

# Effects of ionic strength on the kinetics for $\text{UO}_2$ oxidation

Mohammad Mohsin Hossain, Mats Jonsson \*

*KTH Chemical Science and Engineering, Nuclear Chemistry, Royal Institute of Technology, SE – 100 44 Stockholm, Sweden*

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## Abstract

The effect of ionic strength on the kinetics of  $\text{UO}_2$  oxidation by  $\text{H}_2\text{O}_2$  in aqueous solution has been studied using powder suspensions, where the concentration of  $\text{H}_2\text{O}_2$  was monitored as a function of time. Experiments were performed at 0 and 10 mM  $\text{HCO}_3^-$ .  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  were used to adjust the ionic strength. At 0 mM  $\text{HCO}_3^-$  (where the kinetics is influenced by both oxidation and dissolution) the rate constant for the reaction increases with increasing ionic strength while at 10 mM  $\text{HCO}_3^-$  (where the kinetics is independent of the dissolution of oxidized  $\text{UO}_2$ ) the rate constant is virtually independent of ionic strength. This implies that dissolution of oxidized  $\text{UO}_2$  in the absence of  $\text{HCO}_3^-$  is ionic strength dependent. As expected, the reaction between  $\text{H}_2\text{O}_2$  and  $\text{UO}_2$  is not affected by ionic strength since  $\text{H}_2\text{O}_2$  has no charge. This finding also implies that peroxydicarbonate ( $\text{HCO}_4^-$ ) cannot be an important oxidant under the present conditions.

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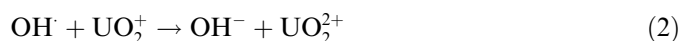
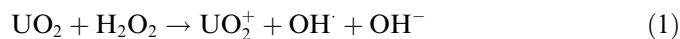
## 1. Introduction

The possible release of toxic and radioactive species from spent nuclear fuel in contact with water in a future repository is expected to depend mainly on the rate of dissolution of the  $\text{UO}_2$  matrix [1]. In the reducing groundwater expected at the depth of a repository,  $\text{UO}_2$  has very low solubility [2]. However, radiolysis of the groundwater will produce reactive radicals and molecular products ( $e_{\text{aq}}^-$ ,  $\text{H}$ ,  $\text{H}_2$  (reductants) and  $\text{OH}^\cdot$ ,  $\text{H}_2\text{O}_2$  (oxidants)) [3] and thereby alter the reducing environment. Secondary reactions will produce  $\text{HO}_2^\cdot$ ,  $\text{O}_2^{\cdot-}$  and  $\text{O}_2$  and with carbonate present in the groundwater,  $\text{CO}_3^{\cdot-}$  will be produced.  $\text{OH}^\cdot$  and  $\text{CO}_3^{\cdot-}$  are both strong one-electron oxidants ( $E^0 = 1.9$  V and 1.59 V vs. NHE, respectively [4,5]), while  $\text{HO}_2^\cdot$  and  $\text{O}_2^{\cdot-}$  are fairly weak one-electron oxidants (depending on pH).  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  on the other hand can act as both one- and two-electron oxidants.

The presence of carbonate affects the kinetics for  $\text{UO}_2$  oxidation not only by converting  $\text{OH}^\cdot$  into  $\text{CO}_3^{\cdot-}$ , but also since it forms soluble complexes with the oxidation prod-

uct,  $\text{UO}_2^{2+}$  [6], and thereby maintains a larger surface area accessible to oxidation. In a recent paper, we studied the effect of  $\text{HCO}_3^-$  concentration on the kinetics for  $\text{UO}_2$  oxidation by  $\text{H}_2\text{O}_2$  [7]. The results show that the consumption of  $\text{H}_2\text{O}_2$  depends on the  $\text{HCO}_3^-$  concentration for concentrations below 1 mM. For higher  $\text{HCO}_3^-$  concentrations, the rate of  $\text{H}_2\text{O}_2$  consumption is independent of  $[\text{HCO}_3^-]$ . From this, we concluded that the oxidation step is the rate limiting process for  $[\text{HCO}_3^-] > 1$  mM, while for lower concentrations the consumption of  $\text{H}_2\text{O}_2$  is significantly influenced by dissolution of  $\text{UO}_2^{2+}$ .

