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Oxidation of UO_2 by radiolytic oxidants

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Abstract

The kinetics of UO_2 oxidation by H_2O_2 has been studied using aqueous suspensions of UO_2-powder. The second order rate constant for the reaction between H_2O_2 and UO_2 has been determined to 8×10^{-7} m/min (based on the surface to solution volume ratio) in the absence of carbonate. By studying the reaction between UO_2 and other oxidants, it is possible to draw conclusions concerning the mechanism. The logarithm of the second order rate constant, $\ln k$, for UO_2 oxidation appears to be linearly related to the one-electron reduction potential, E^0, of the oxidant. This indicates that the rate limiting step in the oxidation of UO_2 is one-electron transfer. A Fenton like mechanism is plausible for the reaction between UO_2 and H_2O_2. The diffusion controlled rate constant in this particular system is approximately 10^3 m/min, and therefore the reactions with $OH^{\cdot}$ and $CO_3^{\cdot -}$ are estimated to be diffusion controlled.

1. Introduction

Spent nuclear fuel mainly consists of uranium dioxide (~95%), UO_2, the remaining 5% being fission products and transuranic elements. The release of toxic and radioactive species from spent nuclear fuel in contact with water is expected to depend mainly on the rate of dissolution of the UO_2 matrix [1]. In reducing ground water UO_2 has very low solubility [2]. However, radiolysis of the ground water will produce reactive radicals and molecular products (e^-_{aq}, $H^{\cdot}$, H_2 (reductants) and $OH^{\cdot}$, H_2O_2 (oxidants)) [3] and thereby alter the reducing environment. A key-question is if and how oxidation by primary radiolysis products and other oxidants formed in the system can increase the dissolution rate of the UO_2 matrix? Secondary reactions will produce $HO_2^{\cdot}$ and O_2 and with carbonate present in the ground water, $CO_3^{\cdot -}$ will be produced. $OH^{\cdot}$ and $CO_3^{\cdot -}$ are both strong one-electron oxidants ($E^0 = 1.9$ and 1.59 V vs. NHE, respectively [4,5]) while $HO_2^{\cdot}$ is a moderately strong one-electron oxidant ($E^0 = 0.79$ V vs. NHE [4]). H_2O_2 and O_2 on the other hand can act both as one- and two-electron oxidants. The difference in potential between the radical oxidants and the molecular oxidants as well as the difference in possible redox reactions is of vital importance for the understanding of radiolytically induced UO_2-dissolution. In the case of H_2O_2 two different redox reactions with UO_2 should be considered, one-electron oxidation (reaction (1)) and two-electron oxidation (reaction (2)):

$$H_2O_2 + UO_{2(s)} \rightarrow UO_2^{+} + OH^{-} + OH^{\cdot} \quad (1)$$

$$H_2O_2 + UO_{2(s)} \rightarrow UO_2^{2+} + 2OH^{-} \quad (2)$$

The effect of radiolysis on spent fuel dissolution is a complex issue, which has been studied and discussed for several decades [1]. Due to the complexity of the spent fuel system it is difficult to conclude how much of the dissolution that can be attributed to radiolysis. To analyze the importance of radiolysis, numerical simulations of the reaction system, including heterogeneous as well as homogeneous reactions must be employed. The outcome of such simulations strongly depends on the quality of the input parameters (rate constants) and on the descriptions of the system (e.g., the geometrical dose distribution). It is therefore important to determine the rate constants as well as the mechanisms for the

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elementary reactions involved in the process, e.g., to separate redox processes and dissolution processes.

