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On the catalytic effects of UO_2(s) and Pd(s) on the reaction between H_2O_2 and H_2 in aqueous solution

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Abstract

The possible catalytic effects of UO_2 and Pd (as a model for noble metal particles) on the reaction between H_2O_2 and H_2 have been studied experimentally. The experiments were performed in aqueous solution using an autoclave. The aqueous solutions were pressurized with H_2 or N_2 and the H_2O_2 concentration was measured as a function of time. The experiments clearly showed that Pd catalyzes the reaction between H_2O_2 and H_2 while UO_2 has no catalytic effect. The rate constant of the reaction between H_2O_2 and H_2 catalyzed by Pd was found to be close to diffusion controlled and independent of the H_2 pressure in the range 1–40 bar. The impact of the catalytic effect on the reaction between H_2O_2 and H_2 on spent nuclear fuel dissolution is, however, fairly small. Other possible effects of noble metal particles are also discussed, e.g. reduction of U(VI) to U(IV) in the liquid and solid phase.

1. Introduction

In Sweden spent nuclear fuel will be placed in a deep repository at a depth of about 500 m, according to the KBS-3 method developed by The Swedish Nuclear Fuel and Waste Management Co. (SKB). The spent fuel consists mainly of UO_2, 95%, the rest being radioactive fission products and actinides. One of the key questions for the safety assessment of a deep repository is the rate of UO_2 dissolution, which is assumed to govern the release rate of the fission products and the actinides. Since damage to the fuel canister is not expected to occur in less than 1000 years [1], it is impossible to study fuel dissolution under relevant conditions. After 1000 years the spent fuel will be less radioactive and the relative α, β and γ dose contribution will be different compared to fresh spent fuel [2]. This problem can be circumvented by studying all the potentially relevant elementary processes and using this knowledge as a basis for simulations.

When spent fuel is directly exposed to groundwater, reactive radicals and molecules will be produced by water radiolysis. Both oxidants ($OH^\bullet$, H_2O_2, $HO_2^\bullet$ and O_2) and reductants (e^-_{aq}, $H^\bullet$ and H_2) are produced. The most important oxidant under deep repository conditions has been shown to be H_2O_2 [3]. H_2O_2 oxidizes UO_2 to soluble UO_2^{2+} and thereby increases the rate of spent fuel dissolution. HCO_3^- in the groundwater enhances the spent fuel dissolution further due to formation of complexes with UO_2^{2+}. The effect of HCO_3^- on the rate constant for oxidation of UO_2 by H_2O_2 is to increase the rate linearly with concentration from 0 to 1 mM. Above 1 mM the rate constant is independent of the carbonate concentration [4].

In several experimental studies on spent fuel dissolution using real spent fuel or α-doped UO_2, the dissolution of the fuel has been found to be slower than expected from the concentration of H_2O_2 produced. A possible rationale for this could be a reaction between H_2O_2 and H_2 producing H_2O, which has been suggested to be catalyzed by the UO_2 surface [5]. Another possible explanation is that solutes present in the water consume H_2O_2 in homogeneous reactions.

In a deep repository, large amounts of H_2 will be produced from anaerobic corrosion of the iron in the canister

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[6]. From previous experiments it is interpreted that H_2 inhibits the dissolution of UO_2 [7]. However, the mechanism for the inhibition is still largely unknown. H_2 slowly reduces U(VI) to U(IV) in aqueous solution and it also reacts with the radiolytically produced oxidants, primarily $OH^{\cdot}$ [8]. These effects are of marginal importance and cannot account for the very efficient inhibition observed in some cases.

Some of the fission products in the spent fuel form nanometer sized noble metal particles, often referred to as ε-Ru- or ε-particles, containing Mo, Ru, Tc, Pd and Rh [9]. These particles contain elements with potential catalytic activity and synthetic noble metal particles have also been shown to be catalysts for reduction by hydrogen. In previous leaching experiments where the leaching solution has been purged with 89.97% Ar + 10% H_2 + 0.03% CO_2, the concentration of ^{99}Tc dropped from 24 ppb to 1.6 ppb in 2 days, while in experiments purged with Ar + 0.03% CO_2 the ^{99}Tc concentration was nearly constant. The decrease of Tc concentration in the first case is probably caused by the reduction of TcO_4^- to $TcO_2(s)$ by H_2 activated on the alloy particles [10].

Electrochemical experiments show that dissolved hydrogen can give more negative corrosion potentials, E_{CORR} for UO_2 when synthetic noble metal particles are incorporated into the UO_2-matrix [11].

