Dynamics of spent nuclear fuel dissolution and radionuclide migration.

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Mats Jonsson

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Nuclear Chemistry

Royal Institute of Technology

SE – 100 44 Stockholm

Deep repository (KBS-3)

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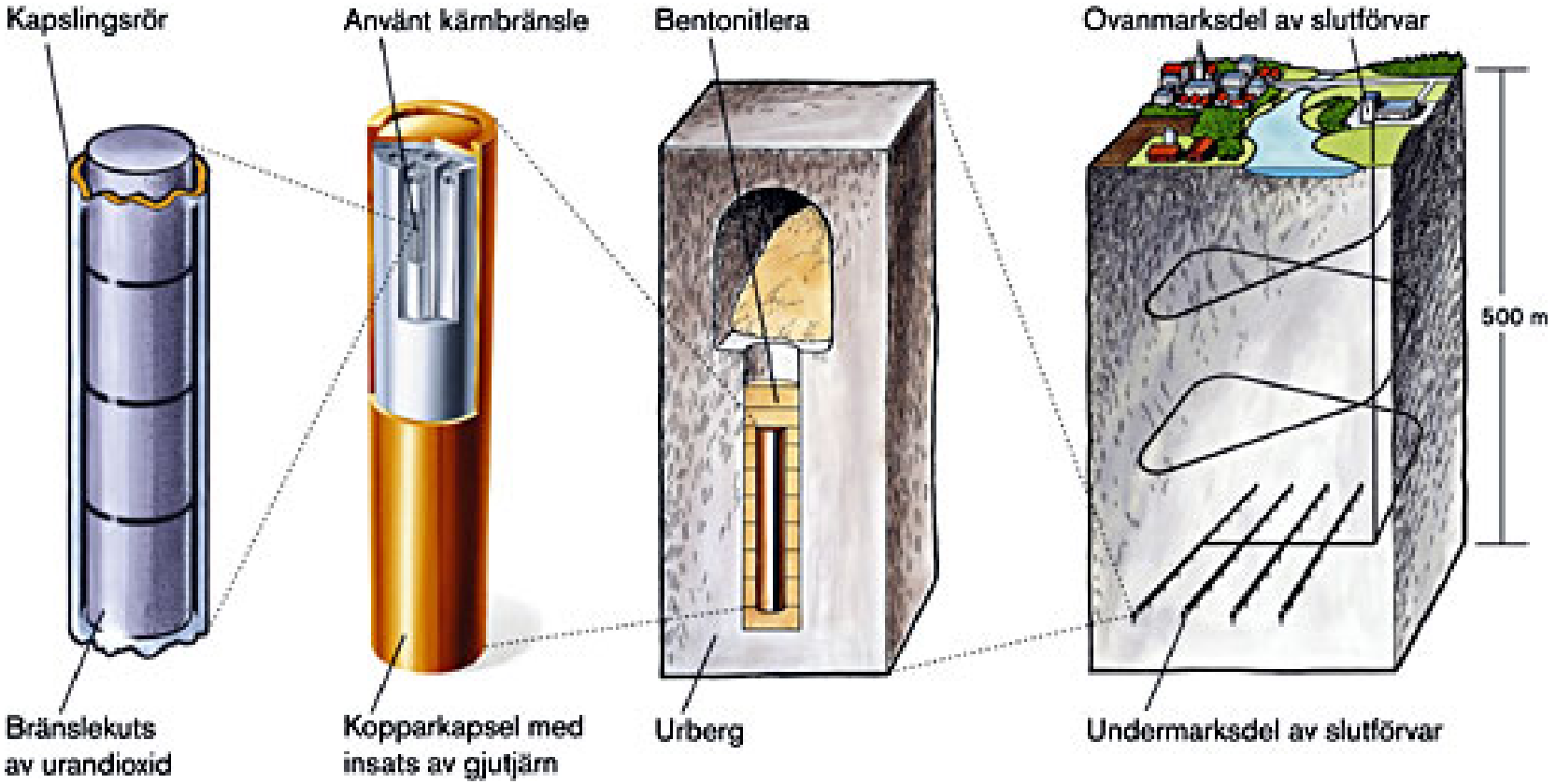

Release of radionuclides

- Canister failure
- Groundwater intrusion

- Dissolution of the fuel matrix

- Transportation of radionuclides
- Retention of radionuclides

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Canister failure

- Defect canister
- Mechanical damage
- Corrosion (discussed in Stockholm today)

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Groundwater intrusion

- Bentonite barrier failure

(due to erosion and changes in groundwater composition)

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Transportation of radionuclides

- Diffusion
- Flowing water

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Retention of radionuclides

- Adsorption (mineral surfaces)
- Redox immobilization
- Precipitation
- Colloid facilitated transport

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Dissolution of Spent Nuclear Fuel

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- Can we predict the rate of dissolution?

Spent nuclear fuel

- 95 % of the spent nuclear fuel is UO_2
- Contains metallic particles (fission products)
- Heterogeneous material

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Dissolution of the UO_2 matrix

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- Radionuclides can only be released if the UO_2 matrix is dissolved.
- UO_2 has very low solubility in groundwater.

Oxidative dissolution of UO_2

- Ox + UO_2 → Red + UO_2^{2+}

- UO_2^{2+} is considerably more soluble than UO_2

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The origin of oxidants?

- Oxidants (and reductants) are produced upon radiolysis of water.

Oxidants	Reductants
$OH^{\bullet}$	e_{aq}^{-}
H_2O_2	H_2
$HO_2^{\bullet}$, O_2	$H^{\bullet}$

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Groundwater components of importance:

- HCO_3^-, Cl^-, etc.
- H_2 (produced upon radiolysis and anaerobic corrosion of Fe)
- Organics

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Observations
(from SNF leaching experiments)

