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Executive summary

In a spent nuclear fuel repository, the engineered barriers are designed to protect humanity from the radiological risks associated with the waste for at least 100 000 years. In Sweden and Finland, the spent fuel will be protected by copper canisters, bentonite clay and 500 meters of crystalline bedrock. Water is not expected to enter the canisters for a very long time; however, when it does, the spent nuclear fuel will start to dissolve, resulting in a release of the radioactivity into the surrounding environment. Therefore, the rate with which the spent nuclear fuel dissolves is central to the safety assessment of the spent fuel repository. In the REDUPP project, this question is investigated through dissolution experiments using analogue materials. There is today an understanding and a general consensus regarding what main processes influence spent fuel dissolution. Spent fuel mainly consists of uranium dioxide, which is nearly insoluble in the absence of oxidants, such as oxygen. However, since it contains radionuclides, it is better the slower the dissolution is. Our present knowledge tells us it will take several millions of years to dissolve all the spent nuclear fuel in the repository, providing the surrounding repository environment keeps oxidants away from the spent fuel. This estimate is based mainly on laboratory experiments using real spent nuclear fuel, and analogue materials, such as uranium dioxide and similar oxides.

Unavoidably, laboratory experiments are of much shorter duration than the time analysed for the safety assessment of the repositories. In order to increase the confidence in the extrapolation of these dissolution rates far into the future, a deeper understanding of the dissolution process is required. An interesting and confounding observation, and recognized problem, is that when results from laboratory dissolution experiments are compared with studies of natural systems, the experimental studies indicate dissolution rates that are orders of magnitude higher. This problem is addressed here by investigating how the surface of a dissolving solid changes during the course of dissolution. It is at the solid-fluid interface that dissolution takes place, and by using the experimental equipment available today, very fine details of the changing surface can be imaged and analysed. Coupling the analysis of the bulk solution with the studies of the surface, it is possible to identify which sites at the surface are most reactive during the dissolution process. Another issue that is being investigated is the effect of using real, natural groundwater instead of the simulated groundwater compositions that were used previously in the experiments.

The dissolution experiments show that the dissolution rates slow down as dissolution proceeds. Dissolution of grain boundaries plays an important part in the first few days of dissolution, resulting in a relatively fast initial dissolution. A strong crystallographic control was observed, leading to faster dissolution for grain boundaries with high misorientation angle. Modelling using Ab Initio Molecular Dynamics, combined with atomistic thermodynamics, predicts dissociative chemisorption of water on the UO_2 surface, leading to a hydroxylated surface. Thus, the first step in the dissolution process is described from first-principles. Overall, the results show the effects of surface properties, especially grain boundaries and surface defects, on measured dissolution rates. Changes in the chemical composition of the fluid will affect the dissolution rate, as will the crystallographic structure of the exposed surfaces. The surface properties are expected to change over time, as could the fluid composition. Thus, these parameters need to be carefully considered when conducting laboratory experiments and when applying these dissolution rates to analyses that cover many thousands of years.

Summary description of project context and objectives

In the safety assessment of a final repository for spent nuclear fuel, release of radioactivity from the repository is controlled by the dissolution of the spent fuel in groundwater. The fuel will be protected from contact with water by a multi-barrier system. Sometime far in the future, the barriers will fail, and water will come in contact with the fuel. Therefore, it is essential to determine the dissolution rate of the aged spent fuel. This cannot be done easily, since the existing spent fuel in the world is not much older than half a century, and the spent fuel that is available for testing has a much higher level of radioactivity than fuel will have thousands of years after disposal. Aged spent fuel has a radiation field that is dominated by alpha decay. A way to simulate the dissolution of aged spent nuclear is to use UO_2 pellets that contain uranium isotopes with relatively short half-lives, so that the level of alpha activity of the material approximates fuel at various times after disposal. This has been done, and many dissolution tests have been performed in this way, indicating very slow dissolution rates (Ollila and Oversby, 2005; Ollila, 2008).

There are two important ways in which the experiments conducted to date with the alpha-doped UO_2 differ from the situation that will occur in the repository under long term disposal conditions. First, the test solutions used do not contain all of the chemical elements that occur in natural ground waters. Some of the trace elements in natural waters may have unexpected effects on the dissolution rate. Second, the fragments used in testing contain sharp edges and defects generated by the crushing process. These sites contain atoms that have fewer bonds than the bulk material and constitute high energy sites. As dissolution occurs, these sites dissolve faster than lower energy sites, such as plane surface sites. As the high energy sites disappear through dissolution, the dissolution rate would then decrease. A general decrease was in fact observed in the previous tests, which were performed one after the other on the same samples (Ollila and Oversby, 2005). This is of importance when considering the translation of the results of laboratory testing into behaviour that will be expected under the conditions of geologic disposal.

One is tempted to explain the discrepancy between the lifetime of UO_2 samples estimated from the results of laboratory testing and the longer lifetime of UO_2 under geologic conditions by appealing to the sensitivity of UO_2 to oxidation by trace amounts of O_2 that cannot be totally eliminated from laboratory testing conditions. This plays a role, but evidence in the geologic literature suggests that other factors are also important. Many studies have been done on the dissolution rates under laboratory conditions of minerals such as quartz and feldspars that are the main components of granitic rocks. The results of these tests have then been used to calculate the weathering rates of rocks. When the dissolution rates for plagioclase are compared with natural weathering rates, the laboratory rates are found to be 3 to 5 orders of magnitude higher (e.g. White et al., 2001). It is possible that the overestimation of dissolution rates from laboratory studies probably comes in large part from the role of high energy sites. With regards to surface maturation, it therefore seems that laboratory testing results in an overestimation of the dissolution rate of crystalline UO_2 by more than 2 orders of magnitude.

Computational modelling is capable of providing insight in the influence of the different energy sites on the dissolution process. Accurate methods of estimating excess energy contained in surface, edge, and point sites are nowadays available through first-principles materials' modelling that is capable of addressing the fine energy differences between different sites. The act of crushing, which is common practice when preparing samples for dissolution testing, generates sharp edges, points, and other surface defects. The atoms on the

surface associated with these features contain fewer chemical bonds than atoms that are on defect-free surfaces. The surface atoms, in turn, contain fewer bonds than atoms that are in the interior. A suitable approach to obtain accurate and detailed insight in how the surface morphology influences the dissolution process is to compute the dissociation energy of surface, edge and corner atoms. Chemical bonding is accurately predicted by first-principles computational techniques (e.g. Yun and Oppeneer, 2011).