The oxidative dissolution of UO_2 is a two-step process according to electrochemical studies. The formation of an oxidized layer of $UO_{2.33}$ is followed by oxidative dissolution of this phase together with the formation of secondary phases [1]. Shoesmith et al. have performed H_2O_2 experiments on UO_2 electrodes. They have found that the oxidation rate is higher with H_2O_2 than with O_2 saturated solutions. However, the corrosion (oxidative dissolution) rate, to soluble UO_2^{2+}, appears to be roughly the same for O_2 and H_2O_2. According to these studies, three regions of behavior are apparent in H_2O_2 solutions [1,6]: (1) At low H_2O_2 concentrations ($\sim 10^{-4}$ M), the oxidative dissolution rate is strongly dependent on H_2O_2 concentration, i.e. reaction order >1 with respect to H_2O_2. (2) For $10^{-4} < [H_2O_2] < 5\times10^{-3}$ M, the corrosion rate is independent of the H_2O_2 concentration. In this concentration range, oxidative dissolution is suggested to occur simultaneously with H_2O_2 decomposition to O_2 and H_2O by radical intermediates ($OH^{\cdot}$ and $HO_2^{\cdot}$) [7,8]. H_2O_2 auto-decomposition, a process that is believed to be catalyzed by the UO_2 surface appears to predominate on surfaces of composition UO_{2+x}, where $x \leqslant 0.33$, i.e. the UO_2 surface contains mixed oxidation states. (3) For $[H_2O_2] > 5\times10^{-3}$ M, the oxidative dissolution rate again increases with H_2O_2 concentration with approximately first order dependence.

de Pablo et al. [9] have shown that the rates of H_2O_2 consumption are higher than the corresponding rates of uranium release. They suggest that this difference can be attributed to both oxidation of uranium in the solid phase and H_2O_2 decomposition by the solid phase acting as a catalyst. The oxidation mechanism of UO_2 is thought to occur via $OH^{\cdot}$ and $HO_2^{\cdot}$. In the presence of carbonate they have found that the dissolution rate is decreased, which is interpreted as a reduction of the efficiency of the oxidant, due to radical scavenging of $OH^{\cdot}$ by HCO_3^- forming $CO_3^{\cdot-}$. $CO_3^{\cdot-}$ is argued to be less reactive than $OH^{\cdot}$.

In this work, we have mainly studied the reaction between UO_2 and H_2O_2, the latter being one of the major products from α-radiolysis. The experiments were performed using aqueous suspensions of fine UO_2 powder. The effect of carbonate on this reaction was also studied. To elucidate the relation between reaction kinetics and oxidant properties we have also studied the kinetics for oxidation of UO_2 by $IrCl_6^{2-}$, MnO_4^- and $Fe(EDTA)^-$.

2. Experimental

2.1. Kinetic studies

The 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 UO_2 powder used in this work has a specific area of 5.85 m^2/g given by BET measurements. The powder was washed one time with 10 mM $NaHCO_3$ and three times with pure water in order to remove U(VI) from the surface. The suspensions (18–20 ml) 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 μm) to stop the reaction and to clear the solution. In Table 1 the experimental conditions for the different oxidants are shown.

The oxidant concentrations were measured by UV/visible spectroscopy (Jasco V-530 UV/VIS-Spectrophotometer). For $Fe(EDTA)^-$, both $Fe(EDTA)^{2-}$ and $Fe(EDTA)^-$ absorbs at 257 nm. In this case the difference in measured molar extinction coefficients, $\varepsilon_{Fe(EDTA)^-} = 9572\ M^{-1}\,cm^{-1}$ and $\varepsilon_{Fe(EDTA)^{2-}} = 13\,007\ M^{-1}\,cm^{-1}$, for the two complexes was used to quantify the consumption of $Fe(EDTA)^-$. The concentration of H_2O_2 was measured indirectly by UV/visible spectroscopy. The H_2O_2 solutions were protected from light during the experiments. We have used I_3^- as 'indicator' for analysis of the hydrogen peroxide concentration at 360 nm where I_3^- absorbs (reaction (3) and (4)).

$$H_2O_2 + 2H^+ + 2I^- \rightarrow 2H_2O + I_2 \tag{3}$$

$$I_2 + I^- \rightarrow I_3^- \tag{4}$$

The sample was mixed with 100 μl potassium iodide (1 M KI) and 100 μl acetate buffer which contained ammonium molybdate (catalyst) (1 M HAc/NaAc, a few drops of 3% $(NH_4)_2Mo_2O_7$ (ADM) to 100 ml solution) and water to a total volume of 2 ml. Using this method, μM concentrations of H_2O_2 are detectable. Detailed information about the I_3^- method can be found in [10–12].

