

Waste Prevention

Impact of H₂ and Consecutive H₂O₂ Exposures on the Oxidative Dissolution of (U_{1-x}Gd_x)O₂ Pellets Under Deep Repository Conditions for Spent Nuclear FuelAnnika Carolin Maier,^{*[a]} Alexandre Barreiro Fidalgo,^[a] and Mats Jonsson^[a]

Abstract: The reactivity of H₂O₂ towards (U_{1-x}Gd_x)O₂ ($x = 0.03, 0.045, 0.08$) in the presence of H₂ was studied experimentally to assess the effect of H₂ on oxidative dissolution of Gd-doped UO₂ under deep repository conditions for spent nuclear fuel. Gd-doped UO₂ was chosen as a model substance for spent nuclear fuel due to its chemical similarity but low radiotoxicity. While H₂O₂ is a radiolysis product capable of driving fuel matrix dissolution, H₂, which is expected to evolve mainly through the corrosion of cast iron canisters encapsulating the fuel, might

limit or even suppress fuel dissolution. Commercial (U_{1-x}Gd_x)O₂ pellets were immersed in 10 mM HCO₃⁻ solutions and consecutively exposed to 2 mM H₂O₂ in an autoclave under either 40 bar H₂ or 5 bar N₂ atmosphere. The results indicate that H₂ does not influence the oxidative dissolution of (U_{1-x}Gd_x)O₂. Instead, the reactivity of the pellets decreases with increasing H₂O₂ exposure due to an irreversible alteration of the pellet surfaces resulting in decreased redox reactivity.

Introduction

To enhance the fuel cycle length in a nuclear reactor, a higher fuel load than needed to maintain critically can be introduced into the reactor when being refueled. To compensate the excess reactivity of the fuel overload at the beginning of the cycle and to maintain criticality, burnable absorbers with high neutron cross-section are often introduced into the reactor core. Ideally, a burnable absorber is depleted at the same rate as the neutron production from the excess fuel decreases.^[1,2] ¹⁵⁵Gd as well as ¹⁵⁷Gd have high neutron cross-sections and can be introduced into the reactor core as burnable absorbers by doping standard UO₂ fuel. In addition, Gd builds up as a fission product in minor quantities in nuclear fuel during in-reactor irradiation. Therefore, Gd-doped UO₂ is part of the nuclear fuel cycle and after being discarded from the nuclear reactor it will eventually be stored in a deep geological repository according to the current plans in many countries.^[3]

After being discarded from a nuclear reactor, used fuel still consists mainly of UO₂ with small fractions (approx. 5 %) of highly radioactive fission products and heavier actinides that are present in different forms within the fuel matrix.^[4,5] Among


the fission products, metallic particles (so called ϵ -particles) containing Mo, Ru, Tc, Pd, Rh and Te precipitate in the UO₂ matrix.^[4,6] These metallic inclusions have been shown to catalyze several reactions of importance for oxidative dissolution of spent nuclear fuel.^[7–10]


Upon barrier failure in a deep geological repository, ground water intrusion is inevitable and the inherent radioactivity from the spent nuclear fuel will cause water radiolysis, producing both reductants and oxidants in close proximity to the spent fuel.^[11] Among the radiolysis products, H₂O₂ has been shown to be the main radiolysis product responsible for oxidative dissolution of UO₂ in what is often considered a plausible scenario for a safety assessment.^[12] There are two competing reaction pathways for H₂O₂ consumption on the surface of UO₂, catalytic decomposition of H₂O₂ forming water and O₂ as well as electron transfer through which U^{IV} is oxidized to U^{VI}. While U^{IV} is almost insoluble, the solubility of uranium increases by several orders of magnitude when it is present as U^{VI}.^[13] The presence of HCO₃⁻ in groundwater will further enhance the solubility of uranium by forming complexes.^[14–16]

In electrochemical studies by Liu et al.^[17] and Kim et al.,^[18] it was shown that the oxidation of UO₂, as well as Gd-doped UO₂ proceeds in two stages, where the first stage is the formation of a thin oxidized surface layer (U_{1-2x}^{IV}U_{2x}^{VO_{2+x}}) and the second stage is the oxidation of this surface layer to U^{VI} which dissolves as UO₂(CO₃)₂²⁻ in carbonate media. In addition, it was shown that Gd-doping in stoichiometric specimens only influences the second stage, while the first stage was found insensitive to doping.

