Radiation Chemistry

Radiation Chemistry

- Absorption of ionizing radiation
- From Physics to Chemistry

When is radiation chemistry of importance?

- Nuclear reactors
- Nuclear materials (in general)
- Biological effects of ionizing radiation
- Atmospheric chemistry
- Tool for studying radical chemistry
- Synthesis of novel materials (e.g. nanoparticles)

Ionizing radiation

- **Radiation with energy > 100 eV**

- Ionization < 15 eV
- Chemical bonds 1-5 eV

Decay energies

- α: 4-9 MeV
- β: 0.02-4 MeV
- γ: 0.1-2 MeV

Ca. 100 000 ionizations per decay!

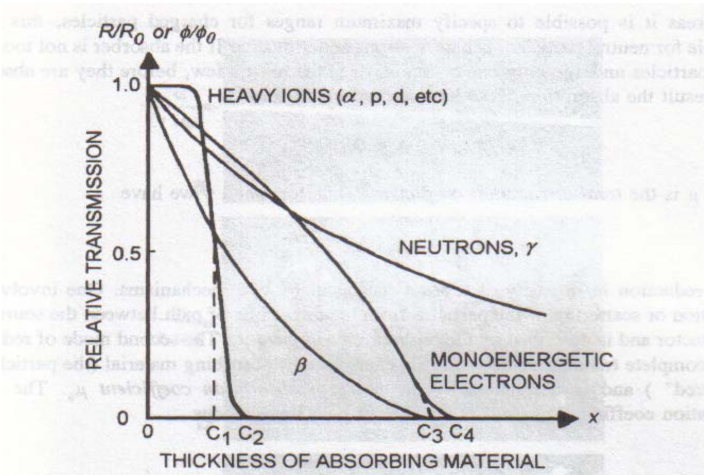
Radiation types

- Protons and heavy ions (*e.g.* α-particles)
- Electrons (β^+ and β^-)
- Photons (γ)
- Neutrons

Absorption of ionizing radiation

- Interactions with the electrons of the absorber
- (Neutrons): Interactions with nuclei resulting in radioactive decay

Relative transmission



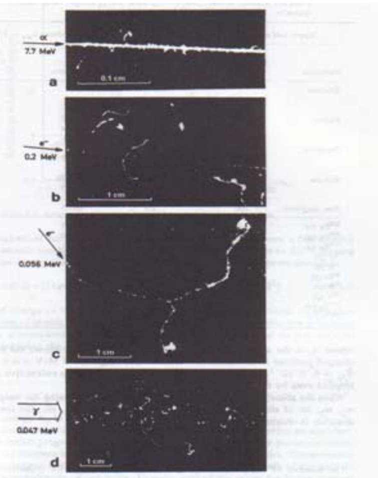
Linear Energy Transfer
LET

$$LET = -dE/dx$$

LET depends on the electron density of the absorber (usually proportional to the physical density)

Radiation (3 MeV)	LET (keV/µm)	cm in air
Electron	0.20	1400
Proton	21	14
Deuteron	34	8.8
α	180	1.7

Absorption



Protons and heavy ions

- The Bethe equation

$$-\frac{dE}{dx}=\frac{4\pi z^2 e^4}{mv^2}NZ\ln\left(\frac{2mv^2}{I}\right)$$

$$-\frac{dE}{dx}\propto\frac{z^2}{v^2}$$

$Z =$ abs. atomic no

$z =$ part. atomic no.

$N =$ no. of absorbing atoms per unit volume

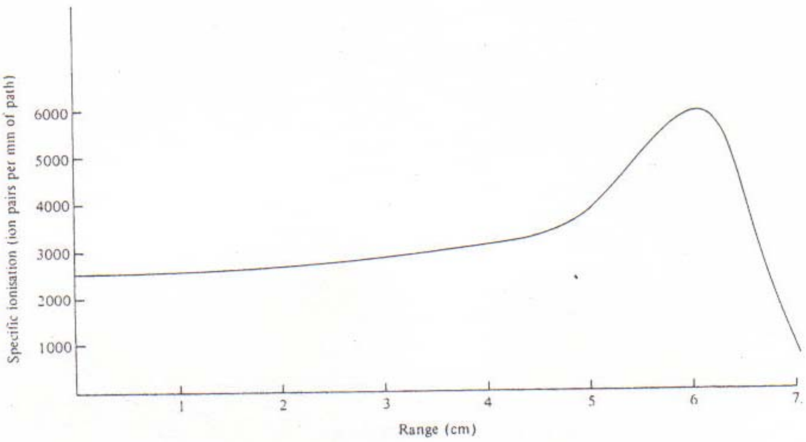
$v =$ velocity

$I =$ ionization potential

$m =$ electron mass

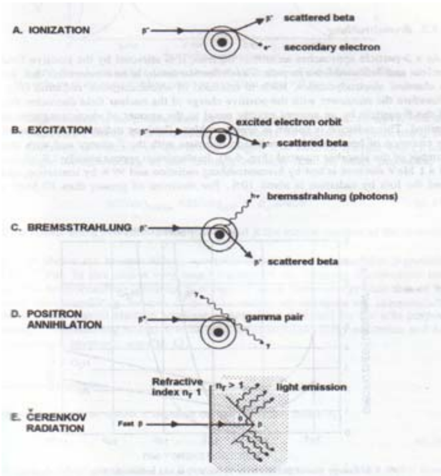
$e =$ particle charge

The Bragg curve
(Heavy charged particles)



$$\text{General}: R\propto E^{3/2}$$

Electrons
(The Bethe equation)

