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Model materials experiments: First dissolution results.

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1 Introduction

The efforts to improve fuel performance in nuclear power generation lead to an increased usage of a various new types of light-water reactor (LWR) fuels including Cr-, Al-, and Si-doped fuels (CEA, 2009, Arborelius, 2006, Massih, 2014). While the improvement of in-reactor performance of these fuels has already been demonstrated, it is still uncertain, whether the corrosion/dissolution behaviour of such fuels in a deep geological repository is similar to conventional spent LWR-fuels. However, the chemical and structural complexity of spent nuclear fuels (SNF) and the associated high beta- and gamma radiation fields impede unravelling all the various concurring dissolution mechanisms from experiments with SNF. Thus within the DisCo project (www.disco-h2020.eu), experiments on irradiated doped fuels are complemented with dissolution studies using systematically produced and carefully characterised UO_2-based model materials to understand the effects of the addition of Cr- or Al-oxide into the fuel matrix on SNF dissolution behaviour under repository relevant conditions. These model materials comprise (i) UO_2 reference materials, and (ii) Cr-/Al-doped UO_2, both, with and without alpha-emitting nuclides such as Pu-238, to address the effects of alpha-radiolysis on the oxidative dissolution of aged SNF after recession of the beta/gamma radiation field in the long-term. Single-effect studies on the dissolution behaviour of the model materials will provide complementary insights and supporting process understanding regarding the performance of modern doped fuels in the repository environment, which cannot be directly obtained from dissolution studies on SNF.

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

The work package started formally in February 2018 and comprises contributions from FZJ, SCK•CEN, CIEMAT, CEA, VTT, University of Cambridge as well as University of Sheffield and is organized according to the following matrix. VTT will conduct leaching experiments also with reference material (UO_2) and chromium doped reference (UO_2 + Cr) if schedule and budget enable those. However, the experiments described in the original plan are prioritized.

Samples	Bicarbonate water reducing, anoxic (H_2) (derived from WP3) (+/- additional components)	Cementitious water (YCWCa) pH ~13.5, Reducing, anoxic (H_2) (derived from WP3)	Synthetic COx water Callovo-Oxfordian Water) (+/- Fe(0))	Natural ground water, with Fe(0)
UO_2 (reference sample)[1]	JUELICH, SCK-CEN, USFD	JUELICH, SCK-CEN		
UO_2 + α-dopant (Pu-238/U-233)	JUELICH, SCK-CEN, VTT	JUELICH, SCK-CEN		VTT
UO_2 + Cr/Al[1]	JUELICH, SCK-CEN, CIEMAT, USFD	JUELICH,SCK-CEN, CIEMAT		
UO_2 + Gd[1]	CIEMAT	CIEMAT		
UO_2 + Cr/Al + α-dopant (Pu-238/U-233)	JUELICH, SCK-CEN, VTT	SCK-CEN, JUELICH		VTT
UO_2 + Gd + α-dopant (Pu-238/U-233)	CIEMAT	CIEMAT		
Homogeneous unirradiated MOX ($U_xPu_{1-x}O_2$) (high α)			CEA	
MOX ($U_xTh_{1-x}O_2$)[1]	UCAM	UCAM		

In the following this reports summarizes the first results on dissolution experiments with model systems focusing on a description of the sample material, a detailed description of the actual leaching conditions and the used experimental setup as well as the first results.

2 Preliminary results of dissolution tests

2.1 Cr/Al/Gd doped UO_2 model systems

2.1.1 Results from SCK•CEN

In order to understand the matrix dissolution of modern LWR fuels and more particularly the effect of Cr on the dissolution rate of the spent fuel, Pu/Cr-doped materials will be prepared next to Cr-doped and UO_2 reference materials, within WP2 of this project. These model materials will be further exposed to two reference waters (young cementitious water at pH 13.5 and bicarbonate water at pH 8.5) in reducing/anoxic conditions, relevant for geological disposal. During the two first years of the project, preparatory tests were carried out with depleted UO_2 and low ^{233}U-doped UO_2 to develop and optimize the method to impose effective reducing/anoxic conditions representative for geological disposal. These preparatory tests are additional to the planned tests with Pu/Cr-doped UO_2.

Description of sample material - The model materials Pu/Cr-doped UO_2 will be synthesised at SCK•CEN according to a protocol developed in close collaboration with FZ Juelich within the WP2 of this project. The Cr-doped UO_2 and the UO_2 reference will be available to start the leaching tests in the third trimester 2019 while the Pu-doped UO_2 and the Pu/Cr doped UO_2 will be completed in the first trimester 2020. Awaiting the model materials, preparatory leaching experiments were performed with depleted UO_2 and low ^{233}U-doped UO_2 pellet. This latter, denominated as F7, has an alpha-activity of 1.45 MBq/gUO_2 and it is representative for a spent fuel age of 100 000 years, which is more than 10 times lower than the target alpha-doping of the proposed Pu/Cr-doped UO_2.

Description of leaching conditions - In order to develop and optimise the leaching procedure to impose effective anoxic/reductive conditions, static dissolution experiments were performed with depleted UO_2 and F7 fuel, either in *Young Cementitious Water Light* at pH 13.5 (YCWCa-L) or in bicarbonate solution at pH 8.5 (= the solution used also in the project First Nuclides, hence denominated as FIN solution, Mennecart et al. 2013), as defined in Table 2.1.1.1. All tests were performed in an Ar glove box with pO_2 below 10 ppm and pCO_2 below the detection limits (< 0.1 ppm) at 25-30 °C.

Three types of experiments were achieved to impose reducing/anoxic conditions. The **first type of tests** was carried out in autoclaves under 10 bar Ar or H_2 (without Pt/Pd catalyst) atmosphere with and without 10 ppm dithionite ($Na_2S_2O_4$) as reducing agent. For this series, the pellets were first annealed at 1000 °C in reducing conditions and pre-leached in 0.1 M KOH during 14 days to reduce or remove any oxidised surface material possibly present at the surface of the UO_2 pellet. Afterwards, the pellets were leached in 35 ml of YCWCa-L (pH 13.5) or in FIN (pH 8.5). In the **second type of tests**, leaching experiments were performed in 30 ml of solution at pH 13.5 or at pH 8.5 either with depleted UO_2 or F7 in autoclaves under H_2 atmosphere in presence of Pt/Pd catalyst to scavenge the oxygen traces inside the

autoclaves. The catalyst is placed in the headspace of the autoclaves to avoid contact with water and consequently to avoid perturbation of the formation of oxygen through radiolysis when this methodology will be transferred to experiments with Pu/Cr-doped UO_2 in the future. Before leaching, the pellets of this series were thoroughly cleaned. This cleaning consists in a pre-washing in 0.01 M NaCl with and without Fe strips for three weeks with frequent solution refreshing (Ollila, 2008) followed by an annealing at 1000 °C in reducing atmosphere and a pre-leaching in 0.001 M KOH with and without Fe strips for one week with daily solution refreshing. The **third type of experiments** consists in a parametric study performed in polyethylene bottles to optimise the pre-treatment protocol of the pellet before leaching at pH 13.5 or pH 8.5 in 30 ml of solution. Three routes were envisaged combining the different steps of pre-treatment as previously described, (A) pre-washing 0.01 M NaCl without annealing nor pre-leaching, (B) annealing, pre-washing and pre-leaching and (C) pre-washing, annealing and pre-leaching.

For all series of experiments, the not-filtered U concentrations were always measured while the ultrafiltered U concentrations (< 3.5 nm), corresponding to dissolved U concentration, were only determined in the leaching step at pH 8.5 or pH 13.5. In addition, when iron was used in the different stage of the preparation, all coupons were rinsed with 1 M HNO_3 in order to estimate the amount of uranium sorbed on the iron surface. The U concentrations were measured by ICP-MS

Table 2.1.1.1: Composition of the two reference leaching solutions

Mol.L^{-1}	Na	K	Ca	SO_4^{2-}	CO_3^{2-}	Cl^-	pH
YCWCa-L	1.3×10^{-1}	3.6×10^{-1}	3.8×10^{-4}	2×10^{-3}	3.7×10^{-4}		13.5
FIN	1.9×10^{-2}				1×10^{-3}	1.9×10^{-2}	8.5

Description of experimental setup - In order to impose a pressure up to 10 bar with Ar or H_2 gas, the leaching experiments were performed in stainless steel autoclaves with a PEEK insert of 50 ml (Figure 2.1.1.1). The cover of the autoclaves is equipped with two valve outlets. One gas outlet consists in a short tube stopping under the cover. The other outlet is a longer tube protruding to a short distance from the bottom of the insert and devoted to the liquid. A manometer is also placed on the top of the autoclave to monitor the variation of gas pressure (Ar or H_2) during the experiment. The cell is filled with 30-35 ml of solution in order to keep enough place in the headspace of the autoclave to install the Pt/Pd catalyst, when is used. These autoclaves will be used also for the tests with Pu/Cr-doped UO_2.

Figure 2.1.1.1: Stainless steel autoclaves

Description of results – Based on the first series of tests, dithionite, even combined with H_2 atmosphere was not effective enough to keep the uranium concentration within the solubility range of UO_2 of 0.3- 3 x10^{-8} M (Neck & Kim, 2001), especially at high pH (Figure 2.2.1.1). For the second series of experiments, Pt/Pd catalyst in presence of H_2 atmosphere was thus considered as another approach to scavenge the oxygen in the system.

Although the Pt/Pd catalyst and the H_2 atmosphere are supposed to consume all O_2 traces in the second series of tests, the soluble U concentration at pH 13.5 ranges between 3 x 10^{-8} M to 8 x 10^{-8} M (UF [U]-empty symbol- Figure 2.1.1.3), close to the UO_2 solubility range but still higher. These results are quite comparable to those obtained at pH 13.5 in experiments in H_2 atmosphere and reducing agent (Figure 2.1.1.2B). Before concluding that the Pt/Pd catalyst is not able to prevent UO_2 oxidation at pH 13.5, the experiment was repeated at pH 13.5 and also tested at pH 8.5 (see further in the text). However, the uranium profile in Figure 2.1.1.3 tends to confirm that uranium is more easily oxidised at high pH (pre-leaching at pH 11 and leaching at pH 13.5) than at neutral pH (pre-washing in 0.01 M NaCl), as already highlighted in the first series (Figure 2.1.1.2). This U increase is clearly observed during the pre-leaching stage (Figure 2.1.1.2.), even though the annealing between the pre-washing and the pre-leaching steps should have avoided a (re)-oxidation of the pellet. Besides a pH effect, two other hypotheses can be considered to explain the U behaviour: the combination of the annealing after the pre-washing may have disturbed the structure of the material, increasing the U release in the pre-leaching solution, or the presence of iron in the pre-leaching stage may be required to block the uranium oxidation. So, a parametric study was initiated to improve the pre-treatment of the UO_2 pellets (third series of experiments in "Description of leaching experiments"), and in parallel complementary tests were carried out in autoclaves with F7 pellets to determine if alpha-doped UO_2 is as sensitive as depleted UO_2 to the oxidation at high pH.

