Available online at www.sciencedirect.com
ScienceDirect
Journal of Nuclear Materials 373 (2008) 186–189
journal of nuclear materials
www.elsevier.com/locate/jnucmat

UO_2 oxidation site densities determined by one- and two-electron oxidants

Mohammad Mohsin Hossain, Mats Jonsson *

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

Received 25 October 2006; accepted 24 May 2007

Abstract

The oxidation site density (number of oxidation sites per m^2) for UO_2 powder was determined by measuring the amount of oxidant needed to fully oxidize the surface (denoted the critical oxidant conversion). The point where the surface becomes fully oxidized is identified by a change in reaction order from first to zeroth order in HCO_3^- free systems. At the critical oxidant conversion the kinetics of the reaction becomes completely governed by dissolution of oxidized UO_2. The oxidants used in this study are H_2O_2 (two-electron oxidant) and $IrCl_6^{2-}$ (one-electron oxidant). The oxidation site densities determined using the two different oxidants are $(2.1 \pm 0.1) \times 10^{-4}$ and $(2.7 \pm 0.5) \times 10^{-4}$ mol m^{-2}, respectively, expressed in two electron equivalents. The fairly good agreement between the two oxidants implies that the methodology used indeed gives a reasonable measure of the oxidation site density. In addition, oxidation site densities for different size fractions of UO_2 powder were determined. The results are discussed in terms of surface roughness.

1. Introduction

The possible release of toxic and radioactive species from spent nuclear fuel in contact with water in a future deep repository is expected to depend mainly on the rate of dissolution of the UO_2 matrix [1]. In the reducing groundwater expected at the depth of a repository, UO_2 has very low solubility [2]. However, radiolysis of the groundwater will produce reactive radicals and molecular products (e_{aq}^-, $H^\bullet$, H_2 (reductants) and $OH^\bullet$, H_2O_2 (oxidants)) [3] and thereby alter the reducing environment. Secondary reactions will produce $HO_2^\bullet$, $O_2^{\bullet-}$ and O_2 and with carbonate present in the groundwater, $CO_3^{\bullet-}$ will be produced. $OH^\bullet$ and $CO_3^{\bullet-}$ are both strong one-electron oxidants ($E^0 = 1.9$ V and 1.59 V vs. NHE, respectively [4,5]) while $HO_2^\bullet$ and $O_2^{\bullet-}$ are fairly weak one-electron oxidants (depending on pH). H_2O_2 and O_2 on the other hand can act both as one- and two-electron oxidants.

In a recent paper, the relative impact of different radiolysis products on oxidative dissolution of UO_2 was studied [6]. For β/γ-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 α-radiolysis, the relative impact of H_2O_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 presence of carbonate affects the kinetics for UO_2 oxidation mainly since it forms soluble complexes with the oxidation product, UO_2^{2+} [7], and thereby maintains a larger surface area accessible to oxidation. In a recent paper we studied the effect of HCO_3^- concentration on the kinetics for UO_2 oxidation by H_2O_2 [8]. The results show that the H_2O_2 consumption rate depends on the HCO_3^- concentration for concentrations below 1 mM. For higher HCO_3^- concentrations, the rate of H_2O_2 consumption is independent of $[HCO_3^-]$. From this we concluded that the oxidation step is the rate limiting process for $[HCO_3^-] > 1$ mM while for lower concentrations the consumption of H_2O_2 is significantly influenced by dissolution of UO_2^{2+}. The $[HCO_3^-]$

---

* Corresponding author. Fax: +46 8 790 8772.
E-mail address: matsj@nuchem.kth.se (M. Jonsson).

0022-3115/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2007.05.042

independent rate constant for UO_2 oxidation by H_2O_2 was determined to be 4.4×10^{-6} m min^{-1}. It should be noted that, in aqueous solutions containing H_2O_2 and HCO_3^-, peroxymonocarbonate (HCO_4^-) can be formed [9]. The reactivity of peroxymonocarbonate towards UO_2 is not known but judging from the reported redox properties it should be similar to that of H_2O_2 [10]. However, very recent studies on the influence of ionic strength on the kinetics for UO_2 oxidation by H_2O_2 indicate that peroxymonocarbonate is of no significance [11].

