Journal of Nuclear Materials 397 (2010) 128–131

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Letter to the Editor

Oxidative dissolution of actinide oxides in H_2O_2 containing aqueous solution – A preliminary study

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ARTICLE INFO

Article history:
Received 16 October 2009
Accepted 6 November 2009

ABSTRACT

Oxidative dissolution of spent nuclear fuel is an important issue in the safety assessment of a future geological repository for spent nuclear fuel. Although UO_2 constitutes, in terms of mass, the majority of the spent fuel material, its main radiotoxicity is (after extended storage times) contained in actinides with half lives shorter than that of 238-uranium, such as isotopes of Np and Pu. Relatively little information is available on the dissolution behavior of Np and Pu in comparable environments. This work investigates the oxidative dissolution of NpO_2 and PuO_2 in non-complexing aqueous solutions containing H_2O_2 and compares their behavior with that of UO_2. We have found that oxidative dissolution takes place for all three actinides in the presence of H_2O_2. Based on the obtained dissolution rates, we would not expect the dissolution of the actinides to be congruent. Instead, in a system without complexing agent, the release rates of Np and Pu are expected to be lower than the U release rate.

1. Introduction

The envisaged geological final disposal of highly radioactive waste demands an investigation of the behavior of the waste materials in geological environments over long time scales. In the event of groundwater intrusion, the release of most radionuclides from spent nuclear fuel will be controlled by the dissolution of the fuel matrix, which (for most fuels) mainly consists of UO_2 [1]. UO_2 has low solubility under the reducing conditions that prevail at the depth of a deep repository, whereas the matrix solubility is increased upon oxidation [2]. When spent fuel comes into contact with water, oxidizing radiolysis products will be formed and the potential for matrix dissolution could increase significantly [3].

Although UO_2 constitutes, in terms of mass, the majority of the spent fuel material, its main radiotoxicity is (after extended storage times) contained in actinides with half lives shorter than that of 238-uranium, such as isotopes of Np and Pu and the point has been raised that potential incongruent dissolution of these actinides may be regarded as a safety-relevant effect when assessing spent fuel behavior [4]. The behavior of uranium dioxide in contact with oxidizing water radiolysis products such as hydrogen peroxide has been extensively investigated in recent years [5] whereas experiments aiming at understanding the radiolytic dissolution kinetics of the homogeneous phases NpO_2 and PuO_2 can not be found in the open literature.

Although Np and Pu are higher homologues of U in the actinide series, it seems improbable that they will display identical oxidation and dissolution kinetics. The consequence of such differences may result in an incongruent dissolution from the spent fuel matrix under radiolytic conditions and deserve attention. This is increasingly important when considering long term deposition of MOX fuel and UO_2-fuel with higher burn-up.

Previous studies on UO_2 have shown that, in a system exposed to α-radiation, H_2O_2 is the major contributor to the oxidative dissolution [6]. This work investigates the kinetics of H_2O_2 consumption in aqueous solutions containing NpO_2 and PuO_2 and compares their behavior with that of UO_2.

2. Experimental

Experiments have been performed where the reaction between actinide oxides and H_2O_2 were studied by mixing aqueous suspensions of AnO_2 powders with H_2O_2 solutions and monitoring the H_2O_2 concentration and the concentration of dissolved An versus time. Radionuclides used in this study are depleted uranium, ^{237}Np and ^{239}Pu. UO_2 was supplied by Westinghouse Atom AB, NpO_2 and PuO_2 were used from Institute for Transuranium Elements (ITU) stocks. Before the start of the experiments the actinide powders were characterized with scanning electron microscope (SEM) to determine the particle size.

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0022-3115/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2009.11.027

Experiments using NpO_2 and PuO_2 were performed in a double glovebox arrangement. Oxygen levels were stabilised in the inner glove box in the range of 1–2 ppm. Experiments measuring H_2O_2 consumption using UO_2 were not performed in a glovebox, instead continuous N_2 purging was used to ensure low O_2 levels. The UO_2 dissolution was measured in separate experiments performed in a glovebox with oxygen levels <0.1 ppm. Actinide oxide powder (30 mg) was mixed with ~20 mM aqueous H_2O_2 solution in a glass vessel. The solution volume was 100 ml in the experiments using NpO_2 and PuO_2 and 20 ml in the case of UO_2. Samples (5 ml) were taken in several time intervals after the start of the experiment.

