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On the impact of reactive solutes on radiation induced oxidative dissolution of UO_2

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ABSTRACT

The impact of 2-propanol (100 mM), NaCl (0.1 – 2 M) and Fe(II)(aq) (10 μM) on the radiation induced oxidative dissolution of UO_2 is investigated experimentally by γ-irradiating a UO_2 pellet immersed in aqueous solution containing 10 mM HCO_3^- together with one of the studied solutes and measure the U(VI) concentration in solution as a function of irradiation time. The solution was saturated with one of the following gases; Air, N_2O, inert gas (N_2 or Ar) in order to vary the experimental conditions and/or avoid the influence of oxygen. The results show that, in the presence of oxygen, 2 M chloride decrease the rate of UO_2 dissolution whereas the dissolution rate increases somewhat in the presence of 100 mM 2-propanol. Under oxygen-free conditions both 2 M chloride, 100 mM 2-propanol and 10 μM Fe(II)(aq) decrease the rate of UO_2 dissolution. The trends in dissolution rates were reproduced by calculations based on previously determined rate constants for UO_2 oxidation and oxidant concentrations obtained from numerical simulation of radiolysis in the corresponding homogeneous systems (taking reactions between the different solutes and the products of water radiolysis as well as changes in oxygen solubility into account). However, the results indicate that we cannot fully account for the G-values in 2 M chloride solution or all reactions involving Cl^- in the aqueous phase. This calls for further studies of the chloride system.

1. Introduction

The release of radioactive species from spent nuclear fuel in a future geological repository is expected to be limited by the rate of dissolution of the UO_2 matrix of the spent fuel [1]. Under the reducing conditions expected at the depth of a deep repository, the solubility of UO_2 is very low and the release of radionuclides is therefore expected to be slow [2]. However, when the spent fuel comes into contact with groundwater, radiolysis of the water will take place producing both oxidizing species ($OH^{\cdot}$, H_2O_2, $HO_2^{\cdot}$ and O_2) and reductants (e^-_{aq}, $H^{\cdot}$, H_2) [3]. When HCO_3^- is present, $OH^{\cdot}$ is converted to $CO_3^{\cdot-}$ by reactions (1) and (2) [4].

$$OH^{\cdot} + CO_3^{2-} \rightarrow CO_3^{\cdot-} + OH^- \quad (1)$$

$$k = 3.9 \times 10^8 \left(\mathrm{L\ mol^{-1}\ s^{-1}}\right)$$

$$OH^{\cdot} + HCO_3^- \rightarrow CO_3^{\cdot-} + H_2O \quad (2)$$

$$k = 8.5 \times 10^6 \left(\mathrm{L\ mol^{-1}\ s^{-1}}\right)$$

The produced oxidants alter the otherwise reducing conditions. When oxidized, the solubility of the UO_2 matrix increases significantly. HCO_3^- present in the groundwater further enhances the dissolution by forming strong soluble complexes with U(VI), thereby a larger surface area available for oxidation is maintained.

Since oxidative dissolution of the UO_2 matrix of spent nuclear fuel is a key issue in the safety assessment of a future deep repository the process has been subject to extensive investigations over the years [1,5]. Relatively fresh spent nuclear fuel has sometimes been used in these experimental studies. However, since the radioactivity of the fuel as well as the relative importance of α-, β- and γ-radiation, affecting the oxidant production, will change considerably with time these experimentally determined dissolution rates can not be used for extrapolations to times relevant for the deep repository. Hence, numerical simulations based on relevant elementary reactions and well established rate constants are needed. Such data is difficult to extract from experiments performed on spent nuclear fuel, due to its inherent complexity. For this reason pure UO_2 has been used as a model substance in several studies. There are however, relatively few studies aiming at elucidating actual rate constants for the elementary reactions involved in the oxidative dissolution process.

In general, oxidative dissolution can be described by the following mechanism:

$$UO_2(s) + OX \rightarrow UO_2^{2+}(s) + RED \quad (3)$$

$$UO_2^{2+}(s) \rightarrow UO_2^{2+}(aq) \quad (4)$$

The dissolution of UO_2^{2+} (s) (reaction (4)) is a fairly slow process in pure water but the rate is increased by HCO_3^- present in the groundwater [6]. HCO_3^- facilitated dissolution has been found to be a diffusion controlled process and at HCO_3^- concentrations above 1 mM the rate limiting step is oxidation [6].

