EURATOM Collaborative Project CAST (CArbon-14 Source Term)

Release of radionuclides from SNF under deep geological repository conditions

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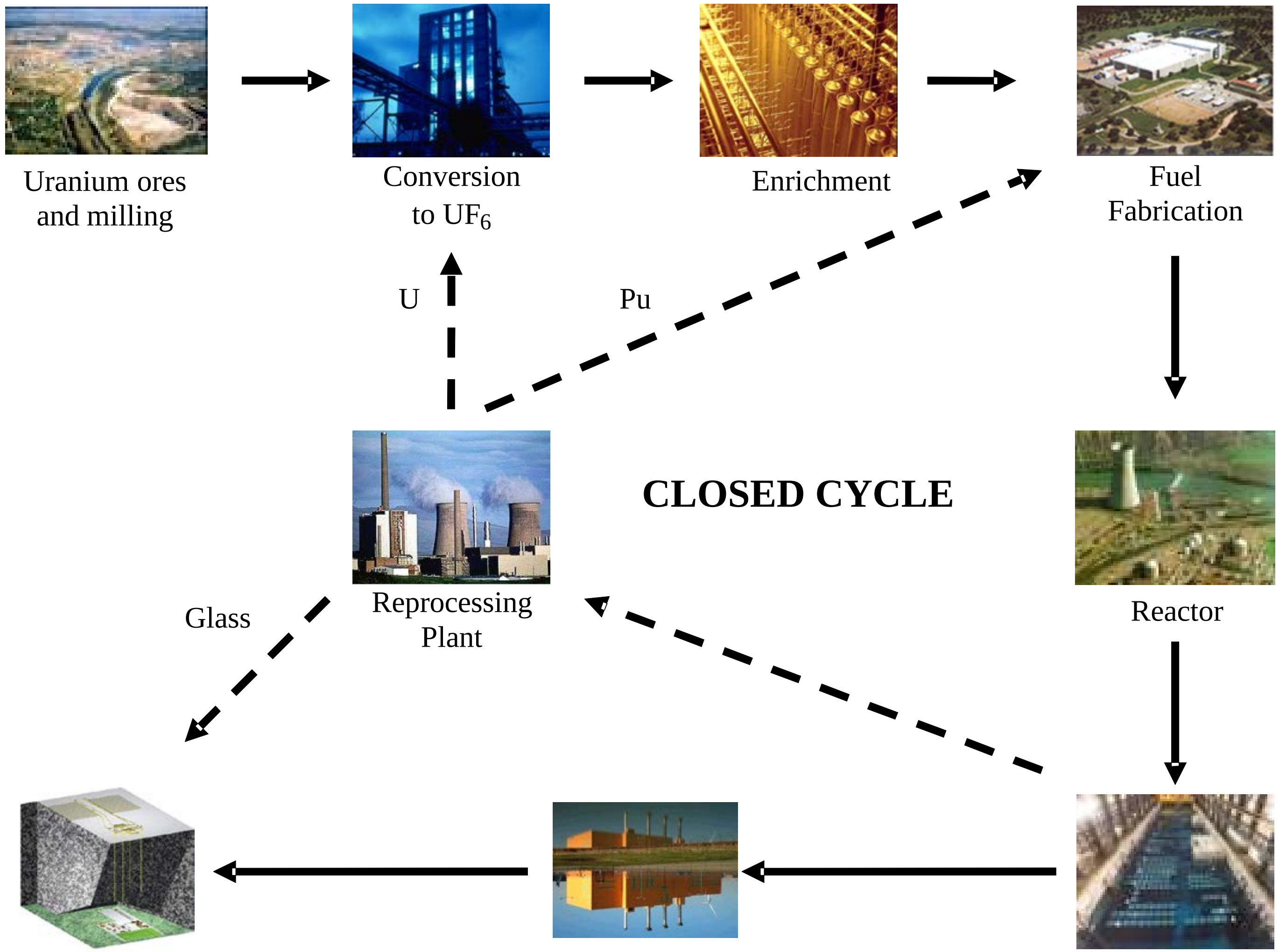
Training Course
C-14 behaviour under repository conditions

5-6 July Karlsruhe(Germany)

Content

- Fuel cycle
- In reactor behaviour
- Geological disposal
- Instant release fraction
- Matrix dissolution

Fuel cycle



Uranium ores and milling

Conversion to UF$_6$

Enrichment

Fuel Fabrication

U

Pu

Reprocessing Plant

CLOSED CYCLE

Reactor

Glass

Geological disposal

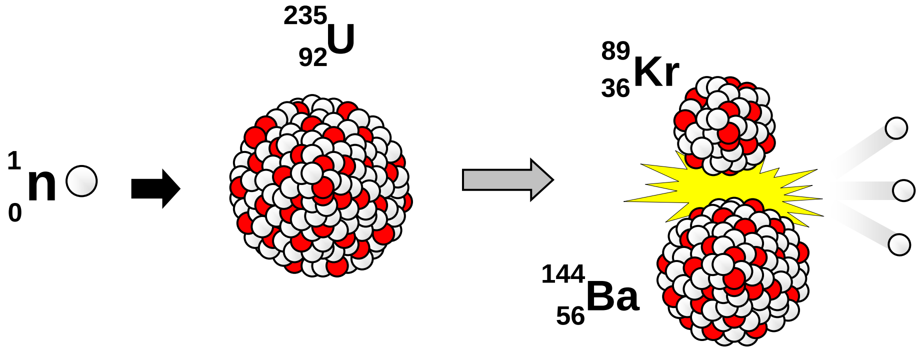
Interim Dry Storage

Pools

OPEN CYCLE

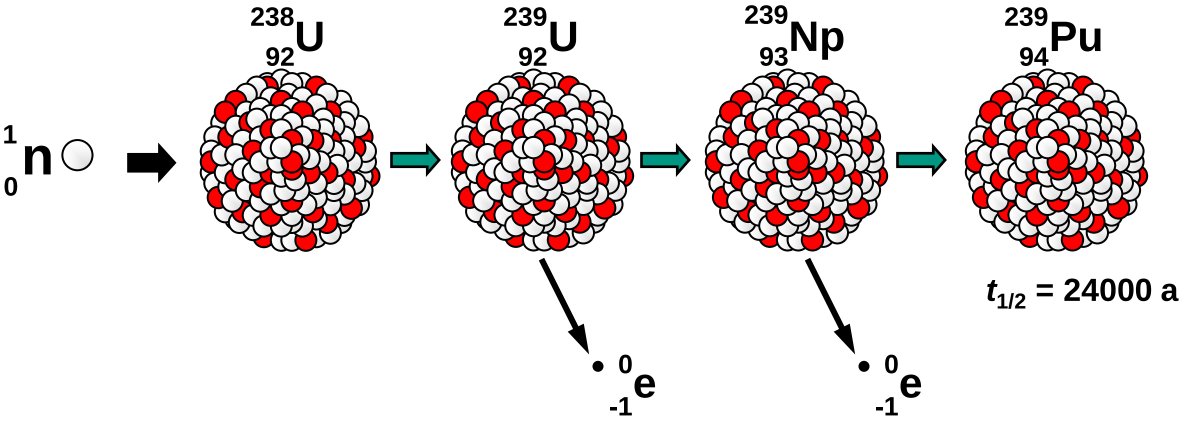
In reactor behavior

Fission



- sustains chain reaction
- produces thermal energy
- 23 GWh/kg (coal, 10 kWh/kg)

Neutron capture



- production of actinides

In reactor behavior

- Production of ^{14}C

- Impurities on the UO_2 of:
  - ^{14}N: impurity level of 25 ppm
  - ^{17}O
- Neutron capture during reactor operation:

$$^{14}N \xrightarrow{(n,p)} {}^{14}C$$

$$^{17}O \xrightarrow{(n,\alpha)} {}^{14}C$$

- Nitrogen reaction is a factor 4 higher than the oxygen reaction

In reactor behavior

- Formation of fission products:
  - High neutron capture cross section
  - Competition with ^{235}U
  - Part of the fuel elements must to be replaced

- The fuel utilization is referred to as burn-up (BU) and represents the cumulative fissions for an irradiation time
  - Ratio of the number of fissions to the number of initial uranium atoms (^{235}U and ^{238}U):

$$BU = \frac{\dot{\mathrm{F}} \cdot t}{N_U}$$

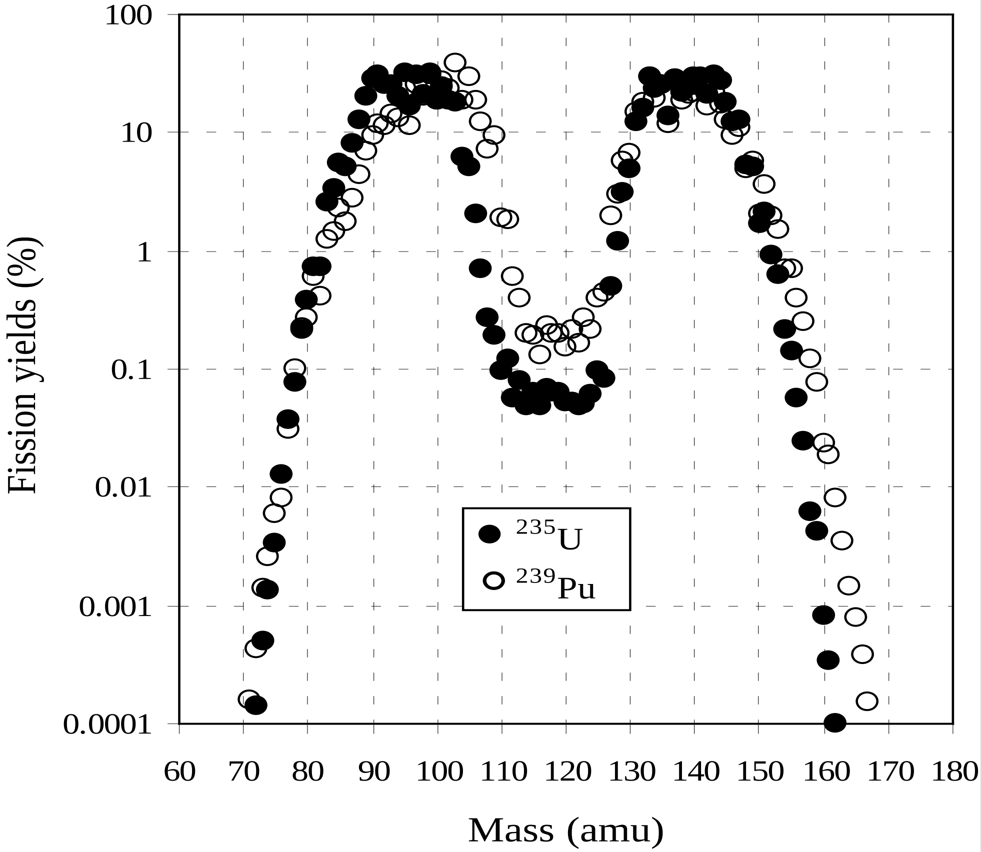
  - Energy produced per unit mass of initial uranium:

$$BU = 950 \cdot \frac{MWd \cdot \dot{\mathrm{F}} \cdot t \cdot kg_{fissioned}}{kg_{fissioned} \cdot N_U \cdot kg_U}$$

