H$_2$O$_2$-Induced Oxidative Dissolution of UO$_2$ in Saline Solutions

Ghada El Jamal,[a] Junyi Li,[a] and Mats Jonsson*[a]

H$_2$O$_2$ is one of the oxidants responsible for driving the process of radiation-induced dissolution of spent nuclear fuel in geological repositories for spent nuclear fuel. As the groundwater composition will vary depending on geographical location as well as on the age of the repository (in relation to glacial cycles, etc.), it is important to elucidate the impact of different groundwater constituents. While several studies have addressed the impact of HCO$_3^-$ and halide ions on the radiation chemistry of water in genera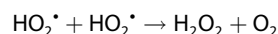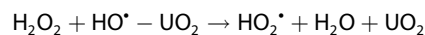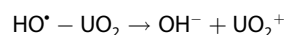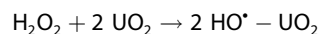l and radiation-induced oxidative dissolution of spent nuclear fuel in particular, very few studies have addressed the impact of halide ions on the mechanism of the reaction between H$_2$O$_2$ and UO$_2$. In this work, the impact of Cl$^-$, Br$^-$ and ClO$_4^-$ on the mechanism and kinetics of H$_2$O$_2$-induced oxidative dissolution of UO$_2$-powder in aqueous suspensions with and without added HCO$_3^-$ has been studied experimentally. The experiments reveal both ionic strength effects and specific ion effects on the kinetics of the reactions involved. These are discussed in connection to the results.

Introduction

Nuclear power constitutes a significant part of the energy supply portfolio in many countries. One of the major issues related to nuclear power is how to handle the highly radioactive nuclear fuel after use in a nuclear reactor. While some countries have decided to reprocess the used nuclear fuel and extract the remaining fissile material for use in new fuel, other countries have decided to keep the used nuclear fuel in repositories until the level of radioactivity has reached that of a natural uranium ore. In most cases the repositories that are discussed are geological repositories composed of multiple natural and engineered barriers to guarantee the integrity of the used nuclear fuel for the desired time period (which is typically 10^5– 10^6 years).[1,2] Even though the various barriers are meant to separate the nuclear fuel from the groundwater and thereby prevent spreading of radionuclides into the environment, safety assessments based on the scenario that groundwater actually comes into contact with the fuel must be carried out. These safety assessments must be based on knowledge about the mechanism and kinetics of fuel dissolution under the relevant conditions. The most commonly used material in commercial nuclear fuels is UO$_2$. Depending on reactor type, the uranium can be enriched in U-235 or be of natural composition. Modern fuels may also contain additives to improve their performance.[3] After use in a nuclear reactor, the majority of the fissile material has been consumed but the fuel matrix is still mainly UO$_2$. It is

therefore very important to understand the behavior of UO$_2$ under repository conditions and also under other conditions when contact between the fuel material and water is a possibility (such as in reactors or storage pools in the event of fuel cladding damage or the event of a nuclear accident).[4]

In general, UO$_2$ has very low solubility in water.[5] However, under oxidizing conditions U(IV) can be oxidized to U(VI) which is significantly more soluble.[1,5] Even though the groundwater conditions at most potential repository sites are reducing rather than oxidizing, the inherent radioactivity of the used fuel will decompose water through radiolysis and thereby create strong oxidants (OH$^•$, H$_2$O$_2$ and HO$_2^•$) capable of oxidizing the UO$_2$.[6] Admittedly, reductants are also produced in water radiolysis (e$_{aq}^-$, H$^•$ and H$_2$) but since UO$_2$ cannot be further reduced by these species, the oxidants dominate the surface reactions. The process of radiation induced oxidative dissolution of UO$_2$ has been thoroughly studied for decades and is therefore fairly well understood.[1,2,7] It has been shown that under the repository conditions prevailing after a few thousand years, H$_2$O$_2$ is the oxidant that mainly drives to oxidative dissolution of UO$_2$.[8] Recently, it was demonstrated that the mechanism of the reaction between H$_2$O$_2$ can be described as follows:[9]

$$H_2O_2 + 2\,UO_2 \rightarrow 2\,HO^• - UO_2$$

$$HO^• - UO_2 \rightarrow OH^- + UO_2^+$$

$$H_2O_2 + HO^• - UO_2 \rightarrow HO_2^• + H_2O + UO_2$$

$$HO_2^• + HO_2^• \rightarrow H_2O_2 + O_2$$

This means that H$_2$O$_2$ oxidizes the UO$_2$ surface in competition with the catalytic decomposition of H$_2$O$_2$ to produce O$_2$ and H$_2$O with a surface-bound hydroxyl radical as a common intermediate for both processes. Catalytic decomposition of H$_2$O$_2$ has been shown to occur on most oxide surfaces.[10] It is also well-established the HCO$_3^-$/CO$_3^{2-}$ in groundwater facilitates

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the dissolution of oxidized uranium and thereby enhances the rate of oxidative dissolution.[11,12]

