



The effect of Y_2O_3 on the dynamics of oxidative dissolution of UO_2

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ABSTRACT

In this work, we have studied the impact of Y_2O_3 on the kinetics of oxidative dissolution of UO_2 and the consumption of H_2O_2 . The second order kinetics of catalytic consumption of H_2O_2 on Y_2O_3 was investigated in aqueous Y_2O_3 powder suspensions by varying the solid surface area to solution volume ratio. The resulting second order rate constant is 10^{-8} m s^{-1} , which is of the same magnitude as for the reaction between H_2O_2 and UO_2 . Powder experiments with mixtures of UO_2 and Y_2O_3 show that Y_2O_3 has no effect on the oxidative dissolution of UO_2 , whereas the consumption of H_2O_2 seems to be slightly slower in the presence of Y_2O_3 and H_2 respectively. UO_2 pellets with solid inclusions of Y_2O_3 show a decrease in oxidative dissolution by a factor of 3.3 and 5.3 under inert and hydrogen atmosphere, respectively. The rate of H_2O_2 consumption is similar for all cases and is well in line with kinetic data from powder experiments. The effects of H_2 and Y_2O_3 on the oxidative dissolution of UO_2 under gamma irradiation are similar to those found in experiments with H_2O_2 . No significant difference in dissolution between inert and reducing atmosphere can be observed for pure UO_2 .

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1. Introduction

Several countries using nuclear energy, plan to dispose their spent nuclear fuel in deep geological repositories. In general, these repositories consist of multiple barriers, where the fuel itself is usually considered to be the innermost barrier. After barrier failure, the dissolution of the uranium dioxide matrix will lead to release of highly radioactive fission products and actinides into the groundwater. Due to the presence of long-lived radionuclides, available experimental data must be extensively extrapolated (10^5 – 10^6 years) to assess the long term safety. Such experimental data include reactions affecting the dissolution and their corresponding rate constants.

Due to the inherent complexity of spent nuclear fuel, it can be difficult to draw mechanistic conclusions on the basis of spent nuclear fuel leaching experiments. Spent nuclear fuel consists of around 95% UO_2 , with the remaining 5% being radioactive fission products and actinides in various chemical states. Furthermore, the ionizing radiation causes radiolysis of the groundwater and, thereby, alters the otherwise reducing conditions. By starting with the simplest system (pure UO_2 [1]) and by gradually increasing the complexity (e.g. inclusions of noble metal particles [2,3], α -emitters [4,5], etc.), the mechanisms and kinetics can be determined and the interdependencies of the parameters can be evaluated. The knowledge about the inventory of the spent nuclear fuel at times relevant in the safety assessment of deep geological repositories

can then, in combination with the basic reaction mechanisms and rate constants, be used to predict the rate of oxidative fuel dissolution.

Relatively fresh spent nuclear fuel has a higher specific activity than the older fuel of significance in the safety analysis. Furthermore, α -radiation will become dominant within a few hundred years, while the importance of β - and γ -radiation decreases with time [6]. Hence, the ratios between the three types of radiation differ significantly between fresh spent nuclear fuel and older fuel of relevance in the safety analysis of a deep repository. While this problem can be circumvented by performing experiments on α -doped (e.g. U-233) UO_2 , other spent fuel properties (e.g. those affected by the presence of fission products) are not reproduced. SIMFUEL (UO_2 containing non-radioactive analogues of the fission products Y, Rh, Pd, Ru, Nd, Zr, Sr, Mo, La, Ce, Ba [7]) is a better chemical model of the fuel inventory, but its specific activity is much lower. Furthermore, the chemical complexity of SIMFUEL is rather significant. A compromise is to dope pure UO_2 with one single type of fission product. In this way, the effect of e.g. noble metal particle inclusions (often called ϵ -particles) and rare-earth metals substituting uranium in the UO_2 matrix (e.g. Y, La, Nd) on the dissolution can be studied independently.