Ollila (2008) investigated the processes of dissolution and precipitation of ^{233}U -doped UO_2 using the isotope dilution method. The U concentrations in higher-ionic-strength solutions (0.5 M – 1 M) were close to the detection limit of the analytical method, indicating significant uncertainties in the measurements. A constant low U concentration in the aqueous phase under reducing conditions, with metallic iron, indicated that the dissolution rate had slowed to zero; however, the isotope dilution method indicated that reactions were still on-going at the fluid-solid interface. It is hypothesized that these continuous dissolution-reprecipitation reactions may be affected by trace elements in the solution. The possible effect of trace elements in natural groundwater is tested here by using low, medium and high ionic strength groundwater from Olkiluoto, Finland. The UO_2 materials containing ^{233}U that have been previously tested by SKB and Posiva in synthetic groundwater and NaCl solutions will be used in these tests. In that way, the results from testing in natural ground waters can be directly compared with those obtained from testing in synthetic ground waters and NaCl solution. If the results are similar, it will provide a significant reduction in the uncertainty for the safety case associated with the behaviour of the waste form under long-term disposal conditions.

To improve our understanding of the relationship between laboratory studies and the results to be expected under geologic disposal conditions, the research reported here monitor both the solution phase and the developments on the surface of the solid. Since the relevant repository conditions are reducing, the goal is not to estimate the rate of oxidation from radiolysis, but rather improve our understanding with regards to surface maturation during the solid-fluid interaction without the complications of redox-reactions at the solid surface. Therefore, in the REDUPP project, the materials studied are ThO_2 , CeO_2 , and CaF_2 ; these have the same crystal structure as UO_2 , but are not sensitive to changes in oxidation state of the cation. These studies are coupled with theoretical calculations of the surface energy of the various fluorite-type surfaces, and possible reactions with these surfaces with water are investigated.

Two main uncertainties are addressed by this project: 1) effects of chemistry of natural ground waters, and 2) effects of changes in surface morphology on experimentally measured dissolution rates. The objectives of the work reported here are to reduce the uncertainty in the dissolution rate to be used in the safety case and thereby increase the confidence that can be placed in our ability to demonstrate that the geologic repository will function as designed. A second objective of this work is to provide for the training of young research workers who can continue to support the research needed in the future concerning radioactive waste disposal.

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Description of main S & T results/foregrounds

The uncertainties investigated in the REDUPP project relate to how well results from laboratory experiments correspond to the expected dissolution behaviour of UO_2 in a repository setting. Experiments to determine dissolution rates of alpha-doped UO_2 have been performed, using natural groundwater rather than synthetic groundwater. Surface maturation and the effects of changing surface geometry during dissolution have been explored using structural analogues such as CaF_2 , CeO_2 and ThO_2 . These materials have same crystal structure as the spent nuclear fuel matrix. The samples were carefully prepared and the solid-state characteristics of the samples were documented before and after dissolution (Godinho et al 2011, Stennett et al 2013, Corkhill et al, Submitted). Data and information from the experiments are used in collaboration with theoretical modelling work, employing ab initio and molecular dynamics simulations, for the ultimate goal of developing a theoretical model for dissolution on fluorite-type materials.

The experimental results presented here are focused on CeO_2 , ThO_2 and UO_2 ; the results from CaF_2 are mainly presented elsewhere (Godinho et al 2011, Godinho et al 2012, Godinho 2013). Results of first-principles calculations, presented below, are mainly based on CaF_2 , but have also been extended to the other fluorite materials.

Sample preparation and characterisation (Work Package 1)

The CeO_2 , ThO_2 and CaF_2 ceramics were prepared from powders that were decomposed at a range of temperatures, and then sintered to produce pellets. The aim was to produce pellets with a microstructure similar to that of spent nuclear fuel. The microstructures produced according to the methods described below are in good agreement with those published for UO_2 fuel (Forsyth, 1995) and SIMFUEL (Lucuta et al., 1991).

Decomposition at 800 °C yielded a CeO_2 powder with most appropriate characteristics for producing a microstructure similar to that of spent nuclear fuel. The powders, decomposed at 800 °C, were pressed into pellets and then sintered at 1700°C to give the largest grain size (between 8 and 20 µm in diameter), the lowest porosity (98.7% theoretical density) and a random crystallographic grain orientation (Evins and Vähänen, 2012; Stennett et al 2013).

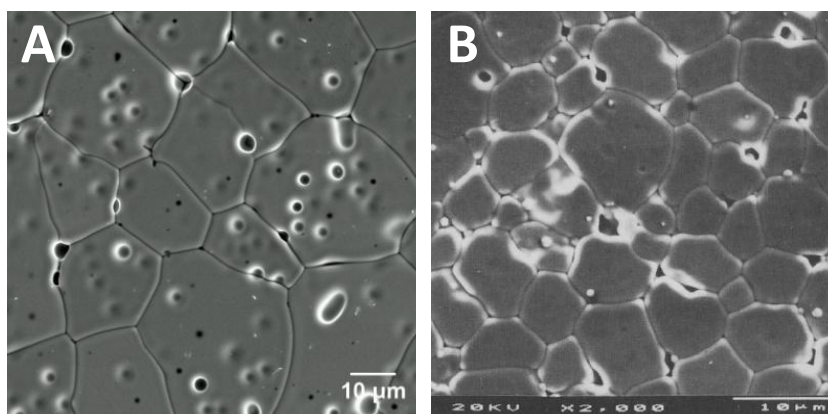


Figure 1. CeO_2 pellet sintered at 1700 °C (this work) compared to SIMFUEL (from Lucuta et al., 1991).

The sintered ThO₂ pellets for this study were prepared from ThO₂ powder with a similar methodology that was used for preparation of CeO₂ pellets. The optimized sintering temperature was found to be 1750 °C, at which 93% of the theoretical density was reached. The ThO₂ pellets have randomly oriented grains between 10 and 20 µm in diameter (Evins et al, 2014, Myllykylä et al, Submitted). Similarly, CaF₂ pellets sintered at 1200°C showed the required microstructures (Godinho et al, 2011).

Dissolution of CeO₂ powders (Work Package 2)

The dissolution study of CeO₂ powders was aimed at investigating the effect of energetically reactive surface sites on the dissolution rate during the first 70 days of dissolution, in conditions far from equilibrium. A full suite of dissolution experiments of CeO₂ in a range of media at pH 2, pH 8.5 and pH 11.7 and at a range of temperatures (40 °C, 70 °C and 90 °C) were conducted; the results were used to calculate normalised dissolution rates. The results show the influence of temperature and pH on dissolution rates (Corkhill et al., 2013). Increasing the surface area (by using smaller size fractions of the powders) did not appear to have the expected effect on dissolution rate: The dissolution rate of 2 – 4 mm particles was higher than that of 75 – 150 µm, which was higher than that of 25 – 50 µm (Evins and Vähänen, 2013).

