Evolution of the surface reactivity of UO_2 exposed to H_2O_2 – Impact on spent nuclear fuel dissolution under repository conditions

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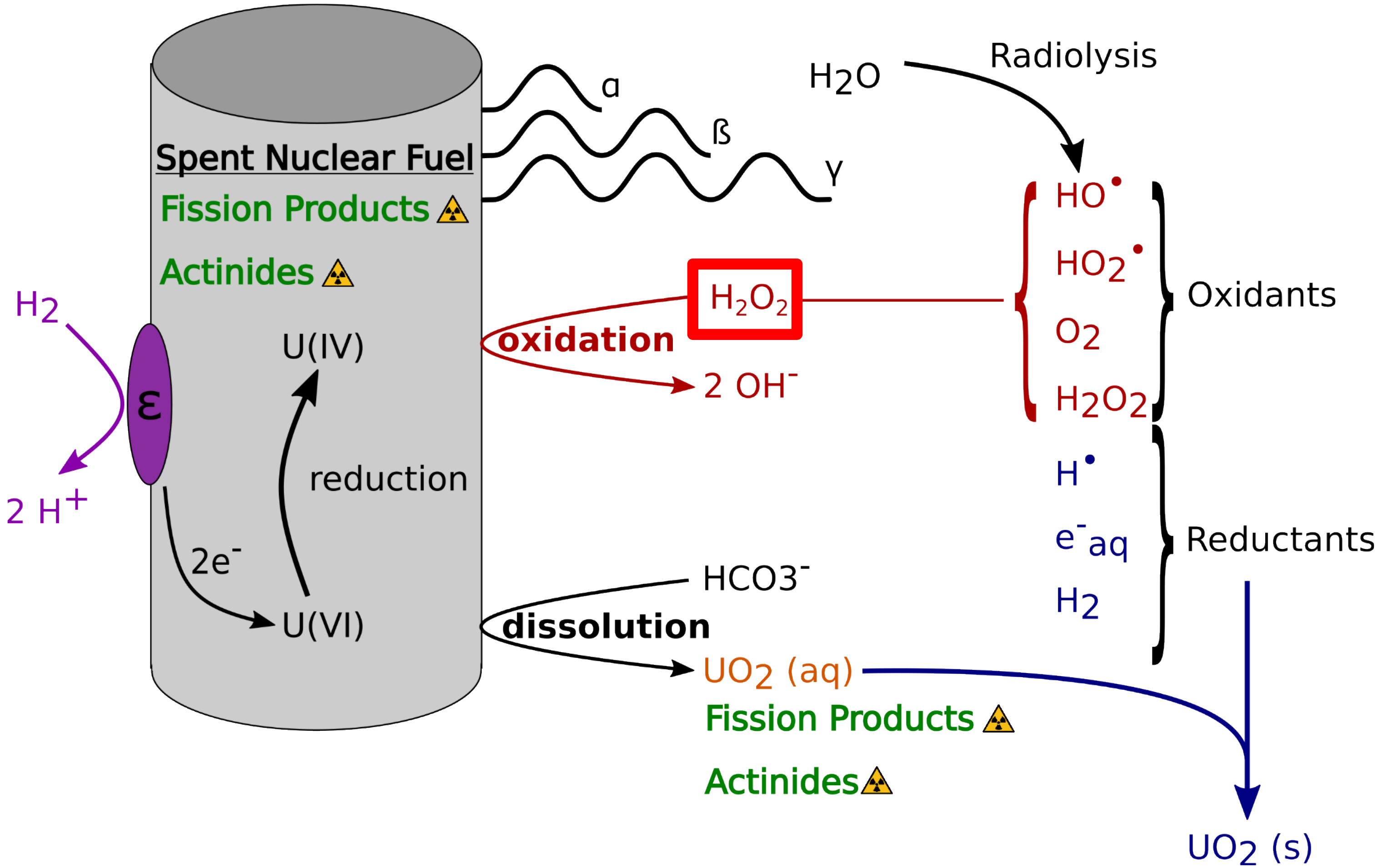
Radiation induced dissolution of spent nuclear fuel
– *Simplified scheme*



