Dynamics of Spent Nuclear Fuel Dissolution

Impact of Catalysis, Matrix Composition and Time Evolution

ANNIKA CAROLIN MAIER

KTH Royal Institute of Technology
School of Engineering Sciences in
Chemistry, Biotechnology and Health
Department of Chemistry
Applied Physical Chemistry
SE-100 44 Stockholm, Sweden

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Avhandlingen försvaras på engelska.

*"Dear little neutronian who lives on a nucleus in an atom of my knee,
if you do not stop jumping around, you are going to cause an atomic
blast and blow up the universe."*

Therese Hance Braithwaite

Abstract

Worldwide, nuclear power produces a large portion of the electricity that we consume every day. While nuclear energy comes with certain advantages, waste originating from its use is of particular concern. As of today, most countries are planning to store spent nuclear fuel in deep geological repositories to protect humans and the environment from this highly radiotoxic waste. Through a number of natural and engineered barriers, a repository is designed to remain intact and keep the radionuclides contained for millennia to come. To assess the safety of a repository, long-term predictions based on model systems are required. Given that one day the barriers of a repository fail, groundwater intrusion is inevitable. Once spent fuel is in contact with groundwater, the mobility of radionuclides in the environment is significantly enhanced. Spent nuclear fuel is a complex material which consists to around 95 % of UO_2 . The remainders are fission products and heavier actinides. In this thesis a bottom up approach is used to study dissolution of UO_2 based model systems with a particular focus on dissolution induced by H_2O_2 . H_2O_2 forms upon water radiolysis and can enhance UO_2 dissolution. The mechanism for H_2O_2 consumption on metals and metal oxides is therefore revisited. It was found that the mechanism for catalytic decomposition of H_2O_2 on Pd differs from that on metal oxides. In addition, coumarin was demonstrated to be an efficient scavenger for reaction intermediates i.e. $\text{HO}^\bullet$. To simulate long-term dissolution under repository conditions, UO_2 and Gd-doped UO_2 pellets were leached to reach high H_2O_2 exposures. Surface passivation reducing the dissolution of UO_2 pellets was found to be accompanied by the formation of an oxidized layer. Studtite, a uranyl peroxide mineral can passivate the UO_2 surface under certain conditions. Upon exposure to γ -radiation studtite was found to dissolve readily, inhibiting passivation of real spent fuel by this surface precipitate.

Sammanfattning

Globalt sett står kärnkraften för en stor del av vår dagliga elproduktion. Kärnkraften har stora fördelar men produktionen av radiotoxiskt avfall utgör ett stort problem. De flesta länder som använder kärnkraft idag planerar att förvara det använda kärnbränslet i geologiska djupförvar för att skydda människor och miljö från radioaktiva ämnen. I ett geologiskt djupförvar används ett antal skyddsbarriärer för att isolera det utbrända kärnbränslet från biosfären. För att göra en säkerhetsanalys för ett geologiskt djupförvar krävs modeller som beskriver tänkbara processer i systemet. Om samtliga skyddsbarriärer brister är intrång av grundvatten oundvikligt. När det utbrända kärnbränslet kommer i kontakt med grundvatten kan bränslet lösas upp vilket leder till att radioaktivitet sprids. Utbränt kärnbränsle är ett mycket komplext material som till 95 % består av UO_2 . Resten är fissionsprodukter och tyngre aktinider som bildas i kärnreaktorn. Vissa av fissionsprodukterna bildar metalliska partiklar i bränslet. I detta arbete har UO_2 använts som modellsystem för utbränt kärnbränsle. H_2O_2 som produceras under radiolys av vatten oxiderar UO_2 vilket leder till ökad löslighet av bränslet. Reaktionsmekanismen för reaktionen mellan H_2O_2 och metalloxider är därför av central betydelse i detta arbete. Även de reaktioner som kan ske på de metalliska partiklarna har studerats. Experimentella resultat visar att reaktionsmekanismen för katalytisk sönderdelning av H_2O_2 på Pd (som modell för de metalliska partiklarna) skiljer sig från mekanismen för katalytisk sönderdelning på metalloxider. Detta arbete har också visat att kumarin fungerar som radikalfångare för ytbunden $\text{HO}^\bullet$. Hydroxylradikaler är en viktig mellanprodukt vid den katalytiska sönderdelningen av H_2O_2 på metalloxider. För att simulera den långsiktiga lösligheten för utbränt kärnbränsle under slutförvarförhållanden genomfördes lakningstester på både UO_2 och Gd-dopade UO_2 kutsar med upprepade tillsatser av H_2O_2 . Detta säkerställer en hög exponeringsnivå för kutsarna. Som en konsekvens av den höga exponeringen kan man detektera en passivering av ytan. För UO_2 kutsar innefattar denna passivering bildandet av ett oxiderat skikt på kutsarnas ytor. Studtit, ett mineral bestående av uranylperoxid som bildas under vissa förhållanden, skulle kunna passivera ytan på liknande sätt. I samband med detta arbete har det visat sig att studtit är oväntat lösligt under påverkan av γ -strålning. Ingen passiverande effekt av studtit kan därför förväntas på ytan av verkligt använt kärnbränsle.

Zusammenfassung

Weltweit liefert Kernenergie einen großen Anteil der Elektrizität, die wir täglich nutzen. Neben einigen Vorteilen die die Nutzung von Kernenergie mit sich bringt, ist die Produktion von stark radiotoxischem Abfall ein großes Problem. Heutzutage planen die meisten Länder die Kernenergie nutzen, den generierten Abfall in geologischen Endlagern zu entsorgen. Durch natürliche sowie technische Barrieren ist ein Endlager darauf ausgelegt über Jahrtausende hinweg intakt zu bleiben, um die Migration von Radionukliden in die Umwelt zu verhindern. Zur Abschätzung der Sicherheit eines Endlagers sind daher langfristige Vorhersagen auf der Basis von Modellsystemen unabdingbar. Trotz aller Vorsichtsmaßnahmen ist der Eintritt von Grundwasser unausweichlich, sollten die Barrieren eines Endlagers versagen. Kommt der ausgebrannte Nuklearbrennstoff in Kontakt mit Grundwasser, ist die Mobilität der darin enthaltenen Radionuklide deutlich erhöht. Ausgebrannter Nuklearbrennstoff ist ein komplexes Material, das zu 95 % aus UO_2 besteht. Der Restbestand sind Spaltprodukte und schwerere Actinoide. In dieser Arbeit wurde ein Bottom-up-Ansatz genutzt, um die Löslichkeit von UO_2 Modellsystemen zu untersuchen. Besonderer Fokus liegt hierbei auf der Löslichkeit von UO_2 unter H_2O_2 Einwirkung. H_2O_2 entsteht bei der Radiolyse von Wasser und kann die Löslichkeit von UO_2 deutlich erhöhen. Der Reaktionsmechanismus für den Verbrauch von H_2O_2 an Metallen und Metalloxiden wird daher in dieser Arbeit erneut aufgegriffen. Die Laborergebnisse zeigen, dass sich der Reaktionsmechanismus für katalytische Zersetzung von H_2O_2 an Pd vom Mechanismus an Metalloxiden unterscheidet. Zusätzlich konnte gezeigt werden, dass Cumarin ein wirksamer Radikalfänger für oberflächengebundene $\text{HO}^\bullet$ ist. Hydroxylradikale sind ein wichtiges Zwischenprodukt bei der katalytischen Zersetzung von H_2O_2 an Metalloxiden. Um die langfristige Löslichkeit von Nuklearbrennstoffen unter Endlagerbedingungen zu simulieren, wurden Löslichkeitsversuche an UO_2 und Gd-dotierten UO_2 Pellets durchgeführt, bei denen durch wiederholte H_2O_2 Zugabe eine hohe H_2O_2 Exposition erreicht wurde. Hierdurch konnte eine Passivierung der Pelletoberflächen, die mit der Bildung einer oxidierten Schicht einhergeht, nachgewiesen werden. Neben der Passivierung durch eine derartige oxidierte Schicht an der Pelletoberfläche kann Studtit, ein Uranylperoxid Mineral, das unter bestimmten Bedingungen entsteht, die Oberfläche auf ähnliche Weise passivie-

ren. Im Rahmen dieser Arbeit wurde jedoch festgestellt, dass Studtit unter Einwirkung von γ -Strahlung leicht löslich ist, und damit keinen passivierenden Effekt auf die Oberfläche von echten ausgebrannten Kernbrennstoffen hat.

List of Articles

I. Confirming the Formation of Hydroxyl Radicals in the Catalytic Decomposition of H_2O_2 on Metal Oxides Using Coumarin as a Probe

A. C. Maier, E. Herceglijia Iglebaek and M. Jonsson
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II. Radiation Induced Dissolution of U_3Si_2 - A Potential Accident Tolerant Fuel

A. C. Maier, A. Benarosch, G. El Jamal and M. Jonsson
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III. High Surface Conversion UO_2 - Leaching Experiments as Model for Long-term Leaching of Spent Nuclear Fuel Under Deep Repository Conditions

A. C. Maier, P. Kegler, M. Klinkenberg, A. Baena, S. Finkeldei, F. Brandt and M. Jonsson
Scientific Reports Submitted Manuscript

IV. H_2O_2 Induced Dissolution of $(\text{U}_{1-x}\text{Gd}_x)\text{O}_2$ Pellets in Aqueous Solution – Impact of H_2 and Consecutive Exposures

A. C. Maier, A. Barreiro Fidalgo and M. Jonsson
Manuscript

V. Stability of Studtite in Aqueous Suspension - Impact of HCO_3^- and Ionizing Radiation on the Dynamics of Dissolution

J. Li, A. C. Maier and M. Jonsson
ACS Appl. Energy Mater. Submitted Manuscript

VI. Pd Catalyzed Surface Reactions of Importance in Radiation Induced Dissolution of Spent Nuclear Fuel Involving H_2

A. C. Maier and M. Jonsson
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Contribution to the Articles

- I. I helped designing the experiments and performed the experiments. I jointly analyzed the data together with my co-authors and wrote parts of the manuscript.
- II. I planned the experimental work and performed most of the experiments. I jointly analyzed the data together with my co-authors and wrote parts of the manuscript.
- III. I formulated the research problem together with my co-authors and designed the experiments accordingly. I participated in performing the experiments, jointly analyzed the data together with my co-authors and wrote major parts of the manuscript.
- IV. I planned and performed the majority of the experiments. I analyzed the data and wrote the manuscript.
- V. I participated in planning and performing the experiments. I participated in the analysis of the data and revised the manuscript.
- VI. I planned and performed the experiments. I jointly analyzed the data together with my co-author and wrote the manuscript.

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1 | Introduction

Today around 450 nuclear reactors are operated worldwide having a total capacity of just below 400 GWe (gigawatt electrical) and accounting for approximately 10% of the global electricity production [1]. The use of nuclear power, which comes with both great benefits as well as great risks, is subject of controversy. Whether or not one is for or against nuclear power, around 10500 metric tons of spent nuclear fuel are discarded from reactors every year (as of 2011), most of which is currently being stored in pools or dry-casks at reactor sites all over the world [2]. Spent nuclear fuel has been generated since the use of nuclear power was established and has to be taken care of, even if all nuclear power plants were shut down today.

Even though fissionable ^{233}U and ^{239}U can be used as fuel from breeding ^{232}Th and ^{238}U , ^{235}U is the most commonly exploited isotope in nuclear fuel. Fission of ^{235}U with thermal neutrons can be described by equation [1],

where ν denotes the number of neutrons that are released and which can initiate fission of another ^{235}U , triggering a chain reaction. If from each fission one of the ejected neutrons initiates further fission, the multiplication factor becomes 1 and the system is called critical. This state is maintained during reactor operation. In contrast, if less than one neutron per fission initiates another fission, the system is called sub-critical and the chain reaction will eventually be disrupted. In turn, when the multiplication factor is higher than 1, i.e. each of the ejected neutrons initiates more than one fission, the system becomes super-

critical [3].

Energy (ΔE) generated through reaction [1] is released to the surrounding moderator and converted into heat which in turn can be used to run turbines driving an electric generator [3].

When a heavy nucleus like ^{235}U undergoes fission, it disintegrates into two fragments which are most likely of different mass. Two maxima for the distribution of fission products exist at mass numbers 95 and 138 [3].

Due to an excess of neutrons the primary fission products are often unstable and decay to form stable daughter isotopes thereby emitting α , β and γ -radiation. In fact, the radioactivity of nuclear fuel increases by a factor of one million to 10^{17} Bq/t during in-reactor irradiation [4].

As most countries do not consider reprocessing of spent nuclear fuel due to the risk of proliferation of nuclear weapons and extra cost, it is considered as waste [5, 6].

In the UN global goals for a sustainable society target 12.4 addresses the responsible management of chemicals and waste [7]. It is stated that by 2020 “the environmentally sound management of chemicals and all wastes throughout their life cycle” should be achieved. Based on international frameworks, the release of chemicals and wastes to “air, water and soil” should be “significantly reduced” to minimize their negative “impact on human health and the environment”.

The International Atomic Energy Agency (IAEA) has classified radioactive wastes of different origins, in which spent nuclear fuel is categorized as high level waste (HLW) due to its high concentration of both, long and short lived radionuclides [8]. It therefore demands a high degree of containment and isolation from the accessible environment to ensure long term safety [8].

A prerequisite for radionuclide migration from a deep geological repository for spent nuclear fuel is dissolution of the fuel. The research on which this thesis is based is focused on improving the understanding of spent nuclear fuel dissolution under deep repository conditions. With respect to the UN goals for a sustainable society, the research presented in this thesis can contribute to achieve safe management of highly radiotoxic spent nuclear fuel and it can help to assess its impact on the environment.

2 | Scientific Background

2.1 Nuclear Fuel

Three isotopes of uranium occur naturally, ^{234}U , ^{235}U and ^{238}U . Out of all the uranium occurring in nature, 99.2742 % is ^{238}U whereas 0.7204 % is ^{235}U [9]. Since ^{234}U is even less abundant than ^{235}U , it is irrelevant for the production of nuclear fuel. The half lives of ^{235}U and ^{238}U are long, $t_{1/2} = 7.04 \times 10^8 \text{ y}$ and $t_{1/2} = 4.468 \times 10^9 \text{ y}$, respectively [9], which results in overall low radioactivity of uranium ores and fuel before it is being used in a nuclear reactor.

Based on the design of a nuclear reactor, different quantities of fissionable ^{235}U are required within the fuel. While CANDU (Canada Deuterium Uranium) reactors make use of natural uranium, the most common grade of enrichment for light water reactors is around 3 % to 5 %. Less common highly enriched fuel contains 20 % or more ^{235}U , whereas weapon grade uranium contains at least 85 % [4].

Mining of uranium usually depends on the nature of the ore deposit. However, almost 50 % of the worlds uranium is mined by in-situ leaching, where reactive solutions are directly injected into the ore body dissolving uranium. Through discharge drill holes the dissolved uranium is pumped back to the surface where it is purified and re-precipitated as so called "yellow cake" for further processing [10–12]. Other prominent methods to extract uranium from a deposit are traditional underground (approx. 32 %) and open pit mining (approx. 14 %) [10].

For the enrichment process, U is converted into a gas, commonly UF_6 . ^{235}U is then concentrated e.g. through selective gas diffusion or by centrifugation, due to its slightly lower mass as compared to ^{238}U [13]. The enriched uranium is further processed to get the desired nuclear fuel.