Initially, the dissolution of crushed CeO₂ is relatively rapid, as seen by a fast initial leaching rate found to occur between 0 and 7 days. During this time, the grain boundaries have undergone significant dissolution compared to the pristine sample, etch pits have formed in some of the grain surfaces (mostly triangular in shape) and some grains appear to have dissolved more than others, as shown by the height contrast between grains. Preferential leaching of some grains and the presence of triangular facets suggests some degree of crystallographic control. Continued dissolution reveals that the normalised dissolution rate data for CeO₂ gets lower and lower and may involve a number of consecutive phases. Finally, a steady state dissolution rate appears to have been reached (Evins and Vähänen, 2013).

The effect of surface characteristics on dissolution rates was investigated by controlling the density of surface defects on the sample surface prior to dissolution. Removal of CeO₂ surface defects was achieved through high temperature annealing whereas oxygen vacancy defects were generated through annealing in oxygen-free environments, producing CeO_{2-x}. Annealing was performed on the (25-50 µm) size fraction at elevated temperatures. Surface area measurements were performed to quantify the removal of reactive surface sites, such as crystal and surface defects, as a function of annealing temperatures. The normalised dissolution rate of non-annealed particles compared to that of particles annealed at 1000 °C show that the normalised dissolution rate for the annealed particles is significantly lower during the first 42 days of leaching than for the non-annealed particles (Evins and Vähänen, 2013). The total Ce³⁺ fraction, determined by X-ray Photoelectron Spectroscopy, was taken as a measurement of oxygen vacancy density. The relative dissolution rates of these materials showed that there is a quantifiable relationship between energetically reactive surface sites and dissolution rate, dependent upon surface area, Ce³⁺ fraction and the solubility of Ce³⁺ and Ce⁴⁺; the greater the defect density, the higher the dissolution rate. This relationship was shown to only be applicable to CeO₂ with disordered defects, and not to isostructural, non-stoichiometric CeO_{2-x} with ordered defects, i.e. Ce₄O₇.

The dissolution data from materials with surface imperfections and defects introduced during sample preparation were fitted by a rate law (Figure 2). The results suggest that the surface

defects are removed relatively fast during the first days of dissolution, however, as the dissolution proceeds, it is a transient effect. Finally, it should be noted that while CeO_2 is isostructural to UO_2 , the defect properties investigated here will be different for UO_2 , which has a significantly different chemical nature.

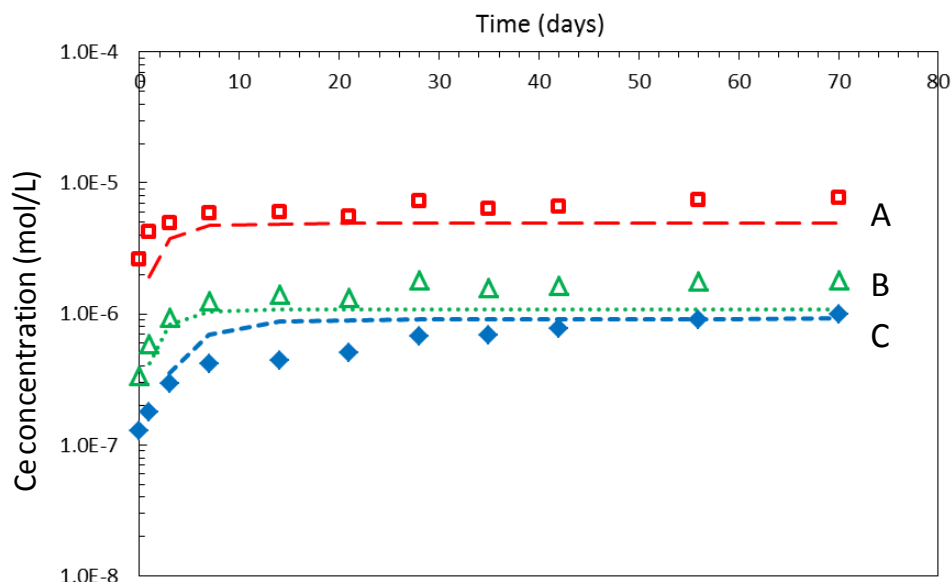


Figure 2. Ce concentration from dissolution at 90°C in 0.01M HNO_3 and modelled data for CeO_2 samples: A) 25 – 50 μm , no annealing; B) 25 – 50 μm annealed at 1000°C in air; and C) 75 – 150 μm particles. Symbols are experimental data and lines are the model fit.

Dissolution of ThO_2 powders (Work Package 3)

In order to optimize the experimental conditions for ThO_2 dissolution, a set of pre-tests were conducted using 2-4 mm sized ThO_2 fragments in two solutions: 1) 0.1 M NaCl ; 2) 0.01 M NaCl with 2 mM NaHCO_3 . The pre-tests were performed under atmospheric conditions at 25°C. High Resolution Inductively Coupled Plasma mass Spectrometry (HR-ICP-MS), with magnetic sector field, allowed the analyses of dissolved Th concentrations of sparingly soluble ThO_2 phases down to 10^{-12} mol/L. Comparing ultrafiltered and unfiltered samples, it is clear that the formation of carbonate/hydroxide complexes are shown to have the expected effect on solubility and dissolution of ThO_2 . The Th concentrations in the solutions stabilised at between 10^{-11} and 10^{-12} mol/l (Evins and Vähänen, 2013). The pH difference might have also some effect on the solubility, as basic conditions are known to decrease the ThO_2 solubility (Neck et al., 2003).

A following set of experiments was performed using two different size fractions and anaerobic conditions. In both solutions the initial, rapid release seems to be greater in the test with smaller size particles, which is expected due to greater reacting surface area to volume ratio (SA/V). Dissolution rate and solubility was found to be greater in 0.01 M HNO_3 (pH ~2) than in 0.1 M NaCl (pH 5-6), as was expected. The measured solubility of Th at pH 2 was found to be a slightly lower than the theoretical solubility of the crystalline ThO_2 . At higher pH (4 to 8), the measured levels (10^{-10} to 10^{-12} mol/L) were between the theoretical solubility of crystalline ThO_2 and $\text{Th}(\text{OH})_4$ (Evins et al., 2014, Myllykylä et al., Submitted).

In one additional set of experiments, a ^{229}Th tracer was used to test if precipitation and/or sorption occurred in the vessel. The results show that precipitation and/or sorption and dissolution occur simultaneously in the vessel (Figure 3; Evins et al, 2014).