In the experiments performed using NpO_2 and PuO_2, one portion of the sample was used for determination of the H_2O_2 concentration using by UV/visible spectroscopy (Lovibond PCCheckit photometer) at 528 nm using DPD (*N*,*N*-diethyl-1,4-phenylene diammoniumsulfate as reagent according to the method described in Refs. [7,8]. Another portion was used for determination of the concentration of dissolved actinide. This was performed by inductively coupled plasma mass spectrometry (ICP-MS). This aliquot was passed through 30 kDa MWCO ultrafilters to remove the colloids from the solution. At the end of the experiments the oxidation state distribution in the aqueous phase was analyzed. This was done by oxidation state separation by solvent extraction using thenoyltrifluoroaceton (TTA) in the case of Pu and DBM (dibenzoylmethane) in the case of Np according to the method described in Refs. [9,10], followed by ICP-MS analysis. The equipment used for ICP-MS was a ThermoFinnigan Element 2 (ThermoFinnigan, Bremen, Germany) installed in a glovebox.

In the experiments performed using UO_2, the H_2O_2 concentration was measured indirectly by UV/visible spectroscopy (S2000 spectrophotometer from WPA) at 360 nm using I_3^- as an indicator. Detailed information about this method can be found in Refs. [11–13]. The concentration of U(VI) in solution was measured by UV/vis spectroscopy at 653 nm using the Arsenazo(III) reagent (ε_{653} = 63,000). Detailed information about this method is found in Refs. [14,15].

In order to remove surface fines and establish a uniform oxidation state (remove pre-oxidized U(VI)) the solid uranium dioxide samples were washed three times with 10 mL and 10 mM HCO_3^- and three times with pure H_2O prior to the experiment with H_2O_2. The surfaces of neptunium and plutonium were not specially treated before the experiments due to the higher stability of their +IV oxidations states, as confirmed by XPS results.

Due to the different specific activities of the actinide oxides [16], the background levels of radiolytically produced H_2O_2 will vary. In order to account for this, background studies were performed for ^{237}Np and ^{239}Pu where the solution consisted of deionised water.

Table 1
Initial H_2O_2 consumption rates, initial actinide release rates and one-electron reduction potential for the AnO_2^+/An^{4+} [16].

	dH_2O_2/dt (mol dm^{-3} s^{-1})	E^0 (mV)	An release rate (mol dm^{-3} s^{-1})
UO_2	12×10^{-7}	380	2.5×10^{-7}
NpO_2	0.9×10^{-7}	640	1.5×10^{-11}
PuO_2	0.28×10^{-7}	1040	4.0×10^{-13}

The uncertainty in the concentration measurements is estimated to ~10%.

3. Results and discussion

Using the present data on H_2O_2 concentration as a function of reaction time, it is possible to determine the relative rates of H_2O_2 induced oxidative dissolution for UO_2, NpO_2 and PuO_2. It should be kept in mind that the rate of H_2O_2 consumption does not necessarily reflect only the relative rate constant for oxidation of the actinide oxide. As the experiments have been performed utilizing aqueous solutions free from potential complexing agents, such as HCO_3^-, the kinetics for H_2O_2 consumption is largely limited by dissolution of the oxidized actinide oxide rather than the redox process [17]. For low conversions, a steady-state approach can be used where the rate of oxidation is identical to the rate of dissolution.

In Fig. 1, the H_2O_2 concentration is plotted versus time for the three different actinide oxides. In Table 1, the initial H_2O_2 consumption rates are shown.

