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H_2 inhibition of radiation induced dissolution of spent nuclear fuel

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ABSTRACT

In order to elucidate the effect of noble metal clusters in spent nuclear fuel on the kinetics of radiation induced spent fuel dissolution we have used Pd particle doped UO_2 pellets. The catalytic effect of Pd particles on the kinetics of radiation induced dissolution of UO_2 during γ-irradiation in HCO_3^- containing solutions purged with N_2 and H_2 was studied in this work. Four pellets with Pd concentrations of 0%, 0.1%, 1% and 3% were produced to mimic spent nuclear fuel. The pellets were placed in 10 mM HCO_3^- aqueous solutions and γ-irradiated, and the dissolution of UO_2^{2+} was measured spectrophotometrically as a function of time. Under N_2 atmosphere, 3% Pd prevent the dissolution of uranium by reduction with the radiolytically produced H_2, while the other pellets show a rate of dissolution of around 1.6×10^{-9} mol m^{-2} s^{-1}. Under H_2 atmosphere already 0.1% Pd effectively prevents the dissolution of uranium, while the rate of dissolution for the pellet without Pd is 1.4×10^{-9} mol m^{-2} s^{-1}. It is also shown in experiments without radiation in aqueous solutions containing H_2O_2 and O_2 that ϵ-particles catalyze the oxidation of the UO_2 matrix by these molecular oxidants, and that the kinetics of the catalyzed reactions is close to diffusion controlled.

1. Introduction

Highly radioactive spent nuclear fuel is one of the major drawbacks of nuclear power. Many countries are planning to store the spent nuclear fuel in geological repositories with multiple barriers keeping the groundwater from reaching the fuel and, in case of barrier failure, radionuclides from reaching the biosphere. In UO_2 based fuel, more than 95% of the spent nuclear fuel still consists of UO_2. The UO_2 matrix is considered to be the innermost barrier of the repository system, due to its low solubility in reducing groundwater [1,2]. However, the radioactivity of the spent fuel leads to radiolysis of water, producing redox-active radical and molecular species. In HCO_3^- containing groundwater, the surface accessible to oxidants is significantly larger than the surface accessible to reductants, due to low steady-state concentration of U(VI) on the fuel surface. Hence, the oxidative species will have the highest impact in this system. The net effect will be oxidation of UO_2 to the more soluble UO_2^{2+}. Thus, radiolysis triggers oxidative dissolution of the fuel matrix. The basic mechanism can be seen in reactions (1) and (2):

$$UO_{2(s)} + Ox \rightarrow UO_{2(s)}^{2+} + Red \tag{1}$$

$$UO_{2(s)}^{2+} \rightarrow UO_{2(aq)}^{2+} \tag{2}$$

The formation of complexes between uranyl and HCO_3^- enhances the dissolution of UO_2^{2+} even further [3–7]. Oxidative dissolution of both UO_2 and spent nuclear fuel has been extensively studied [8,9]. Mechanistic conclusions are difficult to draw from experiments on spent nuclear fuel, due to its inherent complexity. Therefore pure UO_2 systems have been used to quantitatively and qualitatively elucidate the elementary processes involved. The rate constants for reactions between oxidants in solution and solid UO_2 as well as dissolution of oxidized UO_2 in systems with and without HCO_3^- have been determined [10–14]. Using kinetic data and numerical simulations of radiolysis in aqueous solution, the relative impact of the different oxidants has been determined and verified by well controlled experiments on radiation induced oxidative dissolution of UO_2 [15]. The studies show that the only oxidant that has to be considered under deep repository conditions in granitic groundwater is H_2O_2.

It has been shown that H_2 has a considerable inhibiting effect on the dissolution of spent nuclear fuel [16,17]. In a deep repository H_2 is expected to be produced from anaerobic corrosion of the iron part of the canister used to contain the spent nuclear fuel (reaction (3)) and from radiolysis of water,

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \tag{3}$$

In general, there are two possible pathways for H_2 to decrease the dissolution rate, by consuming oxidants in competition with UO_2 and by reduction of oxidized UO_2, reactions (4) and (5),

$$Ox + H_2 \rightarrow Red + 2H^+ \tag{4}$$

$$H_2 + UO_2^{2+} \rightarrow UO_2 + 2H^+ \tag{5}$$

Reaction (5) can take place in solution and on the surface. Reduction by H_2 usually requires a catalyst. Previous studies have