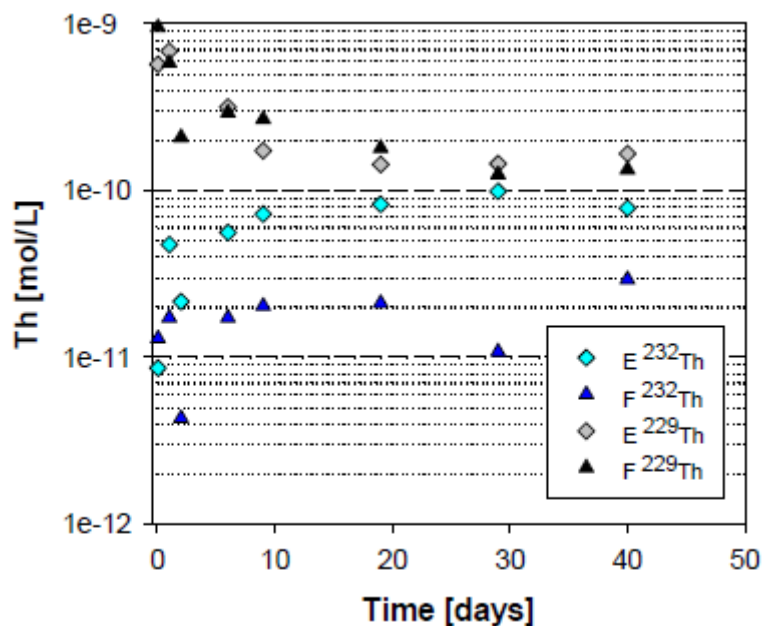


Figure 3. The evolution of ^{232}Th and ^{229}Th concentrations in unfiltered samples. The tests were conducted in 0.01 M NaCl under Ar atmosphere. The tests E (diamonds) and F (triangles) were conducted with 2 to 4 mm particles.

Precipitation/sorption reactions seemed also to happen faster in the test with higher surface area after initial release period. The results of Vandenberg et al. (2010) have also revealed, when using ^{229}Th spiking, that the dissolution/precipitation reactions are dynamic on the solid/solution interface.

These tests have provided high-quality Th solubility data, as well as confirmed that the measured dissolution rate of ThO_2 depends greatly on the chemical conditions such as pH and ligands, which can form complexes. In addition, the sample surface properties, including surface area and crystallinity of the solid, have been shown to affect the results.

Dissolution of alpha-doped UO_2 (Work Package 4)

Three different natural ground waters from Finland were chosen for the isotope dilution tests with ^{233}U -doped UO_2 samples under reducing conditions with Fe. The isotope dilution tests, using 0, 5 and 10% ^{233}U -doped UO_2 samples, were conducted consecutively in brackish (OL-KR6), saline (OL-KR5) and fresh (ONK-PVA) natural ground waters to study possible effects of alpha radiolysis on the dissolution rate of UO_2 . Two series of tests were performed in each groundwater, in which the ratio of UO_2 surface area to water volume was varied. The SA/V ratios were 5 m^{-1} and 15 m^{-1} in the tests with 0 and 5% ^{233}U -doped samples, and 5 m^{-1} and 12.5 m^{-1} in the tests with 10% ^{233}U -doped samples. All the tests were conducted under strongly reducing conditions established by a corroding iron strip in solution.

The first groundwater, a brackish groundwater from Olkiluoto, is a moderately saline groundwater (TDS 6300 mg/l), with slightly alkaline pH 7.7. The dissolution experiments were not started until the pH and alkalinity of the natural ground water had stabilised in Ar atmosphere. The pH was between 8.7 and 8.8 in the presence of iron. The results in the

brackish groundwater are in agreement with previous results of isotope dilution tests in synthetic ground waters (Ollila et al, 2004; Ollila and Oversby, 2005; Ollila, 2008). The changes in the measured $^{235}\text{U}/^{238}\text{U}$ ratios in the solution samples as a function of time show a higher release of ^{238}U from the solid UO_2 samples than the measured ^{238}U concentrations in solution suggest; this suggests U dissolution followed by U precipitation in the vessel or reprecipitation on the solid UO_2 sample. For tests with a surface area to volume ratio (SA/V) of 5 m^{-1} , the results for the different doping levels of 0, 5 and 10% ^{233}U are in agreement with previous findings in synthetic ground waters using similar SA/V (Ollila and Oversby, 2005; Ollila 2008). However, when the SA/V was increased threefold, to $12.5\text{--}15\text{ m}^{-1}$ the results show higher release of ^{238}U from the 10% ^{233}U -doped UO_2 sample, compared with 0 and 5% ^{233}U -doped samples (Ollila et al. 2013). This is in contrast with the other tests with the fresh (ONK-PVA) as well as the more saline groundwater (OL-KR5, TDS 12900 mg/l), where the results do not show elevated ^{238}U release from the 10% doped sample (Figure 4).

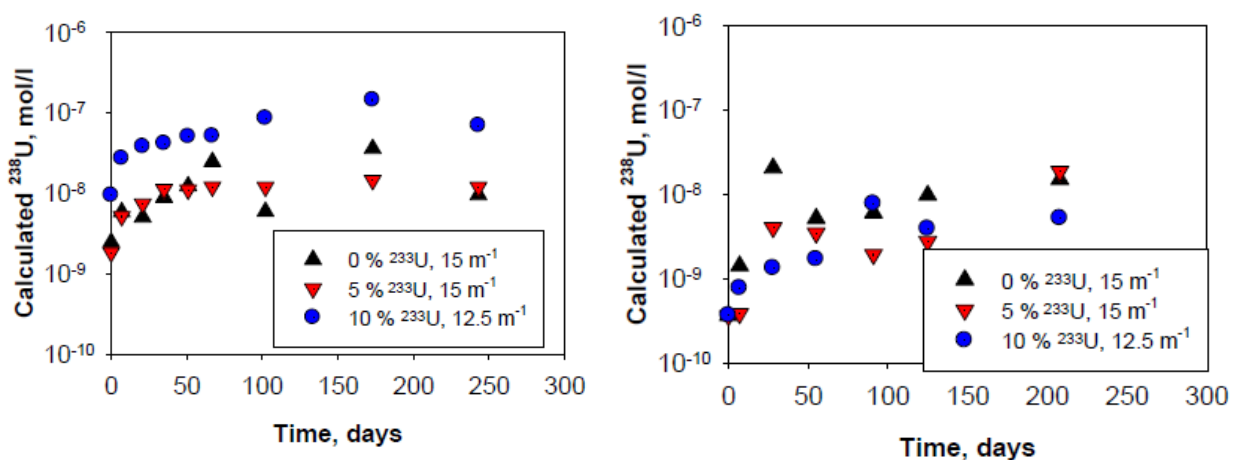


Figure 4. [^{238}U] calculated from the changes in $^{235}\text{U}/^{238}\text{U}$ ratios vs. leaching time. The three different doping levels of the solids were used in the isotope dilution tests in brackish (OL-KR6) groundwater (left) and in saline (OL-KR5) groundwater (right).

The resulting dissolution rates in natural ground waters were generally slightly higher than the rates measured previously in synthetic ground waters. The lowest dissolution rates were measured in saline OL-KR5 groundwater; these rates are in agreement with previous studies in synthetic ground waters. The rates were slightly increased in fresh ONK-PVA groundwater with high carbonate content, and the highest dissolution rate was found in the test with 10% doped UO_2 in brackish water (Evins et al 2014). Further investigations are needed to confirm these results, including i.e. parametric experiments to understand the role of some elements from the groundwater to explain the higher dissolution rate compared to synthetic groundwater.

