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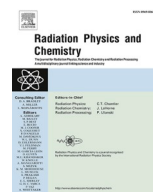
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Citation for the original published paper (version of record):

Hansson, N., Jonsson, M. (2023). Exploring  $H_2$ -effects on radiation-induced oxidative dissolution of  $UO_2$ -based spent nuclear fuel using numerical simulations. Radiation Physics and Chemistry, 210. <http://dx.doi.org/10.1016/j.radphyschem.2023.111055>

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# Exploring H<sub>2</sub>-effects on radiation-induced oxidative dissolution of UO<sub>2</sub>-based spent nuclear fuel using numerical simulations

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## ARTICLE INFO

Handling Editor: Dr. Jay Laverne

### Keywords:

Oxidative dissolution

UO<sub>2</sub>

H<sub>2</sub>O<sub>2</sub>

Hydrogen effect

Surface bound hydroxyl radical

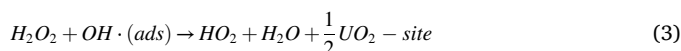
## ABSTRACT

Using a recently developed approach for numerical simulation of radiation-induced oxidative dissolution of spent nuclear fuel, we have explored the impact of three possible contributions to the inhibiting effect of molecular hydrogen. The three contributions are (1) effect on oxidant production in irradiated water, (2) reduction of oxidized uranium catalyzed by noble metal inclusions (fission products) and (3) reaction with surface-bound hydroxyl radicals preventing the oxidation of uranium. The simulations show that the first contribution is of fairly small importance while the second contribution can result in complete inhibition of the oxidative dissolution. This is well in line with previous work. Interestingly, the simulations imply that the third contribution, the reaction between H<sub>2</sub> and the surface-bound hydroxyl radical formed upon reaction between the radiolysis product H<sub>2</sub>O<sub>2</sub> and UO<sub>2</sub>, can account for the inhibition observed in systems where noble metal inclusions are not present. This is discussed in view of previously published experimental data.

## 1. Introduction

Handling the long-term radiotoxic used nuclear fuel is one of the main challenges of the nuclear industry. Several countries have decided to use a once-through nuclear fuel cycle where the used nuclear fuel is placed in a geological repository until the radiotoxicity level has decreased to levels corresponding to a natural uranium ore. This means that the repository must stay intact for 10<sup>5</sup>–10<sup>6</sup> years. To achieve this, a combination of natural and engineered barriers is used. The licensing process relies on safety assessments accounting for various scenarios. One unlikely, yet very relevant, scenario is complete barrier failure allowing groundwater intrusion into the canister containing the used nuclear fuel. Most fuels are based on UO<sub>2</sub>. After use in a reactor, only a few percent of the material has been transformed into fission products and heavier actinides. Therefore, the chemical behavior of used nuclear fuel exposed to groundwater can be expected to be similar to that of UO<sub>2</sub>. In the slightly reducing groundwaters found at several potential repository sites, the solubility of UO<sub>2</sub> is very low and one would expect very slow dissolution of the fuel matrix. However, the highly radioactive fission products and heavier actinides present induce radiolysis of the surrounding groundwater, producing oxidants (OH<sup>•</sup>, HO<sub>2</sub><sup>•</sup> and H<sub>2</sub>O<sub>2</sub>) and reductants (e<sub>aq</sub><sup>-</sup>, H<sup>•</sup> and H<sub>2</sub>). For kinetic reasons, the oxidants will

dominate the initial surface chemistry and oxidize the sparsely soluble UO<sub>2</sub> to significantly more soluble U(VI) and thereby induce oxidative dissolution of the fuel matrix. This process has been extensively studied for decades and the level of mechanistic understanding can be considered to be fairly high. According to some of the more recent studies, the radiolytic oxidant driving the process is primarily H<sub>2</sub>O<sub>2</sub> and the mechanism involves the formation of surface-bound hydroxyl radicals as a common intermediate for oxidation of UO<sub>2</sub> and catalytic decomposition of H<sub>2</sub>O<sub>2</sub> (Ekeröth et al., 2006; Barreiro Fidalgo et al., 2018). These reactions are summarized below.