Reactions between H_2O_2 and the fuel surface

$$H_2O_2 + UO_2 \rightarrow UO_2^{2+} + 2\,OH^- \quad \text{(Dissolution)}$$

$$H_2O_2 + UO_2 \rightarrow H_2O + \tfrac{1}{2}\,O_2 + UO_2$$

$$Dissolution\ yield = \frac{k_{ox}}{k_{ox} + k_{cat}}$$

$$Dissolution\ yield = \frac{\Delta\left[U\right]}{\Delta\left[H_2O_2\right]}$$

Mechanism of catalytic decomposition

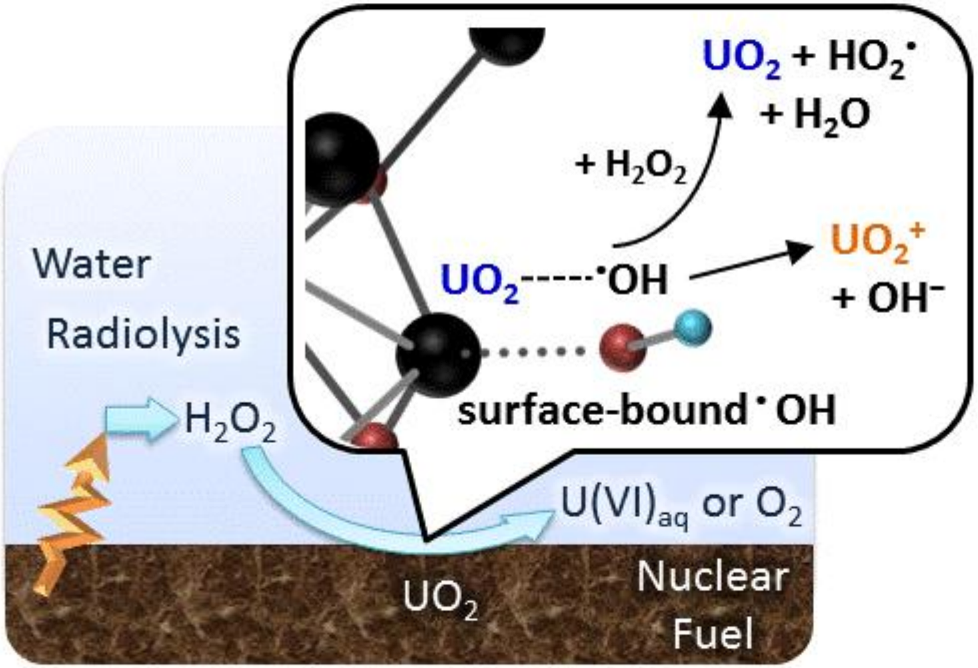
$H_2O_2 \rightarrow 2\ {}^{\bullet}OH(ads)$

${}^{\bullet}OH(ads) + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}$

$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$

$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$

The mechanism of UO_2 oxidation (the role of surface-bond OH)



A. Barreiro Fidalgo, Y. Kumagai, M. Jonsson, J. Coord. Chem. 2018, 71, 1799-1807.

UO_2 continued

$$1/2\,H_2O_2 + UO_2 \rightarrow UO_2 \cdots {}^{\bullet}OH \qquad (1)$$

$$\boxed{H_2O_2 + UO_2 \cdots {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O + UO_2} \qquad (2)$$

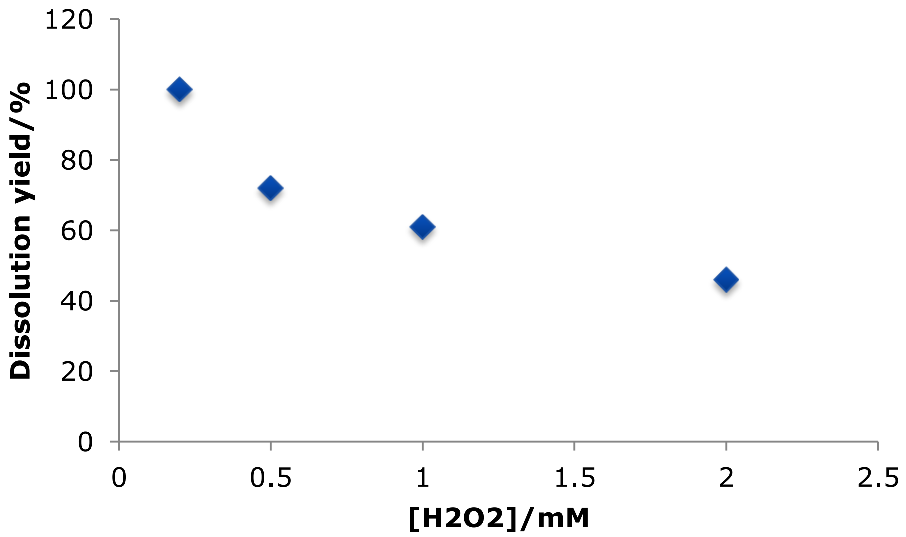
$$2\,HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \qquad (3)$$