The electrochemical reactivity of stoichiometric samples marginally changed when Gd-doping levels varied between 1 % and 5 %, but a decrease in reactivity could be observed at

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under <https://doi.org/10.1002/ejic.202000133>.

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higher doping levels. The unexpected small change in reactivity below 5 % doping was ascribed to a competition between UO_2 -lattice contraction with increasing Gd-content inhibiting oxidation and an increased number of oxygen vacancies formed upon doping with trivalent Gd providing additional interstitial oxygen sites. For slightly hyperstoichiometric specimens the electrochemical reactivity decreased for both stages of oxidation. A continuous loss in reactivity with increasing doping levels was ascribed to the elimination of oxygen vacancies (O_V) by $\text{Gd}^{\text{III}}\text{-O}_V$ clustering leading to a significant lattice contraction. In agreement with these findings it was shown, that oxidative- and radiation induced dissolution of (Gd, U) O_2 pellets decreases with increasing Gd-doping.^[19]

In a deep geological repository for spent nuclear fuel, large quantities of H_2 are expected to evolve mainly through anaerobic corrosion of cast iron canisters.^[20,21] It was previously shown in experiments on Pd-particle doped UO_2 pellets (to mimic the effect of ϵ -particles), that the oxidative dissolution of UO_2 can effectively be inhibited in the presence of H_2 .^[22] The reaction mechanisms for the so called hydrogen effect have been described in several studies.^[10,23] The ϵ -particle catalyzed processes that contribute to the H_2 -effect are the reduction of H_2O_2 and $\text{U}^{\text{VI}}_{\text{aq}}$ by H_2 and the solid phase reduction of U^{VI} by H_2 . The latter is the most efficient process and accounts for the complete inhibition of radiation-induced dissolution of spent nuclear fuel observed already at quite low H_2 -pressures.^[9]

Some authors report a H_2 -effect on UO_2 based materials not containing ϵ -particles, where the $\text{UO}_2(\text{s})$ surface is assumed to catalyze the reduction of U^{VI} in solution.^[24–26] Interestingly this effect was only reported for systems where UO_2 was doped with either ^{233}U , ^{238}Pu , ^{239}Pu or Gd. In systems where un-doped UO_2 was used, a similar effect was not observed.^[27]

It was recently shown that the redox reactivity of un-doped UO_2 pellets towards H_2O_2 decreases with increasing H_2O_2 exposures.^[28] This passivation of the UO_2 surface becomes increasingly important for experiments, which are performed at low surface areas over solution volume ratios (SA/V) or high H_2O_2 exposures, such as in pellet experiments where the SA/V is often around 20 m^{-1} or less and pellets are used for several studies and exposures. The total consumption of H_2O_2 on the surface of a pellet is therefore considerably higher than for powder experiments making the experimental history of the pellet extremely important.

In this study we used commercial Gd-doped UO_2 pellets with different doping levels and exposed them to H_2O_2 in the presence of H_2 or N_2 , respectively. The H_2 effect on doped UO_2 in the absence of ϵ -particles is discussed, taking the sample history and turnover of H_2O_2 on the pellet surface into account.

Results and Discussion

In the first set of experiments, pellets from a previous study in which they were exposed to γ -irradiation as well as H_2O_2 in several consecutive experiments, were being re-used.^[19] Figure 1 shows the results from several H_2O_2 exposures on pellets Gd45 and Gd80 from this study, in the presence (points) and absence (triangles) of H_2 .