When studying the effect of carbonate on the reaction between H_2O_2 and UO_2, the UO_2 powder was washed

Table 1
Experimental conditions

Oxidant	Initial conc. (mM)	Amount of UO_2 (mg)	Volume (ml)	Wave-length (nm)
$IrCl_6^{2-}$	0.1	10–80	20	488
MnO_4^-	0.1	40–80	20	525
H_2O_2	3–9	20–200	18	360[a]
$Fe(EDTA)^-$	0.1	20–80	20	257

[a] I_3^- has been used as indicator of the H_2O_2 concentration according to the reactions:

$H_2O_2 + 2H^+ + 2I^- \rightarrow 2H_2O + I_2$

$I_2 + I^- \rightarrow I_3^-$

three times with $NaHCO_3$ solutions of the same concentration as in the subsequent experiments (1, 10 and 100 mM, respectively). The U(VI) concentrations in these samples were measured using a Scintrex UA-3 Uranium Analyser [13].

2.2. Mechanistic studies

Two methods have been used to investigate if any *free* $OH^{\cdot}$ are formed in the reaction between UO_2 and H_2O_2: (1) chemiluminescence (CL) and (2) spectrophotometrical detection of indigo carmine.

The chemiluminescence method for detection of $OH^{\cdot}$ has been described in detail elsewhere [14]. In summary a trace amount of phthalhydrazide is added to the reaction solution. Phthalhydrazide is a non-chemiluminescent but upon reaction with $OH^{\cdot}$ it forms a chemiluminescent product which can readily be detected. It should be noted that other strong one-electron oxidants do not produce a chemiluminescent product upon reaction with phthalhydrazide. When using this method samples from a suspension of UO_2 (60 mg), H_2O_2 (4.5 mM) and phthalhydrazide (0.5 mM) purged with Argon were taken at different time interval. The samples were filtered (pore size 0.20 μm) and mixed with different reagents and finally analyzed by a BioOrbit 1250 luminometer. A reference sample without UO_2 has also been analyzed in the same way as described above.

In the second method a suspension of UO_2 (40 mg), H_2O_2 (~2 mM) and indigo carmine (5×10^{-5} M) purged with Argon was used. Indigo carmine shows a strong absorption band at 610 nm whereas the product formed upon oxidation of indigo carmine does not absorb at this wavelength. Using this method, it is not possible to distinguish between $OH^{\cdot}$ and other strong oxidants. Samples were taken according to the same procedure as in the CL-method. A reference sample was also used in this reaction system.

3. Results and discussion

In the kinetic studies the UO_2 surface is assumed to be in excess compared to the oxidants. Hence, the reactions can at least initially be treated as being pseudo first order.

3.1. Oxidation of UO_2 by H_2O_2

In Fig. 1 the concentration of H_2O_2 is given as a function of time. The reactivity of H_2O_2 follows first order kinetics when the amount of UO_2 is varied between 50 and 200 mg in absence of carbonate. The second order rate constant can be obtained from the slope (8×10^{-7} m/min) in Fig. 2 where the pseudo first order rate constant, k_1 (min^{-1}) is plotted against the solid surface/total solution volume ratio, S/V (m^{-1}). The second order rate constants, k, for all oxidants studied in this work are presented in Table 2.