In reactor behavior

- The formation of the different fission products depends on its fission yield that represents the probability proportion in which the fission products are formed when the fission occurs

- Fission Yield:
    - Fission products
    - Fissile isotopes
    - Irradiation time
    - Average energy of neutrons
    - Cooling time

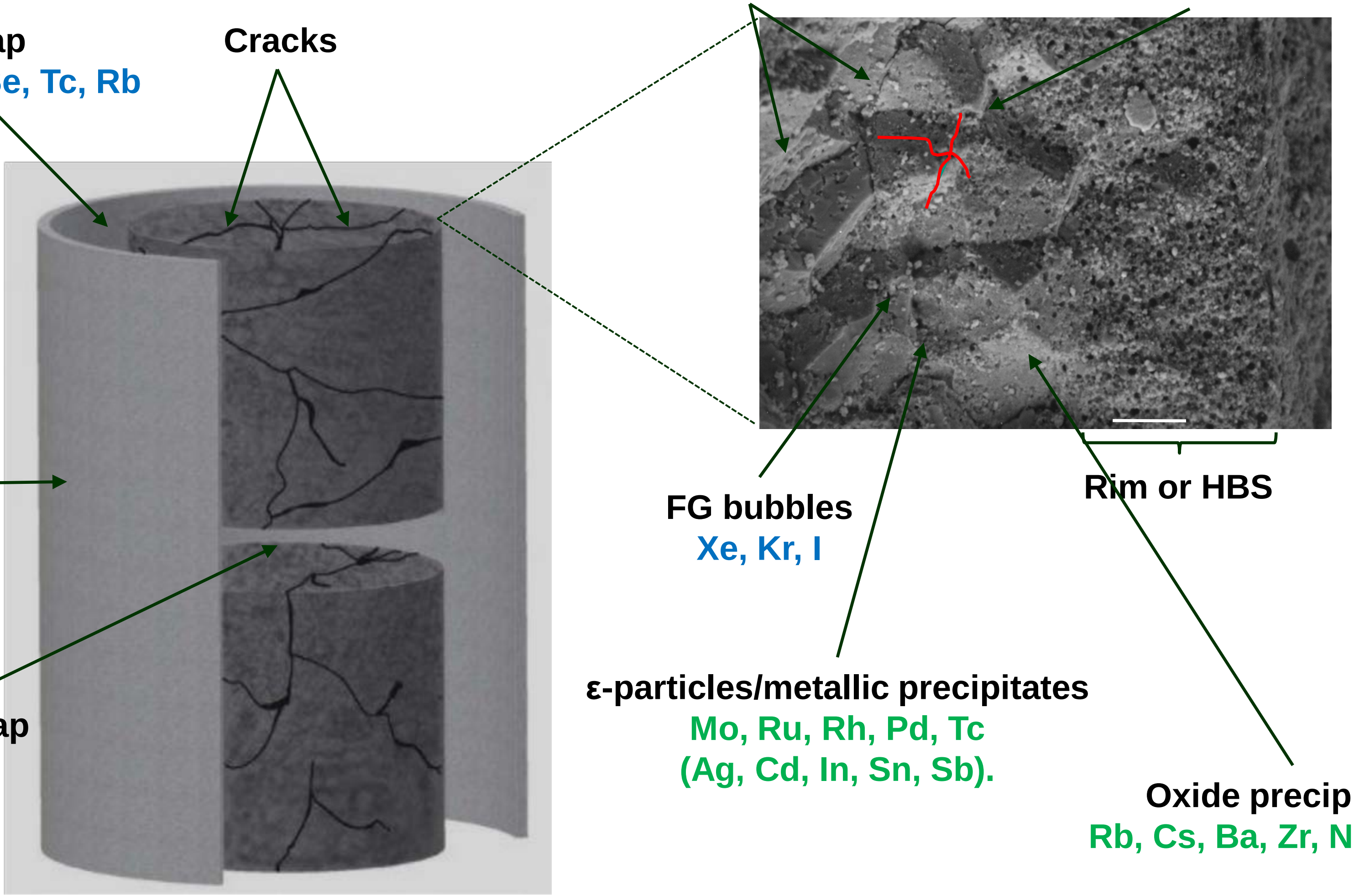


In reactor behavior

Classification

- Fission gases and volatile FP’s:
  - Br, Kr, Rb, I, Xe, Cs and Te
- FP’s forming metallic precipitates:
  - Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Se and Te
- FP’s forming oxide precipitates:
  - Rb, Sr, Zr, Nb, Mo, Se, Te, Cs and Ba
- FP’s dissolved as oxides in the fuel matrix:
  - Rb, Sr, Y, Zr, Nb, Te, Cs, Ba, La, Ce, Pr, Nd, Pm, Sm and Eu

In reactor behaviour



Grains
$(U, An, Ln)O_2$

Grain boundaries
Rb, Sr, Zr, Nb, Mo, Se, Te, Cs, Ba

Gap
C, I, Cs, Se, Tc, Rb

Cracks

Cladding
C, Zr

FG bubbles
Xe, Kr, I

Rim or HBS

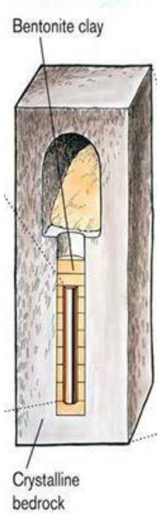
ε-particles/metallic precipitates
Mo, Ru, Rh, Pd, Tc
(Ag, Cd, In, Sn, Sb).

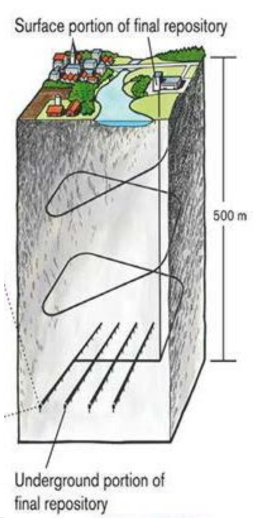
Inter-pellet gap

Oxide precipitates
Rb, Cs, Ba, Zr, Nb, Mo, Tc

Geological disposal

- It is the ultimate step of the nuclear fuel open cycle:
  - Protect the human and his environment from the risks induced by the nuclear waste
  - Limit the consequences for further generations
- It is located at about 400 to 1000 m underground based on:
  - Isolation and confinement capacities of the geological formations.
  - Building of a barriers system around the SNF





Geological disposal

Granite

- + mechanically stable
- + age of rock formation
- + moderate heat conductivity
- + good state of knowledge

- - water bearing fractures
- - moderate retention
- - technical barriers imperative
- - low temperature resistance

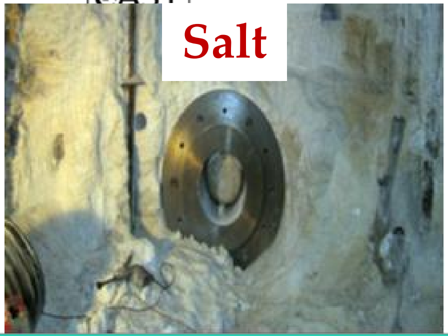
Finland, Sweden, Canada, Japan

Clay

- + tightness
- + plasticity
- + low solubility
- + high retention capacity

- - low heat conductivity
- - low temp. resistance
- - difficult mine construction

Switzerland, France Belgium, Germany



Salt

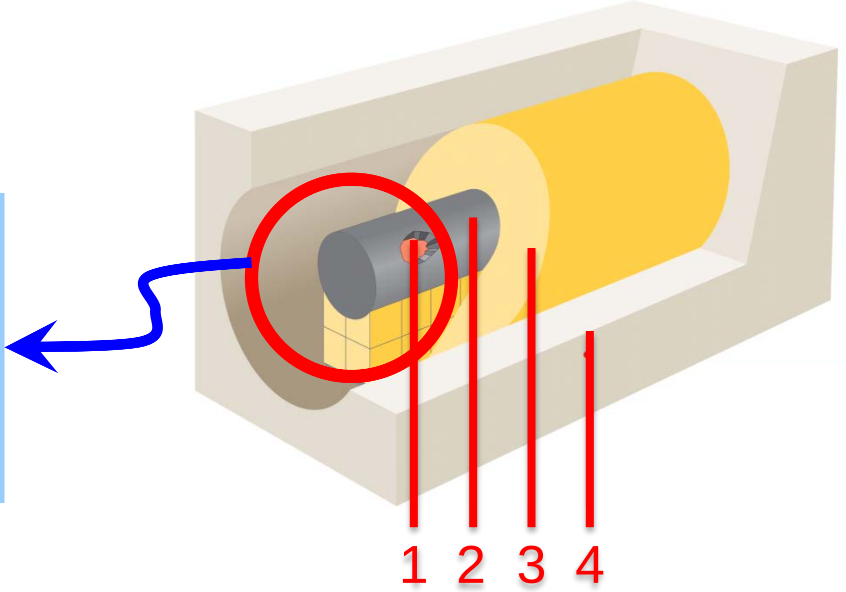
- + tightness
- + plasticity
- + heat conductive
- + high temp. resistance
- + age of existing diapirs
- + good state of knowledge

- - water soluble
- - low retention capacity
- - dissolution

Germany, USA

Geological disposal

- In case of container failure, as a result of several processes, the groundwater will reach the SNF releasing the radionuclides within
- The performance assessment of SNF in a potential future geological disposal system requires the understanding and quantification of the radionuclide release



Groundwater access:

Source term (solubility)