The parametric study (third series of tests) has evidenced that the [U] of the ultrafiltered concentrations are all very low (10^{-8}- 10^{-9} M) and in the range of the UO_2 solubility whatever the considered preparation (Figure 2.1.1.4). These concentrations are also similar to the
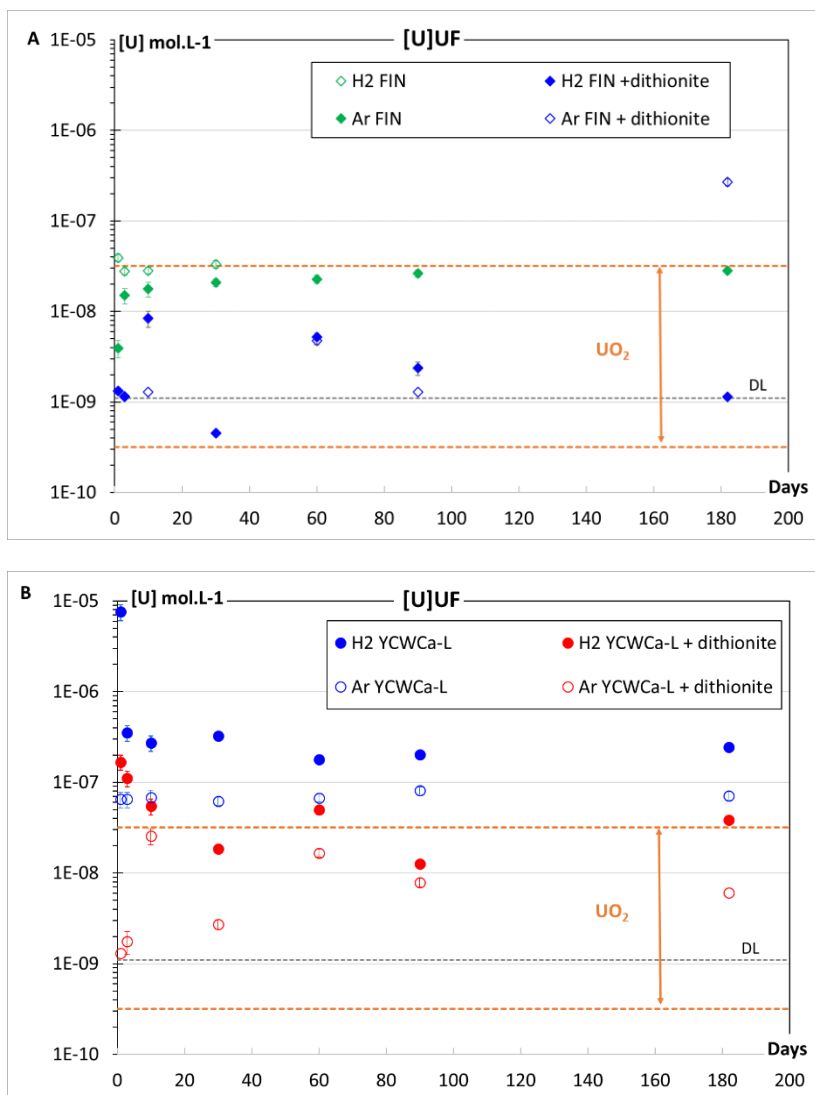
lowest concentrations in autoclaves in the first series (Figure 2.1.1.2). So, a simple pre-washing with/without Fe would be as good as "annealing and dithionite" and better than the "pre-washing-annealing and pre-leaching" with Pt/Pd catalyst in H_2 atmosphere. This suggests that the annealing done after the pre-washing would have an adverse effect on U dissolution, which seems also supported by the larger amount of colloids present in solution (Figure 2.1.1.4C). However, the fact that the ultrafiltered concentrations are low, is considered as an indication that there was little oxidation to U(VI) during the leaching. Currently, we have no explanation for the observed effect of the annealing.

The role of iron in the pre-washing step is not yet fully understood: does it reduce the amount of U(VI) in solution by sorption onto the iron strip, or does it prevent the U oxidation in the pre-washing ? At pH 11 (0.001 M KOH) its effect on the U concentration (Figure 2.1.1.4) seems small. Therefore, the presence of iron does not seem beneficial in our experiments.

The alpha-doped fuel F7 shows slightly higher concentrations than undoped UO_2 in the tests without annealing and pre-leaching (Figure 2.1.1.4A). This is more pronounced in young cementitious than in bicarbonate solution. This alpha effect is not observed for the two other routes of preparation (Figure 2.1.1.4.B and 2.1.1.4C), possibly masked by the disturbing effect of the annealing. This nevertheless suggests that the alpha activity still caused some oxidation, although very little. As the alpha activity of F7 pellet (1,45 MBq/g) is more than 10 times lower than spent fuel after 10 000 years, there is good hope that the tests with the 10 000 year Pu-Cr doped pellets planned for the DisCo programme will show a well quantifiable increasing effect of the alpha activity, that can be compared with the results for Pu doped pellets without Cr. The main objective of the study is indeed to see if Cr doping leads to a different oxidation/dissolution behavior (faster or slower).
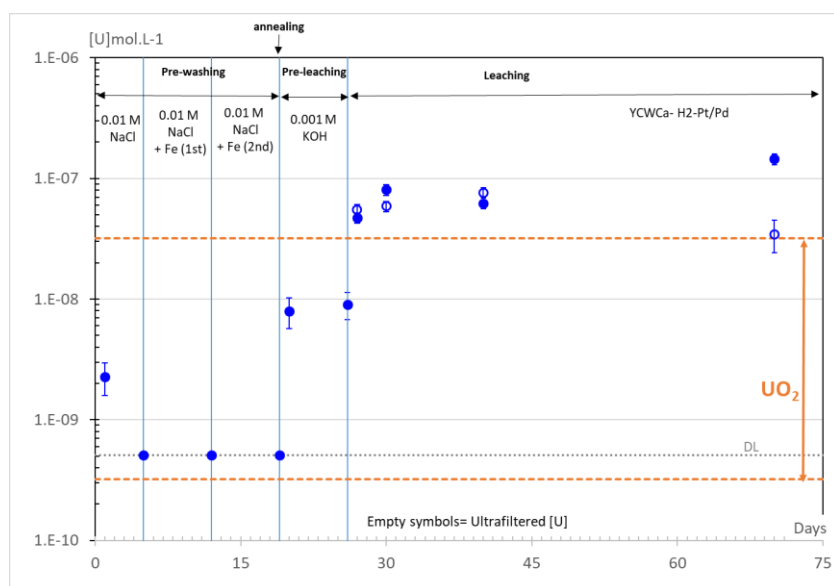
The low uranium concentrations also show that addition of dithionite as reducing agent is not necessary to see the potential impact of the Cr doping. Furthermore, addition of dithionite in solution may even suppress the radiolytical oxidation, and thus mask the potential Cr effect on radiolytical oxidation.

Tests with F7 in autoclaves and H_2 with Pt/Pd catalyst (second type of experiments) show U concentrations of 2 $\times 10^{-9}$ and 10^{-8} M at pH 8.5 and at pH 13.5 respectively, thus in the range of UO_2 solubility (Figure 2.1.1.5). Addition of H_2 seems not clearly useful, as the U concentrations are quite similar to the first series of experiments with dithionite (Figure 2.1.1.2). However, the Pt/Pd catalyst in presence of H_2 atmosphere seems to be more efficient to consume the O_2 traces in the system than the dithionite in solution, as evidenced by the more or less stable U concentration as function of time. The experiments shown in Figure 2.1.1.5 also confirm the results of the previous experiments. Indeed, while the washing step in 0.01 M NaCl was efficient to reduce the U concentration up to 10^{-9} M, even if the role of iron is not clearly demonstrated, the annealing did not stabilise the UO_2 (U concentrations not lower than 10^{-8} M) and the pre-leaching step in 0.001 M KOH leads again to a concentration increase, especially when the leaching is conducted afterwards at pH 8.5.
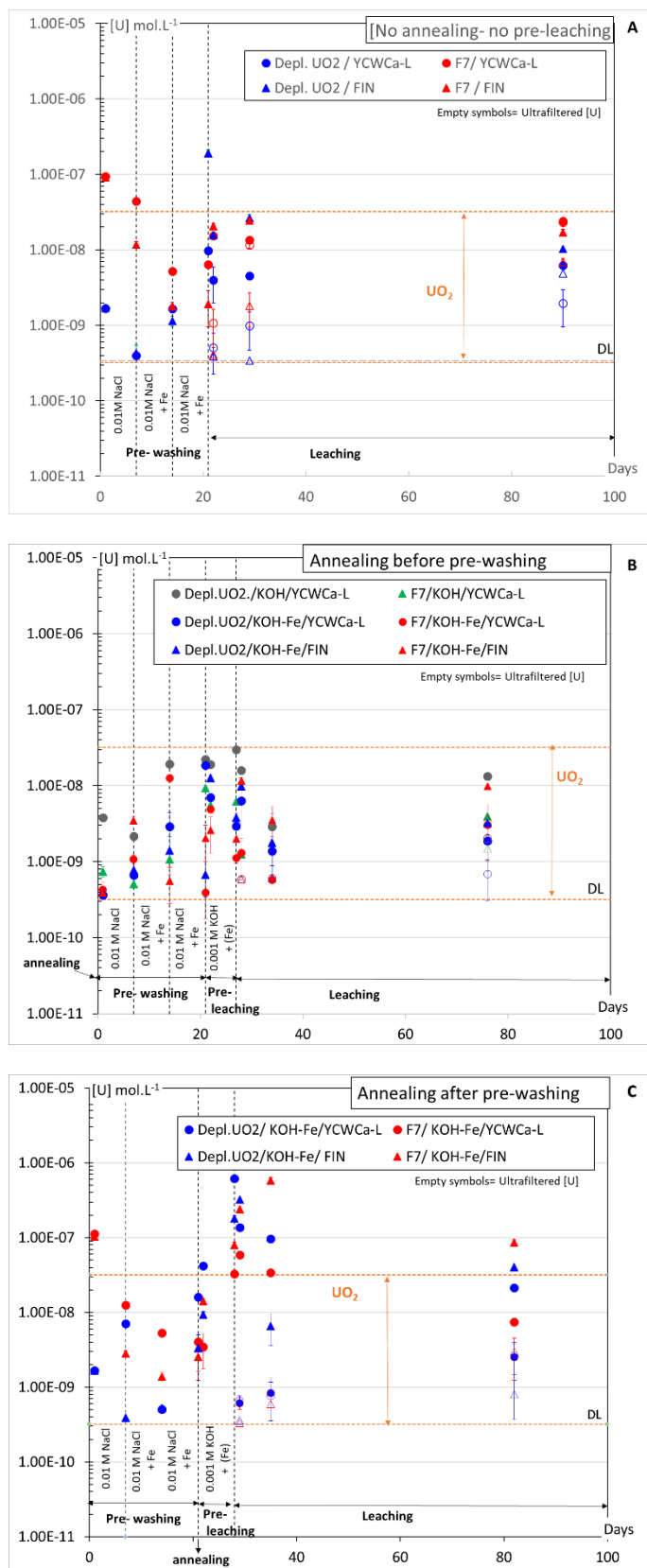
Figure 2.1.1.2: *First type of experiments - U concentration as function of time with depleted UO₂ pellet in autoclave experiments with and without 10 ppm dithionite (Na₂S₂O₄) under Ar and H₂ atmosphere at pH 8.5 in bicarbonate solution-FIN (A) and at pH 13.5 in young cementitious water (YCWCa-L) (B).*