The adsorption site for H<sub>2</sub>O<sub>2</sub> is referred to as UO<sub>2</sub> – site and the surface-bound hydroxyl radical is referred to as OH<sup>•</sup>(ads). In systems where significant amounts of UO<sub>2</sub><sup>2+</sup> are present in solution, H<sub>2</sub>O<sub>2</sub> can form ternary complexes with UO<sub>2</sub><sup>2+</sup> and HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> or with UO<sub>2</sub><sup>2+</sup> and

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<https://doi.org/10.1016/j.radphyschem.2023.111055>

Received 11 April 2023; Received in revised form 17 May 2023; Accepted 22 May 2023

Available online 23 May 2023

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$\text{Cl}^-$  in salt brines (Zanonato et al., 2012). It has been shown that the reactivity of  $\text{H}_2\text{O}_2$  towards the  $\text{UO}_2$ -surface is attributed to the fraction of free  $\text{H}_2\text{O}_2$  (Olsson et al., 2022). Complexed  $\text{H}_2\text{O}_2$  appears to be significantly less reactive.

In general, the overall mechanism for the radiation chemistry of water and the surface reactions involved in oxidative dissolution of the fuel matrix is quite complex. Therefore, numerical models are required for the safety assessment. Very recently, we developed a numerical model with spatial and temporal resolution taking the geometrical dose distribution, radiation chemistry of water and surface reactions into account (Hansson et al., 2023). The surface reactions are described on the basis of the mechanism above. This model can be regarded as a starting point for exploring the potential impact of groundwater constituents.

Molecular hydrogen is a radiolysis product, and it can also be formed upon anoxic corrosion of iron-containing materials. Since canisters for used nuclear fuel are usually constructed with a cast-iron insert for mechanical support, complete barrier failure implies contact between anoxic groundwater and iron. As the depth of the geological repositories is usually hundreds of meters, considerable concentrations of  $\text{H}_2$  can be produced before gas bubbles are formed (Bonin et al., 2000). Hence,  $\text{H}_2$  can become a major groundwater constituent inside a breached canister. There are numerous experimental studies showing that  $\text{H}_2$  can retard or completely inhibit radiation-induced oxidative dissolution of  $\text{UO}_2$ -based materials (Cui et al., 2008; Röllin et al., 2001; Carbol et al., 2005; Broczkowski et al., 2005; Trummer et al., 2008; Eriksen et al., 2008; Muzeau et al., 2009; Carbol et al., 2009b). The impact of  $\text{H}_2$  on the process has partly been attributed to the radiolysis of water where  $\text{H}_2$  will affect the production of oxidants. It has also been shown that fission products present as noble metal inclusions can catalyze the reduction of oxidized  $\text{UO}_2$  by  $\text{H}_2$ . The noble metal inclusions are referred to as  $\epsilon$ -particles and consist of Mo, Tc, Rh, Ru and Pd solid solution. This should be the main effect and complete inhibition is expected already at very low  $\text{H}_2$  concentrations. The noble metal inclusions have also been proposed to catalyze the reaction between  $\text{H}_2\text{O}_2$  and  $\text{H}_2$  as well as the oxidation of  $\text{UO}_2$  by both  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  (Trummer et al., 2008, 2009; Nilsson and Jonsson, 2008a, 2008b; Maier and Jonsson, 2019). A third mechanism that has been discussed is the reaction between  $\text{H}_2$  and the surface-bound hydroxyl radical (Bauhn et al., 2018a). This reaction would compete with the oxidation of  $\text{U(IV)}$  as well as the reaction between  $\text{H}_2\text{O}_2$  and the surface-bound hydroxyl radical and thereby slow-down the oxidative dissolution.

In this work we have added the two surface processes that are believed to contribute to the observed  $\text{H}_2$  effect to the recently developed model. Simulations are performed in order to assess the relative importance of the three  $\text{H}_2$  effects mentioned above.

## 2. Method and models

$\text{UO}_2$  fuel with a dose rate of 1 Gy/h, 5.5 MeV  $\alpha$ -particle energy as well as 95% theoretical density was modelled. The numerical model and the parameters on which it is based are described in detail in Hansson et al. (2023). A  $\text{UO}_2$  surface site density of  $2.1 \cdot 10^{-4} \text{ mol m}^{-2}$  derived in the work of Hossain et al. was used (Hossain et al., 2006). All surface concentrations were expressed using the  $\text{S} \cdot \text{V}^{-1}$  ratio in combination with the surface site density. In all simulations a 50  $\mu\text{m}$  single layer system was modelled for  $10^3$  steps of 100 s each.