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Table 1
Rate constants for the oxidation of UO_2 by the products of radiolysis of water containing HCO_3^- [5,6].

O_2/m s^{-1}	H_2O_2/m s^{-1}	$OH^{\cdot}$/m s^{-1}	$CO_3^{\cdot -}$/m s^{-1}	$O_2^{\cdot -}$/m s^{-1}	$HO_2^{\cdot}$/m s^{-1}
3.9×10^{-10}	7.3×10^{-8}	$1.0 \times 10^{-6*}$	1.0×10^{-6}	1.8×10^{-9}	$1.0 \times 10^{-6*}$

[*] Diffusion controlled rate constants valid for UO_2 pellets (~1 cm).

It has been shown that the oxidation rate is limited by the first electron transfer and that the logarithm of the rate constant for the reaction is linearly dependent on the one-electron reduction potential of the oxidant [7]. Among the oxidants produced in a deep repository, the rate constants for both $OH^{\cdot}$ and $CO_3^{\cdot -}$ are limited by diffusion whereas for example H_2O_2 and O_2 react more slowly [7]. Rate constants for UO_2 oxidation by the products of water radiolysis are given in Table 1.

The impact of a specific oxidant in the oxidative dissolution process depends on the rate constant for the reaction with UO_2 but also on the oxidant concentration. Experimental studies of aqueous solutions containing UO_2 pellets and powder performed under various conditions, in combination with numerical simulations of the systems, reveled that under deep repository conditions (granite groundwater dominated by α-radiolysis), H_2O_2 will be the only oxidant of importance [8].

The production of H_2O_2 in the aqueous phase surrounding spent nuclear fuel is determined by the dose rate and the type of radiation, which in turn depends on the radionuclide inventory of the spent fuel (varies with fuel age and burn up). Furthermore, reactive solutes present at high concentrations in the aqueous phase may influence the radiation chemical yield of H_2O_2 and other radiolysis products. Since the UO_2 dissolution rate can never exceed the rate of H_2O_2 production, the maximum UO_2 dissolution rate is given by the H_2O_2 production rate. Simulations (based on fuel inventory) of the H_2O_2 concentration profile in water surrounding spent nuclear fuel have shown that the surface concentration of H_2O_2 approaches steady-state within a relatively short time (minutes or hours) compared to the time span of interest with regards to a geological deep repository [9]. Hence, the spent fuel dissolution rate at steady-state can be used without loss of accuracy [10].

In order to obtain a more realistic (lower) dissolution rate the effects of surface reactions not leading to oxidative dissolution of UO_2, as well as the effect of reactive solutes have to be taken into account. Surface reactions of potential importance are (a) the reaction between H_2O_2 and H_2 catalyzed by UO_2 or so called ε-particles (metallic particles composed of fission products) present in spent nuclear fuel and (b) the reduction of U(VI)(s) by H_2 catalyzed by ε-particles. The first process has been shown to have little or no influence on the dissolution of spent nuclear fuel [11]. The reduction of U(VI)(s) by H_2 catalyzed by ε-particles has been investigated in experimental studies using Pd as a substitute for ε-particles [12]. These studies have shown that this is indeed an efficient process contributing to inhibition of UO_2 oxidative dissolution. Taking this process into account, experimentally observed spent fuel dissolution rates have been successfully reproduced by calculations using the steady-state approach [13,14].

A large number of both organic and inorganic solutes are expected to be present in the groundwater in a geological repository. Some of these could potentially affect the spent fuel dissolution rate by scavenging oxidants from the system.

The effect of the presence of iron has been discussed in several publications [15–17]. However, very few studies explicitly aiming at elucidating the effect of Fe(II)(aq) are to be found. Amme et al. [18] investigated the effect of Fe(II)(aq) on the UO_2 corrosion by H_2O_2 in a system without complexing agent. In contrast to experiments performed without Fe(II)(aq), no uranyl peroxide (studtite) was found on the UO_2 surface when Fe(II)(aq) and H_2O_2 were present in stoichiometric amounts, indicating that Fe(II)(aq) suppresses the interaction between UO_2 and H_2O_2 by decomposing H_2O_2 in solution. Another possibility could be that Fe(II)(aq) decomposes uranyl peroxide on the surface.