$$\boxed{UO_2 \cdots {}^{\bullet}OH \rightarrow UO_2^{+} + OH^{-}} \qquad (4)$$

Competing reactions

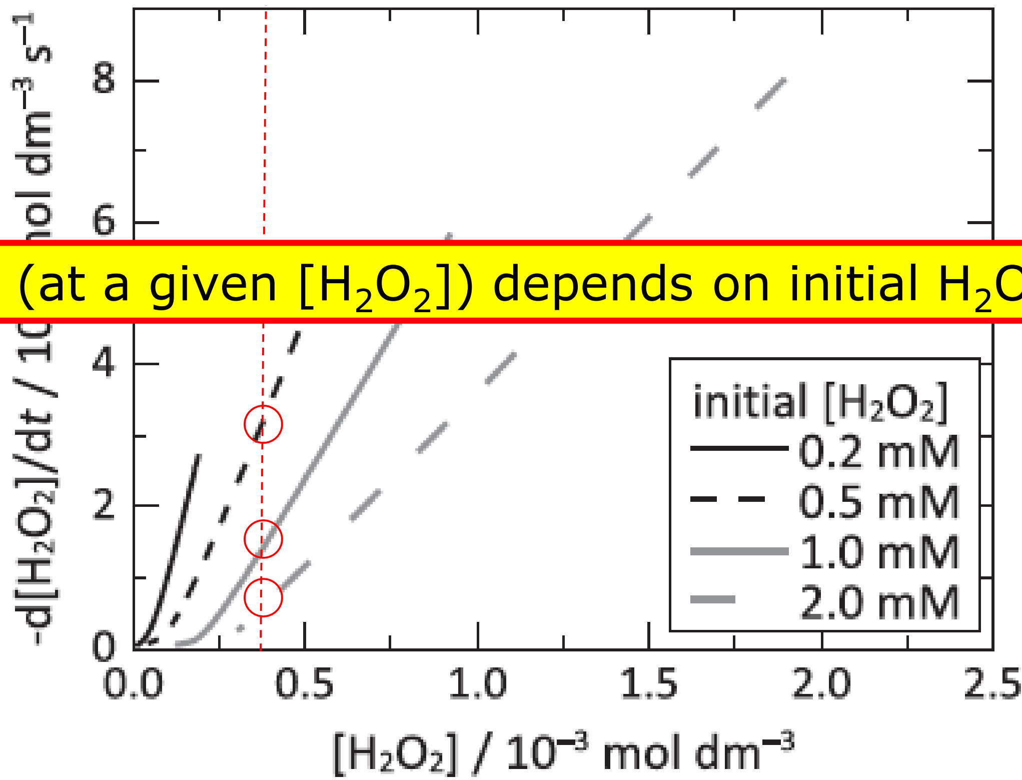
$$Dissolution\ yield = \frac{k_4}{k_4 + k_2\left[H_2O_2\right]}$$

Experimental results



A. Barreiro Fidalgo, Y. Kumagai, M. Jonsson, J. Coord. Chem. 2018, 71, 1799-1807.

Additional observation



The reaction rate (at a given $[H_2O_2]$) depends on initial H_2O_2 concentration

Previous findings

Dissolution yields:

UO_2 powder:40-100%[1]

UO_2 pellet: 15 %[2]

SIMFUEL pellet: 0.2 %[2]

[1] A. Barreiro Fidalgo, Y. Kumagai, M. Jonsson, J. Coord. Chem. 2018, 71, 1799-1807.
[2] S. Nilsson, M. Jonsson, J. of Nucl. Mater., 2011, 410, 89-93

General approach and general assumptions

- HCO_3^- will remove all oxidized Uranium – no secondary phase formation (based on experiments using O_2 as oxidant)