The reactions in the  $\text{H}_2\text{O}_2/\text{UO}_2$  system are reactions (1)–(3). The rate constants for these reactions are referred to as  $\text{ks1}$ ,  $\text{ks2}$  and  $\text{ks3}$ . Reaction (4) is a homogeneous reaction in solution. This reaction and the corresponding rate constant are already included in the general radiolysis model (Hansson et al., 2023). As the product of reaction (2) is  $\text{U(V)}$ , we must also include a surface disproportionation reaction to produce soluble  $\text{U(VI)}$  (Li et al., 2023). This reaction is written as  $\text{U(V)}\text{O}_2 + \text{U(V)}\text{O}_2 \rightarrow \text{U(VI)}\text{O}_2(\text{s})$  with a rate constant denoted  $\text{ks4}$ .

Based on fitting to experimental data, the rate constants were

previously determined to  $\text{ks1} = 0.462 \text{ M}^{-1} \text{ s}^{-1}$ ,  $\text{ks2} = 0.191 \text{ s}^{-1}$ ,  $\text{ks3} = 197 \text{ M}^{-1} \text{ s}^{-1}$  and  $\text{ks4} = 34.1 \text{ M}^{-1} \text{ s}^{-1}$  (Hansson et al., 2023). To quantify the reactive surface the solid surface area to solution volume ratio and a previously determined reactive site density have been used.

The reactions that are required to simulate the impact of  $\text{H}_2$  on radiation induced dissolution of  $\text{UO}_2$  are presented below. In the original version of the model, the rate of dissolution of oxidized uranium was not an issue as there were no competing reactions. Therefore,  $\text{U(VI)}$  was assumed to dissolve as soon as it was formed (Hansson et al., 2023). However, to describe the noble metal particle catalyzed reduction of  $\text{U(VI)}$  back to  $\text{U(IV)}$  we must also consider the kinetics for  $\text{U(VI)}$  dissolution since this is a competing reaction. In a system containing  $\text{HCO}_3^-$ , the rate of  $\text{U(VI)}$  dissolution will depend on the  $\text{HCO}_3^-$  concentration (Hossain et al., 2006) and the rate limiting step can be described as a bimolecular reaction between  $\text{HCO}_3^-$  and oxidized  $\text{UO}_2$ . The reaction between  $\text{H}_2$  and the surface-bound hydroxyl radical can simply be described in the same way as the corresponding reaction for  $\text{H}_2\text{O}_2$  (i.e., analogous to reaction (3)). The noble metal particle catalyzed reduction of  $\text{U(VI)}$  by  $\text{H}_2$  and oxidation of  $\text{U(IV)}$  by  $\text{H}_2\text{O}_2$  are a bit more complicated to describe. Experimentally, the rate limiting step has been found to be the encounter between the solute ( $\text{H}_2$  or  $\text{H}_2\text{O}_2$ ) the noble metal particle (Trummer et al., 2008). To account for this experimental observation, both processes have been divided into two reactions each where the first reaction is rate determining. In the reactions involving noble metal particles,  $\epsilon$  – site denotes the noble metal particle. In the reaction with  $\text{H}_2$ , a hypothetical product “red” is formed while in the reaction with  $\text{H}_2\text{O}_2$ , a hypothetical product “ox” is formed. The reducing product “red” rapidly reduces  $\text{U(VI)}$  to  $\text{U(IV)}$  while the oxidizing product “ox” rapidly oxidizes  $\text{U(IV)}$  to  $\text{U(VI)}$ . This is a way of enabling a system with only bimolecular (or unimolecular) reactions as well as a way of maintaining a realistic mass balance. The reactions mentioned above are summarized in Table 1.

The rate constants of these reactions are discussed in the next section.

## 3. Results and discussion

### 3.1. Rate constants

The dissolution of  $\text{UO}_2^{2+}$  in carbonate solution, described as a bimolecular reaction between  $\text{HCO}_3^-$  and  $\text{U(VI)}$  on the surface as written in Table 1, has been found to be close to diffusion controlled (Hossain et al., 2006). Therefore, we set the value for  $\text{ks5} = 10^3 \text{ M}^{-1} \text{ s}^{-1}$  which corresponds to the diffusion controlled rate constant for a reaction between a solute and the surface in this particular heterogeneous system (i.e., the system for which  $\text{ks1}$ – $\text{ks4}$  were determined) (Jonsson, 2010). The rate constant for the reaction between  $\text{H}_2$  and the surface-bound hydroxyl radical,  $\text{ks6}$ , is not known experimentally. However, from homogeneous reactions in solution we know that the rate constant for the reaction between the hydroxyl radical and  $\text{H}_2$  is more or less the same as the rate constant for the reaction between the hydroxyl radical and  $\text{H}_2\text{O}_2$  (Christensen et al., 1982; Christensen and Sehested, 1983). Based on this,  $\text{ks6}$  could be set equal to  $\text{ks3}$ . However, the surface-bound hydroxyl radical has been shown to be considerably less reactive than the free hydroxyl radical. The reduction potential of the surface-bound hydroxyl radical is more than 300 mV lower than for the free hydroxyl radical