In a previous paper, the kinetics for oxidation of  $\text{UO}_2$  in aqueous solution by various oxidants was studied [8]. From experimental data we were able to establish a linear relationship between the logarithm of the rate constant and the one-electron reduction potential of the oxidant. Both one- and two-electron oxidants were found to follow this relationship and it was, therefore, concluded that the first one-electron transfer is the rate determining step also for two-electron oxidants. This implies that oxidation of  $\text{UO}_2$  by  $\text{H}_2\text{O}_2$  is a Fenton-like two step process:



\* Corresponding author. Fax: +46 8 790 8772.

E-mail address: [matsj@nuchem.kth.se](mailto:matsj@nuchem.kth.se) (M. Jonsson).

where  $k_2 \gg k_1$ . On the basis of the established relationship and simple collision theory [9], the strongest oxidants expected to occur during radiolysis ( $\text{OH}^\cdot$  and  $\text{CO}_3^{\cdot-}$ ) of groundwater would have rate constants limited by diffusion. Hence, both radicals are expected to be equally reactive towards  $\text{UO}_2$ . It should however, be noted that the impact of the two radicals on  $\text{UO}_2$  dissolution may differ considerably due to differences in reactivity towards other species present in the system affecting the life-time of the radicals. Furthermore, a direct comparison between the two radicals is not feasible since they cannot exist under identical conditions, i.e.  $\text{CO}_3^{\cdot-}$  can only be produced in the presence of  $\text{HCO}_3^-/\text{CO}_3^{2-}$ , while  $\text{OH}^\cdot$  will only have a significant life-time in the absence of  $\text{HCO}_3^-/\text{CO}_3^{2-}$  and other radical scavengers.

The kinetic studies were performed in carbonate free solutions and the reported rate constants are, therefore, probably significantly affected by the dissolution of oxidized  $\text{UO}_2$  and, hence, not the accurate rate constants for oxidation. In our recent paper, on the effect of  $\text{HCO}_3^-$  on the kinetics for  $\text{UO}_2$  oxidation, we found that the  $[\text{HCO}_3^-]$  independent rate constant for oxidation by  $\text{H}_2\text{O}_2$  is  $4.4 \times 10^{-6} \text{ m min}^{-1}$  [7]. This value is significantly higher than the value originally reported. The presence of carbonate has also been suggested to reduce the efficiency of the oxidant ( $\text{H}_2\text{O}_2$ ) due to the conversion of  $\text{OH}^\cdot$  into  $\text{CO}_3^{\cdot-}$ , where the latter was claimed to be less reactive towards  $\text{UO}_2$  [10]. However, judging from our previous work, this does not seem to be a plausible explanation. It should be noted that, in aqueous solutions containing  $\text{H}_2\text{O}_2$  and  $\text{HCO}_3^-$ , peroxymonocarbonate ( $\text{HCO}_4^-$ ) can be formed [11]. The reactivity of peroxymonocarbonate towards  $\text{UO}_2$  is not known, but judging from the reported redox properties it should be similar to that of  $\text{H}_2\text{O}_2$  [12].

In a recent paper, the relative impact of different radiolysis products on oxidative dissolution of  $\text{UO}_2$  was studied [13]. For  $\beta/\gamma$ -radiolysis, it was shown that the radical products have a significant impact during the first hours of irradiation. However, for longer irradiation time, the molecular oxidants dominate the system. For  $\alpha$ -radiolysis, the relative impact of  $\text{H}_2\text{O}_2$  was found to be 99.9%–100%. In conclusion, the influence of radical oxidants is expected to be insignificant under deep repository conditions.

The groundwater composition in a repository for spent nuclear fuel is an essential parameter. As has previously been shown, pH and the presence of complexing agents such as  $\text{HCO}_3^-$  significantly affect the rate of oxidative dissolution [7]. However, the general influence of ionic strength has to our knowledge not been quantitatively assessed.

The kinetics of reactions involving ions depends on the ionic strength of the solution according to Eq. (3) [9]:

$$\log k = \log k_0 + 1.02z_A z_B \sqrt{I}, \quad (3)$$

where  $k_0$  denotes the rate constant at zero ionic strength,  $z_A$  and  $z_B$  denote the charge of the reactants and  $I$  is the ionic strength ( $I = \frac{1}{2} \sum_i c_i z_i^2$ ).

Since  $\text{H}_2\text{O}_2$  appears to be the only important oxidant under repository conditions and since  $\text{H}_2\text{O}_2$  has no charge, we would not expect any effect of ionic strength on the rate of spent fuel oxidation. However, this is only true if the concentration of  $\text{HCO}_3^-$  is sufficiently high ( $>1 \text{ mM}$ ) and the kinetics is limited by the oxidation step. The dissolution process is expected to depend on ionic strength.