Depending on the geographical location and to some extent also on glacial cycles, concentrations of groundwater components may vary. Under certain conditions, groundwaters contain high concentrations of Cl^- and to some extent also Br^-.[13] These conditions are also relevant under certain reactor accident scenarios where large amounts of Sea water are pumped into reactors and storage pools to maintain cooling.[4] A number of experimental studies on the radiation chemistry of water containing high concentrations of Cl^- have been reported in the literature[14–31] and there are also several examples of studies of radiation induced dissolution of UO_2 or used nuclear fuel under similar conditions.[32,33] At high halide concentrations, the dominating oxidant in the system may not be H_2O_2.[22,30,32,33] However, even if other oxidants have higher impact, effects of halides on the kinetics and mechanism of H_2O_2 induced oxidative dissolution are still of interest. However, studies focusing on the effects of halide ions on the mechanism and kinetics of H_2O_2 induced oxidative dissolution are scarce in the literature. A previous study has focused on the ionic strength effect on H_2O_2 induced oxidative dissolution of UO_2 and showed that in systems containing 10 mM HCO_3^-, no ionic strength effect on the kinetics of H_2O_2 consumption could be observed.[34] In systems without added HCO_3^-, the rate of H_2O_2 consumption as well as the rate of uranium release were shown to increase with ionic strength.[34] The ionic strength was varied using $NaCl$ and Na_2SO_4 and no difference could be observed between the two electrolytes. It should be noted that the H_2O_2 concentration used in these experiments was 18 mM which is very high compared to what could be expected under repository or accident conditions.

In a very recent paper, the impact of Cl^-, Br^-, HCO_3^- and ClO_4^- on the mechanism and kinetics of catalytic decomposition of H_2O_2 on ZrO_2 was studied experimentally.[35] This paper showed that the surface-bound hydroxyl radicals formed on ZrO_2 were capable of oxidizing Br^- to produce $Br_2^{\bullet-}$ in solutions containing 1 M Br^-. For solutions containing Br^- and HCO_3^-, it was concluded that $Br_2^{\bullet-}$ could oxidize HCO_3^-/CO_3^{2-} to $CO_3^{\bullet-}$. However, direct reactions between surface-bound hydroxyl radicals and Cl^-, HCO_3^-/CO_3^{2-} or ClO_4^- were not observed. Hence, it is possible that Br^- might react in the same way also in the UO_2 system.

In this work we have investigated the impact of Cl^-, Br^- and ClO_4^- on the mechanism and kinetics of H_2O_2 induced oxidative dissolution of UO_2 in HCO_3^-/CO_3^{2-} deficient solutions and the impact of Br^- only in solutions containing 10 mM HCO_3^-. The latter was done to complement the previous study on ionic strength effects and to elucidate the possible reaction between surface-bound hydroxyl radicals and Br^- in the UO_2 system.

Results and Discussion

Experiments were performed for aqueous solutions containing 10 mM HCO_3^- and for aqueous solutions without added HCO_3^-.

The results for solutions containing 10 mM HCO_3^- are presented first.

H_2O_2-induced oxidative dissolution of UO_2 in 10 mM HCO_3^-

A series of experiments were performed in 10 mM HCO_3^-. In Figure 1, the H_2O_2 and uranium concentrations are plotted as a function of time for exposures where the initial H_2O_2 concentration was 0.15 mM.

As can be seen, the rate of H_2O_2 consumption and the rate of uranium dissolution do not vary beyond the experimental uncertainty between the different solution compositions. Hence, no significant effects of the presence of Cl^- and Br^- can be observed. The final uranium concentration is higher than the initial H_2O_2 concentration. This is attributed to the presence of pre-oxidized UO_2 in the interior of the powder particles. In general, this leads to an overestimation of the uranium release.

H_2O_2-exposure experiments were performed also with higher initial H_2O_2-concentrations (0.6 and 2.0 mM) in 10 mM HCO_3^- solutions with and without 1 M Br^-. The results are presented in Figure 2 and Figure 3.

In Figure 2 it is obvious that H_2O_2 is consumed faster and that uranium is dissolved faster in the solution containing 1 M
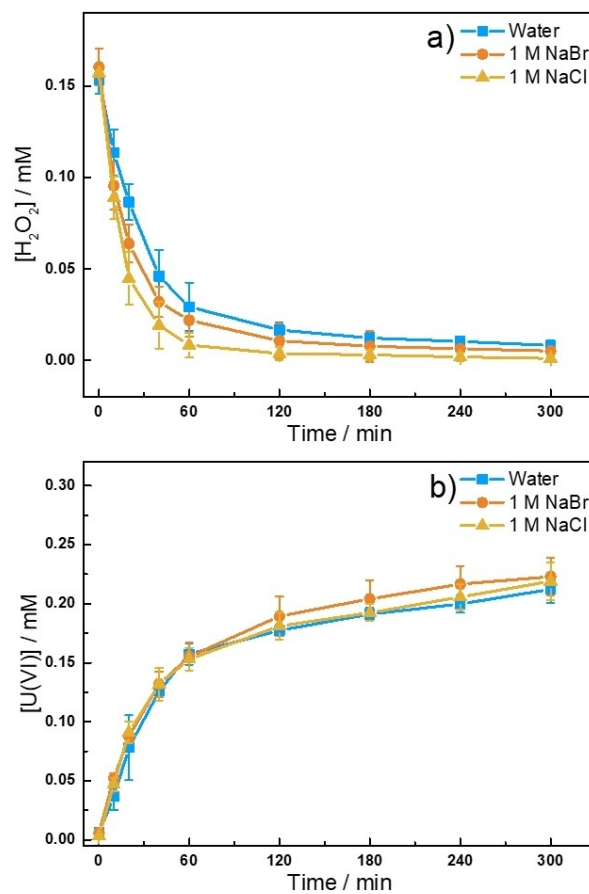