The relative amount of the different metals in noble metal particles varies, but Mo, Ru and Pd seem to represent the largest part of them, over 70% [10,12,13]. Hence, effects of noble metal particles could provide an additional explanation to the observed effect of H_2 on spent fuel dissolution.

In this work we have studied the possible catalytic effects of UO_2 and Pd (as a model for noble metal particles) on the reaction between H_2O_2 and H_2. We also discuss the impact of this effect and other possible effects on the dissolution of spent nuclear fuel.

2. Experimental

All experiments were performed in a glass vessel placed inside an autoclave. The autoclave is equipped with inlet and outlet tubes for pressurizing and sampling and also a stirrer. Experiments without H_2 were also made; in those cases N_2 was used instead. The UO_2 powder was supplied from Westinghouse Atom AB and the Pd powder from Sigma–Aldrich. Chemicals and gases came from Merck, AGA and Air Liquid. Milli-Q filtered water was used throughout.

The effect of H_2 on the reaction of UO_2 with H_2O_2 was first studied. The UO_2 powder (0.5 g per experiment) was washed three times with 10 mM carbonate in order to remove U(VI) from the surface prior to the experiment. The UO_2 powder and 280 ml 10 mM $NaHCO_3$ was bubbled with N_2 and then pressurized with 20 or 40 bar H_2 overnight. The day after, 20 ml H_2O_2 solution was added to give a final concentration of ~0.22 mM. The concentration of H_2O_2 was measured about ten times in 2 h indirectly with I_3^- by UV/visible spectroscopy. The sample volume taken for analysis was approximately 2 ml. Detailed information about the I_3^- method can be found in reference [14–16].

In order to study the possible catalytic effect of Pd on the reaction of H_2O_2 with H_2, 8 mg Pd powder in 280 ml water was bubbled with N_2 for 20 min. The mixture was put in the autoclave and N_2 was blown through for 10 min. The autoclave was then pressurized with H_2 and left overnight. The pressure was varied between 1, 5, 10, 20 and 40 bar. The following day, 20 ml H_2O_2 was added to give a final concentration of ~0.22 mM. The concentration of H_2O_2 was measured over time for 2 h.

The same experiments were done with five different amounts of Pd powder: 4, 8, 12, 16 and 32 mg at 1 and 20 bar H_2.

3. Results and discussion

H_2O_2 reacts with UO_2 in two consecutive single electron transfer steps where the first step is rate determining

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

$$UO_2^+ + OH^{\cdot} \rightarrow UO_2^{2+} + OH^-. \quad (2)$$

The rate constant for oxidation of UO_2 by H_2O_2 is 4.4×10^{-6} m/min [4].

In Fig. 1 the H_2O_2 concentration is plotted as a function of reaction time in the absence and presence of H_2.

As can be seen, the rate of the reaction between UO_2 and H_2O_2 is not significantly affected by H_2. Clearly, these results do not support the previously suggested theory claiming that the UO_2 surface catalyzes the reaction between H_2O_2 and H_2.

In solutions containing H_2O_2 and H_2 (40 bar), no consumption of H_2O_2 was observed in the absence of Pd. Furthermore, in solutions containing only H_2O_2 and Pd, no consumption of H_2O_2 is observed (see Fig. 2). In the experiments with Pd and H_2 present, the H_2O_2 concentration was decreasing over time, which indicates that there is a catalytic effect of Pd. The rate of the reaction increases with increasing amount of Pd powder. In Fig. 2 the

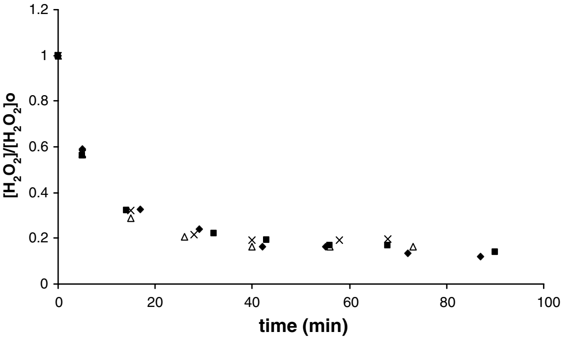

Fig. 1. Normalized concentration of H_2O_2 plotted against reaction time (■ without H_2, ◆ without H_2, △ 40 bar H_2, × 40 bar H_2).