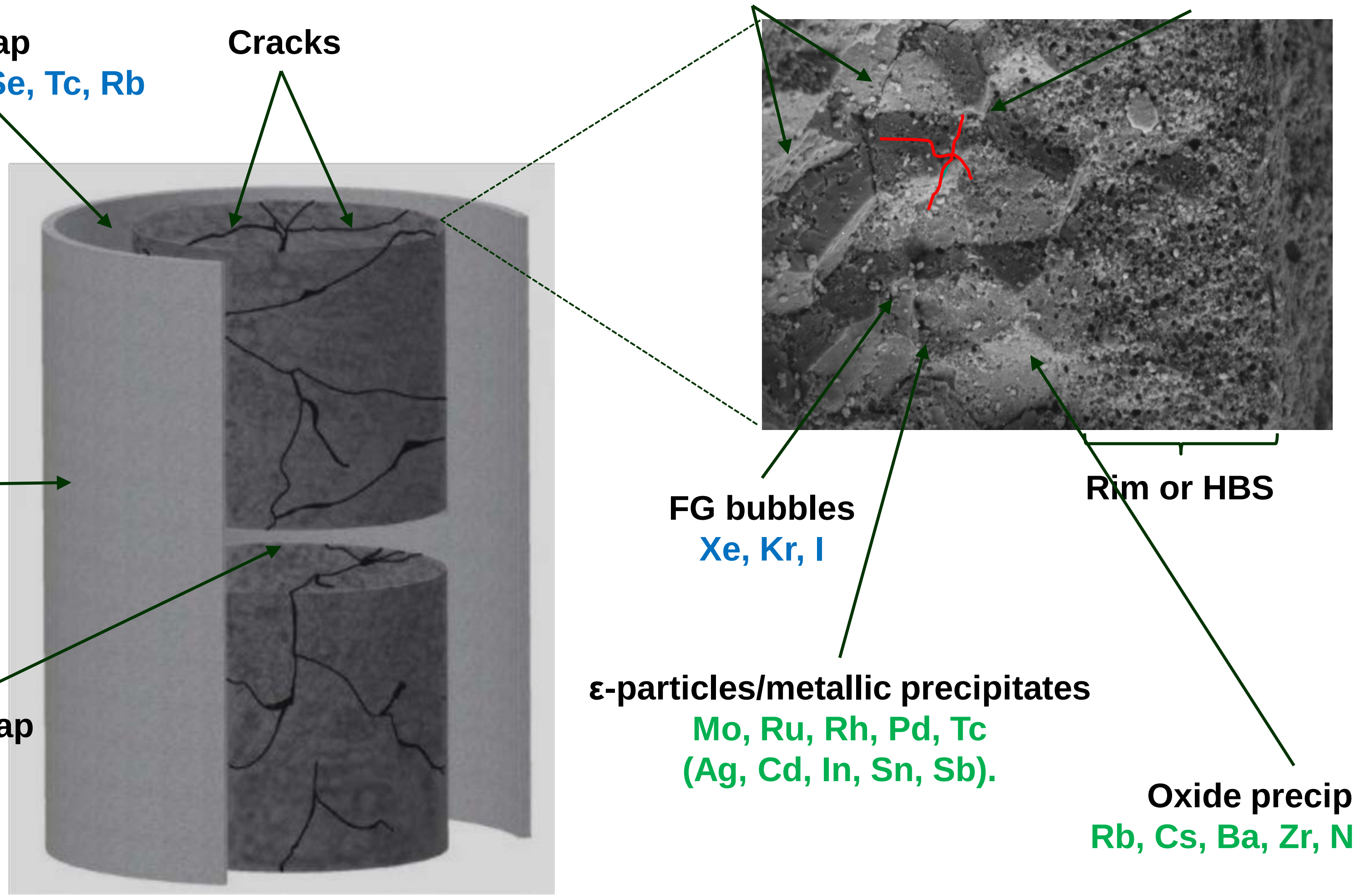
1 **Waste form**

2 **Container**

3 **Engineered barrier**

4 **Geological barrier**

Geological disposal



Gap
C, I, Cs, Se, Tc, Rb

Cracks

Grains
(U, An, Ln)O_2

Grain boundaries
Rb, Sr, Zr, Nb, Mo, Se, Te, Cs, Ba

Cladding
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FG bubbles
Xe, Kr, I

Rim or HBS

Inter-pellet gap

ε-particles/metallic precipitates
Mo, Ru, Rh, Pd, Tc
(Ag, Cd, In, Sn, Sb).

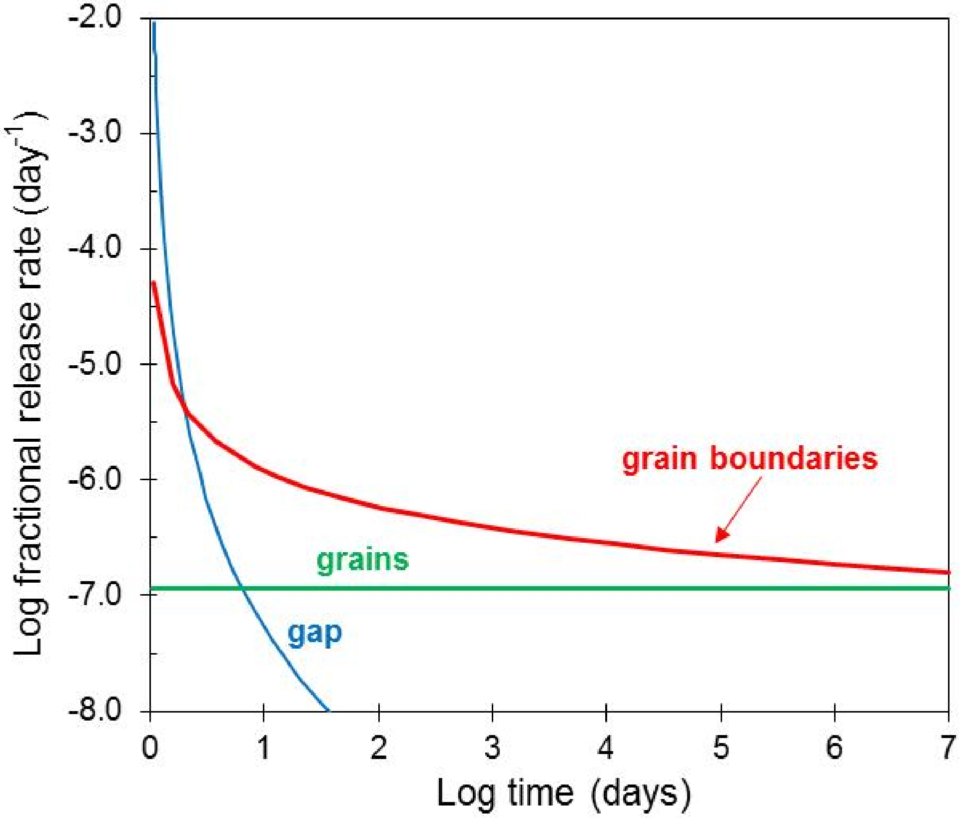
Oxide precipitates
Rb, Cs, Ba, Zr, Nb, Mo, Tc

Geological disposal

- Radionuclide release can be divided into contributions from the three SNF zones: gap, grain boundary and grain matrix

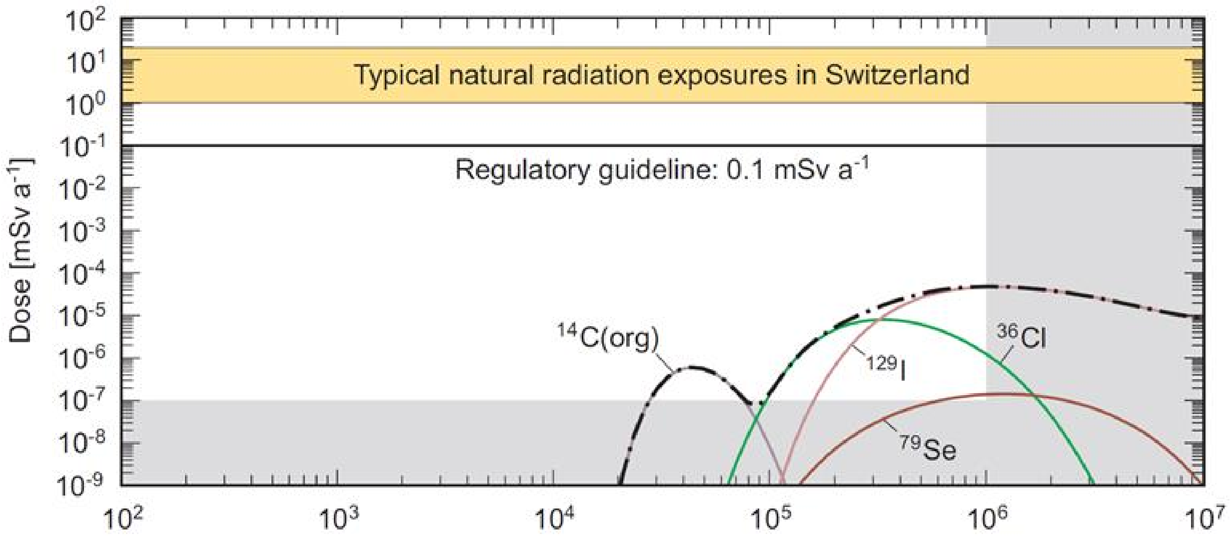
- Instant Release Fraction (IRF)
  - Gap + fractures
  - Grain boundaries
- Matrix dissolution release:

  Grains: 90 % of radionuclides



Geological disposal

- The case of ^{14}C:
- Activation product ^{14}C important contribution to calculated doses in release scenario → especially for organic/gaseous ^{14}C species ($t_{1/2}$ = 5730 years)
- Long-term safety analysis of deep geological repositories for nuclear waste
  → water access into repository needs to be considered