Several experimental studies have been carried out investigating dissolution of spent nuclear fuel and UO_2 in the presence of chloride. Since some countries plan to store spent nuclear fuel in rock salt repositories, highly saline brines (~6 M where stated) have been used in most of these studies [19–23]. In some studies [21–23] dissolution in the chloride containing solutions is compared to the dissolution under chloride-free conditions, showing suppression of the dissolution by the presence of chloride. Wang and Katayama [22] attribute this observation to the formation of a passive film on the UO_2 surface. These studies were however performed in the absence of carbonate. Under these conditions an oxidized layer will build up on the surface, decreasing the surface available to oxidants and consequently reduce the oxidative dissolution rate also in the absence of chloride. In the presence of carbonate, experiments on spent nuclear fuel carried out at lower chloride concentrations (0 – 10 mM) showed similar uranium release rates at the different chloride concentrations [24]. A study of the kinetics UO_2 oxidation by H_2O_2 in aqueous solution containing 10 – 200 mM NaCl revealed that, under HCO_3^- free conditions, the H_2O_2 consumption rate increases with increasing NaCl concentration (i.e. increasing ionic strength) [25] whereas at 10 mM HCO_3^- concentration (i.e. where the kinetics is independent of the dissolution of oxidized UO_2^{2+}[6]), the H_2O_2 consumption rate was shown to be unaffected by the presence of chloride.

In this work we investigate the effect of Fe(II)(aq), chloride and 2-propanol on the rate of UO_2 dissolution. 2-Propanol is used as a model substance for organic substances capable of forming reducing radicals, whereas both Fe(II)(aq) and chloride are naturally occurring substances expected to be present in a geological repository.

Experiments are performed, where the dissolved amount of UO_2^{2+} is measured as a function of time in γ-irradiated aqueous solution containing HCO_3^- and Fe(II)(aq), chloride or 2-propanol and a UO_2 pellet. The solutions were saturated by different gases (inert gas, N_2O, Air) in order to vary the conditions by changing the initial yields of radiolysis products. N_2O promotes the production of $OH^{\cdot}$ (which in turn is converted to $CO_3^{\cdot -}$ in the presence of carbonate) by conversion of the solvated electron according to reaction (5).

$$N_2O + e_{aq}^- \rightarrow N_2 + OH^{\cdot} + OH^- \tag{5}$$

The presence of O_2 promotes the formation of $O_2^{\cdot -}/HO_2^{*}$ by reacting with e_{aq}^- and $H^{\cdot}$ (reactions (6) and (7)) forming $O_2^{\cdot -}/HO_2^{\cdot}$, which in turn is converted to H_2O_2.

$$e_{aq}^- + O_2 \rightarrow O_2^{\cdot -} + H_2O \tag{6}$$

$$H^{\cdot} + O_2 \rightarrow HO_2^{\cdot} \tag{7}$$

The systems are further analyzed by using numerical simulations (MAKSIMA-Chemist [26]). The rate constants used in the simulations were obtained from [4,27,28].

2. Experimental

A depleted UO_2 pellet was immersed in 10 mL aqueous solution. The solution contained 10 mM HCO_3^- and NaCl (2 M), 2-propanol (0.1 M) or Fe(II)(aq) (10 μM). The solution was saturated with one of the following gases; Air, N_2O or Ar. Reference experiments were performed under the same conditions using 10 mM HCO_3^- solutions. The combinations used are shown in Table 2. The solution (containing the UO_2 pellet) was irradiated in a ^{137}Cs γ-source

Table 2
Experimental conditions.

	Air	N_2O	Ar
10 mM HCO_3^-	x	x	x
100 mM 2-PrOH + 10 mM HCO_3^-	x	x	
2 M NaCl + 10 mM HCO_3^-	x	x	
10 μM Fe^{2+} + 10 mM HCO_3^-			x

Gammacell 1000 Elite from MDS Nordion with dose rate 0.15 Gy s^{-1} (determined by Fricke dosimetry [29]). Samples (~1.5 mL) were taken at different time intervals and analyzed for dissolved uranium content.

In the Air and N_2O series UV/Vis spectroscopy (S2000 spectrophotometer from WPA) was used by employing the Arsenazo III method at 653 nm (ε = 63,000 M^{-1} cm^{-1}) described in [30,31]. An aliquot of the sample was mixed with 40 μL 0.03% Arsenazo III reagent and 65 μL 1 M HCl and diluted to a total volume of 1.5 mL. The reaction solutions in these series were buffered by HCO_3^- at pH 8.3.