Rate constants for reactions between solutes and solid surfaces are usually based on the surface area of the solid material, in most cases determined by the BET isotherm. However, studies on the reactivity of different size fractions of UO_2 powder clearly demonstrate that the BET surface is not always an accurate measure of the accessible surface [12]. Rate constants based on oxidation site density and methods for determining oxidation site densities would greatly improve the situation by providing a general basis for comparing the reactivity of suspended solids.

An interesting observation made at very low HCO_3^- concentrations is that the kinetics changes from first to zeroth order during the course of the reaction [8]. The zeroth order behaviour can be attributed to a change in the rate determining step from oxidation to dissolution (not facilitated by HCO_3^-). The H_2O_2 conversion (consumption) at which the reaction order changes for $[HCO_3^-] = 0$ M is referred to as the critical conversion. The critical H_2O_2 conversion increases with increasing amount of UO_2 and closer inspection of the results revealed an almost constant ratio between the critical conversion and the amount of UO_2. In the experimental set up used in the previous work, the concentration of H_2O_2 was reduced by 0.07 mM per mg UO_2 powder when the critical H_2O_2 conversion was reached. As the change in reaction order implies that the surface is saturated (i.e., fully oxidized), the reduction in H_2O_2 concentration at the critical H_2O_2 conversion can be used to estimate the oxidation site density for the UO_2 powder used. In this particular case the estimated oxidation site density was found to be $(2.1 \pm 0.1) \times 10^{-4}$ mol m^{-2} corresponding to (126 ± 5) sites nm^{-2}. This is somewhat lower than the value previously reported by Clarens et al. (165 ± 10 sites nm^{-2}) [13] based on acidic site density.

In this work we have determined the oxidation site density for UO_2 powder using the one-electron oxidant $IrCl_6^{2-}$ in order to compare one- and two-electron oxidants. In addition, we have used the above methodology to determine the oxidation site densities for different size fractions of UO_2 powder previously used in kinetic studies.

2. Experimental

The UO_2 powder was supplied from Westinghouse Atom AB. Chemicals and gases used were of purest grade available and were obtained from Lancaster, 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 (He/N_2, 70/30). The powder was washed with $NaHCO_3$ solution and repeatedly with pre-boiled Millipore water.

In the experiments using $IrCl_6^{2-}$ as oxidant the powder suspensions (100 ml) contained 1.3 mM $IrCl_6^{2-}$ and 25 mg UO_2. For the experiments using different powder size fractions the suspensions (18 ml) contained 18 mM H_2O_2 and 50–150 mg UO_2. In all experiments the suspensions were purged with argon throughout the experiment 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.

The concentration of H_2O_2 was measured indirectly by UV/visible spectroscopy (Jasco V-530 UV/vis-spectrophotometer). 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 (1) and (2)).

$$H_2O_2 + 2H^+ + 2I^- \rightarrow 2H_2O + I_2 \tag{1}$$

$$I_2 + I^- \rightarrow I_3^- \tag{2}$$

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 Refs. [14–16].

The concentration of $IrCl_6^{2-}$ was measured directly by UV/visible spectroscopy at 488 nm.

3. Result and discussion

In aqueous UO_2 powder suspensions free from HCO_3^-, $IrCl_6^{2-}$ displays the same kinetic behaviour as H_2O_2, i.e. the reaction order changes from 1 to 0. However, this behaviour could only be observed at fairly low solid surface area to solution volume ratios. The optimal ratio for observation of the change in kinetics turned out to be approximately 1500 m^{-1}. This results in somewhat higher experimental uncertainty for $IrCl_6^{2-}$ compared to H_2O_2.

The methodology used for determination of oxidation site density can be illustrated by Fig. 1.

As can be seen, the consumption of $IrCl_6^{2-}$ is initially of first order, i.e. the consumption rate depends on the $IrCl_6^{2-}$ concentration, but changes to zeroth order (the rate is independent of $IrCl_6^{2-}$ concentration) after about 10 min. The difference between the initial concentration and the concentration at which the change in reaction order occurs is referred to as the critical conversion. By calculating the amount of oxidant consumed at the critical conversion the oxidation site density can be obtained. The oxidation site densities determined using $IrCl_6^{2-}$ and H_2O_2 for the same UO_2 powder are presented in Table 1.

