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Radiation enhanced reactivity of UO_2

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Abstract

Pure UO_2 is often used as a model compound when studying reactions of importance in a future deep repository for spent nuclear fuel. The reactivity of pure UO_2 is not expected to be identical to the reactivity of the UO_2-matrix of spent nuclear fuel for several reasons. One reason is that the spent fuel, due to the content of radionuclides, is continuously being self-irradiated. The aim of this study is to investigate how irradiation of solid UO_2 surfaces affects their reactivity towards oxidants. The effect of irradiation (γ or electrons) on the reaction between solid UO_2 and MnO_4^- in aqueous solutions containing carbonate has been studied. It was found that irradiation with high doses (>40 kGy) increased the reactivity of the UO_2 to about 1.3 times the reactivity of unirradiated UO_2.

1. Introduction

The knowledge of the dissolution behaviour of spent nuclear fuel is important for the safety analysis of a future deep repository since the release of most radioactive species from the spent fuel is governed by the dissolution of the UO_2-matrix [1]. Under reducing conditions the solubility of the matrix is low due to the low solubility of U(IV), but when oxidized to U(VI) the matrix solubility is significantly increased [2]. Normally the conditions are expected to be reducing in groundwater at the depth of a deep repository but the circumstances can be changed as radiolysis of water will produce a number of oxidizing species, i.e., H_2O_2, O_2, $H^{\cdot}$, $CO_3^{\cdot-}$, and $HO_2^{\cdot}$ [3]. Many studies, aiming at predicting the influence of these species on the dissolution of UO_2, have been performed [1,4–8]. Due to the complexity of the spent fuel system it is however difficult to separate the effect of radiolysis from other factors, and numerical modelling and simulations of the system are necessary. The models used are generally based on the elementary reactions involved in the system and it is therefore important to determine the rate constants and mechanisms for these reactions. Hence, the oxidation of UO_2 by various oxidants has been subject to extensive studies, where pure UO_2 has been used as a model substance for spent fuel [4,7–10].

However, the reactivity of pure UO_2 is not expected to be identical to the reactivity of spent nuclear fuel. Partly because spent fuel contains

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fission products and transuranium elements formed on burning of the fuel, and should thus be regarded as UO_2 containing impurities. The burning process also affects physical properties such as grain structure, grain size, porosity and crack density, even though UO_2, in contrast to many other ceramics, does not become amorphous and no major changes in crystal structure have been detected due to in-reactor irradiation [11,12]. Furthermore, due to the content of radionuclides the fuel is continuously being self-irradiated. In this work the irradiation effects on the reactivity of UO_2 will be discussed. In this experimental study, γ and electron irradiation has been used. It should however be noted, that spent fuel will be exposed to both α-, β- and γ-irradiation. In the long term α will be the dominating type of radiation.

UO_2 is a semiconducting material [2] and it is reasonable to believe that its reactivity is related to the conductivity. Increased electrical conductivity involves increased mobility of electrons which should facilitate and increase the rate of electrochemical reactions. It has been shown that irradiation of metal oxide-semiconductor structures can alter the semi-conducting properties of the material [13]. In stoichiometrically pure UO_2 electric conductivity would require promotion of electrons from the U 5f level to the conduction band. The energy gap is $\sim$1.1 eV and at room temperature the probability for electrons to be transferred to the conduction band is extremely low [14]. However, it is reasonable to believe that the energy deposition in the material due to irradiation could induce such a transfer. Increased electrical conductivity is also gained by hyperstoichiometry as well as by impurities, which can give the material p-type semiconducting properties [15]. Upon irradiation it is also likely that the energy deposit in the material gives rise to structural changes (i.e., effects on grain size etc.) which might affect the reactivity.

In earlier studies, e.g., by Gromov [16] and Matzke [11], it has been observed that the dissolution rate of UO_2 increases as a result of irradiation (or simulated radiation damage). From these observations it is however difficult to draw any conclusions regarding the cause for the increased solubility.

The objective of this work is to investigate how irradiation of solid UO_2 surfaces affects their reactivity towards oxidants. The aim was to study the effect of irradiation of the solid phase without interference from radiolysis of water, for this reason we chose an oxidant which is not a water radiolysis product. Furthermore, the reaction should be slow enough to give a reasonable sampling interval and we also need the method of analysis to be fast so that the analysis time does not interfere too much with the total time for the experiment. Permanganate was found to be a suitable choice due to its relatively low reduction potential (and reactivity) and the possibility to analyse its concentration using UV/Vis spectroscopy.