Interestingly, when a small amount of UO_2 is used (20 mg), the reactivity of H_2O_2 follows zeroth order kinetics with respect to hydrogen peroxide. However, in the presence of 0.1 M $NaHCO_3$, the kinetics is drastically changed as can be seen in Fig. 3. The reaction becomes significantly faster and the kinetics is now of first order. The rationale for this is probably that, at low S/V ratio and in the absence of HCO_3^-, dissolution of $UO_2^{2+}{}_{(surf)}$ at the surface of the UO_2 particles is the rate limiting step rather than the reaction with H_2O_2. Carbonate increases the solubility of $UO_2^{2+}{}_{(surf)}$ [15], shifting the rate limiting step from dissolution to the redox reaction between H_2O_2 and UO_2. Shoesmith has observed

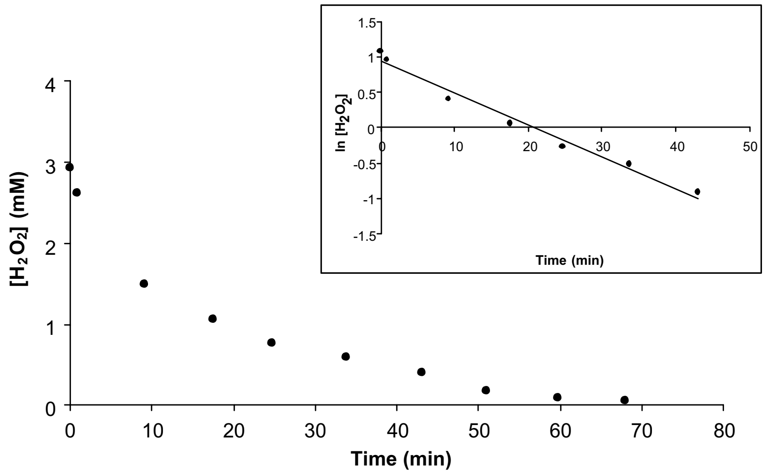

Fig. 1. Concentration of H_2O_2 as a function of reaction time (m_{UO_2} ~ 100 mg).

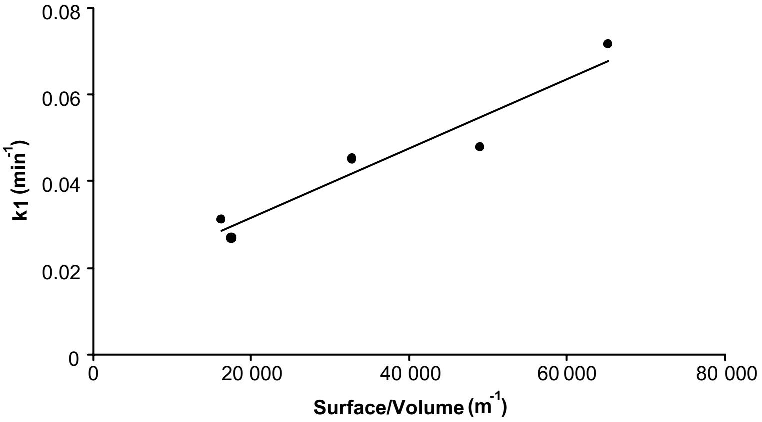

Fig. 2. Pseudo first order rate constants plotted against surface/volume ratio.

Table 2
One electron reduction potentials, E^0, and measured and estimated (italics) second order rate constants, k, for the reaction between UO_2 and various oxidants in the absence of carbonate

E^0 (V)	Rate const. k (m/min)	ln k	Oxidant
0.8665 [21]	4.60×10^{-5}	−9.99	$IrCl_6^{2-}$
0.576 [21]	2.72×10^{-6}	−12.81	MnO_4^-
0.46 [4]	8.05×10^{-7}	−14.03	H_2O_2
0.13[a]	6.20×10^{-8}	−416.60	$Fe(EDTA)^-$
1.9 [4]	*4.28×10^{-1}*	*−0.85*	$OH^\cdot$
1.59 [5]	*2.64×10^{-2}*	*−3.63*	$CO_3^{\cdot-}$
0.79 [4]	*1.99×10^{-5}*	*−10.82*	$HO_2^\cdot$
−0.15 [4]	*4.26×10^{-9}*	*−19.27*	O_2

[a] Measured by cyclic voltammetry.

that when carbonate is added, the accumulation of a corrosion product deposit is prevented. In the absence of carbonate, the accumulation of a corrosion product deposit seems to block the surface sites required for catalyzing H_2O_2 decomposition [1]. At higher S/V ratio the small fraction of $UO_2^{2+}{}_{(surf)}$ does not affect the kinetics significantly.