**Table 1**

The extended surface site reaction system with epsilon particle reactions.

$\text{HCO}_3^- + \text{U(VI)}\text{O}_2(\text{s}) \rightarrow \text{UO}_2\text{CO}_3(\text{aq}) + \text{UO}_2 - \text{site}$	$\text{ks5}$
$\text{OH} \cdot (\text{ads}) + \text{H}_2 \rightarrow \text{H} \cdot + \frac{1}{2} \text{UO}_2 - \text{site} + \text{H}_2\text{O}$	$\text{ks6}$
$\epsilon - \text{site} + \text{H}_2 \rightarrow \text{red}$	$\text{ks7}$
$\text{red} + \text{U(VI)}\text{O}_2(\text{s}) \rightarrow \text{UO}_2 - \text{site} + 2\text{H}^+ + \epsilon - \text{site}$	$\text{ks8}$
$\text{H}_2\text{O}_2 + \epsilon - \text{site} \rightarrow \text{ox}$	$\text{ks9}$
$\text{ox} + \text{UO}_2 - \text{site} \rightarrow \text{U(VI)}\text{O}_2(\text{s}) + \epsilon - \text{site} + 2\text{OH}^-$	$\text{ks10}$

(Lawless et al., 1991). This would imply that hydrogen abstraction from  $H_2$  would not be an exothermic reaction for the surface-bound hydroxyl radical while hydrogen abstraction from  $H_2O_2$  still would be. Hence, it is likely that  $ks_6$  is considerably lower than  $ks_3$ . To account for all possibilities,  $ks_6$  has been varied between 0 and  $10^3 \text{ M}^{-1} \text{ s}^{-1}$ .

Experimental work on  $UO_2$  pellets containing Pd-particles to mimic the effects of noble metal inclusions have shown that the reaction between  $H_2$  and the noble metal inclusions is close to diffusion controlled (Trummer et al., 2008). In other words,  $ks_7$  should be close to  $10^3 \text{ M}^{-1} \text{ s}^{-1}$  (the limit for a diffusion controlled rate constant in this system). The subsequent reaction ( $red + U(VI)O_2(s)$ ) should have a rate constant high enough not to affect the reduction of  $U(VI)$  (i.e., not to become rate-determining) but low enough not to cause numerical problems. A value of  $ks_8 = 10^{16} \text{ M}^{-1} \text{ s}^{-1}$  was found to satisfy these boundary conditions.

Work on the same Pd-containing  $UO_2$  pellets also showed that the noble metal catalyzed oxidation of  $U(IV)$  by  $H_2O_2$  has a rate constant 100 times higher than that of the direct reaction between  $H_2O_2$  and  $UO_2$  (Trummer et al., 2008). For this reason,  $ks_9$  is set to 100 times that of  $ks_1$ . The subsequent reaction ( $ox + U(IV)O_2(s)$ ) has the same rate constant as  $ks_8$  since it must satisfy the same boundary conditions.

### 3.1.1. Impact of $H_2$ on the radiolytic production of oxidants

The impact of  $H_2$  on the oxidative dissolution of  $UO_2$  was explored using the original version of the model (i.e., without the reactions presented in Table 1). In this version, oxidized  $UO_2$  is assumed to dissolve instantly. This is a reasonable assumption for systems containing 10 mM  $HCO_3^-$  but not for systems with  $HCO_3^-$  concentrations lower than 1 mM (Hossain et al., 2006). In Table 2, the absolute dissolution rates for the system without initial  $H_2$  at different dose rates are given along with the relative dissolution rates at different initial  $H_2$  pressures.