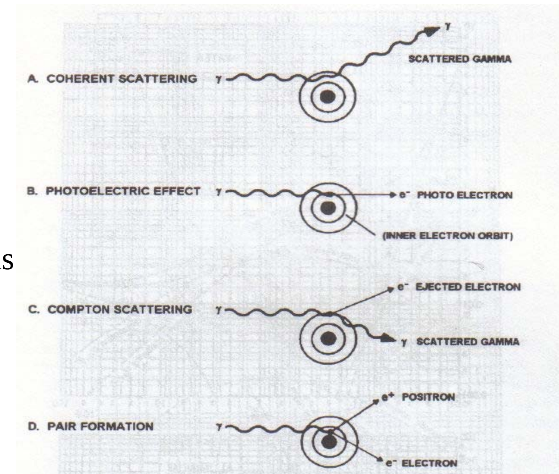


Gamma radiation

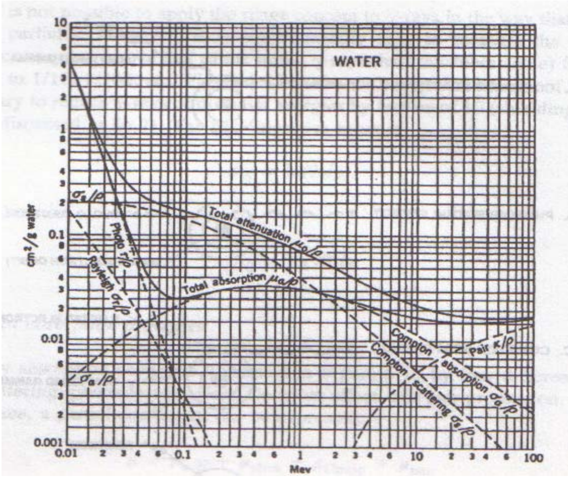
$$-dn = \mu N dx$$

$$N = N_\circ e^{-\mu x}$$

$$N = \text{No. of photons}$$



GAMMA RADIATION



RADIATION SHIELDING

Radiation	Rel. Penetration depth	Shielding
α	1	Paper, skin
β	100	3 mm Al
γ	10 000	Concrete, lead

Keep the distance: r^{-2}!

Absorbed dose

- Unit: 1 Gy (Gray) = 1 J/kg
- 1 Gy = 100 rad

$$D = \frac{dE_{abs}}{dm}$$

$$E_{abs} = E_{in} - E_{out}$$

Radiation Chemistry

- From Physics to Chemistry
- Chemical Effects (G-values)
- Chemical Systems

Radiation effects on gases, liquids and solids

- Gas: Low density, high mobility
- Liquid: High density, intermediate mobility
- Solid: High density, low mobility

Absorption of ionizing radiation

- LET = dE_{abs}/dx

(Depends on charge and velocity of the particle and on the density of the absorber)

- Dose = dE_{abs}/dm

Dose rate

- Proportional to activity/current and LET

- Unit: Gy/s

Radiation chemical yield

- G-value: $G_X=d[X]/dE_{abs}$

- Unit (SI): mol/J
(older unit: number of molecules / 100 eV)

SOLIDS

- Metals: Displacements (heavy particles)

- Inorganic nonmetallic compounds:

-Excitation→Fluorescence

-Crystal defects (heavy particles)

-Decomposition

ORGANIC COMPOUNDS

Table 7.4. *Onsager radii, electron mobilities and free ion yields*

Liquid	r_c (nm)	mobility ($cm^2/V\ s$)	G(free ions) ($\mu mol/J$)
Neopentane	32	55	0.09 – 0.11
Cyclohexane	28	0.35	0.016 – 0.02
Benzene	25	-	0.005 – 0.008
Methanol	2.3	-	0.2
Water	0.7	-	0.28

ORGANIC COMPOUNDS

Table 7.5. *Effects of γ-radiation on organic compounds of technical interest*

Compound	Observed change at (kGy)	Useless at (kGy)	Compound	25% reduction of desired property (kGy)
Olefins	5	10	Teflon	0.1
Silicones	5	50	Cellulose acetate	2
Mineral oils	10	100	Polyethylene	9
Alkyl aromatics	100	500	Polyvinylchloride	10
Polyphenyls	500	5000	Polystyrene	400
			Neoprene, silicon rubber	0.6
			Natural rubber	2.5

TRACK

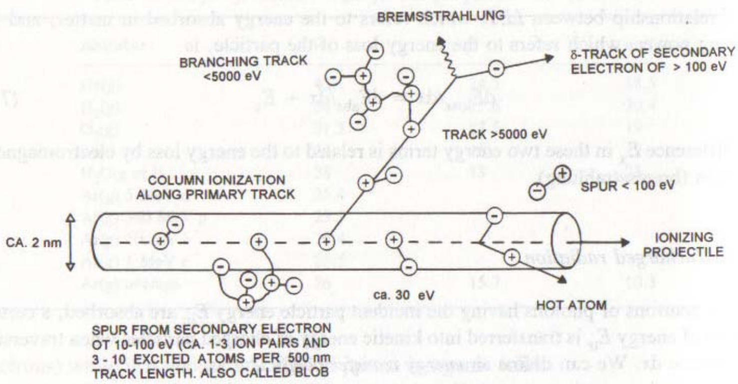
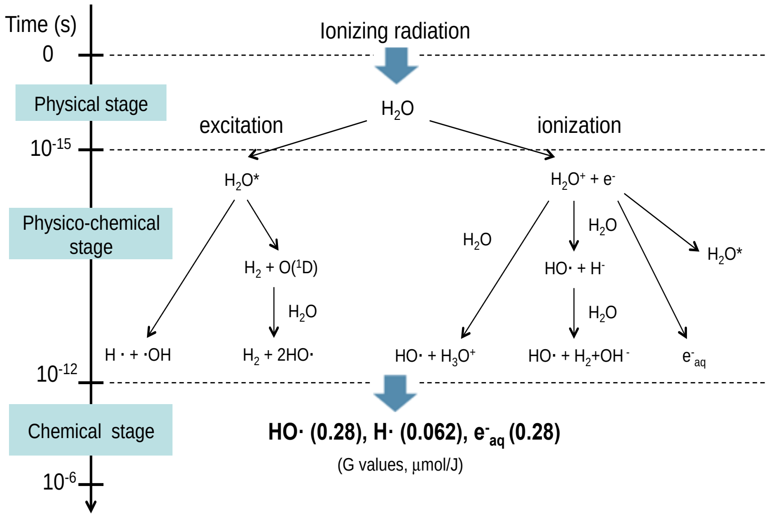
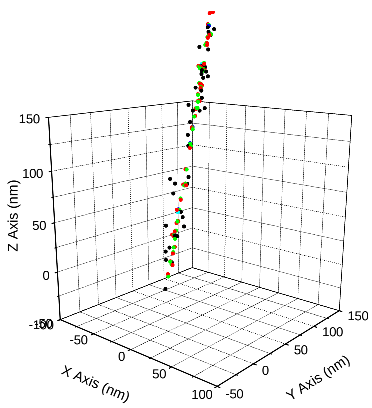


FIG. 7.1. Track formed by energetic ionizing particle in condensed matter. Distances between ion pairs along track are: ~1000 nm γ, 500-100 nm fast electron, ~1 nm slow electron and α.