As can be seen, the initial rate of H_2O_2 consumption is highest for UO_2 followed by NpO_2 and lowest rate is measured for PuO_2. When measuring the H_2O_2 consumption, the available surface area of the oxide to solution volume ratio is a critical parameter. The presented results are based on the assumption that the solid surface area to solution volume ratio is equal in the three experiments. Judging from SEM pictures of the materials, the surface area of the UO_2 powder was estimated to be significantly smaller than for the other materials. In order to obtain similar solid surface area to solution volume ratios, the solution volume was decreased by a factor of five in the experiment using UO_2. No compensation has been made for the difference between NpO_2 and PuO_2. This is probably an underestimation of the differences in surface area between the materials; hence the trend in H_2O_2 consumption could be even more pronounced than shown here. Interestingly,

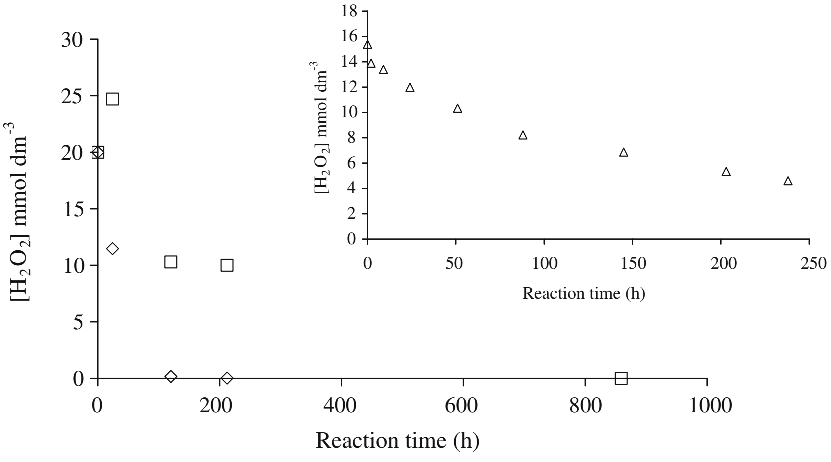

Fig. 1. H_2O_2 concentration as a function of reaction time for (△) UO_2, (□) PuO_2 and (◇) NpO_2.

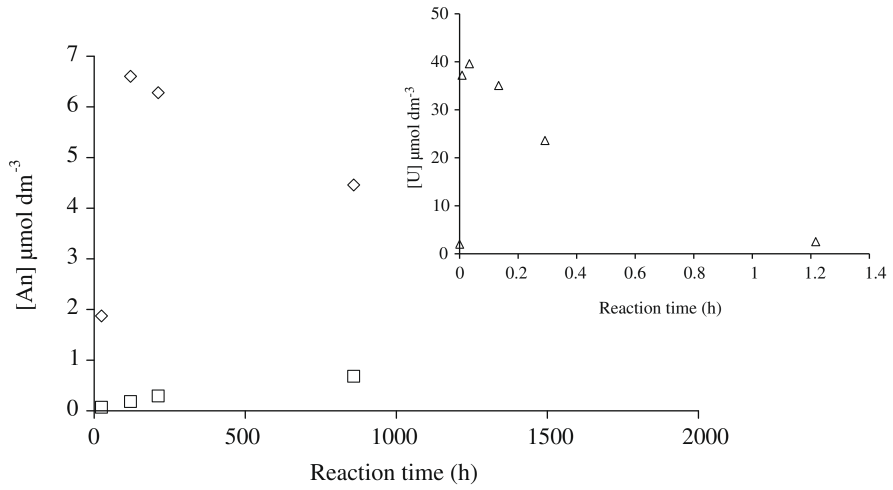

Fig. 2. Dissolved actinide concentration as a function of reaction time for (△) UO_2, (□) PuO_2 and (◇) NpO_2.

Table 2
Fraction of oxidized (oxidation state V and VI) actinide in solution at the end of the experiment, based on concentration of oxidized actinide (oxidation state V and VI) and total actinide concentration in solution.