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shown that uranium dioxide has no catalytic effect on the decomposition of hydrogen peroxide in the presence of H_2 [18]. However, spent nuclear fuel contains nanometer sized clusters of noble metal fission products (Mo, Ru, Tc, Rh, Pd and Te), often referred to as ϵ-particles [19]. Pd has been used experimentally as a substitute for ϵ-particles and has been shown to have a catalytic effect on the reduction by H_2. This includes both reduction of H_2O_2 and $UO_{2(aq)}^{2+}$ [18,20].

These processes could indeed partly account for reduced oxidative dissolution of the UO_2 matrix. However, considering the amount of fission products in spent nuclear fuel, the Pd catalyzed reaction between H_2O_2 and H_2 cannot compete with the reaction between UO_2 and H_2O_2. With the surface area ratio between UO_2 and noble metal particles being around 100, the 20 times higher rate constant for the Pd catalyzed reaction [18] will not be sufficient to inhibit matrix oxidation. Hence, the majority of H_2O_2 will be consumed by UO_2.

The observed inhibition of spent nuclear fuel dissolution in the presence of H_2 is expressed by reduced dissolution of the redox sensitive fuel matrix as well as redox insensitive fission products. The noble metal catalyzed reduction of already dissolved UO_2^{2+} cannot be the main factor, since this will not influence the concentration of the redox insensitive species in solution. This implies that the dissolution of oxidized UO_2 is inhibited on the surface of the pellet, i.e., $UO_{2(s)}^{2+}$ is reduced back to $UO_{2(s)}$ faster than it dissolves. This process was originally suggested by Broczkowski et al. [21].

Recently, experiments using uranium dioxide pellets with varying concentrations of Pd (0, 0.1, 1 and 3 wt%) in H_2O_2 containing aqueous solution under N_2 and H_2 atmospheres have been carried out [22]. The results clearly show that the oxidative dissolution of UO_2 under H_2 atmosphere is reduced with increasing amount of Pd on the surface of the pellet and increasing partial pressure of H_2. The rate constant for the Pd catalyzed $U(VI)_{(s)}$ reduction by H_2 appears to be diffusion controlled ($\approx 10^{-6}$ m s^{-1}). It was also qualitatively shown that Pd catalyzes the oxidation of UO_2 by H_2O_2.

In the present paper, we study the dissolution of uranyl from UO_2 pellets, doped with 0%, 0.1%, 1% and 3% Pd particles in γ-irradiated HCO_3^- containing aqueous solutions under N_2 and H_2 atmosphere. In addition, the noble metal particle catalyzed oxidation of UO_2 by H_2O_2 and O_2 is quantified.

2. Experimental methods

The depleted uranium dioxide powder used in this study came from Westinghouse Atom AB. The sodium hydrogen carbonate solution was prepared with $NaHCO_3$ p.a. from Merck and the water used throughout the experiments was Millipore Milli-Q. The palladium powder with a purity of 99.9+% had an average particle size of 1.0–1.5 μm and was manufactured by Aldrich. The Arsenazo III reagent was mixed from p.a. powder from Fluka.

Four UO_2 pellets with palladium concentrations ranging from 0 to 3 wt% were produced according to the method described in Ref. [22].

Before irradiation, the pellet was washed overnight in 10 mM $NaHCO_3$ solution and then placed in a glass vessel containing 10 mL 10 mM $NaHCO_3$ purged with N_2 or H_2, depending on the desired condition. After placing the pellet in the solution, it was again purged with N_2 or H_2 for a few minutes in order to maintain saturation and to minimize the influence of oxygen. The vessel was then irradiated in a ^{137}Cs gamma source Gammacell 1000 Elite from MDS Nordion with a dose rate of 0.15 Gy s^{-1} (determined using Fricke dosimetry [23]). After the desired irradiation time, the uranyl concentration in solution was measured using the Arsenazo III method with a S2000 spectrophotometer from WPA at a wavelength of 653 nm (ϵ is 63 000 M^{-1} cm^{-1}) described in [24,25]. Sample (1.5 mL) was mixed with 40 μL 0.03% Arsenazo III reagent and 65 μL 1 M HCl. These steps were repeated for different irradiation times for each pellet. The pellet composition and the experimental conditions can be seen in Table 1.