Parallel measurements of both the H_2O_2 consumption and U(VI) formation as a function of carbonate concentration have been performed. The results are shown in Figs. 4 and 5. From these studies it is obvious that the rate of H_2O_2 consumption as well as the initial rate of U(VI) dissolution increase with increasing HCO_3^- concentration. The final concentrations of U(VI) in solution are not in agreement with the initial concentration of H_2O_2, which is consistent with the results from de Pablo et al. [9]. This can probably be attributed to the formation of secondary phases [1]. Consequently, a direct comparison of the kinetics for H_2O_2 consumption and uranium dissolution is not possible without knowledge about the kinetics for precipitation of secondary phases. Shoesmith has shown that for carbonate concentrations (10^{-3} to 10^{-1} M), HCO_3^-/CO_3^{2-} is kinetically involved via the formation of surface intermediates, in the dissolution process [1].

To further elucidate the effect of carbonate we have performed numerical modeling of the following reaction system: [1]

$$UO_2 + H_2O_2 \rightarrow UO_2^{2+}{}_{(surf)} \tag{5}$$

$$UO_2^{2+}{}_{(surf)} + HCO_3^- \rightarrow UO_2^{2+}{}_{(aq)} + UO_2 \tag{6}$$

$$UO_2^{2+}{}_{(aq)} \rightarrow UO_2(X)_{(s)}{}^{2} \tag{7}$$

The experimental results could be quantitatively reproduced when using a k_6/k_5 ratio of 0.25. Experimental and numerical results are given in Fig. 5. Given the good agreement between the experimental results and the numerical simulation it is reasonable to suggest that carbonate simply acts as a complexing agent.

The experiments aimed at analyzing the formation of $OH^\cdot$ in the reaction between UO_2 and H_2O_2 did not result in any detectable $OH^\cdot$ concentrations. Hence, the suggested effect of carbonate as a radical scavenger in the system can be ruled out. These observations, i.e. the absence of *free* $OH^\cdot$ could suggest that the reaction is a two-electron process. However, it cannot be ruled out

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[1] In the numerical modeling of this system, the rate constant for reaction (5) must be based on reaction sites rather than on the surface/volume ratio. As the number of sites per m^2 is unknown for this system we have chosen an arbitrary number and, by trial and error, optmized the system to fit the experimental results. Consequently, the absolute values of k_5 and k_6 are arbitrary numbers. However, the ratio between k_5 and k_6 has significance. k_7 has no effect on the modeling.

[2] $UO_2(X)_{(s)}$ denotes a solid uranyl phase.

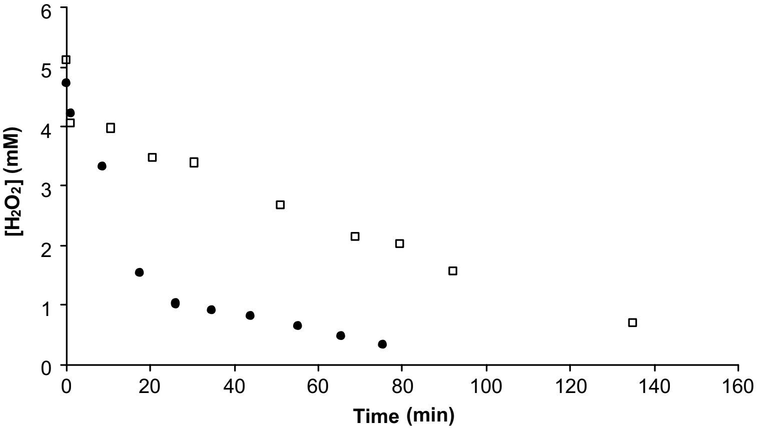

Fig. 3. Concentration of H_2O_2 as a function of reaction time: (●) UO_2 23 mg, 0.1 M HCO_3^-; (□) UO_2 18 mg, no carbonate.