As can be seen,  $H_2$  appears to increase the rate of dissolution slightly for dose rates up to  $2.78 \cdot 10^{-2} \text{ Gy s}^{-1}$ . This effect is only present in solutions with  $HCO_3^-$ , which can scavenge the radicals that cause a protective effect towards  $H_2O_2$  under relatively low dose rates. At higher dose rates and at  $H_2$  pressures above 1 bar, the relative dissolution rate is reduced.

Impact of  $H_2$  reacting with surface-bound hydroxyl radicals.

As stated above, it is reasonable to assume that the rate constant for the reaction between  $H_2$  and the surface-bound hydroxyl radical,  $ks_6$ , should be lower than the corresponding rate constant for  $H_2O_2$ ,  $ks_3$ . In any case, the rate constant cannot exceed what is defined as diffusion controlled in the current system. To explore the impact of this reaction on the dissolution of  $UO_2$ , simulations were performed at a range of  $ks_6$  from 0 to  $10^3 \text{ M}^{-1} \text{ s}^{-1}$  at 40 bar  $H_2$ . The results are shown in Fig. 1.

As can be seen, the maximum possible impact of this reaction is a reduction of the dissolution rate by slightly more than two orders of magnitude. However, it is more reasonable to use a rate constant lower than  $ks_3$ . In the following, we have used a rate constant of  $50 \text{ M}^{-1} \text{ s}^{-1}$  which is 25% of  $ks_3$ . To further explore the impact of this reaction we have determined the steady-state dissolution rate of uranium at different  $H_2$  pressures using  $ks_6 = 50 \text{ M}^{-1} \text{ s}^{-1}$ . The results are summarized in Table 3.

It is interesting to note that the dissolution rate at 0 bar initial  $H_2$  is also affected by including the reaction between  $H_2$  and the surface-

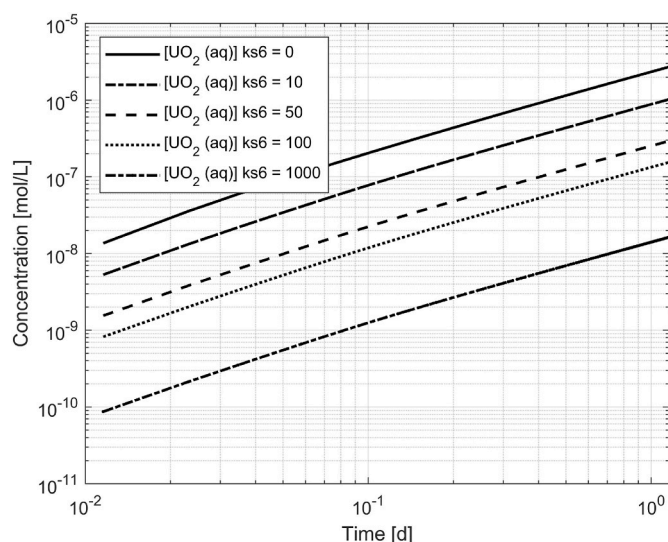


Fig. 1. Different constants for  $ks_6$ , and its influence on the dissolution of  $UO_2$  considering no  $\epsilon$ -particles and a value for  $ks_5 = 10^3 \text{ M}^{-1} \text{ s}^{-1}$  in a 50  $\mu\text{m}$  single layer system with 100 s time steps.

bound hydroxyl radical at higher dose rates. This can be attributed to radiolytically produced  $H_2$ .

Looking at the impact of different initial  $H_2$  pressures it is evident that the relative dissolution rate decreases with increasing  $H_2$  pressure for all dose rates included in the study. It is also evident that the reduction in dissolution rate is most significant at the highest dose rate. However, it should be noted that the main part of this reduction is seen already at 0 bar initial  $H_2$ . At dose rates up to  $2.78 \cdot 10^{-2} \text{ Gy s}^{-1}$ , 40 bar  $H_2$  reduces the rate of dissolution by one order of magnitude. At higher dose rates, the reduction approaches two orders of magnitude.

Impact of noble metal particle catalyzed reactions.

The noble metal particle catalyzed reduction of  $U(VI)$  by  $H_2$  on the surface of  $UO_2$  has previously been claimed to be the major  $H_2$  effect (Trummer and Jonsson, 2010). As discussed above, the fission products present as noble metal inclusions also catalyze oxidation of  $UO_2$ . To explore the impact of noble metal particle catalyzed reactions we simulated the system taking also these reactions into account. The results at 0 bar initial  $H_2$  are summarized in Table 4.