Table 1
Experimental conditions in the γ-irradiated experiments

	Atmosphere	Pd conc. (wt%)	Irradiation time (min)
1	N_2	0, 0.1, 1, 3	0, 30, 75, 120, 165
2	H_2	0, 0.1, 1, 3	0, 30, 75, 120, 165

Background experiments under N_2 atmosphere were performed under the same conditions as in the irradiated case and used for correction. In addition, experiments under O_2 atmosphere (1 bar) were performed without irradiation.

3. Results and discussion

3.1. Catalytic effects on the oxidation of UO_2 by H_2O_2 and O_2

As mentioned above, it was recently shown that Pd has a catalytic effect on the oxidation of UO_2 by H_2O_2 [22]. These experiments were performed in an autoclave using UO_2 pellets with different amount of Pd immersed in aqueous solution to which a controlled amount of H_2O_2 was added. Here, the previous results are used in order to quantify this effect. The rate of H_2O_2 consumption is plotted versus the fraction of palladium in Fig. 1. As can be seen, the consumption of H_2O_2 increases with increasing amount of Pd in the pellet. The rate constant for the Pd catalyzed oxidation by H_2O_2 can be calculated from the slope ($(6.92 \pm 1.52) \times 10^{-6}$ m s^{-1}). The diffusion controlled rate constant for this system is calculated to be on the order of 10^{-6} m s^{-1} using the theory presented in Ref. [26]. Hence, this reaction appears to be diffusion controlled. The rate constant for the Pd catalyzed reaction is more than one order of magnitude higher than the rate constant for the reaction between H_2O_2 and pure UO_2 (7.3×10^{-8} m s^{-1} [10]).

The effect of ϵ-particles on the oxidative dissolution of UO_2 by O_2, and a possible inhibition of the same due to a formation of an oxide film, has been suggested [9]. The suggested catalytic effect is supported by SIMFUEL experiments which clearly showed a faster response of the electrode to O_2 in the presence of ϵ-particles [21]. The experiments performed in this work in solutions saturated with O_2 (1 bar) show that the dissolution of U(VI) increases

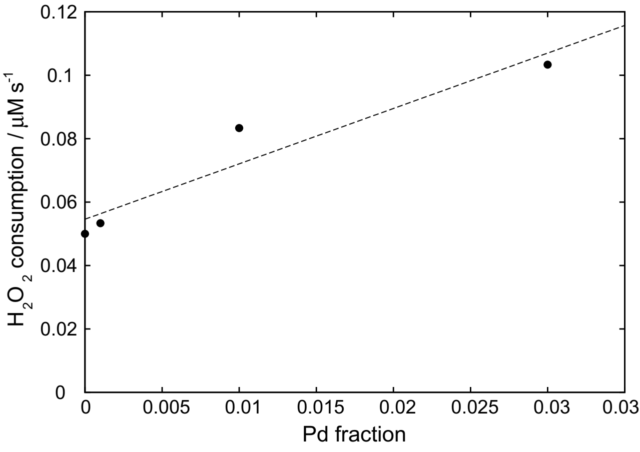

Fig. 1. Consumption of H_2O_2 in N_2 atmosphere as a function of Pd fraction.

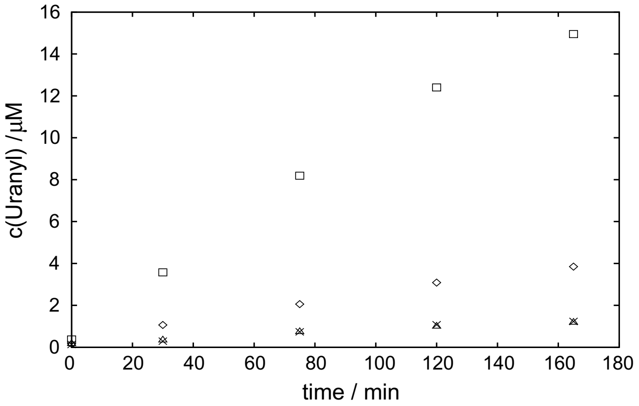

Fig. 2. Dissolution of uranyl in O_2 atmosphere for UO_2 pellets containing 0 wt% (×), 0.1 wt% (△), 1 wt% (◇), and 3 wt% (□) Pd.