Currently, there are two kinds of fuel cycles, "once-through" and "closed" [14]. The once-through cycle implies, that nuclear fuel is only used once in a reactor. After irradiation it is considered waste which requires storage until the level of radioactivity emitted from the spent nuclear fuel reaches the natural background level. During the closed cycle, spent nuclear fuel is reprocessed to recover fissionable ^{235}U and ^{239}Pu which can be re-fabricated into new fuel. As not all of the spent fuel can be reprocessed, high level waste is still being produced, however at a smaller volume as compared to a "once-through" cycle [14].

2.1.1 Standard UO_2 Fuel

After being treated in an enrichment facility, uranium is converted into UO_2 powder, pressed into green pellets and sintered to ceramic UO_2 pellets. Although many factors influence the sintering behavior of UO_2 and the process can be modified depending on the fuel requirements, conventional sintering is usually carried out in a reducing atmosphere (containing H_2) at around 1700°C [15]. The sintered fuel pellets are stacked on top of each other and enclosed within the cladding to make a fuel rod. A number of fuel rods are finally brought together in a fuel assembly.

The use of fuel cladding is crucial to keep fission products contained and to avoid contamination of the moderator. Due to harsh conditions during in-reactor irradiation, there is a high demand on the cladding material when it comes to the neutron absorption cross section, thermal expansion and thermal conductivity, radiation resistance, thermal as well as mechanical stability [16]. Pressurized as well as boiling water reactors usually use a zirconium alloy cladding. It is therefore the most common cladding material used today [16]. The detailed corrosion mechanisms for zirconium alloy cladding is complicated, its final corrosion product is however ZrO_2 [17].

When UO_2 is used in a nuclear reactor its reactivity changes with burn-up. This change in reactivity is mainly attributed to the depletion of ^{235}U which leads to an overall decrease in reactivity of the fuel with time [18]. To improve the performance of a nuclear reactor and minimize the fuel cost as well as the amount of generated waste, enhance-

ment of the fuel cycle length is necessary [19]. Due to the decreasing reactivity with burnup, a higher fuel load than necessary to maintain criticality is usually introduced into the reactor during re-fueling. The excess energy at the beginning of the cycle is compensated for by introducing burnable absorbers [19, 20]. Burnable absorbers have a high neutron cross section and are ideally consumed and transferred into a state of low neutron cross section, at the same rate as the fuel is depleted in ^{235}U . Among others, materials based on gadolinium, boron and erbium are good candidates for burnable absorbers. However, Gd is most commonly used, where the isotopes ^{155}Gd and ^{157}Gd are converted into ^{156}Gd and ^{158}Gd during in-reactor irradiation [19]. Other dopants such as Cr and Al have as well been introduced into the UO_2 matrix to improve the fuel performance [21], but their use and influence is beyond the scope of this thesis.

2.1.2 Crystallographic Information of UO_2

Stoichiometric UO_2 crystallizes in the fluoride structure where each uranium atom is coordinated to eight oxygen atoms. UO_2 has the ability to accommodate various amounts of interstitial oxygen forming hyperstoichiometric UO_{2+x} . Several intermediate structures have been discovered upon the oxidation of UO_2 into the thermodynamically more stable oxide U_3O_8 . The most important intermediate structures are listed in table 1 [22, 23].

Table 1: Structural transformation during the oxidation of UO_2 to U_3O_8 .

O / U crystal system		
<hr/>		
UO_2	2.00	cubic
U_4O_9	2.25	cubic with ordered superstructure
U_3O_7	2.33	tetragonal
U_3O_8	2.66	orthorhombic

The accommodation of interstitial oxygen leads to an increase in the lattice parameter before it results in a change to the cationic sublattice.

Compared to stoichiometric UO_2 , the density of U_3O_8 is 23 % lower [22].

When substituting U in UO_2 upon doping with trivalent lanthanides such as Gd, the crystal lattice contracts (lanthanum being an exception) [24–27]. In the case of Gd-doping, the ionic radii of U^{4+} and Gd^{3+} are fairly similar. The lattice contraction as a result of Gd-doping can be explained through a charge compensation mechanism. When substituting one U^{4+} with one Gd^{3+} , another U^{4+} has to be oxidized to U^{5+} for charge balancing reasons. Since the ionic radius of U^{5+} is smaller compared to U^{4+} the crystal lattice contracts. The charge can also be balanced when two Gd^{3+} replace two U^{4+} leading to the formation of one oxygen vacancy which also causes lattice contraction. Both approaches are considered and debated upon in literature [26, 28–31]. For hyperstoichiometric Gd-doped UO_2 the lattice contraction was found to be stronger than for stoichiometric samples [32].

2.1.3 Accident Tolerant Fuel

Following the severe Fukushima Daiichi accident in 2011, which had a worldwide environmental, political and economic impact, an increasing demand for accident tolerant fuel-clad alternatives emerged [33]. Compared to the standard UO_2 fuel in combination with Zr-based alloy cladding, accident tolerant fuels are desired to have the following properties:

- high thermal conductivity to reduce the thermal energy of the fuel pin
- high heat capacity to reduce the temperature increase as a result of decay heat
- reduced cladding oxidation rate to minimize its degradation and H_2 built-up
- higher resistance to cladding creep to delay bursting of fuel rods

all of which reduce accident progression in a scenario where cooling is lost [34]. In addition to these desired properties which increase the plants safety, the new fuel-clad system must be qualified to be used in existing reactors, where the impact on reactor operation as well as the existing nuclear fuel cycle is minor [35, 36]. Among other materials

U_3Si_2 is currently being discussed as an accident tolerant fuel which could potentially replace UO_2 [37]. U_3Si_2 has several advantages over UO_2 . Despite its lower melting point, U_2Si_2 has a significantly higher thermal conductivity compared to UO_2 [38]. This makes U_3Si_2 an attractive alternative to UO_2 . In addition, due to its higher density, U_3Si_2 comprises a 17 % higher uranium load than standard fuel. This can either allow the possible use of a more corrosion resistant cladding which usually comes with a neutron penalty or it can result in extended fuel cycle lengths or a lower enrichment. Either of the options is beneficial from a safety, as well as an economical perspective [38].

No matter what kind of fuel is used in a nuclear reactor, after it is being discharged it is highly radioactive and has to be placed in interim storage for cooling. Out of the total amount of spent nuclear fuel produced annually, less than 20 % is sent for reprocessing (as of 2011), the rest is being considered for long-term storage [2].

2.1.4 Spent Nuclear Fuel

When spent fuel is discarded from the reactor core, it still consists of approximately 95 % UO_2 , the remainder being fission and activation products as well as transuranium elements [4]. These elements can be classified into four groups based on their appearance in the spent fuel [39]:

- fission gases and volatile fission products like Kr, Xe, Br and I
- fission products which form metallic precipitates and are typically less than 1 μm in diameter, so called ϵ -particles; Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb and Te
- fission products which precipitate as oxides such as Rb, Cs, Ba, Zr, Nb, Mo and Te
- fission products which form oxide solid solutions with the fuel matrix such as Sr, Zr, Nb and the rare earth elements (Y, La, Ce, Pr, Nd, Pm and Sm)

Gaseous fission products usually accumulate along grain boundaries, in cracks, pores or the gap between the fuel and the cladding. Non-gaseous elements either form solid solutions with UO_2 or form metallic precipitates such as ϵ -particles which are often found along grain

boundaries [39, 40]. Continuous transitions between the metallic and oxide precipitates as well as between oxide precipitates and the elements forming solid solutions exist. These transitions depend on the oxygen potential and the burn-up of a fuel pin [39].

Due to a thermal gradient from the center of a pellet to its rim, fission products are not homogeneously distributed throughout the pellet [41]. In addition, fracturing, grain coarsening in the center of the pellet, and a burn-up gradient through the pellet are also the results of the thermal stress. The burn-up increases from the center towards the edge of a pellet which results in a high ^{239}Pu content as well as subdivision of grains and an increase in porosity at the edges of the pellets [42].

The high initial radioactivity of spent nuclear fuel as well as the decay heat originate mostly from the short lived fission products. In general, a radionuclide can emit α -, β - or γ -radiation. The radioactivity of the spent fuel will decrease over time and the relative percentage of emitted radiation changes from predominantly β -radiation for fresh spent fuel to predominantly α -radiation when the fuel ages [43, 44]. α -radiation can be described through the ejection of a He nucleus from the nucleus of the radionuclide. Equation 2 is an example for ^{235}U decaying through the emission of an α -particle [45].

In comparison, β -radiation can be described through the emission of an electron (β^- , equation 3) or a positron (β^+ , equation 4) and occurs when a neutron is transferred into a proton or vice versa [45].

A γ -decay usually follows an α - or β -decay and can be described as the emission of a photon when an excited nucleus relaxes (equation 5) [45].

While γ -radiation penetrates easily through matter, β and especially α -radiation deposit their energy within a short range. The type of shielding which has to be chosen to be protected from a radiation source, therefore strongly depends on the type of emitted radiation. Since spent nuclear fuel contains several long lived isotopes, safe storage and efficient shielding for long time spans is necessary to protect humans and the environment.

2.2 Nuclear Waste Disposal

The risk associated with the disposal of spent nuclear fuel is often described by two terms, hazard as well as accessibility [46]. While the radiotoxicity i.e. the hazard to humans and the environment originating from spent nuclear fuel is high for long time spans, its accessibility can be influenced by safety measures. Several alternative disposal options have been suggested in the past, most of which imply limited accessibility to the spent nuclear fuel [47–49]:

- disposal in outer space
- long term above ground storage
- disposal in wells
- sea disposal
- seabed or subduction zone disposal
- deep underground rock melting
- disposal in ice sheets

Nuclear transmutation has also been considered prior to the final disposal of spent fuel to reduce its long-term radiotoxicity [50]. Currently all of the above mentioned alternatives have either not been implemented (in any country) because of increased risks or they have been abandoned as they are internationally not permitted any longer [51].

Today, most countries consider deep geological repositories in various host rocks (e.g. salt, crystalline bedrock, shale and clay, tuff or basalt [47]) as the best option to dispose spent nuclear fuel [52].

2.3 Safety Requirements for Deep Geological Repositories for Spent Nuclear Fuel and Natural Analogues

Disposal of spent nuclear fuel is a unique challenge for humanity and implies its final emplacement in a deep geological repository without the intention of retrieval after closure [53]. The aims for any disposal site which will receive radioactive waste were summarized in the IAEA safety standards [53] and include:

- "contain the waste"
- "isolate the waste from the accessible biosphere and to reduce substantially the likelihood of, and all possible consequences of, inadvertent human intrusion into the waste"
- "inhibit, reduce and delay the migration of radionuclides at any time from the waste to the accessible biosphere"
- "ensure that the amounts of radionuclides reaching the accessible biosphere due to any migration from the disposal facility are such that possible radiological consequences are acceptably low at all times"

To assess the safety of a deep repository, long term predictions on its evolution become necessary. Such predictions on the site evolution include geologic disturbances such as climate change, changes in groundwater chemistry, etc. Thus, the uncertainty of future events also calls for safety assessments of several alternative futures [49]. Long-term predictions on radionuclide release into the environment are usually based on experiments and modeling [54]. However, leaching experiments on laboratory scale are usually set up for several months or years. These time spans are extremely short compared to the lifetime expected for a deep repository. In addition, neither the dimensions

nor the inhomogeneity of the geological environment can be reconstructed in a laboratory approach [49]. In attempts to circumvent this problem, relevant natural analogues such as uranium ore bodies or archaeological systems have been studied to overcome the inaccessibility of certain features in laboratory experiments and to estimate the usefulness of predictive modeling [49, 54]. Nonetheless, even if short term, experimental approaches on the leaching behavior of both, simple model systems as well as on real spent fuel are extremely important to understand the kinetics and reaction mechanisms involved in spent fuel dissolution.

2.4 The KBS-3 Concept

Today, around 6700 t of spent nuclear fuel are stored in interim storage in Sweden [55]. After interim storage, Sweden is planning to dispose its spent nuclear fuel in a deep geological repository. The Swedish Nuclear Fuel and Waste Management Company (Svensk Kärnbränslehantering, SKB) has developed the KBS-3 multi-barrier model according to which the fuel will be stored 400 m to 700 m underground in granitic bed rock [56]. Both natural and engineered barriers are employed to keep radionuclides contained for a long time.

Figure 1 shows the principle design of the repository and how the barriers i.e. the canister, the clay buffer and the host rock are implemented to prevent migration of radionuclides into the environment.

The innermost barrier of the repository is the copper canister. It consists of a 5 cm thick copper wall to prevent corrosion and a cast iron insert which contains the fuel and provides mechanical strength. The canisters are designed to withstand geological events like earthquakes which could create a shear stress or ice ages which could result in a constant high pressure regime [56, 58]. Each canister will be placed in a vertical hole surrounded by the bentonite clay buffer.

Bentonite contains a high percentage of montmorillonite which has a high capacity to absorb (ground-)water. The absorption of water enables swelling which will induce pressure and eventually seal all gaps. In comparison to the granitic host rock, clay reacts ductile to shear stress. Both, the increase in pressure due to swelling as well as the ductile response to shear stress, keep the canister in place and protect it from minor rock movements. Once saturated with water, clays

Figure 1: The Swedish KBS-3 repository concept. Reprinted with permission of SKB AB [57].

are very impermeable making diffusion of radionuclides the predominant type of transportation through the buffer [56, 58]. In addition, clays have a high sorption capacity for cations. As most radionuclides are present as cations when being dissolved, the clay buffer increases their retention [59].

The outermost barrier of the repository is the granitic bedrock. The Forsmark site, where the Swedish repository is planned to be, is located in a tectonic lens within the Fennoscandian Shield. Tectonic lenses are regions which are only weakly affected by geological events. Therefore, they are less fractured leading to a lower permeability as compared to the surrounding rock [60].

2.5 Dissolution of Spent Nuclear Fuel

Spent nuclear fuel will eventually be in contact with groundwater when all barriers of a repository fail. The radionuclide release upon barrier failure can roughly be divided into three stages [61, 62]. During the first stage, the instant release fraction is released. It is the fraction of the nuclide inventory which will readily dissolve in groundwater. It contains those elements which are volatile and accumulate in the fuel / clad gap as well as in cracks.

During the second stage, nuclide release from segregated material in

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the grain boundaries occurs. This stage is more gradual and can be difficult to distinguish from the third stage [61].

The third and last stage corresponds to long term dissolution, where the release of radionuclides will be governed by the dissolution of the UO_2 matrix [61, 62]. It is expected, that the release of radionuclides into the environment mainly depends on the rate of UO_2 matrix dissolution [63].

In a deep repository, groundwater conditions are expected to be chemically reducing [64] under which UO_2 has a very low solubility [65]. However, due to the inherent radioactivity of the spent nuclear fuel, water radiolysis in close proximity to the fuel can alter this condition. When ionizing radiation is absorbed by water, i.e the energy of the radiation is deposited in water, water molecules can either be ionized or excited, depending on the energy of the radiation (physical stage figure 2). The absorbed energy per mass unit of an absorber is called the absorbed dose. It is measured in Grays, where 1 Gy is 1 J kg^{-1} . In turn, the dose rate is the absorbed dose per time unit (Gy s^{-1}).

Figure 2: Reactions and time line during the radiolysis of water. Readapted after [66, 67].

After the initial event, a number of reactions between H_2O , H_2O^* , H_2O^+ , e^- and their reaction intermediates occur (physico-chemical and chemical stage figure 2). The final products resulting from these reactions are both oxidants (HO^* , HO_2^* , H_2O_2) as well as reductants (H^* , H_2 , e^-_{aq}). At around 10^{-6} s the system can be considered to be homogeneous [66, 67].