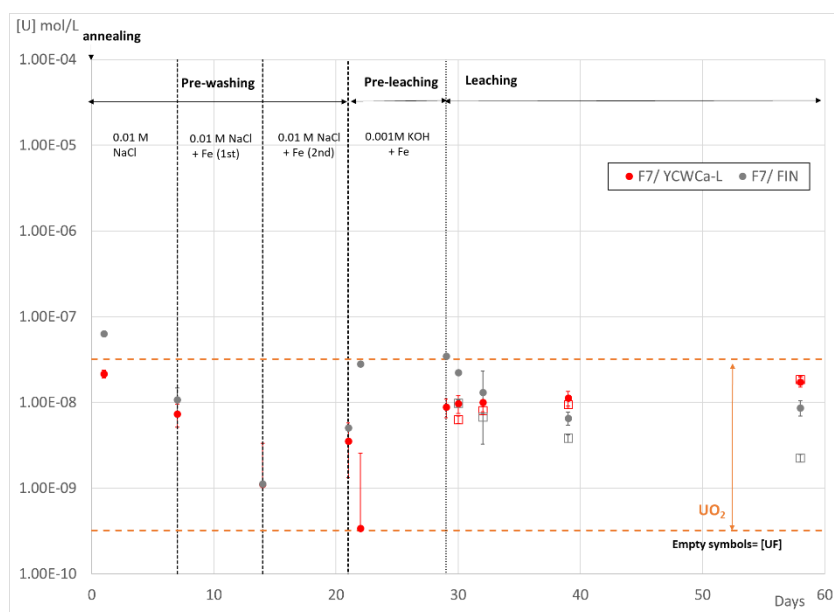*Figure 2.1.1.3*: *Second type of experiments - U concentration as function of time with depleted UO₂ pellet for the autoclave experiment with Pt/Pd catalyst under H₂ atmosphere at pH 13.5 in young cementitious water (YCWCa-L).*

Figure 2.1.1.4: *Third type of experiments - U concentration as function of time with depleted UO$_2$ and F7 pellet as function of annealing, pre-washing with 0.01 M NaCl +(Fe) and pre-leaching with 0.001 M KOH+ (Fe) of the pellet at pH 13.5 in young cementitious water (YCWCa-L) and at pH 8.5 in bicarbonate water (FIN). A- experiments without annealing, no pre-leaching; B- annealing before pre-washing and pre-leaching; C- annealing after pre-washing and before pre-leaching.*

Figure 2.1.1.5: *Second type of experiments - U concentration as function of time with F7 pellet for the autoclave experiment with Pt/Pd catalyst under H_2 atmosphere at pH 13.5 in young cementitious water (YCWCa-L) and pH 8.5 in bicarbonate water (FIN).*

Awaiting the production of model systems Pu-(Cr) doped UO_2, static leaching tests with depleted UO_2 and low alpha-doped UO_2 pellet were performed to optimize the method of the leaching experiments. This preliminary study shows that the addition of dithionite as reducing agent is not necessary to obtain uranium concentrations that are low enough to see a potential impact of Cr doping or of alpha doping. However, a Pt/Pd catalyst in presence of H_2 atmosphere would be helpful to ensure better anoxic/reducing conditions as function of time in the system. It was also demonstrated that pre-treatment of the pellet is a key step of the procedure. While a simple pre-washing in 0.01 M NaCl without iron strips during 3 weeks is sufficient, annealing and pre-leaching in KOH of the pellet is not helpful. Based on these preparatory tests, the further experiments with the model materials will be performed in autoclaves in 10 bar H_2 atmosphere with a Pt/Pd catalyst after a pre-washing of the pellet in 0.01 M NaCl in absence of iron during at least three weeks.

2.1.2 Results from FZJ

Description of sample material - Within WP2, a large variety of UO_2-based materials were produced in the form of sintered pellets. First accelerated dissolution experiments were performed using:

1) pure UO_2 reference pellets with a mean grain diameter of approximately 12 μm and densities between 92.9 to 95 % relative density (compared to the theoretical density of pure UO_2), and

2) Chromium-doped UO_2 pellets doped with 1000 ppm Cr, produced by two different doping methods, namely coprecipitation and wet-coating. The co-precipitation method

lead to a microstructure comparable to the one of pure UO_2 pellets (i.e. grain size ~12 μm) at a relative pellet density of 96.5 to 97.8 %, whereas the wet coating method leads to larger grain sizes (~20 μm) and a relative density of 98.8 % for all used pellets.

Description of leaching conditions - All dissolution experiments were performed in 10 mM bicarbonate ($NaHCO_3$) solutions, prepared from $NaHCO_3$ (pro analysi, Merck) and Milli-Q water, which was de-aerated by boiling for 60 minutes while flushing with argon to remove dissolved oxygen. Immediately before the start of the dissolution experiments, a 0.126 M H_2O_2 solution (pro analysi, Merck) was added to the solution to establish a starting concentration of 2.25 mM H_2O_2, to mimic the oxidative radiolytic dissolution of UO_2. All experiments were performed at room temperature (22°C) under atmospheric conditions.

Description of experimental setup -The experimental set up developed for the dissolution experiments at JUELICH has to fulfil the following requirements (see Figure 2.1.2.1):

• complete coverage of the pellets with test solution during the complete time of the dissolution experiments, considering the loss of volume due to sampling,
• facile sampling of test solution and permanent flushing of the vessels with argon, to exclude ingress of atmospheric oxygen,
• exclusion of light (i.e. vessels have to be light tight) to ensure constant conditions regarding H_2O_2 degradation during the experiments, and
• constant temperature.

Each single dissolution experiment was performed in an extensively washed and preleached 40 mL glass vessel with a layer of glass beads on the bottom (Figure 2.1.2.1b). Each sample vessel was closed using a septum punctured by a glass cannula serving as gas inlet and a cannula used as gas outlet and for sampling of the solution. These cannulae were only in contact with the solution during the sampling procedure. To achieve anoxic conditions the vessels were flushed constantly with argon during the experimental run time.

The setup allowed for the accomplishment of 11 dissolution experiments in parallel. The sample vessels were placed in a massive aluminium block equipped with a water conduit connected to a thermostat for temperature control. Plasticine gaskets were used to close the contact between the vessels and aluminium block and to ensure the light tightness of the vessels. In all experimental runs performed to date, 8 vessels were used for dissolution tests (Figure 2.1.2.1a, blue gaskets) with UO_2 pellets, while 3 vessels were used as blanks to monitor the bulk degradation of H_2O_2 (Figure 2.1.2.1a, red gaskets).
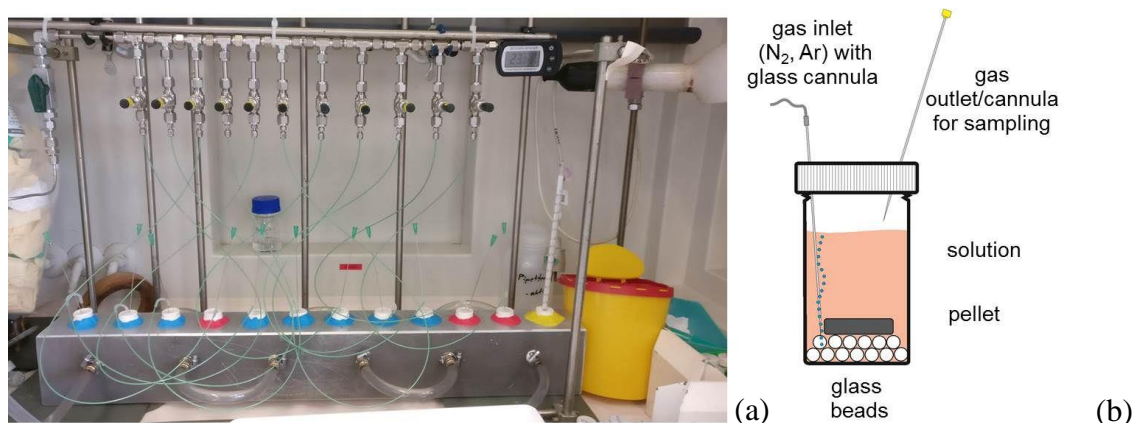
Figure 2.1.2.1: (a) Experimental setup of the dissolution experiments. (b) Schematic drawings of the experimental vessels for the accelerated dissolution experiments.

During all experiments the H_2O_2 and U(VI) concentrations in the solutions were analysed on a regular basis using UV-Vis spectroscopy. After the experiments, the pellets surfaces were examined using optical microscopy, SEM, XRD and Raman spectroscopy.

So far two series of accelerated dissolution experiments have been performed. In the first series pure UO_2 pellets with different densities were used. Three experimental runs of 3 to 5 weeks run time were performed to ensure that the plateau of uranium concentration is reached. The same pellets were used sequentially several times in the dissolution experiments, to assess potential effects of the amorphisation of the pellet surface due to the polishing procedure or of remaining fine grained particles on the pellet surface and in pores, on the initial dissolution rates. Between the experimental runs $NaHCO_3$ solutions were used for thoroughly cleaning the vessels, the parts inside the vessels as well as the pellets itselves to remove surficial U(VI).

In the second series, Cr-doped pellets obtained via different synthesis routes (i.e. co-precipitation and wet coating) and with varying densities were used. In these experiments, a fresh bicarbonate/H_2O_2 solution was added to the solution after 400 hours run time, to test the effect of new oxidants on already leached pellet surfaces.