RADIOLYSIS OF WATER



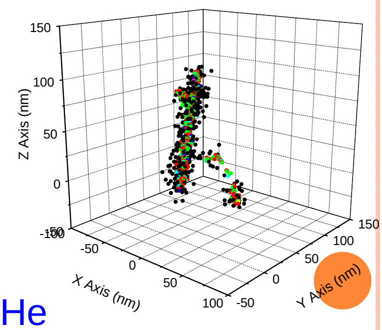
DIFFERENCES IN 10 KEV TRACK SEGMENTS AT 1 PS



10 MeV ^1H

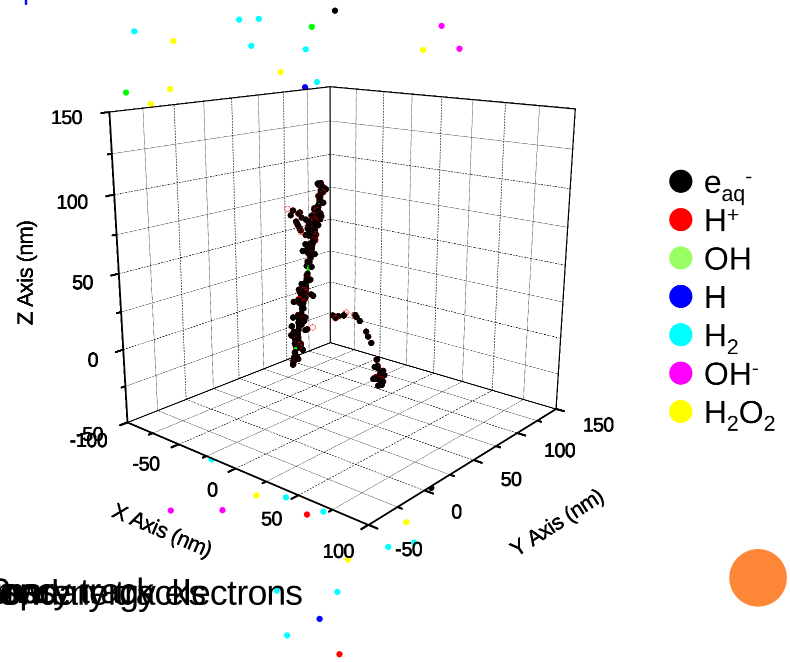
Black : e^-_{aq}
Red : H_3O^+
Green : OH
Blue : H
Cyan : H_2
Magenta : OH^-
Yellow : H_2O_2
Dark yellow : $O(^3P)$

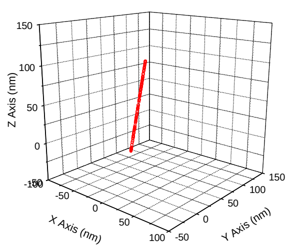
Modern codes give "realistic" track structures.



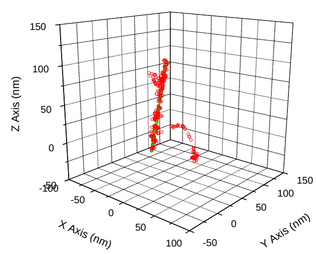
5 MeV ^4He

Development of a 10 keV Section of a 5 MeV $^4He^{2+}$ Ion Track in Water

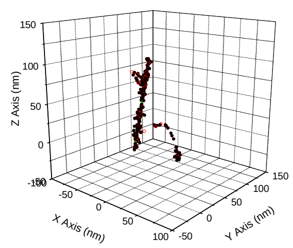




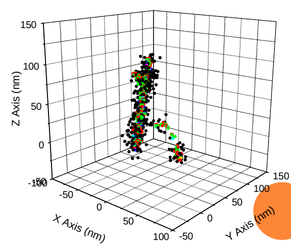
Primary track



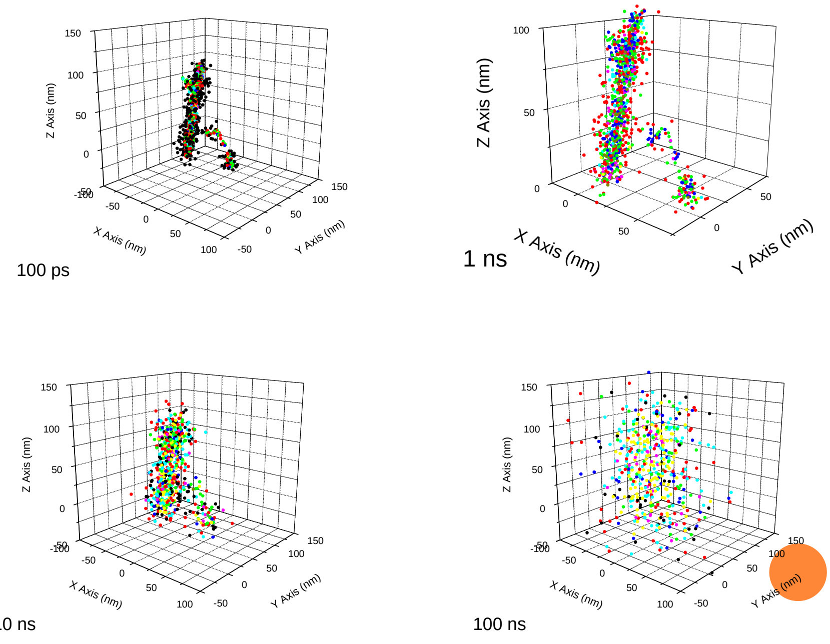
Secondary tracks



Low energy electrons



1 ps



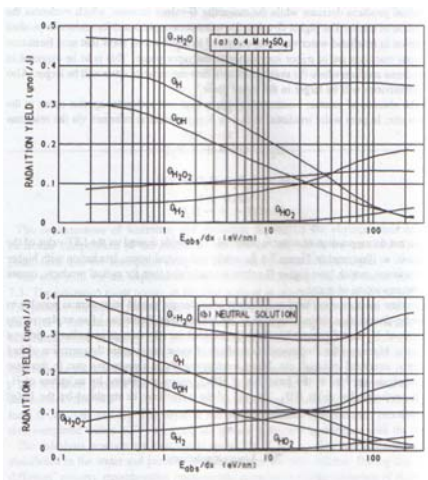
LET AND G-VALUES FOR RADIOLYSIS OF WATER

Radiation	LET	$G(H_2O)$	$G(H_2)$	$G(H_2O_2)$	$G(e^-_{aq})$	$G(H^\bullet)$	$G(HO^\bullet)$	$G(HO_2^\bullet)$
γ, e-	0.24	-0.43	0.047	0.073	0.28	0.062	0.28	0.0027
α (12 MeV)	92	-0.294	0.115	0.112	0.0044	0.028	0.056	0.007