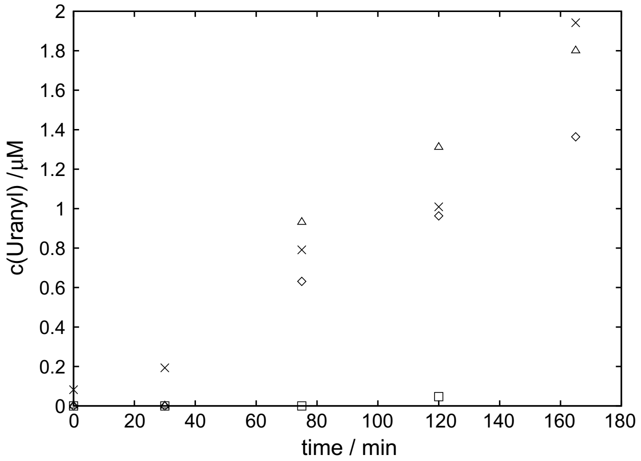

Fig. 3. Dissolution of uranyl in N_2 as a function of irradiation time for UO_2 pellets containing 0 wt% (×), 0.1 wt% (△), 1 wt% (◇), and 3 wt% (□) Pd.

with increasing amount of Pd in the pellet. This indicates that Pd also catalyzes the oxidation of UO_2 by O_2 (Fig. 2). As the experiments were performed under constant O_2-pressure, the rate constant can be estimated indirectly based on the measured UO_2^{2+} dissolution. The rate expressions for the uncatalyzed and catalyzed reactions are shown in the following equations:

$$r = k_{ox}[O_2], \tag{6}$$

$$r_{Pd} = k_{ox}^{Pd}\epsilon_{rel}[O_2], \tag{7}$$

with k_{ox} (3.88×10^{-10} m s^{-1} [15]) and k_{ox}^{Pd} being rate constants for the oxidation of UO_2 by O_2, with and without Pd as a catalyst present, $[O_2]$ the concentration of O_2 and ϵ_{rel} the fraction of Pd on the pellet surface.

The ratio between the U(VI) dissolution rate in the uncatalyzed case and the total U(VI) dissolution in the catalyzed case is given by the following equation:

$$\frac{r}{r + r_{Pd}} = \frac{k_{ox}}{k_{ox} + k_{ox}^{Pd}\epsilon_{rel}}. \tag{8}$$

By rearranging Eq. (8) into Eq. (9), k_{ox}^{Pd} can be calculated from the experimentally determined dissolution rates (slopes in Fig. 2) and the rate constant for the uncatalyzed reaction,

$$k_{ox}^{Pd} = \frac{k_{ox}\left[\left(\frac{r_{Pd}+r}{r}\right) - 1\right]}{\epsilon_{rel}}. \tag{9}$$

The rate constant for this reaction is estimated to be on the order of 10^{-7} m s^{-1}.

In Table 2, the rate constants for oxidation of UO_2 by H_2O_2 and O_2, the corresponding Pd catalyzed reactions, and the Pd catalyzed reduction of UO_2^{2+} by H_2 are summarized. It has been shown that the rate constants for the reactions between UO_2 and the strongest oxidants among the water radiolysis products (e.g. $OH^{\bullet}$, $CO_3^{\bullet-}$) are diffusion controlled [11]. Hence, Pd or ϵ-particles cannot have a catalytic effect on these reactions.

3.2. γ-radiolysis

The results from the experiments in the gamma source under N_2 and H_2 atmosphere, corrected by subtracting the measured U(VI) concentration in the background experiments under inert N_2 atmosphere, are shown in Figs. 3 and 4. It can be seen that the dissolution of the pure UO_2 pellet decreases by around 20% in H_2 atmosphere compared to N_2. The rationale for this is that H_2 reacts with radiolysis products ($OH^{\bullet}$), leading to lower concentrations of oxidants and, thereby, to lower rate of UO_2 matrix oxidation.