- The rate of spent nuclear fuel dissolution is enhanced by HCO_3^-

- Spent nuclear fuel dissolution is inhibited by H_2

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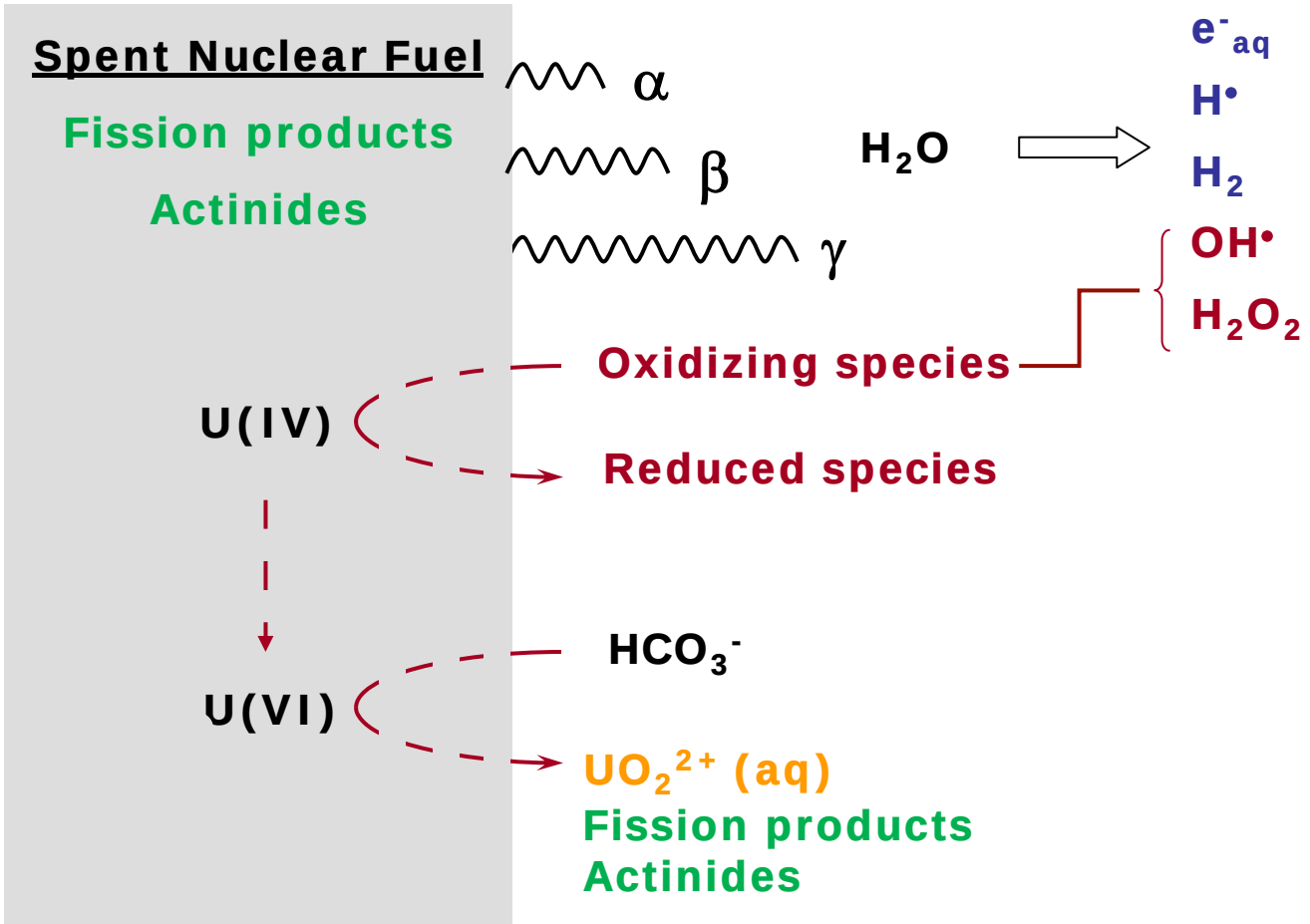

What do we need to describe the system?

- Geometric dose distribution
- Reaction mechanisms and rate constants for surface reactions.
- Water chemistry (incl. Radiation chemistry)
- Formation and effects of secondary phases

- Interfacial radiation chemistry.

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Dose profile
(simulation based on radionuclide inventory)

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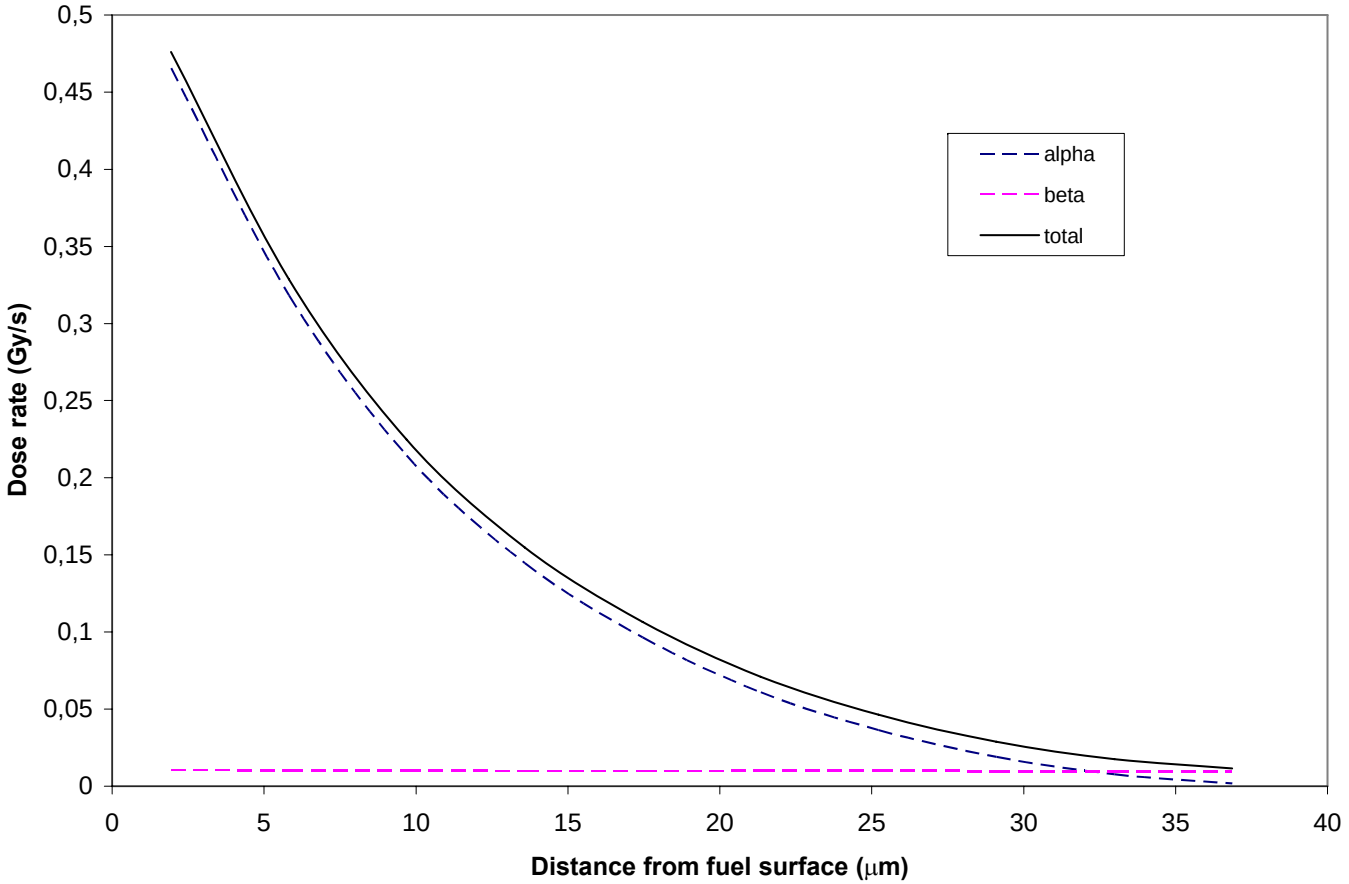
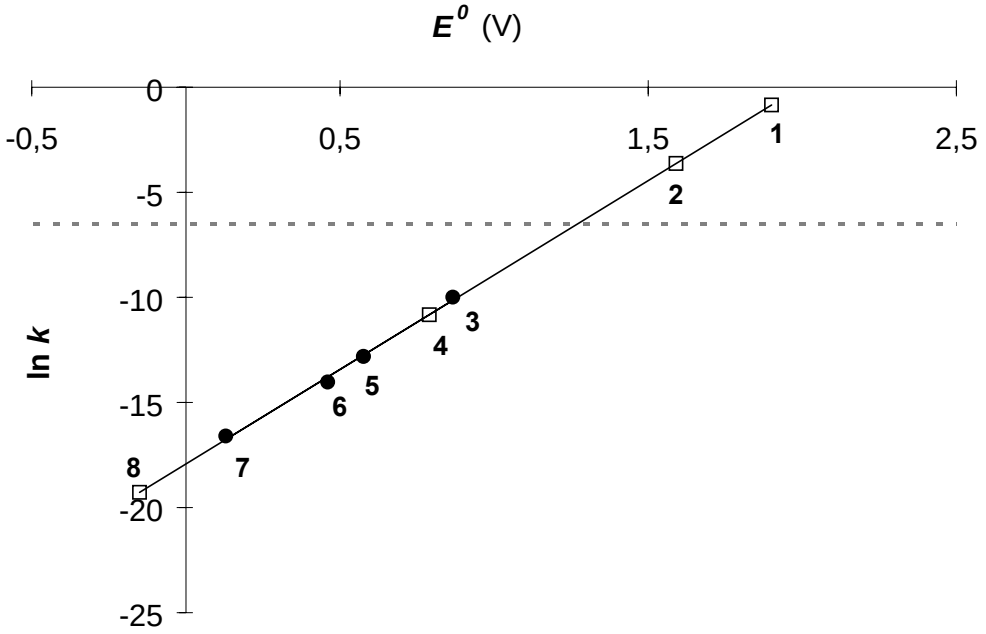