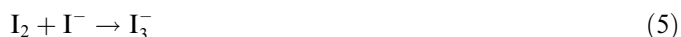
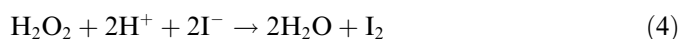
In this work, we have studied the influence of ionic strength on the kinetics for  $\text{UO}_2$  oxidation by  $\text{H}_2\text{O}_2$  in the presence and absence of  $\text{HCO}_3^-$ . The ionic strength was adjusted by using  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$ .

## 2. Experimental

The  $\text{UO}_2$  powder was supplied from Westinghouse Atom AB. Chemicals and gases used were of purest grade available and were obtained from Lancaster, Perstorp AB, Merck, Alfa, BDH and AGA. Millipore Milli-Q filtered water was used throughout. The  $\text{UO}_2$  powder used in this work has a specific surface area of  $5.85 \text{ m}^2/\text{g}$  given by BET measurements. The  $\text{UO}_2$  powder was washed with  $\text{NaHCO}_3$  solutions and pure water prior to the experiments.

The suspensions (18 ml) initially containing 18 mM  $\text{H}_2\text{O}_2$ , 50 mg  $\text{UO}_2$ , 0 or 10 mM  $\text{HCO}_3^-$  and 0–500 mM  $\text{NaCl}$  or 0–200 mM  $\text{Na}_2\text{SO}_4$  were purged with Argon throughout the experiments and stirred by a magnetic stirrer. The sample volume taken for analysis was approximately 2 ml. Before analysis, the solution was filtered (pore size  $0.20 \mu\text{m}$ ) to stop the reaction and to clear the solution.

The concentration of  $\text{H}_2\text{O}_2$  was measured indirectly by UV/visible spectroscopy (Jasco V-530 UV/VIS-Spectrophotometer). The  $\text{H}_2\text{O}_2$  solutions were protected from light during the experiments. We have used  $\text{I}_3^-$  as ‘indicator’ for analysis of the hydrogen peroxide concentration at 360 nm, where  $\text{I}_3^-$  absorbs (reaction (4) and (5)).



The sample was mixed with 100  $\mu\text{l}$  potassium iodide (1 M KI) and 100  $\mu\text{l}$  acetate buffer, which contained ammonium molybdate (catalyst) (1 M HAc/NaAc, a few drops of 3%  $(\text{NH}_4)_2\text{MoO}_7$  (ADM) to 100 ml solution) and water to a total volume of 2 ml. Using this method,  $\mu\text{M}$  concentrations of  $\text{H}_2\text{O}_2$  are detectable. Detailed information about the  $\text{I}_3^-$  method can be found in reference [14–16].

## 3. Result and discussion

In this work, we have performed all experiments at the same surface to volume ratio. Hence, we only have enough data to derive pseudo-first-order rate constants. However, pseudo-first-order rate constants (determined at the same surface to volume ratio) are sufficient when studying the effects of ionic strength on the kinetics for  $\text{UO}_2$  oxidation.

Table 1  
Pseudo-first-order rate constants for the reaction between  $\text{H}_2\text{O}_2$  and  $\text{UO}_2$  at different electrolyte concentrations

Electrolyte	Pseudo-first-order rate constant/ $\text{s}^{-1}$	
	0 mM $\text{HCO}_3^-$	10 mM $\text{HCO}_3^-$
0	$3.2 \times 10^{-4}$	$6.0 \times 10^{-4}$
10 mM $\text{Na}_2\text{SO}_4$	$3.8 \times 10^{-4}$	$5.5 \times 10^{-4}$
50 mM $\text{Na}_2\text{SO}_4$	$6.0 \times 10^{-4}$	$6.0 \times 10^{-4}$
100 mM $\text{Na}_2\text{SO}_4$	$6.5 \times 10^{-4}$	–
200 mM $\text{Na}_2\text{SO}_4$	$4.3 \times 10^{-4}$	$6.7 \times 10^{-4}$
10 mM NaCl	$3.8 \times 10^{-4}$	$6.0 \times 10^{-4}$
50 mM NaCl	$4.7 \times 10^{-4}$	$5.7 \times 10^{-4}$
100 mM NaCl	$4.3 \times 10^{-4}$	–
200 mM NaCl	$4.5 \times 10^{-4}$	$7.3 \times 10^{-4}$
500 mM NaCl	$6.0 \times 10^{-4}$	–

The pseudo-first-order rate constants obtained from the experiments are summarized in Table 1.

