# EFFECTS OF WATER ALPHA RADIOLYSIS ON THE SPENT FUEL MATRIX CORROSION

J.F. Lucchini [a]*, G. Sattonnay [b], C. Ardois [b], C. Jegou [a], C. Corbel [b]

[a] CEA Marcoule, DCC/DRRV/SCD/LECM

[b] CEA Saclay, DSM/DRECAM/SCM/ Laboratoire CEA de Radiolyse

* corresponding author. Tel.: +33-4-66-79-14-22; fax: +33-4-66-79-77-08; e-mail: lucchini@amandine.cea.fr

## ABSTRACT

Within the framework of studies about the long-term behaviour of spent fuel, the mechanism and the kinetics of $UO_2$ alteration require to be known. Water alpha radiolysis is so considered as determining in the corrosion rate of $UO_2$ fuel.

A state of knowledge on this subject is presented. The behaviour of $UO_2$/water interface under irradiation has been investigated as a function of alpha flux using a particle beam provided by a cyclotron. Released amount of uranium, hydrogen peroxide concentration ($H_2O_2$) increased whereas pH decreased when alpha-beam flux increased. The effect of the radiolytic species $H_2O_2$ on the $UO_2$ dissolution out of irradiation was also investigated. The uranium release rate was found smaller for leaching tests with $H_2O_2$ solution than for those performed under irradiation. These results show that others radiolytic species, as OH radical, can be involved in the oxidation/dissolution processes of $UO_2$ under irradiation.

In the future, this study will be continued in ATALANTE's laboratories to verify the radiolysis water impact on spent fuel or $\alpha$-doped $UO_2$.

## INTRODUCTION

The environmental assessment of nuclear used-fuel (composed of $\geq 95$ wt% $UO_2$ for UOX type, depending on its burn-up) disposal requires a prediction of release rates of uranium from the fuel once contact with water is established. Ionizing radiations from the fuel produce chemical species (like $H_2O_2$, $O_2$ and OH radicals) in water, which may cause oxidising conditions near the fuel surface (1,2) and would enhance the dissolution of uranium. After the metallic container lifetime (few hundreds years), water reaching the fuel will be subjected mainly to alpha radiolysis. Therefore, the investigation of the impact of water alpha-radiolysis on the $UO_2$ alteration is necessary to predict the long term behaviour of spent fuel.

This report presents a short state of knowledge on this subject. We performed original experiments on the external alpha radiation effect at the $UO_2$/water interface. We investigated also the specific effect of the radiolytic species $H_2O_2$ on the $UO_2$ corrosion, out of irradiation.

## STATE OF KNOWLEDGE

The dissolution rate of $UO_2$ in aqueous solutions depends on degree of surface oxidation of the fuel, which is governed by the solution redox conditions (1,2). Significant dissolution of uranium is expected to occur once the surface reaches a composition of $UO_{2.33}$ (1,3)

The alpha-radiolysis effects on oxidation and dissolution of $UO_2$ have been previously investigated by two different methods.

The first one consisted of the use of an external alpha-source placed in water to irradiate the $UO_2$/water interface (1,4-6). The corrosion rate was determined by using electrochemical techniques, and it was found to increase with the alpha dose rate. Moreover, according to Sunder et

al., alpha radiolysis effects on the one hand, $H_2O_2$ effects on the other hand, appear to be similar (2).