Fredrik Nielsen and Mats Jonsson, *J. Nucl. Mater.* 2006, 359, 1-7

Oxidation of UO_2

- Rate constants for oxidation of UO_2 as a function of oxidant standard potential.



Ella Ekeroth and Mats Jonsson, *Journal of Nuclear Materials, 2003, 322, 242-248*

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Can the rate constants be used for more complex systems?

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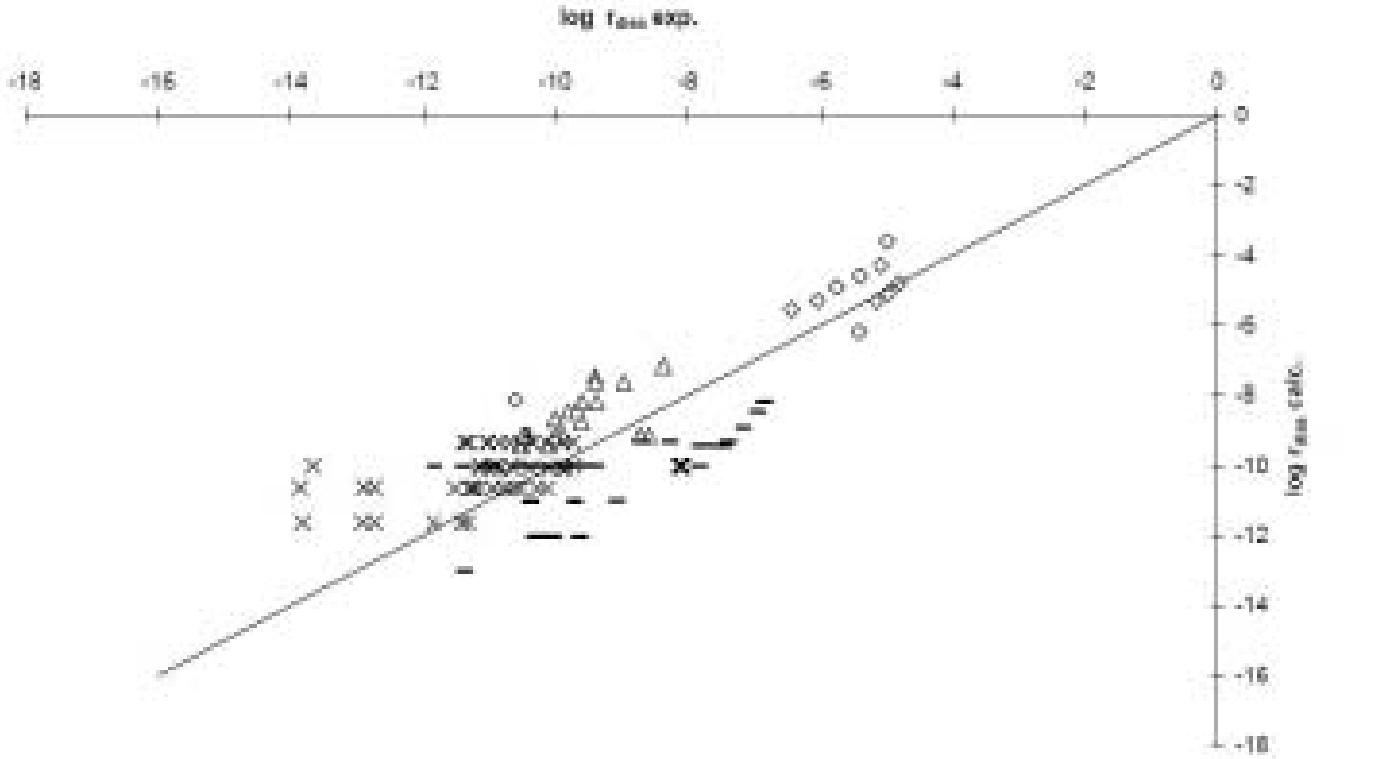

Figure 1. The logarithm of calculated dissolution rates plotted versus the logarithm of experimentally determined dissolution rates [9-18] for different systems; ○ H_2O_2 with carbonate, △ H_2O_2 without carbonate, - O_2 with carbonate, + O_2 without carbonate.