The radiation chemical yield of radiolysis products is referred to as the G-value. It depends on the incoming radiation as well as on the absorber and describes the amount of product produced per energy unit of absorbed dose. Table 2 shows the G-values for both, γ and fast electrons as well as for α -particles in neutral water.

Table 2: Radiation chemical yields ($\mu\text{mol J}^{-1}$) in irradiated neutral water [3].

	$\text{G}(\text{H}_2)$	$\text{G}(\text{H}_2\text{O}_2)$	$\text{G}(\text{e}_{\text{aq}}^-)$	$\text{G}(\text{H}^*)$	$\text{G}(\text{HO}^*)$	$\text{G}(\text{HO}_2^*)$
γ and fast e^-	0.047	0.073	0.28	0.062	0.28	0.0027
12 MeV α	0.115	0.112	0.0044	0.028	0.056	0.007

Among the radiolysis products of water, H_2O_2 has been shown to be the species which is mainly responsible for oxidative dissolution of UO_2 [68]. When U(IV) is oxidized to U(VI) , its solubility and therefore its mobility in the environment increases significantly [69]. The reaction mechanism for oxidation and dissolution of UO_2 by H_2O_2 can be described by reactions 6 and 7 [70].

In contrast, when H_2O_2 is catalytically decomposed on metal oxides, the reaction mechanism can be described by reactions [8], [9] and [10] [71].

The homolytic cleavage of H_2O_2 into two surface bound hydroxyl radicals (reaction [8]) is the prerequisite for this reaction to be spontaneous at room temperature. When H_2O_2 is catalytically decomposed on metal oxides where the metal cation is in its highest oxidation state, further oxidation becomes impossible. In comparison, when H_2O_2 reacts on the surface of UO_2 both, catalytic decomposition as well as uranium oxidation become competing reactions. To quantify the fraction of H_2O_2 consumed during the oxidation of uranium, the dissolution yield has been introduced (equation [11] [72]).

$$\text{Dissolution Yield in \%} = \frac{\Delta[\text{U(VI)}]_{\text{dissolved}}}{\Delta[\text{H}_2\text{O}_2]_{\text{consumed}}} \quad (11)$$

The ratio of uranium being dissolved from the UO_2 surface and H_2O_2 being consumed at the same solid surface makes the yield a surface area independent entity. It can therefore be used to compare experiments where different surface areas over solution volume ratios were used.

2.5.1 The Role of Bicarbonate

Bicarbonate is a very common groundwater constituent and present in various amounts at sites where deep repositories are planned to be built [73]. The presence of HCO_3^- enhances UO_2 dissolution by forming soluble complexes with U(VI) [65]. It was previously shown, that the second order rate constant for UO_2 dissolution, when H_2O_2 was

used as oxidant, becomes independent of the HCO_3^- concentration at HCO_3^- concentrations above 1 mM [74]. This implies that dissolution is the rate limiting step for the reaction between H_2O_2 and UO_2 at HCO_3^- concentrations below 1 mM. At higher HCO_3^- concentrations the rate limiting step is oxidation.

A deficiency of HCO_3^- in groundwaters favors the formation of secondary phases such as studtite, a uranyl peroxide mineral with the chemical formula $\text{UO}_4 \cdot 4\text{H}_2\text{O}$. It has previously been shown, that studtite is the thermodynamically dominant species compared to uranyl oxide hydrates and uranyl silicates in the presence of H_2O_2 [75]. Studtite or its dehydration product metastudtite are the only known peroxide minerals and were first named by J. F. Vaes in 1947 [76, 77].

In HCO_3^- deficient systems studtite was found to precipitate in the presence of UO_2^{2+} and H_2O_2 [78, 79] according to reaction [12] [80].

Studtite was also found to be an alteration product of UO_2 (either irradiated [80, 81] or by H_2O_2 additions [81–83]) as well as on spent nuclear fuel [84, 85] and fuel "lavas" which have been studied after the Chernobyl accident [86].

Since uranium in studtite is present as U(VI), studtite is expected to be insensitive to oxidative dissolution as compared to UO_2 . If studtite forms on the UO_2 surface, where U(VI) can react with H_2O_2 , it might alter the conditions for oxidative dissolution by blocking the UO_2 surface [80].

2.5.2 The H_2 Effect

In a deep geological repository for spent nuclear fuel, H_2 will be produced through water radiolysis as well as through anaerobic corrosion of the cast iron canister [87]. H_2 production through canister corrosion can be described by reactions [13] and [14] [88].

The rate of H_2 production from canister corrosion was roughly estimated to be in the order of $0.4 \text{ mol year}^{-1} \text{ m}^{-2}$, resulting in a H_2 pressure in the order of MPa for a repository having an engineered clay barrier [89]. A total H_2 pressure of around 50 bar was also assumed in reference [90] which results in approx. 38 mM dissolved H_2 at room temperature based on Henry's law.

In literature the H_2 -effect often refers to the inhibition of UO_2 dissolution by H_2 in the presence of ϵ -particles. The inhibiting effect of H_2 , on the dissolution rate of Pd doped UO_2 pellets (to mimic the presence of ϵ -particles) was experimentally studied [91]. In principle, H_2 reduces the rate of UO_2 dissolution through two possible pathways: the solid phase reduction of oxidized U(VI) to U(IV) [92] and by eliminating radiolytic oxidants [93]. The solid phase reduction of U(VI) by H_2 was found to be more efficient than the elimination of radiolytic oxidants and may account for complete inhibition of fuel dissolution even at low H_2 pressures [94].

Figure 3: Scheme of relevant reactions at the interface between the spent fuel surface and groundwater. Reproduced with permission from © Wiley-VHC Verlag GmbH & Co. KGaA.

Even in the absence of ϵ -particles several authors have reported a similar H_2 effect when UO_2 was doped with ^{233}U , ^{238}Pu , ^{239}Pu or Gd [95–97]. In those studies the UO_2 surface was assumed to catalyze the reduction of uranium. However, in experiments performed on un-

doped UO_2 , there was no indication of UO_2^{2+} reduction [98].

Figure 3 summarizes the most important reactions on the spent fuel surface under deep repository conditions. It includes catalytic decomposition of H_2O_2 and U(IV) oxidation by H_2O_2 (orange box), the ϵ -particle catalyzed solid phase reduction of U(VI) (reaction A), U(VI) dissolution (reaction B) which can be facilitated by the presence of HCO_3^- , as well as the most important ϵ -particle catalyzed reactions between H_2O_2 , H_2 , $\text{UO}_2^{2+}(\text{aq})$ and O_2 (blue box).

3 | Aims and Scope

This thesis is based on experimental studies addressing the oxidative dissolution of spent nuclear fuel under deep repository conditions using model substances to mimic real spent fuel. It mainly focuses on interfacial reactions which become relevant, when the spent nuclear fuel is in contact with groundwater. Additionally, important reaction mechanisms are discussed.

Since different sub-topics within the generic term of spent fuel dissolution are addressed, this thesis is divided into five sections:

- 1) The reaction mechanism for catalytic decomposition of H_2O_2 on metal oxide surfaces is revisited. The formation of surface bound hydroxyl radicals is investigated using coumarin as a probe and a comparison to $\text{HO}^\bullet$ radical scavenging by tris is made.
- 2) Radiation induced dissolution of the accident tolerant fuel candidate U_3Si_2 is studied and compared to UO_2 .
- 3) The effect of high H_2O_2 exposures on UO_2 pellets is studied, simulating the long term leaching behavior of spent nuclear fuel. Based on the results of high H_2O_2 exposures on undoped UO_2 , the effect of H_2 and consecutive exposures on Gd-doped UO_2 is also investigated.
- 4) The stability of the secondary mineral studtite is investigated under conditions relevant for a deep geological repository focusing on the impact of HCO_3^- and ionizing radiation.
- 5) ϵ -particle catalyzed reactions of H_2O_2 , O_2 and UO_2^{2+} with H_2 in aqueous suspensions containing Pd are studied, aiming to explore the H_2 pressure dependent regime.

Based on the results presented in 1 - 5 (section 5.1 to section 5.5), the implications for a deep geological repository are discussed in section 5.6, followed by a summary and final concluding remarks.

4 | Materials and Methods

Throughout all experiments Milli-Q was used (18.2 M Ω .cm) and all chemicals were of reagent grade or higher unless otherwise stated.

4.1 Solid Materials

4.1.1 Undoped UO₂ Pellets

Precursor powders for UO₂ pellets were produced by co-precipitation. After precipitating, washing and drying the powders, they were calcined for 5 h at 600 °C in air. Under these conditions the powder is oxidized to U₃O₈. A reduction step at the same temperature was carried out during 5 h in 4 % H₂ in Ar atmosphere, where U₃O₈ is reduced to stoichiometric UO₂. The obtained powders were then pressed and sintered for 10 h to stoichiometric UO₂ at 1700 °C in 4 % H₂ in Ar atmosphere according to [99]. Total densities ranging from approx. 92 % to 96 % were achieved. Polishing of the pellets was done in several steps. For the last step a 0.4 μ m colloidal SiO₂ paste was used. The pellets were then thermally etched for 3 h in 4 % H₂ in Ar atmosphere. The UO₂ pellets were prepared by the staff at Forschungszentrum Jülich in order to be able to use them for the joint research project.

4.1.2 Gd-doped UO₂ Pellets

Commercial Gd-doped UO₂ pellets were supplied from Westinghouse Electric Sweden AB. The pellets were doped with 3 %, 4.5 % and 8 % Gd respectively. A detailed characterization can be found in [100].

4.1.3 Powders

Powders used in suspensions during the experiments are listed in table 3. Specifications for each powder are also given. The stoichiometry of the UO_2 powder was determined by measuring the weight gain through oxidation to U_3O_8 . Conversion into U_3O_8 was confirmed by x-ray diffractometry (XRD). Oxidation was carried out in air at 400 °C for 16 h. Based on this method, the stoichiometry of the UO_2 powder was found to be $\text{UO}_{2.3}$. The powder will hereafter be referred to as UO_2 .

Table 3: Powders used during the experiments.

Powder	Specific Surface Area / m^2g^{-1}	Particle Size / μm	Supplier
ZrO_2 (Paper I)	n.d.	5	Aldrich
U_3Si_2	0.47 ± 0.04	n.d.	In house by arc melting from native Si and U in stoichiometric ratios
UO_2	4.6 ± 0.2	avg. 16	Westinghouse Electric Sweden AB
Pd	1.35 calc.	1.1 ± 0.6	Alfa Aesar
ZrO_2 (Paper V)	6.44 ± 0.05	5	Aldrich
Studtite	n.d.	n.d.	In house through precipitation from dissolved $\text{UO}_2(\text{NO}_3)_2$ in excess H_2O_2

4.2 Instrumentation

4.2.1 Brunauer-Emmett-Teller (BET) Surface Area Analysis

The specific surface areas of the powders used during the experiments (see table 3) were determined through isothermal adsorption and desorption of 30 % He in N₂ on a Micrometrics Flowsorb II 2300 BET device.

4.2.2 X-Ray Diffractometry (XRD)

XRD measurements for papers 2 (section 5.2) and 5 (section 5.4) were carried out on a PANalytical XPert Pro diffractometer using CuK α -radiation (1.5418 Å) a 45 kV voltage, a 30 mA current and Bragg-Brentano geometry. The measurements were carried out at room temperature in air.

Diffractograms in paper 3 (subsection 5.3.2) were recorded on a Bruker D4 Endeavour instrument using CuK α -radiation and Bragg-Brentano geometry. The voltage was set to 40 kV and the current to 40 mA.

4.2.3 Raman Spectroscopy

Raman spectra shown in paper 3 (subsection 5.3.2) were recorded on a Horiba LabRAM HR spectrometer equipped with a Peltier cooled multichannel CCD detector and an objective lens with 50 x magnification. For the measurements a He-Ne laser (λ = 632.8 nm) was used at a power of 17 mW. The spectrometer has a focal length of 800 mm and the spectral resolution was approximately 1 cm⁻¹.

4.2.4 Scanning Electron Microscopy (SEM)

SEM images for paper 6 (section 5.5) were recorded on a Philips FEI XL 30 in low vacuum mode using a secondary electron detector. The microstructures of pellets in paper 3 (subsection 5.3.2) were analyzed using a Thermo Fisher FEI Quanta 200 FEG SEM. Images were recorded in high vacuum mode using both secondary and back-scattered electron detectors.

4.2.5 Inductively coupled plasma - optical emission spectrometry (ICP-OES)

ICP-OES measurements for papers 2 (section 5.2) and 6 (section 5.5) were performed on a Thermo Fisher iCAP 6000 Series instrument. Si in section 5.2 was measured at 198.8 nm, 250.6 nm and 251.6 nm. Pd in section 5.5 was measured at 324.2 nm, 340.4 nm and 360.9 nm. For data analysis an average out of the three individual measurements was used. A calibration in the concentration range of the samples was made before each measurement for both elements using a single element standard. The resulting fit followed the curvilinear regression as described by equation 15.

$$f(x) = A_0 + A_1x + A_2x^2 \quad (15)$$

4.2.6 Gamma Source

For γ -irradiation experiments in paper 2 (section 5.2) and paper 5 (section 5.4), a MDS Nordion 1000 Elite γ -cell was used. The γ -source is ^{137}Cs which has a half life of 30.08 years [9]. ^{137}Cs β -decays to $^{137\text{m}}\text{Ba}$ which in turn has a half life of only 2.552 min and decays through isomeric transition which involves the emission of γ -rays to stable ^{137}Ba according to equation 16 [9].

The dose rate for the sample position used in all the experiments was determined to be 0.11 Gy s^{-1} by Fricke dosimetry [3].

4.2.7 Autoclave

Experiments at high pressures (paper 4, subsection 5.3.3 and paper 6, section 5.5) were carried out in a steel autoclave. A schematic illustration is shown in figure 4. The inner volume of the autoclave where the sample is placed, is made from polyether ether ketone (PEEK) and has a volume of 2 l. The gas inlet can be used to pressurize with the desired gas. The outlet for liquid sampling is also made from PEEK. This material can be considered inert. When powders are used in the

autoclave a paddle stirrer can be used to avoid sedimentation. When pellet experiments are carried out, the stirrer can be completely removed. Due to the pressure in the autoclave, liquid aliquots can be released from the reaction vessel without opening the autoclave.

Figure 4: Schematic illustration of the autoclave setup.

4.3 Methodology

Concentrations of H_2O_2 , U(VI) , $\text{HO}^\bullet$ and 7-hydroxycoumarin were determined spectrophotometrically. The individual methods are described in the following sections.

4.3.1 Ghormley Triiodide Method

H_2O_2 concentrations were measured indirectly using the Ghormley triiodide method [101–103] where I^- is oxidized to I_3^- by H_2O_2 according to reactions 17 and 18.

For the measurement, aqueous samples containing H_2O_2 are taken from the reaction vessel and filtered through $0.2\,\mu\text{m}$ cellulose acetate

syringe filters (when applicable) to separate the liquid phase from the powder. Filtering is not necessary in pellet experiments. 100 μ l 1 M KI are then mixed with 100 μ l 1 M sodium acetate / acetic acid buffer containing ammonium molybdate as a catalyst and 1.8 ml of diluted sample.