In the Ar series the dissolved uranium content was determined by ICP – OES (Varian Vista Ax) in order to avoid influence of Fe(III) (which affects Arsenazo III measurements). In this series, the solution was buffered with 0.1 M TRIZMA® (Tris(hydroxymethyl)amino-methane) buffer at pH 7.1 and the sample/solution preparation took place in a glove-box with Ar atmosphere containing 0.03% CO_2 and <0.1 ppm O_2, in order to avoid precipitation and oxidation of Fe(II) prior to the irradiation.

Prior to the experiment, the UO_2-pellet was washed repeatedly with 10 mM HCO_3^- in order to remove U(VI) from the surface. Experiments in N_2 saturated solutions without γ-irradiation under otherwise identical conditions were performed and used for background correction. The UO_2-pellet was supplied by Westinghouse Atom AB, gases and chemicals were purchased from AGA, Air Liquid, Alfa Aesar, SDS, Fluka, VWR, Sigma – Aldrich and Merck. All experiments were conducted at room temperature and Milli-Q filtered water was used throughout.

3. Results and discussion

In Fig. 1(a) the measured amount of uranium in solution is shown as a function of time for the air-saturated systems. As can be seen in the figure, the measured amount of uranium in solution at the different sampling points is slightly higher in 100 mM 2-propanol solution compared to the reference system, whereas in 2 M chloride the amount of dissolved uranium is lower than in the reference system.

It has previously been shown that in γ-irradiated, air-saturated systems, H_2O_2 is by far the most important oxidant when it comes to oxidative dissolution of UO_2 [8]. An increased dissolution rate in the presence of 2-propanol can be attributed to a series of reactions leading to increased H_2O_2 production. 2-Propanol reacts with $OH^{\cdot}$ (and $H^{\cdot}$) forming a strongly reducing radical (reaction (8) and (9)). In the presence of O_2, reaction (10) takes place producing $O_2^{\cdot-}$, which proceeds to form H_2O_2 through a number of reactions [4].

$$(CH_3)_2CHOH + OH^{\cdot} \rightarrow (CH_3)_2C^{\cdot}OH \tag{8}$$

$$k = 1.9 \times 10^9\ (\mathrm{L\ mol^{-1}\ s^{-1}})$$

$$(CH_3)_2CHOH + H^{\cdot} \rightarrow (CH_3)_2C^{\cdot}OH + H_2 \tag{9}$$

$$k = 7.4 \times 10^7\ (\mathrm{L\ mol^{-1}\ s^{-1}})$$

$$(CH_3)_2C^{\cdot}OH + O_2 \rightarrow O_2^{\cdot-} \tag{10}$$

$$k = 4.2 \times 10^9\ (\mathrm{L\ mol^{-1}\ s^{-1}})$$

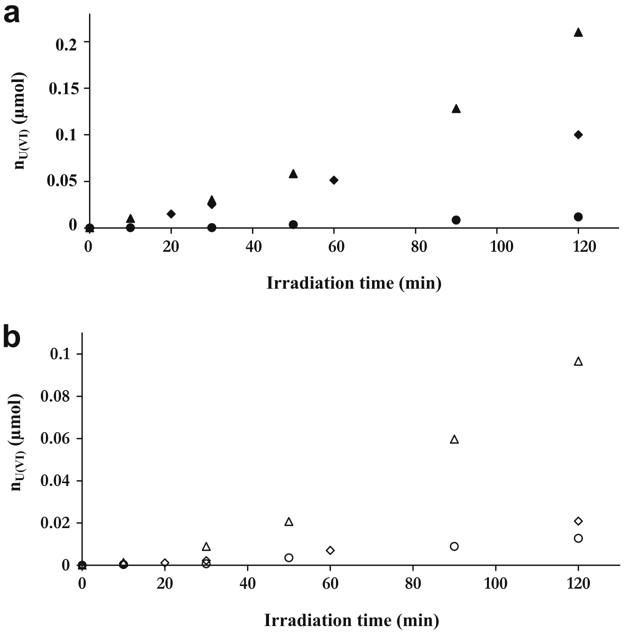

Fig. 1. U(VI) in solution as a function of irradiation time for different air-saturated systems (△/▲) 100 mM 2-PrOH (◇/◆) HCO_3^- reference and (○/●) 2 M Chloride. (a) Experimental results. (b) Calculation.