Olivia Roth and Mats Jonsson, *Cent. Eur. J. Chem.* 2008, 6, 1-14

γ-radiolys (UO_2-suspensioner)

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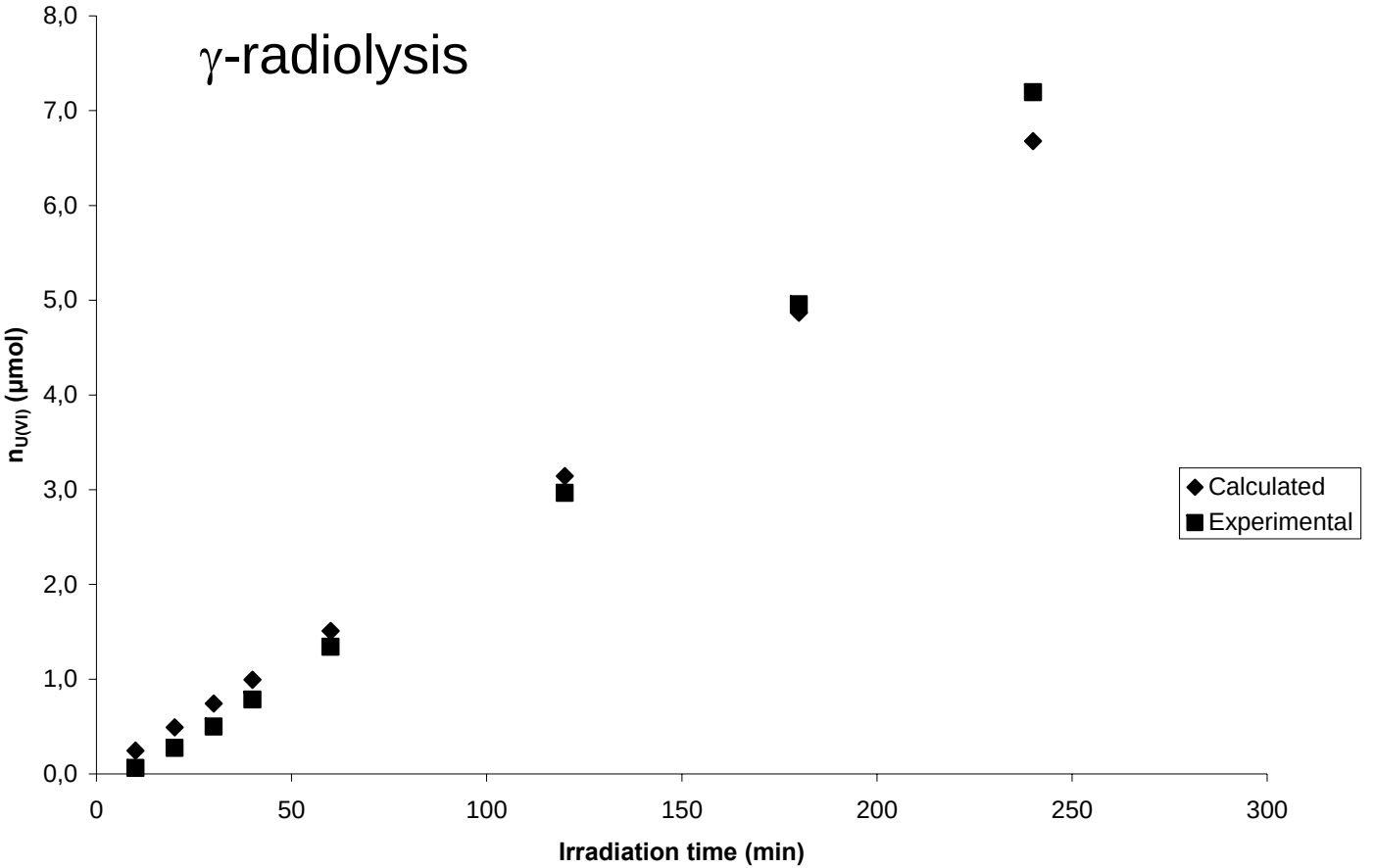

Ella Ekeroth, Olivia Roth and Mats Jonsson *Journal of Nuclear Materials, 2006, 355, 38-46*

Do we have to account for all the radiolysis products?

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Relative impact of oxidants					
H_2O_2	O_2	$O_2^{\cdot-}$	$HO_2^{\cdot}$	$CO_3^{\cdot-}$	$OH^{\cdot}$
100.0 %	0.01 %	0 %	0.03 %	0 %	0 %

[1]E. Ekeroth, O. Roth, M. Jonsson, J. Nucl. Mater. 355 (2006) 38-46.

Conclusion 1

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- We only have to take H_2O_2 into account.