- Pellets can be and are re-used

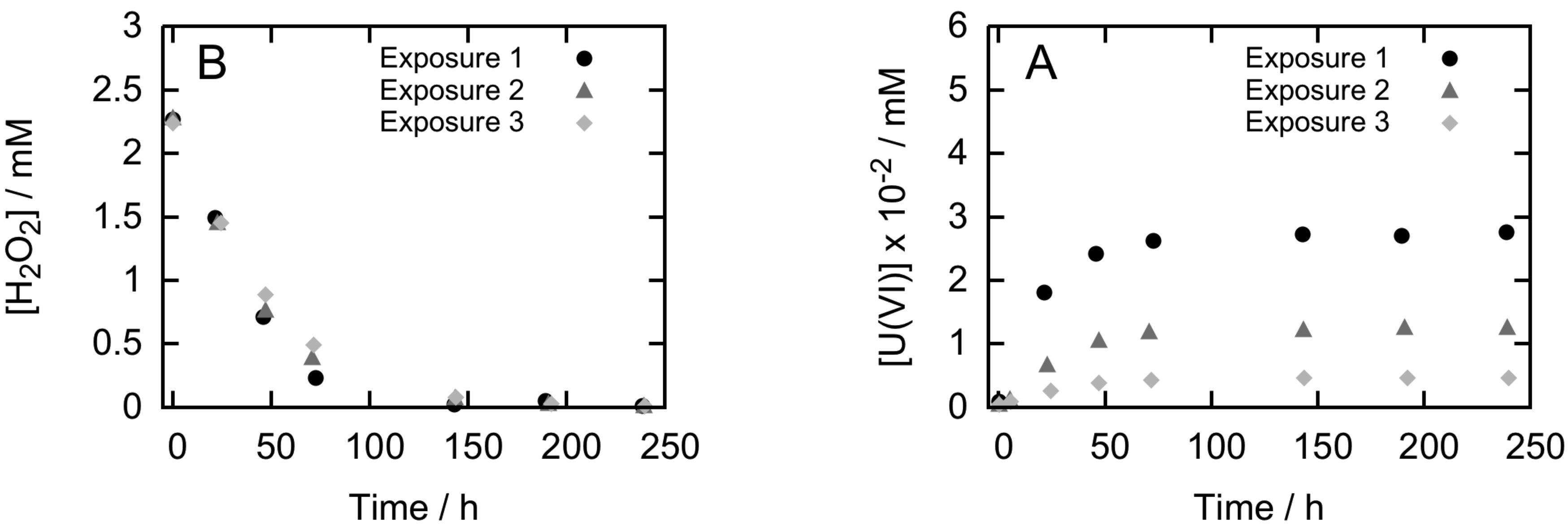
Experiments

- UO_2 pellets have been exposed to H_2O_2 in three consecutive experiments.

- The pellets were thoroughly washed with HCO_3^- between the experiments

- [H_2O_2] and [U(VI)] measured as a function of time. Pellet surfaces characterized using XRD, Raman and SEM before and after exposure.