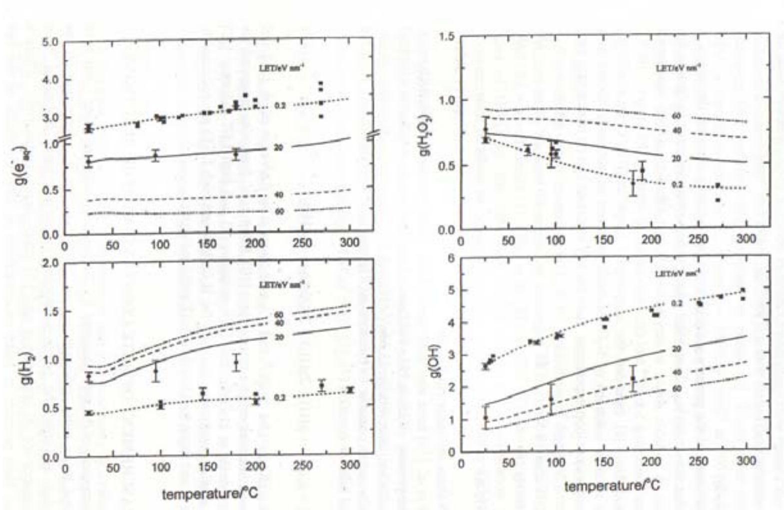
G-VALUES AT HIGH SCAVENGER CONCENTRATIONS

- $G(H_2O_2)$ decreases with increasing hydroxyl radical scavenger concentration.

G-VALUE AS A FUNCTION OF LET



G-value as a function of T



Properties of the radiolysis products

- H_2O_2: Oxidant
- H_2: Reductant (slow)
- $HO^{\bullet}$: Strong oxidant (very reactive)
($HO^{\bullet} \rightarrow O^{\bullet -} + H^+$; pK_a=11.9)
- e^-_{aq}: Strong reductant
- $H^{\bullet}$: Reductant ($H^{\bullet} \rightarrow H^+ + e^-$; pK_a=9.6)

Radiolysis of aqueous solutions containing oxygen

$$H^{\cdot} + O_2 \rightarrow HO_2^{\cdot}$$

$$e^-_{aq} + O_2 \rightarrow O_2^{\cdot -}$$

Radiation chemical effects in nuclear reactors

- Oxidation of metals
- Brittleness (H_2)
- Explosion ($H_2 + O_2$)

Interfacial Photo and Radiation Chemistry

- Surface reactions
- Radiation Chemistry in Heterogeneous systems
- Photochemistry in Heterogeneous systems

The maximum rate constant

$$\frac{d[Solute]}{dt} = -\underbrace{\frac{2k_BT}{3\pi\eta}\frac{R^2_{SolidMol}}{R_{Solute}R_P}}_{k_{\max}}\left(e^{-\frac{E_a}{RT}}\right)[Solute]\frac{N_{SolidMol}}{V}$$

ca 10^{-3} m s^{-1} (µm-sized particles)
ca 10^{-6} m s^{-1} (mm-sized particles)

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

THE G-VALUE DEPENDS ON THE SCAVENGING CAPACITY

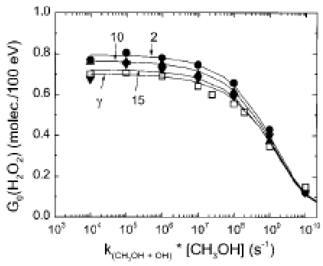


Figure 4. Hydrogen peroxide yields as a function of the scavenging capacity of methanol (25 mM nitrate) with protons of different energies: (●) 2 MeV; (▲) 10 MeV; (▼) 15 MeV. The results with γ rays are (□).

B. Pastina, J. A. LaVerne, *J. Phys. Chem. A*, 1999, 103, 1592-1597

G-VALUE

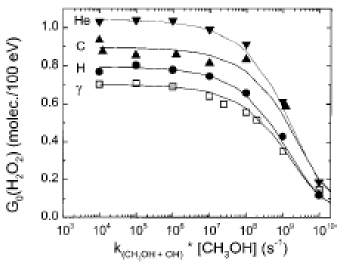


Figure 5. Hydrogen peroxide yields as a function of the scavenging capacity of methanol (25 mM nitrate) for: (□) γ rays; (●) 2 MeV ^1H; (▼) 5 MeV ^4He; (▲) 10 MeV ^{12}C.

B. Pastina, J. A. LaVerne, *J. Phys. Chem. A*, 1999, 103, 1592-1597

$G(H_2O_2)$

- Will be reduced in concentrated solutions (e.g., brines)

Interfacial G-values

- $G(H_2)$ increases with increasing solid surface area to solution volume ratio. This is not the case for H_2O_2.

SiO_2 slurries

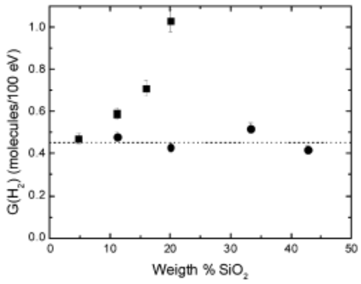


Figure 3. Production of H_2 in aqueous slurries of SiO_2 with 1 mM SeO_4^{2-} and 1 mM Br^-: (●) fused 325 mesh SiO_2 (8.1 m^2/g) and (■) fumed SiO_2 (312 m^2/g). The dotted line is the H_2 yield in water with 1 mM SeO_4^{2-} and 1 mM Br^- but no oxide.

J. A. LaVerne, S. E. Tonnies, *J. Phys. Chem. B*, 2003, 107, 7277-7280

UO_2

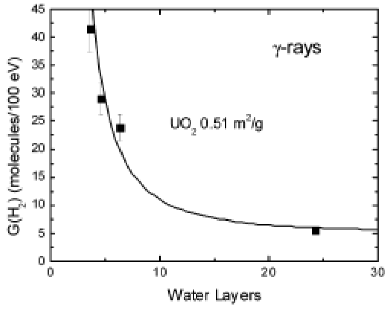


Figure 3. Production of H_2 relative to amount of energy directly deposited by γ-rays in the water adsorbed on UO_2 as a function of the number of water layers. The yield of H_2 in bulk water is 0.45 molecules/100 eV, ref 27.