Four series of experiments were performed where the reactivity of solid UO_2 surfaces towards permanganate was studied. The first series was performed without irradiation of the UO_2 so that effects on the reactivity, arising from several consecutive oxidations of the surface, would be revealed. In the second and third series the reaction between UO_2 and MnO_4^- was studied during irradiation (γ and electrons, respectively) of the solid phase in order to investigate the effect of energy deposition in the material during the reaction. In the fourth series of experiments the solid was irradiated dry (i.e., no solution present) and afterwards treated with permanganate solution, in order to detect permanent changes in reactivity.

2. Experimental

The UO_2 used in this study was obtained from UO_2 pellets supplied by Westinghouse Atom AB. Other chemicals were supplied by Merck. Millipore Milli-Q filtered water was used throughout.

Four series of experiments were performed; detailed information is given below. The solid phase consisted either of a UO_2 pellet, a UO_2 fragment or of a set of two rectangular UO_2 slices ($1 \times 10 \times 8$ mm). The fragment and the slices were cut from a pellet. The UO_2 was washed with 5 mM carbonate solution prior to each experiment in order to remove U(VI) from the surface. In each series the same specimen of UO_2 (pellet, fragment or slices) was used throughout, in order to avoid deviations caused by differences between different individuals (i.e., differences in geometry).

Permanganate, initial concentration 0.6 mM, was used as oxidant in all four series and all solutions contained 5 mM HCO_3^- in order to facilitate the dissolution of U(VI) from the surface [1]. The reactions were studied as a function of time, measuring the Mn(VII) concentration with UV/Vis spectroscopy at 545 nm. During the reactions also Mn(IV) was formed which interfered with the measurement of

Mn(VII). Therefore, the Mn(IV) concentration was measured at 390 nm. The Mn(VII) concentrations were corrected with respect to the Mn(IV) measurements.

The irradiations in series 2 were performed in a ^{60}Co γ-source and in series 3 and 4 a Microtron electron accelerator with electron energy 6–6.5 MeV and a pulse duration of 4 μs was used.

2.1. Series 1

In this experimental series several consecutive oxidations were carried out without irradiation in order to detect possible changes in the reactivity arising from the oxidation of the material. A UO_2 fragment was immersed in 4 ml permanganate solution. Samples were taken every 5 min (during ~80 min), analyzed and poured back into the reaction vessel.

2.2. Series 2

In this series a UO_2 pellet was immersed in 7 ml permanganate solution and the reaction was studied during γ-irradiation of the system (for ~80 min). The results were corrected with respect to the radiolytical decomposition of MnO_4^-, which was measured in separate experiments. Also reference experiments where the reaction was studied without irradiation were performed. Samples were taken and analyzed every 5 min (sampling time ~1 min). The pellet was washed in 5 mM HCO_3^- solution between the irradiations and the reference experiments. The dose rate was measured to 0.06 Gy/s by Fricke dosimetry [3].

2.3. Series 3

The experiments were performed in the PEEK cell shown in Fig. 1. The cell holds 3 mL solution and the solid material (two UO_2 slices) can be placed either inside the cell in contact with the solution, or on the outside in order to provide the same radiation doses but no contact between the solution and the solid.

As in series 2, experiments were performed where the reaction was studied during irradiation of the solid. The results were corrected with respect to the radiolytic decomposition of MnO_4^-, which was measured in separate experiments. Also reference experiments where the reaction was studied without irradiation were performed. The slices were washed overnight in 5 mM HCO_3^- solutions between the irradiations and the reference experiments.

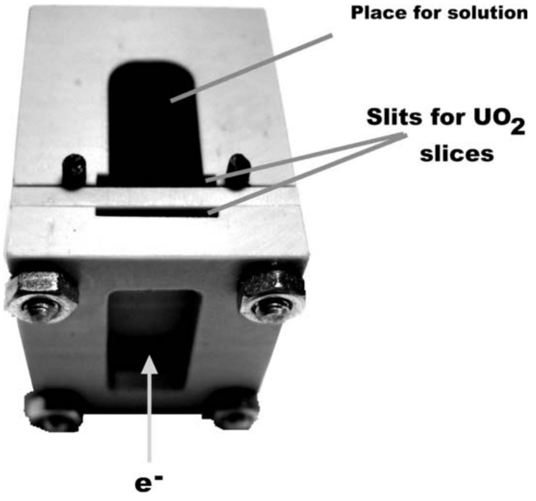

Fig. 1. The PEEK-cell used in electron irradiation experiments.

The irradiation setup was designed so that nearly all the energy was deposited in the solid and irradiation of the solution was minimized. Graphite shielding (28 mm) was used and the cell was placed with the UO_2 slices facing the accelerator. The experiment was performed at 12.5, 25 and 50 Hz pulse frequency. After each minute of irradiation, samples were taken, analyzed and then poured back into the cell. Total time for each experiment was ~45 min, corresponding to 15 min irradiation.