Figure 1. H_2O_2 (a) and uranium (b) concentrations as a function of reaction time for UO_2 suspensions containing 10 mM HCO_3^- and 1 M Br^-, 1 M Cl^- or no additional component. The initial H_2O_2 concentration was 0.15 mM.

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Figure 2. H_2O_2 (a) and uranium (b) concentrations as a function of reaction time for UO_2 suspensions containing 10 mM HCO_3^- and 1 M Br^- or no additional component. The initial H_2O_2 concentration was 0.6 mM.
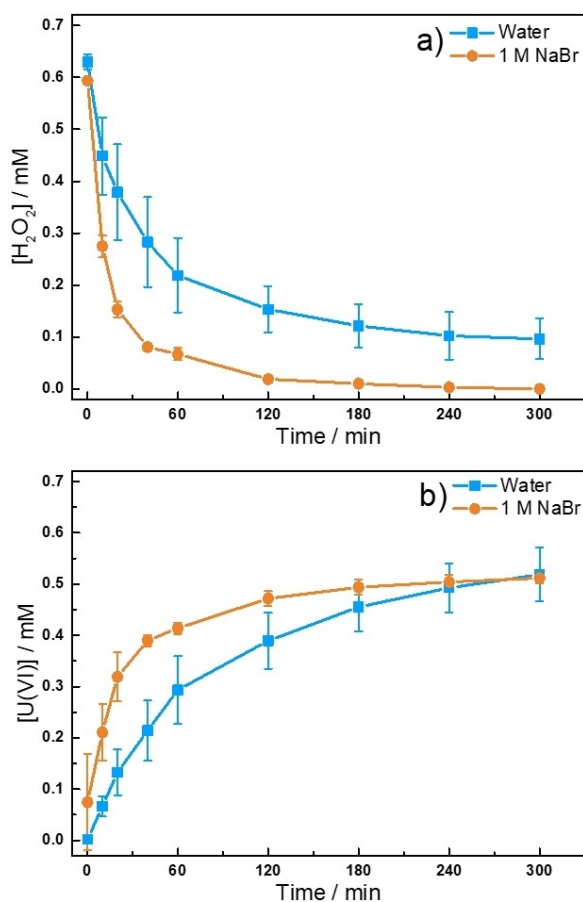

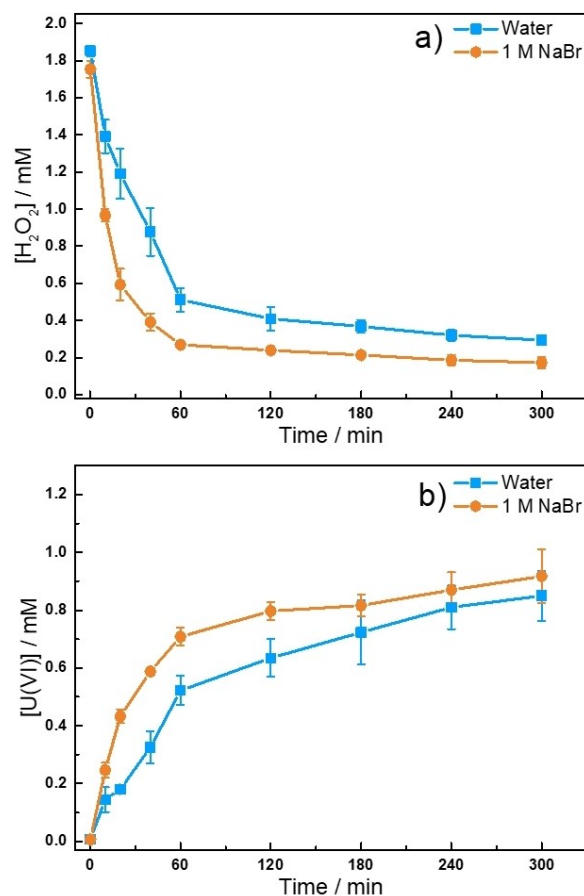**Figure 3.** H_2O_2 (a) and uranium (b) concentrations as a function of reaction time for UO_2 suspensions containing 10 mM HCO_3^- and 1 M Br^- or no additional component. The initial H_2O_2 concentration was 2 mM.

Br^-. In the solution without Br^- the consumption of H_2O_2 appears to stop before reaching a concentration of 0.