The second method to study alpha-radiolysis impact uses $UO_2$ pellets containing alpha emitters ([238]Pu, [239]Pu) (7-9). The leaching of both undoped and Pu-doped $UO_2$ pellets have been studied in a salt brine at 90°C by Gray (7,8). Specific activities of a first set of pellets doped mainly with [239]Pu were $1.06 \times 10^6$ Bq.g$^{-1}$ and $1.72 \times 10^8$ Bq.g$^{-1}$ for a second set doped mainly with [238]Pu. The total uranium mass loss rate from Pu-doped $UO_2$ pellets was about 10 times greater than from undoped pellets. The mass loss rates for the two sets of Pu-doped $UO_2$ pellets were found about equal, which suggests that alpha activity does not take part in these experiments. The uranium release from undoped and [238]Pu-doped $UO_2$ pellets have been investigated by Rondinella et al in demineralized water under anoxic atmosphere at room temperature (9). The specific alpha-activity of a first type of specimen was of $3.76.10^{10}$ Bq.g$^{-1}$ and of $3.76 \times 10^8$ Bq.g$^{-1}$ for a second type. The amounts of uranium released during leaching were 2 to 3 orders of magnitude higher for $\alpha$-doped $UO_2$ than for undoped $UO_2$. Thus, this result indicates a clear alpha-radiolysis effect. In spite of the 100-fold difference in the alpha-decay rates of the two types of investigated specimen, no significant difference was observed in the dissolution behaviour of uranium for the two doped materials.

Despite these studies, reliable estimates of the uranium release rates due to alpha activity are still lacking.

## EXPERIMENTAL

In the present work, a new approach is proposed to investigate how alpha emission from a $UO_2$ surface may affect both the release of uranium at the $UO_2/H_2O$ interface and the alteration of $UO_2$ surface. A high energy $He^{2+}$(alpha)-beam supplied by a cyclotron is used to pass through a $UO_2$ disk and emerges into the water in contact with the disk (see fig.1).

Figure 1 : Schematic diagram of the experimental device for $UO_2$ leaching under irradiation with an alpha-beam.
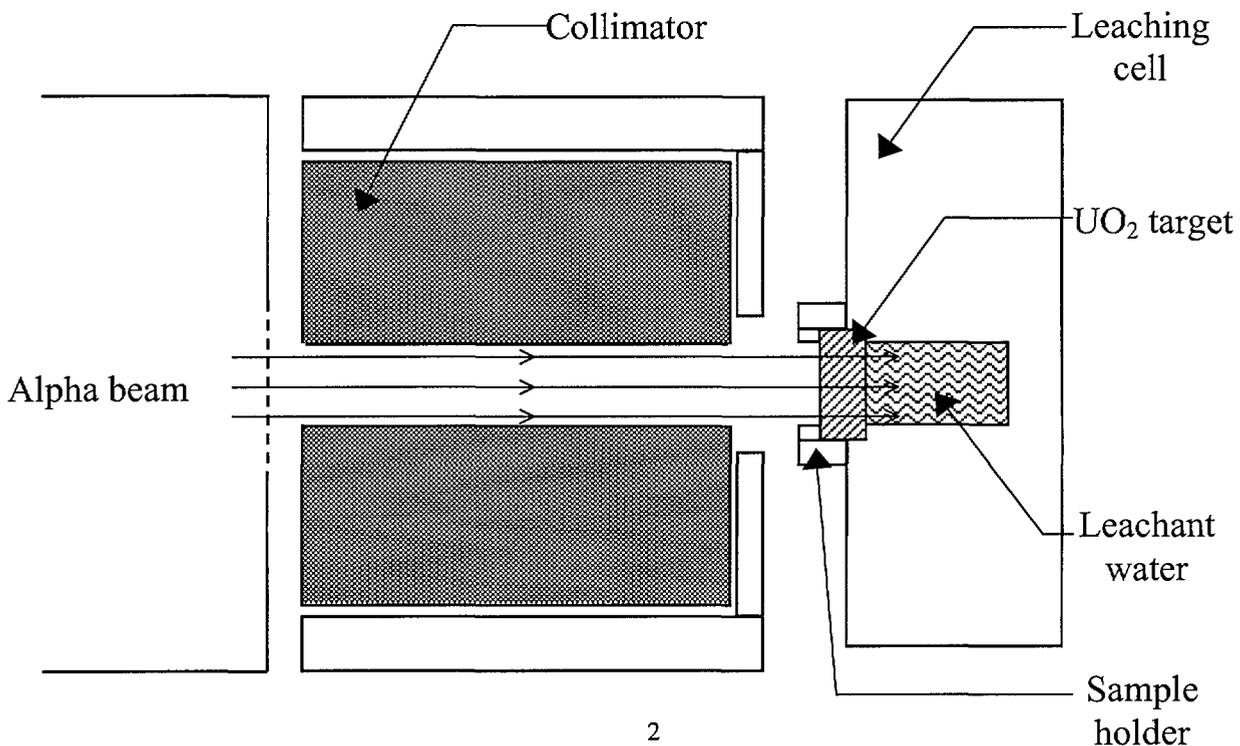
The target is a $UO_2$ sintered pellet, with a 285µm thickness. $\alpha$-beam emerges into the leachant with an energy of about 5 MeV, and its range in water is around 37 µm (according to TRIM code calculations (10)). The leachant is aerated deionized water. Sequential batch dissolution tests are performed on the $UO_2$ sample, at room temperature, before, during and after $\alpha$-irradiation. The irradiation experiments are performed with two alpha-flux : either $3.3 \times 10^{11}$ $\alpha.cm^{-2}.s^{-1}$ or $3.3 \times 10^{10}$ $\alpha.cm^{-2}.s^{-1}$.