The radical formed by reaction (8) and (9) can also scavenge H_2O_2 according to reaction (11) [4].

$$(CH_3)_2C^{\cdot}OH + H_2O_2 \rightarrow CH_3COCH_3 + H_2O + OH^{\cdot} \tag{11}$$

$$k = 7 \times 10^5\ (\mathrm{L\ mol^{-1}\ s^{-1}})$$

This reaction is however relatively slow compared to reaction (8)–(10) and since, in this system, the O_2 concentration is significantly higher than the H_2O_2 concentration, the net effect of 2-propanol addition is increased H_2O_2 concentration leading to increased rate of dissolution. The 2-propanol radical is also capable of reducing U(VI)(aq) back to U(IV)(s). Assuming diffusion controlled kinetics, this reaction decreases the amount of U(VI) in solution at the end of the present experiment by approximately 10%. This effect should however, only affect the measured U(VI) concentration in solution and not the rate of UO_2 dissolution.

Judging from the known reactions between $Cl^-$and the primary products of water radiolysis only (Table 3), we would not expect any effect of chloride on the UO_2 dissolution rate. Cl^- reacts with $OH^{\cdot}$ and is eventually converted to $Cl_2^{\cdot-}$ through a series of reactions. When HCO_3^- is present in the system $CO_3^{\cdot-}$ is formed.

According to these reactions the final products should be identical to the chloride-free system. However, there are other factors that contribute to the observed decrease in dissolution rate. One important factor is the solubility of oxygen, which deceases by

Table 3
Reactions scheme for radiolysis of chloride solutions [26,27].

Reaction	$k(\mathbf{M^{-1}\ s^{-1}})$
$OH^{\cdot}+Cl^- \rightarrow ClOH^{\cdot-}$	3.0×10^9
$ClOH^{\cdot-} \rightarrow OH^{\cdot}+Cl^-$	6.0×10^9
$ClOH^{\cdot-}+Cl^- \rightarrow Cl_2^{\cdot-}+OH^-$	1.0×10^4
$Cl_2^{\cdot-}+OH^- \rightarrow ClOH^{\cdot-}+Cl^-$	4.5×10^7
$Cl_2^{\cdot-} \rightarrow Cl^{\cdot}+Cl^-$	5.7×10^4
$Cl^{\cdot}+Cl^- \rightarrow Cl_2^-$	7.8×10^9
$Cl^{\cdot}+H_2O \rightarrow ClOH^{\cdot-}+H^+$	1.8×10^5
$ClOH^{\cdot-}+H^+ \rightarrow Cl^{\cdot}+ H_2O$	2.4×10^{10}
$Cl_2^{\cdot-}+CO_3^{2-} \rightarrow CO_3^{\cdot-}+2Cl^-$	4.0×10^8
$Cl_2^{\cdot-}+HCO_3^- \rightarrow CO_3^{\cdot-}+2C1^-+H^+$	1.5×10^7

around 50% in 2 M chloride solution [32]. Furthermore, the concentration of radiolysis products will be affected by changes in the G-values due to the presence of OH· scavengers. In a study of radiolysis of chloride solutions, Pucheault et al. [33] found that the G-values of oxidizing radiolysis products in general decrease with increasing chloride concentration. In 2 M chloride solution, $G(H_2O_2)$ was found to be approximately 60% of the value in pure water. This effect is significantly smaller than expected from results presented in reference [34], where it is shown that, at the present OH scavenging capacities (6×10^9 chloride system and 1.9×10^8 2-propanol system), $G(H_2O_2)$ is decreased by ~80% and ~30%, respectively.

In order to further analyze the systems, MAKSIMA-Chemist [26] was used to perform numerical simulations of radiolysis of the different solutions. In the simulations, the reactions discussed above were taken into account, as well as the decreased oxygen solubility. Due to the inconsistency in data reported in the literature, the impact of chloride and 2-propanol on the yield of radiolysis products has not been taken into account in the simulations.

Using oxidant concentrations obtained from the simulations, rate constants for oxidation of UO_2 (Table 1) and the UO_2 surface area exposed to solution, the amount of dissolved U(VI) at each sampling point can be calculated by numerical integration of the previously established expression for the total rate of dissolution (oxidation), Eq. (12) [8]:

$$\text{rate} = \frac{dn_{U(VI)}}{dt} = A_{UO_2} \sum_{ox=1}^{n} k_{ox}[Ox] \frac{n_{e^-}}{2} \tag{12}$$

where $[Ox]$ is the oxidant concentration, k_{ox} is the rate constant and n_{e^-} is the number of electrons involved in the redox process (2 for H_2O_2 and O_2 and 1 for the radicals). A_{UO_2} is the UO_2 surface area available for oxidation, in this case we used the estimated BET surface area of the pellet (the geometrical surface area, 3.66 cm^2, multiplied by three [35]).