Ionizing radiation from radionuclides in the fuel causes water radiolysis, resulting in the production of a mixture of oxidants and reductants. Under deep repository conditions, where the uranium accessible for radiolysis products is mostly in its reduced form (U(IV)), oxidation is kinetically favored [8]. Previous work showed that under granitic deep repository conditions, H_2O_2 is by far the most important radiolytic oxidant [9], promoting oxidation of the sparingly soluble U(IV) [10–12] to U(VI) and its

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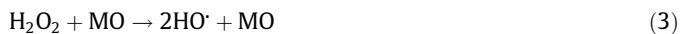
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subsequent dissolution. The solubility of U(VI) is significantly higher and increases even further through complex formation with HCO_3^- present in most groundwaters [13]. The basic mechanism can be seen in reactions (1) and (2).



This mechanism is only valid, if dissolution is not the rate determining step in the oxidative dissolution, which is the case in the presence of a minimum of 1 mM HCO_3^- [14]. In the absence of HCO_3^- , the formation of secondary phases (such as $\text{UO}_3 \cdot y\text{H}_2\text{O}$) is competing with dissolution [15].

Spent nuclear fuel [16–19], SIMFUEL [20,21], UO_2 pellets with palladium (as a model substance for metallic ϵ -phase particles) [2,3], α -doped [4,19] and pure UO_2 [2,3,22] have been studied in dissolution and electrochemical experiments. From experiments under H_2 atmosphere, it has been shown that spent nuclear fuel, α - and Pd-doped UO_2 show lower U(VI) dissolution [2–4,19,23,24], and that the corrosion potential of SIMFUEL is significantly reduced [20]. In the presence of Pd (or ϵ -phase metal particles), this effect is attributed to the catalytic ability of the noble metals in the surface reduction of U(VI) to U(IV) by H_2 [20] (and possibly to low dose rate γ -radiolysis in the case of α -doped UO_2 [25]). In kinetic experiments, pure UO_2 has been shown not to catalyze the reaction between H_2 and H_2O_2 [26]. While the catalytic effect of noble metals and its impact on the dissolution of the uranium dioxide matrix is well known, the possible impact of rare-earth metal oxides on oxidative UO_2 dissolution needs to be investigated further. One possibility for rare-earth metal oxides to decrease the oxidative dissolution of UO_2 is by catalytic decomposition of H_2O_2 . Previous studies have shown that some metal oxides do exhibit this catalytic behavior [27,28]. The catalysis and subsequent reactions are given by reactions (3)–(5).



H_2 can interfere with reaction (4) by competitively reacting with HO^\cdot (reaction (6)).



This will slow down the consumption of H_2O_2 and result in production of reducing H $^\cdot$. The latter being capable of inhibiting oxidative U(VI) dissolution by reacting with both H_2O_2 and U(VI).

The diverse behavior of fission products in the UO_2 matrix can be attributed to their dissimilar solubility [29] and redox properties. The solubility of Pd, Pt and other noble/non-noble metals in this type of oxide is very low and leads to inclusions in the metallic state. Other elements, e.g. many rare earth elements, have a high solubility in the oxide matrix where they substitute for uranium. Some elements are stable in their oxide form, but build their own oxide phases. A number of elements (including Sr and Zr), have a lower solubility than most rare earth elements, but still are present to some extent in the UO_2 matrix. If the concentration of one of these elements is too high, the fraction that exceeds the solubility exists as oxide or metallic inclusions [29].

X-ray photoelectron spectroscopic data on SIMFUEL suggest an increase in U(V) at the expense of U(IV) with increasing trivalent doping [21]. Furthermore, at doping levels up to 3 at.%, the electrical conductivity increases with increasing rare earth content. Between 3 at.% and 6 at.% of trivalent ions, He et al. [21] showed, the electrical resistivity increases again and reaches levels higher

than those of pure UO_2 (1120 and 982 Ω cm, respectively). An increase in doping level has also been found to have an effect on the lattice parameter [21,30–32]. While gadolinium and yttrium lead to a decrease, thorium and lanthanum increase the lattice parameter. In the case of spent nuclear fuel, substitution for tetravalent uranium by trivalent fission products does not lead to a significant oxidation of U(IV) to U(V) and U(VI), due to the reaction of elemental Mo in the fuel and Zr in the cladding with the excess oxygen [33].

Studies on the oxidation kinetics of solid solutions of $\text{UO}_2\text{--M}_2\text{O}_3$ (M = Y, La, Gd) in air have been performed [30,34,35]. The oxidation of pure UO_2 on the one hand is a known two-step reaction,



Solid $\text{UO}_2\text{--M}_2\text{O}_3$ solutions on the other hand show an increase in temperature and kinetic resistance towards U_3O_8 formation with increasing levels of rare earth doping [35]. Furthermore, it has been found that rare earth doping stabilizes U_4O_9 , and no U_3O_7 is formed as an intermediate.