I_3^- absorbs light at $\lambda = 350$ nm. U(VI) in solution absorbs light at slightly shorter wavelengths compared to I_3^- . In samples where concentrations of both, H_2O_2 and U(VI) were measured, triiodide was measured at $\lambda = 360$ nm instead of $\lambda = 350$ nm to avoid an overlap. A calibration for both wavelengths has been made prior to the measurements.

4.3.2 Hantzsch Method

The concentration of hydroxyl-radicals formed during catalytic decomposition of H_2O_2 was also measured indirectly by using the modified Hantzsch method [104]. Tris(hydroxymethyl)-aminomethane (tris) was used as buffer at pH = 7.5 and as a radical scavenger. In the reaction between tris and hydrogen abstracting radicals, formaldehyde forms according to reaction [19].

For the measurements, aliquots are taken from aqueous powder suspensions containing H_2O_2 , tris and a metal or metal oxide powder and filtered through 0.2 μ m cellulose acetate syringe filters to separate the powder from the solution. 1.5 ml of the filtered solution containing formaldehyde (see reaction [19]) is then mixed with 1 ml 0.2 M acetoacetic anilide and 2.5 ml ammonium acetate. Afterwards the mixture is left to react for 15 min at 40 $^\circ$ C. Formaldehyde from the sample reacts with the two reagents according to equation [20], forming a pyridyl derivative

which can be measured at $\lambda = 368$ nm.

ammonia
(ammonium acetate) acetoacetanilide

(20)

pyridyl derivative

The relative yield of formaldehyde from the reaction between $\text{HO}^\bullet$ and tris has been determined to be 35% from radiation chemical experiments [105]. In experiments where $\text{HO}^\bullet$ is formed during catalytic decomposition of H_2O_2 , the overall yield of formaldehyde was found to depend on the surface coverage of both, tris as well as H_2O_2 . The surface coverage in turn depends on the initial concentration of the reagents and their relative affinity towards the surface [106]. The reactions between both, tris and $\text{HO}^\bullet$ (reaction [19]), as well as between H_2O_2 and $\text{HO}^\bullet$ (reaction [9]), are competing reactions. However, if the scavenger concentration i.e. the concentration of tris is high, O_2 formation through reaction [10] becomes negligible [107]. Instead, the probe scavenges $\text{HO}^\bullet$ formed upon cleavage of H_2O_2 on the surface of the powder (reaction [8]).

4.3.3 Hydroxyl Radical Scavenging using Coumarin as a Probe

Instead of tris, coumarin can also be used to scavenge $\text{HO}^\bullet$ according to reaction [21](#).

One of the reaction products, 7-hydroxycoumarin is strongly fluorescent. It can therefore be quantified directly. 7-hydroxycoumarin is a unique product which can only be formed upon the reaction between coumarin and $\text{HO}^\bullet$. In contrast, tris is susceptible to react with any hydrogen abstracting radicals to produce formaldehyde.

However, the same reaction which produces 7-hydroxycoumarin can also produce other products. The relative yield of 7-hydroxycoumarin was quantified from radiation chemical experiments [\[108\]](#) and is 5.7 %.

In comparison to 7-hydroxycoumarin, the other hydroxylated coumarin species are only weakly fluorescent [\[108\]](#). Inferences are therefore negligible during the fluorescence measurements of 7-hydroxycoumarin. However, coumarin itself is poorly fluorescent [\[108\]](#) and due to an inner filtering effect i.e. high absorption of the excitation light by coumarin, the signal of 7-hydroxycoumarin is reduced by the presence of coumarin especially at high probe concentrations [\[109\]](#). The calibration for 7-hydroxycoumarin was therefore made in the presence of 0.05 mM coumarin. The same coumarin concentration was used during the experiments. For the measurements, the excitation wavelength was set to $\lambda = 326 \text{ nm}$. The resulting emission maximum was measured at $\lambda = 456 \text{ nm}$.

4.3.4 Arsenazo III Method

The concentrations of U(VI) in solution were measured by using the Arsenazo III method [110]. A 1.5 ml filtered aliquot sample containing U(VI) is mixed with 40 μl 0.16 wt-% vol^{-1} arsenazo III reagent (1,8-dihydroxynaphthalene-3,6-disulphonicacid-2,7-bis[(azo-2)-phenylarsonicacid]) and 60 μl 1 M HCl. Uranyl forms a complex with the arsenazo III reagent. Its absorbance was measured at $\lambda = 653 \text{ nm}$.

5 | Results and Discussion

5.1 Coumarin as a Probe for Surface Bound Hydroxyl Radicals

When H_2O_2 is catalytically decomposed, water and molecular oxygen are the products being formed according to reaction [22]. The detailed reaction mechanism, reactions [8] to [10], involves the homolytic cleavage of H_2O_2 into two surface bound hydroxyl radicals (reaction [8] [71]). It is important to note, that the lifetime as well as the reactivity of surface bound hydroxyl radicals are not the same as for free hydroxyl radicals [111-113].

Surface bound hydroxyl radicals formed during catalytic decomposition of H_2O_2 on ZrO_2 were first quantified using tris as radical scavenger [105]. After this first study on ZrO_2 , studies on a number of other metal oxides followed, where either tris or methanol were used as radical scavenger [114-116]. Both, tris and methanol can react with $\text{HO}^\bullet$ to form formaldehyde, which in turn can be quantified spectrophotometrically [104]. However, formaldehyde is a product which is not truly unique for $\text{HO}^\bullet$. In fact, any hydrogen abstracting species would produce the same product in the reaction with tris or methanol.

To get a product truly unique for $\text{HO}^\bullet$, coumarin has been used as probe yielding the strongly fluorescent 7-hydroxycoumarin. From heterogeneous photocatalysis and radiation chemical experiments it is known, that coumarin acts as hydroxyl radical scavenger [117, 118]. However, it was not used as a scavenger for surface bound hydroxyl

radicals before.

The results of two sets of experiments, where 2 mM H_2O_2 was catalytically decomposed on the surface of ZrO_2 are shown in figure 5. One set of experiments contained 0.05 mM coumarin (figure 5a) whereas the second set of experiments was carried out in 50 mM tris (figure 5b). In both cases, more than 97.5 % of the initial H_2O_2 was consumed at the end of the experiment. In the background experiments, which also contained 0.05 mM coumarin or 50 mM tris but no ZrO_2 powder, the H_2O_2 consumption was negligible during the time frame of the experiments.

Figure 5: (a) Concentration of 7-hydroxycoumarin measured in 0.05 mM coumarin and (b) concentration of formaldehyde measured in 50 mM tris before (0 s) and after (0.882×10^5 s) the consumption of 2 mM H_2O_2 . Blue triangles are the concentrations of formaldehyde or 7-hydroxycoumarin respectively, turquoise dots are the background signal. Reproduced with permission from © Wiley-VHC Verlag GmbH & Co. KGaA [119].

Despite the appearance of a low background signal, the concentration of 7-hydroxycoumarin formed in the presence of coumarin and ZrO_2 is significant. The strong signal of 7-hydroxycoumarin therefore unambiguously proves, that $\text{HO}^\bullet$ is being formed during catalytic decomposition of H_2O_2 on ZrO_2 . The formation of 7-hydroxycoumarin can be seen as independent evidence for the occurrence of $\text{HO}^\bullet$ as an intermediate species during catalytic decomposition of H_2O_2 in systems containing metal oxide surfaces. The results presented in figure 5 therefore support a $\text{HO}^\bullet$ mediated mechanism for the fraction of H_2O_2 undergoing

Table 4: Results of H_2O_2 experiments where either tris or coumarin have been used as a probe.

	Coumarin / 7-hydroxycoumarin	Tris / CH_2O
concentration of CH_2O / 7-hydroxycoumarin at the end of the experiment	$35 \pm 5 \text{ nM}$	$64 \pm 5 \mu\text{M}$
Scavenged $\text{HO}^\bullet$	$620 \pm 90 \text{ nM}$	$180 \pm 10 \mu\text{M}$
Fraction of scavenged $\text{HO}^\bullet$ per molecule of tris / coumarin	1.2×10^{-2}	3.6×10^{-3}
Fraction of scavenged $\text{HO}^\bullet$ per H_2O_2 consumed	3×10^{-4}	0.09

catalytic decomposition also on UO_2 .

From radiation chemical experiments it is known, that the relative yield of 7-hydroxycoumarin is 5.7 % [108] whereas it is 35 % for tris [105]. By using the relative yields and the experimental results presented in figure 5, the total concentration of scavenged $\text{OH}^\bullet$, as well as the fractions of scavenged $\text{HO}^\bullet$ per probe molecule or per consumed molecule of H_2O_2 can be calculated. The results are shown in table 4. From table 4 it becomes clear that during catalytic decomposition of H_2O_2 under the present conditions (i.e. initial concentrations: 2 mM H_2O_2 and 0.05 mM coumarin or 50 mM tris) only around 1 % of coumarin and less than 0.4 % of tris are consumed. The concentrations of both coumarin and tris can therefore be considered constant throughout the experiment.

Since surface coverage by the radical scavenger has an impact on

the amount of scavenged $\text{HO}^\bullet$, its initial concentration as well as the scavengers capacity to absorb on the surface strongly influence its overall efficiency [106]. Therefore, the maximum scavenging capacity is reached, when the surface is saturated with probe molecules.

It has recently been assessed that both, coumarin and tris have a similar affinity towards the surface of TiO_2 [109]. In addition, the affinity of tris towards TiO_2 and ZrO_2 is similar and formaldehyde formation in both cases was found to become independent of the initial tris concentration above 100 mM [106, 120]. It can therefore be assumed, that surface saturation for both powders is reached at tris or coumarin concentrations around 100 mM.

Since the low solubility of coumarin does not allow for experiments at concentrations high enough to reach surface saturation, coumarin can only be used as a qualitative probe. However, by replacing coumarin with coumarin-3-carboxylic acid this problem could be circumvented based on the higher solubility and surface affinity of the latter [121–123].

As shown in table 4, only 3×10^{-4} hydroxyl radicals are scavenged by coumarin per consumed molecule of H_2O_2 . In contrast, 0.09 hydroxyl radicals are scavenged per consumed H_2O_2 molecule when tris is used as a scavenger. Based on the reaction mechanism, a maximum of two surface bound hydroxyl radicals can be scavenged per consumed H_2O_2 molecule, assuming that the probe scavenges all hydroxyl radicals formed through homolytic cleavage of H_2O_2 (reaction 8). When the scavenger concentration is sufficiently high to scavenge all these surface bound hydroxyl radicals, the key reaction during catalytic decomposition of H_2O_2 , i.e. the reaction between H_2O_2 and $\text{HO}^\bullet$ (reaction 9) becomes negligible. From experiments it is known that the yield of O_2 decreases with increasing scavenger concentration [107] substantiating the discussion above.

In the absence of radical scavengers, only one hydroxyl radical is formed per consumed H_2O_2 , since one of the two surface bound hydroxyl radicals formed during reaction 8 is consumed by H_2O_2 in reaction 9. In comparison to experiments performed in 0.05 mM coumarin, the higher number of scavenged $\text{HO}^\bullet$ per consumed H_2O_2 molecule at an initial tris concentration of 50 mM, significantly influences the sys-

tem. In turn, due to the small number of scavenged $\text{HO}^\bullet$ per consumed H_2O_2 molecule at the coumarin concentration used in this study, the influence on the overall reaction by the presence of coumarin is very small. In the case of coumarin, a low probe concentration allows a significant portion of the $\text{HO}^\bullet$ formed during the cleavage of H_2O_2 (reaction 8) to react with H_2O_2 in a second step (reaction 9). The high sensitivity of coumarin at low probe concentrations makes it an attractive alternative compared to other probes, when low scavenger concentrations are required to minimize their interference. In experiments where the tris concentration was similar or slightly higher compared to the coumarin concentration used here, the measured formaldehyde concentrations were below the detection limit.

5.2 Dissolution of U_3Si_2

5.2.1 H_2O_2 Induced Dissolution of U_3Si_2

50 mg of either U_3Si_2 or UO_2 powder were exposed to 0.2 mM H_2O_2 in aqueous powder suspensions containing 10 mM or 0 mM HCO_3^- . The results for 10 mM HCO_3^- are shown in figure 6 and for 0 mM HCO_3^- in figure 7. Given that the specific surface area of the U_3Si_2 powder is approximately 10 times less than for UO_2 , one has to multiply the reactivity of U_3Si_2 by a factor of 10 to be able to compare the experimental results.

Figure 6: Concentrations as a function of time in 10 mM HCO_3^- (a) H_2O_2 consumption and uranium as well as silicon dissolution from U_3Si_2 ; (b) H_2O_2 consumption and uranium dissolution from UO_2 . Reproduced with permission from © Elsevier [124].

Keeping the different surface areas in mind, it can be seen that in 10 mM HCO_3^- (figure 6a), U_3Si_2 is approximately 5 times more reactive towards H_2O_2 than UO_2 (figure 6b).

When comparing the results for uranium dissolution under these conditions it becomes clear, that the dissolution yield (see equation 11) of UO_2 is significantly higher than that of U_3Si_2 and even exceeds 100%. The dissolution yield exceeding 100% can be attributed to pre-oxidized uranium in hyperstoichiometric UO_2 (for characterization see section 4.1), where some of the uranium is already present as U^{5+} or U^{6+} and therefore readily dissolves. In comparison, the experimentally determined dissolution yield of U_3Si_2 is $30 \pm 5 \%$, which is significantly

lower than the yield of UO_2 . However, compared to the theoretical dissolution yield of 23 % for U_3Si_2 , where both uranium and silicon have to be fully oxidized to be dissolved, this number is not necessarily low. Like for UO_2 , the experimentally determined dissolution yield for U_3Si_2 is higher than the theoretical maximum, indicating that the U_3Si_2 powder is also slightly preoxidized.

In the presence of HCO_3^- the measured concentrations of dissolved silicon and uranium from U_3Si_2 are virtually identical. This is interesting given the elemental ratio of uranium and silicon in U_3Si_2 .

Figure 7: Concentrations as a function of time in 0 mM HCO_3^- (a) H_2O_2 consumption and uranium as well as silicon dissolution from U_3Si_2 ; (b) H_2O_2 consumption and uranium dissolution from UO_2 . Reproduced with permission from © Elsevier [124].

In the absence of HCO_3^- , U_3Si_2 (figure 7a) displays a lower reactivity towards H_2O_2 than in the presence of 10 mM HCO_3^- . The initial release of both uranium and silicon is also slower in the absence of HCO_3^- . While silicon eventually reaches similar concentrations either in the absence or presence of HCO_3^- , the concentration of uranium in the absence of HCO_3^- first increases to reach a maximum, after which it decreases to reach a final concentration of less than $10 \mu\text{M}$ by the end of the experiment. This implies that the solvent (i.e. H_2O) becomes oversaturated with respect to uranium leading to precipitation of the latter. The formation of a secondary phase through precipitation also explains the overall lower reactivity of U_3Si_2 towards H_2O_2 in the absence of HCO_3^- .

When the same experiment in 0 mM HCO_3^- is performed on UO_2 (figure 7b), H_2O_2 is initially consumed very fast. After this initial period, which can be ascribed to fast H_2O_2 adsorption onto the UO_2 surface, the reactivity of UO_2 towards H_2O_2 becomes considerably lower. A rapid initial H_2O_2 consumption cannot be seen for U_3Si_2 because the exposed surface area in experiments on U_3Si_2 is only 10 % of that in UO_2 experiments, limiting surface adsorption.