Description of results - Figure 2.1.2.2 shows the typical evolution of the solution concentrations of U(VI) and H_2O_2 in the accelerated dissolution experiments with time. The evolution of the H_2O_2 concentration vs. time of blank experiments without pellets (figure 2.1.2.2 a) demonstrates that the majority of the H_2O_2 is consumed by degradation on the surfaces inside of the vessel, and only a very minor part (< 1 %) is used up by the oxidation of UO_2. For pure UO_2 pellets (figure 2.1.2.2 b) as well as Cr-doped UO_2 pellets (figure 2.1.2.2 c), the dissolution process is controlled by the concentration of H_2O_2 in solution, i.e. the dissolution (essentially) stops when all H_2O_2 is consumed. The U(VI) concentration in the solutions reached plateau levels that are clearly below the saturation limits of U(VI) phases, such as schoepite or stutdite.
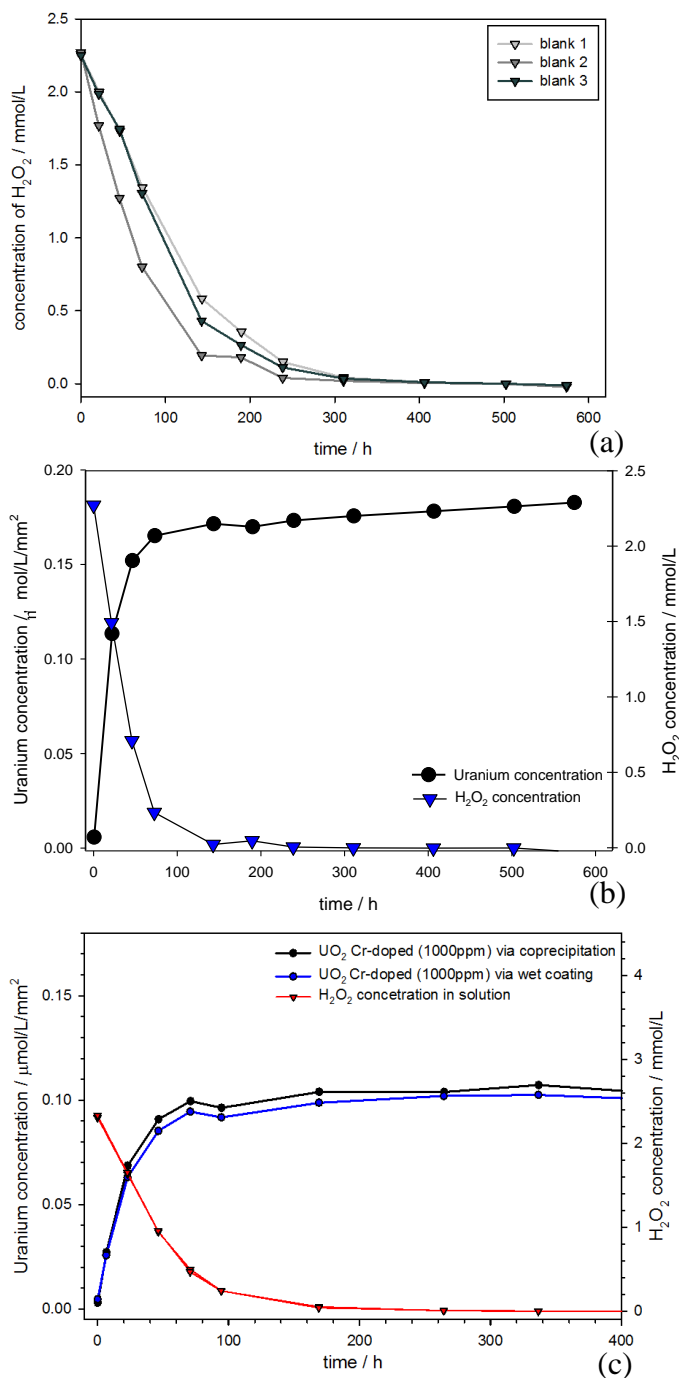
Figure 2.1.2.2: (a) Concentration of H_2O_2 in exemplary blank runs without UO_2 pellets. (b) Solution concentrations of U(VI) - normalised to the geometrical surface area of the pellet - and H_2O_2 vs. time for an experiment using a pure UO_2 pellet. (c) Solution concentrations of U(VI) - normalised to the geometrical surface area of the pellets - and H_2O_2 in two experiments using Cr-doped pellets prepared via co-precipitation, and wet coating, respectively vs. time.

The (initial) dissolution rates of the pellets were determined from the concentrations of dissolved U(VI) obtained within the first 24 hours of the experiments. Figure 2.1.2.3 depicts the data of a pure UO_2 reference pellet (95 % relative density), a pellet Cr-doped by co-precipitation (97.5 % relative density, 1000 ppm Cr) and a pellet doped by wet coating (98.8 % relative density, 1000 ppm Cr). The initial dissolution rates were found to be $1.40 \cdot 10^{-6}$ mol/m$^2\cdot$s for the pure UO_2 reference pellet, $0.78 \cdot 10^{-6}$ mol/m$^2\cdot$s for the pellet doped via co-precipitation and $0.70 \cdot 10^{-6}$ mol/m$^2\cdot$s for the Cr-doped pellet from the wet coating method, respectively. Taking into account the lower relative density of the pure UO_2 pellet and hence its higher reactive surface area, the initial dissolution rates for the shown pellets are rather similar, indicating that the Cr-doping has no significant effect on the oxidative dissolution rates of these UO_2-based materials.
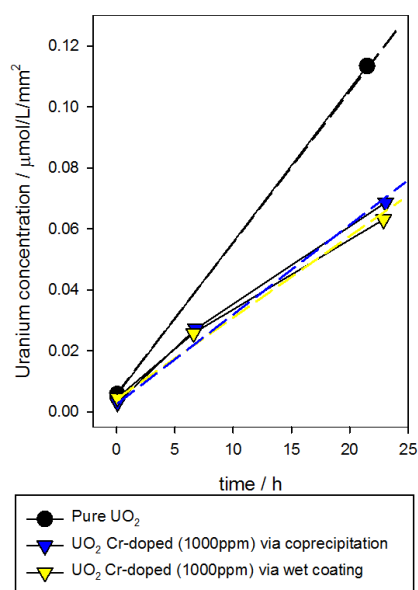

Figure 2.1.2.3: U(VI) concentrations in solution (normalised to the geometrical surface area of the pellets) during the first 24 hours of selected dissolution experiments, using a pure UO_2 reference (95 % relative density, black circles) and two representative Cr-doped UO_2 samples produced by co-precipitation (97.5 % relative density, blue triangles) and by wet coating (98.8 % relative density, yellow triangles).

Repeated experiments with the same pure UO_2 pellets (after cleaning with bicarbonate solution) and following the procedure described above showed an unexpected decrease in the initial dissolution rates and lower plateau levels of the U(VI) concentration in solution from runn to run, in spite of the same initial H_2O_2 concentration in solution (see Figure 2.1.2.4).

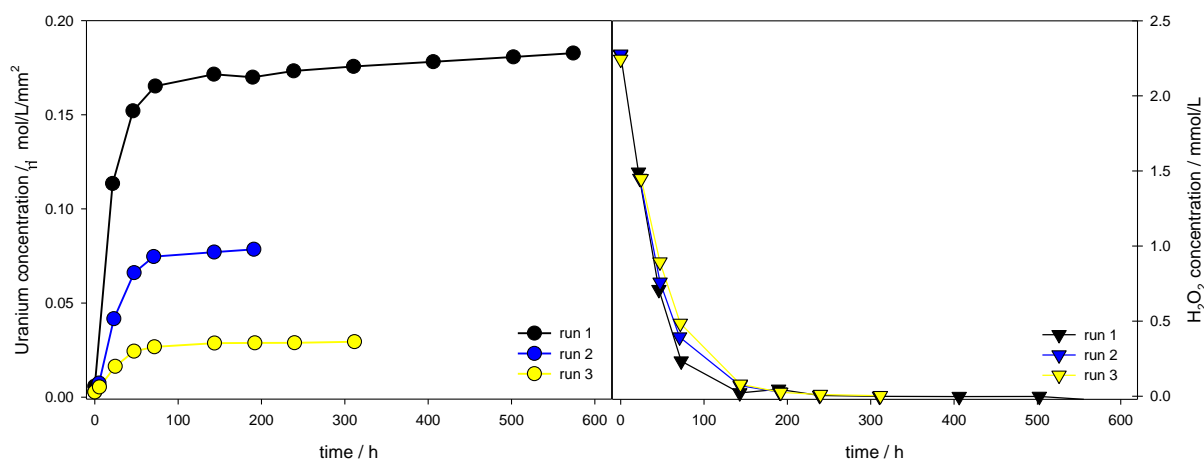*Figure 2.1.2.4: Concentration of uranium (left) and H_2O_2 in solution (right) in repeated experiments using a representative reference sample (i.e pure UO_2) as function of time. Between each run the pellet and the complete experimental setup was extensively washed with $NaHCO_3$ solution.*

A similar "passivation effect" of the pellet surface was also observed during dissolution experiments with Cr-doped pellets, when replenishing the leaching solution and adding additional H_2O_2, after consumption of the initial oxidant (cf. Figure 2.1.2.5). Surprisingly, here the additional H_2O_2 had nearly no effect with respect to the further oxidative dissolution of the pellets, as indicated by the rather small increase in the U(VI) concentration in solution after the H2O2 addition. Again, it can be seen that the method of Cr-doping had no distinct effect on the dissolution behaviour of the doped UO_2-materials.

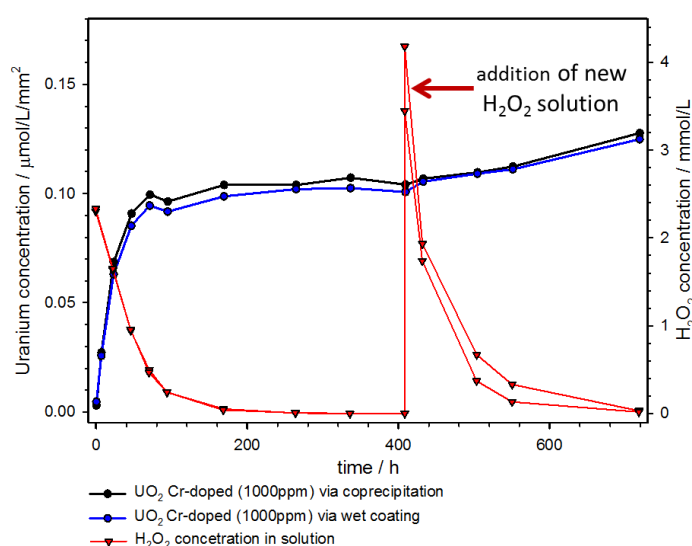*Figure 2.1.2.5: Concentrations of uranium and H_2O_2 in solution depending on run time for two representative Cr-doped UO_2 samples obtained by different doping methods.*

To date SEM, XRD and Raman measurements on pellets after the dissolution experiments have been performed to unravel the reason for the surface "passivation" and the underlying mechanisms. First results suggest that the formation of a secondary phase or the remains of a hyperstoichiometric uraniumoxide on the surface of the pellets, which cannot be completely removed by the washing with bicarbonate solution, might be the cause of the observed dissolution behaviour.