Instant release fraction

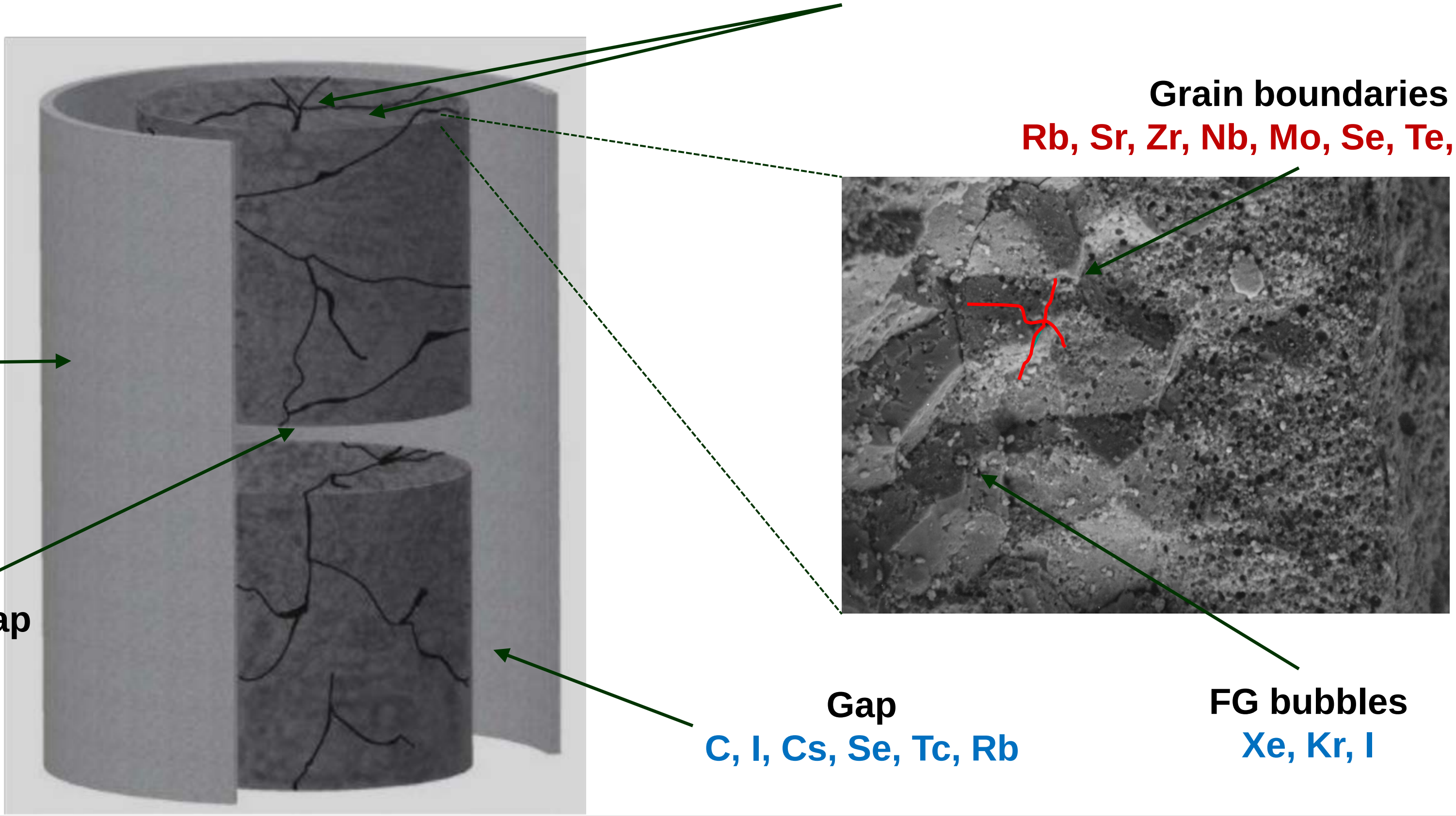
- It is the fraction of the inventory released rapidly when the metal waste package and fuel cladding are first breached
  - Fission gases: Xe and Kr
  - Volatile elements: I, Cs and Cl

- The inventory and segregation of fission-product gases and volatile elements depends on:
  - Burn-up of the fuel
  - Reactor operating condition

- Instantaneous release can vary significantly depending on the type of fuel and its burn-up

Instant release fraction

- The IRF is of particular interest in safety assessments:
  - Long-lived
  - Geochemically mobile



Cracks

Grain boundaries
Rb, Sr, Zr, Nb, Mo, Se, Te, Cs, Ba

Cladding
C, Zr

Inter-pellet gap

Gap
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FG bubbles
Xe, Kr, I

Instant release fraction

Burn-up (GWd/t_{HM})	**48**	**60**	**54.4**	**50.4**		**54.25**		**50.5**		**63**
Sample			OS	S	F	S	F	S	OS	F
FGR	2 (4)	4 (8)	2.3	8.5		13.2		14.1		26.7
Cs	2 (4)	4 (8)	1.3	3.9	4.5	6.2	5.0	3.4	3.7	9.2
I	2 (4)	4 (8)	3.2	15.7	16.4	9.0	3.9	10.8	15.6	11.5
Sr	1 (3)	1(5)	0.083	0.002	0.02	na	na	0.2	0.2	na
^{14}C	10	10	na	na	na	na	na	<1.5	<1	na
Tc	0.1 (3)	0.1 (5)	0.20	0	0	na	na	0.1	0	na
Pd	0.1 (3)	0.1 (5)	na	na	na	na	na	0	0	na
^{36}Cl	10	16	na	na	na	na	na	na	na	na
Sn	-	-	na	na	na	na	na	<0.2	<0.1	na
Mo	-	-	0.51	na	na	na	na	0.3	0.5	na
Rb	-	-	0.28	na	na	na	na			na

- 10 % of the ^{14}C released from the oxide matrix during irradiation.

Geological disposal

- Radionuclide release can be divided into contributions from the three SNF zones: gap, grain boundary and grain matrix

- Instant Release Fraction (IRF)
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- Matrix dissolution release:

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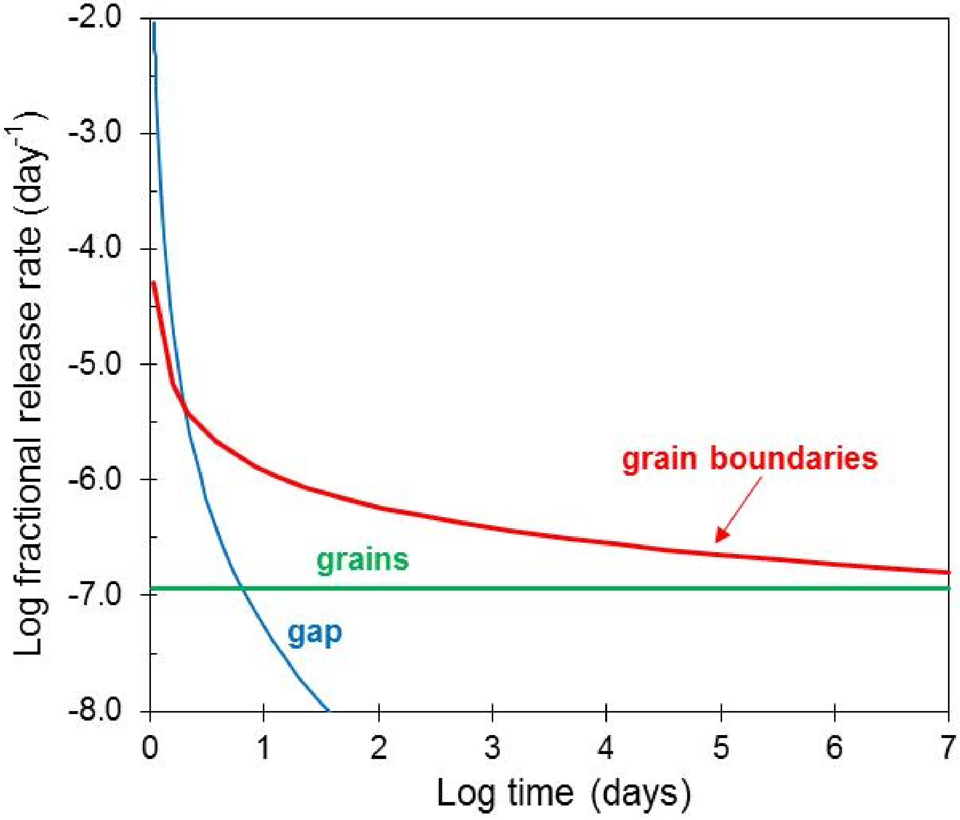
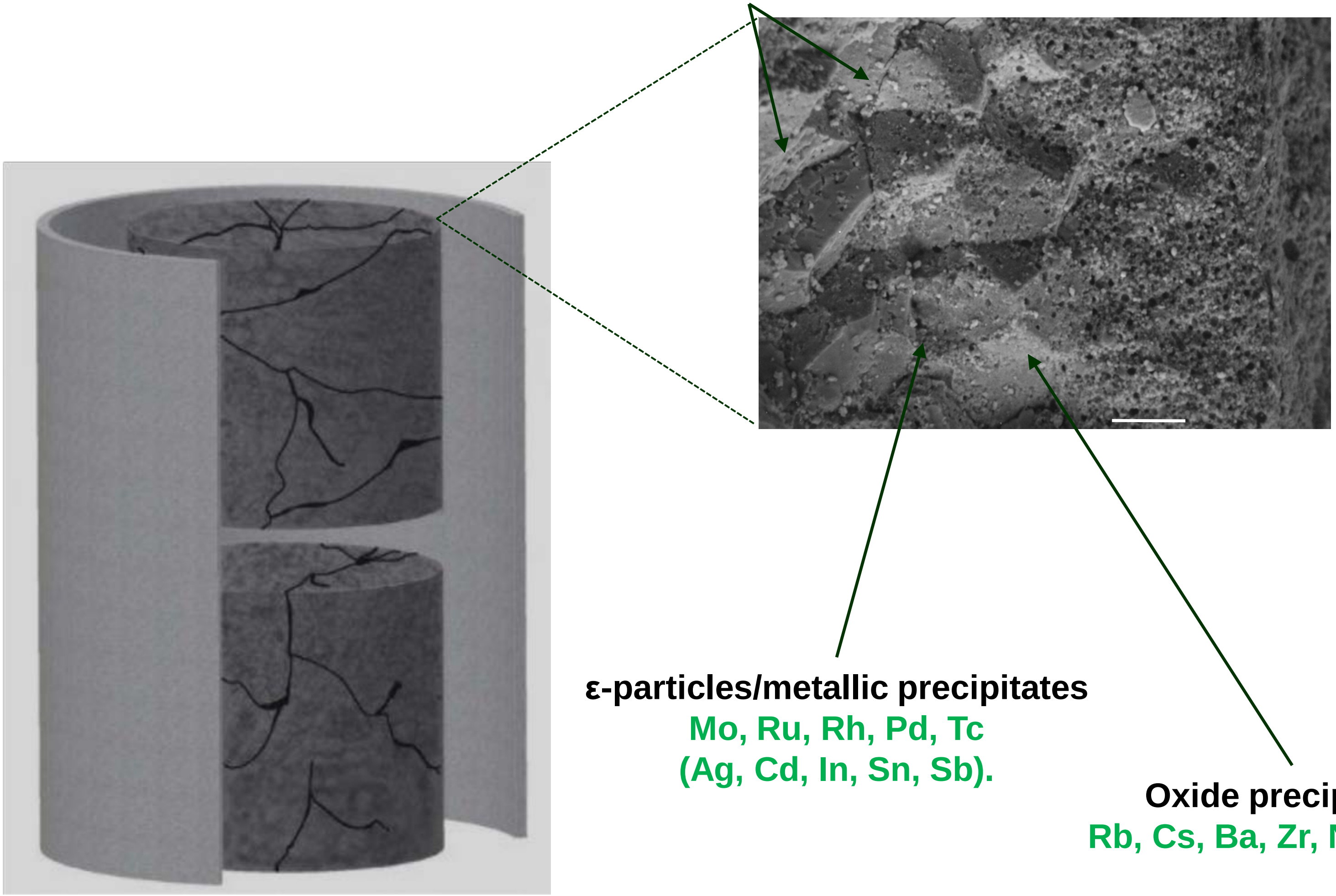