Under continous irradiation the system will reach steady-state

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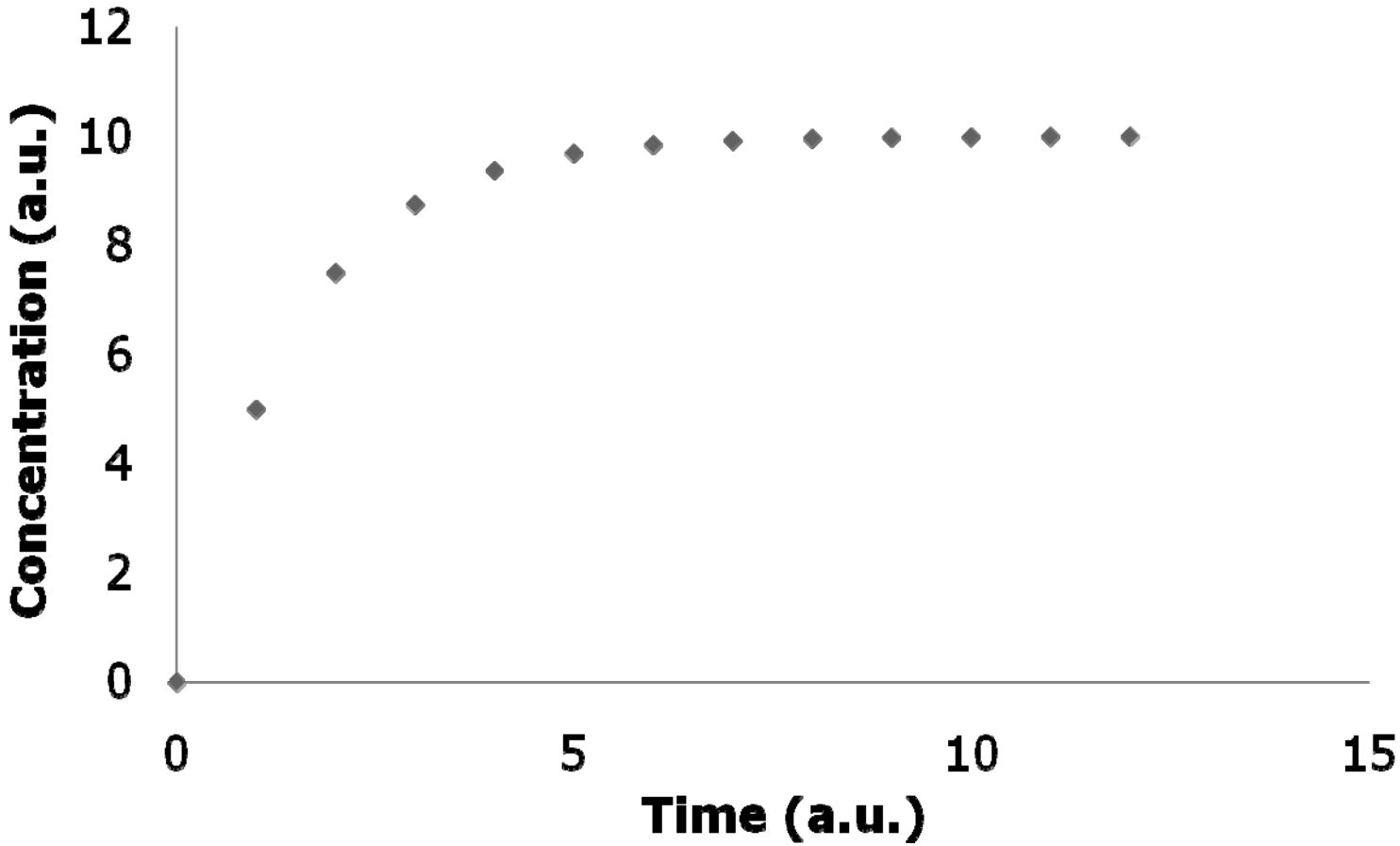

Surface concentration (H_2O_2)
(Simulation)

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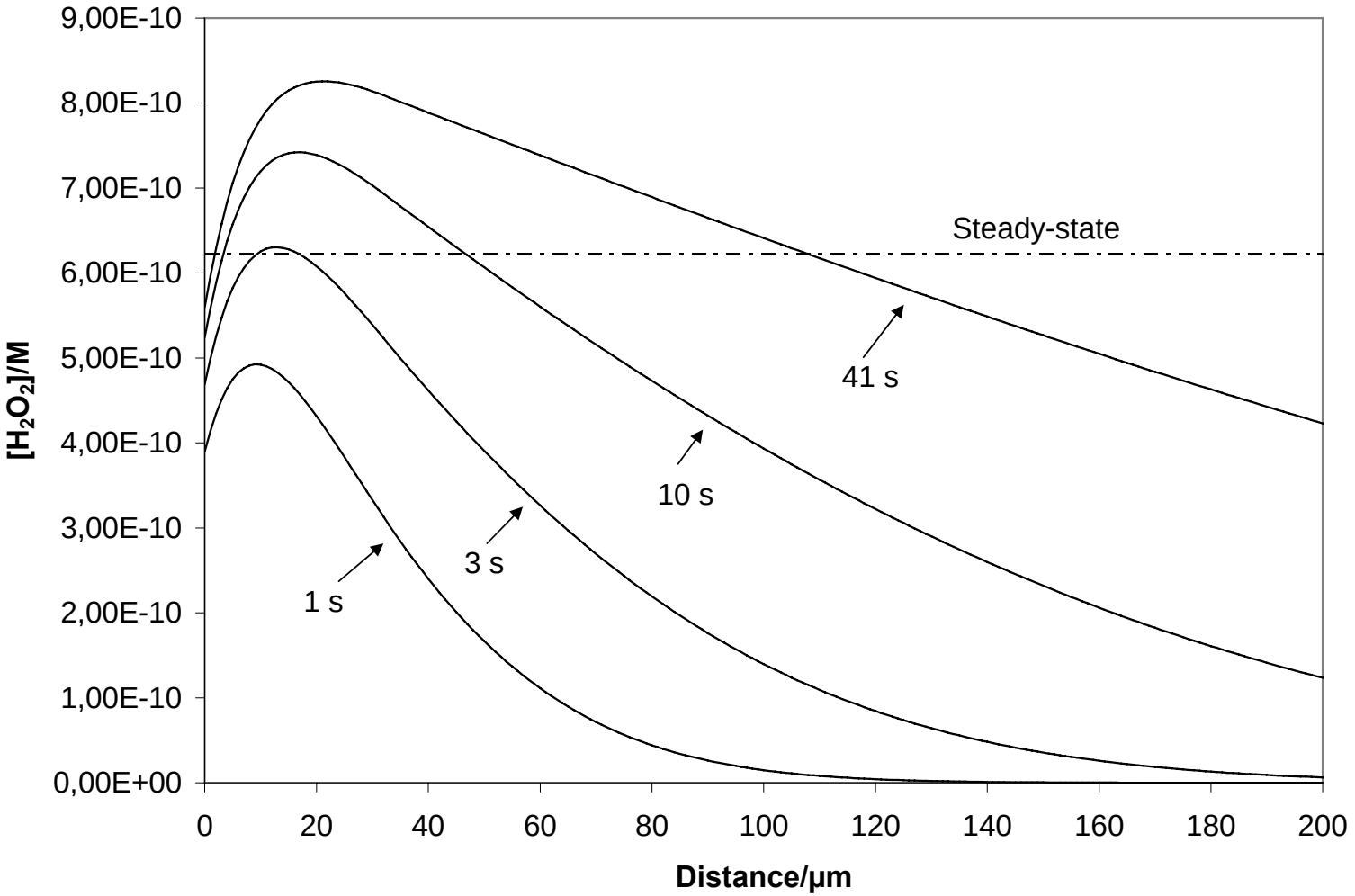

J. Nucl. Mater. 2008, 372, 32-35 and J. Nucl. Mater. 2008, 374, 286-289

Conclusion 2

- We can use the steady-state approximation for H_2O_2.
- Dissolution = f(dose rate)

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The steady-state approach

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$$r_{diss} = r_{ox} - k_{H_2}[H_2]\varepsilon_{rel} =$$

$$0.8\left(\overline{r_{H_2O_2}(\alpha)}\delta_{\max}(\alpha) + \overline{r_{H_2O_2}(\beta)}\delta_{\max}(\beta)\right)\times 10^{-0.6\log k^* - 2.9} - k_{H_2}[H_2]\varepsilon_{rel}$$

Does it work?