The average dose rate (not taking into account that the radiation is pulsed) was measured to 24.3 Gy/s by Fricke dosimetry at 12.5 Hz. The actual dose rate during the pulses is considerably higher (approx. 10^8 Gy/s). Furthermore, it was assumed that the dose rate is proportional to the pulse frequency when calculating the doses at 25 and 50 Hz.

2.4. Series 4

In the last experimental series a fragment of UO_2 was irradiated by the accelerator with no solution present (i.e., in air). The fragment was irradiated 3 times of 15 min each, at 50 Hz pulse frequency. After the irradiation the fragment was washed in 5 mM HCO_3^- solutions for at least 1 h. The fragment was then immersed in 4 ml permanganate solution and the reaction was studied as a function of time (for 2 h), this was repeated 2–3 times after each irradiation and also performed 2 times before the first irradiation.

3. Results and discussion

In the first experimental series eight consecutive oxidations were made without irradiation in order to detect possible changes in the reactivity arising from the oxidation of the material. No such changes were observed.

In the second series the reaction was studied during irradiation in a ^{60}Co γ-source. In these experiments no difference between the reaction during irradiation (corrected for radiolytical decomposition of permanganate) and the reference without irradiation was found.

The irradiation of the UO_2 slices in the electron accelerator (series 3) was performed at three different pulse frequencies (i.e., three different dose rates); 12.5, 25 and 50 Hz. The experimental sequence was the following:

- Reference experiment before irradiation (performed only for 12.5 Hz).
- Study of reaction during irradiation of the solid phase.
- Reference experiment after irradiation.

The same UO_2 specimen was used throughout. The UO_2 was washed with HCO_3^- between each step and in each step fresh MnO_4^- solution was added. The results are shown in Fig. 2(a)–(c), where the normalized MnO_4^- absorbance is plotted versus total reaction time for the reaction during irradiation (corrected for radiolytical decomposition of permanganate) and for the reference experiments with no irradiation.

As can be seen in Fig. 2(a) there is no difference in reactivity between the irradiated case and the reference after irradiation at 12.5 Hz. However, before being irradiated, the UO_2 slice shows significantly lower reactivity than after/during the irradiation.

At higher pulse frequencies (25 and 50 Hz) an increase in reactivity is observed after the irradiations. These experiments show that the reactivity of UO_2 does increase as a result of the irradiation and that the effect is increasing with increasing dose (i.e., increasing pulse frequency at the same irradiation time). This dose dependence is illustrated in Fig. 3, where the difference in absorbance between the reference experiment (after irradiation) and the experiment during irradiation (corrected for radiolytical decomposition of permanganate) after 45 min reaction (corresponding to 15 min of irradiation) has been plotted versus radiation dose.

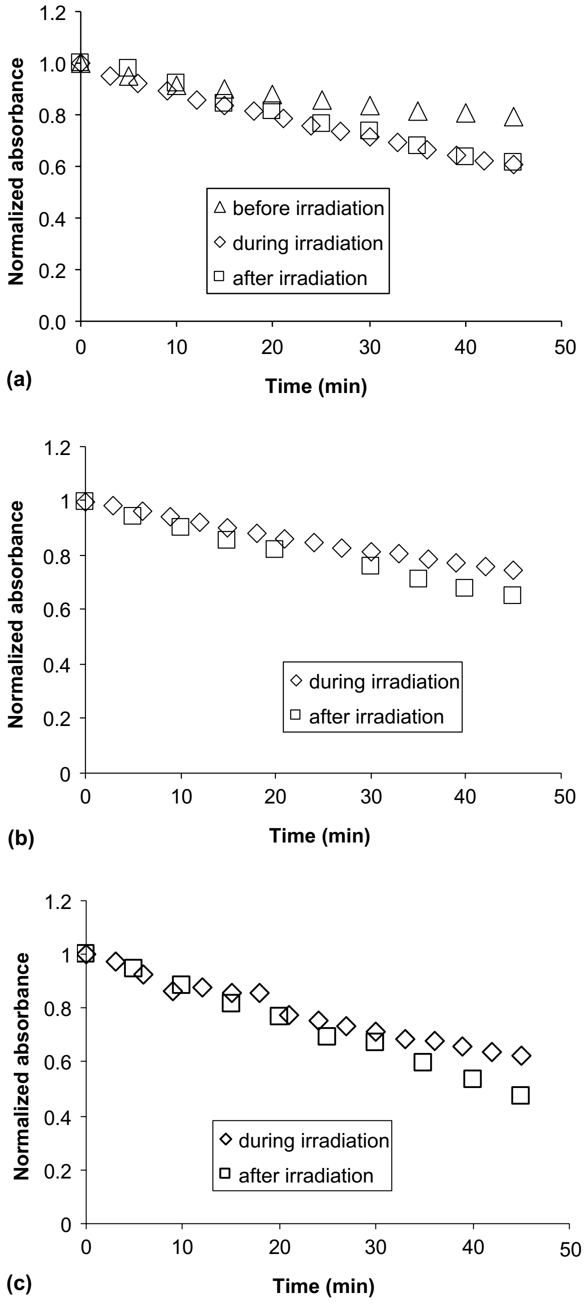

Fig. 2. Normalized absorbance of MnO_4^- versus total reaction time during reaction with UO_2 for irradiation in electron accelerator at (a) 12.5 Hz pulse frequency, (b) 25 Hz pulse frequency, and (c) 50 Hz pulse frequency and corresponding reference experiments.