Johnson *et al*., 1985

Matrix dissolution



Grains
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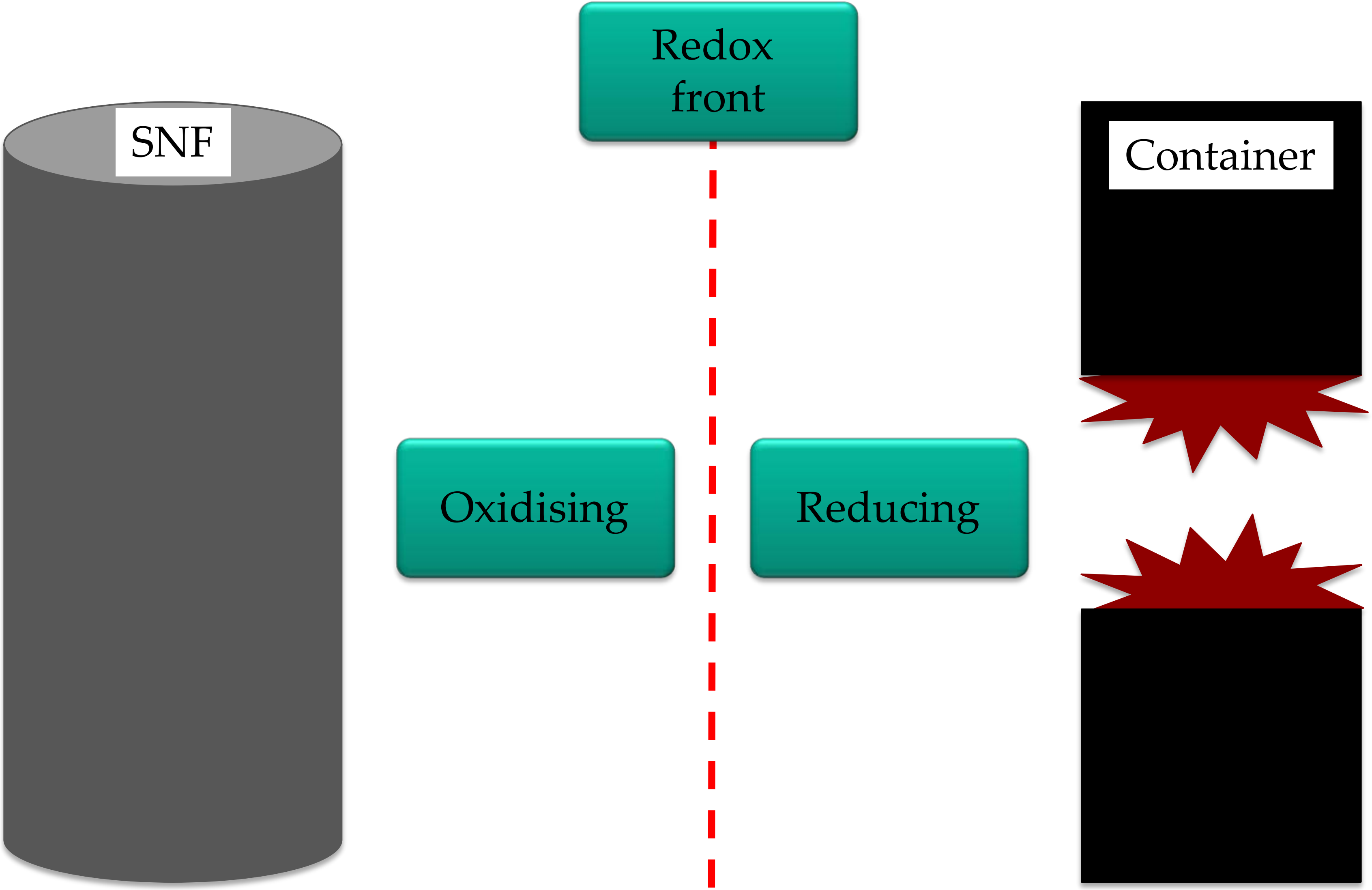
Matrix dissolution



SNF

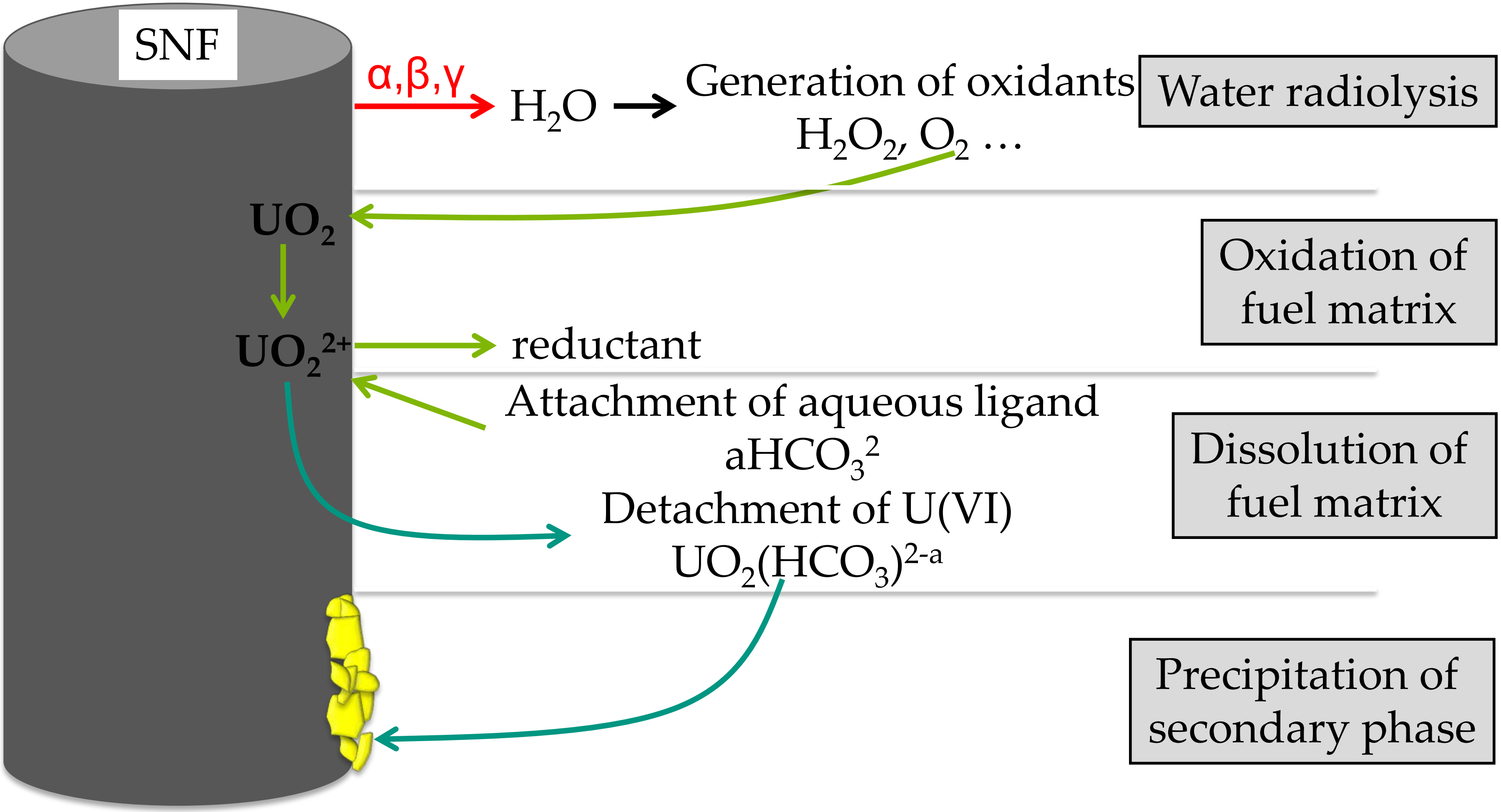
Redox front

Container

Oxidising

Reducing

Matrix dissolution



SNF

α,β,γ $\rightarrow$ H_2O $\rightarrow$ Generation of oxidants

H_2O_2, O_2 …

Water radiolysis

UO_2

UO_2^{2+} $\rightarrow$ reductant

Oxidation of fuel matrix

Attachment of aqueous ligand

$aHCO_3^2$

Detachment of U(VI)

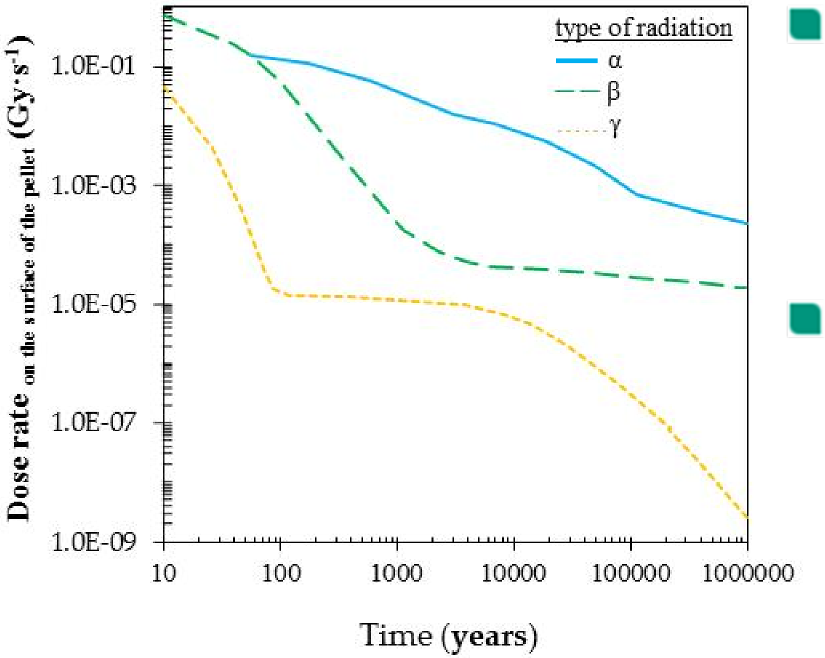
$UO_2(HCO_3)^{2-a}$

Dissolution of fuel matrix

Precipitation of secondary phase

Matrix dissolution

- SNF is a gamma (γ), beta (β) and alpha (α) emitting material with an activity depending on its BU and storing age



- First hundred years dominates the β-radiation:
  - ^{137}Cs (half life of 30.2 years)
  - ^{90}Sr (half life of 28.1 years)
- After 100 hundreds years dominates α-radiation:
  - Transuranides elements (^{241}Am, ^{240}Pu, ^{239}Pu)

