}\text{Cr}_y\text{O}_{2-x}$ pellets, prepared in order to cover all possible scenarios concerning the solubility of Cr_2O_3 in the UO_2 matrix [4, 10], including both the solid solution of Cr_2O_3 in the matrix (solubility limit not reached) and the presence of chromia precipitates (beyond the solubility limit). These samples were analysed and characterised by SEM and XRD. Then, Raman spectroscopy as an analytical technique, and PCA as a multivariate analysis method were used to evaluate whether Raman spectroscopy could be employed to discern between fuels with different grain sizes due to the addition of chromia. Once we have demonstrated that it

is possible to make use of this spectroscopy technique, a detailed evaluation of the Raman spectra is performed.

Thereby, the work is structured as follows: in Section 4.3.2, the fabrication method used to obtain the samples and the characterisation techniques used are described. In addition, the characterisation of raw materials is presented. In Section 4.3.3, SEM images are used to evaluate the effect of chromium in the UO_2 fuel in terms of the increase in grain size, and XRD results are discussed. Also in this section, PCA results show the applicability of Raman as a tool to characterise Cr-doped fuel, and Raman spectra are presented and described in detail. Finally, the conclusions of this work are presented in Section 4.3.4.

4.3.2. Materials and methods

4.3.2.1. Sample preparation

UO_2 and Cr_2O_3 powders were provided by ENUSA and Alfa Aesar, respectively. UO_2 was thermally annealed in a 4.7% $\text{H}_2\text{-N}_2$ atmosphere at 1100°C to attain stoichiometric $\text{UO}_{2.00}$. UO_2 was mixed with weighted amounts of Cr_2O_3 , together with 1^w% of EBS (Ethyl Bis Stearamide, $\text{C}_{38}\text{H}_{76}\text{N}_2\text{O}_2$, supplied by Tokyo Chemical Industry) as binder and lubricant [34], using low-energy ball milling. These batches of mixed powders were then blended for 1 minute at 15 Hz in the mixer mill. Then, following a conventional metallurgical procedure, the mixtures obtained were subjected to uniaxial pressing with an applied pressure of 700 MPa in a press of 25 tons C256C (Power team, Johannesburg, South Africa). After that, a heating process under a 4.7% $\text{H}_2\text{-N}_2$ flow –in order to avoid UO_2 oxidation– was conducted on all the green pellets. All disks were then calcined in three stages (100, 300 and 500°C) at $10^\circ\text{C}\cdot\text{min}^{-1}$ and held up to 4 hours to remove the incorporated EBS, followed by the sintering process at 1675°C for 4 hours ($5^\circ\text{C}\cdot\text{min}^{-1}$). Finally, polishing and thermal annealing were carried out to reveal grains (10 minutes at 1590°C under a 4.7% $\text{H}_2\text{-N}_2$ atmosphere). This fabrication process has been previously tested in our laboratory [35]. As a result, a series of Cr_2O_3 -doped UO_2 solid solutions were obtained. An undoped UO_2 sample was also prepared following the same procedure. Prior to the sintering of the samples, raw powders have been characterised in terms of the Specific Surface Area (SSA) by BET with N_2 (ASAP

2020 Micromeritics) and the mean particle size by Laser Diffraction (Malvern, Series 2600). The results of this characterisation can be seen in Table 4.3.I².

Table 4.3.I. Raw materials characterisation.

Material	SSA (BET) (m ² ·g ⁻¹)	Average particle size (µm)
UO ₂	0.95±0.02	15.23±0.57
Cr ₂ O ₃	3.47±0.02	2.09±0.34

In addition, starting powders have also been measured by Raman spectroscopy and observed by SEM. Raman spectrum of UO₂ powder (Figure 4.3.1 at top) shows the well-known features of uranium dioxide: a) the triply degenerate T_{2g} mode at 445 cm⁻¹, b) the almost indistinguishable LO mode at about 570 cm⁻¹, and c) the first overtone of the LO mode (2LO) centred about 1140 cm⁻¹ [36-38]. These bands are summarised in Table 4.3.II (a-c). In addition, Cr₂O₃ spectrum (Figure 4.3.1 at bottom) shows the classic bands and features described in the literature [39-42]. The corresponding Raman shifts of both materials are shown in Table 4.3.II (d-j), together with the Raman modes that represent. In both cases, spectra shown in Figure 4.3.1 are the sum of 10 spectra of each powder.

Table 4.3.II. Raman modes of starting powders used in this work.

Experimental Raman shifts for UO ₂ (±1 cm ⁻¹)	Raman shifts for UO ₂ (cm ⁻¹) by other authors [37, 38]	Raman mode assigned (UO ₂) [37, 38]
a) 445	445 [37, 38]	T _{2g} [37, 38]
b) 570	575 [37]	LO phonon [38]
c) 1140	1150 [37, 38]	2LO phonon overtone [37, 38]
Experimental Raman shifts for Cr ₂ O ₃ (±1 cm ⁻¹)	Raman shifts for Cr ₂ O ₃ (cm ⁻¹) by other authors [39, 40, 42]	Raman mode assigned (Cr ₂ O ₃) [39, 40, 42]
d) 303	303 [42]	A _{1g} [42]
e) 344	348 [42]	E _g [42]
f) 390	397 [42]	E _g [42]
g) 524	530 [42]	E _g [42]
h) 543	547 [42]	A _{1g} [42]
i) 601	609 [42]	E _g [42]
j) 680	691 [39, 40]	CrO ₂ [39, 40]

² It is important to highlight that the average particle size presented in Table 4.3.I refers to the average diameter of a discrete solid material, in this case a powder, and it is not related with the grain size, which refers to the average diameter of the individual crystal orientations located in poly-crystalline materials, and measured by SEM and presented further on for sintered pellets.

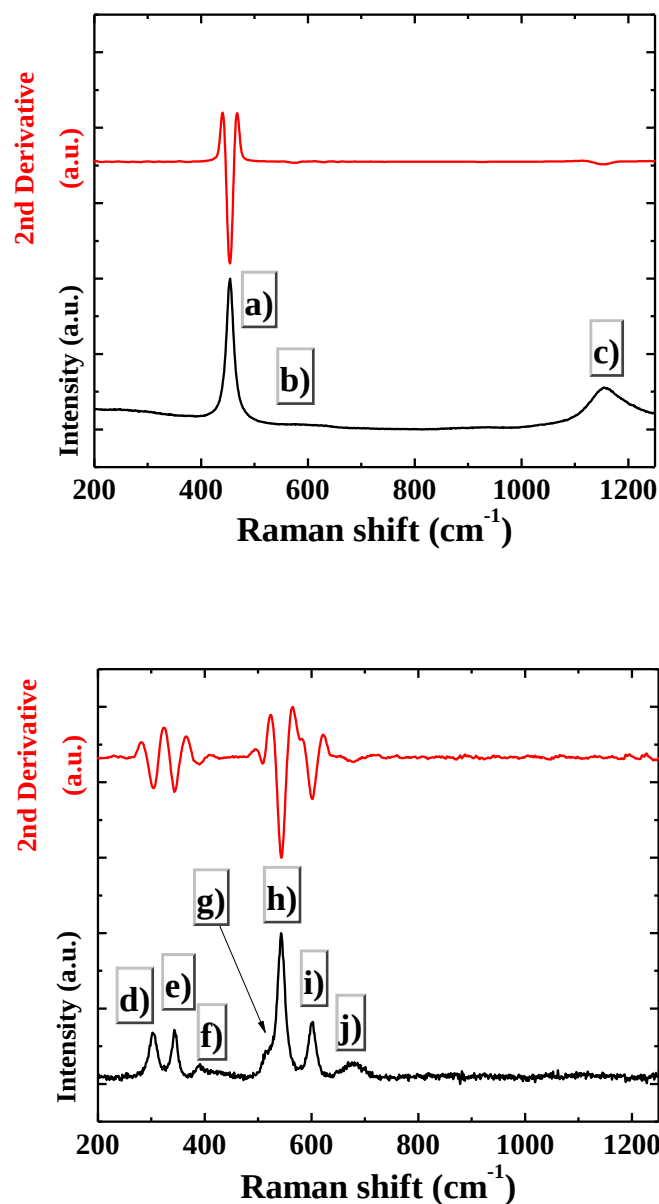


Figure 4.3.1. Raman spectra of UO₂ (top) and Cr₂O₃ (bottom) and 2nd derivative curves. Labels a) to j) correspond to the Raman modes found in the spectra, assigned in Table 4.3.II.

Starting powders have been characterised, in terms of their XRD patterns, and compared with the standards, retrieved from ICDD references 03-065-0285 (UO₂) and 00-006-0504 (Cr₂O₃), in order to confirm the purity of the materials. The results can be seen in Figure 4.3.2.

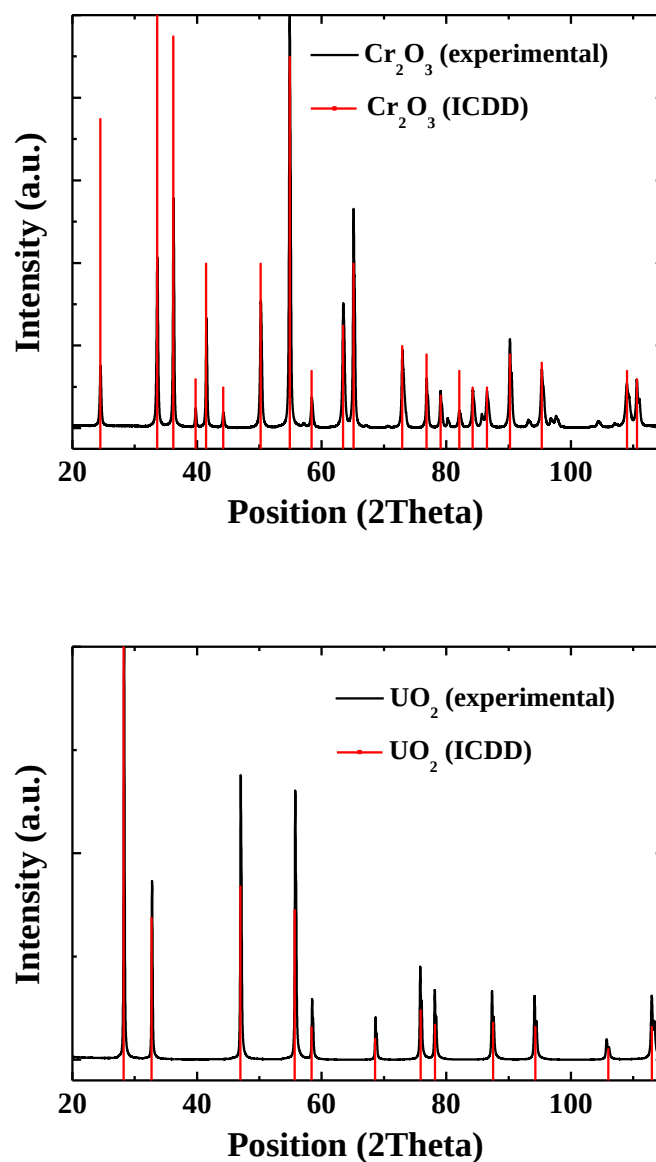


Figure 4.3.2. XRD patterns of starting Cr₂O₃ (top) and UO₂ (bottom), together with their respective ICDD reference data.

Finally, SEM images have been also acquired from each starting powder. A representative example of each one is shown in Figure 4.3.3. In both cases, SEM observations reveal that the powder morphology consists of blunt and round particles, similar to microspheres. This shape is appropriated in the sintering of the pellets [43]. It is also remarkable the fact that particle size of Cr₂O₃ is smaller than UO₂, as presented in Table 4.3.I and seen in Figure 4.3.3.

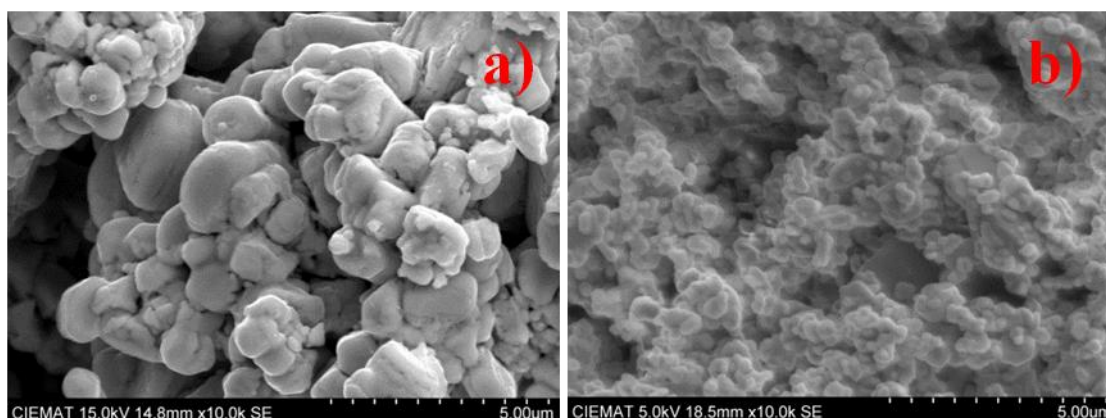


Figure 4.3.3. SEM images of starting powders of a) UO_2 and b) Cr_2O_3 .

4.3.2.2. SEM

Sample surface morphology has been visualised by means of a TM4000 Plus SEM by HITACHI, using a working voltage of 10 kV. The shape of the grains formed with different amounts of dopant was observed, as well as grain size of the samples was estimated by means of the linear intercept method [44]. The microscope is equipped with a Back-Scattering Electrons (BSE) detector, which provides clear images about pellets surfaces components, and a Secondary Electrons (SE) detector, which gives information about the relief of the surfaces. The combination of both has allowed us identifying different precipitates on the surface, which have been related to the segregation of Cr_2O_3 in the pellets.

4.3.2.3. XRD

XRD characterisation was performed by means of a Bruker D8 Advance Eco diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda=1.54056 \text{ \AA}$) and operating at 40 kV and 25 mA. Bragg-Brentano configuration geometry was used. The 2θ range covered was from 20° to 120° , with 0.015° scanning steps and a primary slit of 0.5° . Diffracted radiation was collected by a 1-dimensional Lynx Eye Position Sensitive Detector (PSD). The detector angular aperture was of 2.9° . Four to six XRD patterns were acquired under identical conditions for each sample. The uncertainty of each XRD measurement was estimated as the standard deviation of the individual measurements. Identification of each phase in the samples has been carried out by comparison with the ICDD data files. Finally, lattice parameter of each sample has been calculated by using the unit cell refinement process provided by the software TOPAS (Bruker Analytical X-Ray Systems), taking

the $Fm\bar{3}m$ space group. All systematic sources of error, such as zero displacement, peak positions and goniometer shift, have been corrected by both a correct alignment of the instrument and measurement of a certified pattern of Al_2O_3 .

4.3.2.4. Raman Spectroscopy and PCA

Raman spectra were acquired by using a Horiba LabRAM HR evolution spectrometer (Jobin Yvon Technology) using a He-Ne laser with wavelength equal to 632.8 nm. The laser beam was focused onto the sample through the 50x objective of an Olympus BX41 microscope. The sample is housed in the stage of the microscope without any previous treatment after the fabrication process and the polishing stage. A typical spectrum was obtained in the range $150 - 2500\text{ cm}^{-1}$ within 40 seconds of acquisition time. These acquisition conditions have been confirmed as low enough to not oxidise the surface of the pellets by local heating [45]. Acquired spectra were recalibrated by using the emission lines of a Ne arc-lamp. 10 spectra were acquired for each sample at different locations of the disks due to the heterogeneity of the pellets.

For the processing of the data, acquired spectra were subjected to multivariate analyses. Specifically, Principal Component Analysis (PCA) was carried out with the use of the OriginPro software (OriginLab, Northampton, MA, USA). Raman spectra were first baseline corrected using LabSpec 6.5 Spectroscopy suite (Horiba Scientific).

4.3.3. Results and discussion

In this work, a set of chromia-doped UO_2 disks have been sintered with different Cr_2O_3 concentrations. Table 4.3.III shows the samples fabricated by this pathway.

Table 4.3.III. Definition of samples.

Labelled Material	Cr_2O_3 added (ppm)
UO_2	0
$UO_2\text{--}200Cr_2O_3$	200
$UO_2\text{--}600Cr_2O_3$	600
$UO_2\text{--}1000Cr_2O_3$	1000
$UO_2\text{--}6000Cr_2O_3$	6000

In the next sections, the effect of chromia on the sintered pellets will be studied by using the aforementioned techniques.

4.3.3.1. SEM results

4.3.3.1.1. Grain size

As stated previously, doping UO_2 fuel with chromia has demonstrated to improve the performance of the fuel during irradiation in the reactor by increasing grain size, which allows a higher retention of fission products. In the analysed samples, grain size has been measured by taking SEM images and then using the linear intercept method [46]. Representative images used for the calculation are shown in Figure 4.3.4, where an increase in the grain size can be seen when increasing Cr_2O_3 concentration and compared to pure UO_2 . Quantitative results of the average grain size in the doped pellets studied in this work are plotted in Figure 4.3.5.

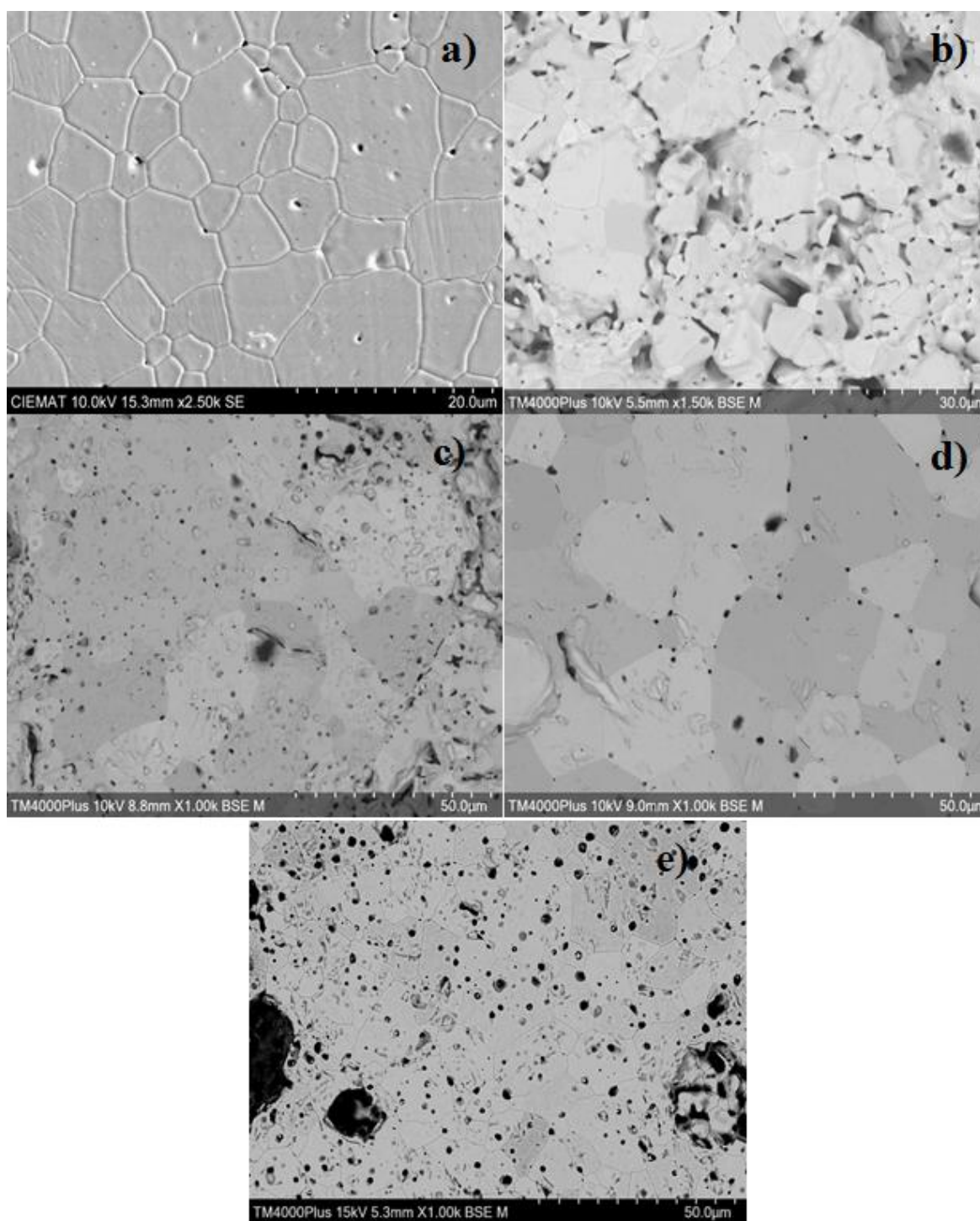


Figure 4.3.4. Representative SEM images of the analysed pellets: a) pure UO_2 , b) $\text{UO}_2_{200}\text{Cr}_2\text{O}_3$, c) $\text{UO}_2_{600}\text{Cr}_2\text{O}_3$, d) $\text{UO}_2_{1000}\text{Cr}_2\text{O}_3$, e) $\text{UO}_2_{6000}\text{Cr}_2\text{O}_3$.

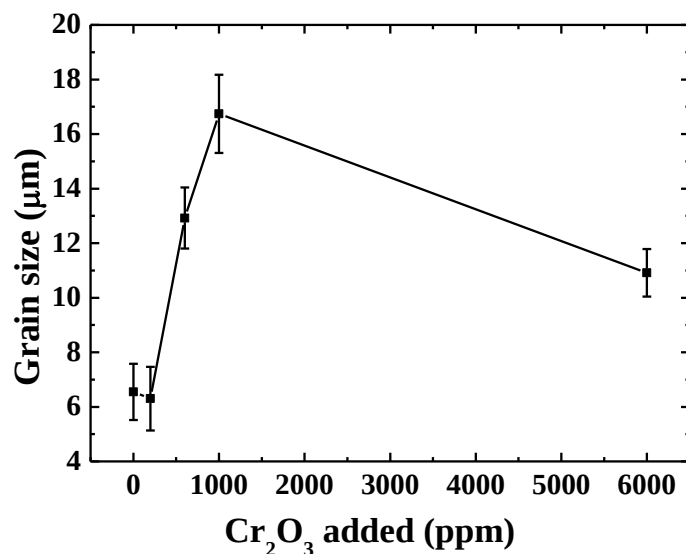


Figure 4.3.5. Average grain size of the studied disks vs Cr_2O_3 content. Uncertainty bands correspond to the repeatability of the measurements.

The distribution of the results shown in Figure 4.3.5 is analogous to grain size curves obtained in the same kind of fuels [7], but varying the absolute values, which depend on the specific sintering and annealing conditions (primarily heat treatment cycles: heating rates, holding time and temperature). Grains of undoped UO_2 (0 ppm of Cr_2O_3 added) have the same average grain size that the Cr-doped sample with the lowest amount of dopant (200 ppm). These similar values suggest that a significant concentration of dopant is needed to appreciate the effects on the grain growth. When increasing Cr_2O_3 concentration, grain sizes are higher, reaching a maximum when 1000 ppm of Cr_2O_3 are added. With even higher values of dopant, average grain size decreases (Figure 4.3.5), thus demonstrating that the solubility limit has been reached and no more chromium enters into the UO_2 matrix. Beyond this solubility limit, excess dopant remains as inclusions in the grain boundaries, as proposed by Bourgeois *et al.* [7]. The presence of such precipitates inhibits the growth of the grains, *i.e.* the maximum grain size is obtained when the solubility limit of Cr^{3+} in UO_2 is reached (Figure 4.3.6).

4.3.3.1.2. Segregated phases

For each sintered disk, SEM images have been taken covering the major part of the surfaces, looking for segregated phases on the pellet. More and bigger precipitates were observed in the samples with a higher Cr_2O_3 content, especially in the sample with the

highest concentration, 6000 ppm. This fact is expected taking into account that, in samples doped with 6000 ppm Cr_2O_3 , chromium is beyond the solubility limit in the UO_2 matrix. However, even though in the other samples the solubility limit has not been reached yet, several small precipitates are still observed. This could be a result of the slow incorporation kinetics of Cr into the UO_2 matrix, and therefore the precipitates could be associated to the remnant of the initial powder particles, that are not dissolved [4].

Two images of representative Cr_2O_3 precipitates are shown in Figure 4.3.6. As can be seen (Figure 4.3.6a), the morphology of the precipitate, its size and the fact that it appears in the grain boundary could lead us to propose a chromium segregation, according to Yang *et al.* [47] and Bourgeois *et al.* [7]. Increasing the Cr_2O_3 concentration and exceeding the solubility limit, sample doped with 6000 ppm, the amount precipitated is much bigger, although it still appears in grain boundaries, as expected (Figure 4.3.6b).

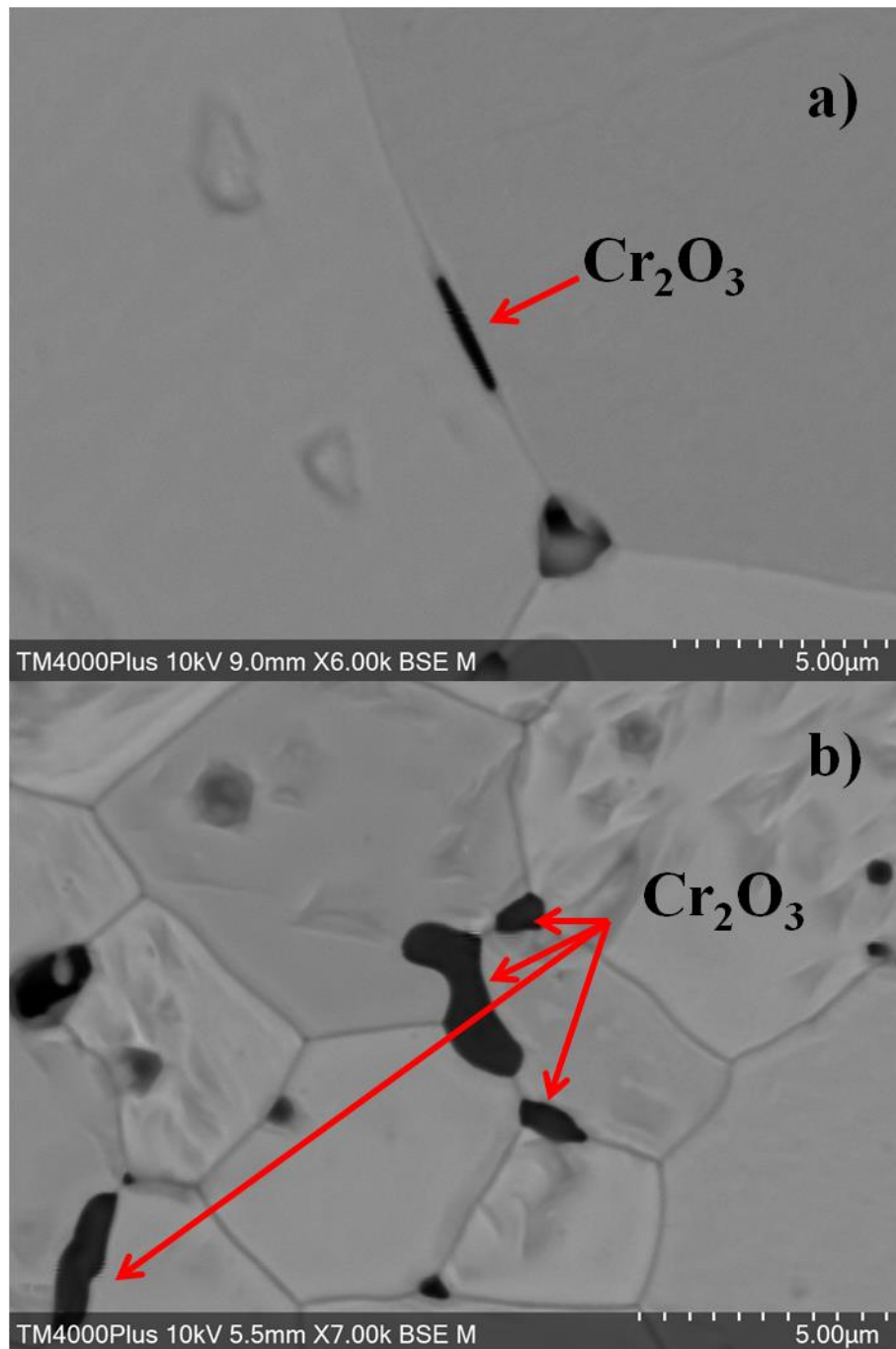


Figure 4.3.6. Back scattered SEM images of chromium precipitates in a grain boundaries in samples doped with a) 1000 ppm and b) 6000 ppm of Cr_2O_3 , respectively.