As can be seen, the pseudo-first-order rate constant for 0 mM  $\text{HCO}_3^-$  increase with increasing ionic strength. For 10 mM  $\text{HCO}_3^-$ , the rate constant is virtually independent of ionic strength. In this case, the rate constant at 0 mM added electrolyte is more or less identical to the maximum rate constant for 0 mM  $\text{HCO}_3^-$  obtained at fairly high ionic strength. The relatively large effect of 10 mM  $\text{HCO}_3^-$  and the low sensitivity to additional increase in electrolyte concentration clearly demonstrates that the major effect of  $\text{HCO}_3^-$  is complexation of  $\text{UO}_2^{2+}$  rather than an ionic strength effect.

In Fig. 1 the logarithm of the pseudo-first-order rate constant is plotted as a function of  $\sqrt{I}$  for 0 and 10 mM  $\text{HCO}_3^-$ .

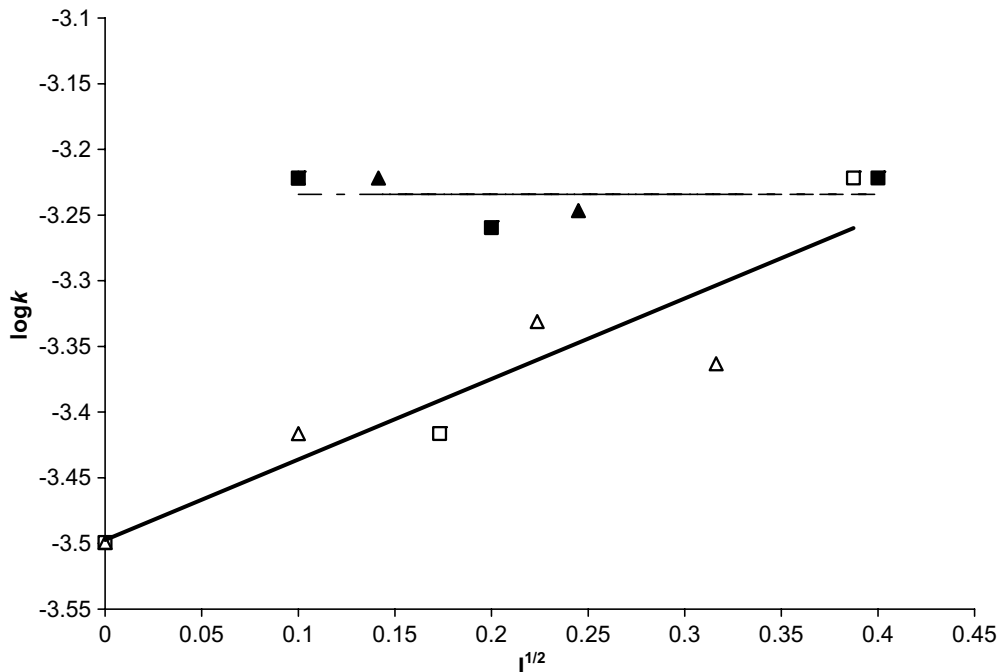


Fig. 1. Logarithm of pseudo-first-order rate constants for the reaction between  $\text{H}_2\text{O}_2$  and  $\text{UO}_2$  plotted against the square root of ionic strength. Open symbols indicate 0 mM  $\text{HCO}_3^-$  and filled symbols indicate 10 mM  $\text{HCO}_3^-$ . Triangles indicate NaCl and squares indicate  $\text{Na}_2\text{SO}_4$ .

As can be seen, there is no significant difference between the two electrolytes. This implies that the observed effect is indeed an ionic strength effect. Again, the figure clearly demonstrates the difference between the system containing  $\text{HCO}_3^-$  and the system where no  $\text{HCO}_3^-$  was added. In the system containing 10 mM  $\text{HCO}_3^-$  the rate limiting step is oxidation and, as expected since  $\text{H}_2\text{O}_2$  is uncharged, the system does not display any ionic strength dependence. Consequently, the ionic strength does not have to be accounted for in spent nuclear fuel dissolution provided the groundwater  $\text{HCO}_3^-$  concentration is sufficiently high ( $>1$  mM). Interestingly, the absence of an ionic strength effect in the system containing 10 mM  $\text{HCO}_3^-$  shows that peroxydicarbonate ( $\text{HCO}_4^-$ ) cannot be an important oxidant under the present conditions. As stated above, the rate limiting step in this system is oxidation rather than dissolution of oxidized  $\text{UO}_2^{2+}$  and, since peroxydicarbonate is an anion, its involvement in the oxidation process would have been revealed by an ionic strength effect. Interestingly, for the system where no  $\text{HCO}_3^-$  was added the ionic strength effect is significant. This implies that the kinetics for dissolution of oxidized  $\text{UO}_2$  is ionic strength dependent. The rationale for this may simply be that the Gibbs free energy for  $\text{UO}_2^{2+}$  in solution decreases with increasing ionic strength (as given by the Debye–Hückel limiting law) [9]. The ionic strength dependence can be quantitatively described by Eq. (6).