Under the aqueous deep repository conditions mentioned above, where only H_2O_2 has to be considered as an oxidant, U(IV) is oxidized to the more soluble U(VI) and will rapidly be removed from the surface by HCO_3^- , resulting in a nearly perfectly reduced surface at any time [36–38]. While the rate of oxidation decreases in air when approaching full conversion to U_3O_8 [39], no such decrease can occur under oxidative aqueous conditions in the presence of HCO_3^- , where the surface properties remain constant.

While the influence of fission products on UO_2 oxidation in air has been studied extensively [39–41], not much is known about the effects of fission products on the kinetics of the oxidative dissolution of UO_2 in aqueous systems. In this work, the effect of yttrium as a model substance for rare earth elements on the dissolution of U(VI) was studied with powder mixtures and $\text{UO}_2\text{--Y}_2\text{O}_3$ solid solutions.

2. Experimental details

The depleted uranium dioxide powder came from Westinghouse Atom AB. The sodium hydrogen carbonate solution was prepared with NaHCO_3 p.a. from Merck, and the water used throughout the experiments was Millipore Milli-Q. The Y_2O_3 powder (99.99%) was purchased from Sigma–Aldrich. The Arsenazo III reagent used to analyze the uranium concentration was mixed from Arsenazo III p.a. powder from Fluka, and the puriss potassium iodide powder for measuring the H_2O_2 concentration came from KEBO lab. Both analytical methods have been described in detail [42–45]. All reagents were used as received.

Seven types of experiments were performed with: (1) Y_2O_3 powder in aqueous H_2O_2 suspension, (2) UO_2 powder in aqueous H_2O_2 suspension, (3) a mixture of UO_2 and Y_2O_3 powder in aqueous H_2O_2 suspension, (4) a pure UO_2 pellet in aqueous H_2O_2 solution, (5) a Y_2O_3 -doped UO_2 pellet in aqueous H_2O_2 solution, (6) a pure UO_2 pellet in aqueous solution exposed to external gamma irradiation and (7) a Y_2O_3 -doped UO_2 pellet in aqueous solution exposed to external gamma irradiation.

Experiments for determining the rate constant for the consumption of H_2O_2 on Y_2O_3 were conducted. A 100 mL solution with 10 mM HCO_3^- and 0.2 mM H_2O_2 was continuously stirred and purged throughout the experiment with N_2 or H_2 , respectively. Y_2O_3 powder was added and the H_2O_2 concentration measured every minute (at longer intervals when the H_2O_2 concentration started to level out). The samples (2 mL) were taken with a plastic syringe and filtrated through a 0.2 μm syringe filter. Five hundred microliter of sample were then analyzed according to the method described in [42–45]. The absorbance of the sample solution

without reagents was measured and compared to pure H₂O to detect background change.

To see possible effects of yttrium on the oxidative dissolution of U(IV), experiments with both, pure UO₂ powder and a mixture of 1 wt.% Y₂O₃ and 99 wt.% UO₂ powder in aqueous suspension containing H₂O₂ were conducted. To clean the UO₂ powder surface from U(VI), it was washed with a 10 mM HCO₃⁻ solution. After sedimentation of the powder, the solution was removed with a pipette and replaced. This procedure was repeated until the concentration of U(VI) reached a constant background level. Two hundred milligram UO₂ and 2 mg Y₂O₃ were then put in 100 mL 10 mM HCO₃⁻, and the solution was continuously stirred and purged with N₂ or H₂, respectively. After the addition of H₂O₂ (final concentration of 0.2 mM), the U(VI) and H₂O₂ concentrations were measured repeatedly, with intervals similar to before. The background dissolution of U(VI) without H₂O₂ was also measured and subtracted.

One pure UO₂ pellet and one with 0.3 wt.% Y₂O₃ as additive were produced by hot-pressing according to the method described in [2].

The pellet experiments were carried out in 2 mM H₂O₂ under inert and hydrogen atmosphere. The pellets were placed in 16 mL 10 mM HCO₃⁻ solution, and the U(VI) and H₂O₂ concentrations were measured after 0, 1, 2, 4 and 5 h. The solutions were purged either with N₂ or with H₂ before the start of the experiment and after each sample had been taken.