2.1.3   Results from VTT

Description of sample material - The first experiments are conducted with old ^{233}U doped UO_2 crushed fragments in the size range of 1.4 to 4 mm. The geometric surface area of the particles is approximately 2 cm^2 per g (This is the surface area of cubes with 3 mm sides and density 10). This sample series contains un-doped UO_2 and doping levels of 5% and 10% simulating the alpha radiation level of 3000 and 10 000 years old spent nuclear fuel (see Table 2.1.3.1) (Ollila et al. 2003). Originally, the un-doped UO_2 pellets, from which the fragments originate, were commercial fuel pellets prepared by ABB. The UO_2 fragments doped with ^{233}U were produced by BNFL (British Nuclear Fuel Limited).

Table 2.1.3.1 The solid UO_2 samples.

UO_2 solid	[^{233}U](%)	[^{235}U](%)	[^{238}U](%)	^{235}U/^{238}U	(g)/experiment
un-doped	0	2.82	97.18	0.029	1, 1, 3
5% ^{233}U-doped (15.7 MBq/g)	5.0	4.5	90.5	0.050	1, 1, 3
10% ^{233}U-doped (31.4 MBq/g)	10.0	4.5	85.5	0.053	1, 1, 2.5

Previously, these ^{233}U-doped UO_2 fragments have been leached in different experimental series during different projects;

- in modified Allard groundwater (Vuorinen et al. 1998), which simulated fresh groundwater conditions

- in NaCl solutions with varying ionic strength (0.01-1.0 M) (Ollila et al. 2003, Ollila & Oversby 2004, 2005, Ollila 2008),

- and in three different kind of natural ground waters from Olkiluoto site (Evins et al 2014, Ollila et al. 2013).

The history of pellets/fragments used for the experiments with higher mass (2.5 to 3 g) is different than the history of the 1 gram samples. The higher mass samples were used (more than 10 years ago) in Chalmers (Gothenburg, Sweden) and the stored under unknown conditions until transported to VTT (Finland) ca 10 years ago.

The old samples have been stored at VTT under anaerobic glove box conditions for 4 years since the last experiments. However, the previous dissolution experiments had been conducted under saline groundwater and thus, the samples required preparation pre-leaching to remove salts possibly precipitated during the storage period. UO_2 fragments were pre-leached twice with bicarbonate (0.01 M NaCl + 2 mM $NaHCO_3$) solution.

Description of leaching conditions - VTT will perform the leaching expriments in bicarbonate reference water and in natural groundwater from Olkiluoto, which is the site selected for the final disposal of spent nuclear fuel in Finland. The "old" ^{233}U-doped fragments will be leached in natural water OL-KR6 groundwater. OL-KR6 water has been sampled form bedrock drilling point 6 from depth 135 m to 137 m via aboveground sampling station. Glass flasks (2 l) were purged with N_2 prior to the sampling to maintain the conditions anaerobic also during transport. After transport to the argon glove box waters were poured into the polyethylene flaks, in which traces of oxygen were detected be at level from 0.00 to 0.02 ppb (analyzed from the water surface).

The natural ground water was kept in Ar atmosphere of the glove box for 12 months and the stability of the water was followed by pH measurement, alkalinity titrations and selected elemental concentrations. An one liter batch of the water was poured into separate polyethylene vessel and iron strips (Fe iron foil; 0,125 mm thick, 99,5%, FE000330 by Goodfellow) were added to precipitate natural uranium away from solution before starting the actual dissolution experiments. The initial uranium level of the OL-KR6 groundwater was 5 • 10^{-9} mol/L (1.2 µg/L). After the uranium concentration had decreased below 10^{-11} mol/l level water was filtrated (0.22 µm pore size) prior to the leaching experiments.

The following experimental series, with new Cr and Cr/α-doped pellets will be conducted with a more saline water originating from the depths from 400 to 450 m, which is closer to the intended disposal level of spent nuclear fuel with solid pellets.

All leaching experiment are performed in the presence of corroding iron under the anaerobic Ar glove box conditions. (O_2 in water ≤0.05 ppb; O_2 in atmosphere 1≤ ppm, T = 25 ± 1 °C). The starting pH was approximately 8 and the Eh can be expected to be as low as -0.4 V to -0.3 V. The alkalinity of the OL-KR6 was 3 mmol /L (HCl uptake) before the start of the experiment. Reference values for main characteristics of natural groundwater OL-KR6 are given in Table 2.1.3.2. It should be noticed that groundwater shows slight temporal variation in nature.

Table 2.1.3.2 The main characteristics of OL-KR6 groundwater. Data for early samplings 2013 and 2016.

	OL-KR6 (2013)	OL-KR6 (2016)
pH	7.6	7.6
Ammonium, NH4 (mg/l)	0.31	0.29
Bicarbonate, HCO3 (mg/l)	159	153
Bromide, Br (mg/l)	12	11
Calcium, Ca (mg/l)	540	530
Chloride, Cl (mg/l)	3340	3340
Dissolved inorg carbon (mg/l)	27	31
Fluoride, F (mg/l)		0.4
Iron, Fe (total) (mg/l)	0.36	0.28
Iron, Fe2 + (mg/l)		0.28
Magnesium, Mg (mg/l)	151	151
Nitrate, NO3 (mg/l)	0.4	0.4
Nitrite, NO2 (mg/l)	0.2	0.2
Nitrogen, N(Total) (mg/l)	0.36	
Non Purgeable Organic Carbon (mg/l)	4.6	5.1
Phosphate, PO4 (mg/l)		0.2
Potassium, K (mg/l)	18	18
Silicate, SiO2 (mg/l)	11	12
Sodium, Na (mg/l)	1460	1460
Strontium, Sr (mg/l)	5.5	5.8
Sulphate, SO4 (mg/l)	404	406
Sulphide, S2 - (mg/l)		0.02
Sulphur, S (total) (mg/l)	130	130
Total dissolved solids (mg/l)	6101	6088
Carbonate alkalinity, HCl uptake (mmol/l)	0.05	0.05
Total acidity, NaOH uptake (mmol/l)	0.18	0.16
Total alkalinity, HCl uptake (mmol/l)	2.6	2.5

Description of experimental setup - Figure 2.1.3.1 illustrates the experimental setup in the polyethylene vessel inside the Argon glove-box. Firstly, 40 mL of Fe-equilibrated, filtered groundwater was added to a test vessel with a fresh iron strip (1.5 x 3 cm, FE000330 by Goodfellow). Next, the solid UO_2 sample (1g or 3 g fragments) in a fused silica saucer was immersed into the solution.

To decrease the uncertainties due to precipitation during leaching experiment an initial spike of $^{235}U/^{238}U$ solution, with isotopic ratio far away of the one of solid UO_2 fragments. This so called isotope dilution method is described more detail in (Ollila, 2008]. The total [U] addition was $3.4 \cdot 10^{-9}$ mol /L.

The closed test vessels were placed in an additional container to protect it from potential fluctuations in the trace oxygen level of the atmosphere of the glove box. The spike solution was allowed to mix with the leaching solution for 2 hours before the initial sampling. The samplings are planned to be taken in intervals at 1, 3, 10, 30, 60 and 90 days.

The ^{238}U concentration and $^{235}U/^{238}U$ isotopic ratio of the leaching solutions will measured with SF-ICP-MS. Depending of the experiments, the evolution of Fe, Cr, Pu concentration will be followed.

Figure 2.1.3.1 Experimental set-up under Ar glove box contitions. UO_2 fragments are placed into silica saucer and Fe strip leans to the wall of the polyethylene vessel.

2.1.4 Results from CIEMAT

In this work, the fabrication of doped UO_2 fuel has been performed. The aim of this investigation is to determine the effect of additives, the presence of H_2 and different types of leachants on UO_2 matrix stability. Solid surface is being characterized by X-Ray Diffraction (XRD), Raman spectroscopy and Scanning Electron Microscopy (SEM-EDX).

Description of sample material - In WP2, fabricated materials were described in detail just as its characterization. All of them were produced by dry-blending. Samples were pressed into pellets at 700 MPa, calcinated and sintered at 1675 °C for 4 hrs in 4.7% H2- N2. Pellets were then polished to 3μm in diamond suspension and thermally etched at 1600 °C to reveal grain boundaries.

a) Chromium-doped UO_2 pellets doped with 600 ppm Cr_2O_3 (UO_2-0.06%Cr_2O_3)

b) Chromium-Aluminium doped UO_2 pellets doped with 500 ppm Cr_2O_3 and 200 ppm Al_2O_3 (UO_2-0.05%Cr_2O_3-0.02%Al_2O_3)

c) Gadolinium-doped UO_2 pellets doped with 4500 ppm Gd_2O_3 (UO_2-4.5%Gd_2O_3)

Description of leaching conditions - To date dissolution experiments have been carried out in sodium perchlorate (20 mM $NaClO_4$) under an N_2/4.7%H_2 atmosphere with a total pressure of (8 ± 1) bar ($pH_2 = 0.37 \pm 1bar$) at 22 ± 3 °C under Ar atmosphere (glove-box with pO_2 bellow 2 ppm). The leachants were prepared adjusting SCK•CEN methodology (Ollila, 2008) and stored in a glove-box under Ar atmosphere. After one month, it was filtrated. The elemental composition, Eh and pH were monitored *ex situ* under anoxic conditions (glovebox atm. <1ppm $[O_2]$). The elemental concentration can be seen in Table 2.1.4.1, with pH 7.2 ± 0.1 and conductivity $2mS\cdot cm^{-1}$.

Table 2.1.4.1: Elemental concentration of the synthetic NaClO₄ 0.02M.

Conc. / mol·l⁻¹	
Na	$(2.18\pm0.03)\cdot10^{-2}$
Mg	$(2.07\pm0.02)\cdot10^{-6}$
Al	$(3.61\pm1)\cdot10^{-10}$
K	$(2.80\pm0.03)\cdot10^{-4}$
Ca	$(2.89\pm0.1)\cdot10^{-6}$
Cr	$(1.9\pm0.4)\cdot10^{-9}$
Mn	$(7.0\pm0.3)\cdot10^{-9}$
Fe	$(3.4\pm0.2)\cdot10^{-8}$
Co	$(3.9\pm0.5)\cdot10^{-10}$
Ni	< LOQ
Cu	$(2.3\pm0.5)\cdot10^{-9}$
Cs	$(1.9\pm0.1)\cdot10^{-10}$
Ba	$(9.9\pm0.1)\cdot10^{-9}$
Ce	$(7.1\pm0.2)\cdot10^{-12}$
Gd	$(9\pm4)\cdot10^{-12}$
Pb	$(5.7\pm0.4)\cdot10^{-10}$
Th	< LOQ
U	$(1.2\pm0.1)\cdot10^{-10}$
Cl-	$1.02\cdot10^{-4}$
ClO^{4-}	$2.11\cdot10^{-2}$

Doped material disk in presence of 300 ml volume of 20 mM NaClO$_4$ solution was fluxed into the autoclave under 8 bar of N$_2$/4.7% H$_2$ pressure. After each sampling each autoclave was refilled with N$_2$/H$_2$ mixture to reach 8 bar and the initial pressure conditions were again established without aqueous replacement. Thereafter, aliquots (2.5 – 5 ml) ml were taken at 0, 6, 14, 20, 27, 41, 54, 63, 76, 111 and 136 days. Additionally, blank test with leaching solution were conducted under the same conditions as well. The aliquots were filtered by ~ 1.5 ml microfiltrated (0.22 μm) and ~ 1.5 ml ultrafiltrated (Amicon Ultra-4 3k Millipore 1 - 2 nm).