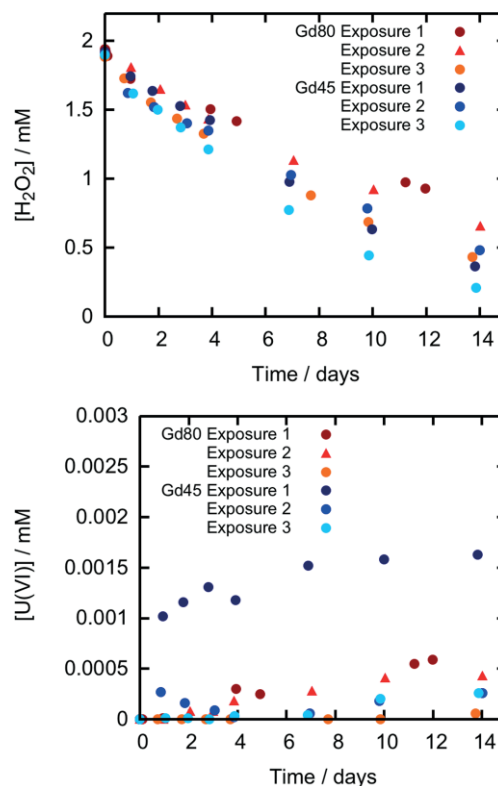


Figure 1. H_2O_2 consumption (top) as well as U^{VI} release (bottom) for pellets Gd45 orange/red and Gd80 green. Points correspond to exposures in 40 bar H_2 and triangles to exposures in 5 bar N_2 .

From Figure 1 top it becomes clear that the reactivity of the pellets towards H_2O_2 is very similar without a significant influence of neither, the atmosphere nor the doping level. Previous exposures under N_2 purging reveal a similar reactivity of the pellets.^[19] Figure 1 bottom shows the corresponding plot for uranium release. The uranium release from all samples is extremely small and close or even below the detection limit of 0.001 mM for the method. Interestingly, the uranium release for the first H_2O_2 exposure for pellet Gd45 is slightly above the detection limit but still well below the release that was previously reported.^[19] Due to the generally low uranium release from pellets Gd80 and Gd45, an inhibiting effect of H_2 could not be observed.

A higher uranium release was observed for the pre-used pellet Gd30, which has a lower doping level than Gd45 and Gd80. Results for both H_2O_2 consumption and uranium release are shown in Figure 2. Three experiments were performed on Gd30. The first exposure to H_2O_2 was in 5 bar N_2 whereas exposure 2 and 3 where in 40 bar H_2 . The H_2O_2 consumption on pellet Gd30 is similar to the consumptions on Gd45 and Gd80. This observation is in line with the previous study.^[19] For the uranium release, we see a similar overall trend as for pellet Gd45, where the first exposure results in a slightly higher uranium release compared to the second and third exposure.

For Gd30 the decrease in uranium release for consecutive H_2O_2 exposures could either be due to the potential effect of H_2 as proposed in,^[24] or it could be due to passivation of the pellet surface at high H_2O_2 exposures.^[28]

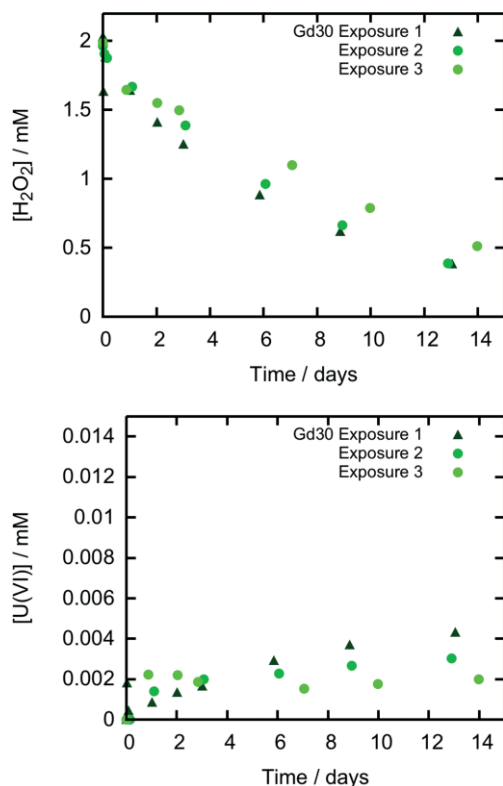


Figure 2. H_2O_2 consumption (top) as well as U^{VI} release (bottom) for pellet Gd30. Points correspond to exposures in 40 bar H_2 and triangles to exposures in 5 bar N_2 .

To assess whether the decrease in uranium release is attributed to passivation of the pellet surface due to previous H_2O_2 -exposures, the experiments were repeated on a pellet (Gd30N) that was not used in previous experiments and therefore never exposed to H_2O_2 . The new pellet was first exposed to 2 mM H_2O_2 in a 40 bar H_2 atmosphere to revert the order of exposures. The second H_2O_2 exposure was under N_2 atmosphere. The results for both exposures are shown in Figure 3.