From these experiments it is also clear that quite high doses (∼40 kGy) are required for the effect to be observed, which explains why no effect was observed from the γ-irradiation where the dose was only 270 Gy. Moreover, the fact that the effect

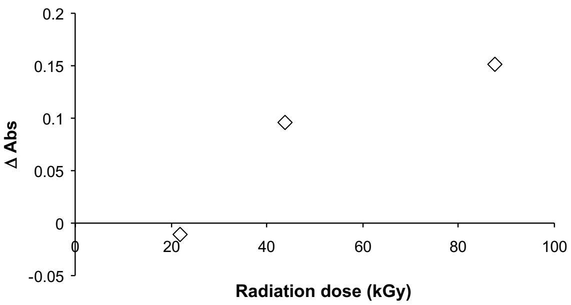

Fig. 3. Difference in MnO_4^- absorbance between irradiated experiment and reference experiment after 45 min total reaction time (corresponding to 15 min irradiation time) versus radiation dose.

remains after the irradiation (for the higher doses, not observed until after the irradiation) implies that the increased reactivity is caused by long-lived changes in the material.

In the fourth series of experiments a fragment of UO_2 was irradiated in air in the electron accelerator at 50 Hz and the reactivity was studied before the first irradiation and after each irradiation. The results are shown in Fig. 4.

Comparing the study made before irradiation of the material with the studies after irradiation we find a clear increase in the rate of the reaction, in consistence with the results from series 3. The effect seems however to be limited to about 1.3 times the reactivity before irradiation (based on the consumed amount of permanganate at the end of the experiments). The largest effect was observed after the first irradiation where the reactivity increased with a factor 1.2, after the second irradiation the reactivity is at its maximum and no further increase in reactivity is observed after the third irradiation.

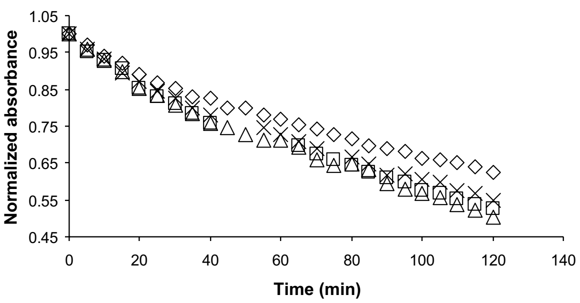

Fig. 4. Normalized MnO_4^- absorbance plotted versus reaction time for reaction with UO_2 before and after irradiation in air. (◇ before irradiation; ×, after one irradiation; Δ, after two irradiations; □, after three irradiations).

As mentioned earlier, in-reactor irradiation causes changes of the physical properties of nuclear fuel. It is known that the surface of the nuclear fuel increases due to in-reactor irradiation, as a result of cracking of the fuel [12], and this would lead to an increased reactivity. For high burn-up spent nuclear fuel a decrease in grain size has been observed at the surface of the fuel, whereas other (interior) parts show an increased grain size [17]. According to a recent experimental study, an increase in particle size would decrease the activation energy and hence increase the rate of the reaction [18]. The causes for the changes in particle size in nuclear fuel are however unclear and it is not possible to draw any conclusions on how electron irradiation affects the particle size, based on these observations. Hence, we cannot attribute the change in reactivity upon irradiation observed in this work directly to a change in particle size, but it is reasonable to believe that the increased reactivity could be caused by changes in the physical properties of the material. In this study, low LET radiation has been used. It is reasonable to believe that the irradiation effect could be even larger in spent nuclear fuel since it has mainly been exposed to high LET radiation.

To summarize, we have found that electron irradiation of UO_2 at doses >40 kGy increases the reactivity of the material. The effect seems to be limited to ~1.3 times the reactivity of unirradiated UO_2 and since the effect is long-lived we conclude that it may arise from permanent changes in the material. This issue must be taken into account when using studies on non-irradiated UO_2 to predict the reactivity of spent nuclear fuel, e.g., in the safety analysis of a future deep repository, since the spent fuel is subject to continuous self-irradiation and should be exposed to doses > 40 kGy after only a few days in the reactor [19]. The dissolution rate would be somewhat increased as a result of the increase in reactivity that arises upon irradiation.

Acknowledgement

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