4.3.3.2. XRD

In order to study the lattice parameter evolution of the UO_2 pellets due to the presence of chromia, XRD was used and the corresponding diffractograms were obtained (Figure 4.3.7). It is known that the crystal structure of UO_2 is cubic, fluorite-type, so the lattice is characterised by only one lattice parameter (a). Diffraction peaks of all prepared

samples were acquired under the same conditions, and a value for the lattice parameters was obtained from each one by using the unit cell refinement method, applying the corresponding error corrections. They are plotted in Figure 4.3.8.

From the diffraction peaks of each sample (Figure 4.3.7a), it can be seen that there is a shift to higher 2θ values with increasing Cr_2O_3 concentration. This effect is clearly observed in the 113° doublet (Figure 4.3.7b), indicating that the lattice parameter of the doped sample is smaller than that of undoped UO_2 , and the higher the concentration of dopant is, the lower lattice parameter value. This fact supports the densification of the samples. This lattice contraction as a consequence of introduction of chromium into the cubic UO_2 lattice is consistent with XRD results from Cardinaels *et al.* [10].

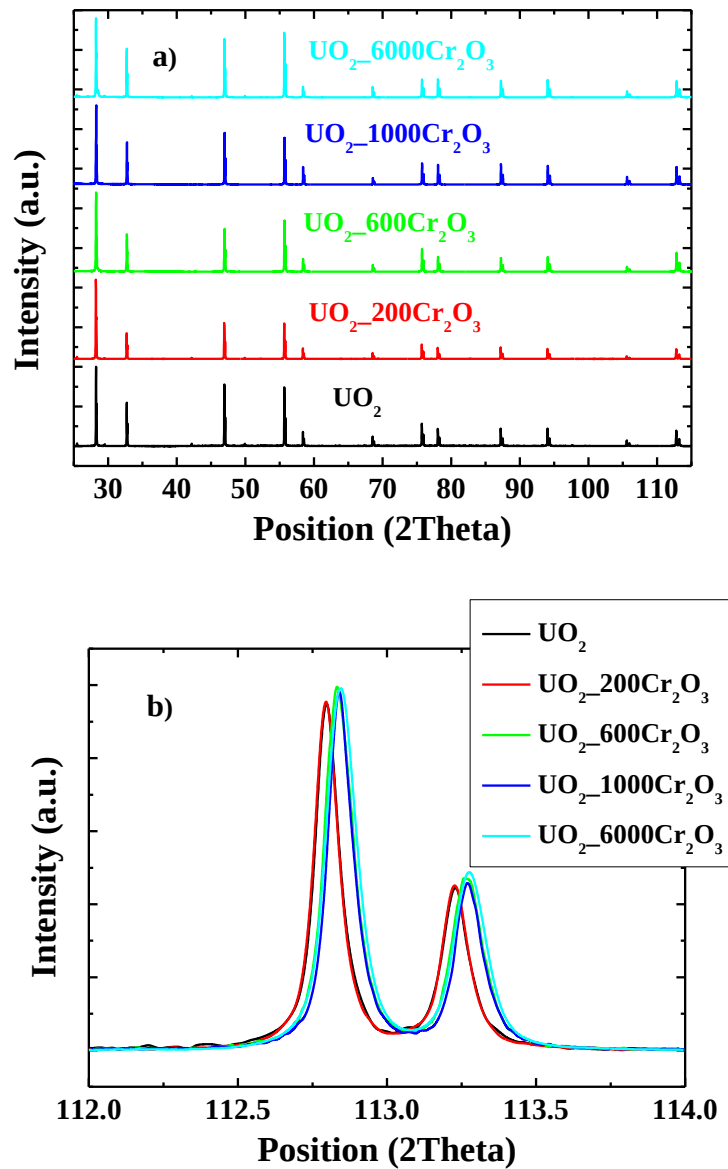


Figure 4.3.7. a) Diffraction patterns of the studied samples and b) the (531) $\text{K}\alpha_{1,2}$ doublet at 113° of the normalised diffraction patterns.

To clearly visualise this lattice contraction as a function of chromium concentration, in Figure 4.3.8 the lattice parameter of the fabricated pellets versus the chromium mixed with the UO_2 in the monoliths fabrication is plotted. It can be seen that lattice parameter decreases linearly as a function of the chromia concentration until the solubility limit is reached. Nevertheless, the sample doped with 6000 ppm of Cr_2O_3 does not follow the same trend, due to the dissolution of the Cr^{3+} into the matrix reached the solubility limit under the conditions used in the fabrication of the pellet in this work, which according to the sintering conditions was established around 1000 ppm of Cr_2O_3 [4, 10].

In the selected range, the decrease in the lattice parameter follows a linear trend according to Equation 1 in a good agreement with Vegard's law, which states that the lattice parameter of solid solutions vary linearly with the composition [48].

$$a(\text{nm}) = -1.92(\pm 0.25) \cdot 10^{-7}[\text{Cr}_2\text{O}_3](\text{ppm}) + 0.54724(\pm 0.00002) \quad (1)$$

The Vegard's law-like behaviour when doping UO_2 with chromia has been also found by other authors [4, 10]. The contraction of the cubic lattice of UO_2 can be explained taking into account the defects that are created with the incorporation of a Cr^{3+} ion. When a U^{4+} ion is substituted by a Cr^{3+} ion, defect clusters are formed in order to maintain electroneutrality within the structure [7, 10]. The charge defect introduced in the lattice can be neutralized whether with the oxidation to U^{5+} by a nearby uranium atom, or by introducing oxygen vacancies. The net result of both effects is a contraction in the lattice parameter [10], specially taking into account that the ionic radius of Cr^{3+} is much smaller than that of U^{4+} (61 and 114 pm, respectively [49]). This has been confirmed by Cardinaels *et al.* [10], by using interatomic potentials calculations.

Although the Vegard's law-like behaviour has been confirmed, it is valid only in the region where a complete solid solution is established [50]. This means that, from the data obtained by XRD, it is possible to deduce a solubility limit of Cr in the UO_2 matrix in these conditions. Assuming that beyond the solubility limit the lattice parameter will not further decrease, from the intersection of the Vegard's line and the horizontal line starting at the point of 6000 ppm of Cr_2O_3 , this limit can be deduced; this calculation is rendered in Figure 4.3.8 (red square). This method has been validated to estimate solubility limits in other systems, such as Nb-doped UO_2 [51]. For the precise mathematical calculation, it has been obtained a solubility limit of (1094 ± 23) ppm of Cr_2O_3 , which corresponds to (748 ± 16) ppm of Cr^{3+} . This value is in good agreement with other studies carried out under similar sintering conditions, as reported by Leenaers *et al.* (860 ± 30 ppm of Cr^{3+} [4]) and Bourgeois *et al.* (750 ppm of Cr^{3+} [7]). In addition, this limit supports the grain size behaviour described in the previous section, as the highest grain size is found in the sample closest to the solubility limit.

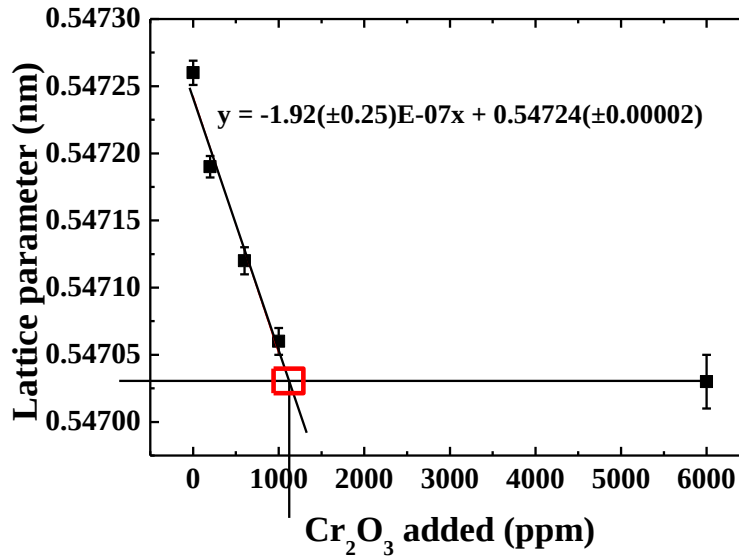


Figure 4.3.8. Lattice parameter vs Cr₂O₃ concentration and graphical calculation of solubility limit of Cr₂O₃ in the UO₂ matrix for the samples studied. Uncertainty bands correspond to the repeatability of the measurements.

Figure 4.3.9 shows a comparison between calculated lattice parameters and the grain size measurements of the chromia-doped UO₂ pellets. It should be highlighted that the maximum grain size is not reached with the lowest lattice parameter value. This is an indicator of the grain growth inhibition by the formation of precipitates in grain boundaries [7], a process that not always occur when solubility limit has been reached (for example due to the slow incorporation kinetics of chromium [4]). In fact, this lattice parameter is reached when doping with a Cr₂O₃ concentration far beyond the solubility limit (6000 ppm), but in this case, the presence of chromia in grain boundary is so high that the average grain size is even lower than pellets doped with 600 ppm of Cr₂O₃. The same reason of low incorporation kinetics of Cr³⁺ could also explain the behaviour of the point labelled as UO₂-200Cr₂O₃ in Figure 4.3.9, which does not follow the linear trend of the grain size values, indicating that a minimum chromium amount may be necessary to promote the enlargement of pellet grains.

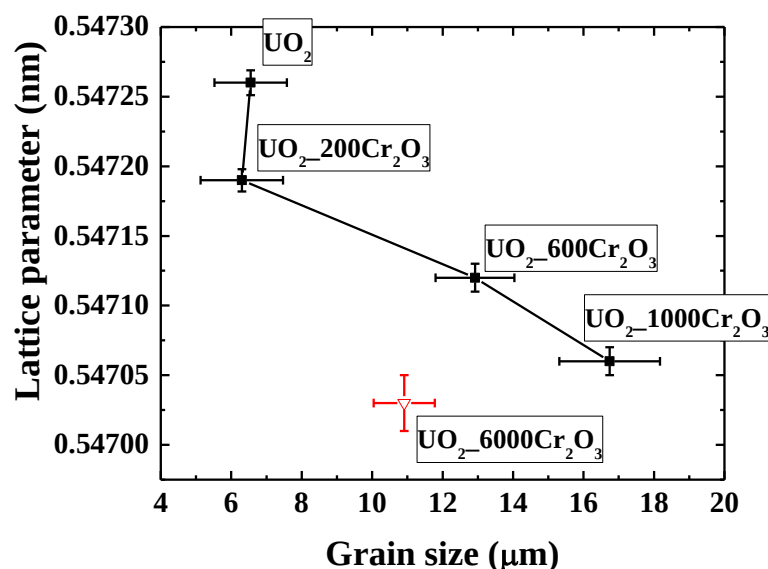


Figure 4.3.9. Lattice parameter vs average grain size of the analysed pellets. Black squares correspond to samples with Cr₂O₃ content lower than the solubility limit, while the open triangle represents the pellet doped with 6000 ppm of Cr₂O₃, which is higher than the solubility limit. Uncertainty bands correspond to the repeatability of the measurements.

4.3.3.3. Raman spectroscopy. Principal Component Analysis (PCA)

Figure 4.3.10 shows Raman spectra acquired from the UO₂ and chromia-doped UO₂ pellets. The plot represents the averaged spectra from 10 individual spectrums recorded at different locations of each disk.

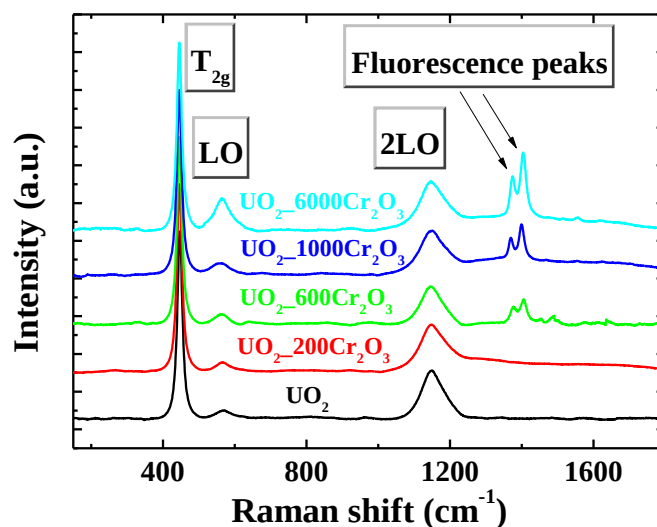


Figure 4.3.10. Raman spectra of chromia-doped UO₂ pellets.

The known Raman features of an undistorted, face-centred cubic structure like undoped UO_2 [45, 52] are seen at Figure 4.3.10. The same assignment that the one shown with powders (Table 4.3.II entries a-c) is used here: T_{2g} mode at 445 cm^{-1} , the LO phonon at 570 cm^{-1} and the first overtone (2LO) at 1140 cm^{-1} . In addition, in some of the Raman spectra acquired from the doped pellets of this study, an extra feature to the previously described has been found. It is an intense doublet at around 1380 cm^{-1} and 1410 cm^{-1} (Figure 4.3.10) that has been associated with fluorescence of Cr_2O_3 by several authors [41, 53-55]. All these features have been individually analysed in Section 4.3.3.4.

Because of the complexity of Raman spectra, a multivariate data analysis, via Principal Component Analysis (PCA), has been used in order to explore similarities and differentiate between samples of UO_2 fuels doped with different amounts of Cr_2O_3 , which have led to different grain size pellets (Figure 4.3.4). Thus, after grouping the spectra by the added amount of Cr_2O_3 into five data set (0, 200, 600, 1000, and 6000 ppm) a PCA has been performed. This analysis reduces the initial spectra data to a number of variables of principal components (PC) [33]. In technical terms, PC approach would neatly simplify the interpretation of our compiled variables by finding patterns in the information provided by the Raman spectral data.

From this analysis, the first result is to calculate in how many PC data can be grouped. This is given by the eigenvalue plot, shown in Figure 4.3.11, and indicating that the greatest impact on the variance of the analysed spectra registered for the five groups previously described can be related to the first three principal components [30]. Actually, the principal components PC1, PC2 and PC3 jointly explain 98.8% of the total variance of the data. PC1, PC2 and PC3 account for 89.8%, 7.7% and 1.3%, respectively.

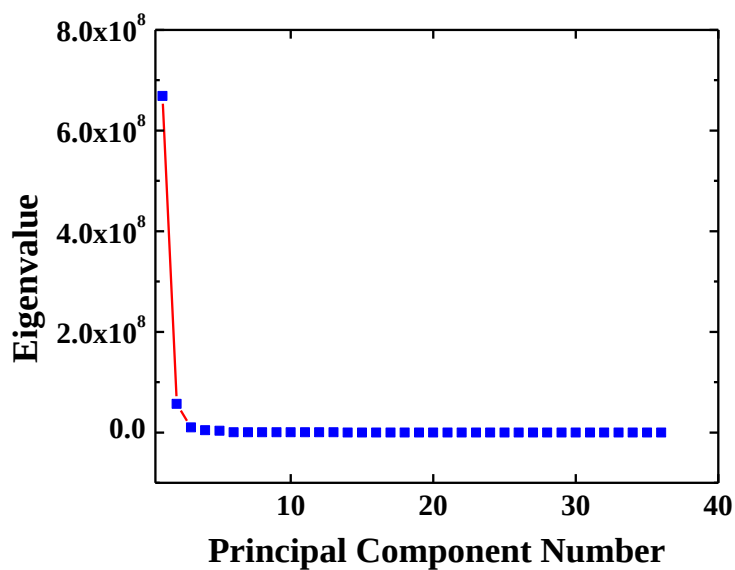


Figure 4.3.11. Plot of eigenvalues for PCA of Raman spectra.

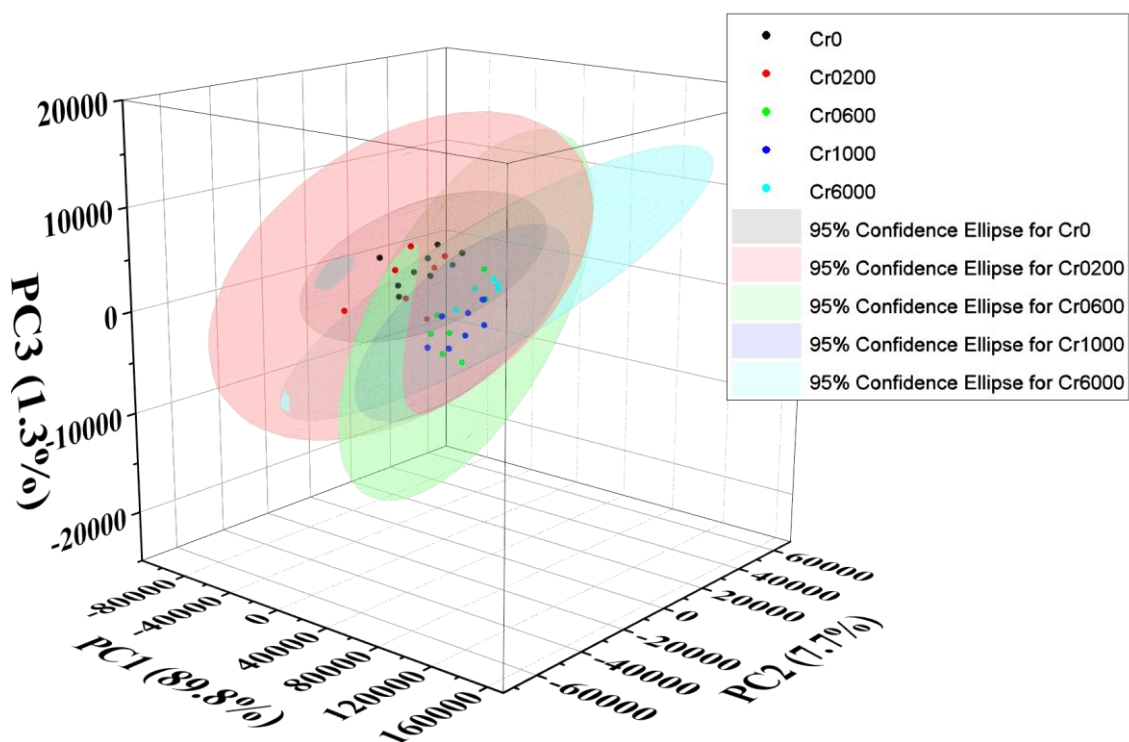


Figure 4.3.12. 3D Score plot of Principal Components and their corresponding confidence (95%) ellipse based on different Cr₂O₃ contents in UO₂ pellets. The total percent variance captured by each PC is shown in brackets along each axis.

Figure 4.3.12 shows a three-dimension score plot of the relation of the three main PCs involved. An in-depth examination of the score plot of these three PCs reveals a clear distinction between the five groups of data regarding the five different amounts of Cr_2O_3 defined before. This indicates that the PCA performed led to a very good discrimination between groups of samples.

4.3.3.4. Raman and fluorescence spectral analysis

4.3.3.4.1. Fluorescence

The presence of the formerly described fluorescence peaks is a consequence of a Cr_2O_3 -enriched region where the Raman laser spot has acquired the spectrum, thus there is chromium present at the surface of the pellet and has not entered in the UO_2 matrix. This hypothesis suggests that the higher Cr_2O_3 precipitates in the pellet-surface, the higher probability of finding fluorescence peaks in the Raman spectra, which are acquired 10 times per pellet randomly along the surface. Despite this reduced statistical sampling, the frequency histogram shown in Figure 4.3.13 confirms this hypothesis. This finding supports the behaviour of Cr_2O_3 previously revealed in the SEM section, as more peaks assigned to the fluorescence of Cr^{3+} are found in the sample that presents more Cr_2O_3 precipitates, *i.e.* $\text{UO}_2\text{-6000Cr}_2\text{O}_3$.

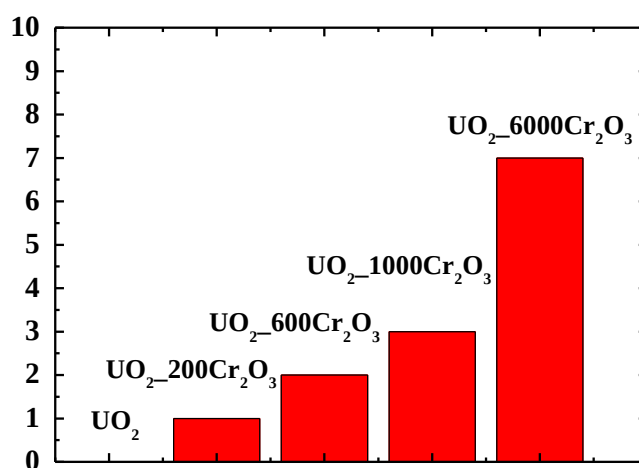


Figure 4.3.13. Number of spectrums showing Cr^{3+} -fluorescence peaks (per 10 spectrums acquired for each sample).

4.3.3.4.2. Raman intensity

On the one hand, T_{2g} and 2LO modes have been analysed in terms of their intensities. The T_{2g} mode involves the U-O bond stretching, and 2LO is attributed to a crystal electric field transition. This latter band has been proposed as a fingerprint for a quasi-perfect fluorite lattice [22, 56].

The observed intensity of the Raman scattered radiation depends, among other factors, on the instrumental and configuration parameters such as laser power or wavelength, optical path variations, sample placement acquisition and accumulation time, etc. Here all these instrumental parameters have been kept constant to perform a comparison of the absolute intensity, which is related to the Raman cross-section. Figure 4.3.14 shows the changes in absolute areas, *i.e.* integrated intensity, of the two mentioned bands. A marked decrease is observed when increasing Cr_2O_3 concentration, due to the distortions introduced in the lattice as a result of the entry of the doping agent. The fact that this area decrease is found in both peaks (445 and 1140 cm^{-1}) may indicate the unlikelihood that they can be attributed to variations in surface roughness.

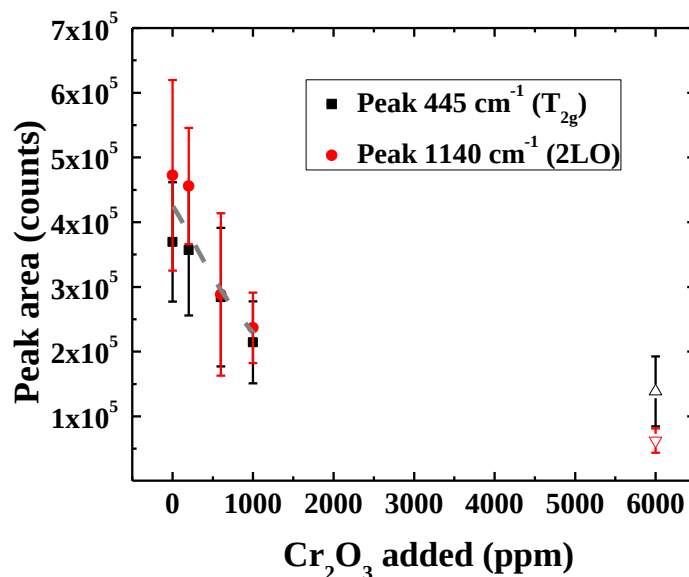


Figure 4.3.14. Area evolution of the T_{2g} (445 cm^{-1}) and 2LO (1140 cm^{-1}) bands with Cr_2O_3 concentration. Solid symbols correspond to samples with Cr_2O_3 content lower than the solubility limit, while open triangles represent the pellet doped with 6000 ppm of Cr_2O_3 , which is higher than the solubility limit. Dashed line represents a guide to the eye to show the general trend of data. Uncertainty bands correspond to the repeatability of the measurements.

4.3.3.4.3. Profile analysis of the LO band

On the other hand, the band at 570 cm^{-1} was analysed in detail. A profile analysis was performed by obtaining the second derivative of the spectra. This analysis revealed the contribution of two Lorentzian peaks, which indicates the presence of an additional feature band centred at 545 cm^{-1} that was not observed in pure UO_2 spectra. This new feature and a more detailed study can be observed in Figure 4.3.15.

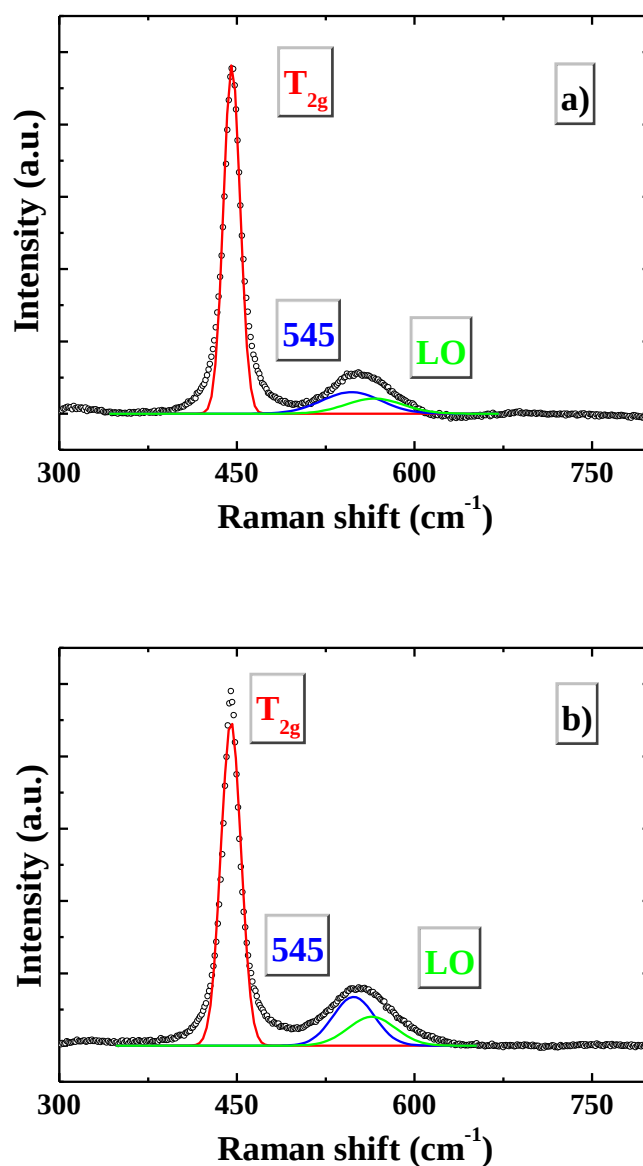


Figure 4.3.15. Raman spectra of a UO_2 disk doped with a) 600 ppm and b) 1000ppm of Cr_2O_3 by Lorentzian peaks at 445, 545 and 570 cm^{-1} .