The data presented in Figure 3 are in good agreement with the data shown in Figure 2. However, it seems like the H_2O_2 consumption stops before reaching a concentration of 0 also in the system containing Br^-. As pointed out in the introduction, the mechanism of H_2O_2-induced oxidative dissolution of UO_2 involves the formation of surface bound hydroxyl radicals that can both oxidize the surface they are bound to and react with H_2O_2 in solution.[9] As a consequence, H_2O_2 is initially consumed by adsorption to the UO_2 surface and as adsorption increases (i.e., the surface becomes saturated) the mode of reaction changes to the reaction with surface bound hydroxyl radicals. It is therefore reasonable to expect a change in the rate constant for H_2O_2 consumption with H_2O_2 conversion. Upon closer inspection of the results, we can see that the first order rate constant based on data for the first 60 minutes of reaction is somewhat higher (ca 40%) for the 0.15 mM initial H_2O_2 concentration ($(4.7 \pm 0.2) \times 10^{-4} \, s^{-1}$) compared to the higher initial concentrations ($(3.3 \pm 0.2) \times 10^{-4} \, s^{-1}$). It is also quite clear that the kinetics deviates from first order for the higher initial H_2O_2-concentrations at higher H_2O_2 conversions, where the reaction is slowed-down considerably.

It has previously been shown that, in addition to the well-known complexes between uranyl and carbonate, peroxide containing complexes can also be formed under certain circumstances.[36,37] To further explore the change in kinetics at higher conversions, we performed speciation calculations for the conditions found at the end of the experiments presented in Figure 3 above (i.e., 10 mM HCO_3^-, 0.8 mM UO_2^{2+} and 0.2 mM H_2O_2). The speciation calculations were performed using Medusa,[38] on the basis of the equilibrium constants reported for the complexes formed in the ternary U(VI)-peroxide-carbonate system.[36] The ionic strength effect (due to the high Br^- concentration in one experiment) was accounted for using the Specific Ion interaction Theory (SIT).[39–43] Interestingly, the speciation calculations show that $(UO_2)_2(O_2)(CO_3)_4^{6-}$ is the dominating peroxide species at the end of both experiments shown in Figure 3, regardless of ionic strength. However, at lower conversions the speciation will display ionic strength dependence. Given the drastic change in kinetics at high conversion, reasonable to assume that $(UO_2)_2(O_2)(CO_3)_4^{6-}$ displays significantly lower reactivity towards UO_2 than H_2O_2 does. This would explain why the H_2O_2 concentration appears to level out at a certain conversion.

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The presence of 1 M Br$^-$ appears to reduce this effect. Indeed, this could partly be an ionic strength effect. The highly negatively charged complex $(UO_2)_2(O_2)(CO_3)_4^{6-}$ will be electrostatically repelled by the negatively charged surface (at this pH) and the high ionic strength at 1 M Br$^-$ could reduce the repulsion and thereby increase the rate of the reaction. However, this would not explain the fact that the initial rate of H$_2$O$_2$ consumption is much higher in the solution containing Br$^-$ since the initially dominating species is H$_2$O$_2$. In a previous study of the kinetics and mechanism of catalytic decomposition of H$_2$O$_2$ on ZrO$_2$ it was shown that Br$^-$ can react with the surface bound hydroxyl radical to produce Br$_2^{\bullet-}$.[35] This reaction was found to increase the rate of H$_2$O$_2$ consumption in the system. Br$_2^{\bullet-}$ is also capable of oxidizing UO$_2$. Hence, this reaction may explain the faster reaction kinetics observed for the systems containing 1 M Br$^-$.

H$_2$O$_2$-induced oxidative dissolution of UO$_2$ in HCO$_3^-$ free solutions

To explore the impact of anions on H$_2$O$_2$ induced oxidative dissolution of UO$_2$ in aqueous solutions without added HCO$_3^-$, a series of experiments were performed. The results are shown in Figure 4, Figure 5 and Figure 6.

Unlike for the systems containing 10 mM HCO$_3^-$, a significant anion effect is observed both for the consumption of H$_2$O$_2$ and the dissolution of uranium at the lowest initial H$_2$O$_2$ concentration. The fastest consumption of H$_2$O$_2$ is observed for the solution containing 1 M ClO$_4^-$. At the same time, virtually no uranium is dissolved in this system. The slowest H$_2$O$_2$ consumption is observed for the solution containing 1 M Cl$^-$ and this is also the solution where most uranium is dissolved in the end. The consumption of H$_2$O$_2$ appears to stop at a concentration of about 0.05 mM which coincidentally is also the final uranium concentration in the system. For the system containing Br$^-$ the trend is similar but the final H$_2$O$_2$ concentration as well as the final uranium concentration are considerably lower. For the pure water system, the trend is slightly different. Rapid initial consumption of H$_2$O$_2$ is followed by considerably slower consumption and the initially rapid dissolution of uranium is followed by a slow reduction in uranium concentration. This behavior is consistent with formation of uranyl peroxo complex followed by precipitation of studtite.[44]