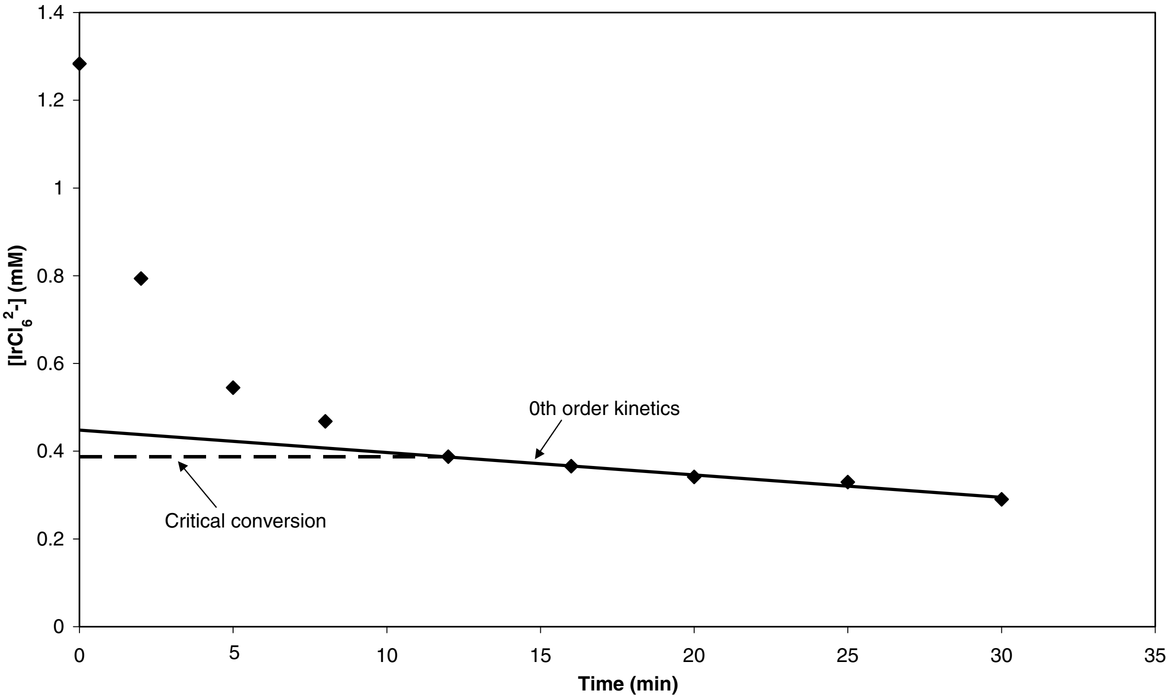

Fig. 1. $IrCl_6^{2-}$ as a function of reaction time (lines showing critical conversion and zeroth order kinetics).

Table 1
UO_2 oxidation site densities determined by H_2O_2 and $IrCl_6^{2-}$

Oxidant	Site density (mol m^{-2})	2-e^- site density (mol m^{-2})
H_2O_2	$(2.1 \pm 0.1) \times 10^{-4}$	$(2.1 \pm 0.1) \times 10^{-4}$
$IrCl_6^{2-}$	$(5.4 \pm 1.0) \times 10^{-4}$	$(2.7 \pm 0.5) \times 10^{-4}$

As can be seen, the oxidation site density determined using $IrCl_6^{2-}$ is more than two times higher than the corresponding value for H_2O_2. However, the direct comparison is not relevant since $IrCl_6^{2-}$ is a one-electron oxidant while H_2O_2 is a two-electron oxidant. Hence, one equivalent of H_2O_2 corresponds to two equivalents of $IrCl_6^{2-}$. It is therefore more relevant to compare the site density based on two-electron transfer (2-e^- density) which also corresponds to the conversion of U(IV) to U(VI). As can be seen in Table 1, both oxidants give similar site densities. Admittedly, the 2-e^- density determined using $IrCl_6^{2-}$ is somewhat higher than the corresponding value for H_2O_2. However, the difference is within experimental uncertainty. This implies that the methodology used indeed gives a reasonable measure of the oxidation site density. Instead of basing heterogeneous rate constants on the solid surface to solution volume ratio it is possible to use the oxidation site concentration. The unit for the second order rate constant would then be the conventional $M^{-1}\ s^{-1}$ used for homogeneous kinetics and the resulting rate constant for the reaction between H_2O_2 and UO_2 is $0.35\ M^{-1}\ s^{-1}$ (4.4×10^{-6} m min^{-1}) [8]. It should be kept in mind that the diffusion limited rate constant for this heterogeneous system is $80\ M^{-1}\ s^{-1}$ (10^{-3} m min^{-1} [17]) which is eight orders of magnitude lower than the diffusion limited rate constant for a homogeneous system. Hence, the use of the more conventional unit for the rate constant could cause confusion.