Post-test characterisation of CeO_2 and ThO_2 (Work package 5)

CeO_2 particles, $25\text{--}50\text{ }\mu\text{m}$ in size, were imaged with Scanning Electron Microscopy (SEM) prior to, and after 350 days of dissolution in nitric acid (pH 2) at $90\text{ }^\circ\text{C}$. At both 0 and 350 days, pores $1\text{--}5\text{ }\mu\text{m}$ in size were present. Prior to dissolution, these pores were filled with fine particles of CeO_2 , which do not seem to present after 350 days of dissolution, suggesting they have been removed or dissolved. Although all small particles $> 1\text{ }\mu\text{m}$ were removed prior to dissolution by washing, it is clear that fines within pores have not been effectively

removed. Therefore, there may be an early contribution from fine particles of CeO_2 , which may be rapidly dissolved.

Other rapidly dissolving features on the surface of the particles are grain boundaries; the particles imaged after 350 days of dissolution have clearly visible grain boundaries which were not observed in pristine samples. This indicates initial, preferential dissolution of these surface sites, possibly reflected by the first stage of rapid dissolution evidenced from solution analysis. To further study the grain boundary dissolution, a CeO_2 polycrystalline monolith was studied using Atomic Force Microscopy (AFM) and Vertical Scanning Interferometry (VSI) before and after dissolution. This reveals preferential removal of material from the grain boundaries in the early stages of dissolution (Figure 5). From day 0 to day 7 of dissolution, the grain boundaries were observed to increase in depth from $0.43\ \mu\text{m}$ to $0.89\ \mu\text{m}$. During this time, a pore within the grain also increased in depth. At 14 days of dissolution, both the grain boundary and pore became more shallow ($0.58\ \mu\text{m}$ for the former), corresponding to a decrease in rate of Ce dissolution, as measured by solution analysis (Evins et al., 2014). A crystallographic control on dissolution was also observed, evident both through different surface retreat rates for grains of different crystallographic orientation, and through different retreat rates of grain boundaries with high or low misorientation angles (Evins et al., 2014; Corkhill et al., Submitted).

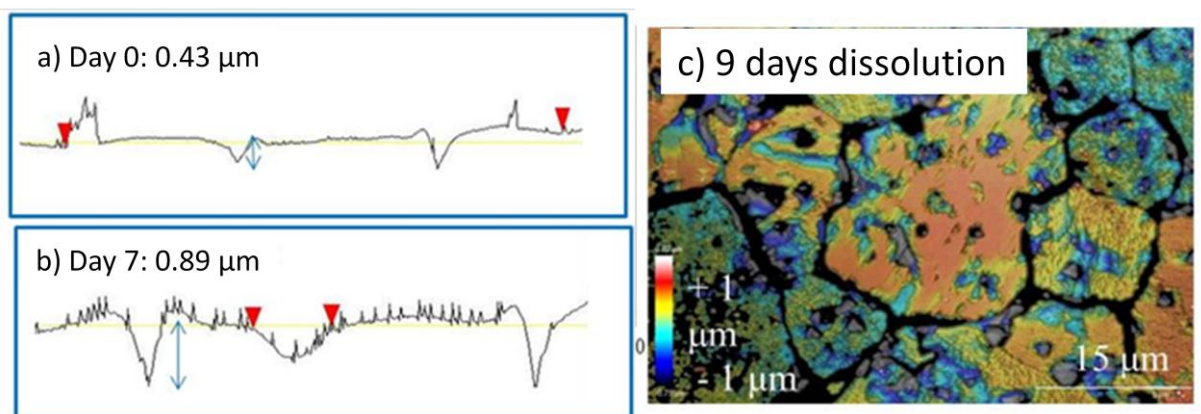


Figure 5. CeO_2 grain boundary dissolution. a) AFM cross section scan showing the surface across grain boundaries. b) AFM cross section scan showing change in grain boundary depth after 7 days dissolution. c) VSI image of a different part of the same sample, showing the preferential dissolution of grain boundaries after 9 days of dissolution.

ThO_2 particles ($80 - 160\ \mu\text{m}$) were imaged by SEM using back-scattered electrons (BSE) before and after dissolution tests. A variable effect on the surfaces by dissolution was observed. Some of the particles or surfaces seemed to have acquired new material precipitated on the surfaces, while others looked like the pristine material. Some particles presented grain rounding and widening of the grain boundaries. The crystallinity and the surface energies of the reacting surfaces of ThO_2 might also have some effects and their relevance to the observed phenomenon should be studied. A ThO_2 monolith was also prepared for post-test analysis by AFM. After 7 days dissolution in 0.01M HNO_3 at 90°C the surface is very rough (Figure 6). It is covered by a layer that makes measuring grain boundaries difficult after 7 days (likely Th-hydroxides). In agreement with what was found for CeO_2 , the grain boundaries with high misorientation angles, e.g. (416)/(506), had a faster retreat rate than grain boundaries with low misorientation angles, e.g. (103)/(506). The research performed suggests a strong crystallographic control on the dissolution of grain boundaries, for both ThO_2 and CeO_2 ,

during the initial phase of dissolution of polycrystalline samples. However, the effect of grain boundaries on the long-term dissolution rate requires further investigation.

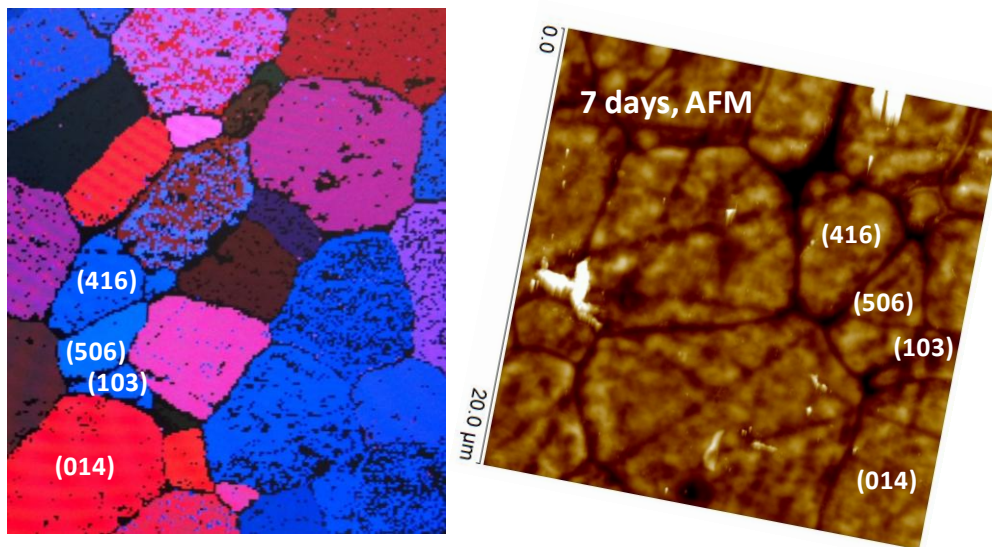


Figure 6. ThO₂ surface imaged by EBSD (left) and, after 7 days dissolution, by AFM (right). The labels give the crystallographic orientation of the grains.