For the higher initial H$_2$O$_2$ concentration, the trends differ a bit compared to the lowest initial H$_2$O$_2$ concentration. Here it is clear that the Cl$^-$ and the Br$^-$ containing solutions behave in very similar ways both with respect to H$_2$O$_2$ consumption and uranium dissolution. These solutions represent the slowest H$_2$O$_2$ consumption where the consumption becomes very slow at a concentration of around 0.3 mM. At the same time, uranium dissolution is largest in these solutions with a final concentration of 0.20–0.25 mM. Again, this indicates that formation of soluble uranyl peroxo complexes is taking place. For pure water the H$_2$O$_2$ consumption is again initially fast, and the uranium concentration initially increases followed by a slow decrease
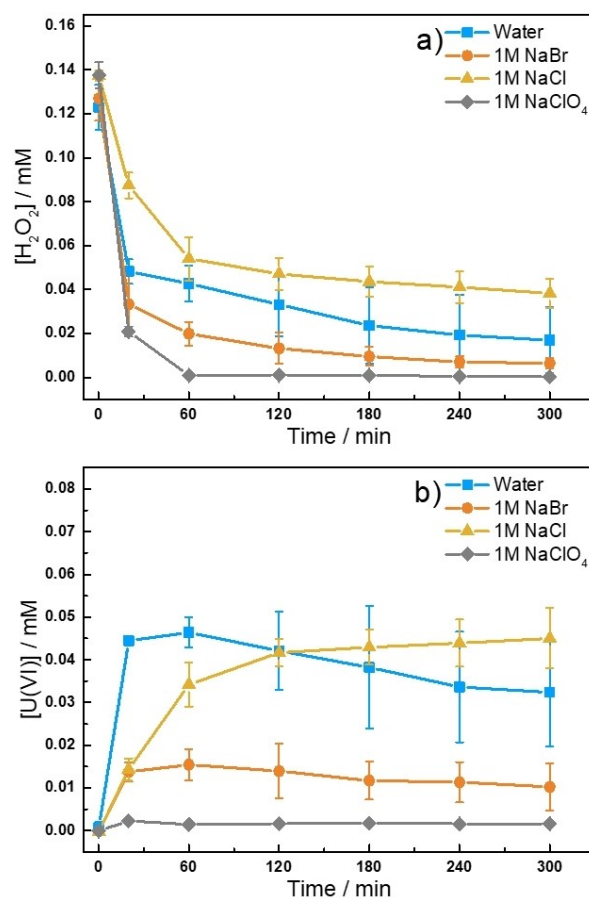

Figure 4. H$_2$O$_2$ (a) and uranium (b) concentrations as a function of reaction time for UO$_2$ suspensions containing bicarbonate free water with and without 1 M NaBr, NaCl or NaClO$_4$. The initial H$_2$O$_2$ concentration was 0.15 mM.

implying that studtite is precipitating.[44] Interestingly, there is a slow increase in uranium concentration also for the solution containing ClO$_4^-$.

For the highest initial H$_2$O$_2$ concentration the trend is relatively similar. The solutions containing Cl$^-$ and Br$^-$ behave similarly to each other and the results again indicate that formation of soluble but fairly unreactive uranyl peroxo complexes is taking place. For the pure water it is evident that much less uranium is dissolved but again the concentration reaches an early maximum whereafter it decreases which is in line with studtite precipitation.[44] In the ClO$_4^-$ system the uranium concentration increases linearly with time but to a level much lower than for Br$^-$ and Cl$^-$.