During one hour of irradiation in our present experiments, alpha doses equivalent to those obtained for several years of spent fuel storage can be accumulated in water. For instance, Sattonnay et al. calculated that the radiation dose deposited by alpha-beam during one hour in the layer of irradiated water near the $UO_2$ surface was $2.6 \times 10^7$ Gy and $2.6 \times 10^8$ Gy for the lower and the higher flux respectively (11). For a PWR spent fuel with a burn-up of 45 $MW.d.kg_U^{-1}$, a cumulated total alpha-dose of $2.10^8$ Gy is reached after ~15 years of cooling time (11).

Similar leaching tests are also performed out of irradiation in the same conditions of pH and $H_2O_2$ concentrations as found under irradiation. They can permit to evaluate the specific effect of the radiolytic species $H_2O_2$ on $UO_2$ dissolution.

The total uranium concentration in each leachate is determined by time resolved laser induced fluorescence (TRLIF). The concentration of hydrogen peroxide in the irradiated solutions is measured by the Ghormley method (12).

## URANIUM RELEASE, HYDROGEN PEROXIDE CONCENTRATION AND PH VALUE IN IRRADIATED SOLUTIONS

Before irradiation, the uranium concentration ( as $UO_2^{2+}$ ) in the leachates is equal to 0.3 $\mu g.L^{-1}$. This value can be taken as a reference level for uranium release rate under aerated deionized water.

Under alpha-irradiation at a flux of $3.3 \times 10^{11}$ $\alpha.cm^{-2}.s^{-1}$, the uranium concentration increases by nearly four orders of magnitude and reaches a constant value of about 2280 $\mu g.L^{-1}$ (see fig.2). The hydrogen peroxide concentration in the irradiated solutions is also constant and equal to about $3.5 \times 10^{-3}$ $mol.L^{-1}$. The final pH for each irradiated solution is found to be equal to 3.8 on average.