Matrix dissolution

- The most important parameter of the SNF dissolution is due to groundwater redox potential in contact with it

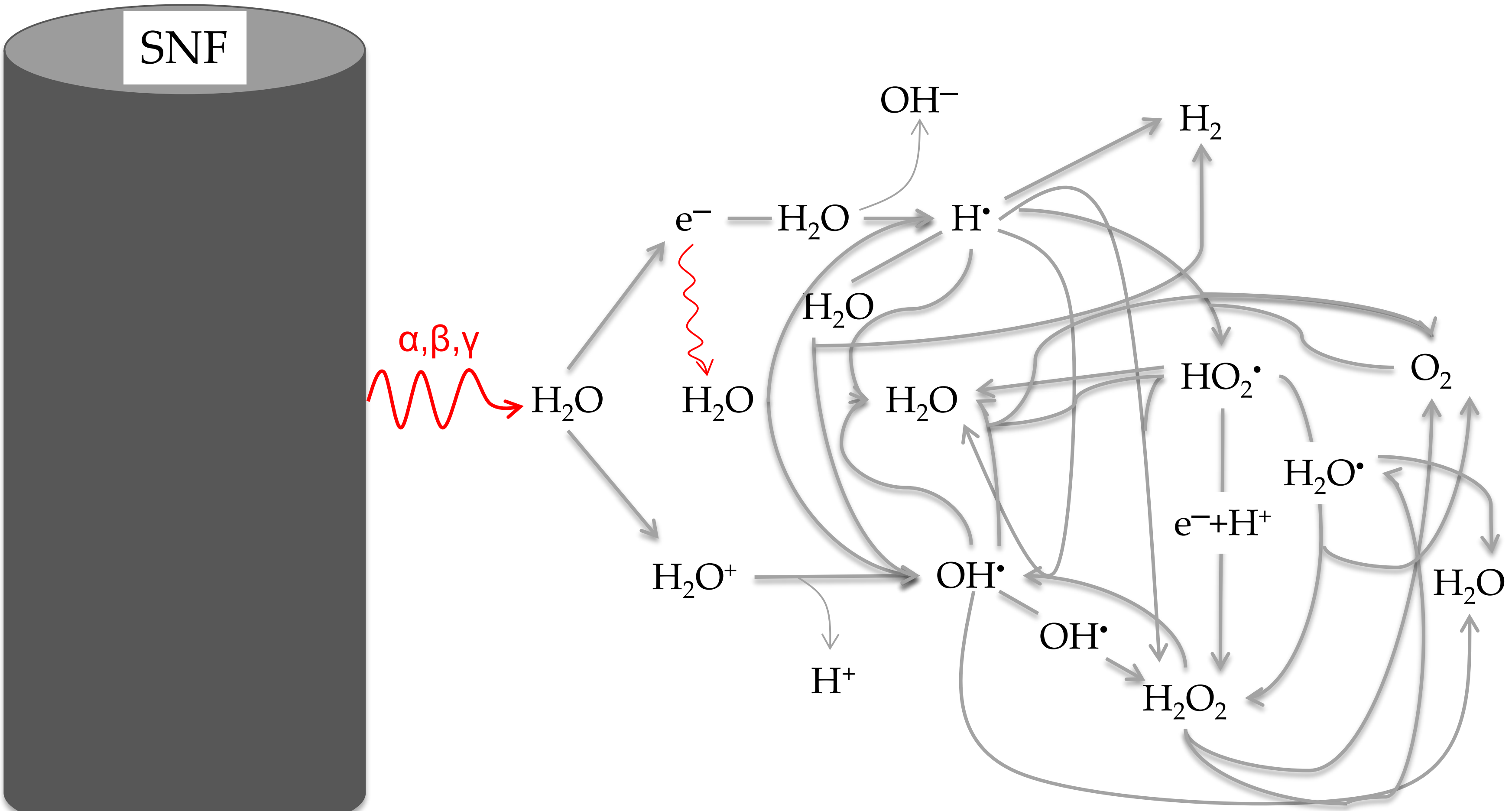
- It will be controlled by water radiolysis
- As a consequence of the water radiolysis:

  - Production of oxidising and reducing species as:
    - Radicals: $OH^{\bullet}$, $O_2^{\bullet-}$, $HO_2^{\bullet}$, e_{aq}, $H^{\bullet}$
    - Molecular form: O_2, H_2O_2, H_2

  - In the case of saline repositories:
    - ClO^{-}, ClO^{2-}, ClO^{3-}

Matrix dissolution

- Water Radiolysis



Fors, 2009

Matrix dissolution

- In deep geological repository the expected conditions are reducing, but the oxidants produced by water radiolysis will lead to oxidising conditions

- Uranium can exist in three different oxidation states:
  - U(IV), U(V) and U(VI)
  - U(VI) is many orders of magnitude more soluble than U(IV)

- This oxidants will be located near to SNF being able to oxidise the UO_2 (as U(IV) in SNF) to a more soluble U(VI)

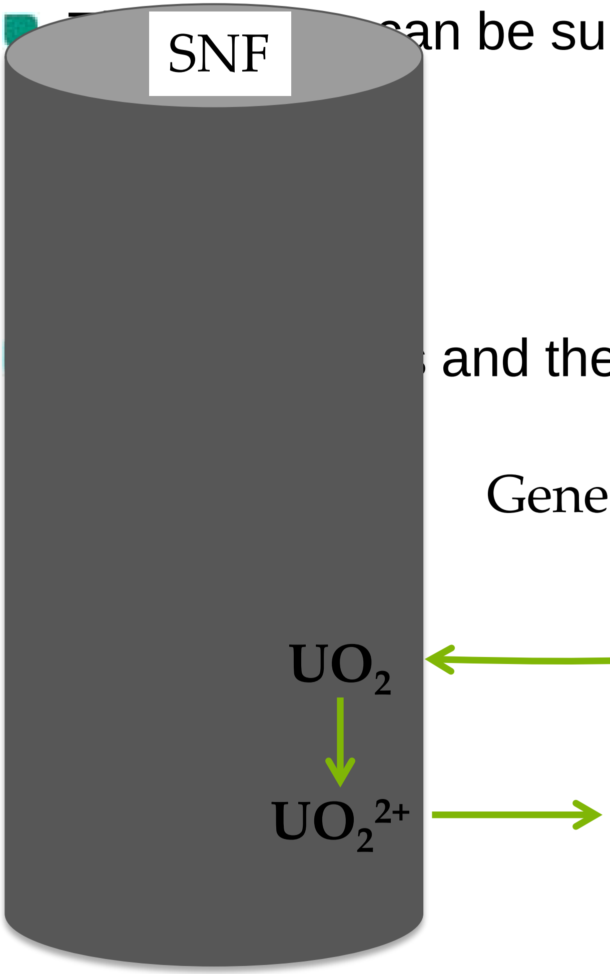
Matrix dissolution

- Oxidation of fuel matrix
- can be summarised as:

$$UO_2 \xrightarrow{\qquad} UO_2^{2+} + 2e^-$$

$$\text{oxidant} + 2e^- \xrightarrow{\qquad} \text{reductant}$$

- and the environment

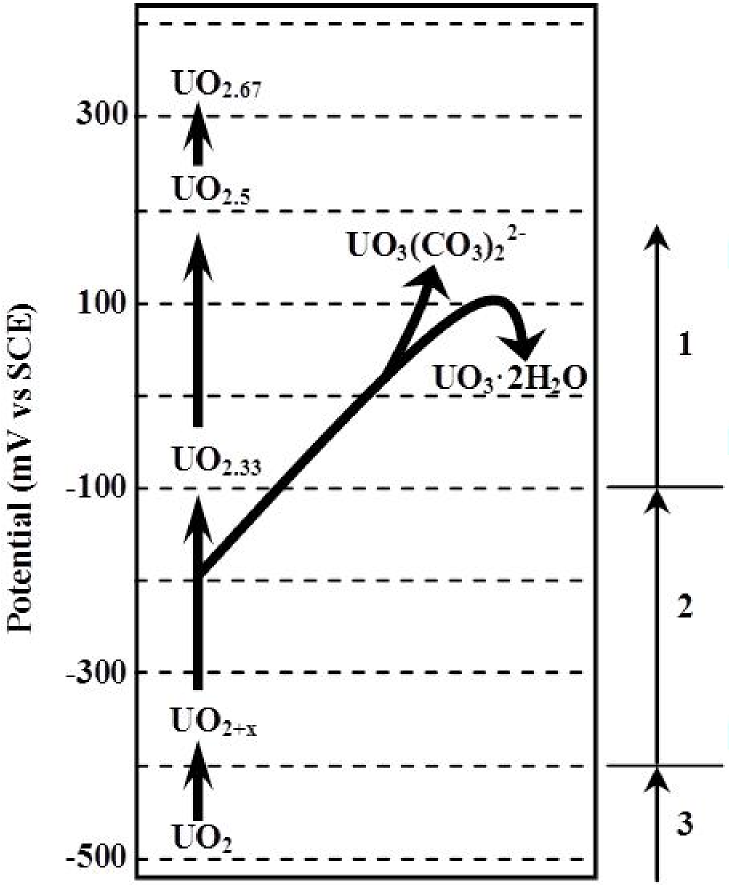


Generation of oxidants by water radiolysis
H_2O_2, O_2 …

Corrosion rate controlled by the slowest reaction

Matrix dissolution

- Oxidation of fuel matrix



Region 1: the dissolution process becomes extensive as the potential increases

Region 2 :

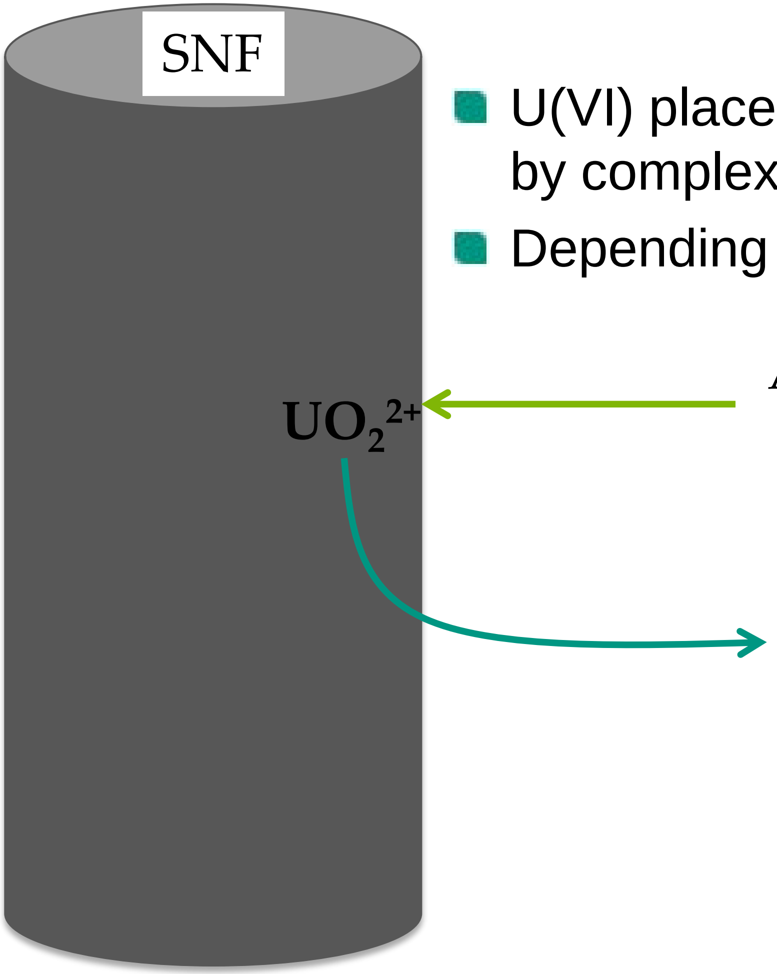
- Irreversible oxidation of UO_2
- Dissolution process starts at -300mV when the UO_2 is oxidised to UO_2^{2+}