In Figure 4.3.15, the LO mode at 570 cm^{-1} increases in intensity with chromia content, together with the band at 545 cm^{-1} . This latter band is not observed for pure UO_2 , and it has been related to the creation of oxygen vacancies in other trivalent-doped UO_2 fuels systems, such as Gd and Dy [20], Nd [24], or La [25]; thus same assignment can be made when doping with Cr^{3+} . This is a result of the charge imbalance produced by the introduction of the trivalent dopant (substitution of a U^{4+} for a Cr^{3+}), and therefore produces a lattice distortion, as confirmed by XRD (see section 4.3.3.2). In addition, the assignment of this feature to the presence of oxygen vacancies can be confirmed by comparing with the Raman spectroscopic studies performed by Rao *et al.* [57] with $\text{ThO}_2\text{-UO}_2$ solid solutions, who did not report the presence of this band from the analysis of Th^{4+} doped UO_2 . In fact, the substitution of U^{4+} by Th^{4+} does not produce a charge imbalance and therefore no oxygen vacancies are created. It is important to highlight that this new band centred around 545 cm^{-1} has been observed only when Cr_2O_3 nominal concentration was beyond 600 ppm (Figure 4.3.16).

The band at 570 cm^{-1} has been ascribed to a first-order LO phonon [36]. Its observation has been related to lattice distortions, causing a breakdown in the selection rules [37], and allowing the appearance of this forbidden Raman scattering mode. As in the previous case, similar bands have been observed in other systems, such as hyperstoichiometric UO_{2+x} [37] and for another kind of doped UO_2 materials [24, 25].

The calculated area of these features and the area ratio relative to that of the T_{2g} band have been plotted against the Cr_2O_3 concentration added at the beginning of the sintering process. This plot can be seen in Figure 4.3.16. This calculated ratio emphasises the dependence of the oxygen vacancies in the matrix structure with increasing chromia content.

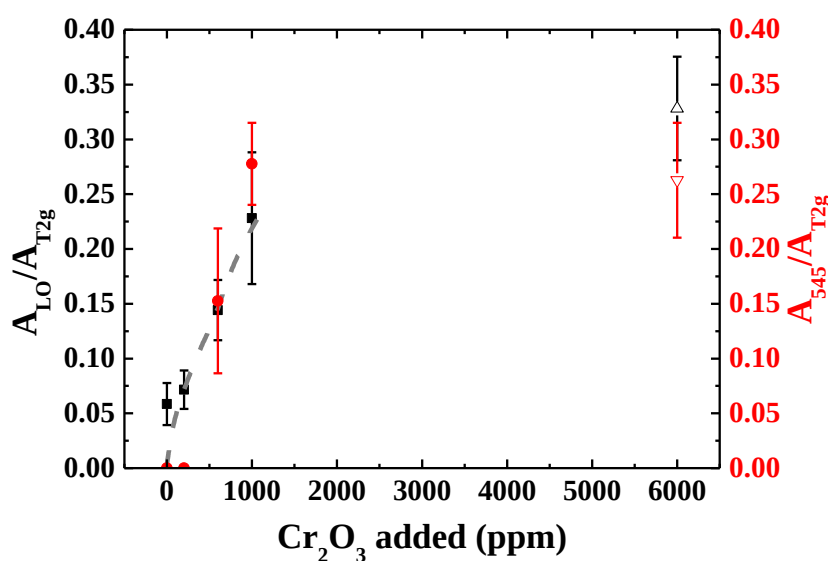


Figure 4.3.16. Evolution of the intensity of the peaks at 570 cm^{-1} (LO band, black squares) and 545 cm^{-1} (red circles), both referred to the T_{2g} band, with the Cr_2O_3 content. Solid symbols correspond to samples with Cr_2O_3 content lower than the solubility limit, while open triangles represent the pellet doped with 6000 ppm of Cr_2O_3 , which is higher than the solubility limit. Dashed line represents a guide to the eye to show the general trend of data. Uncertainty bands correspond to the repeatability of the measurements.

When detected, both the 545 and 570 cm^{-1} area ratios are in the same range, and both undergo the same increase with dopant concentration. These evidences strongly support the assumption that both features are related to the dissolution of Cr^{3+} in the UO_2 solid matrix and then, to defects in the fluorite lattice induced by oxygen vacancies.

Some authors have reported an additional band at $620\text{--}630\text{ cm}^{-1}$ associated with the presence of cuboctahedral clusters of the oxidised phase U_4O_9 , both in UO_2 and rare-earth doped samples [21, 23, 58]. The lack of this band in our spectra testifies that this phase has not been formed on the surfaces of the samples studied in this work, due to the final preparation performed to the pellets during the sintering process (thermal treatment under reducing atmosphere; $4.7\%\text{ H}_2\text{-N}_2$). In addition, it also confirms that no self-oxidation of the sample by laser heating during the measurements has occurred.

As done before for the XRD results (Figure 4.3.9), the area ratio of this band has been compared with the average grain size values of the samples obtained by SEM (Figure 4.3.17). Again, maximum grain size is not reached with maximum $A_{\text{LO}}/A_{\text{T2g}}$, due to the segregation in the grain boundaries of the Cr_2O_3 that has not been incorporated in the UO_2 matrix [4, 7]. It should be highlighted that uncertainty intervals for samples UO_2

and $\text{UO}_2\text{-}200\text{Cr}_2\text{O}_3$ overlap, supporting that a minimum amount of Cr may be needed to promote grain enlargement.

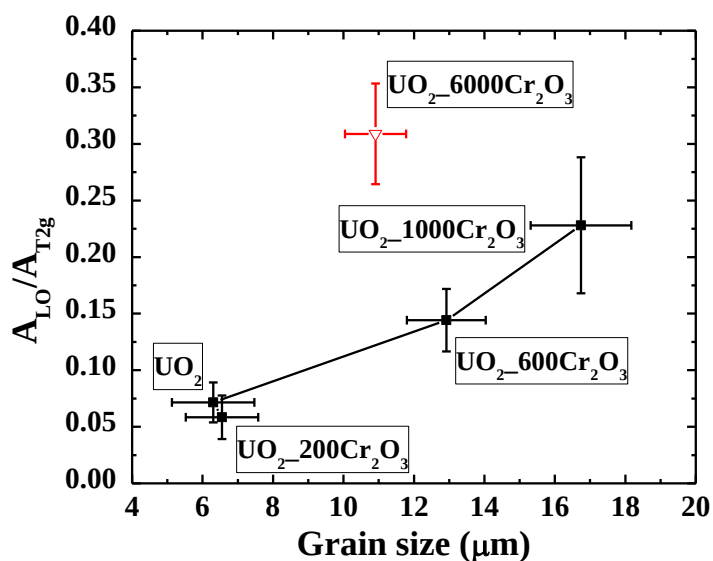


Figure 4.3.17. LO band area ratio vs grain size of the analysed pellets. Black squares correspond to samples with Cr_2O_3 content lower than the solubility limit, while the open triangle represents the pellet doped with 6000 ppm of Cr_2O_3 , which is higher than the solubility limit. Uncertainty bands correspond to the repeatability of the measurements.

Finally, from the combination of both XRD and Raman spectroscopy, one can extract interesting data that may help to understand the dissolution of Cr^{3+} into the UO_2 matrix. In Figure 4.3.18, a plot of the lattice parameter obtained by XRD versus the area ratio of the LO band (570 cm^{-1}) relative to the T_{2g} mode (445 cm^{-1}) obtained by Raman is presented. The tendency shown by the points indicates stabilisation around values close to the calculated solubility limit, approximately near the labelled point $\text{UO}_2\text{-}1000\text{Cr}_2\text{O}_3$, as the decrease in lattice parameter values and the increase in the area ratio are not so marked. The quasi-linear behaviour between the lattice parameter and the area ratio is a further key indicator of the validity of Raman spectroscopy to analyse Cr-doped UO_2 pellets, since the correspondence with a well-established technique such as XRD is almost total.

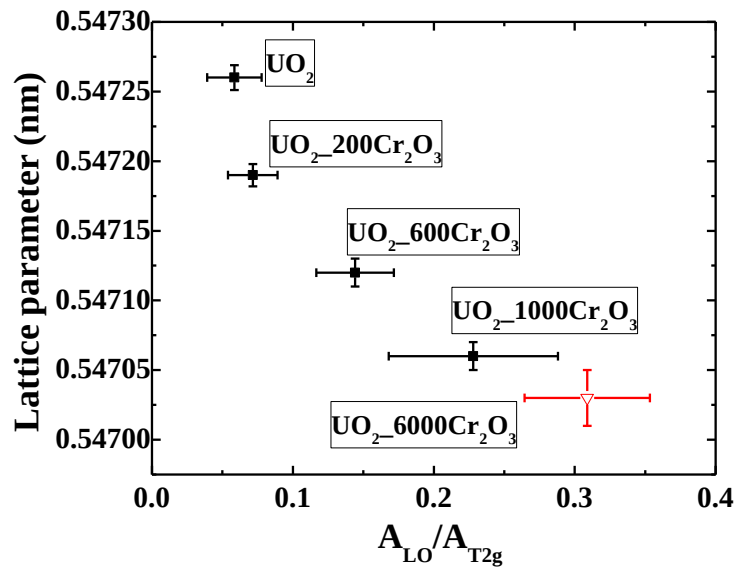


Figure 4.3.18. Lattice parameter vs A_{LO}/A_{T2g} peaks ratio. Black squares correspond to samples with Cr_2O_3 content lower than the solubility limit, while the open triangle represents the pellet doped with 6000 ppm of Cr_2O_3 , which is higher than the solubility limit. Uncertainty bands correspond to the repeatability of the measurements.

4.3.4. Conclusions

Raman spectroscopy has been used to characterise Cr-doped UO_2 pellets for the first time. Its validity to study these samples has been demonstrated by means of the Principal Component Analysis (PCA) and a detailed interpretation of the spectral features. From the statistical analysis, it is found that 98.8% of the total variance of the data is explained by three Principal Components (PC). These PCs coincide with the main Raman features found for the sintered disks. The variation of the Raman modes with Cr_2O_3 concentration is studied and related to the creation of oxygen vacancies due to the entry of Cr^{3+} in the UO_2 matrix.

The study of the grain size of the doped samples reveals that the highest value is found for the sample with the amount of Cr_2O_3 closest to the solubility limit. This is interpreted in terms of the restriction of the grain growth by the presence of segregated phases. SEM images have shown that precipitates of Cr_2O_3 are found to be in the grain boundaries, and that more and bigger precipitates are found for the sample $UO_2-6000Cr_2O_3$. However, Cr_2O_3 -rich areas in the surface of the pellets are also found in samples where the solubility limit has not been reached, probably due to the low incorporation kinetics of Cr. Its presence is supported by the appearance of their

characteristic fluorescence peaks in several Raman spectra. Therefore, the quantity of doping agent and/or fabrication methods for real fuel must be optimised. By XRD, the solubility limit of Cr in these specific sintering conditions is estimated to be (748 ± 16) ppm.

In summary, a systematic measurement protocol by Raman spectroscopy has been successfully developed to characterise Cr-doped UO_2 fuels. Further work on how to implement these protocols to perform *in-situ* measurements on real fuel will be carried out, so realistic tests will be applicable to these new nuclear materials.

Acknowledgements

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4.3.5. References

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Result 4

Testing the oxidation resistance of model materials (ATFs)

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4.4. Result 4. Testing the oxidation resistance of model materials (ATFs)

Abstract

Oxidation of Accident-Tolerant Fuels (ATF) is important from the nuclear safety point of view because it could provoke the release of radioactive material. Despite of the use of ATFs in current nuclear reactors, no studies regarding their oxidation are available. Thus, we propose here an experimental study on Cr_2O_3 -doped UO_2 samples, which were subjected to a thermal treatment ranging from room temperature up to 973K in oxidant conditions. The aim is to assess the potential oxidation resistance of Cr-doped UO_2 based model systems. Next, the effect of oxygen partial pressure and the influence of Cr_2O_3 dopant concentration concentrations on fresh UO_2 fuel oxidation were evaluated. Two oxygen compositions (1 % and 21 % O_2) were used to further evaluate the impact of Cr_2O_3 concentrations on UO_2 oxidation. The results show that, despite no effect of the dopant is found in air (21 % O_2), there is a clear decrease in the oxidation degree at 1 % O_2 . These results are intended to provide a fundamental reference for future investigations of Cr_2O_3 -doped UO_2 corrosion behaviour and performance to be accounted in new designs of storage facilities.

Keywords

Uranium oxide, Accident-Tolerant Fuels (ATF), oxidation, thermal cycling, dry interim storage.

4.4.1. Introduction

The near-term target challenges associated with nuclear energy technology include increasing burnup beyond typically designed limits of around ~ 50 GWd/tU in operating Light Water Reactors (LWR) to expand fuel cycle economy, while not sacrificing the safety margins under normal operating conditions and beyond design basis accident conditions [1-4]. At high burnups, some undesirable processes that could compromise the safety of the fuel, both during irradiation and storage, could take place such as fission gas release enhancement during power transients, fission products (FPs) accumulation and irradiation-induced defects which affects the thermal conductivity of fuel pellets, the occurrence of fuel-clad bonding or clad creep-out [5]. This, added to the

events at the Fukushima-Daiichi plant in Japan in 2011, revealed the susceptibility of UO_2 fuel pellets within a zirconium (Zr) alloy cladding to a station blackout during long-time. This has brought nuclear industry and researchers to come together efforts on improving the resilience response of fuels in severe accident scenarios [6, 7].

A new set of High-Burnup Fuels with enhanced safety margins in the event of an accident (referred as “Accident-Tolerant Fuels, ATFs) are arising as a near-term suitable fuel choice. ATF concept provides enhanced fuel pellet properties to better performance during normal or ab-normal operation and to enable higher burnups and then, extending reactor cycles. A number of ATF designs to direct replacement for the current standard UO_2 fuel/ Zr alloy system have been proposed: for fuels, it includes advanced UO_2 formulations (via additives) and high density uranium fuels (nitride and silicide concepts); and in terms of claddings, developments are focused on innovative alloys or coatings, such as FeCrAl cladding or chromium-coated cladding [6-8].

As the properties of UO_2 are key issues for safe and effective reactor operation, the addition of dopants (metallic or ceramic dopants) in standard UO_2 fuel is used to improve its microstructure during sintering [9, 10]. In UO_2 -doped fuels, the additive in the form of an oxide, acts enlarging fuel grain size, increasing fuel density, providing better fission gas retention and plasticity [9-12]. In particular, these characteristics are well-reached by doping the UO_2 matrix with chromia (Cr_2O_3). Especially important is the enlargement of grain size, which provides improved fission gas retention (by increasing the diffusion path), and reduces fuel swelling. This implies a better resistance upon the interaction of the nuclear fuel pellet to the cladding [7, 13-19]. An anticipated benefit of large grains could also be an enhanced corrosion resistance in the presence of air and water compared to the standard UO_2 [15, 20]. However, testing and data are needed so far to confirm this hypothesis, especially that affecting its thermal oxidation behaviour as a result of thermal cycling during both normal operation and dry interim storage.

The incorporation of Cr atoms into the UO_2 fluorite structure involves charge-compensation to achieve lattice electro-neutrality by positive defect formation, *i.e.* the presence of defect clusters as anion vacancies or the formation of U^{5+} [21, 22]. It is expected that the Cr_2O_3 doping-induced oxygen vacancies [19] would prevent the oxidation of UO_2 compared to the undoped UO_2 samples, which may have positive

effects on fuel corrosion. In fact, the oxidation of undoped UO_2 is described as a two-step reaction UO_2 (cub.) $\rightarrow\text{U}_4\text{O}_9$ (cub.)/ U_3O_7 (tetrag.) $\rightarrow\text{U}_3\text{O}_8$ (orth.) [23-25], which is dependent on temperature, time, physical properties of the material, etc. In any case, the formation of U_3O_8 involves a volume expansion of about 36% [23], which leads to spallation of this phase from the grain surfaces and pulverization of the samples [23, 26]. This may entail a nuclear safety problem for Spent Nuclear Fuel (SNF) management as radionuclides could be released within the environment in case of a confinement failure [27, 28]. Therefore, understanding the role of Cr in the UO_2 matrix against oxidation is of paramount importance. Although previously several studies were devoted to understand the effects of Cr_2O_3 in UO_2 fuels, with respect to the local structure, thermodynamic solubility, manufacturing conditions, and gas release diffusion issues [10, 12, 15-19, 22, 29], a conclusive understanding and its implications of the dry oxidation behaviour of Cr-doped UO_2 has not been established yet. Besides the dopant effect, most of the studies regarding the oxidation of UO_2 -based nuclear fuels have been performed in air, probably following a worst-case scenario. However, new dry storage facilities for storing SNF foresee the possibility of partially inert the loading cell where the fuel is expected to be handled [30], thus bringing to light other alternatives to air that might delay or even prevent this oxidation.

Given the lack of experimental information in the literature on the potential oxidation resistance of ATF, and in particular under modern dry storage conditions, in this work thermal induced oxidation measurements are performed to assess how Cr_2O_3 content and oxygen concentration (21 or 1% O_2) affect corrosion resistance of UO_2 to U_3O_8 , as measured using thermogravimetric analysis. Also, analyses of oxidised products by X-Ray Diffractometry (XRD) and Rietveld Refinement are used to elucidate the U oxidised phases and the fraction of each one, formed as a consequence of the solid/gas reaction of undoped UO_2 and UO_2 -based model materials (as Cr-doped UO_2) with oxygen. To the extent of our knowledge, this fundamental and systematic study is the first analysing the multiple effects (Cr content correlated with microstructure, oxygen concentration and temperature) on the oxidation behaviour of UO_2 . These results are envisioned to provide insights regarding the degradation behaviour of modern doped fuels in the handling, transportation and interim storage of SNF, under both, operational and accidental scenarios.

4.4.2. Materials and methods

4.4.2.1. Sample preparation

The ATFs analogues studied in this work have been prepared following a conventional metallurgical procedure, starting from raw UO_2 and Cr_2O_3 powders provided by ENUSA and Alfa Aesar, respectively; who were mixed in the desired proportions. The fabrication route and an exhaustive characterisation of these samples were published in a previous work, where all the details of the monoliths are given [21].

From this procedure, a set of Cr_2O_3 -doped UO_2 solid solution was obtained. The doping levels (600, 1000 and 6000 ppm of Cr_2O_3) have been selected in order to cover all possible solubility scenarios. Thus, this results in a pellet with a Cr content which is below this solubility limit (600 ppm of Cr_2O_3), another one with a content around the limit (1000 ppm of Cr_2O_3), and finally a monolith with a Cr amount that is beyond the solubility limit of Cr in the UO_2 matrix.

In fact, according to our previous study where these samples were characterised in detail, this limit corresponds to approximately 1094 ± 23 ppm of Cr_2O_3 in these particular sintering conditions [21]. An undoped UO_2 sample was also fabricated by applying the same methodology.

4.4.2.2. Oxidation experiments at different oxygen concentrations

Two different gas mixtures (O_2/N_2) were used during the experiments. For low oxygen availability, a mixture of oxygen and nitrogen in the proportion 1% O_2 -99% N_2 (from now on refereed as 1% O_2) was supplied by Air Liquide. In addition, synthetic air was also provided by Air Liquide, with a licensed composition of $20 \pm 1\%$ O_2 , being the rest N_2 (named as 21% O_2 in the rest of the document). A certified purity higher than 99.999% is guaranteed for all the gases.

The oxidation experiments were carried out by thermogravimetric analyses, using a TGA Q50 thermobalance (TA Instruments). The reactions were done using a gaseous oxidant (21 or 1% O_2) flow at a constant rate of $60 \text{ mL} \cdot \text{min}^{-1}$. The instrument was calibrated in both, temperature of magnetic standards (Curie point, ASTM E-1582) with Alumel, Ni and $\text{Ni}_{0.63}\text{Co}_{0.37}$ alloy standards (427.16 ± 0.31 , 631 ± 1.1 and $1037.4 \pm 1.6\text{K}$, respectively), and weight (200 mg to 1 g calibration weight range). The oxidation of the

pellets were conducted by heating the samples from room temperature up to 973K with a linear heating rate of $10\text{K}\cdot\text{min}^{-1}$. Three replicas for each curve have been performed, leading to the uncertainties calculated for the kinetic parameters analysed. The mass gain curves have been analysed with the software Universal Analysis (TA Instruments).

4.4.2.3. XRD

X-Ray Diffraction (XRD) of the oxidised samples was carried out by means of a Bruker D8 Advance Eco diffractometer using Cu $K\alpha$ radiation ($\lambda=1.54056\text{ \AA}$). The instrument was configured with Bragg-Brentano geometry, and operation parameters of 40 kV and 25 mA. The diffractograms were acquired in the $10\text{-}120^\circ$ 2θ range, with 0.01° scanning steps and a primary slit of 0.5° . A 1D Lynx Eye Position Sensitive Detector (PSD) was used as the detection system, with an angular aperture of 2.9° . The instrument is daily calibrated by measuring a certified pattern of Al_2O_3 .

The phase composition, quantification and structural analyses in the oxidised samples have been obtained by using the HighScore Plus 4.8 software (Malvern-Panalytical) [31]. Phase composition was performed applying Rietveld Quantitative Phase Analysis (RQPA) [32]. Identification of the oxidised compounds of uranium was carried out by using the information available at the Crystallography Open Database (COD) [33]. Peak profile refinement was performed by using Pseudo-Voigt function.

4.4.3. Results

4.4.3.1. Oxidation of raw materials

In order to assess the oxidation of starting UO_2 and Cr_2O_3 powders, both have been subjected to a thermal treatment consisting of heating up to 973K under a continuous airflow. The weight change curves as a function of temperature are presented in Figure 4.4.1A, together with the first derivative of the mass gain curves (Figure 4.4.1B).

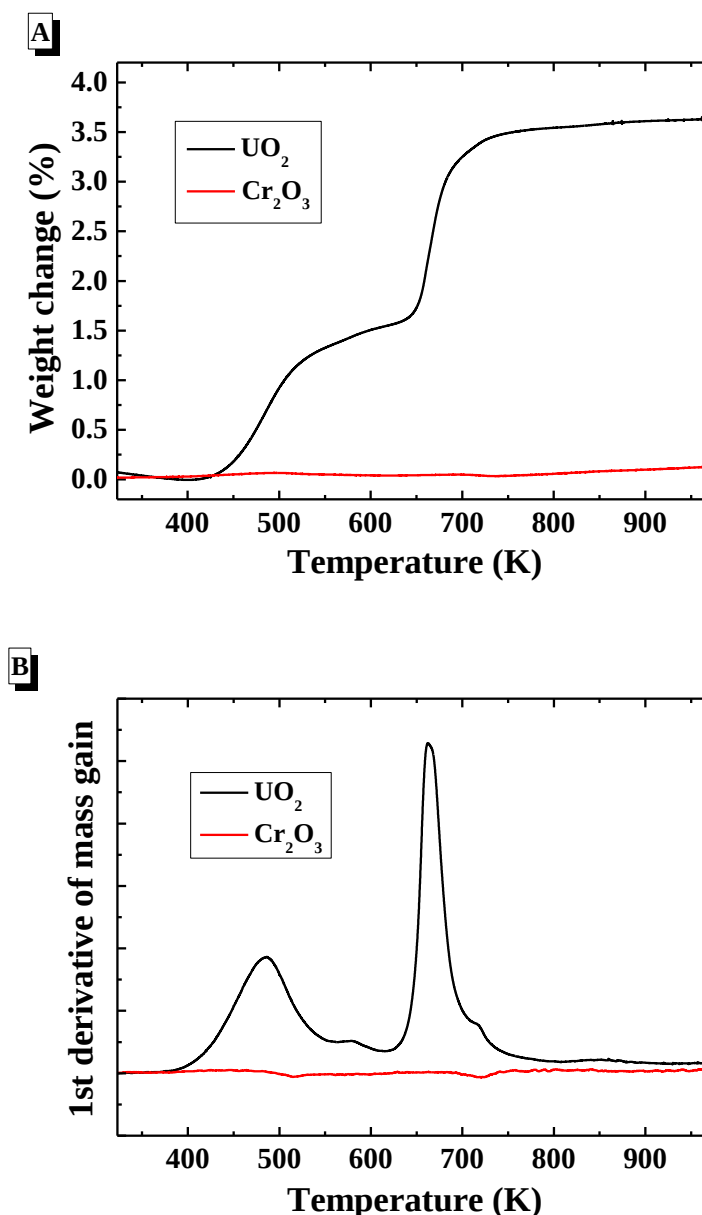


Figure 4.4.1. A) Weight gain curves and B) first derivative of the mass gain curves of starting UO_2 (black) and Cr_2O_3 (red) powders.

The oxidation behaviour of powdered UO_2 is a well-known reaction [23, 34-36]. As previously explained, and as shown in Figure 4.4.1, it consists of a two-step process involving the oxidised phases of uranium that are of interest in this study, *i.e.* (i) $\text{UO}_2 \rightarrow \text{U}_3\text{O}_7$; and (ii) $\text{U}_3\text{O}_7 \rightarrow \text{U}_3\text{O}_8$. This reaction is the most usual oxidation for this nuclear material, which is in powdered form, and follows an oxygen diffusion mechanism for the first step and nucleation and growth for the second [37-40]. This was verified by the presence of two peaks in the derivative of the TGA (Figure 4.4.1B). Regarding Cr_2O_3 , no significant mass changes have been observed during the thermal

treatment applied, proving its thermodynamic stability in these conditions [41]. This fact makes possible to calculate the oxidation of Cr-doped UO_2 pellets as weight gain by UO_2 and its associated oxidised phases, not including mass changes of Cr_2O_3 .

4.4.3.2. *In-situ* oxidation of as-prepared ATFs under different oxygen concentrations

In the case of sintered pellets, the oxidation mechanism in air (21% O_2) of UO_2 proceeds in a different way. In this case, the formation of U_3O_7 and U_3O_8 emerges at the same time, giving place to oxidation curves with only one, well discernible step, while oxygen is diffusing into the UO_2 lattice [23, 26, 42]. The reason relies on the oxidation mechanism itself, as here the first step of the reaction is a surface reaction along the grain boundaries found in the surface of pellets. At the same time that this diffusion is taking place, the grain surface is being cracked, exposing more UO_2 to the oxygen [35, 43]. When U_3O_8 is formed, it spalls from the sample surface as a fine powder [23, 26, 44], another reason why it is important to study the formation of this phase from a nuclear safety perspective [27, 28]. This pulverization effect has been confirmed in our samples, as can be seen in Figure 4.4.2.