From the experiments performed in solutions without added HCO$_3^-$ it can be seen that the amount of dissolved uranium is much lower than the amount of consumed H$_2$O$_2$. This is not entirely unexpected since the solubility of uranium species is in general limited in the absence of HCO$_3^-$. To shed some light on this issue, a series of experiments where 10 mM HCO$_3^-$ was added 3 h after the H$_2$O$_2$ exposure (0.15 mM initial concentration) was initiated were performed. The results are shown in Figure 7.
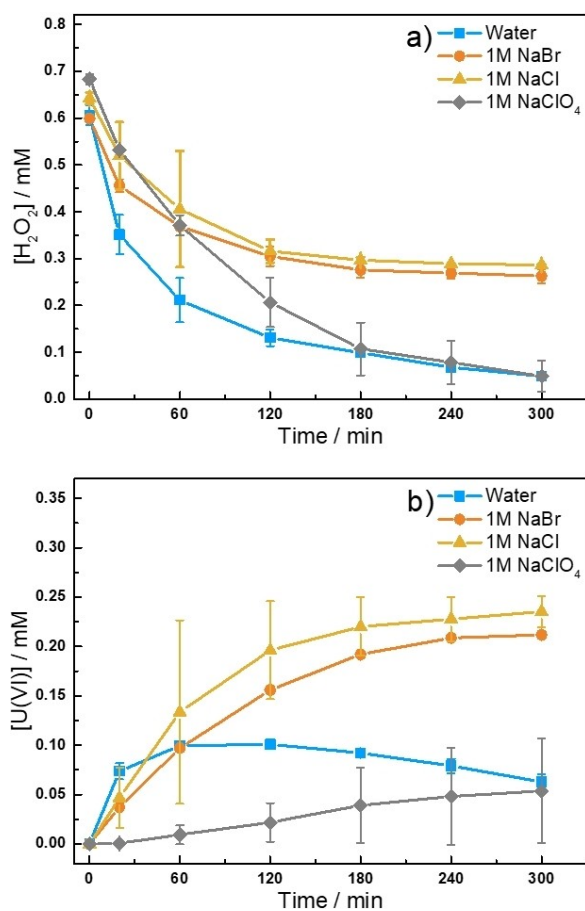
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Figure 5. H_2O_2 (a) and uranium (b) concentrations as a function of reaction time for UO_2 suspensions containing bicarbonate free water with and without 1 M NaBr, NaCl or $NaClO_4$. The initial H_2O_2 concentration was 0.6 mM.
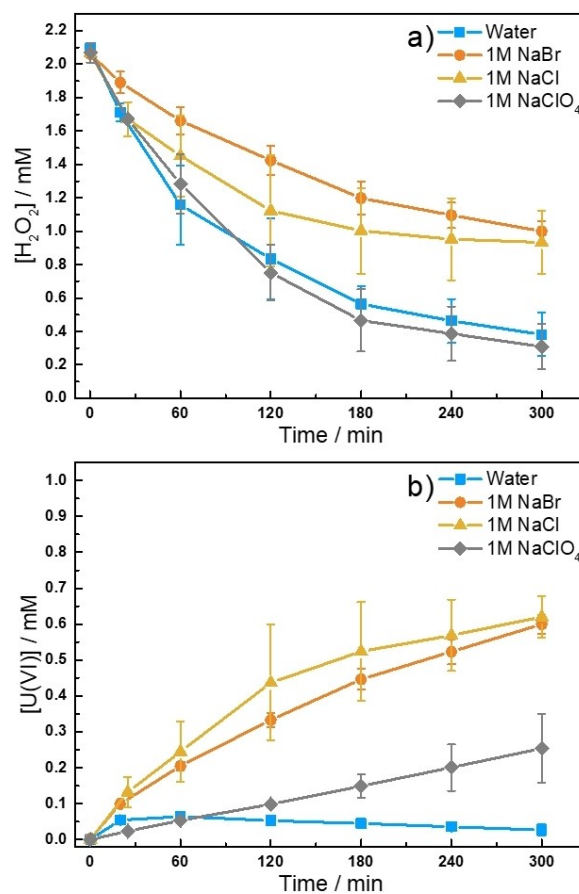

Figure 6. H_2O_2 (a) and uranium (b) concentrations as a function of reaction time for UO_2 suspensions containing bicarbonate free water with and without 1 M NaBr, NaCl or $NaClO_4$. The initial H_2O_2 concentration was 2 mM.

As can be seen, the remaining H_2O_2 is consumed fairly rapidly after the addition of HCO_3^- and the uranium concentration is rapidly increased to the levels seen for the corresponding system containing HCO_3^- from the beginning. This is particularly striking for the ClO_4^- system where H_2O_2 consumption was quantitative while virtually no uranium was dissolved. This implies that the oxidized UO_2 is adsorbed to the surface in the solution containing ClO_4^-.

To test the possible ionic strength effects on the adsorption of UO_2^{2+} to UO_2, simple batch adsorption experiments were carried out where the concentration of UO_2^{2+} was monitored as a function of time for pure water with and without 1 M Cl^-, Br^- and ClO_4^-. The results are presented in Figure 8.

As can be seen, UO_2^{2+} is adsorbed to some extent in pure water and quantitatively in the solutions containing 1 M salt. This implies that there is a significant ionic strength effect favoring adsorption under the present conditions. The fact that we observe a different behavior for the systems containing Br^- and Cl^- as compared to the system containing ClO_4^- in the experiments where we have exposed UO_2 powder to H_2O_2, indicates that Cl^- and Br^- have a stabilizing effect on uranyl peroxo complexes in addition to the ionic strength effect that

favors adsorption of UO_2^{2+}. The stabilization of the uranyl peroxo complexes becomes the dominant effect for Cl^- and Br^- under the present conditions. ClO_4^- only favors adsorption of UO_2^{2+} and therefore the uranyl concentration is too low for uranyl peroxo complexes to be formed at the lowest initial H_2O_2 concentration. At the higher initial H_2O_2 concentrations we observe an increase in the uranium concentration with time and it is also evident that the initial rate constant (based on the first 60 minutes of reaction) for H_2O_2 consumption is considerably lower at the higher initial H_2O_2 concentrations. The estimated initial rate constants for H_2O_2 consumption in pure water are 1.4×10^{-3}, 1.7×10^{-4} and 1.3×10^{-4} s^{-1} for the initial H_2O_2 concentrations 0.15, 0.6 and 2 mM, respectively. This could imply that uranyl-peroxo complexes are formed at the higher initial H_2O_2 concentrations also in solutions containing ClO_4^-.

The impact of UO_2^{2+} was investigated by adding 0.05 mM UO_2^{2+} together with H_2O_2 when starting the exposure experiments. The results are presented in Figure 9.