Table 2
Rate constants for the reactions with H_2O_2, O_2 and H_2

	H_2O_2 (m s^{-1})	O_2 (m s^{-1})	H_2 (m s^{-1})
UO_2/UO_2^{2+}	7.3×10^{-8}	3.88×10^{-10}	–
UO_2/UO_2^{2+} (Pd)	$(6.92 \pm 1.52) \times 10^{-6}$	$\approx 10^{-7}$	$\approx 10^{-6}$

The Pd particles present in the other pellets catalyze the reduction of $UO_{2(s)}^{2+}$ to $UO_{2(s)}$ by H_2 and the oxidation of $UO_{2(s)}$ by O_2 and H_2O_2. The rate of dissolution under N_2 atmosphere lies around 1.6×10^{-9} mol m^{-2} s^{-1} as compared to background experiments for the pellets containing 0%, 0.1% and 1% Pd, while there is virtually no dissolution detectable with a Pd content of 3%. In H_2, the rate of dissolution is 1.4×10^{-9} mol m^{-2} s^{-1} for the pellet without Pd, while there is no dissolution detectable for the pellets containing Pd. In fact, the rate of dissolution is even lower than in the background.

The theoretical dissolution rate is given by the following equation:

$$\begin{aligned} r_{diss} &= r_{ox} - r_{red} \\ &= \sum_{ox}[ox]k_{ox}\frac{S}{V} + \sum_{ox}[ox]k_{ox}^{Pd}\epsilon_{rel}\frac{S}{V} - [H_2]k_{red}\epsilon_{rel}\frac{S}{V}, \end{aligned} \tag{10}$$

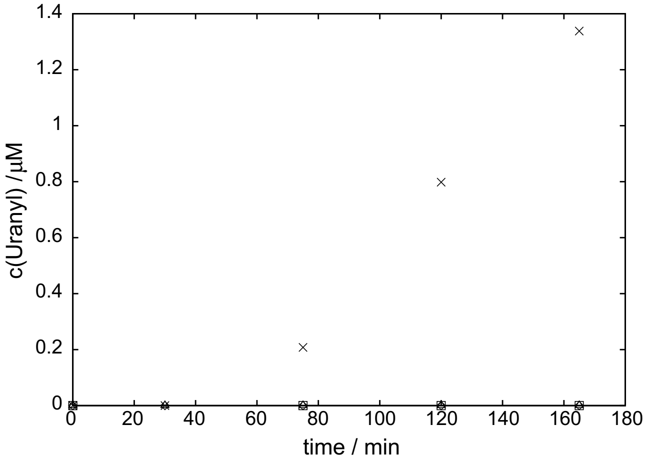

Fig. 4. Dissolution of uranyl in H_2 as a function of irradiation time for UO_2 pellets containing 0 wt% (×), 0.1 wt% (△), 1 wt% (◇), and 3 wt% (□) Pd.

Table 3
Dissolution rates in N_2 background experiments (without irradiation)

	N_2 background ($M\ s^{-1}$)
Pellet 0	$(2.8 \pm 0.9) \times 10^{-11}$
Pellet 0.1	$(3.2 \pm 0.8) \times 10^{-11}$
Pellet 1	$(1.7 \pm 0.1) \times 10^{-10}$
Pellet 3	$(4.1 \pm 0.3) \times 10^{-10}$

with r being the reaction rates for dissolution, oxidation and reduction respectively, [ox] the oxidant concentration, k_{ox} and k_{ox}^{Pd} the rate constants for each oxidant, S the surface area of the pellet, V the volume of the solution, $[H_2]$ the concentration of H_2 in solution and ϵ_{rel} the Pd fraction in the pellet.

When calculating the theoretical dissolution rate, the pellet surface area was taken as three times the geometrical surface area [27]. Oxidant and H_2 concentrations were obtained by using numerical simulations (computed by MAKSIMA-Chemist [28]) of the homogeneous system. The average concentrations during the simulated irradiation time were used in the calculations. Only oxidation by the molecular oxidants (H_2O_2 and O_2) were assumed to be catalyzed by Pd. In the N_2 saturated experiments, the radiolytically produced H_2 (calculated by MAKSIMA-Chemist) was also taken into account. The rate constants used came from Table 2 and Ref. [15].