J. A. LaVerne, L. Tandon, *J. Phys. Chem. B*, 2003, 107, 13623-13628

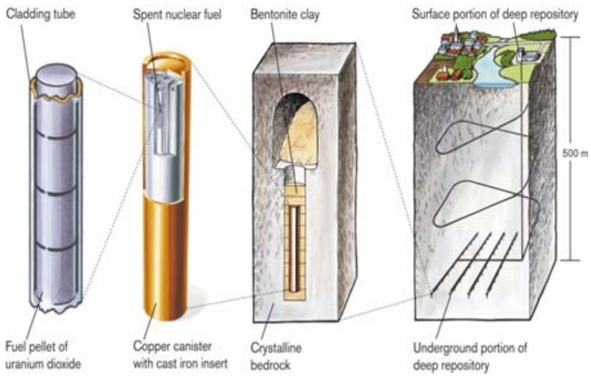
When are interfacial G-values important?

- Surface area to solution volume ratio > 1.6 x 10^7
- Water layer < 60 nm

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

Radiation induced dissolution of spent nuclear fuel under deep repository conditions

Deep geological repository



We want to be able to accurately predict the rate of radionuclide release from spent nuclear fuel in contact with groundwater!

Other relevant radiation induced processes

- Radiation induced corrosion of copper
- Radiation induced changes in Bentonite

Radionuclide release

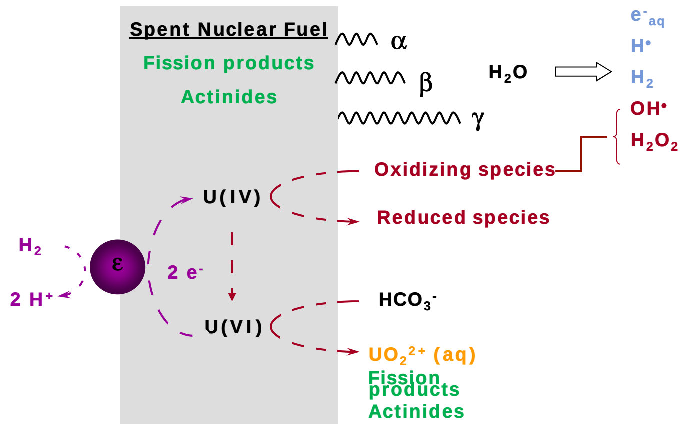
- Instant release
- Matrix dissolution (dissolution of the UO_2 matrix)

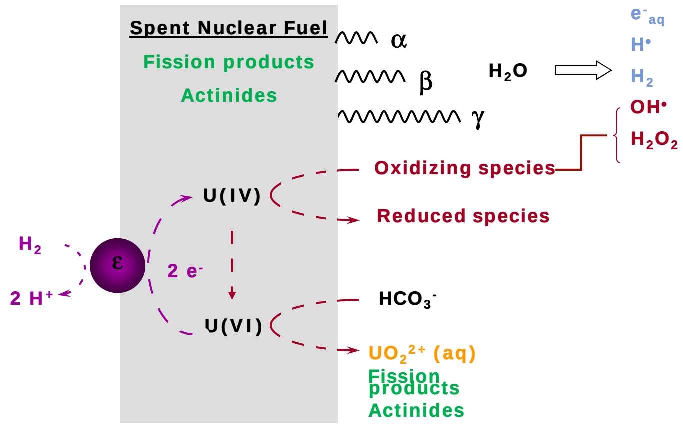
Oxidative (matrix) dissolution

- $Ox + UO_2 \rightarrow UO_2^{2+} \rightarrow UO_2^{2+}(aq)$

KEY PROCESSES

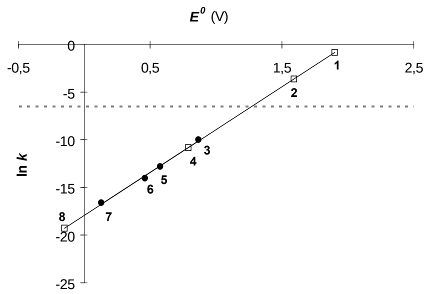
- Groundwater radiolysis
- Surface reactions (redox processes, catalysis and dissolution)





UO_2 OXIDATION KINETICS

- The rate constant for oxidation is a function of reduction potential.



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

RATE CONSTANTS

Oxidant	k (m s^{-1})
H_2O_2	7.3×10^{-8}
O_2	3.6×10^{-10}
$OH^\bullet$	10^{-6}
$CO_3^{\bullet-}$	10^{-6}

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

ARE THE RATE CONSTANTS CONSISTENT WITH EXPERIMENTAL DATA?

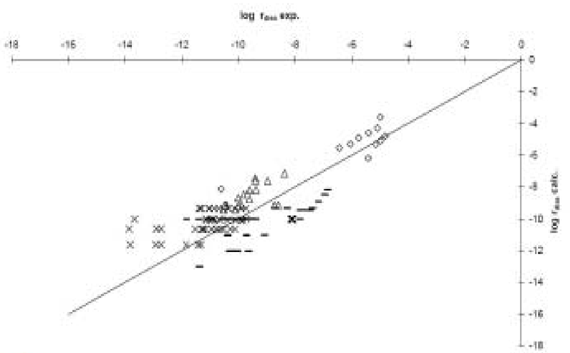


Figure 1. The logarithm of calculated dissolution rates plotted versus the logarithm of experimentally determined dissolution rates [8-16] for different systems; ◇ H_2O_2 with carbonate, △ H_2O_2 without carbonate, - O_2 with carbonate, x O_2 without carbonate.

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

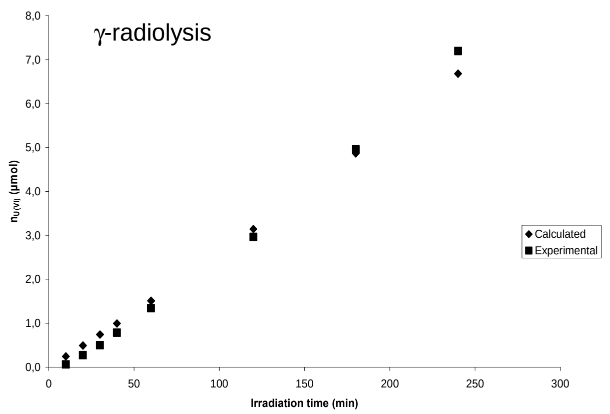
How to use the rate constants for radiation induced UO_2 dissolution

- Total rate of oxidation:

$$rate = \frac{dn_{U(VI)}}{dt} = A_{UO_2} \sum_{ox=1}^{n} k_{ox}[Ox] \frac{n_{e^-}}{2}$$