Figure 4.4.2. Visual pulverization of the undoped UO_2 pellet after being oxidised up to 973K at 21% O_2 .

This reaction has been studied by means of TGA, using as a characterisation parameter the oxygen-to-metal ratio (O/M). This value is widely used to follow the oxidation reaction of UO_2 ; and for undoped, stoichiometric uranium dioxide, it is usually expressed as O/U and it ranges from O/U=2 (UO_2) to O/U=2.67 (U_3O_8). In a more generic way, especially when talking about SNF or doped fuel, it is displayed as O/M, where M refers to a specific metal or element that wants to be also analysed. For this

reason, in this work we use the O/(U+Cr) ratio to follow the reaction of the different ATFs studied.

The O/(U+Cr) ratio is calculated from the weight gain data. For this purpose, we use the method proposed by Kim *et al.* for Gd-doped UO₂ samples [45]. It has been also applied in other similar fuels, such as in the work of Olds *et al.* [46]. We first define the oxygen mass gain, G_o , due to the oxidation in Equation 1.

$$G_o = \frac{m_T - m_i}{m_i} \quad (\text{Eq. 1})$$

Being m_T the mass of the sample at a given temperature, and m_i is the initial mass. Using this value, the O/(U+Cr) ratio is calculated following Equation 2.

$$O/(U + Cr) = 2 + G_o(W_M/16) \quad (\text{Eq. 2})$$

where W_M is the molecular weight of the compound (U_{1-y}Cr_y)O₂. As stated before, different Cr concentrations have been used to obtain the set of UO₂-doped pellets, according to the possible solubility scenarios (Table 4.4.I). In order to calculate the values of y in (U_{1-y}Cr_y)O₂ for each sample and knowing that the solubility limit of Cr₂O₃ in UO₂ in these sintering conditions corresponds to approximately 1094±23 ppm of Cr₂O₃ [21], we assume that, for pellets UO₂_600Cr₂O₃ and UO₂_1000Cr₂O₃ (Table 4.4.I), all the amount of dopant has entered in the UO₂ matrix (*i.e.* 600 and 1000 ppm of Cr₂O₃, respectively). Accordingly, in the case of the sample UO₂_6000Cr₂O₃, with Cr content higher than the solubility limit, we assume that the quantity of dopant here is precisely 1094 ppm of Cr₂O₃. It has been proved that not all the Cr enters in the lattice [47, 48], nevertheless the impact on the calculation of O/(U+Cr) is negligible, given the low solubility of Cr when forms a solid solution with UO₂.

Table 4.4.I. Definition of samples, stoichiometry of the solid solution and molecular weight for the materials studied in this work.

Labelled Material	Cr ₂ O ₃ added (ppm)	(U _{1-y} Cr _y)O ₂	W _M (g·mol ⁻¹)*
UO ₂	0	UO ₂	270.0277
UO ₂ _600Cr ₂ O ₃	600	(U _{1-5.33·10⁻⁴} Cr _{5.33·10⁻⁴})O ₂	269.9006
UO ₂ _1000Cr ₂ O ₃	1000	(U _{1-8.89·10⁻⁴} Cr _{8.89·10⁻⁴})O ₂	269.8615
UO ₂ _6000Cr ₂ O ₃	6000	(U _{1-8.92·10⁻⁴} Cr _{8.92·10⁻⁴})O ₂	269.8609

* Values calculated from atomic weights of the IUPAC Periodic Table of the Elements [49].

Taking into account these considerations, the oxidation curves of the UO₂-based model samples studied in this work vs temperature are presented in Figures 4.4.3 and 4.4.4,

depending on the oxygen concentration used during the experiments. In both cases, they are plotted as $O/(U+Cr)$ vs temperature. For each oxidation curve, the first derivative is also included, in order to obtain the transition temperatures in all the studied conditions.

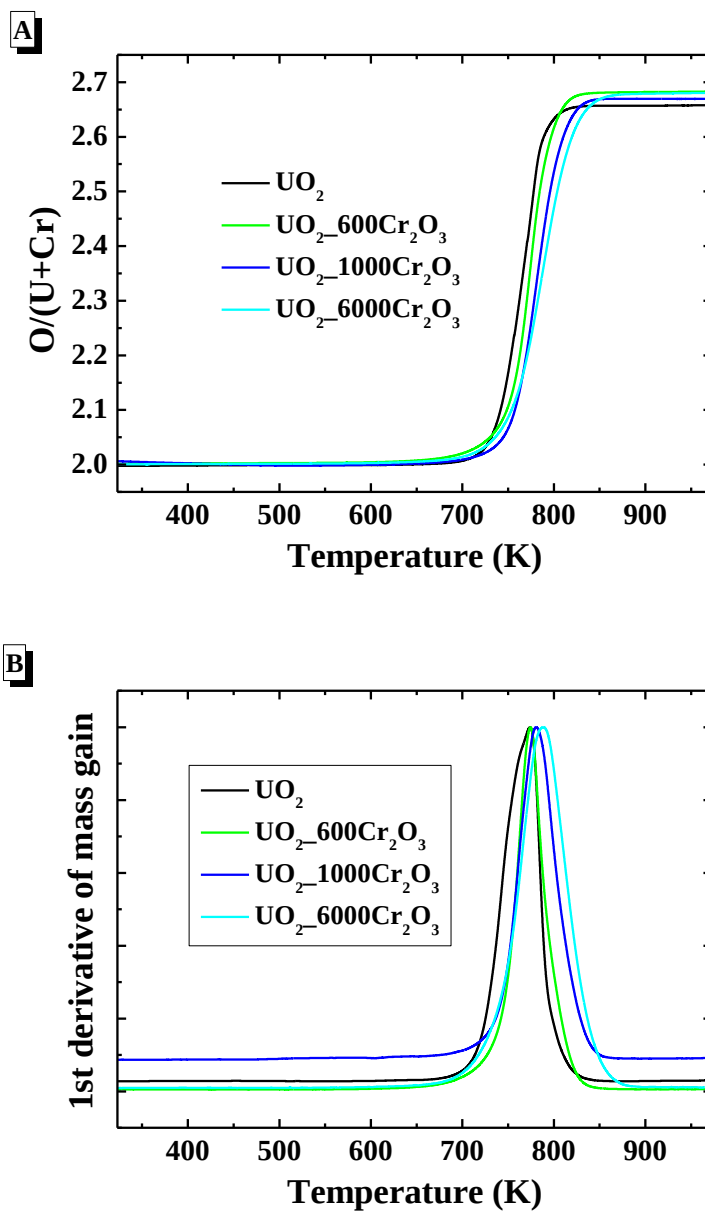


Figure 4.4.3. A) Oxidation curves of the ATFs studied from RT to 973K in air (21% O_2). B) Normalised first derivative of the mass gain curves.

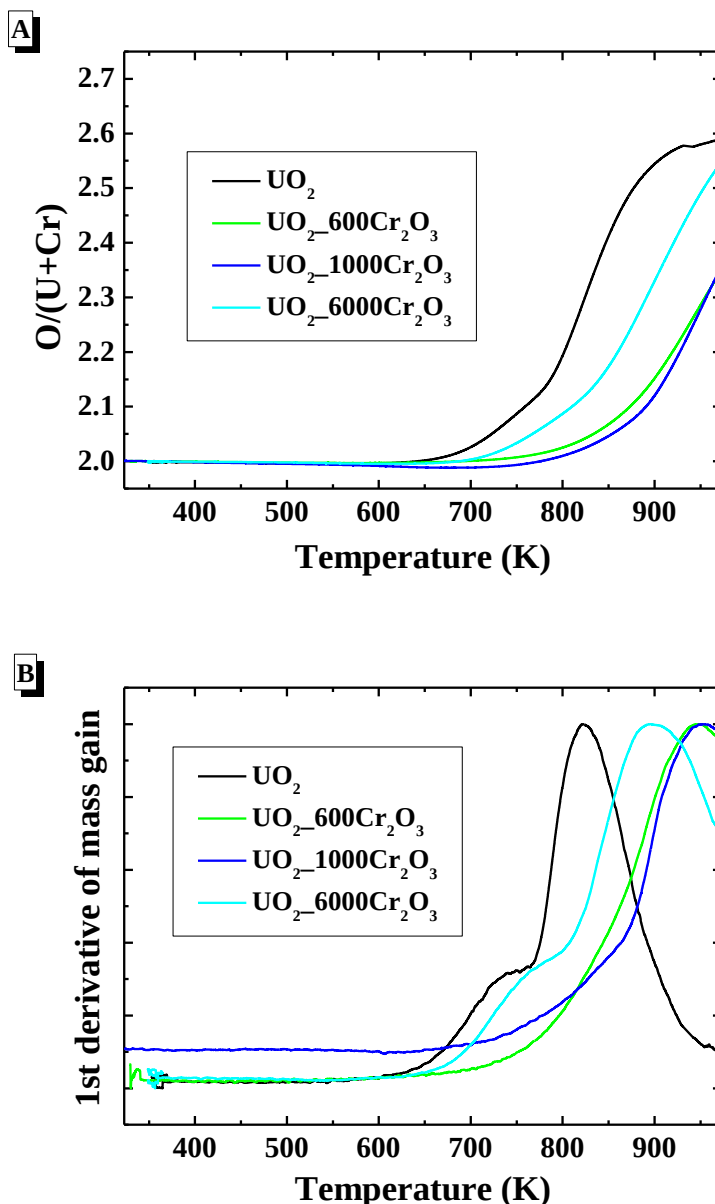


Figure 4.4.4. A) Oxidation curves of the ATFs studied from RT to 973K in 1% O_2 . B) Normalised first derivative of the mass gain curves.

Our results evidenced very different weight gain curves as a function of the Cr content values and oxygen concentration in gas phase. On the one hand, regarding oxidation of the samples in air (Figure 4.4.3A and Figure 4.4.3B), the $\text{O}/(\text{U}+\text{Cr})$ values found are around 2.67 in all cases, meaning total conversion to U_3O_8 . Table 4.4.II shows these ratios. In addition, and also from these figures, it can be seen that in this case the reaction proceeds in one single step, as proved by the first derivative curve of the mass gain. This derivative has been used to calculate the Maximum Reaction Temperature (MRT), which is the temperature corresponding to the maximum of this derivative, and

it is interpreted as a transition temperature. MRTs are also displayed in Table 4.4.II. At 21% O₂, this parameter is around 773K in all cases, a typical value when this thermal procedure is applied to sintered UO₂ samples (see for example MRT for sample F in [25] or Fig. 3 in reference [46]). A detailed analysis of these values displays a slightly growth of MRTs with Cr₂O₃ concentration. However, the increase in MRT in air is almost negligible, being of around 20K in almost the 973K range covered.

On the other hand, thermogravimetric curves carried out by applying the same thermal treatment but with only 1% O₂ present are shown in Figure 4.4.4A and B. The samples oxidised in these conditions present much lower O/(U+Cr) values, as none of them reach the aforementioned 2.67, meaning no complete conversion to U₃O₈. From the first derivative of each curve (Figure 4.4.4B), it seems that the single-step reaction is maintained, in particular for the samples UO₂_600Cr₂O₃ and UO₂_1000Cr₂O₃. However, a local maximum becomes visible for the samples UO₂ and UO₂_6000Cr₂O₃, which could be an indicator of the reaction's deceleration in these conditions. In fact, numerical data confirms this idea. By performing the same analysis of the previous case, MRTs are also calculated from the maximums of the derivative. For the sake of comparison, they are included in Table 4.4.II. From the results, it can be seen that the undoped UO₂ pellet and the one doped with the highest concentration (UO₂_6000Cr₂O₃) present a maximum temperature between 50 and 120K lower than the MRTs of the UO₂_600Cr₂O₃ and UO₂_1000Cr₂O₃ samples. The followed trend is consistent with the O/(U+Cr) values: UO₂ < UO₂_6000Cr₂O₃ < UO₂_1000Cr₂O₃ ~ UO₂_600Cr₂O₃.

Table 4.4.II. Maximum Reaction Temperatures (MRT) and final values of O/(U+Cr) for the samples studied in the different experimental conditions.

Sample	21% O ₂		1% O ₂	
	(O/(U+Cr)) _f	MRT (K)	(O/(U+Cr)) _f	MRT (K)
UO ₂	2.66±0.02	768±2	2.59±0.02	823±3
UO ₂ _600Cr ₂ O ₃	2.68±0.02	774±2	2.34±0.02	954±4
UO ₂ _1000Cr ₂ O ₃	2.68±0.02	781±3	2.35±0.02	943±4
UO ₂ _6000Cr ₂ O ₃	2.67±0.02	789±3	2.53±0.02	898±4

4.4.3.3. XRD analysis of the oxidised pellets

XRD analysis was used to know the amount of U₃O₈ formed in the oxidised samples after the thermal treatment at the different experimental conditions. The changes in the composition of oxidised phases in each of the studied ATFs as a function of the % O₂

could be followed by applying the RQPA [32]. The different phases of uranium oxides have been refined considering the next structures and spatial groups: 1) UO_2 structure has been taken from the $Fm-3m$ group (COD database code 1541665); 2) U_3O_7 from the spatial group $P4mmm$ (COD 1524454); and finally, 3) U_3O_8 has been refined according to the $C222$ group (COD 2310519). The diffraction patterns of these spatial groups are widely known and have been used previously in the identification of different oxidation states of uranium [21, 40, 50-54].

Figure 4.4.5 shows diffraction patterns acquired for the Cr_2O_3 -doped UO_2 samples oxidised up to 973K. Samples oxidised at 21% O_2 (Figure 4.4.5A) show very similar diffraction patterns, corresponding to U_3O_8 , regardless of the Cr_2O_3 doping concentration. A more detailed analysis reveals that the sample $\text{UO}_2\text{-600Cr}_2\text{O}_3$ oxidised in air exhibits a slightly different profile of diffractogram, since the proportion of UO_2 and U_3O_7 after oxidation is slightly higher in this sample (Figure 4.4.6).

On the contrary, the diffraction patterns corresponding to the samples oxidised at lower oxygen partial pressure (1% O_2 , Figure 4.4.5B), are dissimilar. For the samples corresponding to 600 and 1000 ppm of Cr_2O_3 , the diffraction patterns show the presence of U_3O_7 and U_3O_8 , while the diffractograms of samples corresponding to 0 and 6000 ppm of Cr_2O_3 are consistent with U_3O_8 .

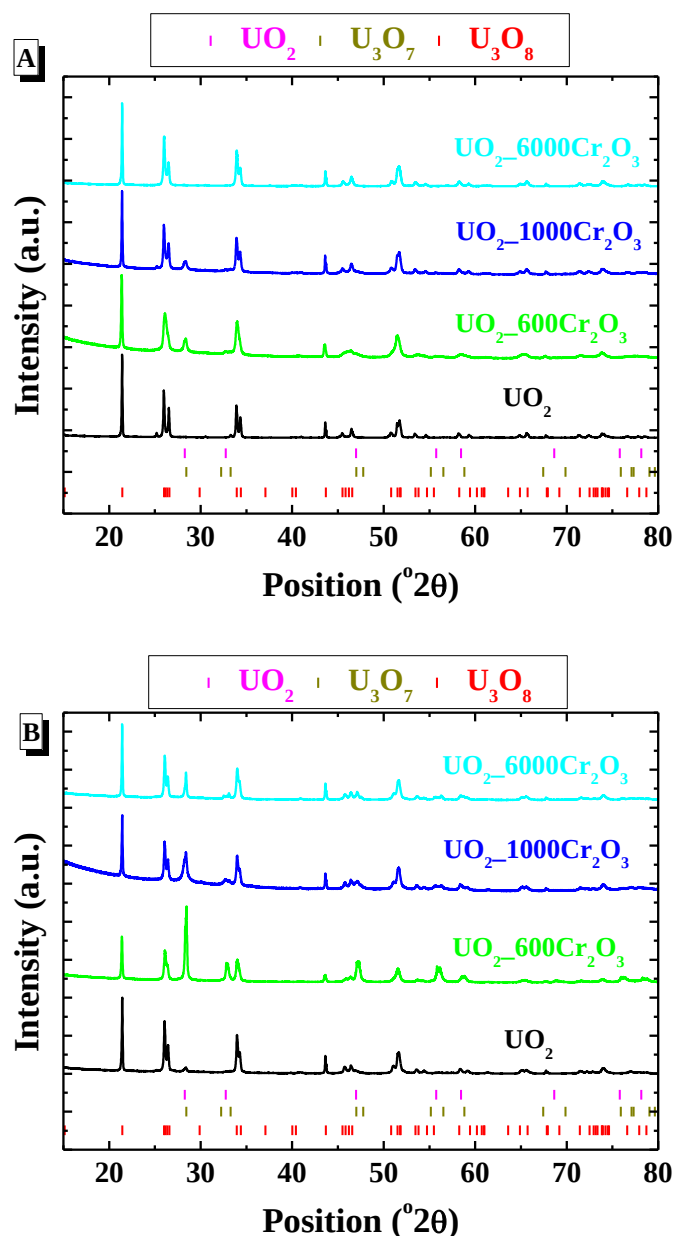


Figure 4.4.5. XRD patterns recorded in the scan range 20-80° of the ATFs after oxidation of the samples in A) 21% O₂ and B) 1% O₂. Pattern B of UO₂ doped with 600, 1000 and 6000 ppm of Cr₂O₃ shows that the oxidation to U₃O₈ has not been completed and peaks associated with UO₂ at 32.7° (2θ), and U₃O₇ at 33.1° (2θ) are present in the pattern.

The composition and amount of the oxidised samples studied in this work is shown in Figure 4.4.6. Regarding the post-oxidation examination of ATFs oxidised in air (Figure 4.4.6A), almost complete conversion to U₃O₈ is observed in all the cases, especially in the undoped and in the UO₂-6000Cr₂O₃ samples, where the transformation is quantitative. In the rest of the Cr-doped UO₂ samples, which are those whose Cr content is below the stoichiometric limit, the amount of UO₂ and U₃O₇ is slightly higher than the limits of the compositional range in Cr. In fact, in the UO₂-600Cr₂O₃ sample the

compositions of UO_2 and U_3O_7 are 3.7 and 11.5%, respectively. In the case of the $\text{UO}_2\text{-1000Cr}_2\text{O}_3$ sample, these percentages are 1.9% of UO_2 and 2.9% of U_3O_7 . These XRD analyses are consistent with the thermal results *i.e.* U_3O_8 formation is practically quantitative for all cases.

The results of the Rietveld refinement carried out in those samples oxidised following the same thermal treatment but with only 1% O_2 present are shown in Figure 4.4.6B. In this case, it is worth highlighting that the UO_2 and U_3O_7 phases are clearly distinguishable in all the oxidised samples, *i.e.* the conversion to U_3O_8 is not complete when the oxygen content is as low as 1% O_2 . Analogously to the previous case, here the undoped and the $\text{UO}_2\text{-6000Cr}_2\text{O}_3$ samples are those in which the proportion of U_3O_8 is the highest, being even higher in the undoped UO_2 oxidised pellet. In addition, the samples doped with an amount of Cr below the solubility limit ($\text{UO}_2\text{-600Cr}_2\text{O}_3$ and $\text{UO}_2\text{-1000Cr}_2\text{O}_3$) present a remarkably greater proportion of the intermediate products UO_2 and U_3O_7 . It was indeed found that the $\text{UO}_2\text{-600Cr}_2\text{O}_3$ sample is composed of a 34.3% of U_3O_7 and a 20.9% of UO_2 . In the case of the $\text{UO}_2\text{-1000Cr}_2\text{O}_3$ sample, the percentages of these phases are 27.7 and 8.1% of U_3O_7 and UO_2 , respectively.

In both cases, the results obtained by applying the RQPA on the experimental diffraction patterns of the oxidised samples are in agreement with the oxidation curves observed by TGA. Concerning the oxidations carried out in air, the huge majority of U_3O_8 obtained are consistent with the results obtained by TGA curves (Figure 4.4.3A), as well as for the experiments performed at 1% O_2 (Figure 4.4.3B) agree well with the calculated percentages of each phase. Also in both cases, those samples doped with Cr below the solubility limit present the highest proportions of the phases UO_2 and U_3O_7 . This effect is particularly highlighted in the case of thermal oxidations at 1% O_2 , which brings to light the contribution of the dopant. This indicates that an optimised composition of Cr as a dopant in UO_2 lattice will slow down the complete conversion from UO_2 to U_3O_8 and the least amount of oxidation will take place lowering the oxygen content.

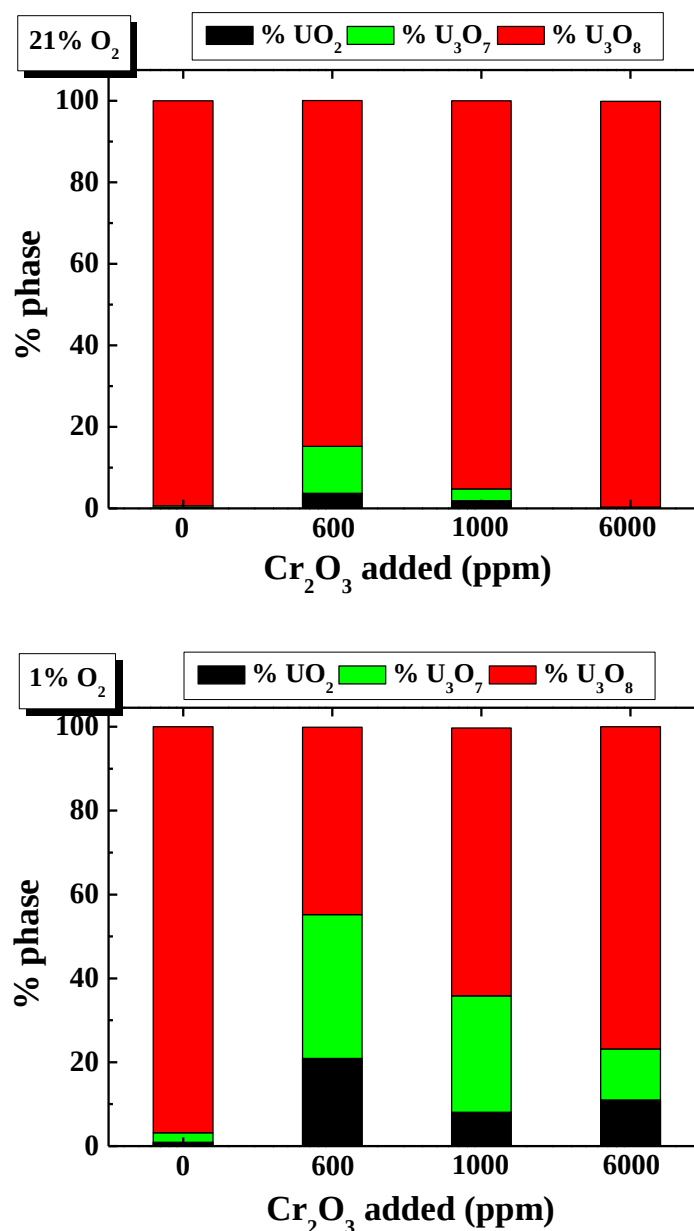


Figure 4.4.6. Composition (in percentage) of the crystalline phases quantified by using the Rietveld refinement method of the samples oxidised at 21% O₂ (top) and 1% O₂ (bottom).

4.4.4. Discussion

The oxidation behaviour of doped UO₂ nuclear fuels have been previously studied with other elements, demonstrating the effect of dopants delaying the formation of U₃O₈ in air, for example Nd and Yb [46], Ce [55], Th [56], Gd [45, 57] and SIMFUEL [58]. On the contrary, our results show that, in the case of doping with Cr, even the highest dopant concentration do not mean the highest resistance to the oxidation. It should be noted that lanthanides and actinides elements have in general a higher solubility limit

than Cr in the UO_2 matrix, thus allowing a higher amount of dopant to stabilise intermedium oxides of UO_2 and limiting the formation of U_3O_8 [58]. Nevertheless, is of great interest that even with low quantities of Cr, the effect on increasing grain size of the pellets is obtained. The microstructural characteristics in UO_2 fuel such as grain sizes, grain boundaries or exposed surface area are known to influence oxygen diffusion. It was reported in literature that the oxidation rate shows great dependence on grain size [35, 59, 60] but does not necessarily implies that grain size would be the only explanation to the slowdown of the UO_2 oxidation. The evidences found here for samples obtained from the same fabrication process and analysed under the same conditions, suggest that over a certain grain size threshold (affected by Cr levels), the oxidation degree depends strongly on oxygen pressure, whereas there is little pressure dependence at atmospheric pressure [23]. Here we study ATFs oxidation in air for the first time, obtaining that the limited quantity of Cr entering the UO_2 matrix has a negligible effect on the oxidation in air, in spite of the grain size increase [21].

It is known that the UO_2 oxidation is a temperature-dependent reaction and ensuring an inert atmosphere discards any effect during SNF dry management. However, at what extent temperature and oxygen concentration would have an impact on the U_3O_8 formation is not established, being the available experimental data very scarce for the undoped UO_2 and inexistent for doped UO_2 . Our results regarding the ATFs oxidation at only 1% O_2 are performed in order to provide new insights in these regard.

The first outstanding result from the oxidation curves at these conditions (Figure 4.4.4A) and the data extracted from the derivative curves (Table 4.4.II), is that a limited oxygen availability makes the overall reaction to proceed slower, making possible that the two theoretical steps of the oxidation of UO_2 become discernible. This feature has been previously reported in isothermal oxidations of fuel pellets [61, 62], being the first time that this effect is noticed in thermal treatments as the applied here (heating from room temperature to 973K). In fact, and from the best of our knowledge, no data has been published regarding thermal oxidation of doped UO_2 in lower oxygen concentrations than air. With the ATFs studied here, the maximum quantity of Cr is very limited; even so the effect of a delayed oxidation is obtained.

From the perspective of the overall reaction, a graphical comparison between both atmospheres used during the oxidation experiments can be seen in Figure 4.4.7. In the

figure, the extent of the reaction is represented by the final values of the average $O/(U+Cr)$ ratio, calculated from the mass gain reached by the oxidised samples [45]. The variation of this parameter is plotted vs the Cr_2O_3 doping concentration. As previously discussed, the values of $O/(U+Cr)$ in air clearly indicate total conversion to U_3O_8 , being around 2.67 in all cases. For the sake of comparison, grain size is added to this plot.

At 1% O_2 the tendency found in the $O/(U+Cr)$ ratio is the same that the aforementioned for MRTs, *i.e.* UO_2 presents the highest one (2.59 ± 0.02), $UO_2\text{-}6000Cr_2O_3$ slightly lower (2.53 ± 0.02), and much lower for $UO_2\text{-}600Cr_2O_3$ (2.34 ± 0.02) and $UO_2\text{-}1000Cr_2O_3$ (2.35 ± 0.02). Taking into account the characteristics of these samples, studied in our previous work [21], which is the increase in grain size with doping Cr concentration up to the solubility limit (Figure 4.4.7), leads us to think that the effect of the grain size at low oxygen concentrations (such as 1% O_2) could be significant in the slowdown of the reaction. The tendency found is analogous for the $O/(U+Cr)_f$ values obtained when oxidising the samples at 1% O_2 , that is the highest ratio is linked to the lowest grain size, corresponding to the UO_2 undoped pellet. The grain size increases with Cr concentration until a maximum is reached for the sample $UO_2\text{-}1000Cr_2O_3$. Grain size here is not too far away from the sample $UO_2\text{-}600Cr_2O_3$, taking into account the uncertainty margins, leading to similar $O/(U+Cr)_f$ ratios. Finally, for the sample $UO_2\text{-}6000Cr_2O_3$, a decrease in the grain size is observed, due to the segregation of Cr in grain boundaries [21]. Accordingly, $O/(U+Cr)_f$ ratio increases again.