The results of the calculations are compared to the experimental values (corrected for background presented in Table 3) and shown in Table 4. In some cases, the dissolution in the background experiment exceeds the dissolution during irradiation in the presence of H_2. The net dissolution rates were taken as zero in these cases as the reduction rate can never exceed the oxidation rate on a fully reduced surface. In general, the experimentally determined dissolution rates are higher than expected from the calculations. However, the trends are reproduced by the calculation. The ratios between the calculated and the measured dissolution rates, in case where dissolution was experimentally observed and calculated, are all around 0.1. Similar experiments with commercially produced pellets show a ratio of 0.5. The difference between the calculated and the measured values could be attributed to the plausible presence of U(VI) in the interior of the pellet and to the difficulty in determining the pellet surface area. U(VI) present inside the pellet is not removed by the pre-treatment with HCO_3^-, but becomes accessible for dissolution when the outer UO_2 layers on the pellet surface are oxidatively dissolved.

Table 4
Comparison between calculated and experimental dissolution rates

	Calculated ($M\ s^{-1}$)		Measured ($M\ s^{-1}$)	
	N_2	H_2	N_2	H_2
Pellet 0	2.95×10^{-11}	1.47×10^{-11}	$(1.8 \pm 0.3) \times 10^{-10}$	$(1.6 \pm 0.3) \times 10^{-10}$
Pellet 0.1	1.88×10^{-11}	(0)	$(2.1 \pm 0.3) \times 10^{-10}$	≈0
Pellet 1	(0)	(0)	$(1.5 \pm 0.3) \times 10^{-10}$	0
Pellet 3	(0)	(0)	≈0	0

Table 5
Impact of the different oxidants on UO_2 oxidation under N_2 atmosphere

	Impact (%)			
	Pellet 0	Pellet 0.1	Pellet 1	Pellet 3
H_2O_2	98.47	41.21	6.61	2.31
H_2O_2 Pd	–	56.20	90.15	94.38
H_2O_2 tot	98.47	97.41	96.76	96.69
O_2	1.13	0.47	0.08	0.03
O_2 Pd	–	1.95	3.13	3.28
O_2 tot	1.13	2.42	3.21	3.31
CO_3^-	0.38	0.16	0.03	0.01
HO_2^-	0.03	0.01	0.00	0.00

The relative impact of the different oxidants on the UO_2 oxidation under N_2 atmosphere is shown in Table 5. The values were obtained by the following equation:

$$\text{Impact} = \frac{k_{ox}[ox]}{\sum_{ox} k_{ox}[ox]}, \qquad (11)$$

using the calculated oxidant concentrations (MAKSIMA-Chemist) after 165 min irradiation, and rate constants in Table 2 and Ref. [15].

It can be seen that H_2O_2 is the most important oxidant in all cases. For the pellet without Pd, almost 99% of the uranyl produced is due to oxidation by H_2O_2. With increasing amount of Pd on the surface of the pellet, the Pd catalyzed reaction between H_2O_2 and UO_2 becomes increasingly important. It should, however, be noted that the total impact of H_2O_2 remains almost constant throughout the series. As can also be seen, O_2 becomes more important with increasing Pd content.

The results of this work clearly demonstrate, that Pd particles catalyze the oxidation of the UO_2 matrix by H_2O_2, and that the reaction is diffusion controlled. It further shows an increase in the rate constant for oxidative dissolution of UO_2 by O_2 by a factor of 250 compared to the uncatalyzed reaction. The experiments during γ-irradiation show that under H_2 atmosphere (1 bar) already 0.1% Pd completely inhibits the oxidative dissolution of UO_2. In the case of N_2, 3% Pd prevent dissolution by reduction with the radiolytically produced H_2. In a previous paper the effect of H_2 on the rate of spent nuclear fuel dissolution for fuels of different age and burn-up was studied [29]. For a fuel age of 100 yr and a burn-up of 38 MWd kg^{-1} U, 0.1 bar H_2 was predicted to be sufficient to completely inhibit the dissolution of the spent nuclear fuel assuming 1% ϵ-particle surface concentration. It was also estimated that an ϵ-particle surface coverage of only 1 ppm would be sufficient to completely stop the nuclear fuel dissolution at a H_2 pressure of 40 bar. These predictions are well in line with the experimental observations presented in this work.