Figure 2 : Released amount of uranium as a function of leaching time under alpha-beam irradiation for a flux of $3.3 \times 10^{11}$ $\alpha.cm^{-2}.s^{-1}$.
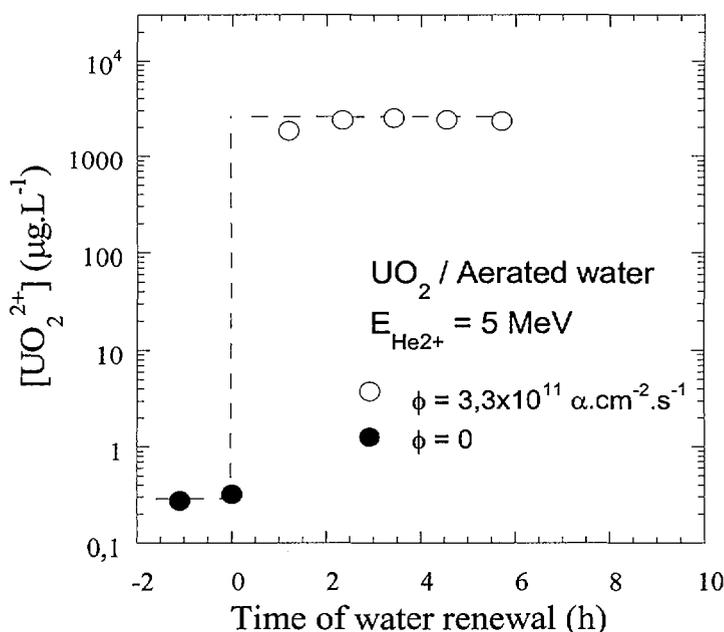
For the lower alpha-flux of $3.3 \times 10^{10}$ $\alpha.cm^{-2}.s^{-1}$, the same behaviour is observed, but the released amount of uranium reaches a lower mean value ($210$ $\mu g.L^{-1}$) than for the higher flux. The hydrogen peroxide concentration is also smaller, $4.8 \times 10^{-4}$ $mol.L^{-1}$, than for the higher alpha-flux and pH decreases to a value of 4.9. The results about the characterisation of irradiated aqueous solutions are summarised in table 1.

Table 1 : Mean values of uranium content, hydrogen peroxide ($H_2O_2$) concentration and pH measured in aqueous solutions for two $UO_2$/water interfaces, irradiated by an alpha-beam at two different flux; leaching tests of one hour each were performed under irradiation.

| Flux ($\alpha.cm^{-2}.s^{-1}$) | [U] ($\mu g_U.L^{-1}$) | [$H_2O_2$] ($mol.L^{-1}$) | pH |
|---|---|---|---|
| $3.3 \times 10^{11}$ | $2280 \pm 230$ | $(3.5 \pm 0.3).10^{-3}$ | $3.8 \pm 0.2$ |
| $3.3 \times 10^{10}$ | $210 \pm 30$ | $(4.8 \pm 0.5).10^{-4}$ | $4.9 \pm 0.3$ |

The concentration of chemical species in solution depends on the alpha-flux : the uranyl and hydrogen peroxide concentrations increased and pH decreased when alpha-flux increased.

## URANIUM RELEASE IN $H_2O_2$ SOLUTIONS

The radiolytic species $H_2O_2$ is supposed to take significantly part in $UO_2$ alteration during leaching tests under irradiation. Therefore, we performed new leaching tests without irradiation but with $H_2O_2$ solutions of $10^{-3}$ $mol.L^{-1}$ concentration and pH=4. These values of pH and $H_2O_2$ concentation are close to those measured in the irradiated solutions at high flux. The results show that the uranium release increases only to ~80 $\mu g.L^{-1}$ (two orders of magnitude smaller than under irradiation) and then decreases to reach the low value of uranium release obtained under deionized water (see fig.3).