From the figure it becomes clear, that the uranium release during the first exposure is higher than the second exposure, which is again higher than the U^{VI} release measured on the pre-used twin pellet Gd30 (Figure 2). The decrease in yield with each new H_2O_2 exposure matches the overall trend from previous observations for un-doped UO_2 pellets.^[28] A plot of dissolution yields vs. H_2O_2 exposures for Gd30N as well as Gd30, Gd45 and Gd80, taking the exposure history of all pellets into account, is shown in Figure 4.

From the figure it becomes clear, that the initial dissolution yields of Gd-doped UO_2 during the first H_2O_2 exposure are generally lower than for un-doped UO_2 ^[19,29] and decrease with increasing doping level due to a change in redox reactivity attributed to increased Gd-doping. In addition, an overall passivating effect as a function of H_2O_2 exposure becomes evident for each pellet implying an additional change in redox reactivity. We ascribe this latter change in redox reactivity to an irreversible alteration of the pellet surface, which is well in line with previous findings for un-doped UO_2 .^[28]

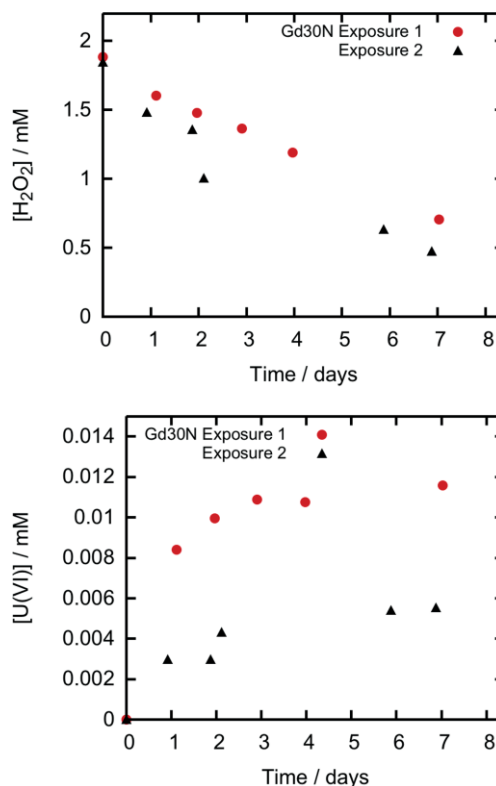


Figure 3. H_2O_2 consumption (top) as well as U^{VI} release (bottom) for pellet Gd30N. Red points correspond to exposures in 40 bar H_2 and black triangles to exposures in 5 bar N_2 .

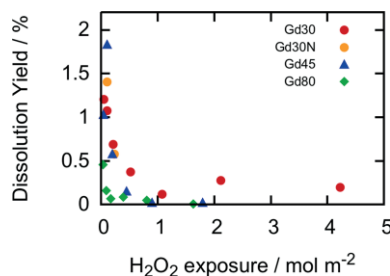


Figure 4. Dissolution yields vs. H_2O_2 exposure for Gd30 red points, Gd30N orange points, Gd45 blue triangles as well as Gd80 green diamonds. Closed symbols are exposures in N_2 , open symbols are exposures in H_2 .

It should be noted that most of the experiments on which Figure 4 is based were carried out under N_2 but some were also carried out under 40 bar H_2 . However, since the trends are continuous without sudden drops in dissolution yields when the atmosphere was changed from N_2 to H_2 , a significant H_2 -effect on H_2O_2 -induced dissolution of Gd-doped UO_2 must be ruled out.

In a previous study, the U^{VI} concentration was found to decrease in systems containing fragments of Gd-doped UO_2 -pellets under H_2 atmosphere. The rate of U^{VI} -decrease was found to depend on the H_2 -pressure.^[24] In these experiments an aqueous solution containing 2 ppm of U^{VI} , 2 mM HCO_3^- and 10 mM NaCl was deoxygenated. Thereafter, fragments of the Gd-doped UO_2 pellets were added to the solution and the uranium concentrations were measured over time in the presence and ab-

sence of H₂. At 5 MPa H₂, the half-life of U^{VI} in solution was about 1 week. Considering that the solid surface area to solution volume ratio was in the order of 5 m⁻¹ we can estimate the second order rate constant to 2 × 10⁻⁷ m s⁻¹. In the present work, the solid surface area to solution volume ratio is slightly higher. Hence, the reduction of U^{VI} could be faster. Nevertheless, the fact that the change in redox reactivity attributed to H₂O₂-exposure history completely overshadows any other effect makes it impossible to assess the potential H₂-effect. However, it should be pointed out that the H₂-effect, if present, does not have a significant impact on H₂O₂-induced dissolution of UO₂.