In addition to grain boundaries and pores, energetically reactive sites that were formed through CeO₂ sample preparation showed an effect on dissolution rate. Facet structures that formed during thermal annealing also exhibited a crystallographic control involving the {111} crystal plane. Upon introduction to dissolution media, they were found to change their morphology in response, suggesting a contribution to dissolution. Dissolution rates were shown to increase by up to 3 orders of magnitude as a result of surface polishing, due to the generation of surface defects and surface strain (Evins et al., 2014; Corkhill et al., Submitted). Thus, defects induced through sample preparation contribute to the initial dissolution rate; however, the observed contribution from the studied facets is small compared to that from grain boundaries. These sample preparation features are not likely to affect the estimated long-term dissolution rates. It should nevertheless be noted that performing dissolution tests with polished samples without any further treatment is likely to cause over-estimation of dissolution rates.

Ab initio modelling and prediction of surface stabilities for fluorite materials (Work package 6)

The most stable surfaces of the fluorite crystal structure are known to be those with the lowest Miller index, i.e. the (111), (110) and (100) surfaces. These are flat surfaces that can be considered as reference planes from which one can build any other higher Miller indexed surface (Godinho et al., 2012). Results presented here are based on the finding that the surface formation energy of any surface within a family of vicinal surfaces of CaF₂ can be described as a function of the number of atomic rows of the terrace, the surface formation energy of the reference surface and a constant that depends exclusively on the structure of the surface. This means that the surface formation energy of any stepped surface only depends on the surface formation energy of the reference plane, the size of the reference plane and the step direction

(Maldonado et al, 2013). These results have also led to the observation that there exists a proportionality relation between the surface formation energies in CaF_2 and CeO_2 , which allows the extension of the model to CeO_2 . Further investigations show that this is so also for ThO_2 and UO_2 . Thus, the surface formation energy of any stepped surface of a fluorite material can be described.

In order to achieve a reliable description of the dissolution processes on the fluorite surfaces, a method using a combination of Ab Initio electronic structure calculations and Molecular Dynamics is used (called AIMD). The results show that the H_2O dissociation process on the CeO_2 (111) surface is virtually barrierless, and the same has been found for UO_2 (Figure 7).

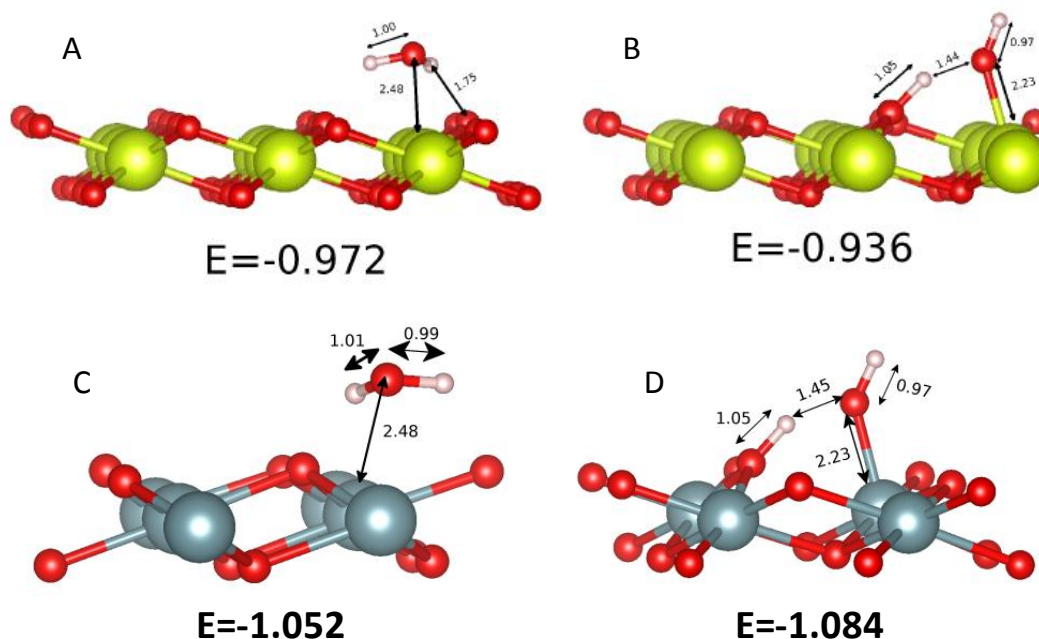


Figure 7. Ball-and-stick models of the (111) surface of CeO_2 and UO_2 . Surface energy is given by E under each image. Bondlengths are given in Å. A) Molecular adsorption of H_2O on CeO_2 (111). B) Dissociative adsorption of H_2O on CeO_2 (111) C) Molecular adsorption of H_2O on UO_2 (111) D) Dissociative adsorption of H_2O on UO_2 (111).

Adsorption, accompanied with a modification of the morphology, has been shown to be favourable. The dissociation process occurs by the rupture of the water molecule into OH^- and H^+ because of the thermal vibration. Then, the H^+ ion bonds to one of the superficial O of CeO_2 , while the OH^- group bonds to one surface Ce (cation). These results suggest that amount of dissociative adsorption of the water molecule onto (111) of CeO_2 is associated with the number of surface cations.

Extending this study to stepped surfaces, involving step edges and terraces, has shown that dissociative adsorption is predicted to occur on the step edges, while molecular adsorption is predicted to occur on the (111) terrace (Maldonado et al, 2014). Connected with these surface reactions is a change in surface morphology on the atomic scale. Ab initio thermodynamics calculations were then used to investigate how the water adsorption process on these different surfaces is affected by environmental conditions. Varying the temperature and the water coverage (H_2O partial pressure) reveals that water adsorption on the step is always more stable on the edge than adsorption on the terrace (Evins et al., 2014; Maldonado et al., 2014). The conclusion drawn from this study is that UO_2 surfaces will always react with water under atmospheric pressure and room temperature, leading to water dissociation. Thus, this work

has allowed the description of the first step of dissolution of the fuel material from first principles.

Research coordination and communication (Work Package 7)

The REDUPP Communication Action Plan (CAP) describes the following tools used for communication and dissemination: Participation in conferences, meetings and workshops external to the project, scientific publications, annual reports, web-site, newsletter, articles in professional magazines & press releases. In addition, project internal and external direct communication is carried out via email.

The project has followed the plan and used every tool listed; further details follow below.