From this table it is evident that the noble metal particle catalyzed reduction of  $U(VI)$  is quite effective already when water radiolysis is the only source of  $H_2$ . At the highest  $ks_7$  (diffusion controlled), oxidative dissolution is effectively inhibited at all dose rates studied while for  $ks_7 = 10^2 \text{ M}^{-1} \text{ s}^{-1}$ , oxidative dissolution still occurs at the three highest dose rates. However, the rate of dissolution is reduced 1-2 orders of magnitude. Simulations at the initial  $H_2$  pressures shown in Table 3 show that the oxidative dissolution is completely inhibited in all cases. To illustrate the efficiency of the inhibition we have identified the minimum initial  $H_2$  pressure required to suppress oxidative dissolution of  $UO_2$  at different dose rates and noble metal particle surface coverage. The results are shown in Table 5.

Table 2

Dissolution rates and relative dissolution rates under varying dose rates and  $H_2$  pressures in 10 mM  $NaHCO_3$  solution without  $H_2$  surface reactions.

D [ $\text{Gy s}^{-1}$ ]	Relative dissolution rate 10 mM $NaHCO_3^-$					
	Dissolution rate [ $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ]	1 [bar]	5 [bar]	10 [bar]	20 [bar]	40 [bar]
$2.78 \cdot 10^{-5}$	$1.2 \cdot 10^{-13}$	1.00	1.01	1.03	1.04	1.05
$2.78 \cdot 10^{-4}$	$1.2 \cdot 10^{-12}$	1.04	1.10	1.11	1.12	1.12
$2.78 \cdot 10^{-3}$	$1.2 \cdot 10^{-11}$	1.06	1.10	1.10	1.10	1.10
$2.78 \cdot 10^{-2}$	$1.3 \cdot 10^{-10}$	1.06	1.07	1.06	1.05	1.04
$2.78 \cdot 10^{-1}$	$1.3 \cdot 10^{-9}$	1.02	0.93	0.87	0.80	0.75
2.78	$1.2 \cdot 10^{-8}$	1.00	0.80	0.61	0.41	0.27

**Table 3**Relative dissolution rates (compared to 0 bar H<sub>2</sub> and ks6 = 0) in 10 mM NaHCO<sub>3</sub> using ks6 = 50 M<sup>-1</sup> s<sup>-1</sup>.

D [Gy·s <sup>-1</sup> ]	Dissolution rate [mol·m <sup>-2</sup> ·s <sup>-1</sup> ] <sup>a</sup>	Relative dissolution rate				
		1 [bar]	5 [bar]	10 [bar]	20 [bar]	40 [bar]
2.78·10 <sup>-5</sup>	1.2·10 <sup>-13</sup>	0.84	0.51	0.35	0.21	0.12
2.78·10 <sup>-4</sup>	1.2·10 <sup>-12</sup>	0.90	0.55	0.37	0.22	0.12
2.78·10 <sup>-3</sup>	1.2·10 <sup>-11</sup>	0.91	0.54	0.35	0.21	0.12
2.78·10 <sup>-2</sup>	1.3·10 <sup>-10</sup>	0.86	0.48	0.31	0.18	0.09
2.78·10 <sup>-1</sup>	8.7·10 <sup>-10</sup>	0.56	0.29	0.18	0.10	0.05
2.78	1.2·10 <sup>-9</sup>	0.10	0.08	0.06	0.03	0.02

<sup>a</sup> Dissolution rates at 0 bar initial H<sub>2</sub> and ks6 = 50 M<sup>-1</sup> s<sup>-1</sup>.**Table 4**

Dissolution rates as a function of dose rate with varying constants ks6 and ks7 with 1% ε-particle surface coverage.