In addition, pellet experiments in a Cs-137MDS Nordion Gammacell 1000 Elite gamma source with a dose rate of 0.15 Gy s⁻¹ (determined by Frickedosimetry [46]) were performed (the oxidants are produced radiolytically). A 10 mL 10 mM HCO₃⁻ solution was purged with N₂ or H₂ respectively, after the pellet had been added. The irradiation times were 24, 48 and 72 h.

In the pellet experiments, a septum was used to sustain the desired atmospheres after purging.

3. Results and discussion

One possible way, by which yttrium(III)oxide could lower the rate of oxidative dissolution of spent nuclear fuel is by catalytic decomposition of H₂O₂. Considering the small amount of rare earth elements in spent nuclear fuel (less than 1%), the reaction rate constant of this decomposition reaction needs to be around two orders of magnitude larger than that of the oxidation of U(IV) to be competitive. In heterogeneous reactions, both, the surface area *S* of the solid material and the volume *V* of the solution are important parameters. These are accounted for by the factor *S/V* in second order rate equations. This factor also leads to the particular dimensions of the reaction rate constants, length per time. The second order rate equation for H₂O₂ consumption on a surface can be seen in Eq. (8), and the oxidative dissolution of UO₂ in Eq. (9).

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = k \frac{S}{V} [\text{H}_2\text{O}_2] \quad (8)$$

$$\frac{d[\text{U(VI)}]}{dt} = k \frac{S}{V} [\text{H}_2\text{O}_2] \quad (9)$$

In powder experiments, the rate constant for oxidative dissolution of U(IV) by H₂O₂ has been determined to $7.3 \times 10^{-8} \text{ m s}^{-1}$ [14]. With the diffusion limit for such a system being on the order of 10^{-6} m s^{-1} , the rate constant for consumption of H₂O₂ on Y₂O₃ cannot be more than 20-times higher than the rate constant for consumption on UO₂. Considering the relative amount of Y₂O₃ in the pellet, this cannot lead to a significant decrease in oxidative dissolution of U(IV).

From experiments with Y₂O₃ powder in aqueous H₂O₂ solutions, the pseudo-first order rate constants were determined. After a certain conversion of H₂O₂, a deviation from first order kinetics

was observed. This is most likely due to a change in rate determining step from adsorption to catalytic decomposition. In order not to underestimate the rate constants, data from the first 5 min. of the reactions were used to calculate the pseudo-first order rate constants. The second order rate constants for the H₂O₂ consumption on Y₂O₃ were obtained by plotting the pseudo-first order rate constants as a function of the solid surface area to solution volume ratio. This is illustrated in Fig. 1. The second order rate constant is given by the slope.

The resulting second order rate constants for the reaction between H₂O₂ and Y₂O₃ in N₂ and H₂ are on the order of 10^{-8} m s^{-1} . Compared to the value for the oxidation of U(IV) by H₂O₂ ($7.3 \times 10^{-8} \text{ m s}^{-1}$), the rate constant for H₂O₂ consumption by Y₂O₃ is of the same magnitude. Decomposition of H₂O₂ on Y₂O₃ is, therefore, not expected to influence the oxidative dissolution of U(IV) significantly at low doping levels.

Powder experiments with UO₂ and 1 wt.% Y₂O₃ in solution were conducted to confirm this. In Fig. 2a, it can be seen that the experiments under inert atmosphere and in H₂ do not show a significant difference in terms of U(VI) dissolution. The H₂O₂ consumption appears to be slightly slower in the Y₂O₃ cases, and also with H₂ being present (Fig. 2b).

Pellet experiments with pure UO₂ and UO₂ doped with 0.3 wt.% Y₂O₃ were conducted in aqueous H₂O₂ solution to study possible effects of incorporated Y₂O₃ on the oxidative dissolution of U(IV). The U(VI) concentration plotted vs. reaction time can be seen in Fig. 3a and the H₂O₂ concentration vs. reaction time in Fig. 3b.

As can be seen, the dissolution of U(VI) is slower in the Y₂O₃ cases. Furthermore, in both cases, with and without yttrium, the dissolution under one bar H₂ is slower than under inert atmosphere. The slight reduction in rate of oxidative dissolution of pure UO₂ under H₂, compared to inert atmosphere, has been observed earlier [2]. The resulting rates are presented in Table 1. The surface area used in the calculations is estimated to three times the geometrical surface area [47].