When comparing the uranium release from UO_2 (figure 7b) to U_3Si_2 (figure 7a) in 0 mM HCO_3^- , it is obvious that in experiments on UO_2 , the uranium concentration does not decrease after reaching a maximum. This implies that a different solid phase is in equilibrium with dissolved uranium in the case of UO_2 as compared to U_3Si_2 .

5.2.2 The Impact of Consecutive H_2O_2 Exposures on the Dissolution of U_3Si_2

To confirm the secondary phase formation as expected from the results presented in figure 7, U_3Si_2 was consecutively exposed to H_2O_2 . In the presence of 10 mM HCO_3^- an initial H_2O_2 concentration of 0.2 mM was chosen, to be able to compare the results to previous experiments. The first order rate constant for H_2O_2 consumption during the first addition is $(3.4 \pm 0.3) \times 10^{-4} \text{ s}^{-1}$, whereas it is $(3.22 \pm 0.04) \times 10^{-4} \text{ s}^{-1}$ for the fifth. The insignificant change in reactivity implies that no significant amount of secondary phase was formed on the U_3Si_2 surface in the presence of 10 mM HCO_3^- upon the consecutive exposures to H_2O_2 .

To promote secondary phase formation, two batches of U_3Si_2 powder were also consecutively exposed to H_2O_2 in 0 mM HCO_3^- . To maximize product formation, the initial H_2O_2 concentration for each exposure was 5 mM and its concentration was measured every 24 h. These experiments were performed in a preparative manner to allow the identification of the secondary phase by XRD. Kinetic data is therefore not available in the same way as for experiments which were performed in 10 mM HCO_3^- . However, while all H_2O_2 was consumed during 24 h after the first addition, only 75% of the H_2O_2 was consumed within 24 h after the fifth addition. This clearly indicates an overall decrease in reactivity. The yellow precipitate which formed upon oxidation of the powder by H_2O_2 was identified as studtite (figure 8). Next to studtite,

its dehydration product metastudtite was also identified. Metastudtite forms when studtite is left to dry in very low humidity under Ar atmosphere. The ratio of studtite and metastudtite varies between the two samples. It is important to note that in all systems studied here (even in the presence of bicarbonate) the formation of studtite is thermodynamically favorable [125]. This will be discussed in more detail in section 5.4.

Figure 8: Diffractograms of U_3Si_2 powder before consecutive exposures to H_2O_2 (blue) and after five exposures to 5 mM H_2O_2 in 0 mM HCO_3^- (turquoise, orange). In one batch (turquoise) metastudtite was predominant after drying, in the other batch (orange) studtite was the predominant species. Indexes for U_3Si_2 from [126], for studtite from [127] and for metastudtite from [77]. Y-axis offset added for clarity. Reproduced with permission from © Elsevier [124].

5.2.3 γ -Radiation Induced Dissolution of U_3Si_2

Figure 9 shows the results of γ -radiation induced dissolution experiments on UO_2 in 10 mM HCO_3^- .

From the experimental results and by taking the background dissolution of UO_2 in 10 mM HCO_3^- into account, the radiation chemical yield for dissolution of UO_2 can be calculated to be $(2.7 \pm 0.2) \times 10^{-8} \text{ mol J}^{-1}$. Measured uranium concentrations during γ -irradiation experiments on

Figure 9: Concentrations of uranium and H_2O_2 measured as a function of irradiation time for samples containing UO_2 and 10 mM HCO_3^- . Reproduced with permission from © Elsevier [124].

several U_3Si_2 samples are only marginally above the detection limit. However, after the background correction from a series of experiments, the respective radiation chemical yield for U_3Si_2 is $(4 \pm 1) \times 10^{-10} \text{ mol J}^{-1}$. When multiplying the radiation chemical yield of U_3Si_2 by a factor of 10, to correct for the effect of surface area, the yields for UO_2 and U_3Si_2 can be compared. Based on these results, the radiation chemical yield is a factor of 5 to 10 times higher in the UO_2 system. This is not surprising considering that the dissolution yield of UO_2 exceeds that of U_3Si_2 by a factor of approximately 4.

For γ -irradiation experiments in 0 mM HCO_3^- , radiation induced dissolution is slower for both materials. The measured uranium concentrations were in fact found to be very close or even below the detection limit of the method making data evaluation impossible.

5.3 Dissolution of UO_2 Resembling Long-term Leaching Conditions

5.3.1 UO_2 Leaching Experiments at High H_2O_2 Exposures

To resemble long term leaching conditions of spent nuclear fuel in a deep repository, five UO_2 pellets (P1 - P5) were consecutively exposed to 2.25 mM H_2O_2 in 40 ml 10 mM HCO_3^- solution. The surface area over solution volume ratio for these experiments ranges between 3.65 m^{-1} and 3.98 m^{-1} , resulting in H_2O_2 exposures of 0.33 mol m^{-2} to 1.36 mol m^{-2} . The high H_2O_2 exposures were reached, after repeating the experiment three times for a given pellet. In comparison, the typical surface area over solution volume ratios for previously published experiments are around 22 m^{-1} for pellets [100, 128] and between 2700 m^{-1} to 10800 m^{-1} for powders [113]. H_2O_2 exposures for these experiments are around 0.08 mol m^{-2} for pellets, whereas for powders exposures range from $1.8 \times 10^{-5} \text{ mol m}^{-2}$ to $7.4 \times 10^{-4} \text{ mol m}^{-2}$. Using similar experimental setups, this difference in surface area over solution volume ratio implies, that the pellets studied here were exposed to approximately 10 times more H_2O_2 per surface area as compared to pellets used in previous experiments. Compared to previous powder experiments, the exposure is approximately three orders of magnitudes higher.

The results of the dissolution experiments for pellets P1 to P5 are shown in figure 8. It should be noted that the background consumption of H_2O_2 is significant during the time frame of the experiments. Since figure 8 shows the measured concentrations for H_2O_2 it is not corrected for the background consumption. The corrected H_2O_2 consumption on the UO_2 surface and the respective dissolution yields for each pellet and exposure are listed in table 5.

From these results it becomes clear, that the dissolution yield decreases with each exposure for a given pellet. This indicates, that the pellet surfaces are continuously being altered despite the presence of 10 mM HCO_3^- during the experiments and extensive washing of the pellets between individual exposures. When plotting the dissolution yield against the accumulated H_2O_2 exposure this trend becomes even more obvious (figure 9).

(a)

(b)

(c)

(d)

(e)

(f)

Figure 8: Measured H_2O_2 (left column) and U(VI) concentrations (right column) vs. time during three consecutive exposures to H_2O_2 . (a, b) Pellet P1, (c, d) pellet P2, (e, f) pellet P3, (g, h) pellet P4, (i, j) pellet P5.

Figure 9: Dissolution yield vs. H_2O_2 exposure for pellets P1-P5. Accumulated exposures are used for the second and third exposure.

CHAPTER 5. RESULTS AND DISCUSSION

Table 5: H_2O_2 consumption and dissolution yields for each pellet and exposure.

Sample	H_2O_2 exposure No.	H_2O_2 consumed on UO_2 / mM	Dissolution Yield / %
P1	# 1	1.20	1.51
	# 2	1.74	1.08
	# 3	1.63	0.53
P2	# 1	1.72	1.98
	# 2	1.80	0.77
	# 3	1.71	0.31
P3	# 1	1.54	2.33
	# 2	1.28	0.79
	# 3	1.77	0.25
P4	# 1	1.72	1.97
	# 2	1.76	0.91
	# 3	1.56	0.26
P5	# 1	1.74	1.62
	# 2	1.60	0.76
	# 3	1.47	0.28

It is interesting to note, that despite the decrease in dissolution yield, the rate of H_2O_2 consumption does not change for the second or third exposure. The decrease in dissolution yield with increasing H_2O_2 exposure implies a change in redox reactivity. However, since more than 98 % of the initial H_2O_2 reacts through catalytic decomposition on the pellet surface anyway, the change in redox reactivity of the pellets by more than a factor of 3 to 4 hardly influences the overall kinetics for H_2O_2 consumption. Due to generally higher dissolution yields in the powder experiments described above, a change in redox reactivity also results in a change of the overall kinetics for H_2O_2 consumption. When combining the results from figure 9 with the high surface area over solution volume ratio experiments on powders [113] and a pellet [128], figure 10a is obtained.

Figure 10: Dissolution yield vs. accumulated H_2O_2 exposure per m^2 for pellets P1-P5 (blue triangles), a UO_2 pellet from [128] (turquoise dot) and UO_2 powders from [113] (orange diamonds); (a) linear axes and (b) logarithmic axes.

While experiments on UO_2 powders imply high surface area over solution volume ratios and therefore low accumulated H_2O_2 exposures per surface area, experiments on pellets P1 to P5 represent the other extreme in term of surface area over solution volume ratio or accumulated exposure. The overall trend shown in figure 10a, links the high dissolution yields previously obtained from powder experiments to the low dissolution yields measured for P1 to P5, through a pellet experiment that has been performed at a surface area over solution volume ratio of approx. 22 m^{-1} . Given the wide range of exposures between

powder and pellet experiments, a logarithmic plot of the same data is presented in figure 10b. Generally it becomes clear, that by increasing H_2O_2 exposure, the dissolution yield for UO_2 decreases. This indicates that UO_2 becomes increasingly resistant to oxidative dissolution by H_2O_2 at high turnovers of the latter. UO_2 specimens, especially pellets are often being re-used for several studies or experiments within this research area. The results presented here clearly demonstrate the importance of the exposure history of individual specimens.

By using the experimental results presented above, one can compare the exposure history of the pellets studied here to a scenario expected in a deep geological repository after barrier failure. Considering a 100 000 year old fuel with a burnup of $55 \text{ MWd kg}^{-1} \text{U}^{-1}$, the maximum dissolution rate due to oxidation by H_2O_2 can be calculated to be $3 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$ [129]. As shown above, the rate of dissolution changes with turnover of H_2O_2 and therefore with time. The time dependent dissolution rates for the same specimens as presented above can be calculated using the maximum dissolution rate of $3 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$ of the 100 000 year old fuel. The results are shown in figure 11a. The same time dependent dissolution rates but with a maximum dissolution rate correlating to a 1000 year old fuel is shown in figure 11b. To reach the same H_2O_2 turnover as on pellets studied here, i.e. 1.36 mol m^{-2} and by using the dissolution rate for the 100 000 year old spent fuel, a contact period between groundwater and the spent fuel surface of just over 14 000 years ($4.5 \times 10^{11} \text{ s}$) is necessary. This time span is reduced to approximately 350 y ($1.1 \times 10^{10} \text{ s}$) when the maximum dissolution rate of the 1000 y old fuel is used. Compared to time spans relevant for the safety assessment of a deep geological repository, these are fairly short periods.

Continuing on the implications for a deep repository, by numerically integrating the curve in figure 10, an estimation can be given on the fraction of fuel which would be dissolved until complete surface passivation is reached. Based to the inherent change in redox reactivity of UO_2 , less than 0.1 % of the total inventory is prone to dissolution.

It is known, that the formation of studtite is thermodynamically favorable even in the presence of 10 mM HCO_3^- [125]. Studtite formation on the surfaces of pellets P1 to P5 could therefore be an explanation for the irreversible alteration of the pellet surfaces upon consecutive

Figure 11: Dissolution rate vs. time for pellets P1-P5 (blue triangles), a UO_2 pellet from [128] (turquoise dot) and UO_2 powders from [113] (orange diamonds); (a) Maximum dissolution rate for a 100 000 y old fuel and $55 \text{ MWd kg}^{-1} \text{U}^{-1}$ (b) Maximum dissolution rate for a 1000 y old fuel and $55 \text{ MWd kg}^{-1} \text{U}^{-1}$.

exposures to H_2O_2 . The precipitation of studtite was previously verified on U_3Si_2 powders after being consecutively exposed to high H_2O_2 concentrations in the absence of HCO_3^- (see subsection 5.2.2). The same has been reported for commercial spent nuclear fuel as well as UO_2 powders and pellets [82, 83, 85, 130]. For doped UO_2 pellets, where the surface reaction with H_2O_2 is dominated by catalytic decomposition of H_2O_2 rather than uranium oxidation, studtite formation could not be observed [130]. A detailed investigation on the stability of studtite in the absence and presence of bicarbonate and H_2O_2 follows in chapter 5.4. To elucidate whether or not secondary phase formation governs the surface alteration of pellets P1 to P5, the pellets were characterized using SEM, XRD and Raman spectroscopy.

5.3.2 UO_2 Solid Phase Characterization

Before and after the three consecutive exposures to H_2O_2 , pellets P1 to P5 have been taken for SEM imaging. BSE images of pellet P3 before (figure 12a) and after (figure 12b) the exposure to H_2O_2 are exemplarily shown.

By comparing the images from before and after dissolution, it becomes clear that dissolution preferentially occurs along grain boundaries. Cracks opening up throughout grains and across grain boundaries

Figure 12: SEM images of (a) P3 before the exposures to H_2O_2 and (b) P3 after three exposures to H_2O_2 . Both images are recorded using a BSE detector.

might be the result of grain boundary dissolution from just below the surface. As a result of grain boundary dissolution, several grains from the matrix seem to have loosened up and fallen out of the UO_2 matrix during the exposure to H_2O_2 . Due to surface roughening after the exposures it becomes clear, that dissolution also occurs on the grains themselves. The increase in contrast between individual grains in image 12b indicates preferential dissolution of several grains, which is most likely based on grain orientation.

In addition to SEM images, XRD patterns were also recorded before (figure 13a) and after (figure 13b) the dissolution experiments. From the XRD patterns of two representative samples (P1 and P5) prior to H_2O_2 exposure, the lattice parameters have been calculated using the Debye-Scherrer method. For both pellets, the calculated lattice parameters, $5.477 \pm 0.002 \text{ \AA}$ for P1 and $5.479 \pm 0.003 \text{ \AA}$ for P5, agree well with literature [99] and thereby confirm the stoichiometry of UO_2 . XRD patterns recorded after three exposures to H_2O_2 reveal small peaks of a secondary phase at higher 2θ angles as compared to stoichiometric UO_2 . These secondary peaks appear to be broadened. Peak broadening can be the result of both, a loss in crystallinity during oxidation leading to the incorporation of interstitial oxygen defects, as well as the occurrence of several over-stoichiometric states of UO_2 .

Figure 13: (a) Diffractograms before H_2O_2 exposure and, (b) after three exposures to H_2O_2 . Y-axis offset is added for clarity. Gray indexes for UO_2 from reference [131], dashed purple indexes for U_4O_9 from reference [132].

Since hyper-stoichiometry unambiguously leads to defect formation, a combination of both phenomena is plausible. Based on positions of the secondary peaks, the highest oxidation state correlates to cubic U_4O_9 . However, no other secondary phase except hyper-stoichiometric UO_2 can be observed.

In agreement with the XRD results, Raman bands of a representative twin pellet of pellets P1 to P5 at 445 cm^{-1} , 918 cm^{-1} and 1150 cm^{-1} confirm the stoichiometric structure of UO_2 prior to the H_2O_2 exposures (figure 14a). After the dissolution experiments new Raman bands corresponding to several states of hyper-stoichiometric UO_2 were observed for all the pellets under study. Raman spectra are exemplarily shown for pellets P1 and P5 (figure 14b and c). A list of these Raman bands and the correlating hyper-stoichiometric phase of UO_2 can be found in table 6.

It should be noted that in comparison to the results from XRD, several distinct hyper-stoichiometric structures and even oxidation states up to U_3O_8 were observed using Raman spectroscopy.