The results from the calculations are shown in Fig. 1(b). In the calculations performed on the 2-propanol systems, the reaction between U(VI) and the 2-propanol radical has also been taken into account. As mentioned above, this reaction decreases the amount of U(VI) in solution at the end of the present experiment by approximately 10%, but does not affect the rate of UO_2 dissolution. Calculated dissolution rates are presented in Table 4.

As can be seen in Fig. 1(b), the calculations are qualitatively in good agreement with the experimental results. However, the calculated uranium amounts are generally lower than the experimentally obtained amounts. Looking at the uranium amounts in the systems with added solutes relative to the HCO_3^- reference in the air-saturated case it can be noted that the impact (i.e. relative change in amount of dissolved uranium) of chloride is underestimated by the calculations, whereas the impact of 2-propanol is significantly overestimated. In an experiment performed using 100 mM NaCl solution saturated with O_2 no significant impact of chloride could be measured compared to the HCO_3^- reference case. In this system $G(H_2O_2)$ is expected to be approximately 30% lower than in pure water according to the results presented in reference [34].

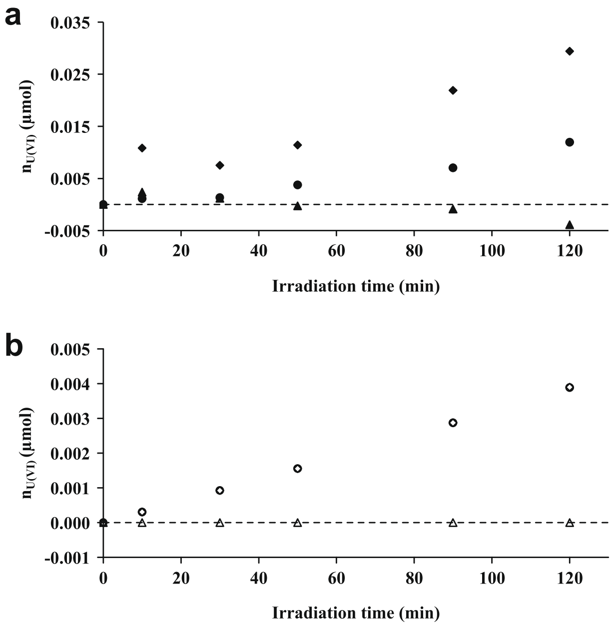

Fig. 2. U(VI) in solution as a function of irradiation time for different N_2O-saturated systems (△/▲) 100 mM 2-PrOH (◇/◆) HCO_3^- reference and (○/●) 2 M Chloride. (a) Experimental results. (b) Calculation.

Under the oxygen-free conditions (N_2O-system), shown in Fig. 2, both 100 mM 2-propanol and 2 M chloride decreases the amount of U(VI) in solution. In the HCO_3^- reference case in the N_2O-saturated system, $CO_3^{\cdot-}$ (produced from OH) is responsible for ~80% of the oxidative UO_2 dissolution, whereas H_2O_2 contributes with ~16% [8]. When 2-propanol is added OH will be effectively scavenged (reaction (8)) consequently the $CO_3^{\cdot-}$ concentration is decreased and the oxidative dissolution will be completely dominated by H_2O_2. As the O_2 concentration is very low in this system, the effect of reaction (10) will be minor and the H_2O_2 concentration will be determined mainly by reaction (8), (9) and (11). Reaction (11) consumes H_2O_2, whereas reaction (8) and (9) remove OH· and H· (H_2O_2 scavengers) and contribute in this way to increased H_2O_2 concentration.

Numerical simulations, performed using methods and considerations as described above, show that the combination of these reactions results in a ~3-fold increase in the H_2O_2 concentration and a ~3-fold decrease in UO_2 dissolution rate (as can be seen in Table 4). This is not consistent with the experimental results, where no dissolved uranium is detected in the 2-propanol system.

However, as the O_2 concentration is low, the reduction of U(VI) by the 2-propanol radical will be favored and have a larger impact here compared to the air-saturated system. Taking this reaction into account no dissolved uranium is expected to be found in this system, as can be seen in Fig. 2(b), where calculated amounts of uranium in solution are shown. As in the air-saturated systems, the calculated uranium amounts are generally lower than mea-

Table 4
Calculated and experimentally determined UO_2 dissolution rates.