Region 3 :

- Small oxidation occurs
- Concentrated to the grain boundaries

Matrix dissolution

- Dissolution of fuel matrix



SNF

UO_2^{2+}

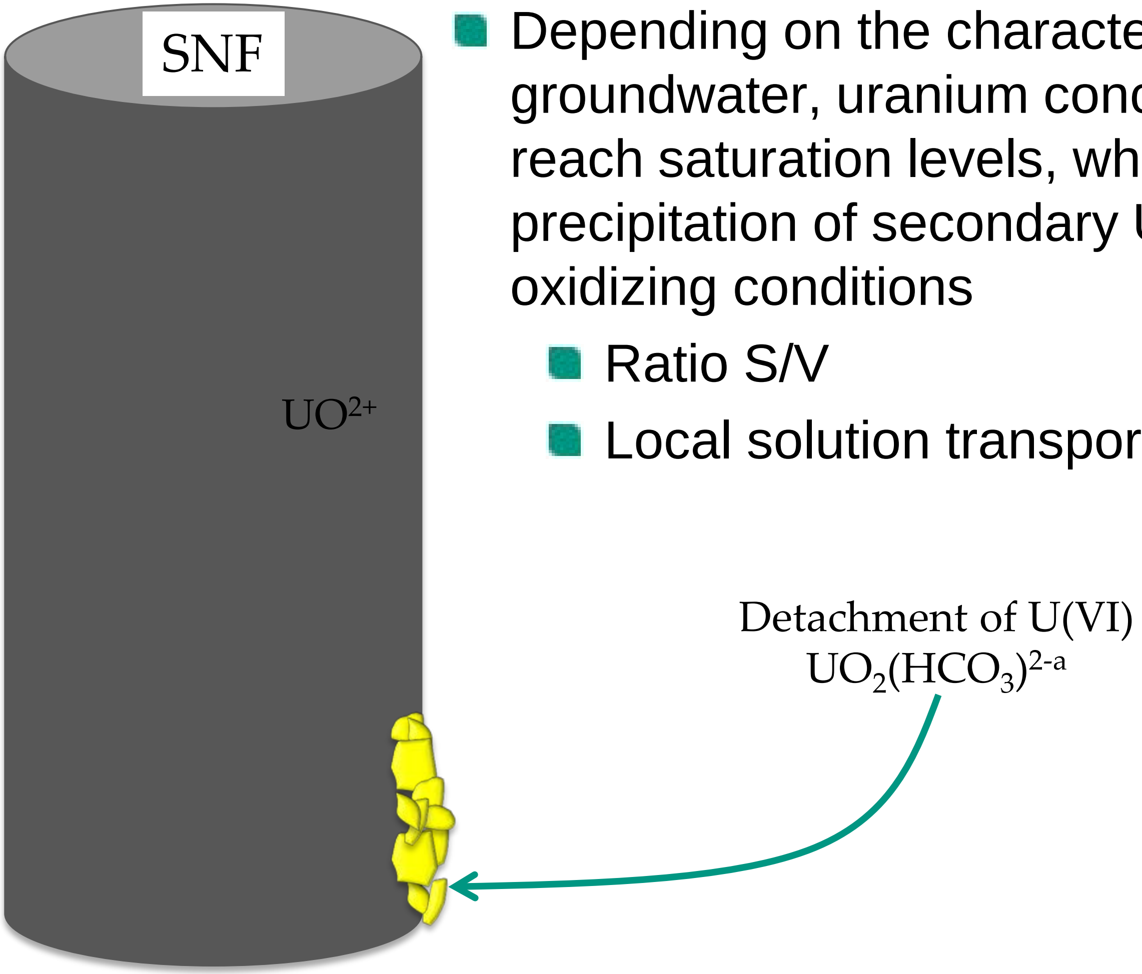
- U(VI) placed at the surface of the SNF is dissolved by complexing ligands
- Depending on characteristics of groundwater

Attachment of aqueous ligand
$aHCO_3^{2}$

Detachment of U(VI)
$UO_2(HCO_3)^{2-a}$

Matrix dissolution

- Precipitation of secondary phases
  - Depending on the characteristics of the groundwater, uranium concentration in solution can reach saturation levels, which will lead to precipitation of secondary U(VI) phases under oxidizing conditions
    - Ratio S/V
    - Local solution transport regime



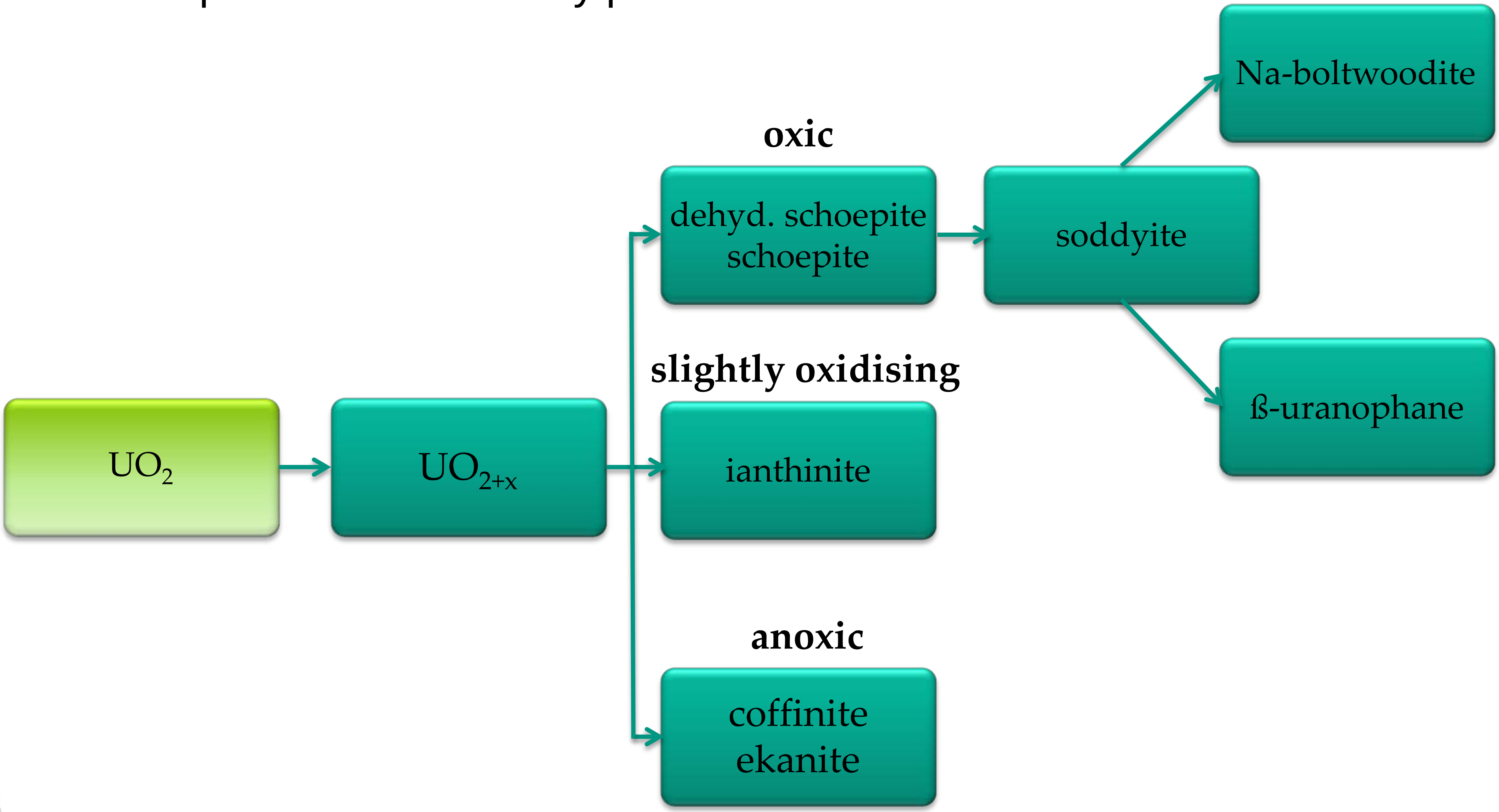
Matrix dissolution

- Precipitation of secondary phases

Authors	Leachant	Secondary phases formed
Wilson (1988), (1990)a,b	J-13 water at 85ºC	Uranophane, Haiweeite, Soddyite
Taylor et al., (1989)	Moisture and DIW	Schoepite
Sunder et al., (1996)	60% saturated steam	Schoepite, soddyite
Forsyth et al., (1992)	DIW	Dehydrated schoepite
Stroes-Gascoyne et al., (1997)	DIW	Schoepite
Finn et al., (1998); Finch et al., (1999)	EJ-13 water, vapour	Vapour: metaschoepite, schoepite LDRe: schoepite, soddyite, Na-boltwoodite HDR: Na-boltwoodite, ß-uranophane
McNamara et al., (2003); Hanson et al., (2005)	DIW	Dry samples: schoepite, metaschoepite Wet samples: studtite, metastudtite
Jégou et al., (2005)	CGW	Na-Si-U-P phases