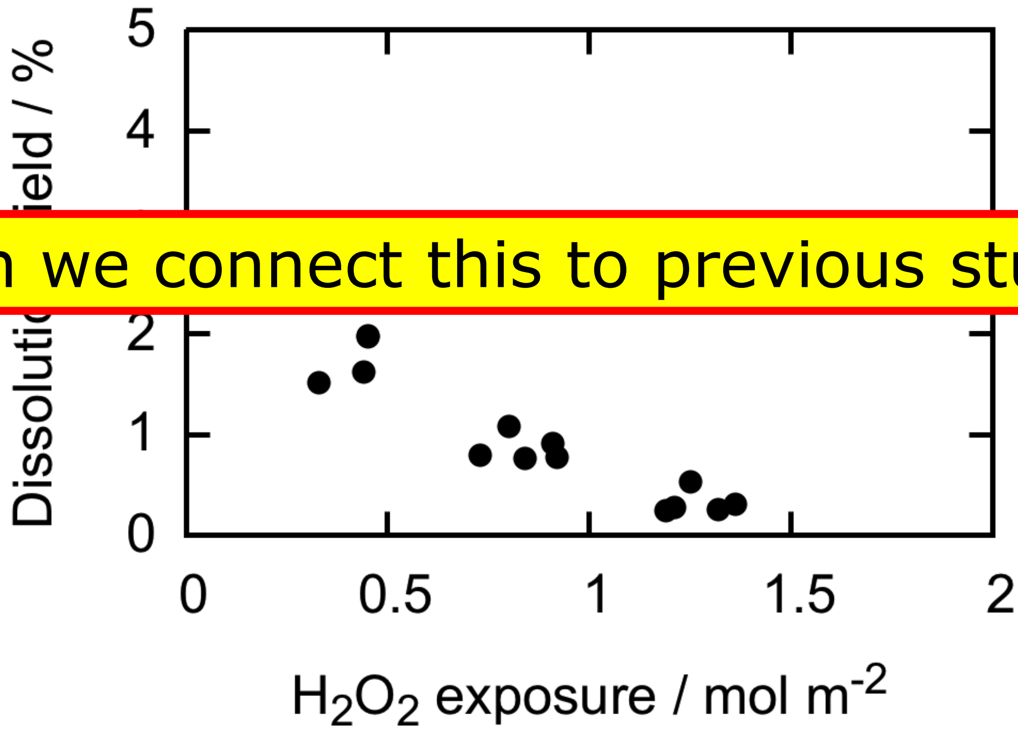
Experimental results



The kinetics for H_2O_2 consumption does not change

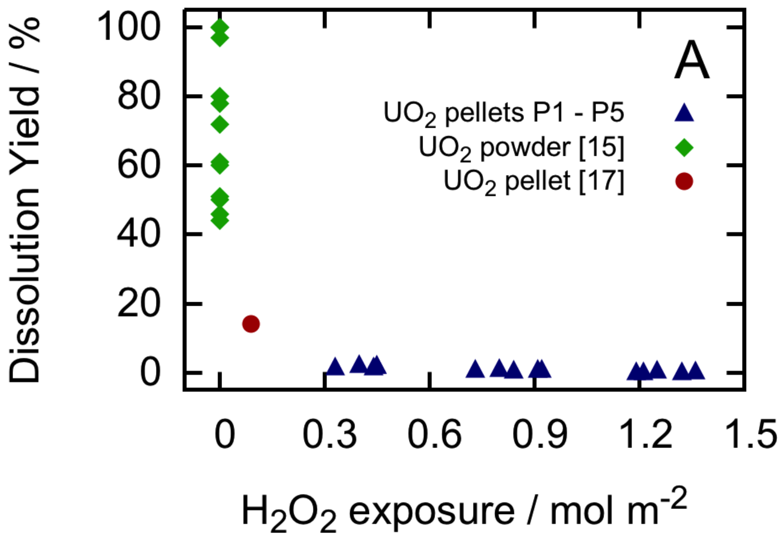
A.C. Maier, P. Kegler, M. Klinkenberg, A. Baena, S. Finkeldei, F. Brandt, M. Jonsson
Submitted to Dalton Transactions

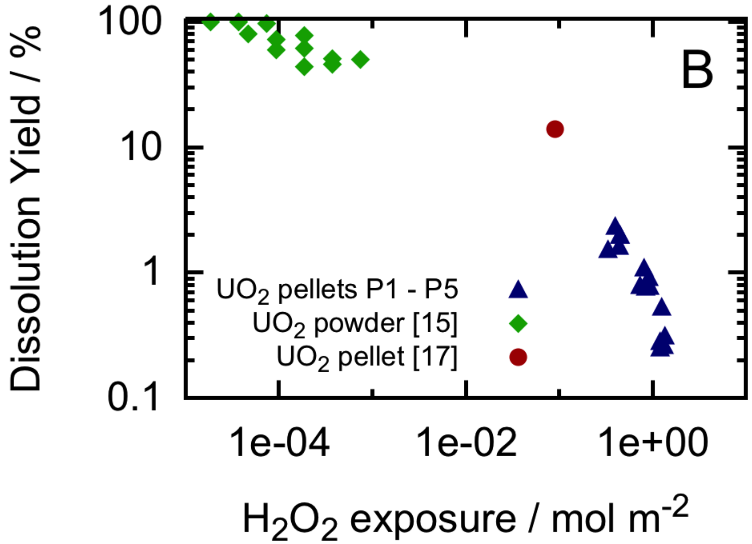
Dissolution yield as a function of exposure (in moles of H_2O_2 per m^2)



Can we connect this to previous studies?

Dissolution yield as a function of exposure (incl. powder exp.)