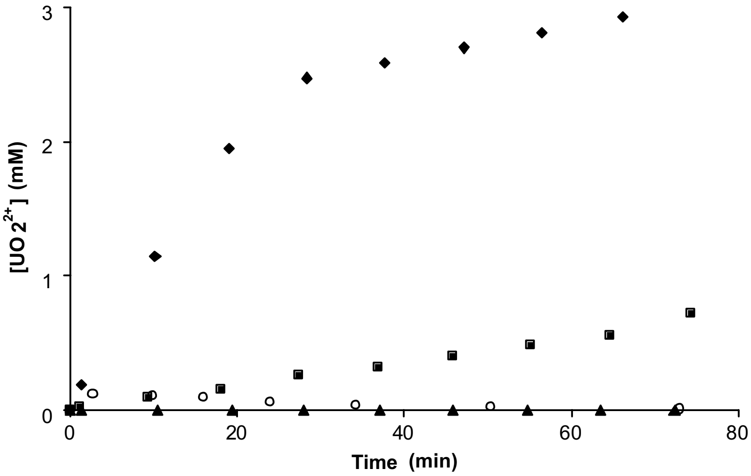

Fig. 4. Concentration of uranyl as a function of reaction time: (◆) UO_2 51 mg, 100 mM HCO_3^-; (■) UO_2 51 mg, 10 mM HCO_3^-; (▲) UO_2 52 mg, 1 mM HCO_3^-; (○) UO_2 100 mg, no carbonate.

that the reaction is a slow one-electron transfer followed by a rapid one-electron transfer.

It should be noted that, in aqueous solutions containing H_2O_2 and HCO_3^-, peroxymonocarbonate (HCO_4^-) is formed [16]. The reactivity of peroxymonocarbonate towards UO_2 is not known but judging from the redox properties [16], it should be very similar to that of H_2O_2.

3.2. Oxidation of UO_2 by other oxidants

To find out more about the mechanism for UO_2 oxidation we performed experiments using other oxidants than H_2O_2. Two of the oxidants, $IrCl_6^{2-}$ and Fe(EDTA)$^-$, are pure one-electron oxidants while the remaining oxidant, MnO_4^-, can act both as one- and two-electron oxidant (as can H_2O_2). In Table 2, the oxidants and their one-electron reduction potentials are listed along with the observed second order rate constants for oxidation of UO_2. As can be seen in the table the strongest oxidant, $IrCl_6^-$, reacts most rapidly with UO_2 while the weakest oxidant, Fe(EDTA)$^-$, displays the lowest reactivity. The difference in reactivity between these two oxidants is nearly three orders of magnitude.

When plotting $\ln k$ for the reaction against the one-electron reduction potential of the oxidant (Fig. 6) we obtain a very good linear correlation indicating that linear free energy relationships are applicable also to this type of surface reaction (i.e., $\ln k \propto \Delta G^0 \propto \Delta E^0$) [17].

The linear relationship could also serve as an indication for the rate determining/limiting step being a one-electron transfer.