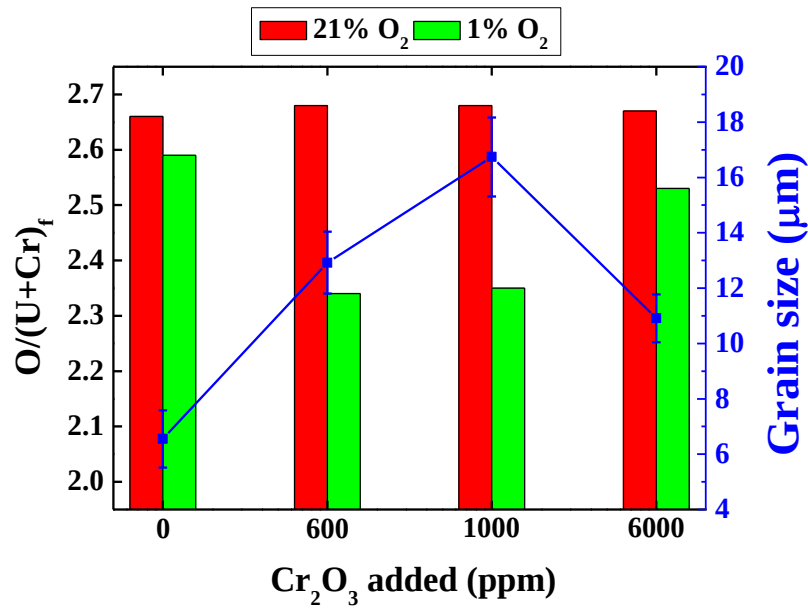


Figure 4.4.7. Final value of $O/(U+Cr)_f$, calculated from mass gain data, and grain size of the oxidised pellets versus Cr_2O_3 concentration at the different oxygen conditions studied.

4.4.5. Conclusions

Accident-Tolerant Fuels (ATFs) are a concept that comprises a set of new technologies of nuclear fuels (including the fuel itself, cladding, etc.) which provides with increased safety margins during operation, allowing increasing burnup in the reactor and improving the performance of the fuel. One of the shortest-term ATF concepts is doping standard UO_2 fuel with elements such as Cr, increasing grain size and delaying the occurrence of some undesirable processes. Given that these new fuels are being currently used in some commercial nuclear plants, its stability at interim storage conditions must be assessed, especially regarding its oxidation behaviour.

It is well-known that lanthanides and actinides doped UO_2 fuels are more resistant to oxidation in air because they provide enhanced stability to the intermediate oxides. However, the experimental results presented in this paper indicate that, when the oxidation of a kind of ATF such as Cr-doped UO_2 pellets is performed in air, the transformation to U_3O_8 is quantitative and no great effect of the dopant is observed, in spite of the measured grain size, which increases with the doping concentration. This is probably due to the low solubility limit of Cr in the UO_2 matrix, compared to the quantities of other dopants traditionally used, such as Th, Ce, La, or SIMFUEL.

This surprising outcome lies in front of the conclusions obtained when lowering the oxygen concentration. When performing the same thermal treatment but with only 1% O₂ present, there is a decrease in the oxidation degree at the same experimental time, demonstrated in: (1) no sample reaches total conversion to U₃O₈ for the oxidation time studied in this work (about 60 minutes), and (2) this slowdown of the reaction is more marked in those samples doped with an amount of Cr below the solubility limit. In this case, this behaviour could be related to grain size, which follows the same tendency that the observed oxidation degree. All in all, when the oxygen availability is low, the dopant effect, even at very low concentrations, in the order of ppm, is very marked, conversely to the previous case.

This fact has direct implications of the storage of this kind of nuclear fuels after irradiation. In fact, from the results of this study it can be derived that combining the use of ATFs with a less oxidant atmosphere during storage (as low as 1% O₂) delays the formation of U₃O₈. This is the first-of-a-kind study, and these conclusions could be extrapolated to other dopants.

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4.4.6. References

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Result 5

Performing a critical review of the database on SNF oxidation

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4.5. Result 5. Performing a critical review of the database on SNF oxidation

Abstract

Oxidation of spent nuclear fuel (SNF) with undetected cladding defects during dry storage might challenge its integrity if high oxygen-content uranium oxides (U_3O_8), characterised by a specific volume about 36% higher than UO_2 's, are formed. As a consequence, an accurate characterisation of the processes involved under anticipated conditions is of utmost significance for nuclear safety, especially taking into account the foreseen lifetime extension of dry, interim storage of SNF. Based on an extensive survey of the open literature on the subject, this paper critically reviews the data available and identifies those initial and boundary conditions at the back-end of the nuclear fuel-cycle, updated to the current trends (higher burnup, new storage designs, etc.), that might affect rates and products of fuel oxidation. The effect of fuel temperature and burnup has been sufficiently addressed to get a qualitative sound characterisation. Temperature has a substantial effect in the range of interest ($<400^\circ\text{C}$) and, according to data, below roughly 200°C oxidation rates slow down substantially and no high O/U stoichiometry oxides get formed. Burnup has been shown to affect oxidation by stabilising intermediate uranium oxides (U_4O_9), but unfortunately the burnup range explored is too narrow (<35 MWd/kgU) and only very limited data is available in the burnup range applicable to modern LWR fuels (50-60 MWd/kgU), thus a direct application to current spent fuel burnups is not recommended. Other environmental variables have been studied; however, raw data are either unavailable or incomplete and a critical assessment has not been feasible. On the grounds of this work, some recommendations based on safety-significant missing data are given.

Keywords

UO_2 oxidation; Spent nuclear fuel; Dry storage; Nuclear waste.

4.5.1. Introduction

There is an international consensus on the suitability of the Deep Geological Repository (DGR) as the safest solution for a definitive disposal of Spent Nuclear Fuel (SNF) [1, 2]. However, delay in site selection, institutional issues and capacity limitation of spent

fuel pools at Nuclear Power Plants (NPPs), have made it necessary to construct and operate new facilities where SNF can be safely stored while DGR are licensed, built and commissioned. These facilities can be Centralised Storage Facilities (CSFs) or Individual Storage Facilities (ISFs), and they are both considered as an interim solution for the management of radioactive waste, including irradiated fuel.

According to IAEA guidelines [3, 4], the safety objectives of an interim storage facility of spent fuel are: to keep the radiation doses below the prescribed limits; to ensure subcriticality of the fuel at every moment; to maintain the confinement of the fuel; and to enable a safe retrieval of SNF, if necessary.

Under dry storage conditions, several processes could challenge the goals above by threatening the integrity of undetected-failed fuel rods. One of these degrading mechanisms is the SNF oxidation. There are some stages at which fuel could be exposed to an oxidant atmosphere, in particular if an undetected cladding breach, such as a pinhole or a hairline crack, exists [5-7]. If this occurs, UO_2 (SNF matrix) oxidation might take place.

UO_2 oxidation is a well-known reaction usually written in the form $\text{UO}_2 \rightarrow \text{U}_4\text{O}_9/\text{U}_3\text{O}_7 \rightarrow \text{U}_3\text{O}_8$ [8-10]. The extent to which this reaction can affect fuel confinement is dependent on prevailing boundary conditions and specific SNF features. In case the reaction progressed up to the end product (in absence of any moisture [11]) and formed the U_3O_8 phase, fuel would jeopardize the cladding performance as the first engineering barrier to prevent fission products escape. This phase entails a volume increase of about 36% with respect to the initial UO_2 , and its formation provokes pulverization and spallation of the initial UO_2 pellet [8, 12, 13]. Therefore, if U_3O_8 is formed in a sufficient amount, and depending on the condition of a pre-existent failure in the fuel cladding, it could provoke failure propagation and even allowing certain release of radioactive material [14-16].

This work gathers and critically reviews the existing literature regarding the SNF oxidation in dry conditions, identifying the most-affecting parameters and bringing to light the drawbacks of the database. Attention is paid to those SNF features which have been substantially affected by the evolution undergone by NPP operation, like burnup discharge. In addition, the temperature effect and the influence of environmental parameters (oxygen partial pressure, moisture and nitrogen oxides content in the air)

have been examined. As an outcome of the analysis carried out, recommendations on research needs in future are made.

4.5.2. Key oxidation boundary conditions

The base case scenario considered as a reference point of the key factors affecting SNF integrity is an interim dry storage facility. At this point, the fuel arrives after being cooled down in the on-site pools at the reactor site, and being dried, loaded into storage casks and transported to the facilities. There are specific requirements that the fuel must meet upon being stored; typically, temperature is one of the most exhaustive because of its importance. The upper limit temperature allowed in inert atmosphere storage conditions for LWR spent fuel is 400°C, based on the requirements given by the US Nuclear Regulatory Commission (NRC) [5-7]. This threshold temperature is based on the peak cladding temperature, and it is applicable to normal conditions of storage and transportation [17], based on the need to avoid creep deformation of the cladding over time [6] and to maintain cladding without a significant amount of radially re-orientated hydrides that may form under normal storage conditions. By using this peak clad temperature for fuel having average assembly burnups less than 45 MWd/kgU, only a small fraction of the rod will experience a significant amount of radially hydride reorientation [6]. It should be noted that, during dry storage of the fuel, there will be a range of temperatures and burnups both in the fuel rods (axial profile) and during the storage time. The database reviewed here focuses on the experiments performed with irradiated fuel simulating specific conditions within this wide range.

Besides storage temperature, the behaviour of spent fuel is significantly affected by the steady-state operation history. Therefore, the burnup at which the fuel is irradiated is an important feature that will have an impact on its properties and long-term stability, as it affects both the fuel final composition (*i.e.* presence of fission products, minor actinides, and other elements) and its microstructure due to defect accumulation (mainly grain size and porosity) [18-22]. The change of these burnup-dependent variables will influence the spent fuel inventory, the mechanical properties (hardness, fracture toughness) of SNF and its oxidation, and therefore must be taken into account in a dry storage scenario. Thus, they are discussed in these terms in the following sections. Because of the marked focus of this review, *i.e.* a critical discussion on the parameters affecting the spent fuel oxidation, some fuel properties related with the oxygen diffusion

in grain-boundaries and more exhaustively studied in the oxidation of unirradiated UO_2 are not included here, such as specific surface area and particle size, and only a brief comment is given in the grain size section.

In addition to the fuel characteristics, the surrounding atmosphere where the fuel is placed must be well-known. In particular, the presence of oxygen in the atmosphere at which the fuel is exposed may produce the oxidation, if the exposure time to O_2 is elevated. In this scenario, the majority of experimental studies carried out with SNF focus on the worst case, which is the unlimited flow of oxygen (*i.e.* air) reaching the fuel. Exploring the possibility of lowering the oxygen content of the atmosphere may constitute an important added value for fuel management. Besides oxygen, the availability of other oxidants (nature and amount) should be addressed. Some of these oxidants may come from residual water that remains in the cask after fuel drying, and can be a source of strong oxidants, such as hydrogen peroxide. Finally, as the drying process finishes by filling the gaps inside the cask with an inert gas (such as Ar, N_2 or He), the radiation coming from the fuel itself may induce the formation of “radiation-induced” oxidant agents. Especially relevant are the nitrogen oxides.

Following the defined boundary conditions, the literature review is performed by dividing the experimental results published through the years according to the studied factors, both intrinsic (specific to SNF attributes) and extrinsic (subjected to external conditions). On the one hand, the intrinsic parameters associated with the fuel properties are addressed. A differentiation is made regarding fuel temperature and fuel chemistry (*i.e.* burnup), affecting the oxidation not only by the presence of fission products and other elements, but also because of the induced change in the physical properties of the fuel. On the other hand, the literature regarding the environmental storage conditions is explored, in terms of the presence of lower oxygen partial pressures than air, oxidants produced by residual moisture, and radiation-induced nitrogen oxides. Credit has been given to the published data, empirical methodologies to perform the oxidation, and how the data were analysed. Thus, this review is focused on consolidating what is already known about SNF oxidation, understanding the consistency among the results reported so far and identifying any knowledge gaps that additional research could contribute to further understanding.

4.5.2.1. Fuel

When nuclear fuel is in operation (*i.e.* it is exposed to a very severe thermal and radiation environment), complex interplay changes regarding composition, mechanical properties, physical parameters, etc., occur. As a result of this interaction, SNF constitutes an extremely complex material that contains almost all of the chemical elements of the periodic table.

The properties of SNF that is stored in dry storage facilities will influence its stability. Among the processes that can threaten this stability, the oxidation of this material if exposed to an oxidising atmosphere at high-enough temperature must be taken into account. These properties are mainly the mentioned temperature and burnup, and the literature regarding their impact on the oxidation reaction will be discussed in this section. A brief comment is dedicated here to the studies regarding the aging effect, which refers to store the fuel in air at low temperature during a long period of time. It seems that a consequence of this long-term storage is a delay in the overall oxidation of the fuel. This is the main conclusion obtained from Wasywich *et al.* [23], who oxidised CANDU fuel (burnup in the range 7-10 MWd/kgU) stored in dry air at 150°C for almost 100 months. An increase in the aging times results in a delay in the weight gain and powder formation, thus it seems that aging used fuel could be beneficial delaying the oxidation of the pellets. Nevertheless, it should be taken in mind that, by definition, ageing refers to the storage of the materials at low temperature, meaning that used fuel must be first cooled-down to an acceptable temperature to be stored in air. Thus, it seems that aging could be useful in ulterior oxidation experiments, but it is not a significant parameter that should be considered regarding storage of fuel.

4.5.2.1.1. Temperature

Temperature is the most important factor affecting both the rate and the extent of the UO_2 oxidation [8]. During normal conditions of storage, there will be a range of temperatures lower than the maximum allowable of 400°C. From the database analysed in this review, U_3O_8 does not appear to be formed in moderate to high burnups below a certain temperature threshold, which seems to be around 250°C [8, 24-26]. In the case of unirradiated UO_2 and low-burnup fuel, there are some evidences indicating that U_3O_8 could be formed at lower temperatures, although at very small amounts and very low oxidation rates [27]. Accordingly, and for the purpose of this work, the discussion of the

database is divided into two different domains: low thermal range ($T < 250^{\circ}\text{C}$), and high thermal range ($T > 250^{\circ}\text{C}$). In any case, other factors, such as the fuel burnup (higher burnups delay the formation of U_3O_8) and the environmental conditions (amount and nature of the oxidant agent, moisture, etc.) must be taken into account. They will be treated in next sections.

Einzigler *et al.* [28] studied the effect of the temperature performing oxidation experiments with “as-irradiated” SNF pellet fragments (LWR fuel, burnup ranging from 30 to 45 MWd/kgU) under a continuous air flow. They selected the temperature range $175\text{--}195^{\circ}\text{C}$, and obtained a stabilisation of the oxygen to metal ratio (O/M) at values around 2.4. XRD post-oxidation analysis allowed them identifying cubic U_4O_9 , and confirming the stabilisation of this phase in irradiated UO_2 [29, 30]. However, they did not report the formation of U_3O_8 in these conditions [28]. In a related study carried out with the same SNF samples, Thomas *et al.* [29] reached the same conclusions, and they proved that this effect should be partially due to the presence of trivalent fission products produced during irradiation, as they obtained similar O/M values with unirradiated, Gd_2O_3 -doped UO_2 . In the same line, Woodley *et al.* [31] studied the air oxidation of irradiated (27 MWd/kgU) fuel fragments between 140 and 225°C . The highest O/M value was reached at this latter temperature and was 2.35 after 400 hours of experiment. They did not report the presence of U_3O_8 . Wasywich *et al.*, [23] oxidised CANDU fuel fragments (irradiated at rather low burnups, 7-10 MWd/kgU) in air at 150°C and came to the same conclusions. Hastings and Novak [27] reported a number of data every 25°C in the range $175\text{--}250^{\circ}\text{C}$ under a continuous air flow for an 8 MWd/kgU burnup fuel coming from irradiated elements which were sectioned in fuel pellets (including cladding). A 15% U_3O_8 conversion was found after approximately 8000 hours at 175°C , and 50 hours at 250°C . At these conditions they calculated a 2% pellet diameter expansion and used these data to forge a safety criterion.

At higher temperatures than 250°C , U_3O_8 is clearly quantifiable and, if it experiences swelling and enough subsequent spallation from the fuel could be even released through the cladding, if breached [8].

Einzigler and Strain [32] studied the behaviour of breached (pinholes and hairline cracks defects with different sized breaches, as well as bare fragments) PWR spent fuel rods (with a burnup of 27 MWd/kgU) oxidising the samples by using a constant air flow at

high temperatures (250-360°C). Under such conditions, the spallation of the fuel was noticed at the first 4 hours for 360°C for the bare fuel fragments, and the resulting weight gain ranged between 2.5 and 3%. This clearly indicates a substantial conversion of UO_2 to U_3O_8 . For the lowest temperature, a plateau at the mentioned weight gains was found, but no spallation was reported, indicating a stabilisation of the U_4O_9 phase. Comparable results were obtained by You *et al.* [33] in the 250-400°C temperature range in their study of the air oxidation (*i.e.* continuous air flow) of PWR fuel rod fragments (35 MWd/kgU), taken by directly cutting the fuel rod without removing the cladding. In fact, even at 400°C weight gain was about only 2%, due to the time limitation of the experiment (oxidation test lasted only 2 hours). These differences in the experimental conditions make difficult to confirm these results in a longer interval. Covering the complete interim storage temperature range, Hastings *et al.* [34] studied the oxidation in air of irradiated CANDU defected fuel elements (8 MWd/kgU). They did not observe weight change at 200°C in air during 24 hours of experiment, but at 400°C in air they reported a severe sheath splitting in less than 24 hours.

A compilation of the experimental results discussed in previous paragraphs is shown in Table 4.5.I. Some of these reported data have been clustered in Figure 4.5.1 as a function of temperature. In order to make a more visual comparison, O/M values have been divided by the experimental time, obtaining a sort of “O/M increase” rate, which is a better indicator of the oxidation rate when comparing different oxidation times. The reason for doing this is the scattering of the measurement’s length, which made a straightforward comparison difficult.

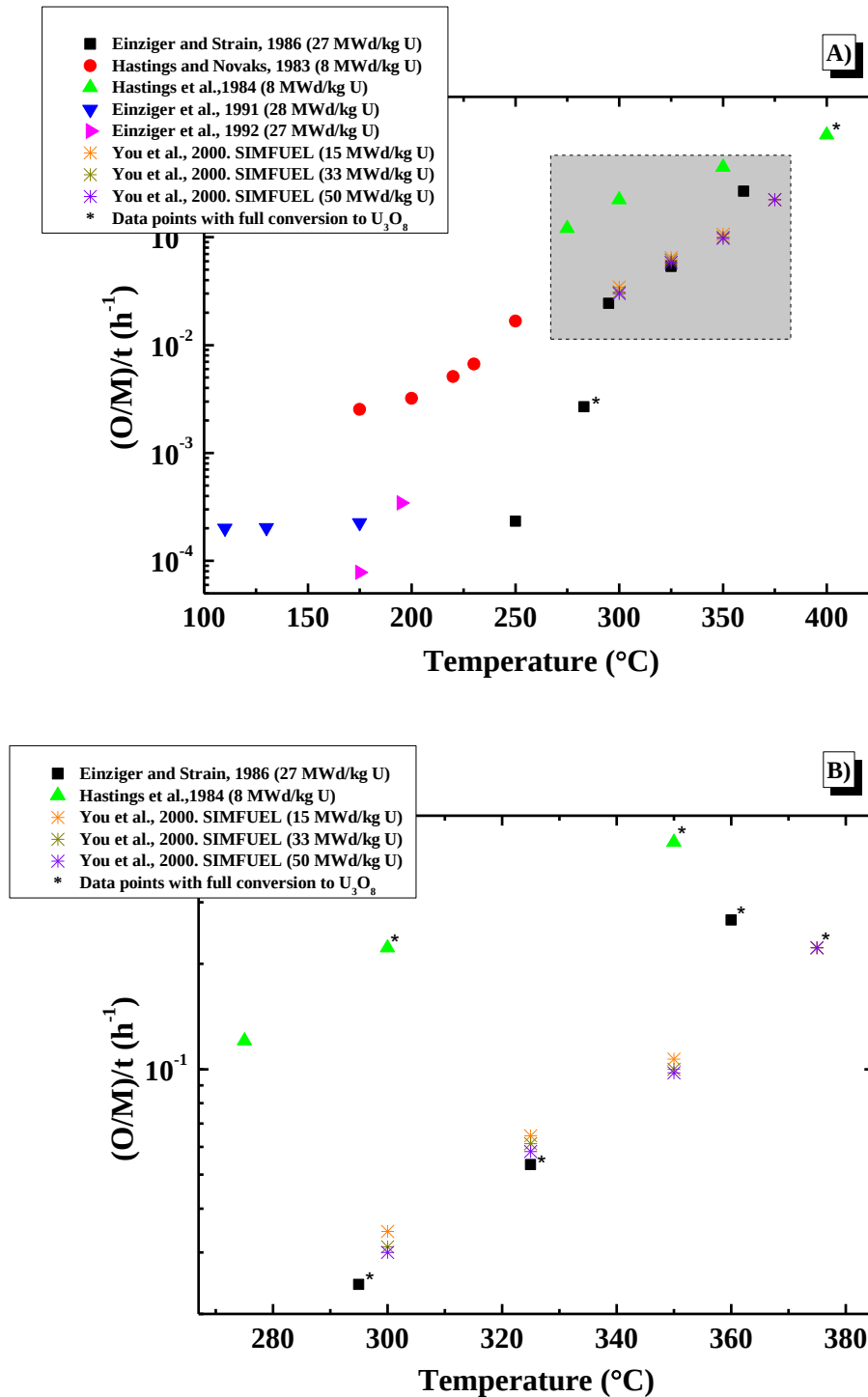


Figure 4.5.1. A) Selected air-oxidation data with SNF samples, showing temperature at which the experiment was carried out and O/M values normalised with experimental time. B)

Expanded region highlighted with a grey box in A). Data correspond to: Einziger and Strain, 1986 [32]; Hastings and Novak, 1983 [27]; Hastings *et al.*, 1984 [34]; Einziger *et al.*, 1991 [35]; Einziger *et al.*, 1992 [28]; and You *et al.*, 2000 [36]. Data marked with an asterisk correspond to those points with full conversion to U_3O_8 (O/M=2.67).

There is a general consensus that UO_2 oxidation at low temperatures (lower than 250°C) for moderate and high burnups (higher than 20 MWd/kgU) does not result in a

significant fraction of UO_2 transformed in U_3O_8 . Even with very long experiments (as is the case of the data by Einziger *et al.*, 1991 and 1992, Figure 4.5.1A in blue and pink), the oxidation rate remains low. With higher temperatures and enough exposition time to the oxidant, full conversion to U_3O_8 is reached (black and green points in Figure 4.5.1B at 300°C and higher).

From the analysis of the available literature reported, one may note:

- The need for more experimental data at high temperatures (higher than 350°C) (Figure 4.5.1), in particular at medium and high burnup levels (see next section). Given the interest in this range because the potential formation of U_3O_8 , it would be necessary to have more experimental data points for irradiated fuels to support the two plotted values (black and green points). Some previous reports have highlighted this need, in particular for extrapolate prediction models about the incubation time of U_3O_8 as a function of temperature and burnup [37].
- U_3O_8 is formed only above 250°C (except the small conversions for extremely long times obtained by Hastings and Novak [27], as pointed out before); however, the influence of other parameters could change this value to some extent. In this regard, the burnup effect might be especially relevant (next section). This threshold has been proved consistent with the semi-empirical model proposed in CRWMS (Equation 33 in [38]), which was later supported by Hanson *et al.*, [37]. The latter was specific pointing that at or below 240°C, only oxidation to $\text{UO}_{2.4}$ would occur after more than three weeks. However, the equation used for these estimates is only valid for burnups lower than 40 MWd/kgU. Further data at higher burnups would be necessary to stretch the correlation domain beyond 40 MWd/kgU.
- The existing data (Figure 4.5.1 and Table 4.5.I) show the burnup limitation to values of 35 MWd/kgU (from You *et al.*, 1992 [33]). Given the current irradiation of fuels to average burnups around 50-55 MWd/kgU, the proposed extension of the database to high temperatures and burnups should be targeted.
- By using SIMFUEL, Cobos *et al.* [39] observed the oxidation kinetics by heating samples up to 1000°C simulating burnups from 25 to 200 MWd/kgU, at a linear heat rate of 1°C/min. They found that local burnups of 80 MWd/kgU, would induce a slowdown of the oxidation to the point that at very high local burnups (150 MWd/kgU), U_3O_8 was not detected, even at 1000°C. This effect of

the simulated burnup on the delay of the oxidation was later made by You *et al.* [36] too (Figs. 1 & 2), with samples specifically simulating local burnups in the range 15-50 MWd/kgU.

- As can be seen in Figure 4.5.1 (where You *et al.* data have been included) normalisation of the O/M values with respect to time brings to light that similar conclusions may be drawn for high-temperature data. The point at 375°C is U_3O_8 for all the SIMFUEL experiments (Figure 4.5.1B). At lower temperatures, although SIMFUEL O/M rate increase with temperature shows the same order that the ones from SNF (black and green points in Figure 4.5.1B), no effect of differences in the simulated burnup is noted. If credit is given to this observation, it would mean that burnup effect might become saturated at a certain concentration of fission products corresponding to burnups between 8 MWd/kgU and 15 MWd/kgU; in other words, over a burnup threshold the slowdown effect would remain the same. Of course, extrapolation of this outcome to burnups high enough to develop the rim region would not be supported by any experimental evidence. Even if fuel composition can be simulated with these analogues, the micro-structure of high burnup fuels (*i.e.* cracks and HBS) should also be replicated, as it might affect the access of oxygen to the fuel matrix. For example, Choi *et al.* declared that SIMFUEL does not replicate features such as grain-boundary segregation of volatile elements, or distribution of fission products within the pellet [40]. This is an important aspect when integral fuel performance is concerned, as it is the case of oxidation where both fuel composition and macro and micro-structure (*i.e.* cracks and HBS) might play a role as enhancers of oxygen reach to fuel matrix.