As can be seen in Figure 9, the UO_2^{2+} concentration drops quickly initially for the solutions containing Cl^-, Br^- and ClO_4^-. This is due to the ionic strength facilitated adsorption of UO_2^{2+} on UO_2. For pure water no significant adsorption is observed. After a short time, the uranium concentration increases in all

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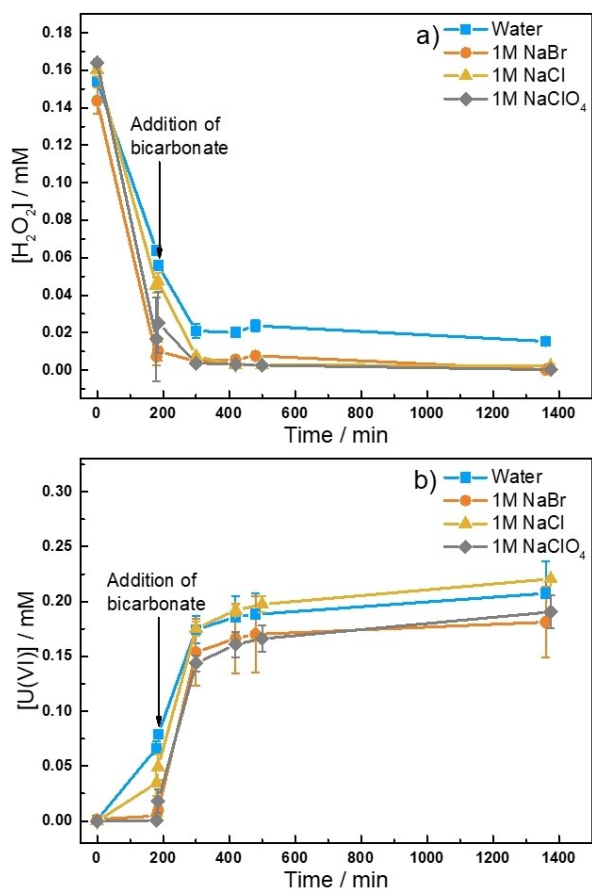**Figure 7.** H_2O_2 (a) and uranium (b) concentrations as a function of reaction time for UO_2 suspensions containing pure water with and without 1 M NaBr, NaCl or $NaClO_4$. The initial H_2O_2 concentration was 0.15 mM and 10 mM HCO_3^- was added to the suspensions after 180 minutes.
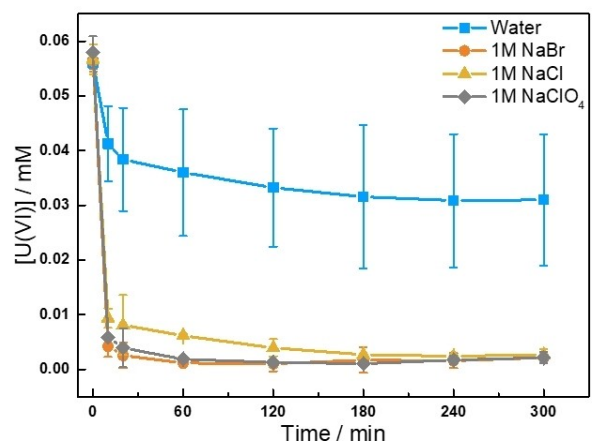

Figure 8. Uranium concentrations as a function of reaction time for UO_2-suspensions containing pure water with and without 1 M NaBr, NaCl or $NaClO_4$. The initial UO_2^{2+} concentration was 0.06 mM and the pH was set to 7.

systems to levels that are fairly close to the ones observed in the corresponding solutions without initially added UO_2^{2+} (Figure 4). In general, the rate of H_2O_2 consumption is slightly
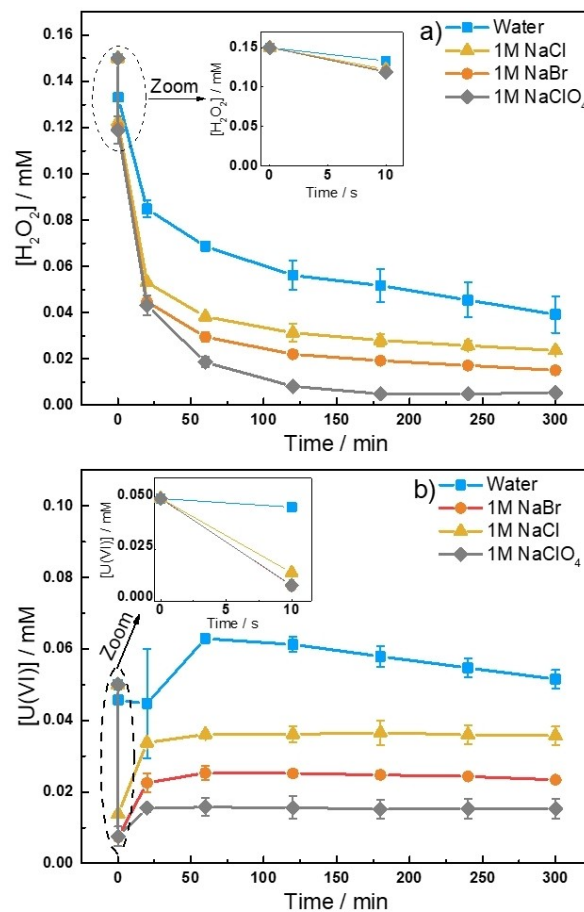

Figure 9. H_2O_2 (a) and uranium (b) concentrations as a function of reaction time for UO_2-suspensions containing pure water with and without 1 M NaBr, NaCl or $NaClO_4$. The initial H_2O_2 concentration was 0.15 mM and the initial UO_2^{2+} concentration was 0.05 mM at pH 7.

lower for the systems where UO_2^{2+} is initially present. This can probably be attributed to the formation of uranyl peroxo complexes.