	Background experiment			Experiment with added H_2O_2		
	Oxidized concentration (μmol dm^{-3})	Total concentration (μmol dm^{-3})	Oxidized fraction	Oxidized concentration (μmol dm^{-3})	Total concentration (μmol dm^{-3})	Oxidized fraction
NpO_2	3.3	8.1	0.41	4.1	4.4	0.93
PuO_2	0.09	0.12	0.78	0.7	0.68	1.03

the relative trend in reactivity towards H_2O_2 parallels the trend in oxidation potential for the three oxides (UO_2 has the lowest potential while PuO_2 has the highest potential [16]).

The observed trend in H_2O_2 consumption is qualitatively confirmed by the initial rate of actinide release (Table 1, Fig. 2). In the initial phase of the experiments the actinide concentration increases with increasing reaction time in all three cases. At longer reaction times the concentration of U and Np decreases, whereas the Pu concentration continues to increase. This can probably be attributed to the larger propensity of U and Np to form stable solid peroxide complexes [18,19]. Furthermore, the concentration of dissolved Pu is comparatively low, which limits the formation of the peroxide complex.

It should also be noted that, while the redox reactivity of the actinide oxides towards H_2O_2 is expected to depend on the redox potential of the actinide oxide, the rate of surface catalyzed decomposition of H_2O_2 is expected to be independent of the redox properties and therefore similar for all three oxides, as previously observed for other metal oxides [17,20–22]. Hence, the impact of the catalytic decomposition route (on the overall H_2O_2 decomposition) is expected to increase in the order $UO_2 < NpO_2 < PuO_2$. As a direct consequence, the oxidative dissolution yield is expected to decrease in the order $UO_2 > NpO_2 > PuO_2$.

The background experiments where no H_2O_2 was added revealed very low U release rate. The Pu background release rate was around 15% of the release rate in the H_2O_2 experiment. In the Np case the background release rate is approximately 10% of the initial release rate in the H_2O_2 experiment. However, since the Np concentration is decreasing at longer times in the presence of H_2O_2, the background concentration will, with time, exceed the Np concentration in the H_2O_2 experiment.

When analyzing the distribution of oxidation states in the dissolved Np and Pu at the end of the experiments performed in the presence of H_2O_2 and in the background experiments, it was found that H_2O_2 addition increased the fraction of oxidized material. The distribution of oxidation states is presented in Table 2.

This finding indicates that an oxidation reaction is indeed involved in the dissolution mechanism.

H_2O_2 produced by NpO_2 under the test conditions was below the detection limit of 1 μM during the whole experiment (35 days). The H_2O_2 produced by $^{239}PuO_2$ was found to be negligible compared to the amount of added H_2O_2. Decomposition of H_2O_2 caused by test conditions (i.e. vessel, atmosphere, surrounding light) was measured to be negligible in the concentrations used.

In conclusion, we have found that oxidative dissolution takes place for all three actinides in the presence of H_2O_2 and that the trend in dissolution rate parallels the trend in redox potential of the oxides. However, from the present data we can not draw any conclusions regarding the individual trends for the oxidation and dissolution mechanisms, respectively. In order to gain information on a mechanistic level, experiments with excess of solid material and varying surface to solution volume ratio are needed. Furthermore, the use of a complexing agent would be necessary in order to determine the true rate and rate constant of oxidation without influence of dissolution of oxidized species from the surface.

Based on the dissolution rates obtained in this work, we would not expect the dissolution of the actinides to be congruent. Instead, in a system without complexing agent, the release rates for Np and Pu are expected to be lower than the U release rate. However, in the presence of complexing agents and in systems where the oxides occur in mixed phases these dissolution rates may not be applicable.

Acknowledgements

We acknowledge the support of Mr. G. Rasmussen and K. Luetzenkirchen for providing us with analytical support, and H. Thiele and T. Wiss for analytical electron microscopy on the materials used. Further acknowledgements go to the safety and health services at Institute for Transuranium Elements (ITU). The work was performed under the ACTINET-6 Network of Excellence on actinide sciences, Joint Research Project No. JRP 02-09. The Swedish Nuclear Fuel and Waste Management Co. (SKB) is gratefully acknowledged for financial support.

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