Based on the literature review and in representative data included in Figure 4.5.1 and Table 4.5.I, another limitation of the database is also emphasised. Most of the results shown that the studies of the oxidation of irradiated fuel in dry storage conditions are based upon data from over 30 years ago, where experiments were carried out by means of available techniques, *i.e.* samples tested in a furnace and measured by weight gains or thermogravimetric analyses, measuring the weight change (and, by extension, the O/M ratio) against time at a given temperature. The use of these techniques lies on their property to study the fuel oxidation *in-situ*, thus providing a direct signal of the reaction progress in real time. By setting up the temperature and the atmosphere at which the

reaction takes place, it can be well-controlled. Nevertheless, by only measuring the fuel weight change, an averaged O/M is obtained; however, U_3O_8 could form during the mass increase and in a significant quantity to propagate a defected cladding. This effect is particularly well pointed out in the study by Colle *et al.* [41], who obtained the air-oxidation curve at 397°C of high burnup fuel (65 MWd/kgU) at different intervals, and performed XRD measurements at each data point, revealing the presence of orthorhombic U_3O_8 when O/M=2.4 (Fig. 3 of the reference). In order to overcome this, there are currently characterisation methods to get an early detection of U_3O_8 that would be advisable and would extend the knowledge to “realistic” systems. Especially interesting are the techniques exploring the surface of the sample, as it is known from the oxidation mechanism that U_3O_8 spalls from the fuel grains and appears at the pellet surface. In this regard, the use of alternative *in-situ* methods, for example modifying Raman spectroscopy or XRD set-ups, would be appropriate. In the latter technique, a recent paper has demonstrated that special sample holders allow introducing UO_2 in dedicated heaters, where the laser can be focused in order to produce the diffraction phenomenon [42]. By this method, diffractograms are continuously acquired and, depending on the acquisition conditions, the U_3O_8 formation can be detected earlier than the visual detection of powder [43]. In the case of Raman spectroscopy, its applicability as an *in-situ* technique goes beyond, as the experimental set-up is simpler, and new equipment consisting of a fiber that can be remotely controlled open new pathways in the analysis of spent fuel oxidation [44-46]. The particular Raman spectrum of U_3O_8 , together with its powerful Raman signal, makes an early detection of this compound feasible. The new capabilities provided by these techniques allow going deeper into the safety during storage of spent fuel, making possible the early detection of U_3O_8 in the appropriate conditions.

Table 4.5.I. Selected data of oxidation of SNF from a variety of burnups, temperature and experimental time.

Reference	Fuel	BU (MWd/kgU)	Temp (°C)	Time (h)	O/M _f
Einziger and Strain, 1986 [32]	PWR	27	360	10	2.67
			325	50	2.67
			295	110	2.67
			283	1000	2.67
			250	10000	2.33
Hastings and Novaks, 1983 [27]	CANDU	8	250	150	2.50
			230	350	2.33
			220	425	2.17
			200	650	2.08
			175	800	2.03
Hastings <i>et al.</i> , 1984 [34]	CANDU	8	400	3	2.67
			350	6	2.67
			300	12	2.67
			275	18	2.17
Einziger <i>et al.</i> , 1991 [35]	PWR	28	175	10000	2.26
			130	10000	2.03
			110	10000	2.01
You <i>et al.</i> , 1992 [33]	PWR	35	400	2.5	2.42
			375	2.5	2.33
			350	4	2.25
			325	30	2.25
			300	40	2.25
Einziger <i>et al.</i> , 1992 [28]	PWR	27	195	7000	2.40
			175	30000	2.35
You <i>et al.</i> , 2000 [36]	SIMFUEL	15 ⁽¹⁾	375	12	2.67
			350	25	2.5
			325	40	2.45
			300	75	2.33
You <i>et al.</i> , 2000 [36]	SIMFUEL	33 ⁽¹⁾	375	12	2.67
			350	25	2.50
			325	40	2.45
			300	75	2.33
You <i>et al.</i> , 2000 [36]	SIMFUEL	50 ⁽¹⁾	375	12	2.67
			350	25	2.44
			325	40	2.33
			300	75	2.25

⁽¹⁾Burnup obtained from the average composition of simulated fuel, as indicated in the reference

4.5.2.1.2. Burnup

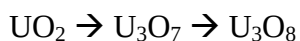
Burnup is the fission energy produced per fuel unit mass over time. It describes how extensive fuel irradiation has been and, as a consequence, it is an indirect characterisation of SNF composition [18-20, 47], which is known not to be uniform across fuel pellet. However, the fuel burnup is generally described in terms of the

average burnup of the entire fuel assembly when assessing the acceptable contents and occasionally, as the rod with the highest burnup within the fuel assembly in terms of peak rod average burnup when evaluating the fuel cladding integrity in the materials and structural examination [17].

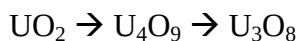
In addition, fuel microstructure changes along irradiation and at high average burnup (>50 MWd/kgU) a peripheral rim, characterised by much smaller grain size and high porosity, is formed (High Burnup Structure, HBS) [48]. In this region, Pu isotopes and fission products concentrations get substantially higher levels than in the pellet core [49-53]. At average burnups of 60-65 MWd/kgU, this region thickness has been observed to be around 100 μm [52]. Presumably, the HBS region, with its distinctive features, might affect fuel oxidation, as discussed next.

It is worth noting that since the onset of commercial use of nuclear energy, LWR spent nuclear fuels have been discharged from reactors with average burnups in the range 20-50 MWd/kgU [54]. The current trend is to increase burnup [55, 56] to 70-80 MWd/kgU with advanced technologically fuels [48].

The effect of burnup on fuel oxidation under dry storage conditions has been investigated experimentally. Oxidation of unirradiated fuel and low burnup fuels, mainly CANDU (6-12 MWd/kgU), has been shown to go through U_3O_7 as intermediate product before turning into U_3O_8 [8, 14, 23, 30, 43, 57-59]. At higher burnups (20-50 MWd/kgU), though, the reaction route has been seen to proceed through U_4O_9 instead [60, 61], which can be stabilised even at O/M values up to 2.4 (due to the extra oxygen atoms that the U_4O_9 structure is able to accommodate [30]). Therefore, experimental data support the following 2-step oxidation paths:



Burnup less than 12 MWd/kgU



Burnup in the range 20-50 MWd/kgU

A graphical comparison of the O/M ratio at the end of tests between different burnup ranges is shown in Figure 4.5.2. The available data have been clustered according to the burnup ranges discussed above and extended over 60 MWd/kgU, for two temperatures: 200°C (black) and 300°C (red).

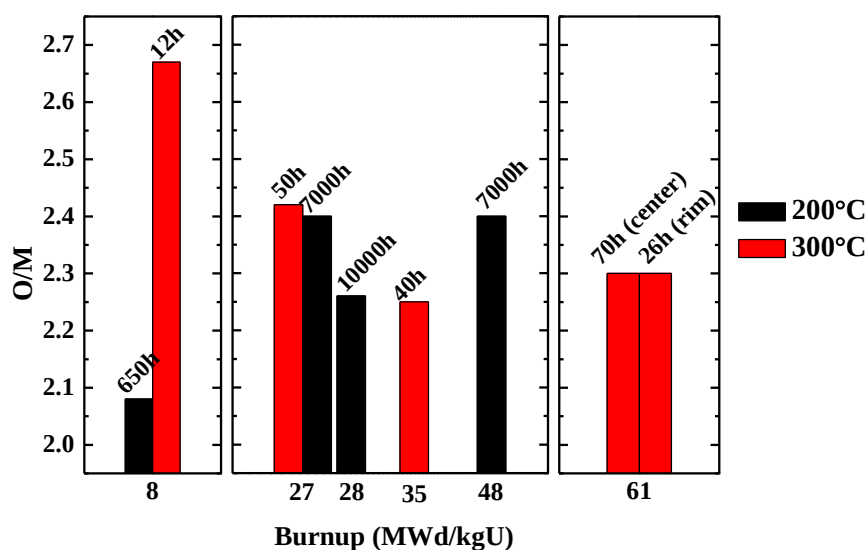


Figure 4.5.2. Relation of O/M with burnup, divided into three regions of interest, for a set of experimental values published in the literature, divided into two temperature regions (200°C, black bars and 300°C, red bars) for the sake of clarity. Data correspond, from left to right, to Hastings and Novaks, 1983 [27]; Hastings *et al.*, 1984 [34]; Einziger and Strain, 1986 [32]; Einziger *et al.*, 1992 [28]; Einziger *et al.*, 1991 [35]; You *et al.*, 1992 [33]; Einziger *et al.*, 1992 [28]; Hanson *et al.*, 2008 [37]. The time of each experiment is indicated above the corresponding bar.

According to Figure 4.5.2, the temperature effect is quite noticeable at low burnups [27, 34]: weak oxidation occurs at 200°C (O/M=2.1) after 650 hours, but full conversion to U_3O_8 is reached (O/M=2.67) in only 12 hours at 300°C [32]. This fast oxidation at 300°C is consistent with the observations made for unirradiated fuel [8, 30].

At the mid burnup range (20-50 MWd/kgU), observations look drastically different. At high temperature (300°C), after more than 2-3 times the same reaction time as in the low burnup range, oxidation is notably less developed, O/M ratio being between 2.25 (40 h) and 2.42 (50 h); in other words, under same thermal conditions (300°C), burnup hinders fuel oxidation development. At 200°C, after over 7000 h reaction time, oxidation attains sort of the same level, with O/M ratios between 2.25 and 2.4. Namely, for the mid-range burnup some fuel oxidation seems to be feasible at 200°C but it would take about 10 months to reach the same oxidation level as shown in 2 days at 300°C. The two data points from Einziger *et al.* [28] (27 and 48 MWd/kgU), and also the observation at 28 MWd/kgU [29], just illustrate this: no difference in oxidation level, despite the nearly double factor in burnup, is obtained for the first oxidation reaction, *i.e.* formation of

UO_{2.4}. In fact, such a slow oxidation in mid-range burnups at low temperatures has been interpreted as a stabilisation of the intermediate phase (U₄O₉) [30]. This effect is not observed for higher temperatures (300°C) and low burnup, as pointed out in Figure 4.5.2. This interpretation would also support the idea that the influence of burnup on the overall oxidation process begins to be significant at medium-high burnups, where U₄O₉ becomes very stable and delays the formation of U₃O₈. This behaviour has not been observed in the lowest burnup range (Figure 4.5.2).

The correlation discussed above between burnup and oxidation, based on the data at low and mid-range burnup in Figure 4.5.2, was qualitatively confirmed by Gilbert *et al.* [62]. They oxidised a number of LWR fragments from different locations of a fuel rod irradiated to an average of burnup of 29 MWd/kgU in air at temperatures ranging from 220 to 283°C. According to their observations, the samples from areas with a higher local burnup took longer to reach U₃O₈. The authors postulated that burnup enhanced the diffusion rates of oxygen through the grain boundaries (thus increasing the oxidation rate during the first step of the oxidation), but the associated fission products stabilised U₄O₉ and therefore delayed the spallation of U₃O₈ from the pellet surface.

At burnup higher than 50 MWd/kgU, Hanson *et al.* [37] obtained a weight-gain oxidation curve of a highly-irradiated (average burnup 60.9 MWd/kgU) fuel at 305°C, differentiating from the fuel fragments coming from the centre of the pellet and those coming from the peripheral zone. As shown in Figure 4.5.2, no significant differences exist between the two fragments (rim and pellet centre) used in the oxidation experiment, except that in the case of the rim fragment oxidation got steady about three times faster (oxidation rate). According to the authors, no hard conclusion can be settled on the HBS effect on the extension of oxidation, due to the release of fission gases during the oxidation, which caused a sample weight loss and, as a consequence, prevented the accurate measurement of O/M ratio. As for comparison with the previous burnup range at the same temperature, again the major difference is how fast the first step of the oxidation process took place. No U₃O₈ was reported at any time even at 300°C, which contrasts with observations at the low burnup interval.

From Figure 4.5.2 and the above discussion, we might conclude that burnup accelerates oxidation to intermediate products (*i.e.* U₃O₇ or U₄O₉) but hinders U₃O₈ formation, at least in the time scales (longer than 10 months) considered during the experiments done.

This said, the experimental evidences are few, particularly at really high burnup, and further experimental data would be helpful to support the observed trends.

Some attempts have been made in order to fill this gap. For example, Papaioannou *et al.* [63] carried out the oxidation of LWR de-cladded fragments irradiated with nominal burnups of 50 and 65 MWd/kgU at 300, 350 and 400°C in air. While at 300°C they reported a similar behaviour for both fuels, at higher temperatures they found that the fragments irradiated at 65 MWd/kgU oxidised faster than those of 50 MWd/kgU. They attributed this to an enhanced porosity (and thus, a higher surface area) of the former sample, allowing faster oxygen diffusion. However, the authors did not distinguish between “centre” and “rim”, as Hanson’s did, and thus their conclusions should be interpreted as an average behaviour, so a clear effect of the HBS cannot be warranted.

Colle *et al.* [41] reported results of a 65 MWd/kgU UO₂ fragment oxidation in air at 397°C to U₃O₈. They reported the onset of U₃O₈ formation within 2 hours of experiment and complete conversion to this phase in 2 days. However, according to the authors’ discussion it might be that the actual burnup of the sample was rather lower than what thought to be. So, it is uncertain whether this data can be used to characterise oxidation in the high or in the mid burnup interval, but anyway at nearly 400°C.

Jegou *et al.* [46] studied the oxidation of irradiated UO₂ (60 MWd/kgU) and MOX (47 MWd/kgU) fuels employing Raman spectroscopy. The authors identified a stabilisation of the U₄O₉ phase and a resistance to the formation of U₃O₈, especially in the rim regions and in zones close to Pu agglomerates, in the case of MOX sample. Unfortunately, these data cannot be used quantitatively because the temperature at which the experiments were carried out is unclear, as they used the laser-heating method to oxidise the sample.

Burnup is a parameter that not only affects the SNF oxidation by itself, but also provokes a number of changes in the material that could also affect the oxidation reaction. The main “burnup-induced” feature is the previously mentioned HBS, with associated changes in the rim zone of the pellets, mainly in its mechanical properties (different porosity and grain size with respect to the pellet centre). Some attempts of addressing the impact of these parameters on the SNF oxidation have been carried out:

- Porosity: According to the oxidation mechanism, in theory a fuel with higher open porosity would oxidise faster, as there are open pathways for oxygen entry to carry out the reaction in the bulk of the pellet. In fact, Thomas *et al.* [64] pointed out that the oxidation of LWR fragments (nominal burnup 28.4 MWd/kgU) at 175°C in air was non-uniform, being enhanced at the pellet rim. They associated this fact to the local porosity found in this region of the pellet, probably due to the accumulation of fission-gas microbubbles in this zone; and did not link it to the larger pores located in the centre of the pellet. However, they claimed that “no burnup-induced microstructural effects” were observed in the pellet rim, stating that the enhanced oxidation of the region was solely due to fission-gas bubbles. Indeed, it is unlikely that a proper HBS was formed with such a low burnup, but a first approach was described. Same authors [65] reported an enhanced oxidation near fabrication-induced porosity, explaining that these micro-pores open pathways for oxygen diffusion in the grain boundaries. However, in the Hanson’s work previously described (average burnup 60.9 MWd/kgU, air-oxidation at 305°C), it is affirmed that “the presence of the HBS did not accelerate oxidation because of the fine-grained, high-surface-area structure” [37]. Therefore, the effect of porosity, particularly at the HBS, on the oxidation remains unknown. The competition of effects between higher porosity (enhancing oxidation) vs accumulation of plutonium and other fission products (lowering oxidation) in the outer region of the fuel and its impact on the oxidation is still not clear, and more experimentation in this regard is highly recommended.
- Grain size: Grain size affects the oxidation of used fuel, also because of the mechanism itself: oxygen diffusion along grain boundaries. Therefore, it is expected that this process will be faster in smaller grains. A very recent paper has shown this effect, among others, by an extensive theoretical study [66]. In fact, this influence will be probably due to a combination of effects: besides the oxidation mechanism, smaller grains imply a higher specific surface area of UO_2 exposed to the oxidant agent. However, from the published works studying this parameter, it seems that its importance is observed only under a certain threshold size. Thomas *et al.* [29] reported an oxidation behaviour independent from grain size under their experimental conditions (LWR fuel, burnup range 27-48 MWd/kgU, air oxidation at 175 and 195°C). They selected fuel fragments with

grain sizes ranging from 7-15 to 20-30 μm . The small range studied may be a reason of this insensitivity. In addition, the selected temperature range is probably too low to observe significant changes in the reaction (*i.e.* no U_3O_8 is expected). Thomas and Einziger [67] attributed it to an indication of cracking in the pellet surface, which would “refine the grain size” and accelerate the oxidation in both small and large grains [67]. Also, an increase in the oxidation reaction rate with decreasing grain size, for samples with grain size below 5 μm was reported by Wood and Bannister [68]. At higher temperatures, Bennett *et al.* [69] observed the effect of grain size in the oxidation of irradiated UO_2 fragments (11.7-26.7 MWd/kgU) in air at 175-400°C. They reported a positive correlation between grain size and the time to start observing U_3O_8 , namely “*induction time*”, also confirmed by Wood and Bannister [68] and Kinugasa *et al.* [70]. The latter authors reported not only the positive correlation between induction time of oxidation and grain size, but also that the size of the U_3O_8 powder particles formed by oxidation increased with larger grain size [70].

Besides the comments about the impact of burnup and its associated features on the SNF oxidation, the observation about the suitability of modern techniques to characterise the reaction and detect an early formation of U_3O_8 is very pertinent here. Indeed, new methods such as the aforementioned modifications on XRD and Raman spectroscopy experimental set-ups assure quality control of the samples. In the particular case of burnup, *in-situ* image techniques are especially recommended for following the morphological changes associated to the oxidation, for example cracking of grains, the impact of porosity, etc. Some attempts using *in-situ* scanning electron microscopy configurations have been already published for unirradiated UO_2 [12].

4.5.2.2. Environmental composition

A number of environmental factors (*i.e.*, variables characterising the medium around SNF) may impact SNF oxidation rates and extension. Those that drew attention of most past research are reviewed and discussed next.

4.5.2.2.1. Oxygen partial pressure

The vast majority of the experiments investigating the oxidation of SNF in dry storage conditions are carried out with an unlimited air flow, *i.e.* 21% O_2 , from the reviewed literature so far. This fact is likely a consequence of the worst-case that could take place

at a dry storage facility. However, lower O_2 concentrations were of interest, as O_2 starved environments might be considered as a preventive measure at any stage of the SNF management.

A sound relation between oxygen partial pressure and oxidation rate has not been established yet. Nakamura *et al.* [71] oxidised artificially defected fuel rods irradiated within the burnup range 14-30.6 MWd/kgU. Temperatures ranged from 200 to 240°C at the atmospheres studied contained 1, 5 and 21% O_2 in argon mixtures. As expected, they concluded that oxidation rates were faster in air than with lower oxygen concentrations; even in air flow samples experienced very little deformation. The limited temperature range, where presumably U_3O_8 is not formed, prevented any further conclusions of the effect of oxygen concentration. Kolyadin *et al.* [72] studied the oxidation of SNF (irradiated with burnups between 10.07 and 19.7 MWd/kgU) at 300°C. In this case, the selected oxygen atmospheres were composed by 0.08, 0.48 and 1.3% O_2 in N_2 . Their conclusions were similar to Nakamura *et al.*, *i.e.* the reaction rate decreased when the oxygen content was low.

In short, despite qualitative information is available, no quantitative data can be used to set a sort of correlation.

4.5.2.2.2. Residual moisture

Besides oxygen, the impact of other oxidants with a higher oxidation potential, which could be present in the considered scenario, should be explored. These oxidants could be formed from residual contents of water that remain in the cask after fuel drying [73]. The U/H_2O reaction rate is strongly influenced by temperature and relative humidity [74], fitting an Arrhenius kinetic dependence. Even though it is known that small amounts of moisture in air significantly increase the reaction rate of uranium relative to dry oxygen [74], most of the studies regarding the fuel corrosion by the effect of water are focused on its oxidative dissolution, relative to the definitive disposal of SNF, and not to its oxidation because of humidity. As the former process would correspond to definitive disposal of SNF, it is out of the scope of this work.

Thus, water can affect the oxidation rate of SNF in three ways [75]:

- As a medium for intermediate phase reaction.
- As a reagent for the formation of hydrated compounds.

- As a source of radiolytic oxidants, such as H_2O_2 and various free radicals. In particular, the radiolytically generated hydroxyl radical ($\text{OH}\cdot$) is formed from radiolysis of water [76] and, besides its high reactivity forming hydrogen peroxide by recombination or also reacting rapidly with reducing materials, its interest remains in its high oxidation potential (around 4 times higher than the oxygen one [16]).

Although extensive work regarding these three processes has been carried out with unirradiated UO_2 [75, 77-79], some authors have emphasised the difficulty to study the moisture content with used fuel [78], which is the main knowledge gap of the impact of the residual moisture on SNF oxidation. Fundamental studies on the impact of moisture on the SNF oxidation were also performed and different results have been reported. On the one hand, several authors have reported an effect of moisture under certain experimental circumstances. The oxidation of CANDU fuel (average burnup 8.3 MWd/kgU) at 150°C with limited air and 100% of relative humidity was studied by Wasywich *et al.* [23]. One of the outcomes of the work was that the presence of moisture promotes a more generally distributed oxidation on UO_2 grain boundaries. However, they did not report an impact of this fact on the fuel performance at the dry storage facility. It is important to highlight that these conclusions were obtained under a limited air supply, which could distort the results. Leenaers *et al.* [80] carried out microscopic observations of BWR fuel rods (irradiated with an average burnup of 23 MWd/kgU) stored for 25 years at ambient temperature (dry air for 10 years and a moist environment, consisting of $0.4\pm0.2\%$ of H_2O , for the remaining 15 years). They concluded that moisture accelerates the oxidation process also at ambient temperatures, and found that grain boundaries are affected. However, even though oxidation was detected, they concluded that spent fuel still showed a generally good condition, minimising the detected impact of moisture.

On the other hand, several studies have shown that relative humidity (lower than 33%), has no effect on the rate of oxidation [8, 29, 31, 81, 82]. Woodley *et al.* [31] oxidised PWR fuel samples between 140 and 225°C (burnup around 26 MWd/kgU) with water vapour partial pressures varying over four orders of magnitude. They reported no significant effect of these conditions on the oxidation rate. The hypothesis given by these authors lie on the SNF oxidation mechanism itself: as oxygen diffusion proceeds along grain boundaries, and this diffusion is fast due to fission gas bubbles and

mechanical defects on the pellet surface, the oxidation up to U_4O_9 can be considered to occur at the same time throughout the sample. In such conditions, the presence of moisture is unlikely to accelerate the process [8, 78]. This final conclusion is supported by a recent report by Shukla *et al.* [83], who specified that no significant fuel reconfiguration is needed to control criticality, and no major loss of fuel internals are expected in dry storage facilities due to residual water.

Regarding radiolysis-assisted fuel oxidation of residual water, the UO_2 could be oxidised or form hydrated uranium oxides (uranium secondary phases), such as schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$) or studtite ($(\text{UO}_2)_2\text{O}_2 \cdot 4(\text{H}_2\text{O})$) [75, 78], depending on the relative humidity. In this sense, additional systematic oxidation experiments using humid air or (partially) inert gas, in order to study in detail the impact of radiolytic decomposition of residual water (i.e., radiolysis) in the oxidation would be valuable.

4.5.2.2.3. Nitrogen oxides

Radiation coming out from fission products and actinides present in the SNF might change the cover gas in which fuel is stored. In particular, if this filling gas is nitrogen, the interaction with the radiation could result in the formation of strong oxidants, like nitrogen oxides (general formula NO_x) [8, 84, 85]. The reaction between NO_x and residual water could yield nitric acid, although its concentration should be low and the effect on the fuel oxidation minor [86].

Limited experimental studies have been found concerning the specific effect of NO_x formation on the oxidation rate of SNF. In [87], Campbell *et al.* oxidised LWR pellets (irradiated with burnups ranging from 8 to 34 MWd/kgU) in static air at temperatures ranging from 200°C to 220°C with and without an external gamma source of 0.556 Gy/s. They found that oxidation rates for samples exposed to gamma field were significantly higher, and attributed this to the formation of NO_x compounds in the static air [8]. Few studies have been focused on the particular effect of NO_2 [9, 87-89]. Oxidation experiments with UO_2 fragments from CANDU fuel in air and in air+ NO_2 mixtures (up to 1 vol.% NO_2) were described by McEachern *et al.* [89], who concluded not only that there is an increase in the oxidation rate, but also that the formation of higher oxides than U_3O_8 (i.e. UO_3) takes place in presence of NO_2 . These observations indicate that the enhancement of the oxidation by effect of the nitrogen oxides should be considered in dry storage scenarios [85].

4.5.3. Conclusions and recommendations

In this work, a thorough critical review of the available data regarding the impact of different factors on the SNF oxidation has been carried out. Credit has been given to the data, the facilities and the experimental procedures to perform the oxidation, being thus this review focused on revising eventual knowledge gaps and consistency among the results reported so far.

Besides this consideration, the assessment of the existing database concerning the behaviour of SNF when exposed to oxidising atmospheres in a dry interim storage scenario has pointed out significant knowledge-gaps and uncertainties that need to be addressed to ensure its reliable application in the current nuclear operation scenario, where the new tendencies (increasing irradiation fuel cycle length and higher burnup to expand the operational yield of existing LWRs, use new fuel designs with accident-tolerant fuel, etc.) require a literature update. One of the main outcomes of this review is that available data are very scarce for some relevant indicators, such as the temperature and burnup. Based on the highlighted gaps of the empirical database and remaining work previously discussed, some specific recommendations for R&D are provided here:

- **Temperature:** There are large data gaps concerning the impact of temperature on SNF oxidation. In spite of covering the expected temperature range in a dry storage facility, the reported data are few and, at some points, only one/two experiments have been carried out, thus preventing a proper reproducibility analysis. The discrepancies found in the experiments performed under similar conditions, in particular at high temperature ($>350^{\circ}\text{C}$) reveal the lack of robust conclusions in this temperature region, especially important because it is feasible during dry storage of the fuel and it ensures the formation of U_3O_8 . In addition, it is highlighted that most of the reviewed studies correspond to experimental campaigns carried out around 30 years ago, and mainly using thermogravimetric methods as analysis techniques, measuring the “bulk” oxidation in terms of the progress of the O/M ratio. The use of modern techniques, with capability to detect early formation of U_3O_8 and able to analyse small quantities of samples is highly recommended.
- **Burnup:** There is a general knowledge of the effect of burnup on the oxidation, in particular at low-medium burnups. However, the conclusions obtained from

this review need to be supported by a robust experimental database, especially at high burnups, being increasingly more common in current nuclear power plants. The assessment on the oxidation behaviour of SNF and the impact of high burnup fuel should be evaluated in terms of its anticipated consequences under dry storage conditions. Research activities and an adequate experimental database are required for a full understanding of the SNF oxidation mechanism (including fuels with burnup higher than 50 MWd/kgU), where the current database is scarce and present some inconsistencies. Also here, complementary experimental techniques could be used in addition to traditional thermogravimetric approaches, always ensuring a correct control in all the affecting parameters (in particular the control of the fuel temperature). Added to this issue, a systematic approach on oxidation tests is highly recommended, not only by means of conventional techniques for investigating the effect of burnup but accounting the development on analysis techniques to properly determine the oxidation phases formed at each stage. Image techniques, which can be configured for *in-situ* tracking of the reaction, are highly recommended here.