The pH is being measured at every sampling interval with a pH Glass Electrode (Metrohm 6.0233.100) and pH-meter 905 Titrando (Metrohm). The pH electrode is calibrated with commercial pH buffer solutions (Reagecon pH 4.00 (Ref. 1040-49K01), Reagecon pH 7.00 (Ref.1070-79K01), Panreac pH 9.00 (Ref. 293166). Redox potential is being measured with an Ag/AgCl Combined Pt-ring Electrode (Metrohm 6.0451.100).

Soluble element concentration leached U, Cr, Al and Gd among other low concentrated metals, were analysed by Inducted Coupled Plasma Mass Spectrometry ICP-MS (iCAP Qc Thermo Fisher Sci.). Samples were conditioned with 10% HNO$_3$ solution. The limit of detection (LOD) of ICP-MS is in the range of ppt (pg·g^{-1}) and the limit of quantification (LOQ) in the ppb range (ng·g^{-1}). Uncertainty of the elemental concentration measured by this technique is 10 to 15%.

Description of experimental setup - Static leaching experiments are being performed in stainless steel autoclaves with reaction vessels made of PEEK (419 ml of total volume). Four valves in the lid allow aqueous sampling, gas injection and extraction and fourth valve is insert for in-situ temperature control in case of high temperature experiments (Rodriguez-Villagra et al., 2018) (Figure 2.1.4.1). The experiment was installed inside an argon glove box (O2 < 1 ppm) in order to ensure anoxic/reducing conditions.

Figure 2.1.4.1.- View of leaching experimental set up installed at CIEMAT in Ar glove box under 8 bar of 4.7% H$_2$-N$_2$.

Description of results - Leaching experiments results under anoxic conditions performed in presence of $NaClO_4$ with cumulative contact time of 136 days are plotted in figure 2.1.4.2, where no measurable uranium concentration released into the aqueous phase were observed (in a range between 10^{-9} to 10^{-8} mol·l^{-1}). The results indicate extremely low matrix dissolution after experimental time, close to the UO_2 solubility limit. Besides, the dopants analysed concentrations (Cr, Al, Gd) in solution were at the same order of magnitude than the own leachant and no further important release was observed.

Most of quantified elements in solution were in the range of aqueous leachant concentration. Thus any dissolution bellow aqueous leachant concentration (10^{-10} M for U, 10^{-9} M for Cr, 10^{-10} M for Al and 10^{-12} M for Gd) will mask the release of those elements from the solid matrix under such experimental conditions. Redox experimental conditions measured were Eh = -20 mV (at pH ~ 6.8).
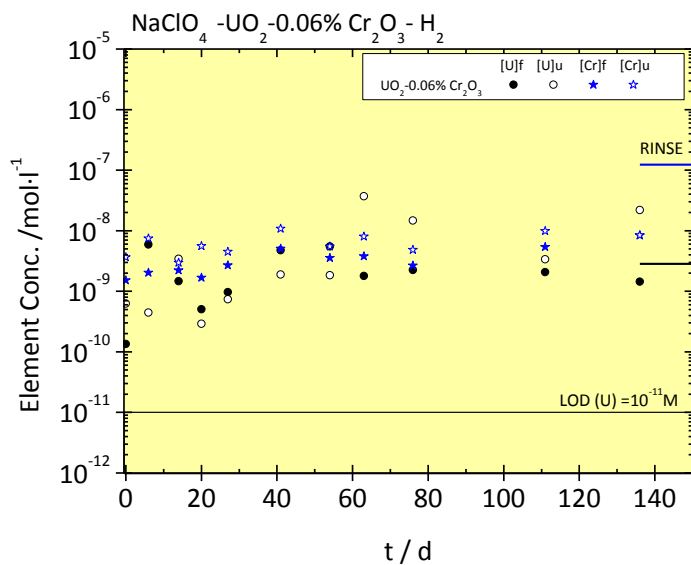
The normalized dissolution rates of the pellets (related to geometric surface area) could not have been evaluated from the concentrations because of the analytical background cannot distinguish between electrolyte concentrations and the presence of solid UO_2 samples.

SEM, XRD (fig. 2.1.4.3) and Raman (fig. 2.1.4.4) post leaching characterization on the surface of the pellets after the dissolution experiments with 0.02 M $NaClO_4$ have been performed and the results suggest no evidence of defects or microstructural alteration by-products on the pellet surfaces.

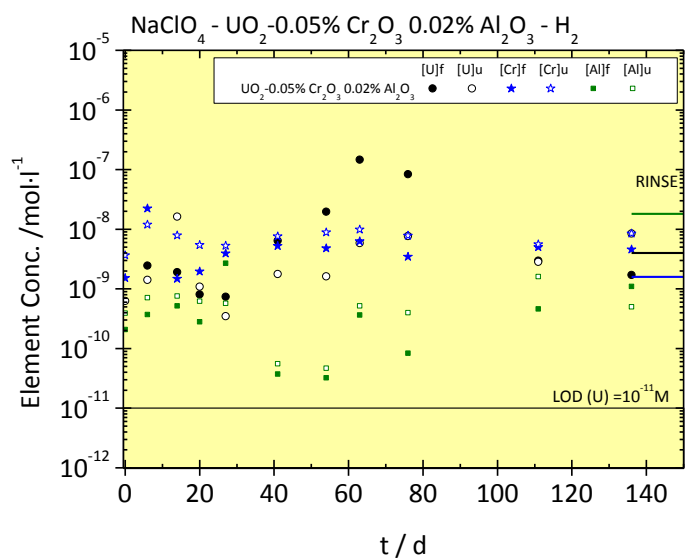In summary, initial dissolution data have been obtained for UO_2 doped in "inert" aqueous solution. The outcomes show no different effects on the dissolution behaviour between the leached kinds of doped UO_2 pellets.

Stability doped UO_2 studies by leaching experiments in presence of high carbonated and cementitious water (YCW-Ca) are being carried out and the results will be shown in the next deliverable report.
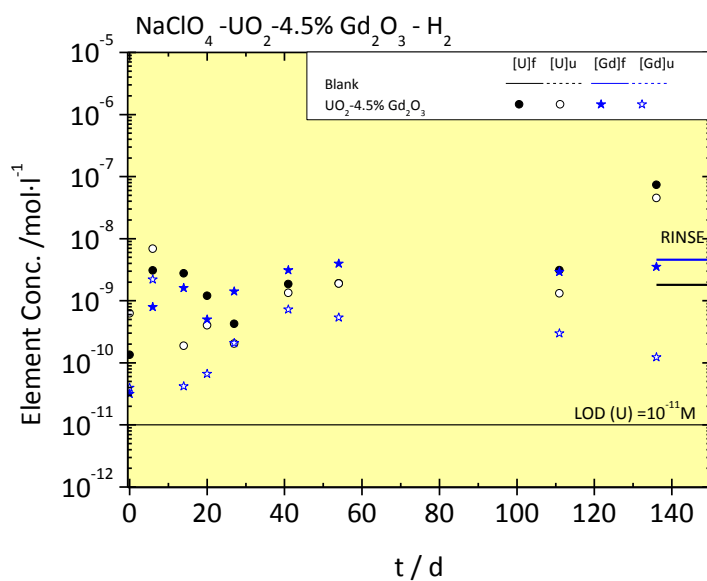
a)

b)

Figure 2.1.4.2.- U and Cr concentration as a function of leaching time of a) UO_2-0.06 w%Cr_2O_3, b) UO_2-0.05w%Cr_2O_3-0.02 w%Al_2O_3 and c) UO_2-4.5 w%Gd_2O_3.

DisCo

XRD (pre-leaching)

XRD (post-leaching)

a)

b)

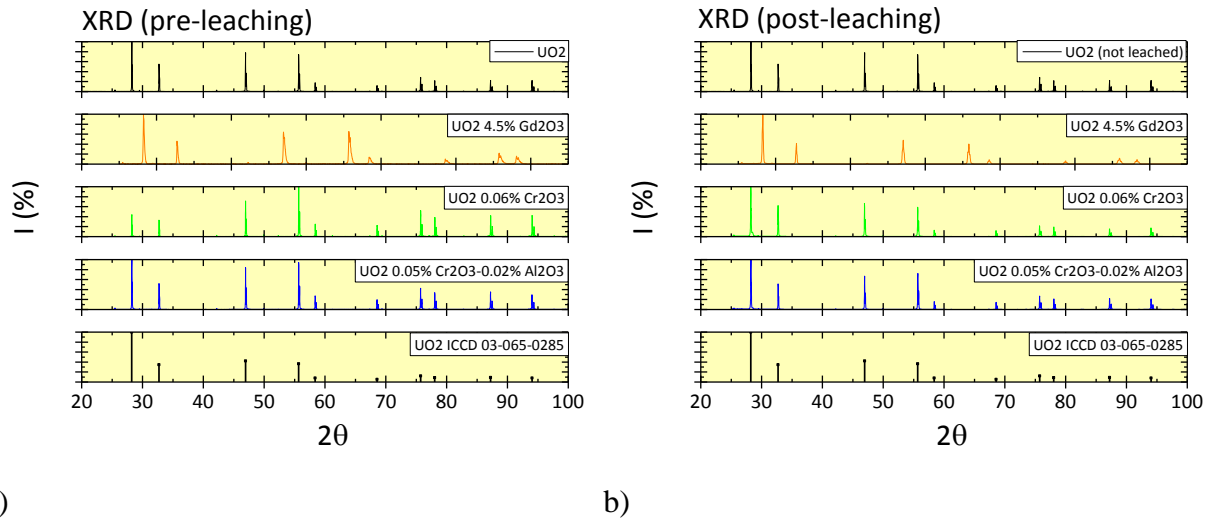*Figure 2.1.4.3.- XRD of solid sample pre-leaching (a) and after 136 days of leaching time (b) for UO$_2$-0.06^{w}/$_{o}$Cr$_2$O$_3$, UO$_2$-0.05^{w}/$_{o}$Cr$_2$O$_3$-0.02^{w}/$_{o}$Al$_2$O$_3$ and UO$_2$-4.5^{w}/$_{o}$Gd$_2$O$_3$ compared to UO$_2$ spectra.*
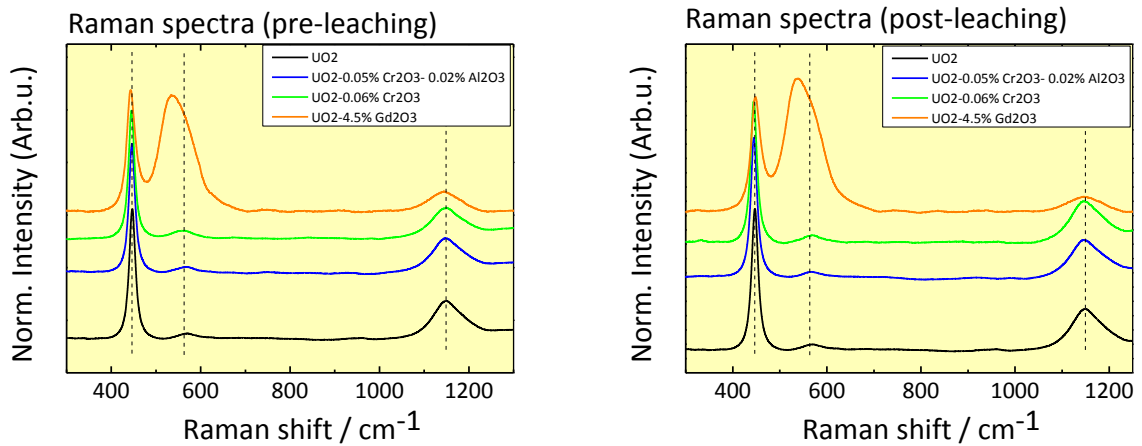