Dose rate (Gy·s <sup>-1</sup> )	Dissolution rate [mol·m <sup>-2</sup> ·s <sup>-1</sup> ]				
	ks6 = 0, ks7 = 0	ks6 = 50, ks7 = 0	ks6 = 50, ks7 = 10 <sup>2</sup>	ks6 = 50, ks7 = 10 <sup>3</sup>	ks6 = 50, ks7 = 10 <sup>4</sup>
2.78·10 <sup>-5</sup>	1.2·10 <sup>-13</sup>	1.2·10 <sup>-13</sup>	2.5·10 <sup>-22</sup>	1.2·10 <sup>-22</sup>	1.2·10 <sup>-22</sup>
2.78·10 <sup>-4</sup>	1.2·10 <sup>-12</sup>	1.2·10 <sup>-12</sup>	2.6·10 <sup>-22</sup>	1.2·10 <sup>-22</sup>	1.2·10 <sup>-22</sup>
2.78·10 <sup>-3</sup>	1.2·10 <sup>-11</sup>	1.2·10 <sup>-11</sup>	8.1·10 <sup>-22</sup>	4.7·10 <sup>-22</sup>	4.7·10 <sup>-22</sup>
2.78·10 <sup>-2</sup>	1.3·10 <sup>-10</sup>	1.3·10 <sup>-10</sup>	9.8·10 <sup>-13</sup>	6.4·10 <sup>-21</sup>	6.4·10 <sup>-21</sup>
2.78·10 <sup>-1</sup>	1.3·10 <sup>-9</sup>	8.7·10 <sup>-10</sup>	1.8·10 <sup>-11</sup>	1.9·10 <sup>-18</sup>	1.9·10 <sup>-18</sup>
2.78	1.2·10 <sup>-8</sup>	1.2·10 <sup>-9</sup>	5.4·10 <sup>-10</sup>	3.5·10 <sup>-17</sup>	3.5·10 <sup>-17</sup>

**Table 5**Initial hydrogen pressures required to suppress UO<sub>2</sub> oxidative dissolution as a function of ε-particle surface coverage and dose rate with ks7 = 10<sup>2</sup> M<sup>-1</sup> s<sup>-1</sup> and ks6 = 50 M<sup>-1</sup> s<sup>-1</sup>.

D [Gy·s <sup>-1</sup> ]	H <sub>2</sub> pressure [bar]		
	ε = 0.1%	ε = 1%	ε = 3%
2.78·10 <sup>-5</sup>	0.0	0.0	0.0
2.78·10 <sup>-4</sup>	0.0	0.0	0.0
2.78·10 <sup>-3</sup>	1.7·10 <sup>-3</sup>	0.0	0.0
2.78·10 <sup>-2</sup>	4.4·10 <sup>-2</sup>	5.7·10 <sup>-3</sup>	0.0
2.78·10 <sup>-1</sup>	4.4·10 <sup>-1</sup>	1.7·10 <sup>-1</sup>	8.0·10 <sup>-2</sup>
2.78	2.7	1.5	9.9·10 <sup>-1</sup>

### 3.1.2. Comparison to literature data

The impact of H<sub>2</sub> on the concentration of H<sub>2</sub>O<sub>2</sub> upon alpha radiolysis has been explored experimentally by Pastina and LaVerne (2001), and was also discussed by Trummer and Jonsson (2010). The results of the simulations presented in this work are in line with the work by Pastina and LaVerne. In the work by Pastina and LaVerne, experiments clearly showed that H<sub>2</sub> (800 μM) has an insignificant effect on the H<sub>2</sub>O<sub>2</sub> concentration upon irradiating an aqueous solution initially containing 50 μM H<sub>2</sub>O<sub>2</sub> with 5 MeV He<sup>2+</sup>.

Experimental data on the impact of the reaction between H<sub>2</sub> and the surface-bound hydroxyl radical are not fully consistent. In a study by Nilsson and Jonsson (2008a), the kinetics for H<sub>2</sub>O<sub>2</sub> consumption on UO<sub>2</sub>-powder was studied in solutions containing 0 and 40 bar initial H<sub>2</sub>. It is evident from these results that the kinetics for H<sub>2</sub>O<sub>2</sub> consumption is not significantly affected by 40 bar H<sub>2</sub>. The initial H<sub>2</sub>O<sub>2</sub> concentration in this work was 0.22 mM which is roughly 150 times lower than the H<sub>2</sub> concentration. At H<sub>2</sub>O<sub>2</sub> concentrations around 0.2 mM, the impact of the reaction between H<sub>2</sub>O<sub>2</sub> and the surface-bound hydroxyl radical is very small. Hence, the experimental observation does not rule out a possible reaction between H<sub>2</sub> and the surface-bound hydroxyl radical. Carbol et al. (2009a), studied the effect of H<sub>2</sub> on the uranium dissolution from U-233 doped UO<sub>2</sub> and found that H<sub>2</sub> has a strong inhibiting effect. This effect could potentially be attributed to the reaction between H<sub>2</sub> and the surface-bound hydroxyl radical. However, the observed effect is much stronger than would be expected from the simulations carried out in this work. In the work by Bauhn et al., D<sub>2</sub> was found to inhibit radiation