- Porosity: The formation of the HBS at the pellet rim as a consequence of an increased burnup during operation has brought to light the need to better understand the effect of porosity on the oxidation. It seems that a higher porosity would not accelerate the reaction at certain conditions, but the lack of data is evident, being this recommendation related to the requirement of more experiments with fuels irradiated at higher burnups.
- Grain size: The current nuclear operation scenario points out to the fabrication of fuel pellets with the highest grain size achievable, in order to improve the performance of the fuel during both irradiation in the reactor and storage [37, 90], giving place to new fuel designs such as the so-called Accident-Tolerant Fuels (ATFs). The study of the oxidation of these materials at storage conditions, because of their use, is necessary to confirm the enhanced safety that they claim to provide. Nevertheless, it should also be mentioned that although the study of the fuel oxidation in these conditions deserves credit, it seems that grain size will play a secondary role, *i.e.* its impact on the oxidation will not be major.
- Oxygen partial pressure: In contrast to the effect of oxygen on the oxidation reaction on unirradiated UO_2 that has been widely studied through the years [9,

91-97], there is an evident gap of knowledge regarding the impact of lowering the oxygen concentration on the oxidation of SNF. Experimentation with fresh surrogates is broader, but the impact on real irradiated pellets still needs to be assessed. Alternative designs of dry storage facilities, that foresee the possibility to partially inertise the dependencies where SNF is placed, support this recommended experimentation.

- Residual moisture: There is an evident sparsity of conclusions regarding the effect of moisture on SNF oxidation. The variability of experimental conditions (*i.e.* temperature, level of humidity, burnup of the fuel, etc.) makes it difficult to compare effects. Integrated tests with well-defined boundary conditions, preferably those expected in a dry storage facility, would be desirable. Nevertheless, it seems that the effect of water is not primordial compared to other variables given the success of the current drying processes, and the proposed experimentation could be considered as “non-critical”.
- Nitrogen oxides: The few experimental data found regarding the effect of nitrogen oxides on the oxidation of SNF have revealed that these oxides could significantly enhance the reaction. Given the feasibility to fill the storage casks with N₂ after drying, or the possibility that radiation could provoke the radiolysis of air, this effect should be given more credit, and integrated studies with SNF and gaseous atmospheres containing NO₂ would be desirable.

According to previous discussions, comprehending the aspects that control the U₃O₈ formation from SNF at dry interim storage conditions is essential for ensuring the integrity of fuel rod cladding and providing assurance that the correct gaps are being addressed. In general, the lack of consistent and systematic work on irradiated fuel oxidation is underlined, especially regarding to fuel characterisation and well-defined experimental conditions during the conducted tests. Precise solid phase characterisation both before and after the thermal dry oxidation experiments is required. Given the complexity of the spent fuel characterisation, more efforts focusing on thoroughly comprehending and standardizing the empirical approaches should be taken into account. In this regard, the use of alternative *in-situ* methods, *e.g.* modifying Raman spectroscopy or XRD set-ups, would be appropriate. Also, the degree of conservatism in using unirradiated UO₂ or SIMFUEL as a surrogate of SNF and its relationship with SNF behaviour (an appropriate definition of the applicability ranges and limitations) should be evaluated.

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4.5.4. References

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Result 6

Applying the acquired knowledge to the oxidation of high-burnup SNF

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4.6. Result 6. Applying the acquired knowledge to the oxidation of high-burnup SNF

Abstract

In this work we have studied, for the first time, the oxidation of highly-irradiated Spent Nuclear Fuel (SNF) at *in-situ* conditions, with a controlled temperature and atmosphere, and measuring in the same experiment the oxidation in both the pellet centre and the rim. The oxidation of the SNF matrix is of paramount importance from the nuclear fuel safe storage point of view, mainly because the potential threat that the formation of the oxidised phase U_3O_8 entails. In this work a measurement protocol for following *in-situ* the oxidation of SNF at controlled conditions (350°C, constant air flow), based on the use of Raman spectroscopy as the measuring technique, is presented. The installation of the set-up inside a hot cell has been successfully applied. The radial surface oxidation of the irradiated fuel sample (63 MWd/kgU) is followed. In the centre, U_3O_8 is obtained after 62 hours. In the pellet periphery, the first spectrum of U_3O_8 is not observed until almost 92 hours, although even after that not-oxidised spectra are still acquired. These results evidence that the higher local burnup and increase of fission products could enhance the oxidation resistance of the fuel in these conditions. This is the first time that this effect is proved in a temperature-controlled oxidation, single experiment.

Keywords

Spent Nuclear Fuel; oxidation, dry interim storage, high burnup, U_3O_8

4.6.1. Introduction

Spent Nuclear Fuel (SNF) is a complex material in which, due to the own nuclear reactions for energy production, a variety of elements are contained in different chemical forms. Additionally, irradiation damage modifies the crystalline structure, altering its lattice vibrations. The radiation emitted by SNF further complicates the system, making it extremely difficult to handle and more challenging to manage than other wastes, with extremely long storage times. Accordingly, the behaviour of SNF must be understood and evaluated at each and every stage of the back-end of the nuclear fuel cycle [1, 2]. Among them, dry interim storage represents an intermediate step in nuclear waste management before its final disposal. Understanding the behaviour of the

fuel in this scenario is critical, since it will define the design of storage facilities and it will describe the initial state of the fuel at the disposal stage [3].

One of the main concerns about the SNF integrity during dry storage is the potential oxidation of the SNF matrix, *i.e.* UO_2 , as the main component of most of current nuclear fuels. UO_2 oxidation is a process dependent on both the physicochemical changes associated to irradiation (basically the burnup, related to the inventory) and the boundary conditions (mainly temperature, presence of oxidant agents, moisture, etc.) [4]. Some knowledge gaps are arising in the nuclear fuel oxidation field, due to the current tendency to increase burnup during irradiation, as a way to improve the performance of the fuel [5-7]. In fact, at average burnups higher than 45 GWd/t_{HM}, the higher density of epithermal neutron resonance absorption by ^{238}U at the pellet outer edge, or rim, leads to a local enrichment in ^{239}Pu , and therefore to a higher local fission density. This fact makes that the local burnup at the pellet periphery is around 2-3 times higher than in the pellet centre. A consequence of this enhanced burnup is increasing the porosity and the grain division in this area, making it different to the rest of the pellet, and thus called High Burnup Structure (HBS) [8-12].

While significant experimental work has been done in the past in studying oxidation of fresh UO_2 , very scarce data concerning fuel oxidation for LWR fuel at medium-high burnups is available in the literature. In addition, the conclusions reached are sparse. For example, while Papaioannou *et al.* [13] reported an enhanced oxidation of fuel fragments irradiated at higher burnups (65 vs 50 MWd/kgU) at 350 and 400°C; Hanson *et al.* [14] stated that no different behaviour was found at 300°C between irradiated fragments (60.9 MWd/kgU) coming from the centre and from the peripheral zone.

The previously cited results, as well as other published works about the SNF oxidation at lower burnups, have often been obtained by conventional thermal analysis techniques, such as thermogravimetry, which provide limited information about the structural properties [15-19], measuring the “bulk” of the oxidation in terms of the variation in the O/M ratio. In this regard, Raman spectroscopy is presented as an interesting alternative technique, since its characteristics as a punctual method for measuring the surface of the samples allows an early detection of U_3O_8 , which could be critical for nuclear facilities safety. In addition, it is able to follow the changes in the UO_2 oxidation by identifying the Raman signal of the involved oxides (*i.e.* UO_{2+x} ,

$\text{U}_4\text{O}_9/\text{U}_3\text{O}_7$, U_3O_8) [20-26]; and allows following a systematic *in-situ* analysis of the reaction through the use of adapted systems [27, 28]. These systems provide not only with selected environmental conditions (temperature, gas composition, etc.), but also with enhanced radiation protection of workers, since they encapsulate the radioactive material and can be installed inside glove boxes or hot cells. The aforementioned punctual behaviour of Raman also allows distinguishing between the different parts of the fuel pellet in the same experimental conditions.

The study of the SNF oxidation by using Raman spectroscopy is limited up to date, being it widely used for fresh fuel, as previously mentioned. In fact, and for the best of our knowledge, only the study of Jegou *et al.* [29] has tried to evaluate the oxidation mechanism of high-burnup SNF. These authors used the laser heating method to give evidence of the unlike oxidation resistance of the different parts of the pellets (centre/rim). Here, we propose going one step beyond, since our aim is to provide an experimental approach to study the thermal air oxidation of highly-irradiated nuclear fuel by using a temperature-controlled pressure stage, following the reaction by Raman spectroscopy. This measurement protocol has been successfully tested with unirradiated fuel in our laboratory [25, 27]. The results of this work provide, for the first time with this technique, new data regarding the oxidation of spent fuel at the foreseen conditions of storage.

4.6.2. Experimental

4.6.2.1. Material: Irradiated UO_2 fuel

The selected SNF was irradiated in a commercial PWR reactor with a linear power density of 255 W/cm, and provided by Westinghouse. Average burnup of the fuel rod was 63 MWd/kgU, with a measured Fission Gas Release (FGR) of 13.6%.

The fuel sample was cut from the fuel rod in the cutting machine available at the JRC facilities, obtaining a disk with an approximate diameter of 10 mm and a thickness of around 4.5 mm. The sample cut was carried out in the middle of a fuel pellet, so no inter-pellet zones (dishing) are present for the studied disk [30]. In order not to damage the sample, in particular the edge zone, the fuel was not de-cladded, keeping the Zr cladding during the oxidation experiment.

4.6.2.2. Raman spectroscopy devices

Raman spectra of the irradiated fuel samples were acquired by means of a Renishaw in Via Raman microscope spectrometer, equipped with a 785 nm laser. The main instrument is placed outside the hot cell, being the laser conducted to the microscope through an optic fiber that enters in the cell. The spectrometer is connected to a nuclearized optical microscope developed by Renishaw, prepared *ad-hoc* to be used in the hot cells. Inside the cell, the microscope focuses the laser beam onto the fuel segments surface through a 50x objective by Leica. The scattered radiation was then collected and dispersed through an 1800 grooves per mm grating, obtaining a spectral resolution better than 1 cm^{-1} per pixel. The laser power was adjusted to 1.1 mW, measured at the end of the fiber optics. These conditions are low enough to ensure that no self-oxidation of the fuel has been produced because of the laser [29]. Typical acquisition conditions consisted of 120 seconds of acquisition time and 5 accumulations per spectrum, using the software WiRE 5.5 for visualisation of the optical images and the Raman spectra. The spectral range was defined at $100\text{-}1300\text{ cm}^{-1}$, where the main Raman features of the uranium compounds appear [20, 22, 25, 31]. The instrument is daily calibrated by using a Si standard and using its emission line at 520 cm^{-1} .

For the *in-situ* measurements, the fuel sample was placed inside a Linkam THMS600 temperature-controlled pressure stage. This device has been previously used and the measurement protocol optimised at CIEMAT in order to follow the oxidation of UO_2 surrogates [25, 27, 32], developing a protocol that now is implemented here. A picture of this Linkam stage is presented in Figure 4.6.1, where its main components have been numbered. Inside the chamber, the temperature is controlled by a T96-6 temperature controller, which provides temperature stability better than 0.05°C .

The oxidation experiment consisted of heating the sample at $50^\circ\text{C}\cdot\text{min}^{-1}$ up to 350°C , keeping this temperature for the full duration of the experiment. Both the heating and the isothermal stages were performed under a constant air flow of $80\text{ mL}\cdot\text{min}^{-1}$, measured by a Brooks Instrument Sho-rate flowmeter.

4.6.3. Results

4.6.3.1. Experimental set-up inside the hot cell

The Linkam stage described in the previous section was used as a sort of autoclave, where controlled conditions of temperature and pressure can be defined. Prior to the installation inside the hot cell, the device was subjected to previous tests in order to check the absence of gaseous leakages, resistance of the glass window, movement of the sample holder and temperature control. As a result of these tests, the method was optimised and the experimental conditions decided, in terms of airflow and working temperature. In particular, the glass window is resistant to a gas pressure of 1 atm, which can be regulated including the flowmeter in the gas line, previous to the gas inlet of the stage.

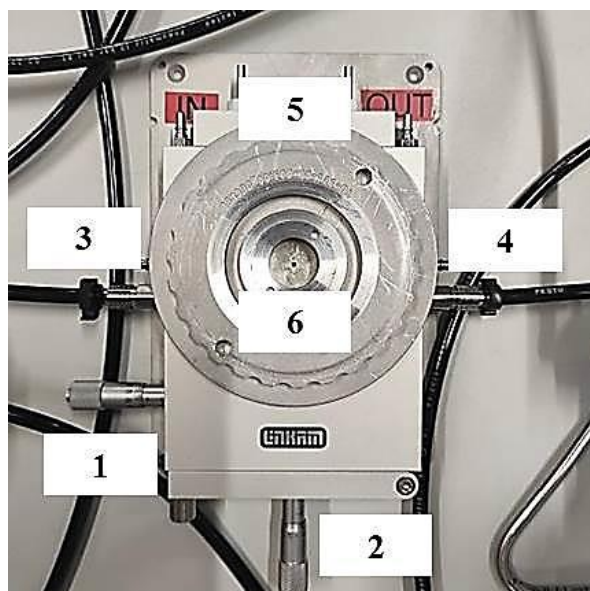


Figure 4.6.1. Overhead view of the Linkam THMS600 stage and its main components: (1) sample positioner (y axis); (2) sample positioner (x axis); (3) gas inlet; (4) gas outlet; (5) stage's lid and (6) central window.

Once the irradiated fuel sample is placed inside the chamber, the lid is closed (point 5 in Figure 4.6.1) and the objective is positioned to focus the sample through the glass window (point 6). After that, airflow is connected to the inlet and outlet connections (points 3 and 4 in Figure 4.6.1), being the experiment ready to begin. In Figure 4.6.2, a couple of pictures with the final set-up are shown.

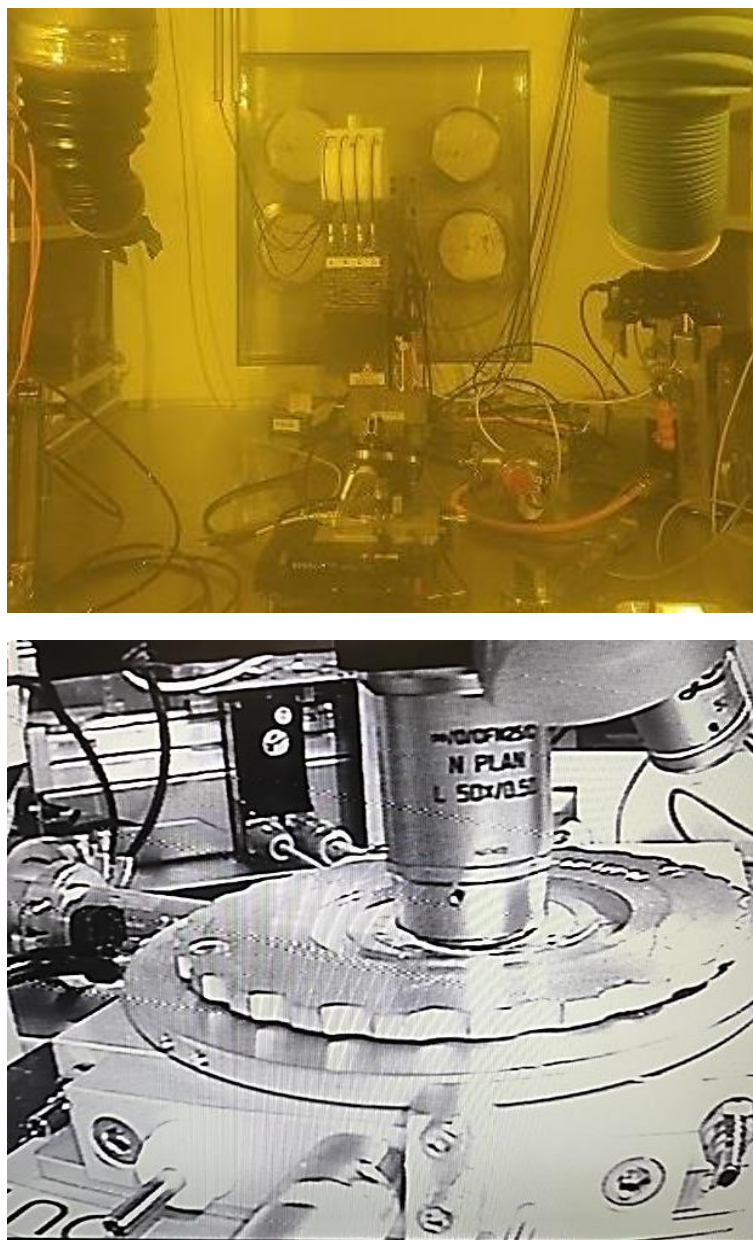
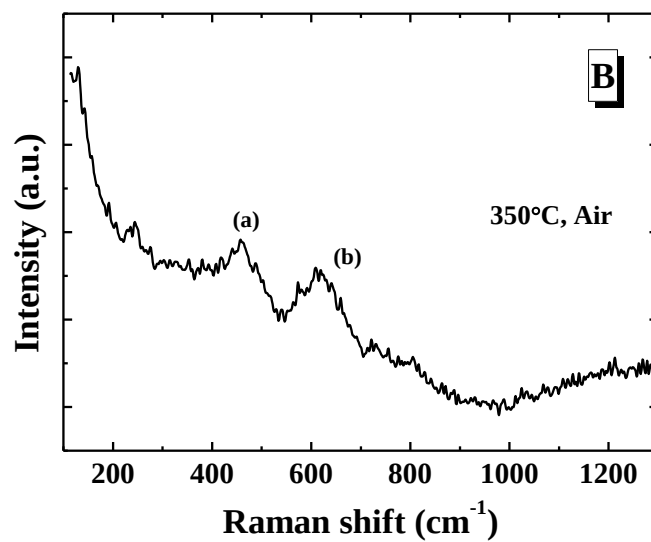
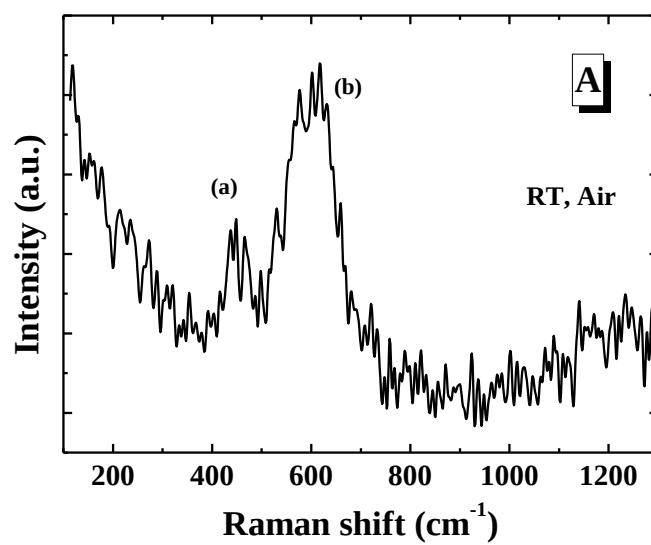


Figure 4.6.2. Final disposition of the Linkam stage, where it will be moved with the telemanipulators (up); and optical image of the measurement, with the 50x objective focused onto the sample through the Linkam's window (down).

4.6.3.2. Raman signatures of the oxidised phases in the oxidation of the Spent Nuclear Fuel matrix

The experimental set-up described in the previous section has allowed us following *in-situ* the oxidation of highly-irradiated nuclear fuel by means of Raman spectroscopy. This technique has demonstrated to be suitable to follow this reaction, since it allows identifying the different uranium oxides involved in the oxidation of UO_2 , known as the SNF matrix [20, 21, 25, 33-39].



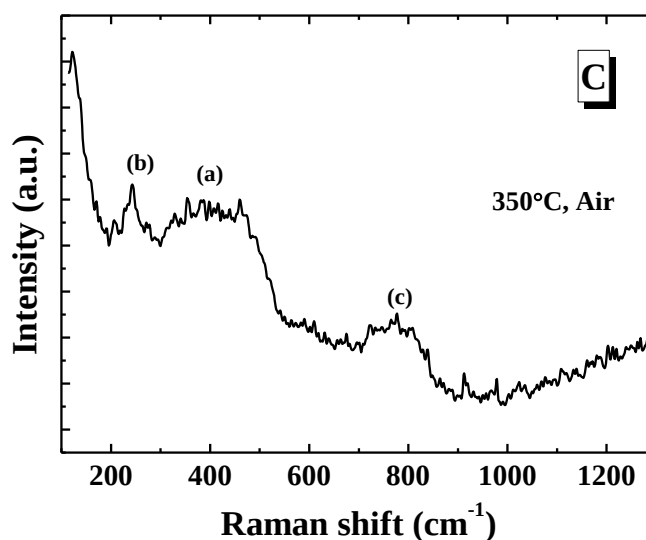


Figure 4.6.3. Raman spectra of the uranium oxides involved in the oxidation of SNF, being (A) UO_2 , (B) U_4O_9 and (C) U_3O_8 .

In Figure 4.6.3, representative spectra of the different uranium oxides involved during the oxidation of the SNF matrix [29, 40] are presented. Regarding UO_2 , Figure 4.6.3A, the first Raman band observed is the T_{2g} mode at around 445 cm^{-1} (a). In this compound, the presence of defects in the fluorite structure allows the appearance of Raman modes that otherwise would be forbidden and are not seen in pure UO_2 [20, 41]. In the case of irradiation-induced defects, there is a general consensus that the consequence in the Raman spectrum is the formation of three additional bands, which sometimes overlap forming the so-called “defects band” (labelled as (b) in Figure 4.6.3A). Typically, the three bands are named U1, U2 and U3 [29, 40, 42, 43]. U1 ($\sim 530\text{ cm}^{-1}$) has been recently associated to the signature of local UO_{2-x} sub-stoichiometry defects [42]. U2 ($\sim 575\text{ cm}^{-1}$) is assigned to the T_{1u} LO phonon, forbidden for a perfect fluorite crystal but allowed because of the defects. Finally, U3 ($\sim 635\text{ cm}^{-1}$) is assigned to structural defects related to the cuboctahedra symmetry of U_4O_9 . It should be noted that in the theoretical spectrum of UO_2 there is an additional band at $\sim 1150\text{ cm}^{-1}$, which is the first overtone of the previously mentioned LO phonon (and thus called 2LO [34]). However, in our spectra this band is not observed because of the excitation wavelength employed (785 nm). A recent paper by Karcher *et al.* has proved this effect and used a variety of laser wavelengths for different purposes [44].

Regarding U_4O_9 and U_3O_8 , Raman spectra of these phases are also shown in Figure 4.6.3, and their main features described below:

- With respect to irradiated UO_2 , the T_{2g} mode of U_4O_9 (Figure 4.6.3B, band (a)) suffers a shift to higher wavenumbers (typically from 445 to 455 cm^{-1}), as well as an increase in the bandwidth due to oxidation and increase of temperature [21, 25, 45]. In addition, there is a change in the intensity ratio of T_{2g} and “defects bands” (Figure 4.6.3B, band (b)) because of the intensity growth of the 630 cm^{-1} band, identified with the U3 peak in the previous discussion [21, 29]. In this sense, Fig. 3 in [42] is particularly illustrative.
- In the case of U_3O_8 (Figure 4.6.3C), a different pattern is presented, as a result of the crystal transition from cubic to orthorhombic [46, 47]. This is characterised by the presence of a band at 240 cm^{-1} (b), a broad range between 300 and 500 cm^{-1} (a), and an extra feature at 800 cm^{-1} (c). These specific spectral features allow a quick and unambiguous identification of this oxide, which as aforementioned is important from the nuclear safety point of view. The possibility of following the reaction by analysing these different Raman signals can be extrapolated to the rest of uranium oxidised phases, thus validating the use of this technique for the purpose of this work.

4.6.3.3. *In-situ* Raman study of the Spent Nuclear Fuel oxidation

The spectral fingerprint of each phase has been used as a basis to detect phase transitions in the study of the thermal air oxidation of an irradiated fuel disk by using Raman spectroscopy with the Linkam device adapted inside a hot cell, as explained before. The sample surface has been divided into two well-differentiated regions (see Figure 4.6.5 for clarity), following the criterion given by Serrano-Purroy *et al.* [10]:

- On the one hand, the central part of the sample has been defined from the pellet centre up to 6 mm in radial position, where a region characterised by the presence of cracks due to irradiation is found. During the experiments, Raman spectra have been randomly acquired within this 6 mm circular limit.
- On the other hand, a second region is defined at the periphery of the disk, very close to the cladding (not farther than 1 mm from the cladding).

The results of the Raman spectra acquired in these two zones are presented in Figure 4.6.4A and Figure 4.6.4B, respectively. For the sake of clarity in the evolution of the spectral features, representative spectra obtained during the experiment are plotted. The complete dataset is shown in Figure 4.6.S.1A and Figure 4.6.S.1B of the supplementary information.

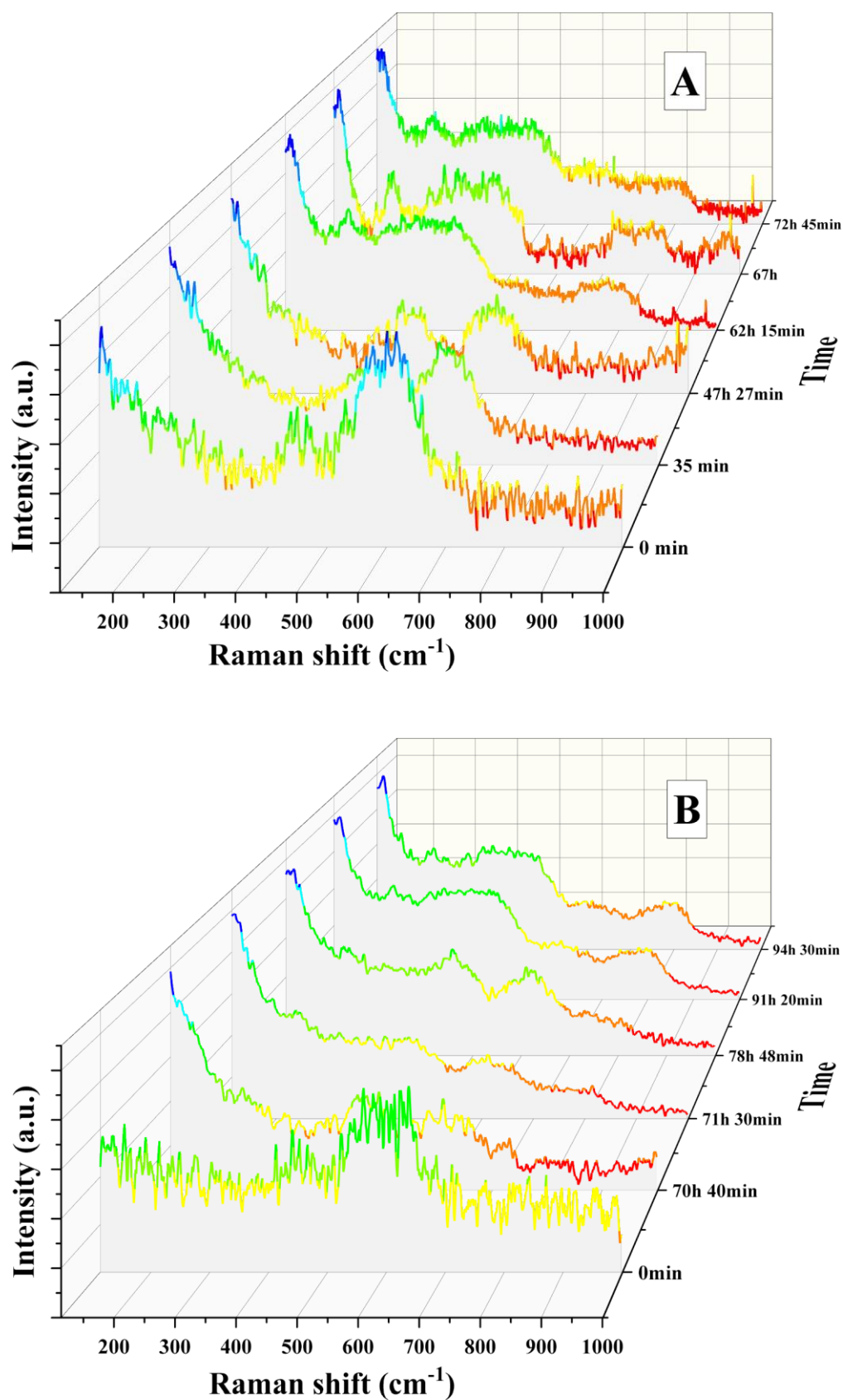


Figure 4.6.4. Representative Raman spectra acquired during the thermal air oxidation experiment of the irradiated UO_2 sample at the A) centre and B) close to the cladding. For the sake of clarity, time axis is not scaled.