Figure 3 : Uranium release as a function of leaching time in a $H_2O_2$ solution with a concentration of $10^{-3}$ $mol.L^{-1}$ and pH=4.
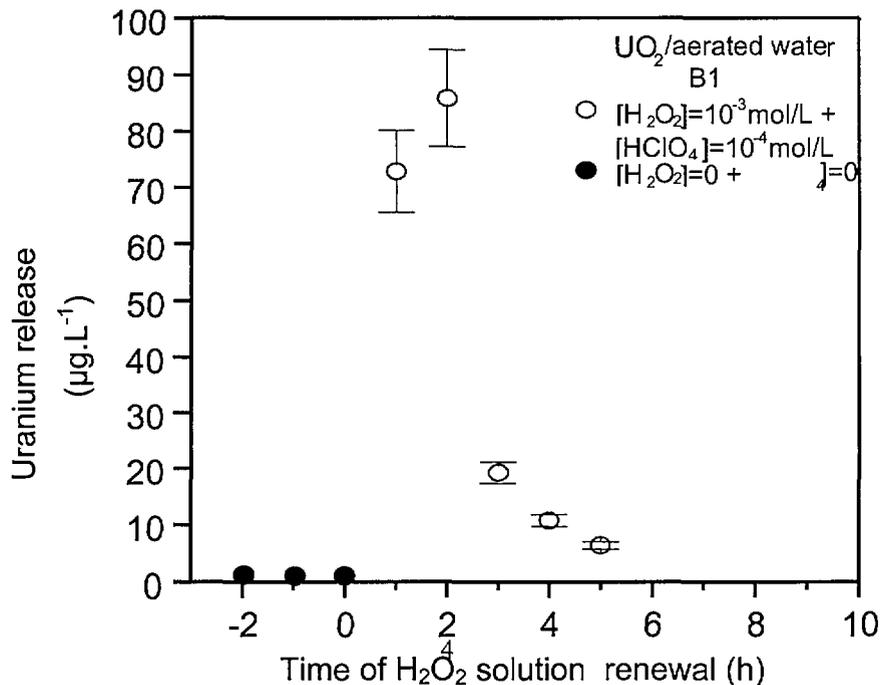
$H_2O_2$ concentration effects on $UO_2$ dissolution are not so significant as expected. $H_3O^+$ and $H_2O_2$ concentrations only can not explain the whole uranium release reached during irradiation in water.

## DISCUSSION

The results show that uranium release and hydrogen peroxide concentration increase whereas pH decreases in the irradiated solutions when the alpha-beam flux increases. Therefore, we can conclude that, at high-flux, the released amount of uranium depends on the radiation dose deposited by the alpha-beam in the aqueous solution. Such an alpha-flux dependence was found neither by Rondinella et al (9), nor by Gray et al (7,8) in experiments with alpha-doped $UO_2$. On the other hand, for studies of the $UO_2$ oxidation using external alpha-sources of various fluxes, at ambient temperature and in near-neutral solutions, oxidation of $UO_2$ by the alpha radiolysis of water was reported to be a function of the strength of the alpha flux (6). However, the alpha-fluxes used in all these experiments were smaller compared to those of the present investigation.

The uranium release in water is much higher for leaching tests under irradiation than for leaching experiments only with $H_2O_2$ solutions and out of irradiation. Moreover, the uranium concentration remains constant in the irradiated solutions whereas it decreases during leaching tests with $H_2O_2$ out of irradiation. From these different results, we can conclude that the others radiolytic species produced by water irradiation, as OH radical for instance, should also take a large part in the $UO_2$ oxidation/dissolution processes under irradiation.

Nevertheless, the $H_2O_2$ radiolytic species is involved in the formation of an alteration product on $UO_2$ surface during alpha-beam irradiation of the $UO_2$/deionised water interface (11). Sattonnay et al. show that an alteration product with a yellow colour is formed on $UO_2$ surface (11). This compound is identified by X-ray diffractometry : it is hydrated uranium peroxide ($UO_4.2H_2O$ or $UO_2(O_2).2H_2O$), called metastudtite. The reaction of metastudtite precipitation out of irradiation is usually given by the following equation:

$$UO_2^{2+} + H_2O_2 \rightarrow UO_4 + 2H^+ \qquad (R.1)$$

As the hydrogen peroxide is a product of water radiolysis, the formation of uranium peroxide can be considered as an effect of the water radiolysis. Moreover, the reaction (R.1) produces two $H^+$ ions, which may partially explain that pH decreases in the irradiated solutions.

Therefore, the leaching of $UO_2$ surface under irradiation involves complex processes with probably the contribution of all the chemical species (and not only $H_2O_2$) produced by water radiolysis for $UO_2$ oxidation, then the passage of uranium in aqueous solution and finally the implication of the radiolytic species $H_2O_2$ in the formation of hydrated uranium peroxide.

The possibility of uranium peroxide occurrence on spent fuel surface is discussed in details in (11). It was concluded that for very long-term leaching experiments, hydrated uranium peroxide precipitation may occur on spent fuel surface. Such a formation of secondary uranyl phases on $UO_2$ surface may influence the dissolution rate of uranium, because of their influence on the concentrations of uranyl ions in solution.