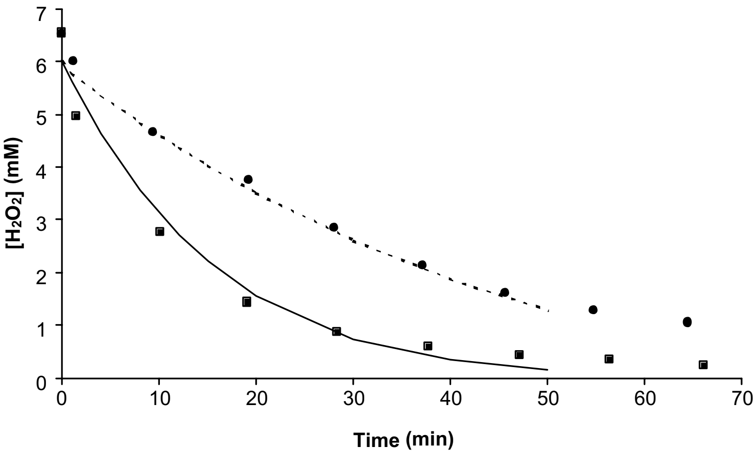

Fig. 5. Concentration of H_2O_2 as a function of reaction time at two different carbonate concentrations: (■) UO_2 51 mg, 100 mM HCO_3^-; (●) UO_2 52 mg, 10 mM HCO_3^-; (—) UO_2 50 mg, 100 mM HCO_3^- (numerical modeling according to reaction (5)–(7)); (- - -) UO_2 50 mg, HCO_3^- 10 mM (numerical modeling according to reaction (5)–(7)).

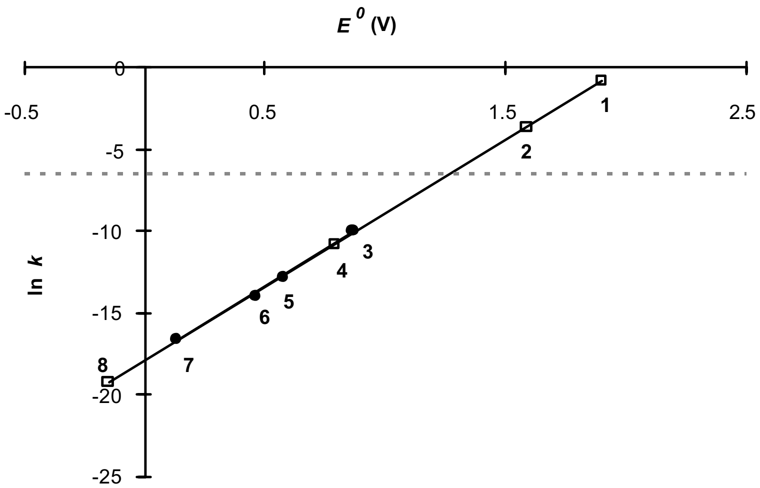

Fig. 6. The logarithm of the second order rate constant, ln *k*, for oxidation of UO_2 plotted against the one-electron reduction potential of the oxidant, E^0: the dashed line represents the diffusion limit; ● experimental data; □ values estimated from the linear relationship between ln *k* and E^0 (1. OH·, 2. $CO_3^{\cdot-}$, 3. $IrCl_6^{2-}$, 4. $HO_2^{\cdot}$, 5. MnO_4^-, 6. H_2O_2, 7. $Fe(EDTA)^-$ and 8. O_2).

Hence, a plausible mechanism for the reaction between UO_2 and H_2O_2 is a slow one-electron transfer step producing U(V) and OH· (reaction (8)) followed by a very rapid reduction of OH· to OH^-. This mechanism has also been proposed by Nicol and Needes as quoted by Shoesmith et al. [18]. The U(V) could either be oxidized directly to U(VI) by OH· or undergo disproportionation with another U(V) in the matrix producing U(IV) and U(VI) (reaction (9)). The primary step is analogous to the Fenton reaction.

$$UO_2 + H_2O_2 \rightarrow UO^+_{2\,(surf)} + OH^{\cdot} + OH^- \qquad (8)$$

$$UO^+_{2\,(surf)} + UO^+_{2\,(surf)} \rightarrow UO^{2+}_{2\,(surf)} + UO_2 \qquad (9)$$

If we allow ourselves to extrapolate the linear relationship established in Fig. 6 we can predict the rate constant for oxidation of UO_2 by OH·. The predicted rate constant (see Table 2) is almost six orders of magnitude higher than the observed rate constant for the reaction between H_2O_2 and UO_2. The predicted rate constant for the reaction between $CO_3^{\cdot-}$ and UO_2 is one order of magnitude lower than that of OH·.