Given the insensitivity of x-rays to distortions in the anionic sub-lattice, such distortions remain unnoticed by XRD and the presented results are therefore not surprising. However, due to the attenuation length of photons when penetrating matter, it is expected that the majority of the signal detected during XRD measurements originates from a

Figure 14: (a) Raman spectra before the exposure to H_2O_2 recorded at two different locations on a twin pellet of pellets P1 - P5. Raman spectra after three exposures to H_2O_2 recorded at three different locations for pellets P1 (b) and P5 (c).

greater depth as compared to the signal collected during the Raman measurements. This could be an indication, that the highest oxidation states observed, only form very close to the surface during oxidation of UO_2 by H_2O_2 .

Table 6: Raman bands of pellets P1 to P5 after three exposures to H_2O_2 .

UO_2 [133, 134]	445 cm^{-1} , 918 cm^{-1} , 1150 cm^{-1}
$UO_{2.03}$ [133]	445 cm^{-1} , 562 cm^{-1} , 623 cm^{-1} , 1150 cm^{-1}
$UO_{2.24}$ [133]	459 cm^{-1} , 547 cm^{-1} , 637 cm^{-1} , 1150 cm^{-1}
$\alpha\text{-}U_3O_8$ [135]	343 cm^{-1} , 351 cm^{-1} , 412 cm^{-1} , 483 cm^{-1} , 738 cm^{-1} , 811 cm^{-1}

5.3.3 $(U_{1-x}Gd_x)O_2$ Leaching Experiments at High H_2O_2 Exposures under H_2 or N_2 Atmosphere

In several previous studies, a hydrogen effect in the absence of ϵ -particles, where dissolved U(VI) is reduced to U(IV), has been described. The reduction reaction was proposed to be catalyzed by the presence of UO_2 -based solid materials that were either doped with α -emitters (^{233}U , ^{238}Pu , ^{239}Pu) or Gd [95–97]. However, a similar effect could not be confirmed for un-doped UO_2 [98]. To assess the effect of H_2 on the oxidative dissolution of Gd-doped UO_2 , commercial $U_{1-x}Gd_xO_2$ pellets with Gd-doping levels of 3 wt-%, 4.5 wt-% and 8 wt-% were exposed to H_2O_2 for several times in either N_2 or H_2 atmosphere. The pellets, hereafter referred to as Gd30, Gd45 and Gd80, were previously used and characterized [100] and their exposure history has been taken into account during data analysis. To evaluate the effect of surface passivation at high H_2O_2 exposures, a comparison between a pellet (Gd30N) which has never been used for experiments and its twin (Gd30) which already has an exposure history, is made.

The results from dissolution experiments for pellets Gd45 and Gd80 are presented in figure 15.

Despite some scattering in the data, it can be seen that the consumption of H_2O_2 (figure 15a) is similar for each exposure and pellet despite

Figure 15: Measured concentrations of (a) H_2O_2 and (b) U(VI) as a function of time for pellets Gd45 (red-yellow) and Gd80 (blue-cyan). Dots correspond to exposures in 40 bar H_2 , triangles are exposures in 5 bar N_2 .

differences in atmosphere or doping level. In comparison, the release of U(VI) is close to the detection limit for all datasets except the first exposure for pellet Gd45 where the release of uranium is highest. In general, the release of U(VI) from both pellets is lower than previously reported [100].

The results of dissolution experiments of Gd30 are shown in figure 16.

Figure 16: Measured concentrations of (a) H_2O_2 and (b) release of U(VI) for pellet Gd30. Dots correspond to exposures in 40 bar H_2 , triangles are exposures in 5 bar N_2 .

Also for this pellet it can be seen that the consumption of H_2O_2 is simi-

lar for each H_2O_2 exposure (figure 16a) and is in line with the measured concentrations from experiments on Gd45 and Gd80. The release of U(VI) (figure 16a) is marginally higher as compared to Gd80 and Gd45 and seems to decrease slightly for each H_2O_2 exposure.

To assess the influence of surface passivation, an effect which has been discussed in the previous chapter and which has been demonstrated to be irreversible despite excessive washing of the UO_2 specimens in 10 mM HCO_3^- , the exposures to H_2O_2 were repeated on a new pellet Gd30N. The H_2O_2 concentrations measured as a function of time are presented in figure 17a. The corresponding plot for U(VI) release from Gd30N is shown in figure 17b. To evaluate the influence of the atmosphere, the pellet was first exposed to H_2O_2 at 40 bar H_2 before repeating the experiment in N_2 atmosphere.

Figure 17: Measured concentrations of (a) H_2O_2 and (b) U(VI) as a function of time for pellet Gd30N. Dots are exposures in 40 bar H_2 , triangles exposures in 5 bar N_2 .

The results presented in figure 17 clearly show, that the release of U(VI) is higher during the first exposure in H_2 than during the second exposure in N_2 . Dissolution during the second exposure is in turn higher than the U(VI) concentrations measured for the pre-used twin pellet Gd30 (figure 16). This trend is well in line with the surface passivation previously discussed for un-doped UO_2 . By plotting the dissolution yield of the Gd-doped pellets vs. accumulated H_2O_2 exposure and by taking their exposure history from the previous study into account [100], figure 18 is obtained.

In agreement with the results for un-doped UO_2 pellets, also for Gd-

Figure 18: Dissolution yield vs. accumulated H_2O_2 exposure per m^2 for pellets Gd80 (orange diamonds), Gd45 (red points), Gd30 (blue triangles) and Gd30N (turquoise triangles).

doped pellets the dissolution yield is highest during the first exposure to H_2O_2 and decreases with H_2O_2 turnover. The dissolution yield for the first exposure is higher for pellets with lower Gd-doping levels, and decreases with increasing doping levels. The decrease in dissolution yield for increasing Gd-doping can be attributed to a change in redox reactivity, where the percentage of H_2O_2 reacting through catalytic decomposition increases with increasing doping level. Moreover, the decrease in dissolution yield at high H_2O_2 exposures, can be attributed to an irreversible change in redox reactivity.

When plotting the data shown in figure 18 only the H_2O_2 exposure history of each pellet is considered and the atmosphere under which the individual exposure was carried out is neglected. Since the trends observed in figure 18 are continuous despite the negligence of atmosphere, it can be concluded, that the effect of surface passivation at high H_2O_2 turnovers exceeds any possible H_2 effect.

5.4 Studtite Stability in Aqueous Suspensions

Under deep repository conditions, studtite ($(\text{UO}_2)_2\text{O}_7 \cdot 4(\text{H}_2\text{O})$) can form on the spent fuel surface in the presence of H_2O_2 and UO_2^{2+} . Precipitation of studtite on the UO_2 surface has been found to reduce its reactivity [83, 130]. In addition, the generally low solubility of studtite ([125]) might also affect the long term stability of the fuel. Despite studtite being sparingly soluble, it has recently been reported that nanocluster formation can anyway solubilize studtite under certain conditions [136, 137].

As part of this thesis, the solubility of studtite was studied under conditions which are relevant for a deep repository by using aqueous powder suspensions containing 0 mM HCO_3^- or 10 mM HCO_3^- . Studtite was precipitated from acidified solutions containing $\text{UO}_2(\text{NO}_3)_2$ and excess H_2O_2 . After drying the precipitate in either air or Ar atmosphere, it was analyzed by x-ray diffractometry to confirm studtite formation.

Figure 19: Diffractograms of studtite powder dried in air (turquoise) and Metastudtite powder dried in Ar (orange), with indexes for studtite from [138] and for metastudtite from [77].

It is interesting to note that powders which were dried in air could be identified as studtite, whereas powders which were dried in an

Ar glovebox were identified as metastudtite (figure 19). Since metastudtite is the dehydration product of studtite, dehydration in the glovebox is probably due to the very low humidity which can promote this phase transformation (< 0.1 ppm H_2O).

5.4.1 Impact of HCO_3^- and H_2O_2 on the Dissolution of Studtite

To study studtite dissolution in the presence of H_2O_2 , studtite powder that was washed but not dried has been exposed to aqueous solutions containing either 10 mM HCO_3^- or 0 mM HCO_3^- under constant N_2 purging. Since the powder was not dried prior to the experiments, dehydration into metastudtite is very unlikely. Both, H_2O_2 and U(VI) concentrations were measured as a function of time. The results are shown in figure 20.

Figure 20: Concentrations of (a) H_2O_2 and (b) U(VI) as a function of time for aqueous suspensions containing 40 mg studtite powder in 10 mM HCO_3^- (blue triangles) and 0 mM HCO_3^- (turquoise dots).

From the figure it becomes clear that the presence of HCO_3^- facilitates dissolution of studtite by forming complexes. Under the current experimental conditions the solubility limit of studtite is approximately $40 \mu\text{M}$. Reactions 23 - 25 describe the equilibria in the system. In addition, the equilibrium constants are given for each reaction.

The calculated solubility limit matches the measured concentrations of H_2O_2 from dissolution experiments in 10 mM HCO_3^- well. However, the U(VI) concentration at the end of the experiment is approximately three to four times higher than the concentration of H_2O_2 . While the U(VI) concentration keeps increasing throughout the experiment, the H_2O_2 concentration seems to reach a maximum.

When studtite congruently dissolves, the ratio between H_2O_2 and U(VI) should be 1:1. The fact that U(VI) concentration is significantly higher as compared to the H_2O_2 concentration implies, that H_2O_2 is being consumed in the system. From a thermodynamical point of view, H_2O_2 consumption in the system would favor further studtite dissolution. It should be noted that $1 \times 10^{-4} \text{ mol l}^{-1}$ of dissolved U(VI) at the end of the experiment (figure 20) corresponds to less than 3 % of the studtite powder being dissolved.

In the absence of HCO_3^- , the measured U(VI) and H_2O_2 concentrations are close to the detection limit. Dissolution kinetics in 0 mM HCO_3^- can therefore not be assessed. This result is in good agreement with the low solubility of studtite that was previously reported i.e. $3.6 \times 10^{-9} \text{ M}$ [125].

Results of studtite dissolution experiments where 0.2 mM H_2O_2 was added initially are presented in figure 21.

In the absence of HCO_3^- (figure 21a), the concentration of U(VI) hardly increases and is close to the detection limit of 1 μM . In addition, the initial H_2O_2 concentration remains constant within the time frame of the experiment. While H_2O_2 is catalytically decomposed on a number of metal oxides [115] including UO_2 [72], these results demonstrate that H_2O_2 is not reactive towards studtite. Studtite precipitation on the surface of spent nuclear fuel could therefore lead to reduced reactivity of

Figure 21: Concentrations of H_2O_2 (turquoise dots) and U(VI) (blue triangles) as a function of time for aqueous suspensions containing 40 mg studtite powder in (a) 0 mM HCO_3^- and (b) 10 mM HCO_3^-

fuel towards radiolytic oxidants as it has previously been described for UO_2 [83, 130].

H_2O_2 is expected to suppress the dissolution of studtite, even in the presence of HCO_3^- and the solubility limit can be calculated to be approximately $7 \mu\text{M}$ under the present conditions [125, 139]. The experimental results of studtite dissolution in the presence of 10 mM HCO_3^- and an initial H_2O_2 concentration of 0.2 mM are shown in figure 21b. As can be seen from the figure, H_2O_2 as well as U(VI) reach a maximum after which the concentrations decrease. While the H_2O_2 concentration decreases significantly, the decrease in U(VI) concentration is less pronounced. Since dissolved U(VI) reaches almost the same concentration with or without H_2O_2 being present, studtite dissolution seems to be independent of the H_2O_2 concentration.

To investigate the mechanism behind the observed H_2O_2 consumption, three sets of samples were prepared. Each set of experiments was carried out in triplicates to assure reproducibility. The first set of samples contained 0.05 mM $\text{UO}_2(\text{NO}_3)_2$, 0.1 mM H_2O_2 and 10 mM HCO_3^- in 25 ml water. The second set contained the same concentration of H_2O_2 and HCO_3^- but no $\text{UO}_2(\text{NO}_3)_2$ was added. The third set was a replica of the first set, however 0.05 mM $\text{UO}_2(\text{NO}_3)_2$ was replaced by 0.1 mM NaNO_3 , to assess the influence of the NO_3^- ions.

H_2O_2 and U(VI) (when applicable) concentrations were measured over time and the results are presented in figure 22. The measured H_2O_2 concentrations of set 1 are shown as turquoise dots. Blue triangles give the respective U(VI) concentrations. Results of set 2 are shown in red diamonds and results of set 3 in orange pentagons.

Figure 22: Concentrations of H_2O_2 (turquoise dots, red diamonds, orange pentagons) and U(VI) (blue triangles) as a function of time in aqueous solutions. Set 1 (turquoise and blue) originally contains 0.05 mM $\text{UO}_2(\text{NO}_3)_2$, 0.1 mM H_2O_2 and 10 mM HCO_3^- ; Set 2 (red diamonds) originally contains 0.1 mM H_2O_2 and 10 mM HCO_3^- ; Set 3 (orange pentagons) originally contains 0.1 mM NaNO_3 , 0.1 mM H_2O_2 and 10 mM HCO_3^- .

From figure 22 it can be seen that the consumption of H_2O_2 is almost negligible for samples which do not contain $\text{UO}_2(\text{NO}_3)_2$ (sets 2 and 3). However, in the presence of $\text{UO}_2(\text{NO}_3)_2$, H_2O_2 is consumed at a much higher rate as compared to the background experiments (sets 2 and 3). Since the concentration of UO_2^{2+} remains constant while H_2O_2 is being consumed, the results from these experiments indicate that H_2O_2 is catalytically decomposed on uranyl carbonate complexes.

5.4.2 Impact of γ -Radiation on the Dissolution of Studtite

Results of γ -irradiation experiments on aqueous studtite powder suspensions in 0 mM HCO_3^- under constant N_2 purging are shown in figure 23.

As can be seen, neither the concentration of H_2O_2 nor U(VI) increase within the time frame of the experiment. It should be noted that the

Figure 23: Concentrations of H_2O_2 (turquoise dots) and U(VI) (blue triangles) as a function of time in aqueous suspensions containing 40 mg studtite powder (0 mM HCO_3^-) exposed to γ -irradiation.

detection limit of H_2O_2 is around 5 μM and around 1 μM for U(VI) . The apparent decrease in H_2O_2 is therefore negligible.

Results of γ -irradiation experiments in 10 mM HCO_3^- are shown in figure 24, together with the results of unirradiated samples.

Figure 24: Concentrations of (a) H_2O_2 and (b) U(VI) as a function of time for aqueous powder suspensions containing 40 mg studtite powder and 10 mM HCO_3^- . Turquoise dots for γ -irradiated samples and blue triangles for unirradiated samples.

From the graph it becomes clear, that studtite dissolution is significantly enhanced under γ -irradiation. While in the unirradiated system the U(VI) concentration reaches approximately 0.07 mM after 8 h the concentration is approximately a factor of 10 higher under irradiation

(0.72 mM). The H_2O_2 concentrations measured under irradiation are also higher than the concentration measured without irradiation but only by a factor around 3. The ratio of dissolved U(VI) to H_2O_2 is around 7 under irradiation, while the same ratio is around 2 without irradiation. Since H_2O_2 can be consumed through reactions with aqueous radiolysis products, the relatively low H_2O_2 concentrations with respect to dissolved U(VI) under irradiation experiments can partly be explained. Anyway, the extremely high U(VI) concentrations reached under irradiation are by far higher than the solubility limit of studtite in HCO_3^- containing solutions. For spent nuclear fuel in a deep repository this implies that studtite which could form on the surface of the spent fuel becomes highly soluble in the presence of HCO_3^- , due to the inherent radioactivity of the fuel. A surface passivating effect due to studtite formation, which reduces spent fuel dissolution can therefore not be expected in HCO_3^- containing water.