The consumption of H₂O₂ in Fig. 3b seems to be slightly slower with Y₂O₃-doping. The rates of H₂O₂ consumption can be seen in Table 2, together with the value calculated from the rate constant based on experiments with UO₂ powder [14]. The difference between the calculated and the measured values is less than a factor of 2.

When looking at the molar yields of U(VI) per consumed H₂O₂ (corresponding to the oxidative part of the H₂O₂ reactivity towards the surface), the difference between pure UO₂ ($(5.6 \pm 0.5)\%$ in N₂, $(4.2 \pm 0.2)\%$ in H₂) and Y₂O₃-doped UO₂ ($(2.5 \pm 0.3)\%$ in N₂,

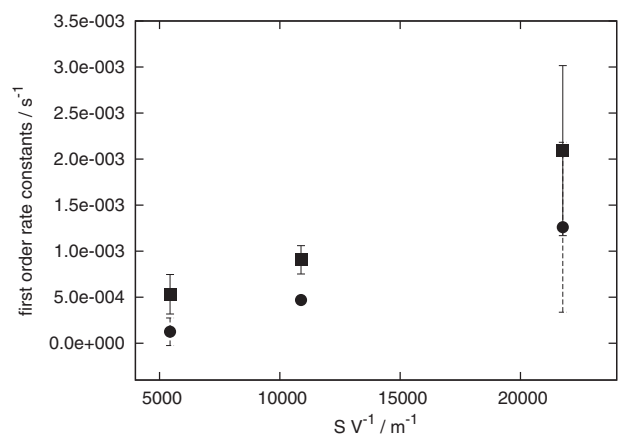


Fig. 1. First order rate constants vs. surface/volume ratio to determine the second order rate constants for the H₂O₂ consumption on Y₂O₃ under inert (squares) and H₂ (circles) atmosphere.

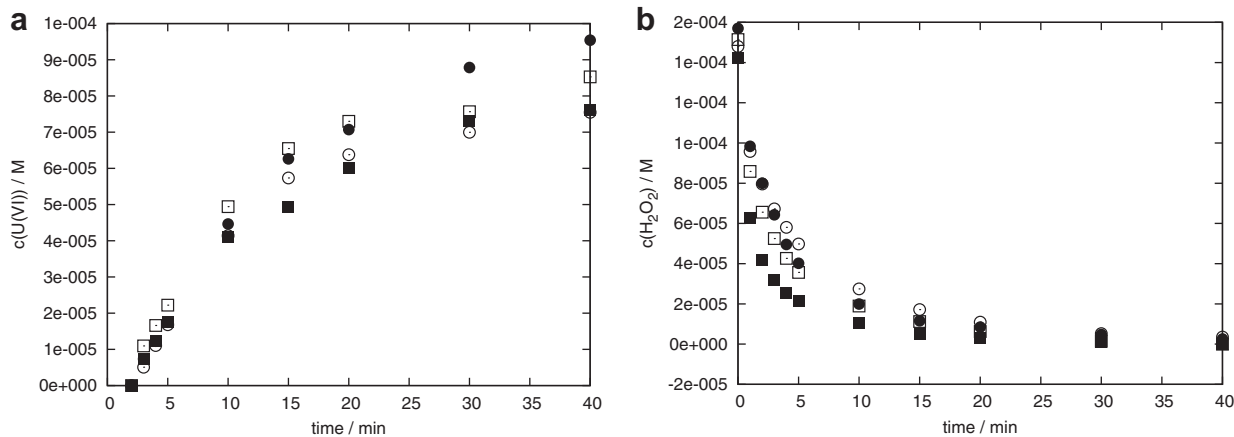


Fig. 2. U(VI) concentration (a) and H₂O₂ consumption (b) vs. time in powder experiments in 0.2 mM H₂O₂ with UO₂ in N₂ (filled squares)/H₂ (unfilled squares) and with UO₂ + Y₂O₃ in N₂ (filled circles)/H₂ (unfilled circles).