Meetings and workshops

The project participants have met at three Annual Meetings. The first meeting was held in Stockholm in April 2012, the second meeting was held in Sheffield in May 2013, and the third and final meeting was arranged as an open conference which took place in February 2014 in Stockholm, Sweden. This meeting had the title: "REDUPP International workshop on Surface Reactivity and Dissolution of Spent Nuclear Fuel Materials". It was attended by ca. 60 people from Europe and overseas. The abstracts from the conference are published as an appendix to the REDUPP Final report (Posiva Working report 2014-12).

Two smaller, informal workshops were held; the first in Stockholm in September 2011, and the second in Uppsala in September 2012.

The Project website

The web site address is: www.skb.se/REDUPP. It includes a Member Area which requires a Login which has been provided to the project participants. The web site was used for announcing the final open conference; it will continue to be available until 2019, five years after the end of the project.

Annual reports

Annual reports have been published as Posiva Working Reports 2012-28, 2013-15 and 2014-12, available on the REDUPP web site as well as on www.posiva.fi. The reports describe the work performed in the different work packages. The audience is expected mainly to be different Nuclear Waste Management Organisations, and the participants in the IGD-TP platform (Implementing Geological Disposal-Technology Platform).

Peer-reviewed articles

Overall, the REDUPP project has submitted 8 manuscripts for publication. At the end of the project, 6 peer-reviewed articles are published, and two are presently under review.

1. Godinho, J.R.A., Piazzolo, S., Stennett, M.C. and Hyatt, N.C. (2011). Sintering of CaF₂ pellets as nuclear fuel analogue for surface stability experiments. *Journal of Nuclear Materials*, 419, 46-51.
2. Stennett M.C., Corkhill C.L., Marshall, L.A. and Hyatt, N.C. (2013). Preparation, characterisation and dissolution of a CeO₂ analogue for UO₂ nuclear fuel. *Journal of Nuclear Materials* 432, 182-188.

3. Corkhill, C.L, Bailey, D. J., Thornber, S.M., Stennett, M. C. and Hyatt, N. C. (2013). Reducing the uncertainty of nuclear fuel dissolution: an investigation of UO₂ analogue CeO₂. Mater. Res. Soc. Symp. Proc. Vol. 1518, DOI: 10.1557/op2013.90
4. Maldonado, P., Godinho, J. R. A., Evins, L. Z., and Oppeneer, P. M. (2013). Ab Initio Prediction of Surface Stability of Fluorite Materials and Experimental Verification. Journal of Physical Chemistry C, 117, 6639–6650.
5. Ollila K., Myllykylä, E., Tanhua-Tyrkkö, M. and Lavonen. T. (2013). Dissolution rate of alpha-doped UO₂ in natural groundwater. Journal of Nuclear Materials 442, 320–325.
6. Maldonado, P., Evins, L.Z., Oppeneer, P.M. (2014). Ab Initio Atomistic Thermodynamics of Water Reacting with Uranium Dioxide Surfaces. Journal Physical Chemistry C, 118, 8491-8500.
7. Myllykylä, E., Lavonen, T., Stennett, M., Corkhill, C., Ollila, K., Hyatt, N. (Submitted) Dissolution study of ThO₂ with analogue microstructure to UO₂ of nuclear fuel matrix. Submitted to Radiochimica Acta.
8. Corkhill, C. L., Myllykylä, E., Bailey, D. J., Thornber, S. M., Qi, J., Maldonado, P., Stennett, M. C., Hamilton, A., and Hyatt, N. C. (Submitted). The contribution of energetically reactive surface features to the dissolution of CeO₂ and ThO₂ analogues for spent nuclear fuel. Submitted to ACS Applied Materials and Interfaces.

Conference reports and proceedings

1. Stennett, M.C., Corkhill, C. L., Bailey, D. Thornber, S., Hyatt, N.C., Maldonado, P., Oppeneer, P.M., Myllykylä E., Ollila K., Vähänen M., Salo V., and Evins, L. Z. (2013). Investigating the Effect of Surfaces During Dissolution of Materials with a Fluorite Structure (REDUPP). In Valls, Buckau and Duro (Eds.) Proceedings of the EURADISS 2012 Workshop, JRC Scientific and policy reports, JRC 81587, pp A95-A108.
2. Evins, L. Z., Corkhill, C. L., Stennett, M.C., Hyatt, N.C., Maldonado, P., Oppeneer, P.M., Myllykylä E., Ollila K., Godinho, J., Juhola, P. and Vähänen M. (2014). How the surface properties of spent nuclear fuel materials influence dissolution: Results of the REDUPP project. In: Proceedings of the 8th European Commission conference on the management of radioactive waste, Euradwaste'13, 14-16 October 2013, Vilnius, Lithuania (in preparation).
3. Corkhill, C.L., Bailey, D.J., Thornber, S., Stennett, M.C., and Hyatt, N.C. (2014). The disposal of spent nuclear fuel: The effect of high energy surface sites on dissolution rate. P20, In: Proceedings of the 8th European Commission conference on the management of radioactive waste, Euradwaste'13, 14-16 October 2013, Vilnius, Lithuania (in preparation).
4. Maldonado P., Godinho, J.R.A., Evins, L.Z. and Oppeneer, P.M. (2014). Surface Reactivity and Dissolution of Spent nuclear Fuel: The Value of First-principles Computational Modelling, P21. In: Proceedings of the 8th European Commission conference on the management of radioactive waste, Euradwaste'13, 14-16 October 2013, Vilnius, Lithuania (in preparation).

Papers in professional magazines

1. Hyatt, N.H. and Evins, L.Z. (2011) Safety - The Swedish Way. *Materials World* 19(7), 20-22.
2. Evins, L.Z. (2013) REDUPP - the final steps. In: Pan European Network Science and Technology vol. 7, June 2013, pp 66-67.
<http://www.paneuropeannetworks.com/ST7/#66>
3. Evins, L.Z. (2014) Rate of spent fuel dissolution In: Pan European Network Science and Technology vol. 10, March 2014, p 58.
<http://www.paneuropeannetworks.com/ST10/#58>

Newsletters

Five Newsletters were sent out to interested parties during the project. These newsletters are posted on the REDUPP web site www.skb.se/REDUPP as well as on the EC website: http://cordis.europa.eu/fp7/euratom-fission/funded-reports_en.html

Press releases

Research collaboration between The University of Sheffield and Japan was described by a press release and this resulted in the appearance of REDUPP in the local Sheffield newspaper "The Star". The article featured the Sheffield-Japan collaboration and explained that Sheffield University has been awarded a grant from the Japan Society for the Promotion of Science, which has allowed REDUPP participant Claire Corkhill to visit Kyushu University in Japan.

Lecture Series

The REDUPP Lecture series, with the theme Surface reactivity and surface processes during dissolution, is now finished. In total, nine lectures were held.