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Material (Dose rate)	$p(H_2)$	$[HCO_3^-]$ (mol dm^{-3})	Time (days)	Calc. final conc (mol dm^{-3})	Calc. diss rate (mol dm^{-3} d^{-1})	Experimental final conc. (mol dm^{-3})
10 % U-233 (99 Gy/h)	(Ar)	1.68×10^{-3}	47	7.05×10^{-8}	1.50×10^{-9}	6.40×10^{-8}
10 % U-233 (99 Gy/h)	(1,2 % O2)	1.07×10^{-3}	126	1.96×10^{-6}	1.56×10^{-8}	5.69×10^{-7}
SF (α = 828 Gy/h β = 31 Gy/h)	(Ar)	10×10^{-3}	40	1.42×10^{-4}	3.54×10^{-6}	$5,96\times10^{-5}$
SF (α = 828 Gy/h β = 31 Gy/h)	5 bar	10×10^{-3}	376	0	0	1.70×10^{-10}

Why does H_2 inhibit SNF dissolution?

- H_2 reduces the concentration of H_2O_2 produced by radiolysis
- Reduction of U(VI) to U(IV) in solution (no inhibition)
- Catalyzed reduction of U(VI) in the pellet

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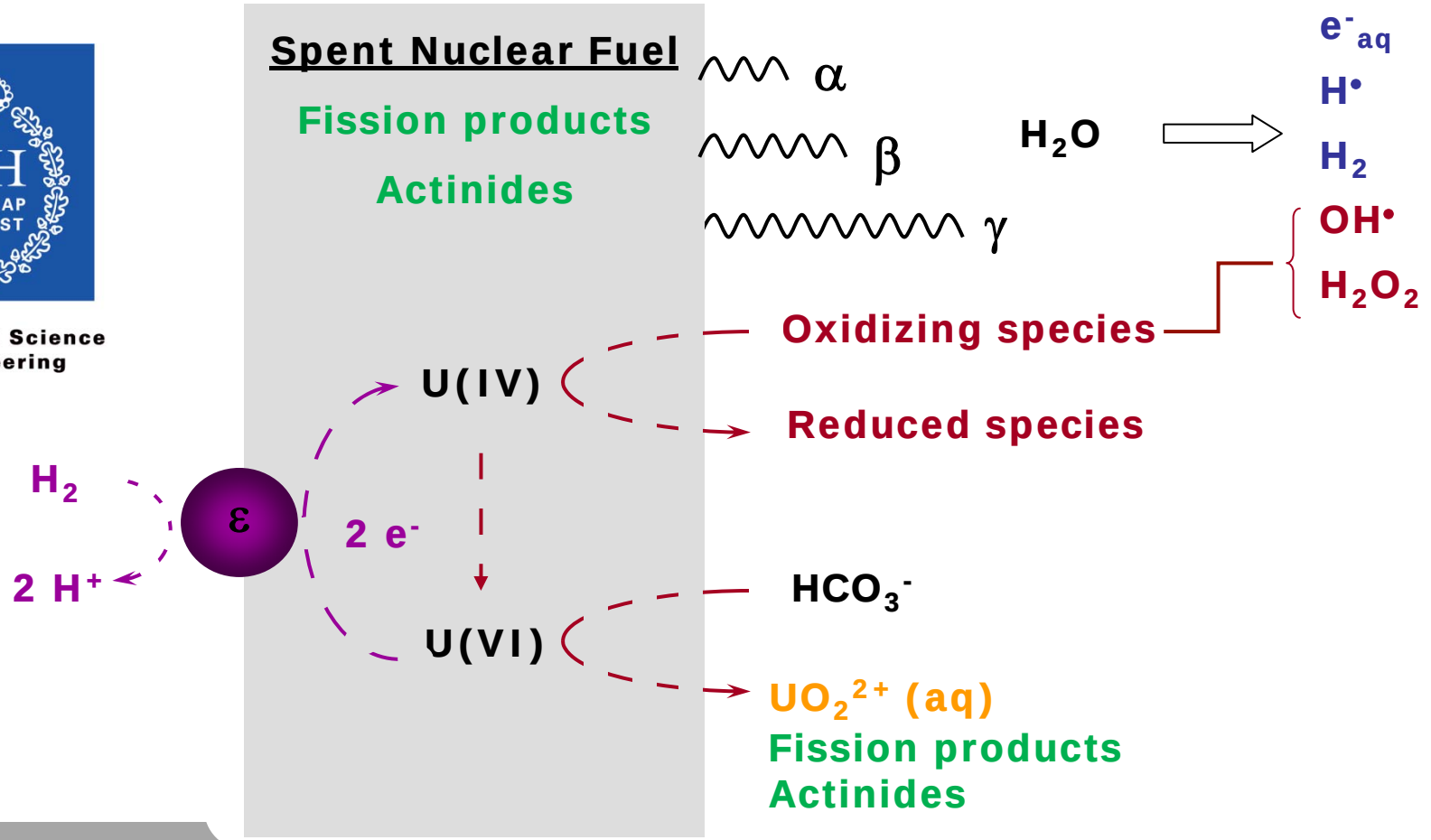