Concerning the centre of the disk (Figure 4.6.4A), the spectra evolution follows very clearly the changes associated to the oxidation from UO_2 to U_4O_9 , *i.e.* intensity increase of the 630 cm^{-1} band (U_3), widening and shifting to higher wavenumbers of the T_{2g} band. At approximately 62 hours, the first U_3O_8 spectrum becomes clearly visible. The progress in the oxidation seems to be quite homogeneous in different central parts of the surface, since the U_3O_8 pattern is obtained in all the points after that first initial time of 62 hours.

Regarding the measurements close to the cladding (Figure 4.6.4B), there is a sustained tendency to find U_4O_9 spectra at longer times. In fact, the first U_3O_8 Raman spectrum is not found until 91 hours of experiment. Unlike the sample centre, longer measurement times do not imply to obtain only U_3O_8 spectra. In fact, the last spectrum of the experiment corresponds to U_4O_9 , and it was acquired after 115 hours of thermal treatment at 350°C (see Figure 4.6.5).

4.6.4. Discussion

The experimental set-up described in the previous section has allowed us, for the first time, following *in-situ* the oxidation of highly-irradiated nuclear fuel by Raman spectroscopy at controlled conditions of gas and temperature. The possibility of using a punctual technique has provided with the opportunity to discriminate between different locations within the sample, enabling the measurements in different zones at different times. This makes it possible to explore the different behaviour of the regions present in a spent nuclear fuel pellet (centre/rim).

These results are shown in Figure 4.6.5, where representative spectra obtained at different times are plotted as a function of the sample region where they were acquired. For the sake of comparison, these spectra have been chosen starting from the time when the U_3O_8 phase (in red in Figure 4.6.5) is firstly observed. By doing so, one can compare with other spectra acquired in other parts of the sample, where U_4O_9 still remains (in black in Figure 4.6.5).

Starting from the centre, marked with green arrows, the aforementioned Raman pattern of U_3O_8 is obtained from 62 hours (peak at ~ 240 , broad region between 300-500, and a wide band centred at $\sim 800\text{ cm}^{-1}$) [25, 29, 44, 48, 49]. This same pattern is maintained with time, as it is seen in other spectra acquired in the central part of the fuel (67h and

72h 45min). The presence of other low-intensity bands, such as the one centred at 600 cm^{-1} of the 72h 45min spectrum, could be an indicator of a $\text{U}_3\text{O}_8 + \text{U}_4\text{O}_9$ mixture. Nevertheless, the U_3O_8 phase is prevalent in this zone at these times.

On the other hand, in blue arrows are marked the regions corresponding to the disk edge, being very close to the cladding (Figure 4.6.5). The first spectrum shown, 79 hours, is clearly related to the U_4O_9 phase (T_{2g} band at 455 cm^{-1} and “defects” band centred at 630 cm^{-1}) [21, 29]. This first spectrum already demonstrates the oxidation resistance of this edge area compared to the centre, since this spectrum has been acquired later than the ones of the centre, which belong to U_3O_8 . Later on, there is a second U_4O_9 spectrum in other rim-zone, acquired at 83h 30min. At 91h 30min, the first U_3O_8 Raman pattern is obtained, almost 30 hours later compared to the centre. Nevertheless, the oxidation is far from being complete in the whole sample. In fact, the last spectrum shown in Figure 4.6.5, acquired after 115 hours of thermal treatment in other part of the sample edge, shows that the U_4O_9 phase is still present.

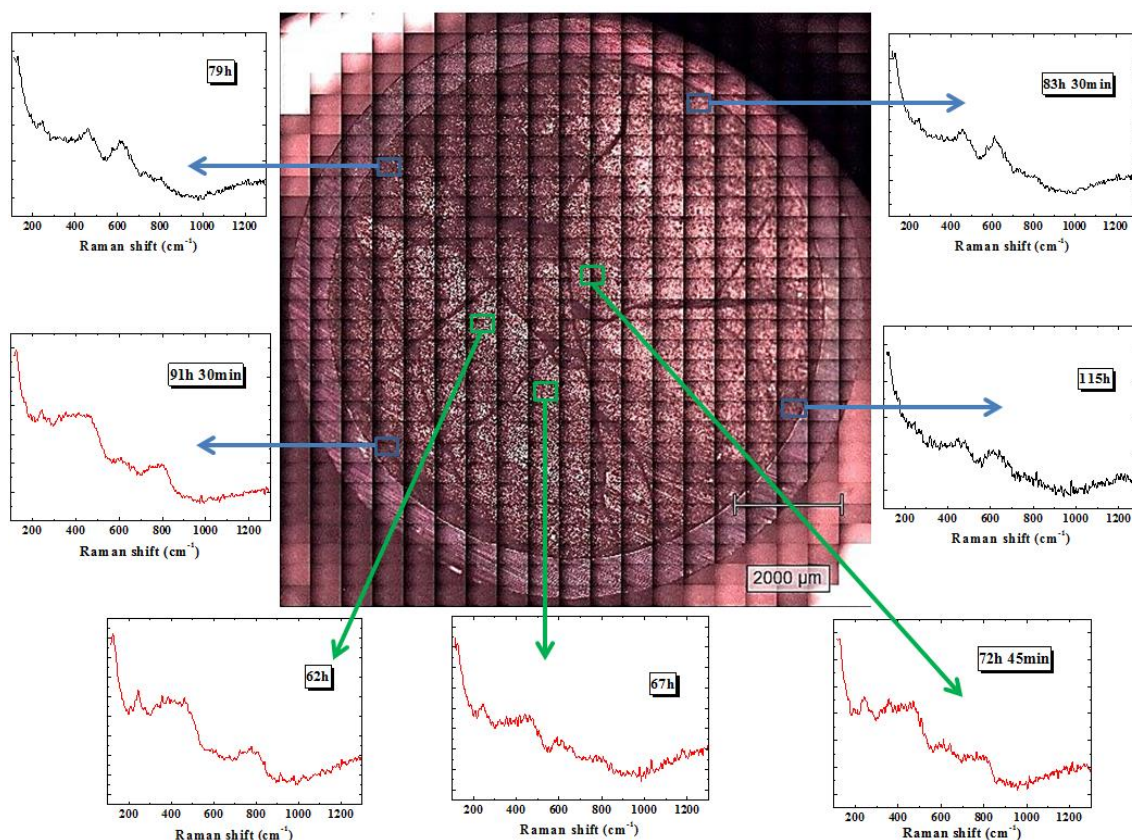


Figure 4.6.5. The appearance of irradiated fuel sample and Raman spectra acquired at different zones of the sample: disk centre (green arrows) and close to the cladding (blue arrows). The spectra in red are characteristic of U_3O_8 , while the ones in black are characteristic of U_4O_9 . The label of each spectrum corresponds to the experimental time when it was acquired.

The oxidation behaviour of the rim, especially important taking into account the current trend to extend the burnup of nuclear fuels in operating reactors [50-52] and the subsequent formation of the HBS [9, 53, 54], has been a matter of debate. Basically, and given the characteristics of the restructured rim of the fuel pellet at high burnup, there is theoretically a competition of effects regarding its oxidation [4]. On the one hand, the accumulation of Pu and fission products in this region, increasing the local burnup [8, 53], would delay the formation of U_3O_8 . There are several studies in the literature regarding the delaying role of dopants in the UO_2 matrix; in particular the studies with SIMFUEL, as the ultimate doped fuel, are clearly representative [55-57]. On the other hand, the mechanical changes associated to the HBS imply smaller grains and enhanced porosity in the zone, which would accelerate the oxidation because of the presence of more open pathways for O_2 entry [58]. Some experimental results have challenged the existence of open porosity in the HBS, in terms of gaseous fission products release [59].

There are examples for both possibilities in the literature, which reinforce the lack of consensus about this matter. For example, Papaionannou *et al.* [13], used thermogravimetric analysis (TGA) to oxidise de-cladded fuel fragments irradiated with nominal burnups of 50 and 65 MWd/kgU at 300, 350 and 400°C in air. At 300°C they reported a similar oxidation behaviour for both fuels; however, at 400°C they observed that the fragments irradiated at 65 MWd/kgU oxidised faster than those of 50 MWd/kgU. They justified this observation as a consequence of the enhanced porosity of the higher-burnup sample, allowing faster oxygen diffusion. Unfortunately, as they studied fuel fragments, they reported an average behaviour, not making the distinction between centre and rim of the same fragment. Thus, a direct conclusion about the HBS impact cannot be derived.

Other authors have reported that no difference exist between both effects. This is the case of Hanson *et al.* [14], who oxidised highly irradiated (average burnup 60.9 MWd/kgU) fuel fragments at 305°C in air, also by means of TGA. Unlike Papaionannou *et al.*, they did the distinction between fragments of the pellet centre from those of the pellet rim. From their results, no significant differences are observed in the oxidation curves (Figure 2 of the reference) and, as the authors themselves reported, “the presence of the HBS did not accelerate oxidation because of the fine-grained, high-surface-area structure” [14].

Nevertheless, the results of this study point to a higher impact of the higher local burnup (and thus the accumulation of Pu and fission products) delaying the formation of U_3O_8 , as shown in Figure 4.6.5 and earlier discussed. The characteristics of Raman spectroscopy as the measuring technique have allowed performing an integral study with the full surface of the disk, being not necessary to make fragments from it. The enhanced oxidation resistance of the rim zone proved here is in agreement with the findings of Jegou *et al.* [29], who also used Raman spectroscopy to analyse irradiated UO_2 (60 MWd/kgHM) and MOX (47 MWd/kgHM) fuels. The difference of their method is that they did not heat at a precise temperature control, since they used laser heating as the tool to oxidise the sample. In our case, the air oxidation is performed *in-situ* at 350°C. In any case, they also observed a higher oxidation resistance in the zones close to the cladding. In fact, the highest resistance was found in Pu agglomerates of the MOX sample, obtaining only M_4O_9 -like Raman spectra, therefore confirming the role of the higher Pu concentration in this region (understanding Pu as a dopant which stabilises the fluorite structure of UO_2). In our work, a temporal frame is given for this enhanced stability of the rim zone, which is of application to the specific experimental conditions (oxidation at 350°C under flowing air).

4.6.5. Conclusions

In this work, Raman spectroscopy has been used for the first time to follow *in-situ* the oxidation of highly-irradiated SNF (63 MWd/kgU) at controlled conditions of temperature (isothermal at 350°C) and gas conditions (continuous air flow). For doing so, a systematic measurement protocol has been optimised by using a temperature-controlled Linkam stage. The device has been previously employed to study the oxidation of fresh nuclear fuel (UO_2) at controlled conditions [25], validating its use for studying real (*i.e.* irradiated) fuel. The installation and set-up of the instrument and the associated equipment inside a hot cell has been successfully carried out.

During the experiment, Raman spectra have been continuously acquired at different regions of the fuel pellet surface, distinguishing between two main areas: the central part of the sample and a thin region at the periphery of the disk, very close to the cladding (not far than 1 mm from the cladding). On the one hand, Raman spectra of the centre shows the known transformation of the SNF matrix oxidation ($\text{UO}_2 \rightarrow \text{U}_4\text{O}_9 \rightarrow \text{U}_3\text{O}_8$) in a temporal frame of approximately 62 hours, being this the time when the first

U₃O₈ spectrum is observed. The oxidation in this region seems to be quite homogeneous, since the rest of the spectra acquired here until the end of the experiment correspond to U₃O₈.

On the other hand, oxidation close to the cladding follows the same sequence of oxides, but the occurrence of U₄O₉ spectra is much higher, obtaining the first U₃O₈ signal after more than 91 hours. Unlike the previous case, there are still zones at the pellet rim where oxidation has not been completed, acquiring U₄O₉ Raman bands even after 115 hours, being the heterogeneity of the oxidation very marked. The results of this work point to an enhanced oxidation resistance of this area, probably due to the accumulation of fission products and Pu in the area, which stabilises U₄O₉ and delays the formation of U₃O₈.

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SUPPLEMENTARY INFORMATION

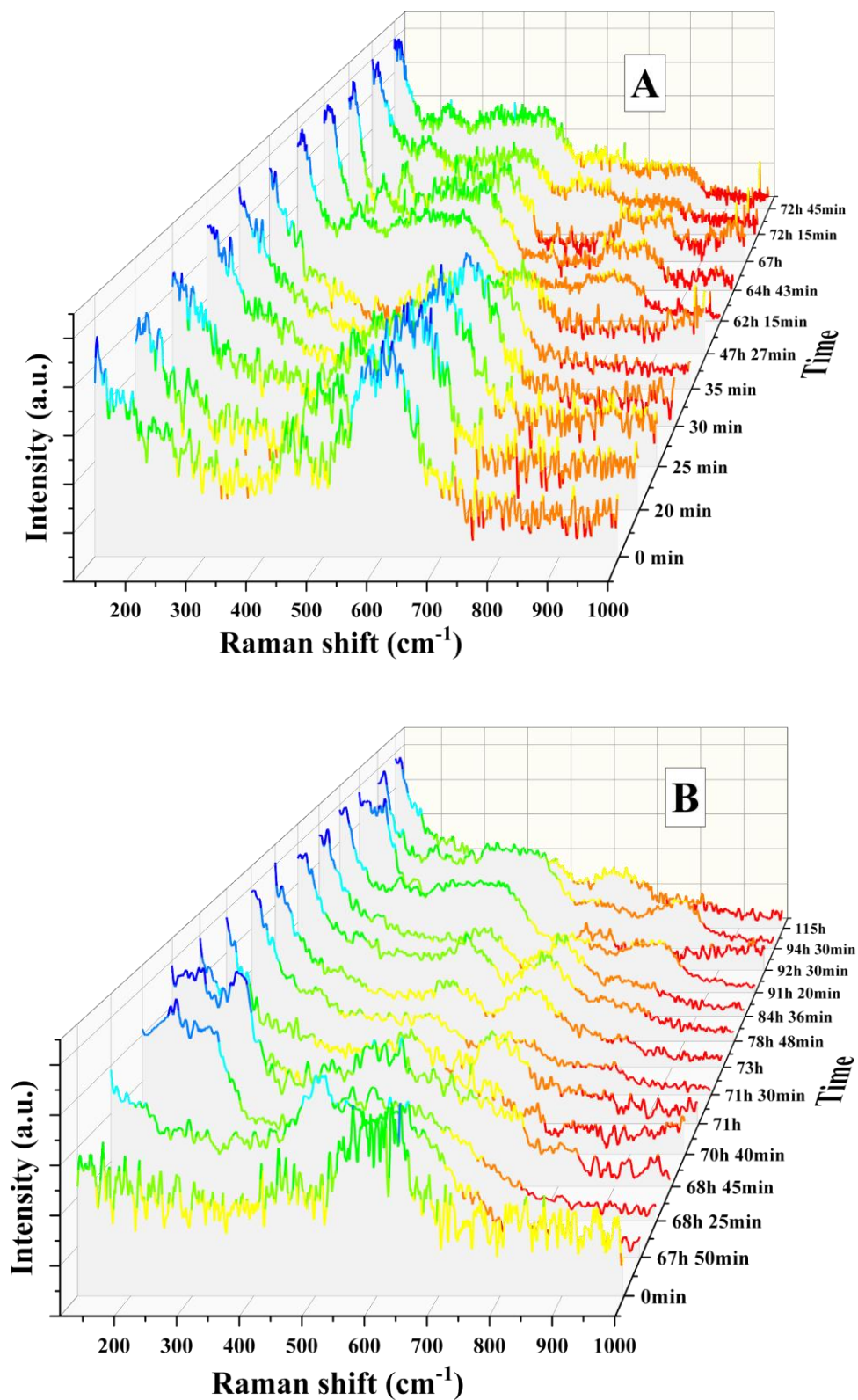


Figure 4.6.S.1. Raman spectra acquired during the thermal air oxidation experiment of the irradiated UO_2 sample at the A) centre and B) close to the cladding. For the sake of clarity, time axis is not scaled.

Chapter V

General Discussion

5. GENERAL DISCUSSION

The work performed in this PhD thesis contributes to the understanding of the parameters affecting the spent nuclear fuel oxidation from different perspectives. The sequence followed during the accomplished Results (Chapter IV) has allowed starting from the basics up to the real case, both in the physical form of the UO_2 samples studied (unirradiated powder, unirradiated pellets, spent fuel pellets) and in the complexity of the system (undoped UO_2 , Cr-doped UO_2 , spent nuclear fuel).

For doing so, specific outcomes have been obtained through the fulfilment of the objectives and tasks proposed in Chapter II. In particular:

- Task 1.1. A set of unirradiated UO_2 powdered surrogates were prepared. Such model materials will allow studying the impact of different effects on their oxidation. On the one hand, the preparation route was investigated by comparing the materials obtained via ADU purification (*i.e.* no internal stresses due to sintering), labelled as P1, and obtained from the milling of sintered pellets, named P3. On the other hand, the effect of the particle size distribution was studied by analysing a surrogate with a more uniform particle size, *i.e.* narrow PSD (P2) and another one with a wide PSD (P3), both with comparable median particle sizes. All of them were compared to a UO_2 pellet fragment used as a reference. The origin of the material is the most affecting parameter to the oxidation reaction, since P1 is the fastest material to oxidise. The particle size distribution effect proves that a narrower PSD exhibits faster oxidation than a wide one, *i.e.* P2 oxidises faster in this regard. This demonstrates that P3 shows a more similar behaviour to the UO_2 precursor used as a reference, and the frequently used fuel analogues coming from the recycling of other materials (such as P1) may differ too much from the reality that they try to simulate. In other words, P3 still meets the conservative criterion (*i.e.* the oxidation reactions is faster than the reference), but in a more realistic way. This conclusion is of paramount importance to the nuclear field, because many times the impossibility of working with real fuel makes the selection of an appropriate surrogate key in the design of the experiments.
- Task 1.2. A measurement protocol for monitoring UO_2 oxidation at *in-situ* conditions was developed and optimised by using a temperature stage (Linkam)

coupled to the Raman spectrometer. The experimental campaign consisted in oxidation experiments at forecast conditions of dry storage facilities for spent nuclear fuel when failed rods may be exposed to oxidising atmospheres, *i.e.* temperature in the region 200-400°C and oxygen partial pressure between 0.1 and 21 %O₂. The inclusion of reduced oxygen levels relative to air provides new and relevant data to the scarce database. The intention was to determine the quantitative effect of oxygen starvation on the U₃O₈ induction time (*i.e.* the integral reaction kinetics) at different thermal conditions. The UO₂ surrogate used was the material described in the previous task, named as P3. As expected, the results indicate that temperature is the main factor affecting the oxidation reaction, rather than the oxygen concentration, up to maximum oxygen level under consideration. In fact, at 400°C the formation of U₃O₈ occurs only within 2 hours, even at oxygen concentrations as low as 0.1%. On the other hand, at 200°C no U₃O₈ is detected after three days of exposure, even under the most oxidant atmosphere (air). At intermediate temperatures, 300°C, a delay in the U₃O₈ formation with decreasing oxygen concentrations is detected. These results are the first ones obtained in these conditions from very short time ranges, since the spectral acquisition begins only after two minutes of experiment. From the fuel storage point of view, the results are important in the design of nuclear fuel storage facilities, in particular eventual discharge cells for the fuel under controlled temperature and oxygen environmental conditions.

- Task 2.1. The growing interest in the nuclear industry in using ATFs led to study these innovative materials, in particular the Cr-doped UO₂ fuel. Specifically, a set of (U,Cr)O₂ pellets was prepared with different Cr concentrations, covering all the possible scenarios regarding the solubility of Cr in the UO₂ matrix as solid solution. The fabrication route followed was similar to the one used at an industrial level. The study of the grain size confirms that the highest value is found for the sample with the amount of Cr closest to the solubility limit. By using XRD, this limit is estimated to be (748±16) ppm of Cr in the specific sintering conditions employed. In addition, Raman spectroscopy is used for the first time to study this kind of materials, being the intensity of the defects band of the samples related to grain size. Statistical analysis by using PCA reinforces the suitability of Raman, since 98.8% of the total variance of the data is

explained by three Principal Components, which are precisely related to the main Raman features observed in the spectra.

- Task 2.2. In order to assess the stability behaviour of ATFs at interim dry storage conditions, in particular with regard to the eventual formation of U_3O_8 , the previously prepared Cr-doped UO_2 samples were subjected to oxidation experiments. The selected conditions ensure the reaction to proceed to U_3O_8 starting from unirradiated UO_2 , as obtained in Result 1. These were maintained for doped fuel, for the sake of comparison. Although it is well-known that UO_2 oxidation is delayed because of the presence of dopants in the matrix, in this case the experiments conducted in air show that there is not a great effect of Cr, obtaining almost total conversion to U_3O_8 in all cases. This behaviour is probably due to the low amount added because of the solubility of Cr in the UO_2 matrix, compared to other elements. Surprisingly, when the same oxidations are performed with only 1% O_2 present, Cr starts playing a considerable role. In fact, the slowdown of the reaction is more marked in those samples doped with an amount of Cr below the solubility limit, forming barely 50% of U_3O_8 in some cases, even at 700°C. This is the first time that ATFs are evaluated in front of their oxidation, not only in air, but also in environments with lower oxygen contents. The combination of ATFs and less oxidant atmospheres than air results in fuel enhanced resistance to oxidation.
- Task 3.1. The transition from the studied nuclear fuel surrogates to spent nuclear fuel is based on an elaborated critical review of the available literature on SNF oxidation. Knowledge gaps in the different parameters impacting the reaction are pointed out. This review provides specific recommendations, updated to the current nuclear fuel sector, in order to fulfil these gaps. Among them, it is especially emphasised the lack of robust conclusions at relatively high temperatures (>350°C), being the formation of U_3O_8 in this region very feasible. Regarding burnup, there is a clear gap at the high region (>50 MWd/kgU), which becomes even more relevant under the current nuclear power plants conditions. Burnup-related parameters, such as porosity and grain size, should also be evaluated in front of the likely HBS that will appear at these high burnups. Oxygen partial pressure could affect the SNF oxidation, being the experimental database in this matter even scarcer than in the case of unirradiated UO_2 . Other parameters, such as moisture and NO_x are also of interest, but their

impact on the SNF oxidation is expected to be lower. A cross-cutting conclusion can also be drawn. Traditional techniques have provided very valuable results, in particular measuring the “bulk” oxidation in terms of the progress of the O/M ratio. However, it is recommended to complement them with modern techniques, which allow an *in-situ* monitoring of the oxidation reaction and detecting an early formation of U_3O_8 , as a way to improve the safe storage of the fuel from the very first moment.

- Task 3.2. Based on the previous recommendations, and as a part of an international collaboration between CIEMAT and JRC reached under the frame of this PhD thesis, an experimental set-up has been installed inside a hot cell in order to study the oxidation of highly-irradiated UO_2 fuel. The method is based on the use of the Linkam temperature stage for *in-situ* monitoring the oxidation reaction by Raman spectroscopy, already described and successfully applied in Task 1.2. The measurement protocol has been modified to fit the particularities of working in hot cells, and a number of previous tests have been performed to optimise the experimental conditions. After that, one oxidation experiment (350°C, continuous air flow) has been carried out with a spent fuel sample at high burnup (UO_2 irradiated at 63 MWd/kgU). This is the first time that this kind of experiments is carried out at controlled temperature. In fact, the characteristics of Raman spectroscopy as the measuring technique have allowed following oxidation at different regions of the samples, distinguishing between centre and close to the cladding areas. The reason for doing that is the known restructuration of the fuel at the pellet rim. From the analysis of the acquired Raman spectra, it is inferred that formation of U_3O_8 proceeds faster at the central part of the pellet. Conversely, the oxidation reaction is delayed at the pellet rim, probably due to the accumulation of Pu and FP in this region. These conclusions point out to an enhanced oxidation resistance of the High Burnup Structure (HBS) formed at the pellet periphery, conversely to other studies that report a lack of impact or even an accelerated oxidation.

Apart from the above particular conclusions, drawn from the results gathered in Chapter IV, some general outcomes comprising the main objectives proposed in Chapter II can also be highlighted. They represent the global contributions of this work.

- Objective 1: A “realistically conservative” nuclear fuel powdered surrogate has been prepared and characterised in detail, in particular studying the impact of its preparation nature and PSD on its oxidation to U_3O_8 . This material has been employed as the substrate to perform oxidation experiments at *in-situ* conditions in a range of temperatures and oxygen concentrations, following an optimised protocol that can be directly applied to study the spent nuclear fuel behaviour under representative conditions of a dry storage facility.
- Objective 2: A set of Cr-doped UO_2 pellets, as one of the shortest-term ATFs, have been fabricated. The characterisation has included confirmation of the grain size increase due to the presence of Cr, and calculation of the solubility limit in the sintering conditions used. Oxidation to U_3O_8 does not seem to be affected in air. With lower oxygen concentrations, there is an effect of the dopant delaying the reaction, being more marked in those samples with Cr content below the solubility limit.
- Objective 3: Insights from Objectives 1 (a new, *in-situ* oxidation protocol) and 2 (oxidation of ATFs for the first time) are combined to study real (*i.e.* irradiated) nuclear fuel. The transition is supported by a review of the SNF oxidation database. A preliminary study on the experimental set-up in the hot cells and testing the method with irradiated UO_2 is carried out. This work opens the door to perform oxidation experiments with other nuclear materials, in particular with commercially irradiated Cr-doped UO_2 fuels.

All in all, this PhD thesis covers some key knowledge gaps arising from the current scenario in the nuclear sector. The potential oxidation of SNF, that could happen in dry storage scenarios, has been studied at upgraded conditions (including less oxidant atmospheres than air), with newer nuclear fuel technology (ATFs) and applied to high-burnup irradiated fuel. The grounds of the work, which have allowed acquiring the knowledge to transfer it to real spent fuel, demonstrate the critical and useful role that experimentation with nuclear surrogates plays in the nuclear field.