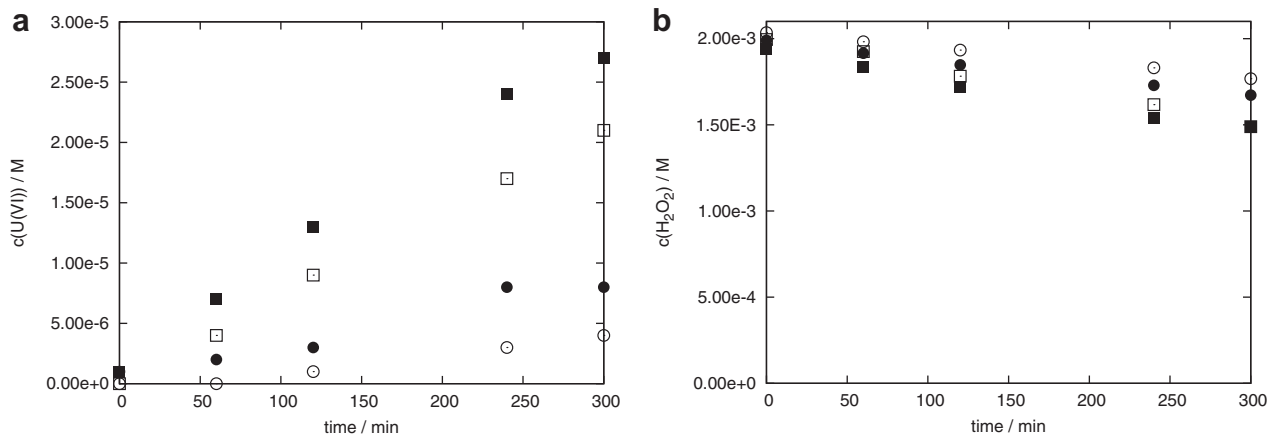


Fig. 3. U(VI) concentration (a) and H₂O₂ concentration (b) vs. time in pellet experiments in 2 mM H₂O₂ with UO₂ in N₂ (filled squares)/H₂ (unfilled squares) and with Y₂O₃-doped UO₂ in N₂ (filled circles)/H₂ (unfilled circles).

Table 1
Oxidative U(IV) dissolution rates and ratios with and without Y₂O₃-doping.

	UO ₂ /mol m ⁻² s ⁻¹	UO ₂ -Y ₂ O ₃ /mol m ⁻² s ⁻¹	UO ₂ /UO ₂ -Y ₂ O ₃ ratio
Inert atmosphere	(13.0 ± 0.7) × 10 ⁻⁹	(4.0 ± 0.5) × 10 ⁻⁹	3.3 ± 0.4
Hydrogen	(10.5 ± 0.3) × 10 ⁻⁹	(2.0 ± 0.1) × 10 ⁻⁹	5.3 ± 0.4

Table 2
Measured H₂O₂ consumption and the calculated value in mol m⁻³ s⁻¹.

	UO ₂	UO ₂ -Y ₂ O ₃	Calculated
Inert atmosphere	(25.5 ± 1.7) × 10 ⁻⁶	(17.5 ± 0.5) × 10 ⁻⁶	(16 ± 1) × 10 ⁻⁶
Hydrogen	(28.0 ± 1.3) × 10 ⁻⁶	(8.8 ± 0.2) × 10 ⁻⁶	

(1.5 ± 0.1)% in H₂) is more than a factor of two. As shown above, the rate constant for the reaction between H₂O₂ and Y₂O₃ is of the same magnitude as the H₂O₂ reactivity towards UO₂. Hence, a surface coverage of 50% Y₂O₃ would be required to account for the observed difference in oxidation yields. This seems unlikely for a material with 0.3 wt.% Y₂O₃.

One possibility for incorporated Y₂O₃ to decrease the dissolution of the UO₂ matrix could be due to a change in the matrix oxide structure. Beside a decrease in the lattice parameter and a stabilization of the U₄O₉ phase with increasing yttrium content, electrochemical experiments on SIMFUEL, by He et al. [21], showed a

decrease in current for dissolution (UO_{2+x} → UO₂²⁺) with an increase in doping level. The changes in the oxide structure could lead to the observed change in electrochemical behavior and the decrease in the oxidative dissolution of U(IV).

SEM images of the pure UO₂ pellet and the one doped with 0.3 wt.% Y₂O₃ can be seen in Fig. 4.