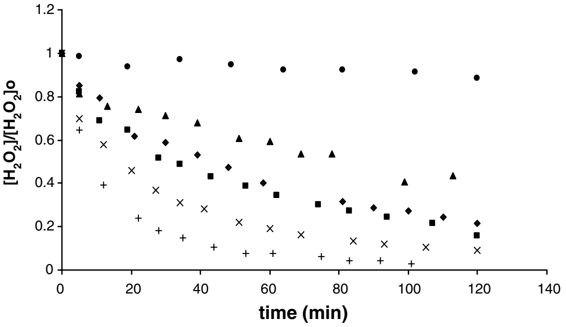

Fig. 2. Normalized concentration of H_2O_2 plotted against reaction time at 1 bar H_2 with different amounts of Pd (● without H_2 8 mg, ▲ 4 mg, ◆ 8 mg, ■ 12 mg, × 16 mg, + 32 mg).

normalized concentration of H_2O_2 is plotted as a function of time for different amounts of Pd.

When reducing the H_2 pressure we did not observe any decrease in reaction rate. The catalytic effect of Pd seems to be independent of the H_2 pressure in the range of 1–40 bar. This is shown in Fig. 3. Consequently, the Pd surface appears to be saturated by H_2 already at 1 bar.

By plotting $\ln([H_2O_2]/[H_2O_2]_o)$ against time we obtain straight lines indicating first order kinetics. The slopes give us pseudo first order rate constants, k_1 (min^{-1}). By plotting k_1 against the solid surface to solution volume ratio, S/V (m^{-1}), the second order rate constant, k (m/min), can be determined from the slope (Fig. 4). k is here $(1.3 \pm 0.1) \times 10^{-3}$ m/min. This is very close to the diffusion limit for particle suspensions, which indicates that Pd lowers the activation energy for the reaction dramatically. The different solid surface area/total solution volume ratios, $S/V\,(\text{m}^{-1})$ were calculated using the average particle size ($r = 0.625\ \mu\text{m}$) assuming spherical geometry. The pseudo first order rate constants and the solid surface to solution volume ratios are presented in Table 1.

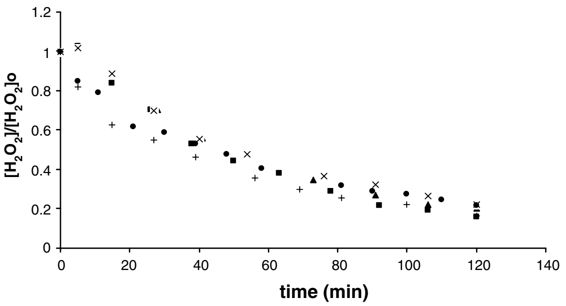

Fig. 3. Normalized concentration of H_2O_2 plotted against reaction time with 8 mg Pd at different H_2 pressures. (□ 40 bar, ▲ 20 bar, × 10 bar, + 5 bar, ● 1 bar).

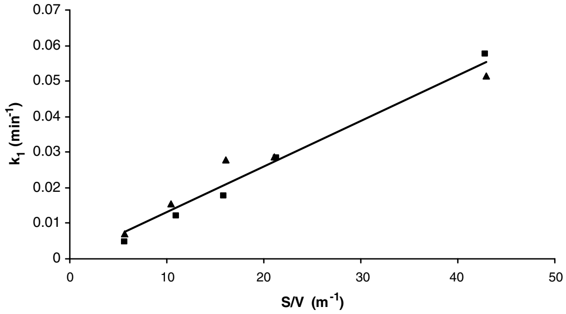

Fig. 4. Pseudo first order rate constants, k_1 (min^{-1}) plotted against the solid surface/total solution volume ratio, S/V (m^{-1}) at 1 and 20 bar H_2, respectively, (■ 1 bar, △ 20 bar).

Table 1
Details for calculations of the second order rate constant, k, at 1 bar H_2

Pd (mg)	S/V (m^{-1})	k_1 (min^{-1})
4.2	5.6	0.0048
8.2	10.93	0.01206
11.9	15.87	0.01762
16	21.33	0.0284
32.1	42.8	0.0575