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References

[1] R.L. Segall, R.S.C. Smart, J. Nowotny, Surface and Near-surface Chemistry of Oxide Materials, Elsevier Science Publishers B.V., 1988.
[2] D. Rai, A.R. Felmy, J.L. Ryan, Inorg. Chem. 29 (1990) 260.
[3] I. Grenthe, F. Diego, F. Salvatore, G. Riccio, J. Chem. Soc. 11 (1984) 2439.
[4] J. de Pablo, I. Casas, J. Gim'enez, M. Molera, M. Rovira, L. Duro, J. Bruno, Geochim. Chosmochim. Acta 63 (1999) 3097.
[5] D.E. Grandstaff, Econ. Geol. 71 (1976) 1493.
[6] W.J. Gray, J.C. Tait, S.A. Steward, D.W. Shoesmith, in: Fifth Annual International Conference, La Grange Park, IL, 1994, p. 2597.
[7] E.M. Pierce, J.P. Icenhower, R.J. Serne, J.G. Catalano, J. Nucl. Mater. 345 (2005) 206.
[8] O. Roth, M. Jonsson, Cent. Eur. J. Chem. 6 (2008) 1. and references therein.
[9] D.W. Shoesmith, J. Nucl. Mater. 282 (1) (2000) 1. and references therein.
[10] M.M. Hossain, E. Ekeroth, M. Jonsson, J. Nucl. Mater. 358 (2006) 202.
[11] E. Ekeroth, M. Jonsson, J. Nucl. Mater. 322 (2003) 242.
[12] L.E. Eary, L.M. Cathles, Metall. Trans. B 14B (1983) 325.
[13] J. de Pablo, I. Casas, J. Giménez, M. Molera, M. Rovira, L. Duro, J. Bruno, Geochim. Chosmochim. Acta 63 (1999) 3097.
[14] J. Merino, E. Cera, J. Bruno, J. Quinones, I. Casas, F. Clarens, J. Giménez, J. de Pablo, M. Rovira, A. Martinez-Esparza, J. Nucl. Mater. 346 (2005) 40.
[15] E. Ekeroth, O. Roth, M. Jonsson, J. Nucl. Mater. 355 (2006) 38.
[16] T.E. Eriksen, M. Jonsson, Tech. Rep. TR-07-06, Svensk Kärnbränslehantering AB, August 2007.
[17] P. Carbol, J. Cobos-Sabathe, J.-P. Glatz, C. Ronchi, V. Rondinella, D.H. Wegen, T. Wiss, A. Loida, V. Metz, B. Kienzler, K. Spahiu, B. Grambow, J. Quiones, A.M.E. Valiente, Tech. Rep. TR-05-09, Svensk Kärnbränslehantering AB, March 2005.

[18] S. Nilsson, M. Jonsson, J. Nucl. Mater. 372 (2008) 160.
[19] H. Kleykamp, J. Nucl. Mater. 131 (1985) 221.
[20] S. Nilsson, M. Jonsson, J. Nucl. Mater. 374 (2008) 290.
[21] M.E. Broczkoswki, J.J. Noel, D.W. Shoesmith, J. Nucl. Mater. 346 (2005) 16.
[22] M. Trummer, S. Nilsson, M. Jonsson, J. Nucl. Mater. 378 (2008) 55.
[23] J.W.T. Spinks, R.J. Woods, An Introduction to Radiation Chemistry, 3rd Ed., John Wiley, New York, 1990.
[24] I.K. Kressin, Anal. Chem. 56 (12) (1984) 2269.
[25] S.B. Savvin, Talanta 8 (1961) 673.
[26] R.D. Astumian, Z.A. Schelly, J. Am. Chem. Soc. 106 (1984) 304.
[27] I. Casas, J. Giménez, V. Marti, M.E. Torrero, J. de Pablo, Mater. Res. Soc. Symp. Proc. 294 (1993) 61.
[28] M.B. Carver, D.V. Hanley, K.R. Chaplin, MAKSIMA-Chemist a program for mass action kinetics simulation by automatic chemical equation manipulation and integration using stiff techniques, Tech. Rep., Atomic Energy of Canada Limited – Chalk River Nuclear Laboratories, Ontario, 1979.
[29] M. Jonsson, F. Nielsen, O. Roth, E. Ekeroth, S. Nilsson, M.M. Hossain, Environ. Sci. Technol. 41 (2007) 7087.