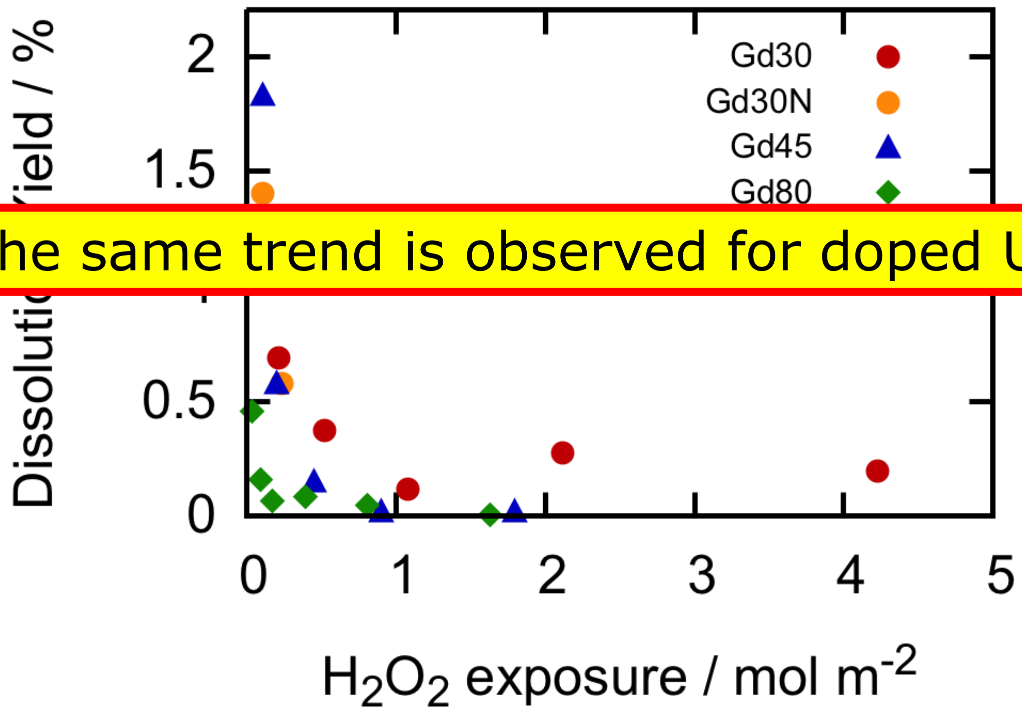




Observations

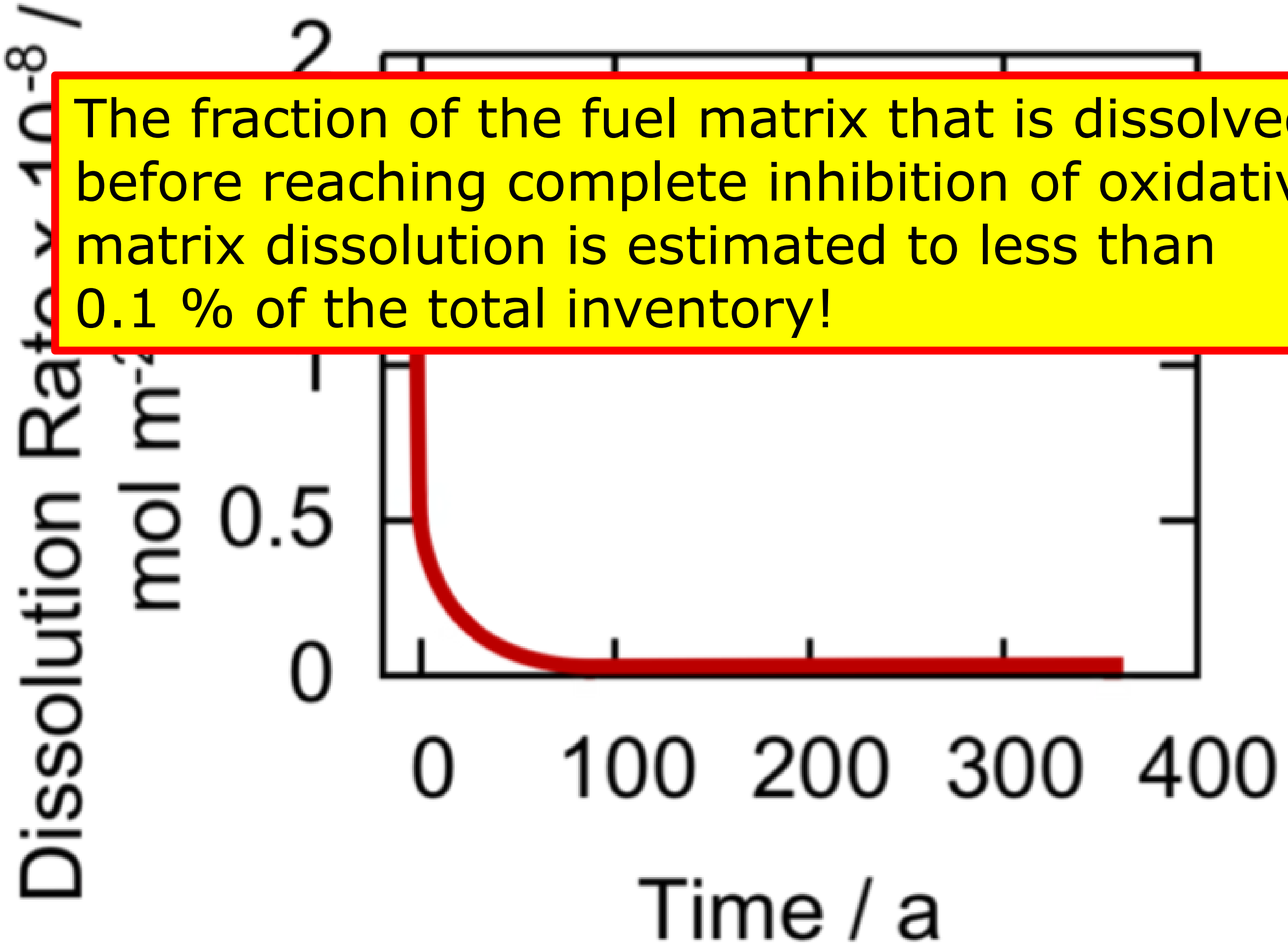
- The dissolution yield decreases with increasing exposure to H_2O_2: This is attributed to decreasing redox reactivity of the surface.
- XRD and Raman shows that the UO_2 surface becomes irreversibly oxidized – HCO_3^- does not remove the oxidized phase (the oxidized phase is NOT studtite)