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

Γ-radiolysis of UO_2-suspensions



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

RELATIVE IMPACT OF (α-) RADIOLYSIS PRODUCTS

$$\text{rate} = \frac{dn_{\text{U(VI)}}}{dt} = A_{\text{UO}_2} \sum_{ox=1}^{n} k_{\text{ox}} [\text{Ox}] \frac{n_{\text{e}^-}}{2}$$

	H_2O_2	O_2	$O_2^{\bullet-}$	$HO_2^{\bullet}$	$CO_3^{\bullet-}$	$OH^{\bullet}$
No additives	100.0 %	0.01 %	0 %	0.03 %	0 %	0 %
H_2 (40 bar)	99.9 %	0 %	0 %	0.02 %	0 %	0.03 %
H_2 (40 bar) HCO_3^- (10 mM)	100.0 %	0 %	0 %	0 %	0.02 %	0 %
HCO_3^- (10 mM)	99.9 %	0.09 %	0 %	0 %	0 %	0 %

H_2O_2 is the major oxidant!

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

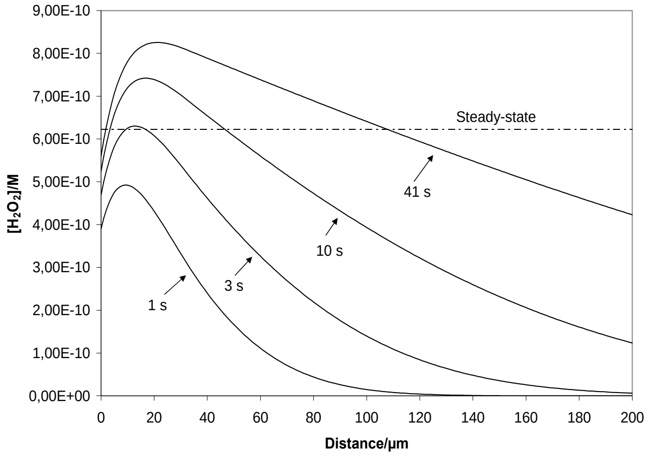
RATE OF H_2O_2 PRODUCTION

$$r_{H_2O_2} = \int_{x=0}^{x_{\max}} \dot{D}(x) \times \rho \times G(H_2O_2)dx$$

Can this be simplified?

Mats Jonsson, Fredrik Nielsen, Olivia Roth, Ella Ekeroth, Sara Nilsson, Mohammad Mohsin Hossain, *Environ Sci. Technol.* 2007, *41*, 7087-7093

SURFACE CONCENTRATIONS
(SIMPLE NUMERICAL SIMULATIONS)



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

STEADY-STATE

- 90% of the steady-state (surface) concentration is reached in a very short time (Seconds-Minutes)

DOES THE STEADY-STATE APPROACH WORK?

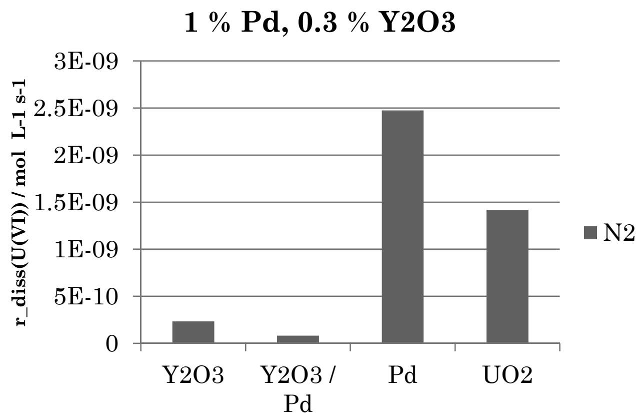
Material (Dose rate)	$p(H_2)$	$[HCO_3^-]$ (mol dm^{-3})	Time (days)	Calc. final conc (mol dm^{-3})	Calc. diss rate (mol dm^{-3} d^{-1})	Experimental final conc. (mol dm^{-3})
10 % U-233 (99 Gy/h)	(Ar)	1.68×10^{-3}	47	7.05×10^{-8}	1.50×10^{-9}	6.40×10^{-8}
10 % U-233 (99 Gy/h)	(1,2 % O2)	1.07×10^{-3}	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}

FACTORS AFFECTING (LOWERING) THE STEADY-STATE CONCENTRATION OF H_2O_2

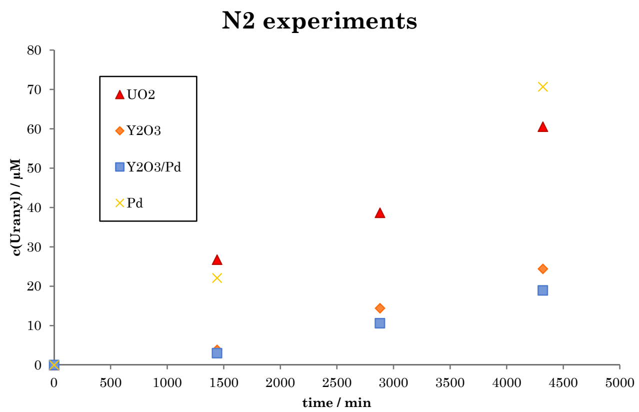
- Surface reaction (UO_2 oxidation, Catalytic decomposition, H_2 and ε-particles, surface area, radiation enhanced reactivity[1])
- Homogeneous reactions (e.g. $H_2O_2 + Fe^{2+}$)[2]
- β- and γ-radiolysis

1. Olivia Roth, Sara Nilsson and Mats Jonsson *Journal of Nuclear Materials, 2006, 354, 131-136*
2. O. Roth, M. Jonsson, J. Nucl. Mater. 2009, 385, 595-600

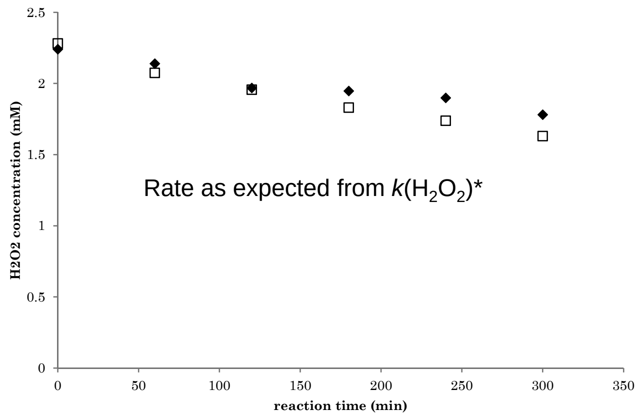
H_2O_2 INDUCED OXIDATIVE DISSOLUTION (DOPED UO_2 PELLETS)