The lecture series started in conjunction with the first Annual Meeting on the 26 April, 2012, with Lecture #1:

- Virginia Oversby (VMO Konsult): "Spent fuel dissolution under repository conditions – why laboratory measurements always overestimate."

Lectures #2 and #3 were held in 9 September 2012 in conjunction with the second informal Workshop in Uppsala.

- David Shoesmith (Western University, Canada): "The Influence of In-reactor Irradiation on the Chemical/Electrochemical Reactivity of Uranium Dioxide."
- Peter Oppeneer (Uppsala University): "Modeling of nuclear fuel materials using first-principles calculations."

At all three first lectures there were approximately 15 project-external people attending and contributing to the discussions.

Five lectures, #4 to #8, were held in Sheffield 7 May 2013 in conjunction with the second annual meeting:

- Joaquin Cobos-Sabate (Ciemat): "Studies on spent fuel stability during repository conditions"
- Thomas Gouder (ITU): "Surface Science Investigations of Spent Fuel Corrosion Processes"
- Mark Read (Birmingham University): "Computational modelling of the Bulk and Surface Chemistry of Nuclear Fuel Materials"

- Jonathan Icenhower (Lawrence Berkeley National Lab): “Determining glass dissolution rates using interferometry and the role of uncertainties associated with surface area”
- Thorsten Geisler (University of Bonn): ”An alternative model for silicate glass corrosion”

Approximately 30 project-external people attended these lectures.

The final lecture, REDUPP Lecture #9, was held in Stockholm on the 19 February 2014:

- Rodney C Ewing (Stanford University): "The simplicity and complexity of the fluorite structure"

This lecture was held in conjunction with the final REDUPP meeting, and there was an audience of ca 60 people.

Project management (Work Package 8)

The tasks within this Work Package relates to the Grant and Consortium Agreements.

The Consortium Agreement states that there should be a project Steering Committee which will meet at appropriate intervals. In total three such Steering Committee meetings have been held in conjunction with the Annual Meetings (April 2012, May 2013 and February 2014).

The deliverables connected to this WP are the two Periodic reports, and the Final administrative report, to be submitted to the EC. The current document is the Final administrative report.

Conclusions

- The CeO₂ experiments show fast initial leaching rates followed by slower leach rates. Studies on monolithic, polycrystalline samples show fast grain boundary dissolution, and the formation of triangular etch pits suggests a crystallographic control on leaching.
- The ThO₂ experiments show that chemical conditions such as pH and presence of complexing ligands elevate the Th solubility and affect the dissolution rate. It was shown that dissolution occurs in coincidence with precipitation and/or sorption in the vessel, and the crystallinity and surface features of the dissolving material affect the dissolution.
- The three different natural ground waters affect ²³³U-doped UO₂ dissolution differently; however they all result in a slightly elevated dissolution rate compared to previous experiments with synthetic groundwater. This difference is only seen in samples with high surface area to fluid volume ratio, indicating that the effect is related to the exposed surface. Significantly, dissolution rates are lowest in the most saline groundwater, which contains the highest amount of trace elements such as Br. The addition of an isotope tracer reveals that dissolution occurs in conjunction with precipitation and/or sorption in the reaction vessel.
- First-principles modelling of fluorite surfaces has been used to establish surface energies and to predict the order of surface stability. A combination of terraces and

steps oriented in the directions of crystallographic reference planes is used to express the surface formation energy as dependent on the geometry of the planes involved.

- Reactions of these surfaces H_2O have been described using Ab Initio Molecular Dynamics, and atomistic thermodynamics. This shows that dissociative chemisorption of water will always occur on UO_2 surfaces under ambient conditions, leading to a hydroxylated surface. This is the first step in mechanistically describing, from first principles, the dissolution reaction.
- Overall, measured dissolution rates are affected both by surface properties and by fluid composition. Notably, the crystallographic structure of the exposed surface also influences the interfacial reactions. These parameters should be carefully considered when measuring dissolution rates in the laboratory, and when extrapolating these rates far into the future.
- All deliverables have been submitted, and the project members have published the results in peer-reviewed journals. Various dissemination activities have been carried out, including a final open conference at the end of the project. Training and outreach have been successfully implemented through the REDUPP Lecture Series.

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Potential impact and main dissemination activities and exploitation results

This project concerns improving our knowledge regarding long-term dissolution rates of spent nuclear fuel, a core issue in the safety assessments of geologic repositories for high level waste. Thus, this project has improved the confidence to our ability to safely dispose of these wastes and to protect the health and wellbeing of human beings and the environment. As our confidence in the post-disposal performance of the repository increases, public acceptance for nuclear energy and repository disposal safety should also increase. The results are expected to have an impact in both applied and basic research, since our work is deeply rooted in fundamental scientific questions regarding the dissolution process and how surfaces change during solid-fluid interaction.

The scientific literature has, for many years, documented an apparent discrepancy between dissolution rates measured in laboratory studies and in natural systems. Laboratory results often indicate much faster weathering and dissolution rates; the suggested reasons for this discrepancy are many. The REDUPP project has provided yet another piece in the puzzle for this general scientific problem. The cross-disciplinary approach of the REDUPP project is also a show case for successful collaboration between researchers from different fields. Training is an important issue in the nuclear field; it is essential to have continuous knowledge transfer in order to secure a pool of skilled personnel for current and future facilities. The project has provided training through the REDUPP Lecture Series, as well as through employing early-career scientists and directly involving students in the activities. Studying materials with low solubility require high precision analytical data, which is attained through analyses by High Resolution ICP-MS; thereby this project has also contributed to the development of analytical skills and methods, personnel training and improvement of data bases.

The results are published in a series of reports and in several peer-reviewed scientific journals (e.g. Journal of Nuclear Materials, Journal of Physical Chemistry C). The articles have been cited in articles in other peer-reviewed journals (e.g. International Journal of Applied Ceramic Technology, Geochimica et Cosmochimica Acta). The project web page and the newsletters inform the public and interested organisations of the activities and results of the project. Public events carried out are the publication of the annual reports and newsletters, which have been distributed to interested organisations and are available on the project web page. The sectors expected to show an interest in our work is both nuclear waste management industry and research departments throughout the world. The REDUPP project has been presented in two volumes of the Pan European Network's Science and Technology section, ensuring dissemination to non-experts and policymakers across Europe. In addition, the final project meeting was arranged as open scientific conference which was attended by 60 people from Europe and overseas. The abstracts from this meeting are found as an Appendix to the final project report (Posiva Working Report 2014-12). In particular, the project has maintained a close collaboration with the other organisations involved in the European Technology Platform for Implementing Geological Disposal (IGD-TP). It is clear that international collaboration is necessary to achieve the goals of IGD-TP, and the REDUPP project has helped to strengthen communication between countries in a range of research areas. By ensuring efficient knowledge transfer between the experienced people in the field and young scientists this project contributes to the future European competitiveness in nuclear waste management.