Doped UO_2



The same trend is observed for doped UO_2!

Impact on the safety assessment



The fraction of the fuel matrix that is dissolved before reaching complete inhibition of oxidative matrix dissolution is estimated to less than 0.1 % of the total inventory!

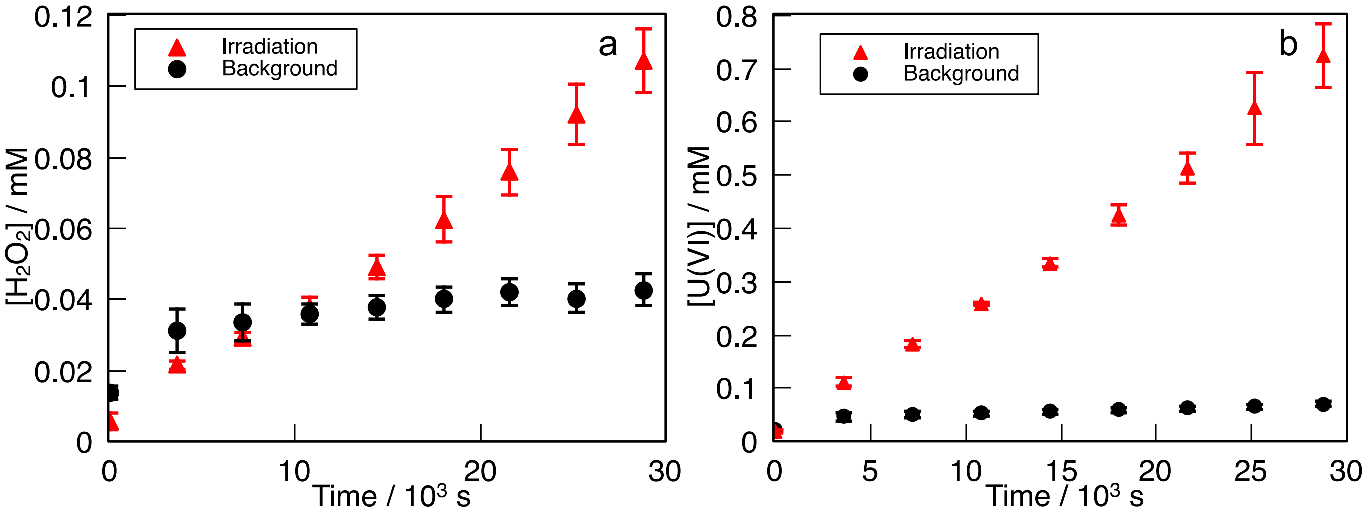
On the stability of studtite

- Studtite ($(UO_2)O_2(H_2O)_4$, uranyl peroxide) was γ-irradiated in aqueous solution containing HCO_3^- and in pure water

γ-irradiated studtite

No dissolution in pure water (without HCO_3^-)

HCO_3^-



Studtite is efficiently dissolved upon irradiation!