The use of an alpha beam supplied by an accelerator may strongly increase the radiolysis effects and enhance the kinetic of oxidation/dissolution or secondary phase precipitation processes which would be too slow to be observable during the leaching experiments at low dose rate. The short-term experiments at high dose rate may allow to model the long-term behaviour of spent fuel in contact with water.

## CONCLUSION

5

In order to investigate the effects of alpha-irradiation on the $UO_2$ surface alteration and on the uranium release in aqueous solution, an interface $UO_2$/water was irradiated under high flux with an external alpha beam supplied by a cyclotron. In addition, the effect of the radiolytic species $H_2O_2$ on the $UO_2$ dissolution out of irradiation was also investigated.

The following results were obtained :

(i) high uranium and $H_2O_2$ concentrations are measured and pH decreases in the irradiated solutions. The release of uranium increases by four orders of magnitude in aerated deionized water for the highest alpha-flux; the released amount of uranium depends on alpha-flux;

(ii) The uranium release in water was found smaller for leaching tests performed only with $H_2O_2$ solutions than for those under irradiation. An explanation is that others radiolytic species, as OH radical for instance, are involved in the $UO_2$ oxidation/dissolution processes under irradiation.

## PERSPECTIVES

In order to evaluate the water radiolysis impact on the long-term behaviour of spent fuel, this work must be also carried out on $\alpha$-doped $UO_2$ or on spent fuel itself. A greater total dose in water around than the one delivered by the radioactive sample can be supplied by an external gamma source for instance. This kind of experiment requires DHA's hot cells, which are devoted to highly radioactive material studies in the ATALANTE facility.

## ACKNOWLEDGEMENTS

## REFERENCES

1.  S. SUNDER and D.W. SHOESMITH, "Chemistry of uranium dioxide fuel dissolution in relation to the disposal of used nuclear fuel", Atomic Energy of Canada Limited, AECL-10395 (1991)
2.  D.W. SHOESMITH and S. SUNDER, "An electrochemistry-based model for the dissolution of uranium dioxide", Atomic Energy of Canada Limited, AECL-10488 (1991).
3.  L.H. JOHNSON and D.W. SHOESMITH, in: "Radioactive Waste Forms for the Future", eds W. Lutze and R.C. Ewing, (North-Holland, Amsterdam, 1988) pp. 635-698.
4.  M.G. BAILEY, L.H. JOHNSON and D.W. SHOESMITH, Corros. Sci. 25 (1985) 233.
5.  S. SUNDER, G.D. BOYER and N.H. MILLER, J. Nucl. Mater. 175 (1990) 163.
6.  S. SUNDER, D.W. SHOESMITH and N.H. MILLER, J. Nucl. Mater. 244 (1997) 66.
7.  W.J. GRAY, "Effect of surface oxidation, alpha radiolysis, and salt brine composition on spent fuel and uranium dioxide leaching performance: Salt Repository Project", Pac. Northwest Lab.,Richland,WA,USA., Report PNL/SRP-6689 (1988).
8.  W.J. GRAY, Mater. Res. Soc. Symp. Proc. 176 (1990) 141.
9.  V.V. RONDINELLA, H. MATZKE, J. COBOS and T. WISS, Mater. Res. Soc. Symp. Proc. 556 (1999) 447.

10. J.F. ZIEGLER, J.P. BIERSACK and U. LITTMARK, "The Stopping and Range of Ions in Solids" (Pergamon Press, New York, 1985).

11. G. SATTONNAY, C. ARDOIS, C. CORBEL, J.F. LUCCHINI, M.F. BARTHE, F. GARRIDO, D.GOSSET, submitted in Journal of Nuclear Materials.

12. A.O. ALLEN, J. HOCHANADEL, J.A. GHORMLEY and T.W. DAVIS, J. Phys. Chem. 56 (1952) 575.