RADIATION (Γ) INDUCED DISSOLUTION

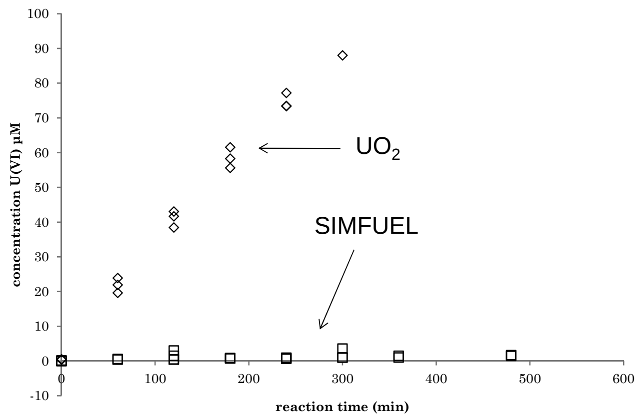


H_2O_2 CONSUMPTION SIMFUEL/UO_2

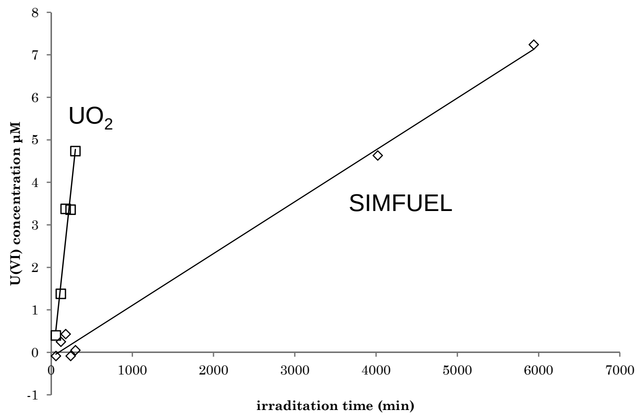


*M. M. Hossain, E. Ekeroth, M. Jonsson. *J. Nucl. Mater.* 2006, ***358***, 202-208

H_2O_2 INDUCED U(VI) DISSOLUTION SIMFUEL/UO_2



Radiation (Γ) induced dissolution of SIMFUEL/UO_2



What happens to H_2O_2?

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

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

$$Yield = \frac{k_{ox}}{k_{ox} + k_{cat}}$$

CATALYTIC DECOMPOSITION OF H_2O_2

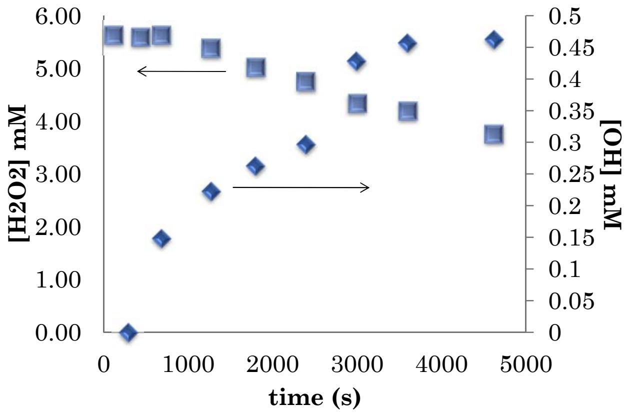
$H_2O_2 \rightarrow 2HO^{\bullet}$ (surface catalyzed)

$HO^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot}$
$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow O_2 + H_2O_2$

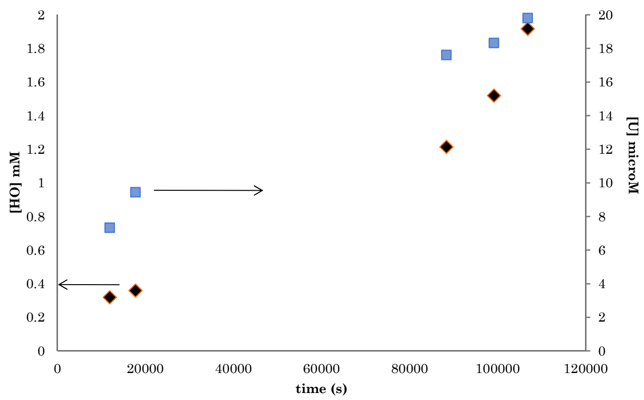
$\Sigma\ 2H_2O_2 \rightarrow O_2 + 2H_2O$

(ZrO_2) Cláudio Lousada and Mats Jonsson, *J. Phys. Chem. C, 2010*, 114 (25)

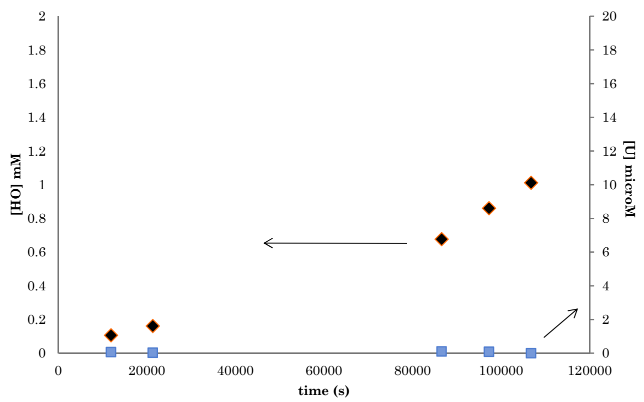
UO_2 POWDER



UO_2 PELLET



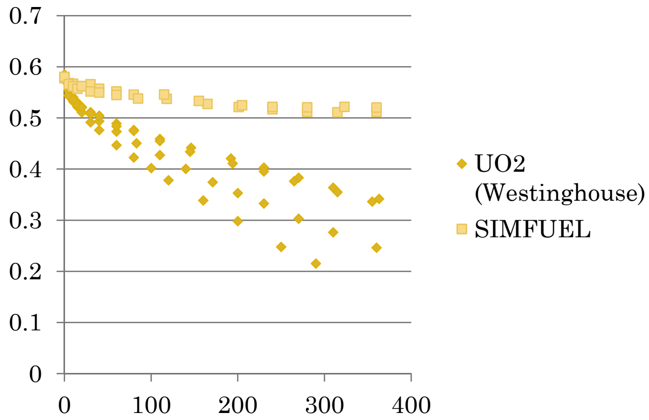
SIMFUEL PELLET



Dissolution yields based on OH/U(VI)

- UO_2 powder: 83 % *(80 % [U(VI)]/[H_2O_2])*
- UO_2 pellet: 2 % *(14 %)*
- SIMFUEL pellet: 0 % *(0.2 %)*
- Catalytic decomposition is the main reaction path for H_2O_2 on pellets!