J. Li, A. C. Maier, M. Jonsson, revised version submitted to ACS Applied Energy Materials

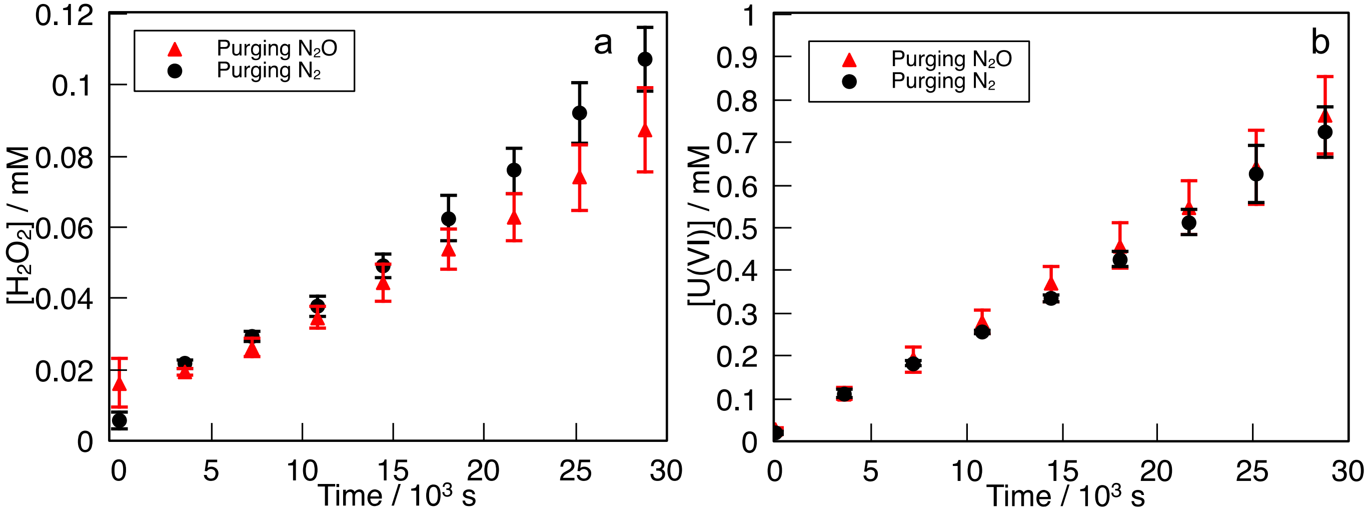
Conclusions

- The uranium dissolution yield decreases with H_2O_2 exposure. This is attributed to a change in redox reactivity due to irreversible oxidation of the UO_2 surface.
- The fraction of the fuel matrix that is dissolved before reaching complete inhibition of oxidative matrix dissolution is estimated to be less than 0.1 % of the total inventory.
- Studtite solubility is strongly affected by irradiation in aqueous solution containing HCO_3^- (no effect in aqueous solution free from HCO_3^-).

Acknowledgements

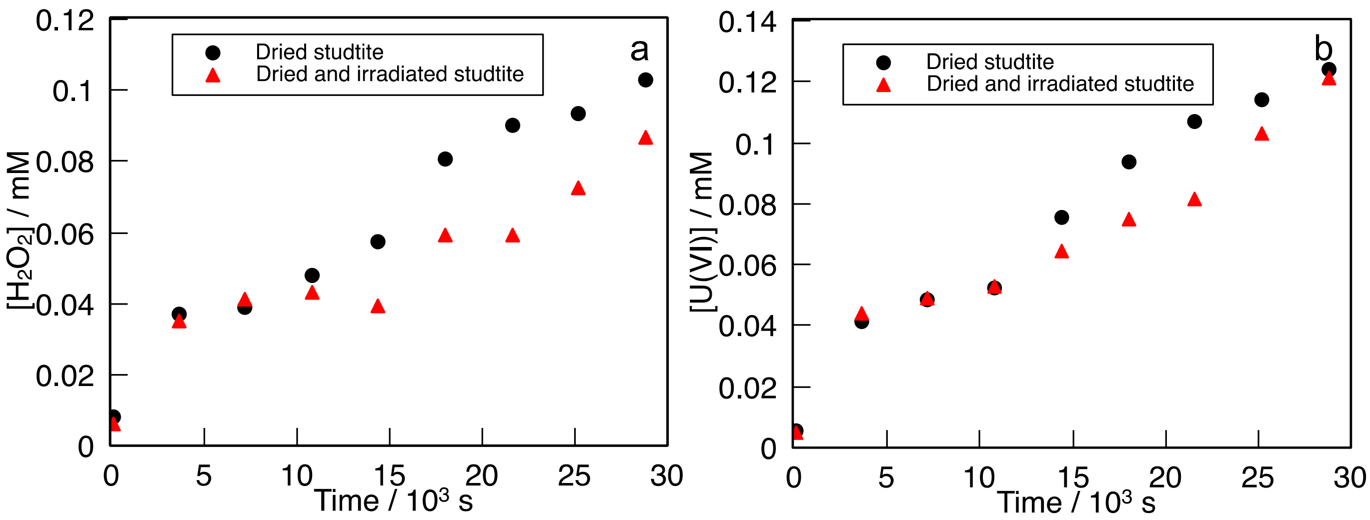
The Swedish Nuclear Fuel Management Co. (SKB) is gratefully acknowledged for financial support

Impact of N_2O/N_2



No significant differences!

Dry-irradiation (Studtite irradiated as dry powder followed by exposure to aqueous solution containing HCO_3^-)



No significant effect of dry-irradiation!