However, for this specific system we have estimated the diffusion controlled rate constant to be approximately 10^{-3} m/min ($\ln k = -6.5$) [19]. Hence, the rate of oxidation by OH· and $CO_3^{\cdot-}$ should be strictly limited by diffusion, i.e. the rate constant should be identical for both oxidants (~10^3 m/min). Consequently, OH· formed at the UO_2 surface upon one-electron reduction of H_2O_2 are expected to react instantly with the UO_2 matrix.

We have also predicted the reactivity of $HO_2^{\cdot}$ and O_2 towards UO_2. Interestingly, the H_2O_2 reduction is ~190 times faster than the predicted O_2 reduction on UO_2, which is in very good agreement with experimental observations by Shoesmith et al. [8]. If we compare the estimated rate constant for diffusion limited reactions, e.g. $OH^{\cdot}$ reduction with that for H_2O_2 reduction on UO_2, $OH^{\cdot}$ reacts 1.5×10^3 times faster than H_2O_2. According to Christensen and Bjergbakke [20] the $k[OH^{\cdot}]/k[H_2O_2]$ ratio is 4×10^6 which is ~2500 times faster than our results indicate.

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References

[1] D.W. Shoesmith, J. Nucl. Mater. 282 (2000) 1.
[2] R.L. Segall, R.S.C. Smart, in: J. Nowotny, L.-C. Dufour (Eds.), Surface and Near-Surface Chemistry of Oxide Materials, Elsevier, Amsterdam, 1988, p. 527.
[3] J.W.T. Spinks, R.J. Woods, An Introduction to Radiation Chemistry, John Wiley, New York, 1964.
[4] P. Wardman, J. Phys. Chem. Ref. Data 18 (1989) 1637.
[5] R.E. Huie, C.L. Clifton, Radiat. Phys. Chem. 38 (1991) 477.
[6] D.W. Shoesmith, S. Sunder, J. Nucl. Mater. 190 (1992) 20.
[7] S. Sunder, D.W. Shoesmith, Mater. Res. Soc. Symp. Proc. 84 (1987) 103.
[8] D.W. Shoesmith, S. Sunder, Mater. Res. Soc. Symp. Proc. 50 (1985) 309.
[9] J. de Pablo, I. Casas, Mater. Res. Soc. Symp. Proc. 663 (2001) 409.
[10] W.A. Patrick, H.B. Wagner, Anal. Chem. 21 (1949) 1279.
[11] T.C.J. Ovenston, W.T. Rees, Analyst 75 (1950) 204.
[12] Y. Nimura, K. Itagaki, Nippon Suisan Gakk. 58 (1992) 1129.
[13] J.C. Robbins, CIM Bull. 71 (1978) 61.
[14] S. Backa, K. Jansbro, Holzforschung 51 (1997) 557.
[15] I. Grenthe, F. Diego, J. Chem. Soc. Dalton Trans. 11 (1984) 2439.
[16] D.E. Richardson, H. Yao, J. Am. Chem. Society 122 (2000) 1729.
[17] W. Stumm, J.J. Morgan, Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, 3rd Ed., John Wiley, New York, 1996.
[18] D.W. Shoesmith, S. Sunder, in: J. Lipkowski, P.N. Ross (Eds.), The Electrochemistry of Novel Materials, VCH, New York, 1994, p. 297.
[19] K.J. Laidler, Chemical Kinetics, 3rd Ed., Harper & Row, New York, 1987.
[20] H. Christensen, E. Bjergbakke, Mater. Res. Soc. Symp. Proc. 84 (1987) 115.
[21] A.J. Bard, R. Parsons, Standard Potentials in Aqueous Solution, Marcel Dekker, New York, 1985.