induced oxidative dissolution of (U,Pu)O<sub>2</sub> were the α-particles originate from Pu (Bauhn et al., 2018a). As this material was unirradiated, noble metal inclusions are not present and the most likely explanation to the observed effect is the reaction between D<sub>2</sub> and surface-bound hydroxyl radical. The observed product, HDO, is also the product that would be expected from this reaction. However, it could also be formed from other reactions. Hansson et al. (2021) studied α-radiation induced oxidative dissolution of UO<sub>2</sub> under Ar and 10 bar H<sub>2</sub>, respectively. The α-source was external and was separated by 30 μm from the UO<sub>2</sub> pellet. H<sub>2</sub> was found to reduce the oxidative dissolution also in this case and the most probable reason for this is again the reaction between H<sub>2</sub> and the surface-bound hydroxyl radical. The rate of oxidative dissolution is reduced by one order of magnitude which is well in line with our simulated results.

In addition to the experimental studies mentioned above there are numerous studies where noble metal inclusions are present. Broczkowski et al. have studied SIMFUEL containing various concentrations of noble metal inclusions using electrochemical techniques (Broczkowski et al., 2005, 2007). These studies have clearly shown that the corrosion potential is greatly reduced by H<sub>2</sub> for pellets containing noble metal inclusions. The response at a given H<sub>2</sub> pressure is proportional to the number density of the noble metal inclusions. Bauhn et al. (2018b), studied a SIMFUEL pellet with 339 mm<sup>2</sup> surface area, ~2% ε-particles (Lucuta et al., 1991), in 100 mL 10 mM NaHCO<sub>3</sub> with an initial concentration of 2.5 mM H<sub>2</sub>O<sub>2</sub> at a D<sub>2</sub> pressure of 10 bar over approximately 150 h. An oxidation yield (defined as the amount of dissolved uranium per amount of consumed H<sub>2</sub>O<sub>2</sub>) of 1.69·10<sup>-4</sup> was obtained. This implies that the oxidative dissolution was effectively inhibited which is perfectly in line with the model used in the simulations. Carbol et al. studied the impact of H<sub>2</sub> on the leaching of irradiated MOX fuel as well high burn-up structured UO<sub>2</sub> fuel (Fors et al., 2009; Carbol et al., 2009b). In both cases, dissolution was completely inhibited by H<sub>2</sub>. In these cases, the inhibition can most probably be attributed to the noble metal inclusions. More recently, Ekeröth et al. demonstrated that H<sub>2</sub> can inhibit radiation induced dissolution of UO<sub>2</sub>-based fuel already at low pressures (Ekeröth et al., 2020). The fact that radiolytic H<sub>2</sub> production is sufficient to stop the uranium dissolution has been confirmed in spent nuclear fuel leaching experiments where gases are not allowed to escape the reaction vessel, i.e., in sealed ampoules (Eriksen and Jonsson, 2007).

## 4. Conclusions

In this work we have incorporated two different surface processes accounting for H<sub>2</sub> inhibition of radiation induced dissolution of UO<sub>2</sub>-based fuel in a numerical model recently developed. The two processes are the reaction between H<sub>2</sub> and the surface-bound hydroxyl radical which prevents oxidation of UO<sub>2</sub> and noble metal particle catalyzed H<sub>2</sub>-reduction of U(VI) on the UO<sub>2</sub> surface. The rate constants for the two processes were assessed based on existing literature data. Based on simulations we were able to assess the relative impact of the two processes and it turned out that the noble metal inclusion catalyzed process is by far the most efficient one. Simulations show that even radiolytically produced H<sub>2</sub> is sufficient to completely stop radiation induced oxidative dissolution of UO<sub>2</sub>-based fuel, perfectly in line with experimental



finding. The successful inclusion of these two surface processes into the model opens up for more detailed studies of the impact of other groundwater constituents.

### Author statement

N.L. Hansson: Conceptualization, Formal analysis, Investigation, Methodology, Software, Validation, Visualization, Writing – original draft. M. Jonsson: Conceptualization, Methodology, Project administration, Supervision, Validation, Writing – review & editing.

### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Mats Jonsson reports financial support was provided by Swedish Nuclear Fuel and Waste Management Co.

### Data availability

Data will be made available on request.

### Acknowledgements

The Swedish Nuclear Fuel and Waste Management Company (SKB) is gratefully acknowledged for financial support.

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