	Calculated dissolution rate (mol s^{-1})			Experimental dissolution rate (mol s^{-1})		
	N_2O	Air	Ar	N_2O	Air	Ar
10 mM HCO_3^-	5.4×10^{-13}	3.0×10^{-12}	3.8×10^{-13}	4.1×10^{-12}	1.4×10^{-11}	7.1×10^{-13}
100 mM 2-PrOH + 10 mM HCO_3^-	2.0×10^{-13}*	1.5×10^{-11}*		0	2.9×10^{-11}	
2 M NaCl + 10 mM HCO_3^-	5.4×10^{-13}	1.8×10^{-12}		1.6×10^{-12}	1.7×10^{-11}	
10 µM Fe^{2+} + 10 mM HCO_3^-			1.8×10^{-13}			2.2×10^{-13}

* Not accounting for reduction of U(VI)(aq) by 2-PrOH·.

sured experimentally. It can also be noted that, judging from the calculations, no change in dissolved amount of uranium is expected from the addition of chloride whereas a decrease in uranium amount is experimentally observed.

In the air-saturated system, the effect of chloride could, at least partially, be explained by the decrease in O_2 solubility. In the N_2O-saturated system no such effect is expected. The effect is also not likely due to surface passivation. In reference [6] it was shown that the rate constant for the reaction between H_2O_2 and UO_2 was unaffected by the presence of chloride up to at least 200 mM in the presence of HCO_3^-. Judging from these observations, the impact of chloride can not be attributed to passive film formation. This indicates that the impact of chloride is controlled by the chemistry in the aqueous phase.

The effect of chloride on the G-values of the water radiolysis products is likely an important factor. As mentioned above, the radiation chemical yield of H_2O_2 as well as other oxidants is expected to be decreased by the presence of chloride [33,34]. The literature data is however, too scarce to quantify the impact on the rate of UO_2 dissolution.

In general, the experimentally determined uranium amounts presented in this study are higher than expected from the calculations. This can partly be attributed to the rather large uncertainty in the estimation of the UO_2 surface area available for oxidation. Another contributing factor could be the presence of U(VI) in the pellet interior. U(VI) present inside the pellet is not removed by the pretreatment with HCO_3^-, but becomes accessible for dissolution when the outer UO_2 layers on the pellet surface are oxidatively dissolved.

In Fig. 3 the results from the experiments performed with Fe(II)(aq) are shown together with results from the simulation of the system. The amount of dissolved uranium is decreased by the presence of Fe(II)(aq) and, as in the previous systems, the qualitative agreement between measured and calculated uranium amounts is good.

In the Ar-saturated reference system both H_2O_2 and $CO_3^{\cdot -}$ will have significant impact on the UO_2 oxidative dissolution (73% and 24%, respectively) [8]. In presence of Fe(II)(aq) the concentration of both oxidants will be reduced since Fe(II)(aq) is oxidized by both H_2O_2 and $OH^\cdot$ (or $CO_3^{\cdot -}$ in HCO_3^- containing solutions) according to reaction (13) (the Fenton reaction) [28] and reaction (14) [4]. Fe(II)(aq) is also capable of consuming other oxidants in the system e.g. $HO_2^\cdot$.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\cdot + OH^- \tag{13}$$

$$k = 6.90 \times 10^4 \ (L\ mol^{-1}\ s^{-1})$$

$$Fe^{2+} + OH^- \rightarrow Fe^{3+} + OH^- \tag{14}$$

$$k = 4.30 \times 10^8 \ (L\ mol^{-1}\ s^{-1})$$

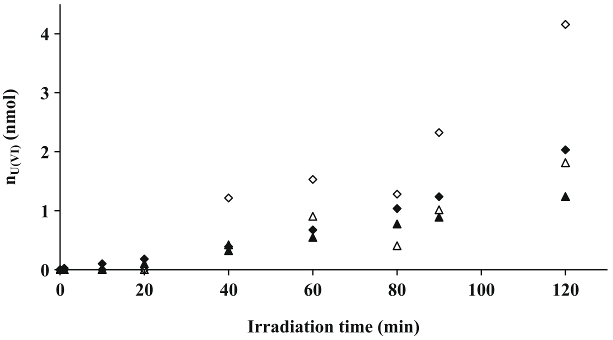

Fig. 3. U(VI) in solution as a function of irradiation time for different Ar-saturated systems (△/▲) 10 YM Fe(II)(aq) and (◇/◆) HCO_3^- reference. Filled symbols correspond to calculated U(VI) amounts.