The observed effect of H₂O₂-exposure history must be accounted for in future studies of H₂-effects on oxidative dissolution of UO₂-based materials. In addition, it would be advisable to re-evaluate previously published studies on this matter in view of the findings presented here. However, this requires detailed knowledge about the exposure history of the specimens used in the study.

Conclusion

The experimental results presented above give new insights on the effect of Gd-doping on the oxidative dissolution of (U_{1-x}Gd_x)O₂ (x = 0.03, 0.045, 0.08) under deep repository conditions. It was found that the uranium release from Gd-doped pellets is lower as compared to un-doped UO₂ pellets and decreases with increasing Gd-content as a larger fraction of the H₂O₂ undergoes catalytic decomposition on the pellet surface instead of oxidizing uranium when specimens are doped with Gd. In addition, it was found that the presence of 40 bar H₂ does not have an inhibiting effect on the oxidative dissolution of (U_{1-x}Gd_x)O₂ (x = 0.03, 0.045, 0.08). Instead the experimental results indicate an irreversible alteration of the pellet surfaces at high H₂O₂ exposures, which implies an additional change in redox reactivity. The passivation of specimens at high H₂O₂ exposures and their exposure history are crucial for future research and should also be considered for α-doped samples due to the constant production of radiolysis products including H₂O₂ on the UO₂ surface.

Experimental Section

Commercial UO₂ pellets with different Gd-doping levels were supplied from Westinghouse Electric Sweden AB and are listed in Table 1. Pellets Gd30, Gd45 and Gd80 were previously used and characterized.^[19] Pellet Gd30N is a twin pellet of Gd30 but it was not used for any experiments before being used in this study. Between individual experiments all pellets were stored in 10 mM HCO₃⁻ solution to facilitate the removal of an oxidized surface layer.

Table 1. Overview of Gd-doped pellets used in this study.

Sample ID	Gd-doping /wt-%
Gd30	3.0
Gd45	4.5
Gd80	8.0
Gd30N	3.0

Purified water (18.2 MΩ cm, Merck MilliQ) was used throughout the experiments and chemicals were of reagent grade unless otherwise stated.

Prior to an experiment each pellet was placed in 20 mL of fresh HCO₃⁻ solution for 16 h. Afterwards, the pellet was washed at least three more times in 50 mL of 10 mM HCO₃⁻ solution for 1 h under constant N₂ purging (≥ 99.999 %, Strandmøllen), or the washing was repeated until no further uranium release could be detected. After washing, the pellet was placed in fresh HCO₃⁻ solution and H₂O₂ was added immediately to reach a total volume of 50 mL, a HCO₃⁻ concentration of 10 mM and a H₂O₂ concentration of 2 mM. After the addition of H₂O₂, a 2 mL sample was taken from the solution to measure H₂O₂ and U^{VI} concentrations. The reaction vessel was then transferred into an aerated 2 L autoclave. The autoclave was closed and pressurized to 40 bar with H₂ (≥ 99.995 % Strandmøllen) or to 5 bar with N₂ within 15 min after the H₂O₂ addition.

U^{VI} as well as H₂O₂ concentrations in solution were measured over time on a UV/Vis spectrophotometer. U^{VI} was measured at 653 nm using the Arsenazo III method,^[30] whereas H₂O₂ was measured at 360 nm using the Ghormley triiodide method.^[31]

Acknowledgments

The Swedish Nuclear and Fuel Waste Management Company (SKB) is gratefully acknowledged for financial support. Westinghouse Electric Sweden is gratefully acknowledged for providing the pellets.

Keywords: Oxidative dissolution · Uranium · Surface chemistry · Kinetics · Spent nuclear fuel

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Received: February 10, 2020