Conclusion

The experiments performed in this work show that Cl^- and Br^- have no effect on the kinetics for H_2O_2-induced oxidative dissolution of UO_2 in aqueous solutions containing 10 mM HCO_3^- for initial H_2O_2 concentrations of 0.15 mM. At higher initial H_2O_2 concentrations (0.6 and 2 mM) in systems containing 10 mM HCO_3^-, 1 M Br^- increases the rate of H_2O_2 consumption as well as the rate of uranium dissolution. The observed difference in kinetics is proposed to be attributed to ionic strength effects on the reaction between highly charged uranyl-carbonate-peroxo complexes and the UO_2 surface and possibly also to reactions between surface-bound hydroxyl radicals and Br^- analogous to what has recently been observed on ZrO_2 surfaces.

For systems without added HCO_3^-, the presence of Cl^-, Br^- and ClO_4^- influences the reaction kinetics for all initial H_2O_2

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concentrations investigated. As the different anions influence the kinetics to different extent it is quite clear that we have both ionic strength effects and specific ion effects. The general ionic strength effect appears to be mainly connected to adsorption of UO_2^{2+} and the adsorption is enhanced by increased ionic strength. In solutions containing 1 M ClO_4^-, H_2O_2 is quantitatively consumed while the release of UO_2^{2+} is very limited. The pure ionic strength effect is mainly displayed by ClO_4^-. Cl^- and Br^-, on the other hand, both slow down the consumption of H_2O_2 and enhances the dissolution of UO_2^{2+}. This is interpreted as formation of uranyl-peroxo complexes stabilized by Cl^- and Br^-. In pure water, the reaction dynamics show clear signs of studtite formation as oxidation of UO_2 proceeds. This is not observed in the presence of the ClO_4^-, Cl^- or Br^-. The results of this work imply that uranyl-peroxo complexes are of importance when describing the reaction mechanism of H_2O_2-induced dissolution of UO_2 in systems containing Cl^- and Br^- as well as in systems containing HCO_3^-.

Experimental Section

Material Preparation and Characterization

Depleted UO_2 powder was supplied from Westinghouse Electric Sweden AB. The stoichiometry of the powder has previously been determined by weight gain through oxidation in air at 400 °C for 16 h.[45] The resulting U_3O_8 phase was confirmed by XRD measurements. The UO_2 powder was found to be hyperstoichiometric ($UO_{2.3}$).[46]

H_2O_2-exposure experiments

Aqueous powder suspensions of UO_2 were prepared with and without 10 mM $NaHCO_3$ (Merck). Purified water (18.2 MW cm, Merck MilliQ) was used for all experiments. Before each experiment the UO_2 powder was washed three times for 25 minutes in 10 mM bicarbonate solution to remove pre-oxidized uranium from the surface. An extra wash with 10 mL of MQ water performed for 5 minutes to remove any residual bicarbonate from the powder. The chemicals used in all experiments are of reagent grade or higher unless otherwise stated. 50 mg UO_2 powder was added to a total volume of 25 ml of aqueous solution. The solution containers were always protected from light. All experiments were carried out at room temperature and the suspensions were purged with N_2 ($\geq$ 99.999%, Standmøllen) throughout the washing procedure and the experiment. The solutions of high ionic strength contained 1 M of $NaBr$, $NaCl$ or $NaClO_4$. Solutions initially containing uranyl were prepared by dissolving uranyl nitrate ($UO_2(NO_3)_2 \cdot 6H_2O$) in water. For solutions not containing HCO_3^-, the initial pH was adjusted to 7 using NaOH. The pH was measured at the beginning and at the end of the experiment and it was in general found to change by less than 0.5 pH units during the experiment.

The reaction solutions contained 0.15–2 mM H_2O_2 (J.T. Baker). The concentration of H_2O_2 was measured indirectly using the Ghormley triiodide method,[47,48] where I^- is oxidized to I_3^- by H_2O_2. The absorbance of I_3^- was measured at 360 nm by UV/Vis spectrophotometry. The concentration of U(VI) in solution was measured using the Arsenazo III method,[49] where uranyl reacts with the Arsenazo III reagent forming a complex in acidic solution. The absorbance of the complex is measured at 653 nm by UV/Vis spectrophotometry. Samples from the reaction solution were filtered through 0.2 µm

cellulose acetate syringe filters immediately to stop the reaction between H_2O_2 and UO_2.

Conflict of Interest

The authors declare no conflict of interest.

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