To evaluate whether increased dissolution is a matter of radiolytic reductants, the same experiments were repeated under N_2O purging. N_2O reacts with solvated electrons, rapidly converting them into $\text{HO}^\bullet$ through reactions [26] and [27].

In HCO_3^- containing solutions the hydroxyl radicals are in turn rapidly converted into carbonate radical anions ($\text{CO}_3^{\bullet-}$).

It is hard to imagine that the radiolytic oxidants induce dissolution of studtite, as uranium in studite is already present as U^{6+} . Whether it is the radiolytic oxidants or reductants which induce dissolution, a clear change in studtite dissolution kinetics should be observed upon purging with N_2O , as the latter doubles the radiolytic yield of $\text{HO}^\bullet$. The results of the irradiation experiments under N_2O purging are presented in figure [25] together with the results of N_2 purged experiments.

As can be seen, the significant change of the chemical conditions upon purging with N_2O does not change the dissolution kinetics of studtite.

Figure 25: Concentrations of (a) H_2O_2 and (b) U(VI) as a function of time for aqueous powder suspensions containing 40 mg studtite powder and 10 mM HCO_3^- . Samples purged with N_2O (turquoise dots) or N_2 (blue triangles).

H_2O_2 as well as U(VI) concentrations measured under N_2O agree well with the data for N_2 purging. This result clearly shows that neither radiolytic reductants like the solvated electron, nor the radiolytic oxidants have a significant effect on studtite dissolution under γ -irradiation.

To explore whether irradiation has a direct impact on the integrity of studtite, 3 studtite samples of 40 mg each were synthesized and left to dry on the bench top. After drying, 2 samples were irradiated for 8 h (2.9×10^4 s). After the irradiation one sample was taken for XRD analysis whereas the other sample was exposed to 10 mM HCO_3^- together with the sample that was not irradiated. The results of the dissolution experiments are presented in figure 26.

From figure 26 it can be seen that the measured concentrations of both H_2O_2 as well as U(VI) coincide whether or not studtite powder was irradiated prior to being exposed to 10 mM HCO_3^- . In addition, the diffractogram of the irradiated powder does not reveal any structural changes compared to the unirradiated powder. These results indicate that γ -irradiation does not induce permanent changes in studtite. However, the high U(VI) concentrations measured under irradiation for studtite powder suspension containing 10 mM HCO_3^- could still be the result of reversible transient changes to studtite based on direct deposition of radiation quenched by the presence of HCO_3^- . Since changing the solution chemistry through purging with either N_2 or N_2O did not change

Figure 26: Concentrations of (a) H_2O_2 and (b) U(VI) as a function of time for dried (blue triangles) and dried and irradiated (turquoise dots) studtite powders immersed in aqueous solutions containing 10 mM HCO_3^- after irradiation.

the outcome of the experiments, the direct involvement of both e_{aq}^- or $\text{CO}_3^{\cdot-}$ can be excluded. One can speculate that nanocluster formation under irradiation significantly enhances the solubility of studtite.

5.5 Pd Catalyzed Reactions Involving H₂

5.5.1 Pd Catalyzed Reduction of UO₂²⁺ by H₂

It has been proposed, that ϵ -particles, often mimicked by Pd, catalyze a number of reactions of concern during the radiation induced dissolution of spent nuclear fuel [92–94, 129, 140]. One reaction of importance is the Pd catalyzed reduction of UO₂²⁺ in the presence of H₂ (reaction 28), which was found to be independent of the H₂ partial pressure between 1.5 bar and 40 bar [140]. In the same study it has also been shown, that UO₂²⁺ is not reduced in the same system in the absence of H₂.

To explore the H₂ pressure dependent regime, Pd suspensions containing UO₂²⁺ at different H₂ partial pressures were prepared and U(VI) concentrations were measured as a function of time. To ensure that the H₂ pressure dependent regime can be identified, the aqueous Pd powder suspensions containing 2 mM HCO₃[−] and an initial UO₂²⁺ concentration of 10 μ M were continuously purged in a closed system using pre-mixed gases containing 100 %, 5 %, 0.5 %, 0.05 % or 0 % H₂ in N₂.

Table 7: Gas mixtures and respective H₂ partial pressures during UO₂²⁺ reduction experiments.

H ₂ partial pressure / %	H ₂ partial pressure / bar
100	1.01
5	5.1 × 10 ^{−2}
0.5	5.1 × 10 ^{−3}
0.05	5.1 × 10 ^{−4}
0.00	0.00

The resulting H_2 partial pressures are listed in table 7 and the experimental results are presented in figure 27.

Figure 27: Concentration of UO_2^{2+} as a function of reaction time and p_{H_2} . Blue triangles = 1.01 bar H_2 , turquoise dots = 5.1×10^{-2} bar, cyan diamonds = 5.1×10^{-3} bar, orange pentagons = 5.1×10^{-4} bar and red squares = 0.00 bar. Reproduced with permission from © Wiley-VCH Verlag GmbH & Co. KGaA [141].

The results shown in figure 27 clearly demonstrate, that reaction 28 is indeed catalyzed by Pd and the H_2 partial pressure dependence below 1 bar becomes evident. Already at 5.1×10^{-2} bar the rate of uranyl reduction is significantly reduced. The most significant change in reactivity becomes apparent between 5.1×10^{-3} bar and 5.1×10^{-4} bar. This change in reactivity can partly be ascribed to a prolonged initial lag phase at low H_2 partial pressures. While at 1.01 bar H_2 7 % of the initial UO_2^{2+} is reduced after 35 min, only 4 % is reduced at 5.1×10^{-3} bar and 2.5 % at 5.1×10^{-4} bar during the same time interval.

It should be noted that the initial lag time for each experiment can be attributed to the intake of around 14 μM oxygen into the system during the injection of uranyl. In the presence of Pd, H_2O_2 can be formed from gaseous H_2 and O_2 . H_2O_2 in turn can re-oxidize UO_2 among other possible reaction pathways. No matter in which particular way O_2 reacts in the system, it efficiently counteracts H_2 in the process of UO_2^{2+} reduction. UO_2^{2+} reduction therefore becomes only evident after the oxidants are being consumed.

5.5.2 Pd Catalyzed Reaction Between H₂ and H₂O₂

In a previous study it has been shown, that next to being an efficient catalyst for the reduction of UO₂²⁺, Pd also catalyzes the reaction between H₂O₂ and H₂ according to reaction [29] [93]. A more detailed reaction mechanism is proposed here as shown in reactions [30] and [31]. Experimental results where H₂O₂ concentrations were measured as a function of time and H₂ partial pressure are shown in figure [28]. From the figure it becomes evident, that reaction [29] becomes dependent on the H₂ partial pressure below 1 bar and the pseudo first order rate constants are reported in table [8].

Figure 28: Concentration of H₂O₂ measured as a function of time and p_{H₂} in aqueous Pd powder suspensions. Blue triangles = 1.01 bar H₂, turquoise dots = 5.1 × 10⁻² bar, cyan diamonds = 5.1 × 10⁻³ bar, orange pentagons = 5.1 × 10⁻⁴ bar and red squares = 0.00 bar. Reproduced with permission from © Wiley-VHC Verlag GmbH & Co. KGaA [141].

Table 8: Pseudo-first order rate constants at different H_2 partial pressures for the consumption of H_2O_2 in suspensions containing Pd particles.

H_2 partial pressure / bar	k_1 / s^{-1}	R^2
1.01	$(9.3 \pm 0.5) \times 10^{-4}$	0.9945
5.1×10^{-2}	$(8.8 \pm 0.4) \times 10^{-4}$	0.9963
5.1×10^{-3}	$(4.32 \pm 0.06) \times 10^{-4}$	0.9997
5.1×10^{-4}	$(2.198 \pm 0.006) \times 10^{-4}$	0.9999
0.00	$(1.91 \pm 0.07) \times 10^{-4}$	0.9974

Despite the intake of approximately 15 μM oxygen into the system during the injection of H_2O_2 , a lag phase which would be comparable to the uranyl experiments could not be observed. Since the initial concentration on H_2O_2 is approximately one order of magnitude higher than the concentration of oxygen, the appearance of a similar lag phase is unlikely.

It was found that H_2O_2 consumption follows first order kinetics for a given H_2 partial pressure, where the pseudo first order rate constants decrease with decreasing H_2 partial pressure (figure 29a). This implies that reaction 31 is rate determining resulting in a constant concentration of surface adsorbed H_2 .

The rate law for H_2O_2 consumption on Pd in the presence of H_2 can be expressed as shown in equation 32.

$$-\frac{d[H_2O_2]}{dt} = k[H_2O_2] \cdot \Theta \quad (32)$$

where Θ denotes the fractional coverage of the Pd surface by H_2 . This equation can be simplified to equation 33

$$-\frac{d[H_2O_2]}{dt} = k^*[H_2O_2] \quad (33)$$

Considering that the fast reaction between H_2 and Pd results in a constant concentration of surface adsorbed hydrogen. It should be kept in mind, that k^* is the measured rate constant for the total H_2O_2 consumption in the system from which the rate constant for catalytic decomposition of H_2O_2 in the absence of H_2 is subtracted.

Figure 29: (a) First order rate constants k_1 for H_2O_2 consumption as a function of p_{H_2} and (b) Langmuir Hinshelwood kinetics of H_2O_2 consumption. Reproduced with permission from © Wiley-VHC Verlag GmbH & Co. KGaA [141].

Using the Langmuir isotherm to describe Θ , where $\Theta = k^* k^{-1}$ and K the equilibrium constant, equation 34 is obtained.

$$k^* = \frac{k \cdot K \cdot [\text{H}_2]}{K \cdot [\text{H}_2] + 1} \quad (34)$$

Inversion of equation 34 gives a linear relationship (equation 35) which can be plotted in combination with the experimental data (figure 29b).

$$\frac{1}{k^*} = \frac{1}{k} + \frac{1}{k \cdot K \cdot [\text{H}_2]} \quad (35)$$

From the intercept of the linear fit i.e. $1.09 \times 10^3 \text{ s}$ (figure 29b), the second order rate constant k can be calculated to be $9.2 \times 10^{-4} \text{ s}^{-1}$. It

should be kept in mind that k is only valid for the surface area over solution volume ratio used in these experiments. In turn, from the slope ($1.34 \times 10^{-2} \text{ s M}$) of the linear fit the equilibrium constant K for H_2 adsorption can be determined to be $8.1 \times 10^4 \text{ M}^{-1}$.

In a previous study [93] a H_2 pressure dependence was not observed above 1 bar resulting in a rate expression as shown in equation [36].

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = k_2[\text{H}_2\text{O}_2] \cdot \frac{\text{SA}}{V} \quad (36)$$

Under these conditions the H_2 pressure independent second order rate constant was determined to be $2.2 \times 10^{-5} \text{ m s}^{-1}$. Using the experimental results presented above, the H_2 pressure independent rate constant can be calculated to be $2.4 \times 10^{-5} \text{ m s}^{-1}$ and the overall rate expression which combines the H_2 pressure independent regime with the H_2 pressure dependent regime can be written as shown in equation [37].

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = k_2[\text{H}_2\text{O}_2] \cdot \frac{\text{SA}}{V} \cdot \Theta \quad (37)$$

Using μm sized powder suspensions, the diffusion controlled rate constant has been reported to be in the order of 10^{-3} [142]. The experimental results presented above are therefore clearly not diffusion controlled.

It is important to note, that when purging and stirring of the aqueous powder suspensions is prolonged, the reactivity of the Pd powder significantly decreases. This phenomenon has been observed for both, H_2O_2 experiments as well as for UO_2^{2+} reduction experiments. Results of experiments where H_2O_2 concentrations were measured as a function of time under N_2 purging are exemplarily shown in figure [30]. Here, the powder was either purged and stirred for 16 h or for 30 min respectively before the injection of H_2O_2 .

Figure 30: Concentration of H₂O₂ as a function of time under N₂ purging. 30 min purging + stirring before H₂O₂ injection (blue triangles), 16 h purging + stirring before the injection of H₂O₂ (turquoise dots). Reproduced with permission from © Wiley-VHC Verlag GmbH & Co. KGaA [141].

It has previously been described that particle agglomeration is a common phenomenon, reducing the overall catalytic activity of Pd powders by reducing the accessible surface area of the catalyst [143]. SE-SEM images (figure 31) of the Pd powder used in this study were recorded after stirring and purging the powder for 6 h, 16 h or 22 h respectively. From the images it can be seen, that the Pd powder agglomerates and the agglomerate size increases with time.

Figure 31: SE-SEM images of Pd powder that was exposed to (a) water without stirring and purging, (b) Pd powder that was stirred and purged for 30 min before the injection of H₂O₂ (total stirring time approx. 6 h) and (c) Pd powder that was stirred and purged for 16 h before the injection of H₂O₂ (total stirring time approx. 22 h). Reproduced with permission from © Wiley-VHC Verlag GmbH & Co. KGaA [141].

The decrease in reactivity shown in figure 30 can therefore qualitatively be correlated to the observed particle agglomeration.

The reactivity of Pd towards H_2O_2 or UO_2^{2+} has previously been reported to be very low [93]. Before initiating experiments by injecting H_2O_2 or UO_2^{2+} , the powders from this previous study were stirred over night in an autoclave. The decrease in reactivity due to particle agglomeration for the experimental results presented above therefore also connect the data reported here to previous works [93, 140].

Despite the decrease in reactivity due to particle agglomeration, the data presented here clearly shows that H_2O_2 is catalytically decomposed on the surface of Pd. To gain insights into the reaction mechanism of catalytic decomposition of H_2O_2 on Pd, experiments were performed under N_2 purging in the presence of 20 mM tris. Since ZrO_2 has already been used in section 5.1 to get insights in the reaction mechanism of H_2O_2 decomposition and it has been subject of several mechanistic studies [105, 106, 114], experiments were also carried out on ZrO_2 for comparison. The measured H_2O_2 concentrations for experiments on Pd, ZrO_2 or in the absence of any powder are shown in figure 32.

Since hydroxyl radicals are measured indirectly after being converted into CH_2O according to reactions 19 and 20, the measured CH_2O concentrations are shown in figure 32.

Figure 32: (a) H_2O_2 and (b) CH_2O concentrations measured as a function of time. Reproduced with permission from © Wiley-VHC Verlag GmbH & Co. KGaA [141].

As can be seen in figure 32 the reactivity of H_2O_2 towards Pd is higher

as compared to ZrO_2 . It should be noted, that the surface area over solution volume ratio is a factor of 10 higher in the ZrO_2 experiments. To be able to compare the results, one should speed up the reaction on Pd by a factor of 10, which pronounces the different reactivities even more. In addition, in experiments on ZrO_2 in the presence of tris a significant amount of CH_2O is being formed. Since the concentration of $\text{HO}^\bullet$ is proportional to the yield of CH_2O , tris can be used as a quantitative probe for $\text{HO}^\bullet$. In contrast to the ZrO_2 experiments, CH_2O formation in Pd experiments overlaps with the background signal. The absence of a signal can be the results of several factors influencing formaldehyde formation. If hydroxyl radicals are formed during catalytic decomposition of H_2O_2 on Pd, surface adsorption could be stronger compared to ZrO_2 . If the $\text{HO}^\bullet$ radicals would adsorb strongly to the surface of Pd, a lack of desorption could explain the absence of measurable formaldehyde. However, if strongly adsorbed $\text{HO}^\bullet$ cannot be scavenged by tris, scavenging by H_2O_2 through the competing reaction is unlikely to occur either. As a result, $\text{HO}^\bullet$ radicals would accumulate on the surface of Pd, blocking the reactive sites and therefore change the reaction kinetics over time.