As can be seen, the grain boundaries are easily identified on the pure UO₂ pellet while the Y₂O₃-doped pellet lacks this feature, suggesting a smaller surface area of the doped pellet. This could partly explain the difference in reactivity towards H₂O₂. Due to the small amounts of Y₂O₃ in the UO₂ matrix, no yttrium can be detected by EDX.

The dissolution of U(VI) during gamma irradiation can be seen in Fig. 5. The effects of hydrogen and Y₂O₃ on the oxidative dissolution are similar to the experiments with H₂O₂, but no significant difference in dissolution can be observed between inert and reducing atmosphere with the pure UO₂ pellet. The oxidative dissolution of U(IV) is slower than in the experiments in 2 mM H₂O₂ aqueous solutions, since the H₂O₂ concentration is lower. Also here, the ratios between the oxidative dissolution rates of the pure UO₂ and the Y₂O₃-doped pellet are around three and five in N₂ and H₂, respectively.

The relative increase in catalytically decomposed H₂O₂ in experiments with Y₂O₃-doped UO₂ pellets is in line with the mechanism shown in reactions (3)–(5). With the doped metal oxide matrix being more resistant to oxidation, catalytic decomposition is

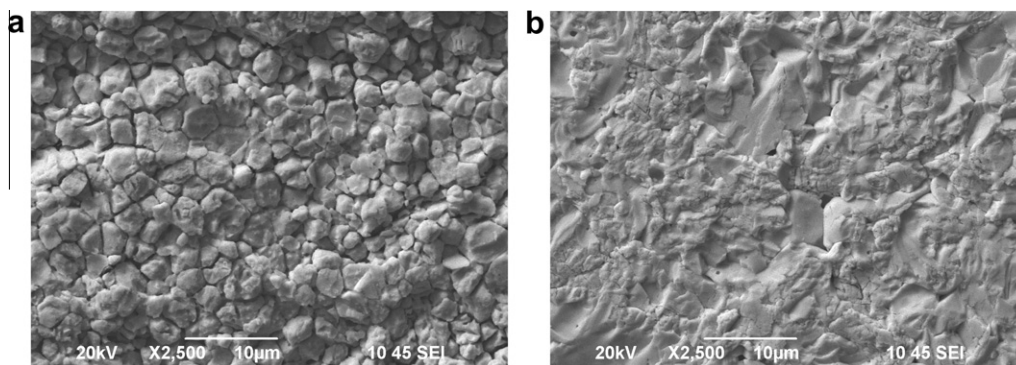


Fig. 4. SEM images of the pure UO₂ pellet (a) and with 0.3 wt.% Y₂O₃ inclusions (b).

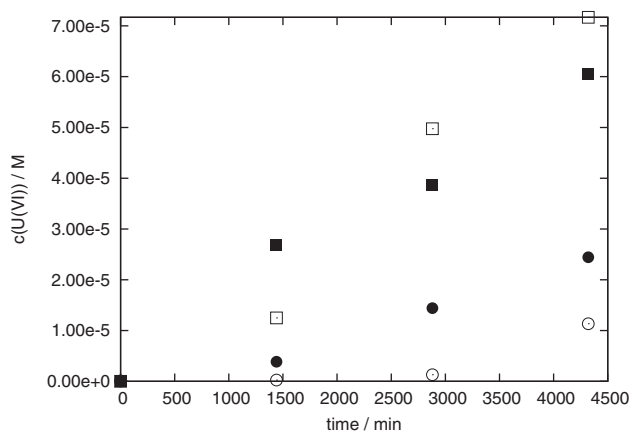


Fig. 5. U(VI) concentration vs. time in pellet experiments during γ -irradiation with UO₂ in N₂ (filled squares)/H₂ (unfilled squares) and with Y₂O₃-doped UO₂ in N₂ (filled circles)/H₂ (unfilled circles).

avored. This is most likely due to a raise in activation energy for the oxidation reaction. The larger effect of H₂ on the consumption of H₂O₂ and the molar yields of U(VI) per consumed H₂O₂ can be explained by reaction (6).

In conclusion, Y₂O₃ inclusions decrease the reactivity of UO₂ towards H₂O₂ and the molar yields for the oxidative dissolution of U(IV). In order to fully explain the effect of trivalent doping, further investigation is needed.

Acknowledgments

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