It should be noted that the surface site density is significantly larger than expected from the lattice parameters for UO_2. This could imply that the oxidation must progress several atom layers deep before zeroth order kinetics is obtained. However, it should also be kept in mind that the surface are on which the site density is based was obtained from the BET specific surface area. The BET isotherm could underestimate the specific surface area considerably giving rise to high surface site density values.

As mentioned above, kinetic studies on different size fractions of UO_2 powder gave some unexpected results. Furthermore, BET measurements displayed no significant difference in specific surface area between the four size fractions used (<20, 20–41, 41–72 and > 72 μm). This observation is to some extent explained by SEM-studies revealing significant differences in surface structure between the size fractions. The larger fractions have a rougher surface than the smaller fractions. Hence, the BET surface area for the larger particles will deviate significantly from the geometrical surface area based on particle radius. On the basis of particle size alone we would expect the smaller particles to have a larger specific surface area than the larger particles. In order to shed some more light on the difference between different size fractions we have determined the oxidation site density for the four size fractions mentioned above using H_2O_2. This was done by determining the critical conversion for different solid surface area to solution volume ratios. In Fig. 2 the critical conversion is plotted against the surface to volume ratio for the largest size fraction.

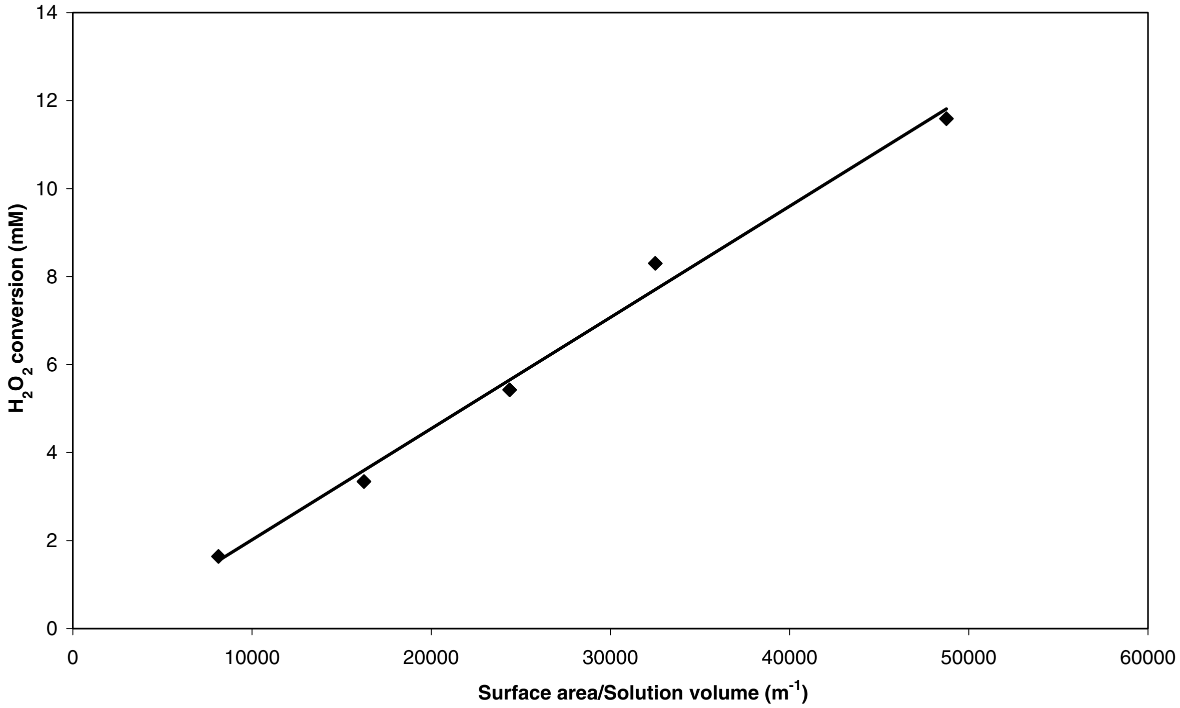

Fig. 2. Critical H_2O_2 conversion plotted against UO_2 surface to solution volume ratio.

Table 2
Oxidation site densities based on H_2O_2 consumption for different powder size fractions

Size fraction (μm)	Oxidation site density (mol m^{-2})
>72	$(2.5 \pm 0.1) \times 10^{-4}$
41–72	$(2.3 \pm 0.2) \times 10^{-4}$
20–41	$(2.1 \pm 0.2) \times 10^{-4}$
<20	$(2.1 \pm 0.1) \times 10^{-4}$

The slope of this plot directly gives the oxidation site density. The resulting oxidation site densities for the four size fractions are given in Table 2.