Another factor which could reduce the formation of formaldehyde is the affinity of tris to adsorb on the surface of Pd. Surface adsorption of tris on ZrO_2 has been found to be poor [105]. Therefore the relative yield of scavenged $\text{HO}^\bullet$ is low. Surface adsorption of tris on Pd has not been assessed. However, several studies describe the interaction of tris with the Pd surface through its primary amino group [144–146]. This makes the assumption, that surface adsorption of tris is not the limiting factor for this reaction to occur, reasonable. Therefore, the results presented in figure 32 indicate, that $\text{HO}^\bullet$ is not being formed on Pd during catalytic decomposition of H_2O_2 . As a consequence one has to assume that the reaction mechanism for catalytic decomposition of H_2O_2 on Pd differs from that on ZrO_2 which contradicts literature [147–149]. A different reaction mechanism which does not involve the $\text{HO}^\bullet$ was proposed in the 1960s but was not considered in recent literature [150–152].

5.5.3 Pd Catalyzed Reaction Between H_2 and O_2

To obtain a better understanding of the catalytic activity of ϵ -particles, reactions involving O_2 and H_2 were studied. Both H_2 and O_2 are

molecular radiolysis products and it has been known since the beginning of the 20th century that H_2O_2 can form from its elements on Pd catalysts according to reaction [38] [153]. Similar to the reaction on Pd, catalytic activity for this reaction has also been reported for ZrO_2 [154].

Results of experiments where aqueous Pd suspensions containing 20 mM tris were exposed to 0.2 bar O_2 and 40 bar H_2 are presented in figure [33]. As can be seen from figure [33] the formation of H_2O_2 mainly occurs within the first 50 h (0.18×10^6) after pressurizing the autoclave with H_2 . Based on the oxygen concentration in air and the volume of the reaction vessel the maximum theoretical H_2O_2 concentration that can be reached is 190 mM. However, due to the simultaneous production as well as consumption of H_2O_2 and the frequency at which samples were taken from the reaction vessel, the highest measured H_2O_2 concentration of 0.7 mM is well below the theoretical maximum. Also in these experiments where a large amount of H_2O_2 is constantly produced and consumed, the formation of formaldehyde is very low, indicating that $\text{HO}^\bullet$ is indeed no intermediate species in neither the formation nor the successive decomposition of H_2O_2 on the Pd surface.

Figure 33: Concentrations of H_2O_2 and CH_2O measured as a function of time in aqueous Pd powder suspensions at $p_{\text{H}_2} = 40$ bar and $p_{\text{O}_2} = 0.2$ bar. The data is collected from two repetitions of identical experiments to assure reproducibility. Reproduced with permission from © Wiley-VHC Verlag GmbH & Co. KGaA [141].

Since a similar catalytic behavior was recently proposed for ZrO_2 , autoclave experiments in the presence of O_2 and H_2 were repeated and Pd powder was replaced by ZrO_2 . The results are presented in figure 34. In the previously published study on ZrO_2 , the CH_2O concentration reached approximately $225\ \mu\text{M}$ after 300 h ($1.1 \times 10^6\ \text{s}$) and H_2O_2 was detected as an intermediate product [154]. The formaldehyde concentrations from this previous study correlate well with the results shown here for experiments where the autoclave was equipped with a PEEK stirrer. However, when performing the same experiment in the absence of ZrO_2 the measured CH_2O concentrations are approximately the same in the presence of the PEEK stirrer. Only when the PEEK stirrer is removed or replaced by a glass stirrer, the formation of CH_2O becomes negligible.

Figure 34: (a) H_2O_2 and (b) CH_2O concentrations as a function of time on ZrO_2 or without powder at $p_{\text{H}_2} = 40\ \text{bar}$ and $p_{\text{O}_2} = 0.2\ \text{bar}$. Note the detection limit for H_2O_2 of approximately $1 \times 10^{-5}\ \text{M}$. Reproduced with permission from © Wiley-VHC Verlag GmbH & Co. KGaA [141].

In the previously published work discussed above, PEEK was assumed to be inert and the published data was not corrected for the background signal which is obtained in the absence of ZrO_2 . Therefore, it was concluded that ZrO_2 also catalyzes the reaction between H_2 and O_2 to form H_2O_2 . Based on the results presented here, the catalytic activity which was previously assigned to ZrO_2 has to be ascribed to a contamination of the PEEK stirrer.

5.6 Implications for a Deep Repository

In this thesis several aspects counteracting oxidative dissolution of spent nuclear fuel under deep repository conditions have been addressed. The effects directly involving the UO_2 matrix are the ϵ -particle catalyzed reduction of H_2O_2 as well as the ϵ -particle mediated solid phase reduction of U(VI) . Both reactions depend on the concentration of dissolved H_2 up to $p_{\text{H}_2} = 1$ bar. H_2 pressure independent second order rate constants (i.e. $p_{\text{H}_2} \geq 1$ bar) for the most important reactions involved in UO_2 dissolution are listed in table 9. Since the rate of a reaction between a solute and a solid changes with particle size of the solid, the given rate constants are normalized for reactions involving a pellet.

Table 9: H_2 pressure independent second order rate constants.

	H_2 independent second order rate constant / m s^{-1}	Reference
k_{Pd}	2.40×10^{-9}	Paper VI
k_{UO_2}	4.57×10^{-11}	[74]
k_{uranyl}	$1.20 \cdot 10^{-9}$	[140]
$k_{\text{solid red.}}$	4×10^{-7}	[155]

In subsection 5.5.2 it is shown that H_2O_2 is consumed on the surface of Pd, where Pd powder has been used to study reactions which are also expected to occur on ϵ -particles. Since the rate of reduction of H_2O_2 on Pd is dependent on the H_2 partial pressure up to 1 bar, this effect could compete with the oxidative dissolution of spent nuclear fuel, by reducing the total amount of oxidants with increasing H_2 pressures. Taking the rate constants from table 9 into account, the H_2 pressure dependent expression 37 can be solved using the Langmuir isotherm (equation 34) for the adsorption of H_2 on Pd. By varying the ϵ -particle surface coverage of a pellet one can further calculate the percentage

CHAPTER 5. RESULTS AND DISCUSSION

of H_2O_2 reacting on the Pd instead of the UO_2 surface. These results are shown in figure 35, where in (a) the ϵ -particle surface coverage is varied for several H_2 pressures and in (b) the H_2 pressure is varied for several surface coverages.

Figure 35: Percentage of H_2O_2 reacting on Pd instead of UO_2 on the surface of a fuel pellet (a) H_2 partial pressure dependence (b) Pd surface coverage dependence.

As can be seen from figure 35, a maximum of approximately 35 % of H_2O_2 can react on ϵ -particles instead of reacting with UO_2 , when the ϵ -particle surface coverage reaches 1 % and the H_2 pressure exceeds 1 bar. With respect to the dissolution of spent nuclear fuel, this effect is insufficient to completely inhibit fuel dissolution, despite its ability to reduce the amount of H_2O_2 by up to 35 %.

Another effect which reduces the dissolution of UO_2 is the ϵ -particle mediated solid phase reduction of U(VI). By calculating and comparing the rates of UO_2 dissolution one can estimate the importance of each effect individually. The oxidation rate taking only H_2O_2 consumption on Pd into account can be calculated using equation 39. Note that in this case the rate of oxidation is equal to the rate of dissolution.

$$r_{\text{ox}} = r_{\text{H}_2\text{O}_2\text{prod.}} \cdot \text{Dissolution Yield} \cdot \frac{(1-x)k_{\text{UO}_2}}{(1-x)k_{\text{UO}_2} + x \left(\frac{k_{\text{Pd}} \cdot K_{\text{eq}} \cdot [\text{H}_2]}{(K_{\text{eq}} \cdot [\text{H}_2]) + 1} \right)} \quad (39)$$

In turn, the rate of dissolution taking only the ϵ -particle mediated solid phase reduction into account can be calculated using equation 40,

$$r_{\text{diss}} = r_{\text{H}_2\text{O}_2\text{prod.}} \cdot \text{Dissolution Yield} - (k_{\text{solidred.}} \cdot x \cdot [\text{H}_2]) \quad (40)$$

where $r_{\text{H}_2\text{O}_2\text{ prod.}}$ denotes the rate of H_2O_2 production (here for a 55 MWd/kgU fuel at different ages [156]), x the fraction of surface covered by Pd and K_{eq} the equilibrium constant for adsorption of H_2 on Pd. The rates of dissolution for different H_2 partial pressures, pessimistically assuming a dissolution yield of 20 %, are shown in figure 36. The results for the 55 MWd/kgU fuel at 1000 y are presented in (a) and at 100 000 y in (b). The dissolution rates for each age and effect were calculated for 0.1 % or 1 % surface coverage respectively.

Figure 36: H_2 pressure dependent dissolution rate of a 55 MWd/kgU spent nuclear fuel with 0.1 % ϵ -particle surface coverage (blue, turquoise and cyan lines) or 1 % ϵ -particle surface coverage (red, orange and yellow lines). Effect of H_2O_2 reacting with Pd instead of UO_2 (red and blue). Effect of U(VI) solid phase reduction (turquoise and orange). Both effects combined (cyan and yellow). (a) 1000 y old fuel, (b) 100 000 y old fuel.

The combination of the two effects results in a H_2 pressure dependent dissolution rate which is very similar to the rate of dissolution based on the effect of solid phase reduction alone. In fact, when the critical H_2 pressure is reached, i.e. the pressure where dissolution is completely inhibited, around 99.4 % of the inhibition is due to the effect of solid

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phase reduction at 0.1 % and 1 % surface coverage for the 100 000 y old fuel. For the same fuel at an age of 1000 y ca. 96 % or ca. 86 % (for 0.1 % and 1 % surface coverage respectively) of the inhibition are due to the effect of solid phase reduction. In comparison, when the dissolution yield is decreased to 2 %, around 99.9 % of the inhibition is due to the solid phase reduction for the 100 000 y old fuel, whereas it is approximately 97.6 % or 98.3 % for the 1000 y with a surface coverage of 1 % or 0.1 % respectively. From this result it can be concluded that the ϵ -particle mediated solid phase reduction is the most important effect which efficiently reduces the dissolution of spent nuclear fuel in the presence of H_2 .

Figure 37: Critical p_{H_2} depending on the ϵ -particle surface coverage and the dissolution yield for a fuel with a burnup of 55 MWd/kgU at an age of (a) 1000 y and (b) 100 000 y.

By solely accounting for the effect of ϵ -particle mediated solid phase reduction competing with oxidation of the UO_2 matrix, one can calculate the critical H_2 pressure depending on the ϵ -particle surface coverage and the dissolution yield. A three dimensional map for the 55 MWd/kgU fuel is presented in figure 37, where (a) is based on the oxidation rate at 1000 y and (b) is based on the oxidation rate at 100 000 y.

The figure clearly demonstrates, that the highest critical H_2 pressures are reached at low ϵ -particle surface coverage and high dissolution yields. As described in subsection 5.3.1 the dissolution yield decreases with increasing H_2O_2 exposure. It is therefore expected to be highest for young spent fuel just after contact between groundwater and the spent nuclear fuel has been established.

Based on the calculations presented above it becomes clear that a very low H_2 pressure is sufficient to completely inhibit spent fuel dissolution. One has to keep in mind that the expected H_2 pressure in a repository of the KBS-3 type is around 50 bar 90.

6 | Summary and Concluding Remarks

In this thesis a number of different subtopics under the generic term of "radiation induced oxidative dissolution of spent nuclear fuel under deep repository conditions" have been addressed.

It has been shown that coumarin can be used as a selective probe for hydroxyl radicals which form during catalytic decomposition of H_2O_2 on metal oxide surfaces. Low concentrations of coumarin are sufficient to scavenge $\text{HO}^\bullet$ without altering the surface chemistry and yielding a product which is truly unique for hydroxyl radicals.

In addition to this mechanistic study, oxidative dissolution of the accident tolerant fuel candidate U_3Si_2 has been investigated. It has been shown, that U_3Si_2 powder is more reactive towards H_2O_2 than UO_2 powder. However, since both Si and U have to be oxidized by H_2O_2 the overall dissolution yield of U_3Si_2 is significantly lower than for UO_2 . The lower dissolution yield for U_3Si_2 is also reflected under γ -irradiation.

The leaching behavior of UO_2 pellets has been studied at high H_2O_2 exposures. It has been shown that the UO_2 surface gradually passivates with increasing H_2O_2 turnover. This passivation can be ascribed to a drastic change in redox reactivity of the pellets and is accompanied by an alteration of the pellet surfaces. Post leaching examination of the UO_2 pellets using various surface characterization techniques shows, that the surface alteration involves oxidation to various compositions of UO_{2+x} or even U_3O_8 . Within this area of research, it is common to use pellets or pellet fragments for several studies. The results presented in this thesis clearly demonstrate how important it is to keep track of the exposure history of these specimens. Leaching experiments performed on $(\text{U}_{1-x}\text{Gd}_x)\text{O}_2$ reveal a similar passivation

effect at high H_2O_2 exposures, even for the doped material. An effect of H_2 on oxidative dissolution of $(\text{U}_{1-x}\text{Gd}_x)\text{O}_2$ was not observed.

An alteration product of UO_2 which is expected to precipitate as secondary phase from solutions containing UO_2^{2+} and H_2O_2 is studtite. The results presented in this thesis confirm the low solubility of studtite in bicarbonate deficient aqueous solutions, even under γ -irradiation. In contrast, in the presence of the common groundwater constituent HCO_3^- , studtite readily dissolves and measured U(VI) concentrations exceed the solubility limit. Enhanced dissolution in the presence of HCO_3^- occurs especially under γ -irradiation. One can speculate that nanocluster formation is favored under irradiation reducing the stability of studtite. The high release of uranium from studtite under irradiation clearly indicates, that studtite would not form on the surface of real spent fuel in HCO_3^- containing groundwater due to its inherent radioactivity. Spent fuel surface passivation due to studtite formation can therefore be ruled out. Furthermore, it has been found that uranyl carbonate complexes catalyze the decomposition of H_2O_2 . The solubility of studtite however seems unaffected by the presence of H_2O_2 .

From experiments which were performed to obtain new insights on the effect of H_2 on spent nuclear fuel dissolution, the H_2 pressure dependent regime has been identified at $p_{\text{H}_2} \leq 5.1 \times 10^{-2}$ bar for both, the reduction of UO_2^{2+} as well as the consumption of H_2O_2 using Pd as a model substance for ϵ -particles. Even in the absence of H_2 , H_2O_2 is catalytically decomposed on Pd where the rate of H_2O_2 consumption is found to decrease when Pd particles agglomerate. The results presented in this thesis indicate that the reaction mechanism for catalytic decomposition of H_2O_2 differs from the reaction mechanism which has been proposed for metal oxides. In addition, it is well known that H_2O_2 can form from its elements in the presence of small quantities of Pd. A similar catalytic activity recently proposed for ZrO_2 could not be confirmed.

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