Oxidation of UO_2 by MnO_4^-



Oxidation of UO_2 by MnO_4^-

Reactivity (doped UO_2):

$Y_2O_3/Pd < Y_2O_3 < UO_2 < Pd$

Activation energies (MnO_4^-)

UO_2 (Westinghouse): 7.4 kJ mol^{-1}

SIMFUEL: 12.9 kJ mol^{-1}

The redox reactivity of doped UO_2

- Pure one-electron oxidants are more reactive towards UO_2 than SIMFUEL.
- The difference decreases with increasing reduction potential of the oxidant.
- The main effect of doping is reduced redox reactivity.

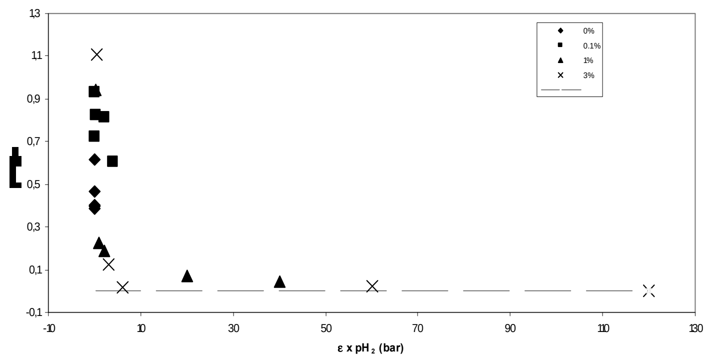
Linear Energy Transfer (Heavy ions)

$$-\frac{dE}{dx} \propto \frac{z^2}{v^2}$$

$$z = \text{atomic no.}$$
$$v = \text{velocity}$$

NOBLE METAL CATALYZED REDUCTION BY H_2

INHIBITION OF H_2O_2 INDUCED DISSOLUTION



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

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

ACCOUNTING FOR SOLID PHASE REACTIVITY

Surface		*k*/m s^{-1}	
	O_2	H_2O_2	H_2
UO_2	3.9×10^{-10}	7.3×10^{-8}	--
UO_2/UO_2^{2+}(Pd)	10^{-7}	10^{-6}	1×10^{-6}
UO_2 (irrad.)	5.1×10^{-10}	9.5×10^{-8}	--

Olivia Roth, Martin Trummer and Mats Jonsson, *Research on Chemical Intermediates*, In press

ACCOUNTING FOR SOLID PHASE REACTIVITY

Solid	Dissolution rate / mol m^{-2} s^{-1}				
	Max	H_2 (40 bar)	H_2 (40 bar) 10^{-2} M HCO_3^-	GW	GW H_2 (40 bar)
UO_2	8.7×10^{-11}	2.7×10^{-12}	2.9×10^{-11}	1.4×10^{-13} (5.6×10^{-13})	1.4×10^{-13} (3.5×10^{-13})
UO_2 + ε-part	8.7×10^{-11}	0	0	1.4×10^{-13} (5.6×10^{-13})	0

Olivia Roth, Martin Trummer and Mats Jonsson, *Research on Chemical Intermediates*, In press

Spent fuel leaching (closed system)

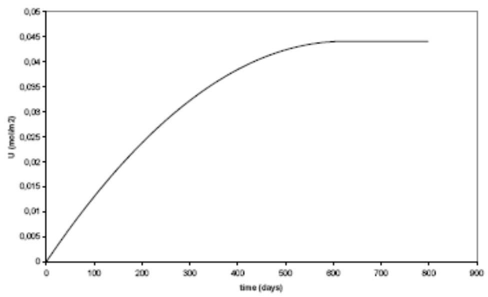


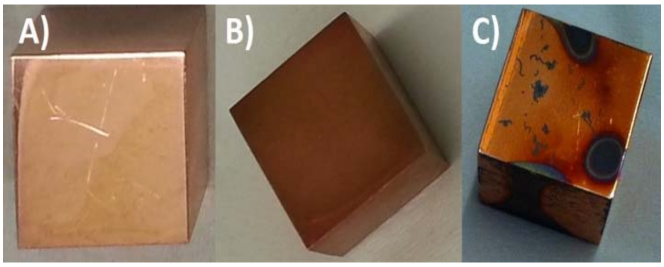
Figure 5. Dynamics of spent nuclear fuel dissolution taking UO_2 oxidation by H_2O_2, H_2 production and noble metal particle catalyzed reduction of $UO_2^{2+}(s)$ by H_2 into account.

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

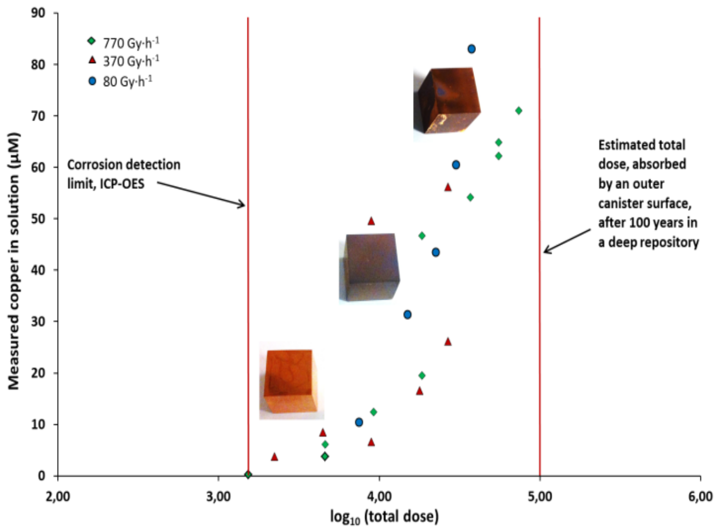
Radiation induced corrosion of copper

- Upon irradiation (in solution) the copper conc. increases with dose.
- The oxide layer grows to ca 100 nm
- Exposure to H_2O_2 does not have this effect.
- The copper concentrations in solution are higher than the oxide solubility and do not match the amount of oxidant produced from radiolysis.

Radiation Induced Corrosion of Cu



Radiation induced corrosion of Cu



Photocatalysis

- TiO_2
- Kinetics (Adsorption)
- Mechanism (Production of hydroxyl radicals)

Quantum yield