$$\log \frac{k}{k_0} = (0.61 \pm 0.13)\sqrt{I}. \quad (6)$$

As has been shown previously, for  $\text{HCO}_3^-$  free systems, the kinetics for  $\text{H}_2\text{O}_2$  consumption changes from initially being

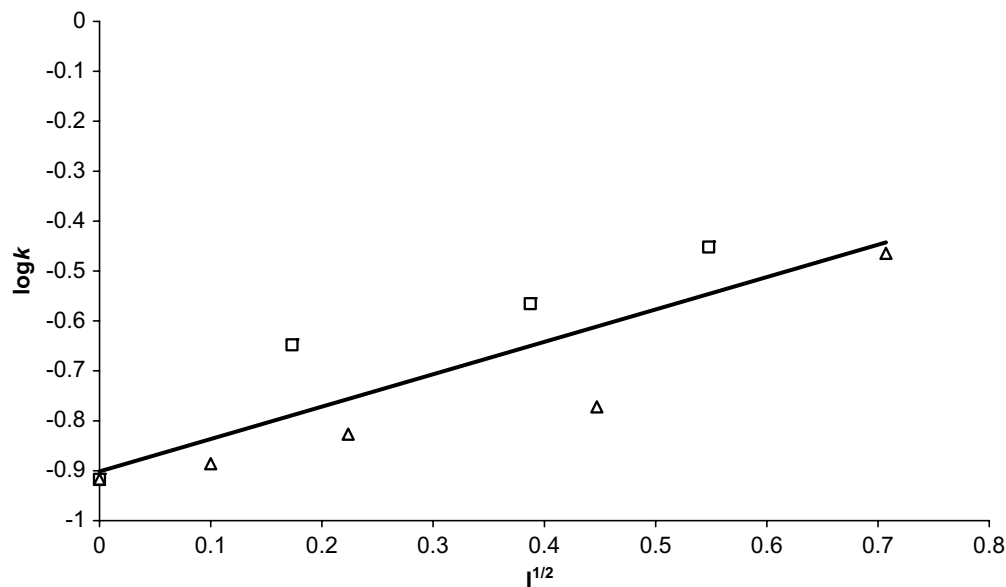


Fig. 2. Logarithm of the zeroth order rate of  $\text{UO}_2^{2+}$  dissolution plotted against the square root of ionic strength at 0 mM  $\text{HCO}_3^-$ . Triangles indicate NaCl and squares indicate  $\text{Na}_2\text{SO}_4$ .

of first order to zeroth order, where the consumption is completely governed by dissolution [7]. The rationale for the change in reaction order is that the surface becomes saturated with oxidized  $\text{UO}_2$  and the rate of consumption of  $\text{H}_2\text{O}_2$  thereby becomes identical to the rate of  $\text{UO}_2^{2+}$  dissolution. In Fig. 2 the logarithm of the zeroth order rate of dissolution is plotted as a function of  $\sqrt{I}$  for 0 mM  $\text{HCO}_3^-$ .

There is, however, an apparent difference between the two electrolytes. Upon closer inspection, the difference has no statistical significance (based on the uncertainties in the slopes for the two sets of data). The ionic strength dependence on the zeroth order dissolution kinetics can be quantitatively described by Eq. (7).

$$\log \frac{k}{k_0} = (0.65 \pm 0.17)\sqrt{I}. \quad (7)$$

Interestingly, the ionic strength dependence is slightly higher for the zeroth order dissolution kinetics than for the  $\text{H}_2\text{O}_2$  consumption in the  $\text{HCO}_3^-$  free system. However, the difference is very small, which indicates that the pseudo-first-order  $\text{H}_2\text{O}_2$  consumption is largely limited by dissolution in the absence of  $\text{HCO}_3^-$ .

#### Acknowledgement

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