Raman spectra (pre-leaching)

Raman spectra (post-leaching)

Figure2.1.4.4.- Raman spectra of solid sample pre-leaching (a) and after 136 days of leaching time (b) for UO$_2$-0.06^{w}/$_{o}$Cr$_2$O$_3$, UO$_2$-0.05^{w}/$_{o}$Cr$_2$O$_3$-0.02^{w}/$_{o}$Al$_2$O$_3$ and UO$_2$-4.5^{w}/$_{o}$Gd$_2$O$_3$ compared to UO$_2$ spectra.

2.1.5   Results from USFD

Materials developed for investigation in dissolution experiments were synthesised via the nitrates co-precipitation method using uranium nitrate hexahydrate and chromium nitrate nonahydrate solutions precipitated with an excess ammonium hydroxide at pH 8-10. Powders of uranium dioxide doped with 0, 100, 600, 1200, 1800 and 2400ppm Cr were obtained from calcination at 750°C for 4 hrs in 5% H_2: 95% N_2 and milled at 35 Hz for 15 minutes before being pressed into 6 mm pellets at 500 MPa, and sintered at 1700 °C for 8 hrs in 5% H_2: 95% N_2. Pellets were then polished to 1µm in diamond suspension and thermally etched at 1600 °C to reveal grain boundaries. XRD confirmed the fluorite structure of UO_2 for all samples and Cr incorporation was confirmed by ICP-OES analysis of supernatants obtained during precipitation, the average grain size was 5-10 µm depending on the Cr concentration.

Static oxidative leaching experiments were conducted in 1 mM $NaHCO_3$ + 19 mM NaCl simulant groundwater solution at 30°C in air. To date, experiments have run a total of 56 days and the pH monitored throughout; pH 7-8 is maintained for the duration of the experiment.

Duplicate pellets of each Cr concentration (0, 100, 600, 1200, 1800 and 2400ppm) in UO_2 were placed in PTFE baskets and submerged into vessels with a total volume of 50ml simulant groundwater solution. At each sample point, the vessel was agitated and 2ml of solution removed for analysis via ICP-MS and replaced by 2ml of fresh simulant groundwater solution. Sample points were days 1,3,7,14 and then weekly; the results presented are from 56 days of dissolution, however the experiment is still ongoing. A dilution of 1:10 in 1% Ultra-pure HNO_3 solution was carried out for each sample before the elemental concentration, in ppt, of Cr and U measured using ICP-MS analysis. Calibration was carried out using several standard solutions made up from certified standards of U and Cr in solution. Equation 1 was then used to calculate the normalised mass loss ($N_L(i)$) of each element (i) as a function of time (t), normalising by the geometric surface area (GSA), the mass fraction (f_i) of element in sample and mass of sample pre dissolution ($m_{i\,(t-1)}$).

$$N_L(i) = \frac{m_i\,(t)}{f_i \times GSA \times m_{i\,(t-1)}} \qquad (1)$$

Figure 2.1.5.1 of the normalised mass loss of uranium shows that there is an increase in dissolution with time. This continues, seemingly linearly until day 51 where N_L (U) begins to plateau. This could be due to oxidation of the pellet surface, creating a passivation layer, as is expected for UO_2 (Rodriguez-Villagra, 2018), however, continued sampling over longer timescales is required before this can be concluded. In relation to the Cr content, the general trend is such that at higher Cr concentrations, the dissolution is reduced, as seen in the literature (Wang, 2009) suggesting that UO_2 becomes more refractory with increasing Cr, however, this relationship does not follow a decisive trend; 600 ppm Cr appears to be more durable than 1200 ppm and 1800 ppm Cr. It should be noted that the concentration of Cr in UO_2 is low and therefore changes between samples are very small. More investigation of the dissolution as a function of dopant concentration is required. It can also be noted that the

normalised mass loss in these samples is low, in the order of $\times 10^{-5}$ g.m^{-2}, more analysis for longer time periods is required.
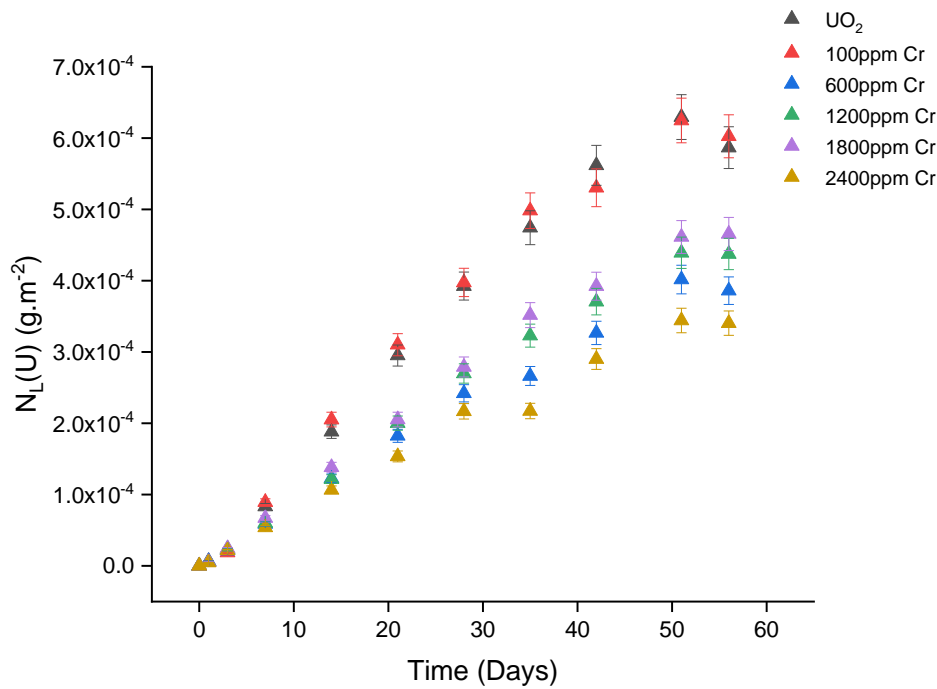

Figure 2.1.5.1. Normalised mass loss of U ($N_L(U)$) as a function of time for UO$_2$ used as reference and Cr-doped UO$_2$ pellets. All values are average of duplicates.

In conclusion, inital dissolution data have been obtained for UO$_2$ doped with increasing concentration of Cr in bicarbonate ground water solution, the results of which show, as expected, the durability increases with increasing Cr. Future work will include ongoing sampling of the above experiment as well as additional dissolution experiments at 60 °C. The rate of dissolution as a function of Cr will be evaluated and the microstructural influence invested via SEM and vertical scanning interferometry imaging to compare changes before and after dissolution. It will be interesting to normalise the dissolution data to the specific surface area of each pellet (rather than the geometric surface area, as performed here) to determine the surface area effects of Cr doped UO$_2$ on dissolution.

2.2 MOX related model systems

2.2.1 Results from CEA

Description of sample material - Homogeneous (U$_{0.73}$Pu$_{0.27}$)O$_2$ solid solution pellets (1 cm thickness and 5.4 mm diameter) were fabricated in 1985 at CEA Cadarache (COCA Process) and stored over 30 years at room temperature under air in a hot-cell. The initial stoichiometry was O/M: 1.983 and the density was 10.421 g cm^{-3}. Table 2.2.1.1 shows the initial isotopic composition of the sample. The damage level of the sample due to the accumulation of alpha decays during the 30 years of storage was calculated as 0.58 dpa by considering each alpha

decay event produces 1750 atomic displacements in UO_2 due to the recoil nucleus (~100 keV) and the alpha particle (5–6 MeV). After 30 years of storage period, one of the pellets was cut into ~2 mm thickness disks, which were then annealed at 1373 K for 6 h (heating and cooling rate 5°C/min) under Ar/H_2 4% atmosphere to recover the radiation damage and to adjust the stoichiometry of the sample. The pellets were characterized by EPMA, XRD and Raman spectroscopy to check the homogeneity of the plutonium distribution and to collect structural information.

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

Table 2.2.1.1: Initial isotopic composition of the sample (November 1985) in weight.

Description of leaching conditions - The leaching solution was a synthetic groundwater representative of Callovian-Oxfordian groundwater. A simplified groundwater composition was calculated by the BRGM (French Office of Geological and Mining Research) and validated by Andra (French National Radioactive Waste Management Agency) from analyses of samples coming from the site of the Meuse/Haute-Marne laboratory (France) and from Andra's regional boreholes. The composition is given in Table 2.2.1.2, and the pH was around 7.2-7.5.

	$[Na^+]$	$[K^+]$	$[Ca^{2+}]$	$[Mg^{2+}]$	$[Sr^{2+}]$	$[Cl^-]$	$[SO_4^{2-}]$	$[HCO_3^-]$	$[Si]$
$mg.L^{-1}$	993	39.1	341	131	17.5	1454	1412	146	5.62
$mol.L^{-1}$	0.0432	0.0010	0.0085	0.0054	0.0002	0.0410	0.0147	0.0024	0.0002

Table 2.2.1.2: *C*omposition of the synthetic Callovian-Oxfordian groundwater at 25°C.