To elucidate the impact of the noble metal particle catalyzed reaction between H_2O_2 and H_2 on spent fuel dissolution we have compared three different cases (surface coverage). Simulations of the H_2O_2 concentration as a function of time in a system taking radiolytic production, consumption of H_2O_2 in a surface reaction and diffusion into account show that the surface concentration approaches steady state fairly rapidly [17]. The presence of noble metal particles would increase the rate constant for H_2O_2 consumption at the surface and thereby lower the steady state concentration. The direct consequence of this would be a lower rate of UO_2 oxidation. Using the recently published rate constant for the reaction between H_2O_2 and UO_2 and the rate constant for the Pd catalyzed reaction between H_2O_2 and H_2 determined in this work, we can calculate the reduction in steady state concentration as a function of noble metal particle surface coverage. For fuel containing 0.1%, 1% or 2% noble metal particles, the steady state concentration and thereby the dissolution rate is reduced by a factor 1.3, 3.9 and 6.9, respectively. Consequently, the maximum effect of noble metal particles, taking only the reaction between H_2O_2 and H_2 into account is fairly small. However, noble metal particles could possibly also catalyze the reduction of U(VI) to U(IV) by H_2 both in the liquid phase and in the solid. The first type of reduction would not inhibit spent fuel dissolution, but it would lower the concentrations of redox sensitive radionuclides in the liquid phase. The second type of reduction would, on the other hand, inhibit the dissolution by reducing soluble U(VI) back to insoluble U(IV) in the solid phase. The maximum impact of the solid phase reduction can be estimated assuming the noble metal particle catalyzed process to be diffusion controlled and equal to the rate of oxidation ($H_2O_2 + UO_2$). At 40 bar H_2 an noble metal particle content of 1 ppm would be sufficient to cancel the radiation induced oxidation of the fuel matrix completely (fuel age 100 years). Judging from inventory data, the fraction of noble metal particles in spent nuclear fuel is expected to be in the order 1% [18]. Hence, this process alone could account for the inhibiting effect of H_2.

4. Conclusions

The experiments conducted in this work do not reveal any catalytic effect of UO_2 on the reaction between H_2O_2 and H_2. However, the reaction is effectively catalyzed by Pd. The rate of the reaction is increasing linearly with the amount of Pd and the second order rate constant is virtually diffusion controlled. The rate of the reaction is independent of the H_2 pressure in the range of 1–40 bar. Calculations of the influence of noble metal particles on the dissolution rate show that the effect is fairly small. Real noble metal particles are expected to have the same or even lower effect than Pd. However, if noble metal particles catalyze the reduction of U(VI) to U(IV) in the solid phase, at 40 bar H_2 an noble metal particle content of only 1 ppm is sufficient to cancel the radiation induced oxidation completely.

Acknowledgement

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References

[1] Swedish Nuclear Fuel and Waste Management Co. SKB Technical Report, TR-06-09, 2006, p. 403.
[2] F. Nielsen, M. Jonsson, J. Nucl. Mater. 359 (2006) 1.
[3] E. Ekeroth, M. Jonsson, J. Nucl. Mater. 322 (2003) 242.
[4] M.M. Hossain, E. Ekeroth, M. Jonsson, J. Nucl. Mater. 358 (2006) 202.
[5] J.C. Wren, D.W. Shoesmith, S. Sunder, J. Electrochem. Soc. 152 (11) (2005) B470.
[6] N.R. Smart, D.J. Blackwood, L. Werme, Swedish Nuclear Fuel and Waste Management Co. SKB Technical Report, 2001, TR-01-22, p. 1.
[7] P. Carbol, J. Cobos-Sabate, J.-P. Glatz, C. Ronchi, V. Rondinella, D.H. Wegen, T. Wiss, A. Loida, V. Metz, B. Kienzler, K. Spahiu, B. Grambow, J. Quinones, A. Martinez, E. Valiente, Swedish Nuclear Fuel and Waste Management Co. SKB Technical Report, 2005, TR-05-09, p. 124.
[8] E. Ekeroth, M. Jonsson, T.E. Eriksen, K. Ljungqvist, S. Kovacs, I. Puigdomenech, J. Nucl. Mater. 334 (2004) 35.
[9] H. Kleykamp, Nucl. Technol. 80 (1988) 412.
[10] D. Cui, J. Low, C.J. Sjöstedt, K. Spahiu, Radiochim. Acta 92 (2004) 551.
[11] M.E. Broczkowski, J.J. Noël, D.W. Shoesmith, J. Nucl. Mater. 346 (2005) 16.
[12] D. Cui, T. Eriksen, U.-B. Eklund, Mater. Res. Soc. Symp. Proc. 663 (2001) 427.
[13] H. Kleycamp, J. Nucl. Mater. 171 (1990) 181.
[14] W.A. Patrik, H.B. Wagner, Anal. Chem. 21 (10) (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 (6) (1992) 1129.
[17] F. Nielsen, K. Lundahl, M. Jonsson, J. Nucl. Mater., in press, doi:10.1016/j.jnucmat.2007.01.279.
[18] R. Håkansson, Swedish Nuclear Fuel and waste Management Co. SKB Technical Report, R-99-74.