Matrix dissolution

- Precipitation of secondary phases



UO$_2$

UO$_{2+x}$

oxic

dehyd. schoepite
schoepite

soddyite

Na-boltwoodite

ß-uranophane

slightly oxidising

ianthinite

anoxic

coffinite
ekanite

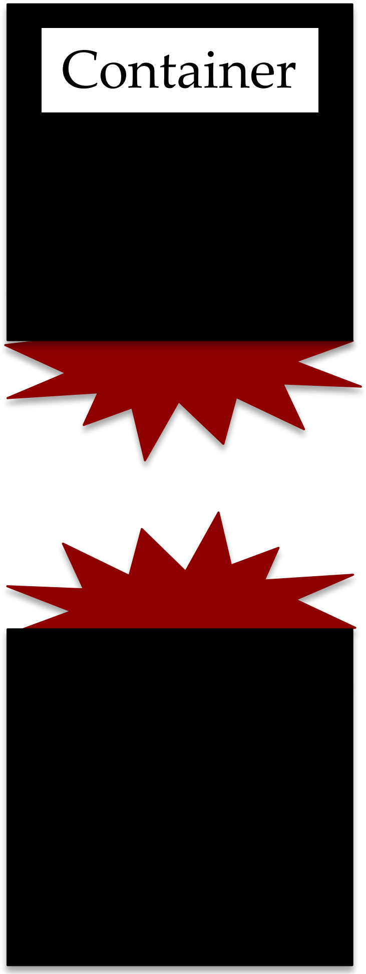
Matrix dissolution

- Precipitation of secondary phases

- These secondary phases could have certain effects:
    - Suppress the corrosion process of UO_2 by blocking the SNF surface
    - Restrict the diffusive mass transport of species to and from SNF surface
    - Adsorb or incorporate others radionuclides released during the SNF corrosion delaying their release to groundwater
    - Lead to a local acidification within the pores in the secondary phase or within defects in SNF by restricting the diffusion of dissolved UO_2^{2+}

Container corrosion

- The oxygen trapped in the repository after its closure will be consumed by bacteria and reducing minerals:
    - Groundwater becomes anoxic
    - Water in contact with iron canister starts the anaerobic corrosion of iron



$$Fe + 2H_2O \longleftrightarrow Fe(OH)_2 + H_2\uparrow$$

$$3Fe + 4H_2O \longleftrightarrow Fe_3O_4 + 4H_2\uparrow$$

Container corrosion

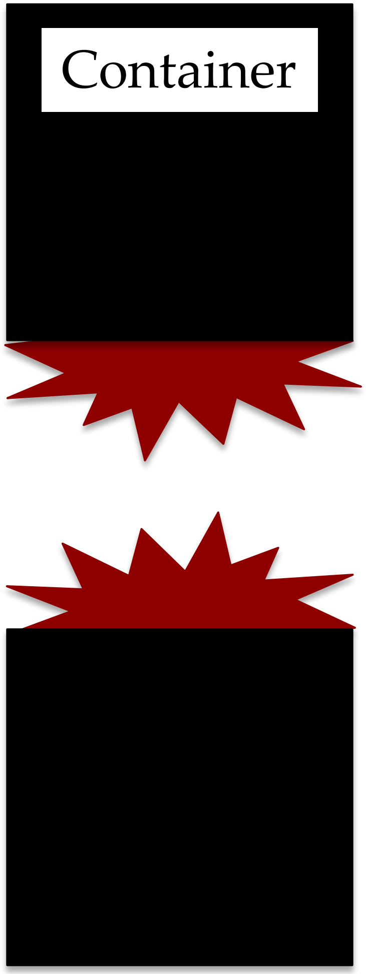
- Accumulation of H_2 in the canister
- Increase of H_2 pressure: formation of gas bubbles
- H_2 pressure ≥ 5MPa remains until α-activity threshold is reached (10000 years)
- Fe and H_2 may react with: radiolytic products and corrosion products from the SNF
- Fuel corrosion in presence of iron:
  - Fenton reaction:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\bullet} + OH^{-}$$

  - In presence of H_2:

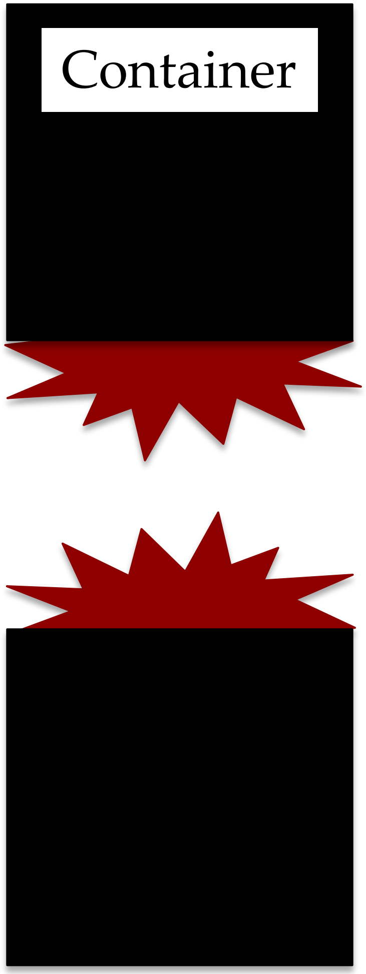
$$Fe^{2+} + OH^{\bullet} \longrightarrow Fe^{3+} + OH^{-}$$

$$H_2 + OH^{\bullet} \longrightarrow H^{\bullet} + H_2O$$

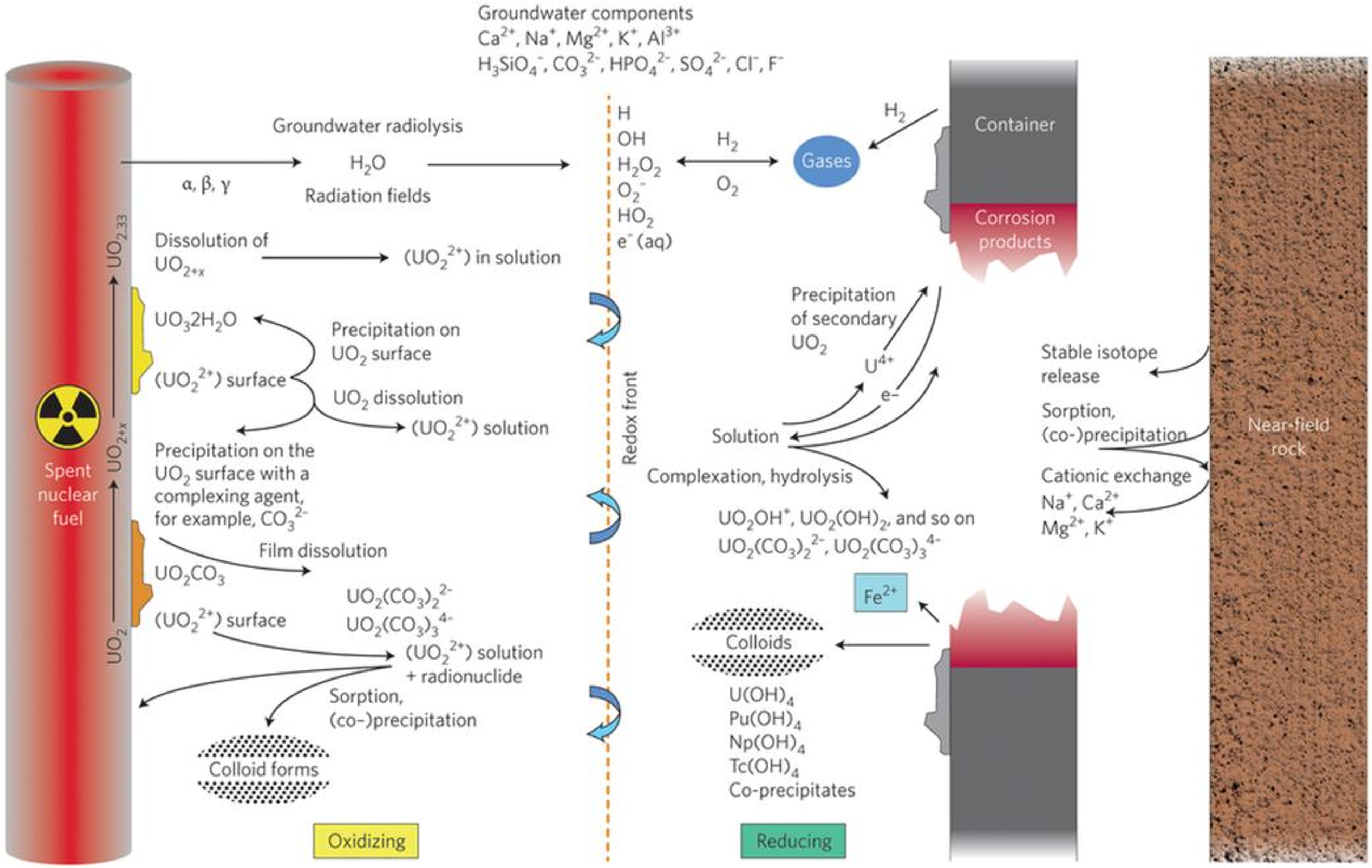


Container corrosion

- Fuel corrosion in presence of H_2:
  - Suppression of fuel corrosion and radionuclide release
  - Consumption of radiolytic oxidants by H_2 is a surface catalysed process



Summary


Groundwater components
Ca^{2+}, Na^{+}, Mg^{2+}, K^{+}, Al^{3+}
$H_3SiO_4^{-}$, CO_3^{2-}, HPO_4^{2-}, SO_4^{2-}, Cl^{-}, F^{-}
Groundwater radiolysis
H_2O
α, β, γ
Radiation fields
H
OH
H_2O_2
O_2^{-}
HO_2
e^{-} (aq)
H_2
O_2
Gases
H_2
Container
Corrosion products
$UO_{2.33}$
Dissolution of UO_{2+x}
(UO_2^{2+}) in solution
UO_32H_2O
Precipitation on UO_2 surface
(UO_2^{2+}) surface
UO_2 dissolution
(UO_2^{2+}) solution
UO_{2+x}
Spent nuclear fuel
Precipitation on the UO_2 surface with a complexing agent, for example, CO_3^{2-}
Film dissolution
UO_2CO_3
(UO_2^{2+}) surface
UO_2
$UO_2(CO_3)_2^{2-}$
$UO_2(CO_3)_3^{4-}$
(UO_2^{2+}) solution + radionuclide
Sorption, (co-)precipitation
Colloid forms
Oxidizing
Redox front
Precipitation of secondary UO_2
U^{4+}
e-
Solution
Complexation, hydrolysis
UO_2OH^{+}, $UO_2(OH)_2$, and so on
$UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$
Fe^{2+}
Colloids
$U(OH)_4$
$Pu(OH)_4$
$Np(OH)_4$
$Tc(OH)_4$
Co-precipitates
Reducing
Stable isotope release
Sorption, (co-)precipitation
Cationic exchange
Na^{+}, Ca^{2+}
Mg^{2+}, K^{+}
Near-field rock

Thank you for your attention