This solution was put in contact with an iron foil for 3 months before introducing the MOX pellets. This first step was intended to ensure the presence of corrosion products on the iron foil surface, to obtain a solution chemistry containing Fe^{2+} ions not initially present in the synthetic COx water, and to have reducing conditions when the MOX pellets were introduced at a later date.

Description of experimental setup - Due to the Pu content of the MOX pellets, the experiment was performed inside a glove box in vacuum compared to the laboratory atmosphere. The atmosphere inside the glove box was argon (O_2 < 1 ppm) in order to ensure anoxic conditions. The leaching reactors were airtight and all the parts in contact with solution were in annealed titanium dioxide. Titanium is relatively inert chemically for radiolytical species, and as the objective was to study the influence of iron on MOX dissolution any possible iron contribution from the experimental equipment had to be

avoided. Samples were collected without opening the reactor through a sampling valve, thanks to the overpressure inside the reactor.

a) Precorrosion step of the iron foil (From November 2017 to January 2018)

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

The iron foil was first pre-corroded in 180 mL of synthetic COx water for around 80-90 days in the absence of the MOX pellets. The iron foil was slightly curved to enable maximum contact with water, and placed on the platform immediately under the pellet support. Once the leaching reactor had been closed, it was purged with a mixture Ar/CO_2 3000 ppm for 2h30 and then put under a pressure of 3.5 bars. The leaching solution was regularly sampled over time.

b) Long term leaching experiment with the homogeneous MOX fuel pellets (From Feb 2018 to May 2019)

After the iron pre-corrosion phase, the reactor was opened to add two MOX pellets with an alpha activity of 2.2×10^9 Bq/g, which were placed on a support above the iron foil. The reactor was then closed again, purged with a mixture of Ar/CO_2 3000 ppm for 30 min, and returned to a pressure of 3.5 bars with the same gas mixture. This experiment, which began in February 2018, was the subject of solution samplings over the last 15 months. Solution analyses are underway to determine the actinides releases from the MOX pellets, the evolution of groundwater chemistry and the contribution of the iron foil. The leaching experiment was stopped after 15 months of leaching in May 2019. The solid samples were recovered for surface characterizations by SEM and Raman spectroscopy in the next weeks. Acidic rinses of the vessel were also carried out in order to perform complete mass balances and quantify the alteration. The first leaching data are presented here and all the information will be available at the end of 2019 for the modelling part.

Description of results - Figure 2.2.1.1 shows the two MOX pellets extracted from the sample holder at the end of the leaching experiment. The iron foil has lost its metallic luster and appears gray because of the development of corrosion products. Surface characterization is underway but the drop in calcium concentrations (Figure 2.2.1.2) suggests already the precipitation of phases such as calcium carbonates.
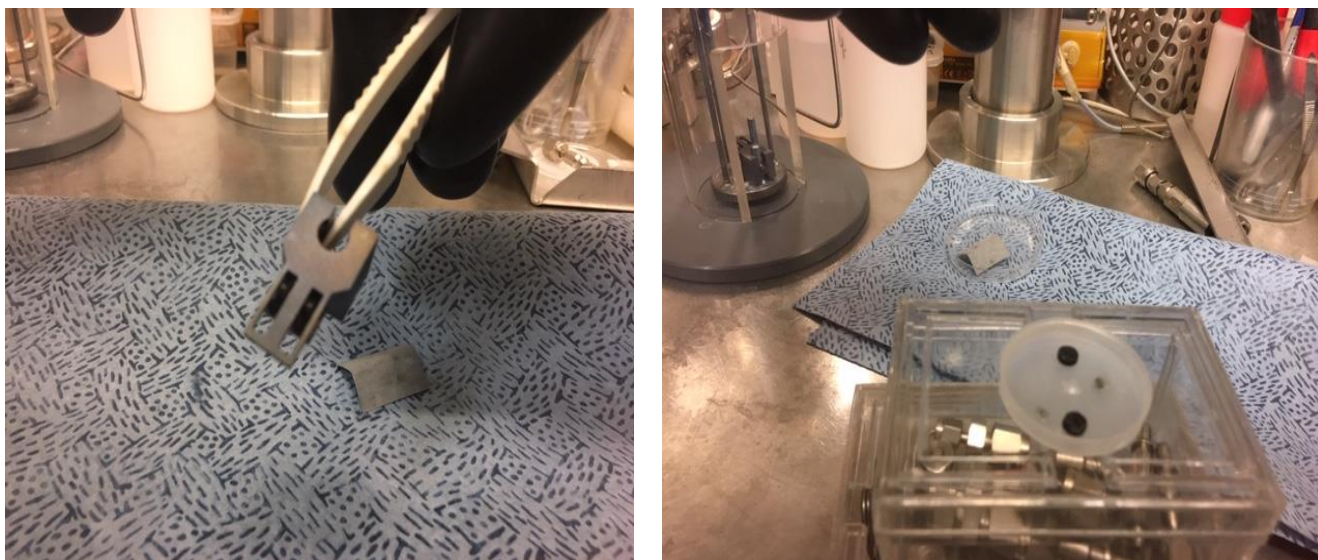
Figure 2.2.1.1: View of the samples (MOX pellets and iron foil) at the end of the leaching experiment.
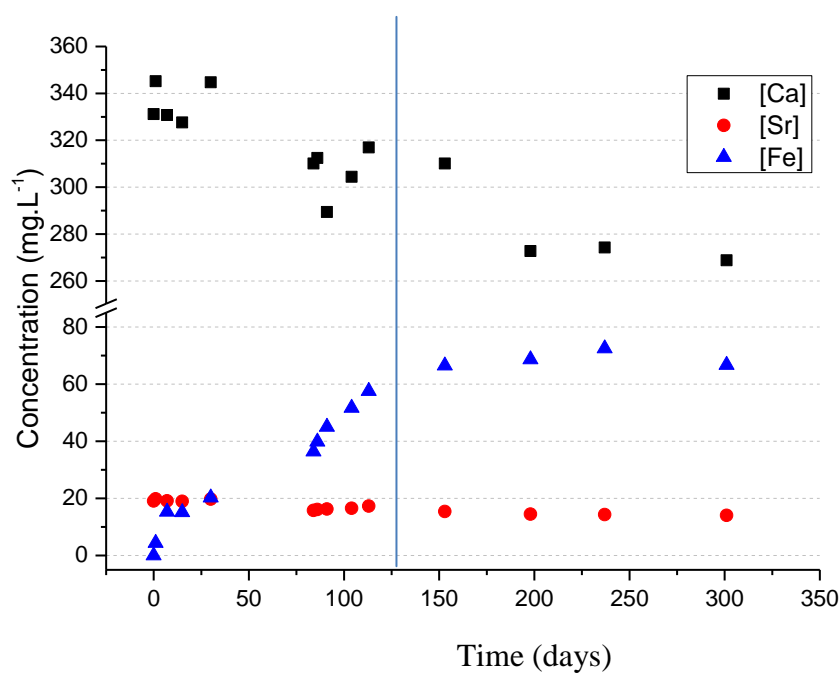

Figure 2.2.1.2: Evolution of the water chemistry as a function of time. The MOX pellets were introduced after three months of corrosion of the iron foil (vertical line).

The first uranium results indicate a significant effect of iron on the oxidative dissolution of this homogeneous MOX fuel. Uranium concentrations are less than 1 $\mu g.L^{-1}$ after seven months of leaching. These results are similar to those obtained on Pu-doped UO_2 or on heterogeneous Mimas MOX fuels (Figure 2.2.1.3).
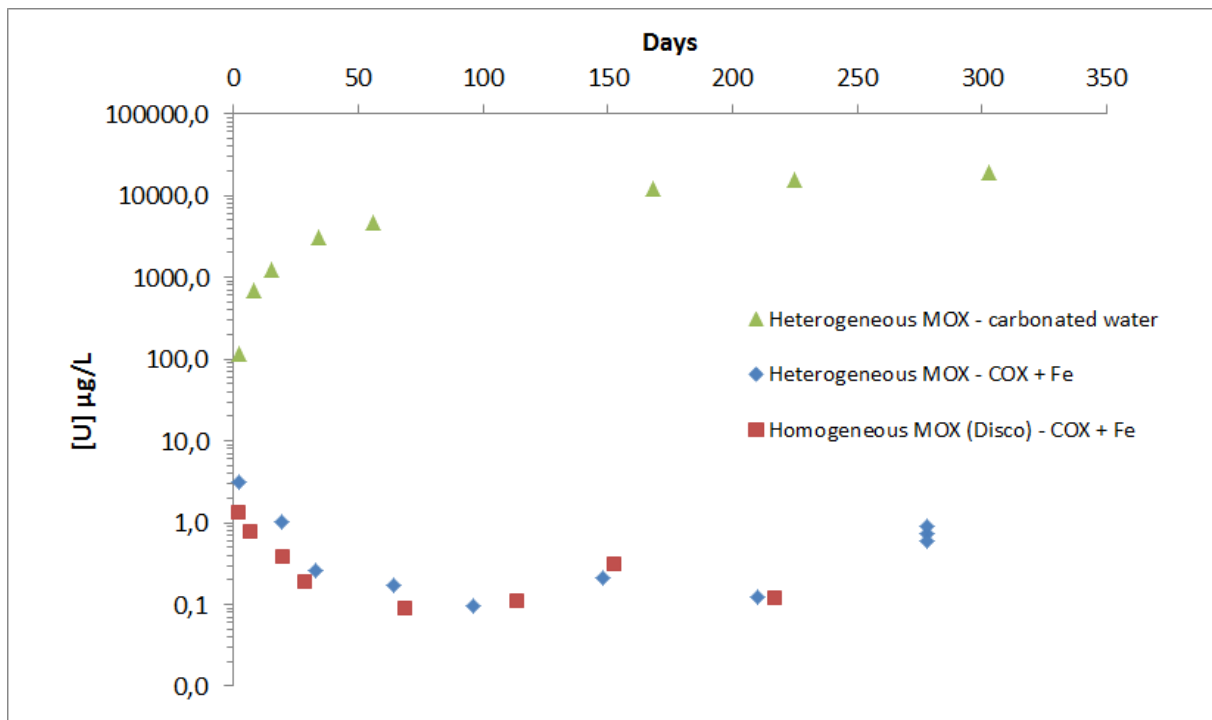
Figure 2.2.1.3: Evolution of the uranium concentrations as a function of time in a carbonated water for an heterogeneous Mimas MOX fuel (M Odorowski thesis) and for homogeneous and heterogeneous MOX fuels in a synthetic COX water + metallic iron.

3 Concluding perspective

This report summarizes the first results from dissolution experiments performed by WP 4 participants. It will be updated in project month 36 (May 2020).

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