As can be seen, the oxidation site density appears to increase with particle size. The difference is however barely statistically significant (error margins based on the uncertainty in the slope when plotting the critical conversion against the surface to volume ratio). Furthermore, it should be stressed that such a trend is not expected for a uniform material where the surface structure is similar for all size fractions. The trend observed for the material used here can probably be attributed to the surface roughness which is significantly higher for the larger particles. The rougher surface has more defects which could act as oxidation sites. The observed oxidation site densities are fairly close to the values presented in Table 1.

This finding again demonstrates the problems that can occur when comparing the kinetics for different types of solid materials. The surface roughness is not accommodated by simple geometrical theories describing the kinetics in particle suspensions [18]. In order to improve the theoretical treatment of the kinetics of particle suspensions one must also include the surface roughness.

Acknowledgement

SKB is gratefully acknowledged for financial support.

References

[1] D.W. Shoesmith, J. Nucl. Mater. 282 (2000) 1.
[2] R.L. Segall, R.S.C. Smart, P.S. Turner, in: L.-C. Dufour (Ed.), Surface and Near-Surface Chemistry of Oxide Materials, Elsevier Science Publishers BV, 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, P. Neta, Rad. Phys. Chem. 38 (1991) 477.
[6] E. Ekeroth, O. Roth, M. Jonsson, J. Nucl. Mater. 355 (2006) 38.
[7] I. Grenthe, F. Diego, F. Salvatore, G. Riccio, J. Chem. Soc. Dalton Trans. 11 (1984) 2439.
[8] M.M. Hossain, E. Ekeroth, M. Jonsson, J. Nucl. Mater. 358 (2006) 202.
[9] D.E. Richardson, H. Yao, K.M. Frank, D.A. Bennett, J. Am. Chem. Soc. 122 (2000) 1729.
[10] A.B. Ross, B.H.J. Bielski, G.V. Buxton, D.E. Cabelli, C.L. Greenstock, W.P. Helman, R.E. Huie, J. Grodkowski, P. Neta, NDRL/NIST Solution Kinetics Database, 1992.
[11] M.M. Hossain, M. Jonsson, J. Nucl. Mater. 373 (2008) 190.
[12] O. Roth, T. Bönnemark, M. Jonsson, J. Nucl. Mater. 353 (2006) 75.
[13] F. Clarens, J. de Pablo, I. Casas, J. Giménex, M. Rovira, Mater. Res. Soc. Symp. Proc. 807 (2004) 71.
[14] W.A. Patrick, H.B. Wagner, Anal. Chem. 21 (1949) 1279.
[15] T.C.J. Ovenston, W.T. Rees, Analyst 75 (1950) 204.
[16] Y. Nimura, K. Itagaki, K. Nanba, Nippon Suisan Gakk. 58 (1992) 1129.
[17] E. Ekeroth, M. Jonsson, J. Nucl. Mater. 322 (2003) 242.
[18] R.D. Astumian, Z.A. Schelly, J. Am. Chem. Soc. 106 (1984) 304.