The produced Fe(III) can be reduced back to Fe(II) by e.g. $HO_2^\cdot/O_2^{\cdot -}$ or e_{aq}^- causing a self-sustaining cycle regenerating Fe(II). However, at neutral pH the solubility of Fe(III) is low and, with time, Fe(III) will be removed from solution by precipitation.

Fe(II)(aq) is also potentially capable of reducing U(VI) on the UO_2 surface. However, since HCO_3^- is in large excess compared to Fe(II)(aq), the rate of carbonate facilitated dissolution of U(VI) from the surface will be much higher than the reduction even if the reduction is assumed to be diffusion controlled.

To summarize, we have studied the effect of 2-propanol, chloride and Fe(II)(aq) on oxidative dissolution of UO_2 in γ-irradiated system under air-saturated and oxygen-free conditions experimentally. Theoretical dissolution rates and amounts of uranium in solution in the corresponding systems were calculated using numerical simulations of the systems using MAKSIMA-Chemist [26] not taking surface reactions involving 2-propanol, chloride or Fe(II)(aq) species into account. The trend in the impact of each solute could be reproduced by the calculations. However, the calculated dissolution rates in general fall below the experimentally observed dissolution rates. These observations could probably be attributed to the presence of pre-oxidized uranium in the pellet interior and to the uncertainty in the estimation of the UO_2 surface area available for oxidation.

As can be seen in Table 4, the experimental results show that 2 M chloride decreases the rate of UO_2 dissolution, both in air-saturated and oxygen-free systems. In the air-saturated system, the decrease could, at least to some extent, be explained by decreased oxygen solubility. Furthermore, the presence of chloride, will affect the yield of radiolysis products [33,34], which in turn will affect the UO_2 dissolution rate. This effect will also contribute to decreased dissolution rates in the presence of chloride. However, quantification of this effect requires further studies of radiolysis of chloride solutions.

100 mM 2-propanol was shown to give a slight increase in dissolution rate under air-saturated conditions, whereas an apparent inhibition of the dissolution was observed under oxygen-free conditions. Under the corresponding conditions in the absence of 2-propanol, H_2O_2 will be the dominating oxidant in the air-saturated system whereas $CO_3^{\cdot -}$ will dominate in the oxygen-free system. The observed increase in dissolution rate can be attributed to increasing H_2O_2 concentrations partly due to removal of $OH^\cdot$ and $H^\cdot$ (acting as H_2O_2 scavengers) by 2-propanol and partly due to the reaction between O_2 and the 2-propanol radical leading to increasing H_2O_2 production. Under oxygen-free conditions the removal of $OH^\cdot$ (and consequently $CO_3^{\cdot -}$) will, in combination with H_2O_2 scavenging by the 2-propanol radical, give a slight decrease in dissolution rate in the studied system, as shown in by the calculated results presented in Table 4. The apparent inhibition observed experimentally in this system is attributed to the reduction of U(VI) by the 2-propanol radical in solution. It should be emphasized that this reaction will only affect the concentration in aqueous phase and not the rate of dissolution of the solid material. The presence of 2-propanol will probably also affect the G-values of the different radiolysis products to some extent, however, the effect will however be smaller than in the chloride system due to the smaller $OH^\cdot$ scavenging capacity [34].

Experiments performed under oxygen-free conditions show that Fe(II)(aq) significantly decreases the dissolution rate. These results are in line with the effect of reactive solutes (Fe(II)(aq)) predicted in reference [10], where calculations showed that a steady-state concentration of 1 μM Fe(II)(aq) would decrease the spent fuel dissolution rate under steady-state conditions with a factor of ~50. The results are however not directly comparable since the dissolution rates in the present work were not obtained under steady-state conditions.

In conclusion, the results presented here show that both Fe(II)(aq) and chloride have strongly inhibiting effects on radiation induced oxidative dissolution of UO_2 under oxygen-free (i.e. deep repository) conditions. Organic substances have been shown to increase the dissolution rate in systems where H_2O_2 is the dominating oxidant, as expected under deep repository conditions. This proves the importance of taking the effects of reactive solutes on the steady-state H_2O_2 concentration into account when simulating dissolution of spent nuclear fuel under deep repository conditions.

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