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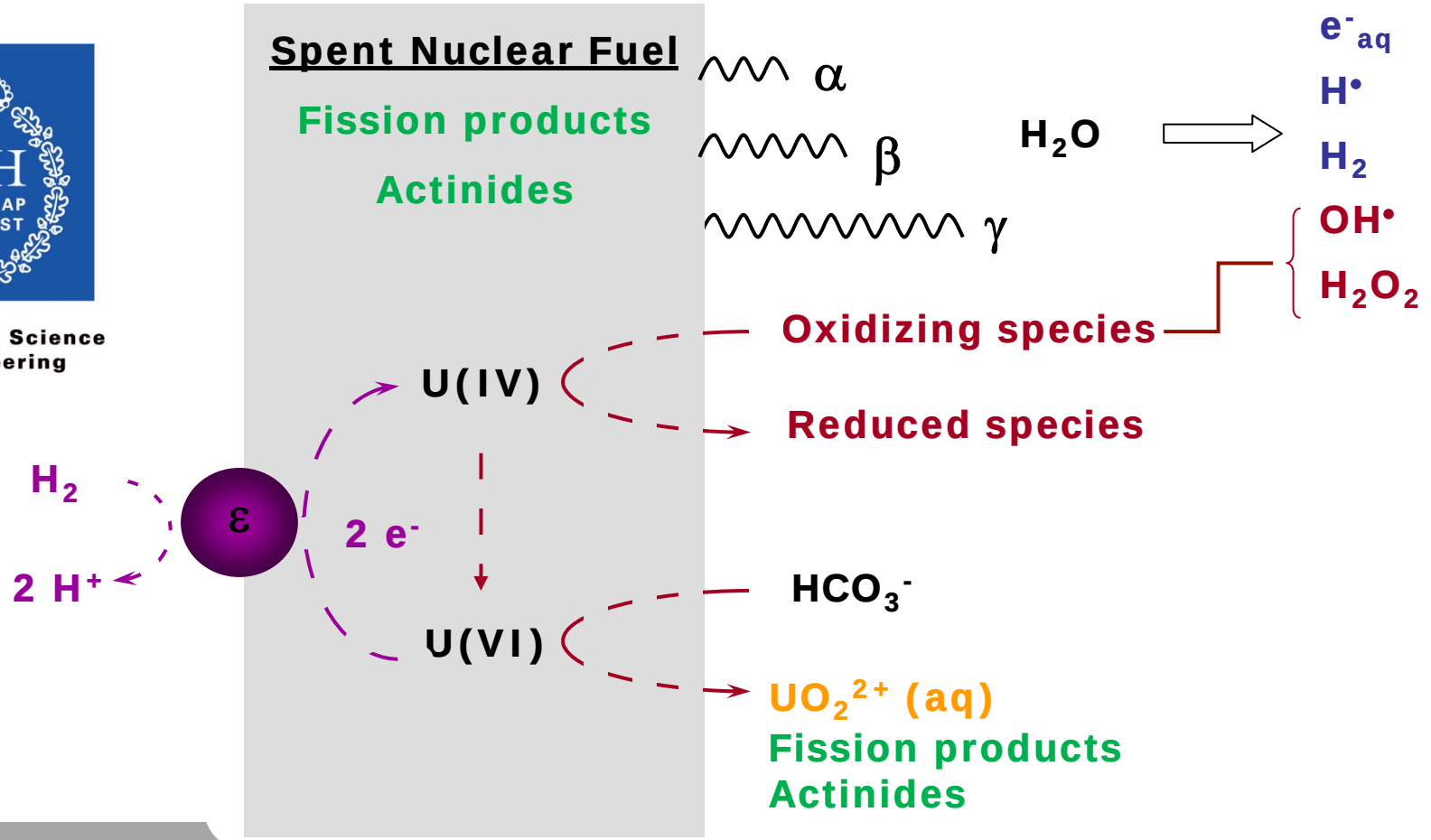

Quantifying the H_2 effect

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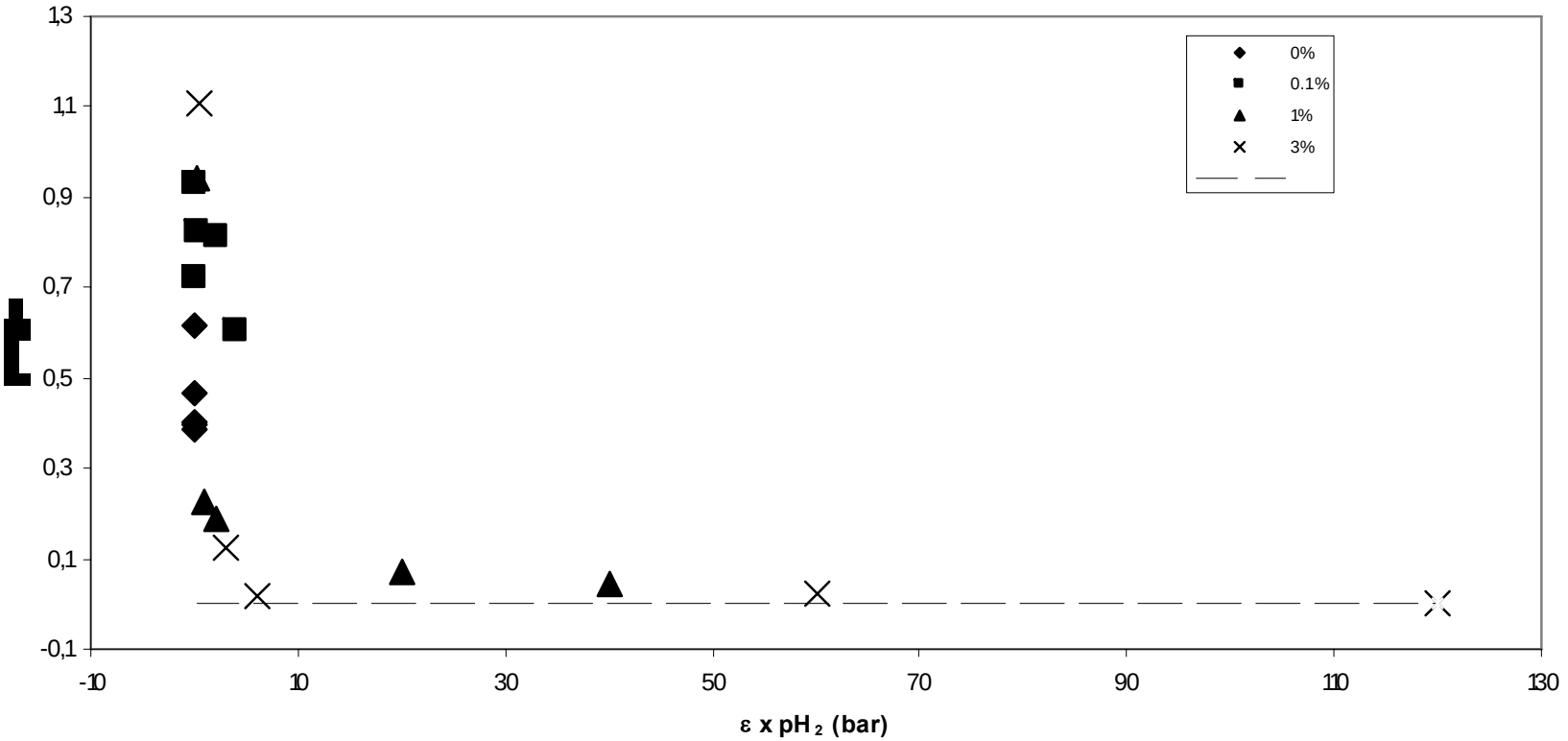

$k = 10^{-6}$ m s^{-1} (diff. limited)

Martin Trummer, Sara Nilsson and Mats Jonsson, *J. Nucl. Mater.* 2008, 378, 55-59

How much H_2 is needed to completely inhibit dissolution?

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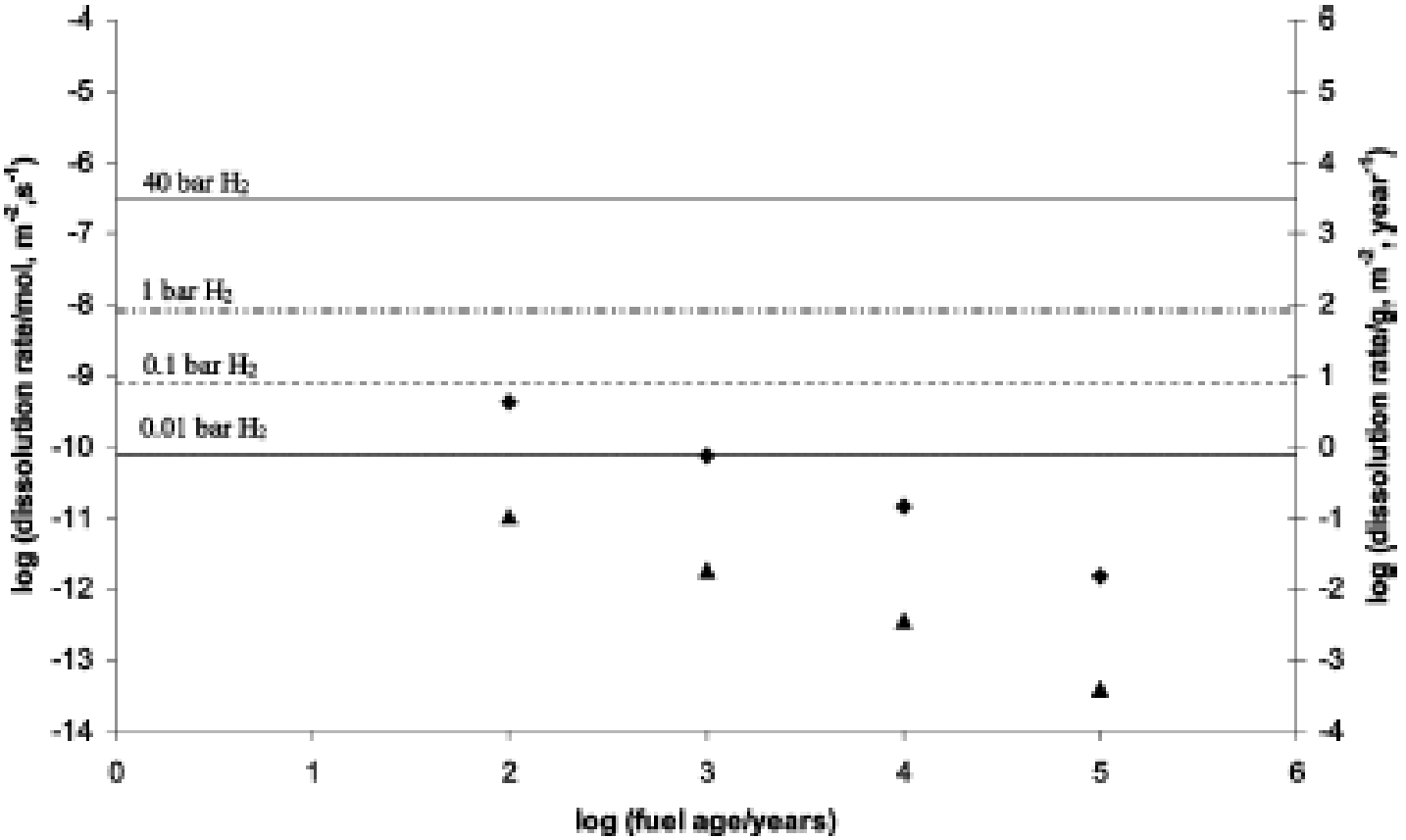

Closed system(H_2 produced from radiolysis)

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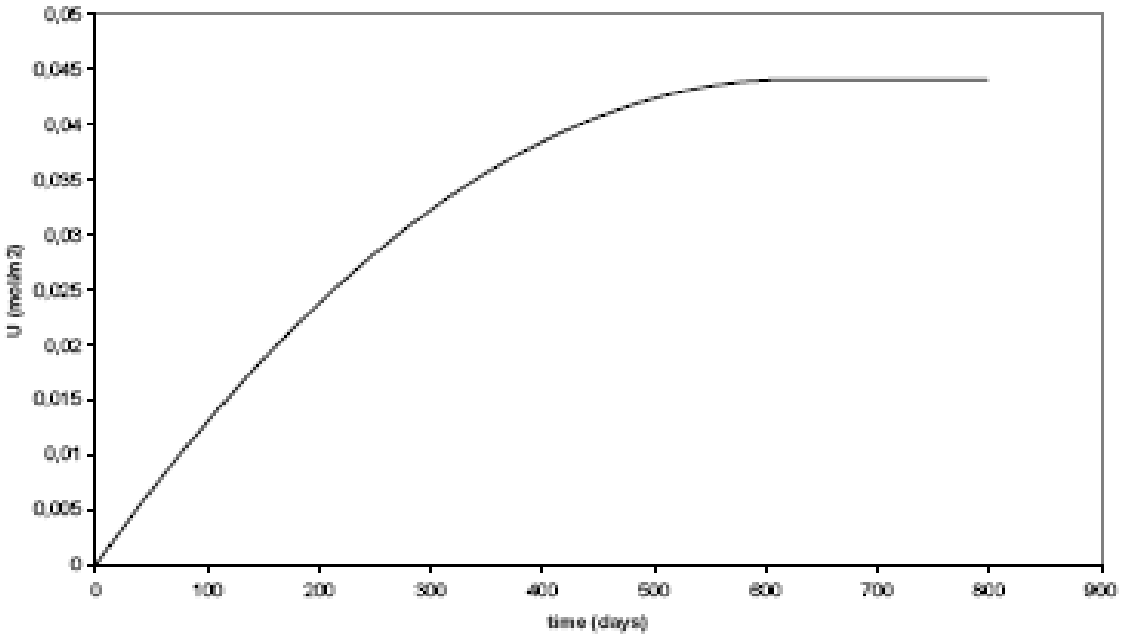

Figure 5. Dynamics of spent nuclear fuel dissolution taking UO_2 oxidation by H_2O_2, H_2 production and noble metal particle catalyzed reduction of $UO_2^{2+}(s)$ by H_2 into account.

Radiation induced processes at solid-liquid interfaces.
Mats Jonsson, in *Recent Trends in Radiation Chemistry*, Eds. J. F. Wishart and B. S. M. Rao, World Scientific, in press

Conclusion 3

- H_2 inhibits radiation induced dissolution of spent nuclear fuel at very low partial pressure.

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Acknowledgements

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