CArbon-14 Source Term

CAST

CAST Training Course 1 (D7.13)

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Dissemination Level		
PU	Public	**X**
RE	Restricted to the partners of the CAST project	
CO	Confidential, only for specific distribution list defined on this document	

CAST – Project Overview

The CAST project (CArbon-14 Source Term) aims to develop understanding of the potential release mechanisms of carbon-14 from radioactive waste materials under conditions relevant to waste packaging and disposal to underground geological disposal facilities. The project focuses on the release of carbon-14 as dissolved and gaseous species from irradiated metals (steels, Zircaloys), irradiated graphite and from ion-exchange materials.

The CAST consortium brings together 33 partners with a range of skills and competencies in the management of radioactive wastes containing carbon-14, geological disposal research, safety case development and experimental work on gas generation. The consortium consists of national waste management organisations, research institutes, universities and commercial organisations.

The objectives of the CAST project are to gain new scientific understanding of the rate of release of carbon-14 from the corrosion of irradiated steels and Zircaloys and from the leaching of ion-exchange resins and irradiated graphites under geological disposal conditions, its speciation and how these relate to carbon-14 inventory and aqueous conditions. These results will be evaluated in the context of national safety assessments and disseminated to interested stakeholders. The new understanding should be of relevance to national safety assessment stakeholders and will also provide an opportunity for training for early career researchers.

For more information, please visit the CAST website at:
http://www.projectcast.eu

CAST		
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Training Course 1

Executive Summary

This report contains the presentations made at Training Course 1 of CAST held on 5th and 6th July 2016 at Karlsruhe Institute of Technology.

The length of the Executive Summary will depend on the report but please aim for a maximum of no more than 2 to 3 pages.

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1 Introduction

This report contains the presentations made at Training Course 1 of CAST held on 5th and 6th July 2016 at Karlsruhe Institute of Technology C-14 behaviour under repository conditions:

Vanessa Montoya, C-14 in wastes from LWR and its relevance to the long-term safety of waste disposal;

R. Dagan, M. Herm, V. Metz, M. Becker, Production of C-14 in fuel elements of light water reactors – introduction to calculation methods and related NEA databases;

E. González-Robles, Release of radionuclides from SNF under deep geological repository conditions;

Felix Himmerkus, Waste Management of LLW / ILW at HDB;

Michel Herm, Separation and analysis of gaseous/dissolved C-14 compounds in structural parts of irradiated LWR fuel elements; and

Volker Metz, 14C behaviour under repository conditions – application to geo-chemical based long-term safety analysis for a underground disposal system.

EURATOM Collaborative Project CAST
(CArbon-14 Source Term)

Training Course

C-14 behaviour under repository conditions

Tuesday, 5. July, 2016

KIT-INE seminar room

9:00 Welcome, introduction to the course and practical information (V. Montoya, KIT-INE)

9:10 Overview on C-14 in waste streams from commercial light water reactors and its relevance to the long-term safety of C-14 bearing waste disposal (V. Montoya, KIT-INE)

9:55 Production of C-14 in fuel elements of light water reactors – introduction to calculation methods and related NEA databases (R. Dagan, KIT-INR)

10:40 Coffee break

11:00 Release of Instant Release Fraction of C-14 from Spent Nuclear Fuel under conditions of a deep geological repository (E. González-Robles, KIT-INE)

11:45 Waste management of (C-14 bearing) low / intermediate level waste (F. Himmerkus, WAK-HDB)

12:30 Lunch break in KIT Cantina

L/ILW facilities of Hauptabteilung Dekontaminationsbetriebe (KIT, Campus North)

13:30 Visit to low / intermediate level waste treatment, decontamination, conditioning and interim storage facilities (F. Himmerkus, WAK-HDB)

17:30 Pick-up and transfer to hotels in Karlsruhe
19:00 Dinner

Wednesday, 6. July, 2016

KIT-INE seminar room

9:00 Separation and analysis of gaseous / dissolved C-14 compounds in structural parts of irradiated LWR fuel elements (M. Herm, KIT-INE)

9:45 C-14 behaviour under repository conditions – application to geochemical based long-term safety analysis for a underground disposal system (V. Metz, KIT-INE)

10:30 Brief introduction into practical training, radiation protection instructions, filling-in forms (V. Metz, KIT-INE)

10:40 Coffee break

KIT-INE controlled area

11:00 Practical training for working with glove boxes, handling of radioactive laboratory waste and analytical techniques for determination and speciation of radionuclides under disposal relevant conditions (E.Bohnert / M. Herm, KIT-INE)

12:30 Lunch break in KIT Cantina

13:30 Visit to laboratories with open radioactivity, shielded box line with high level waste and C-14 separation and analysis facility (E. González-Robles / M. Herm, KIT-INE)

group (A) Raman-spectroscopy and optical microscopy of SNF in shielded box line
group (B) surface analytics (SEM, XPS)

17:00 Summary discussion in INE seminar room

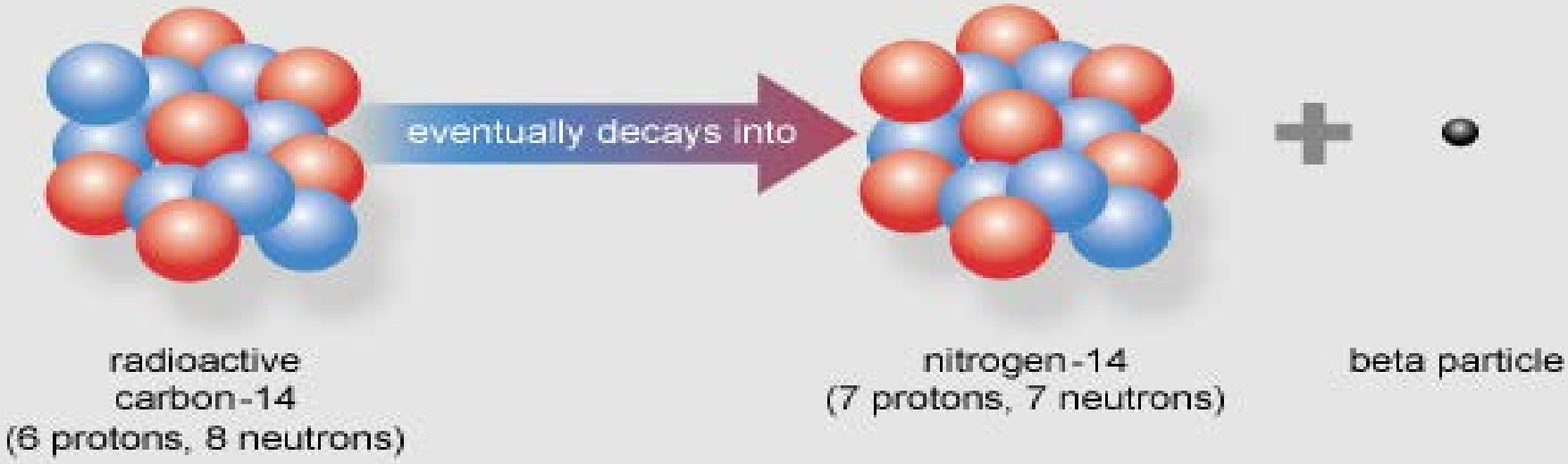
17:30 Pick-up and transfer to Karlsruhe

C-14 in wastes from LWR and its relevance to the long-term safety of waste disposal

Vanessa Montoya (vanessa.montoya@kit.edu)

INSTITUT FÜR NUKLEARE ENTSORGUNG (INE)

5. 07. 2016, Karlsruhe, Germany



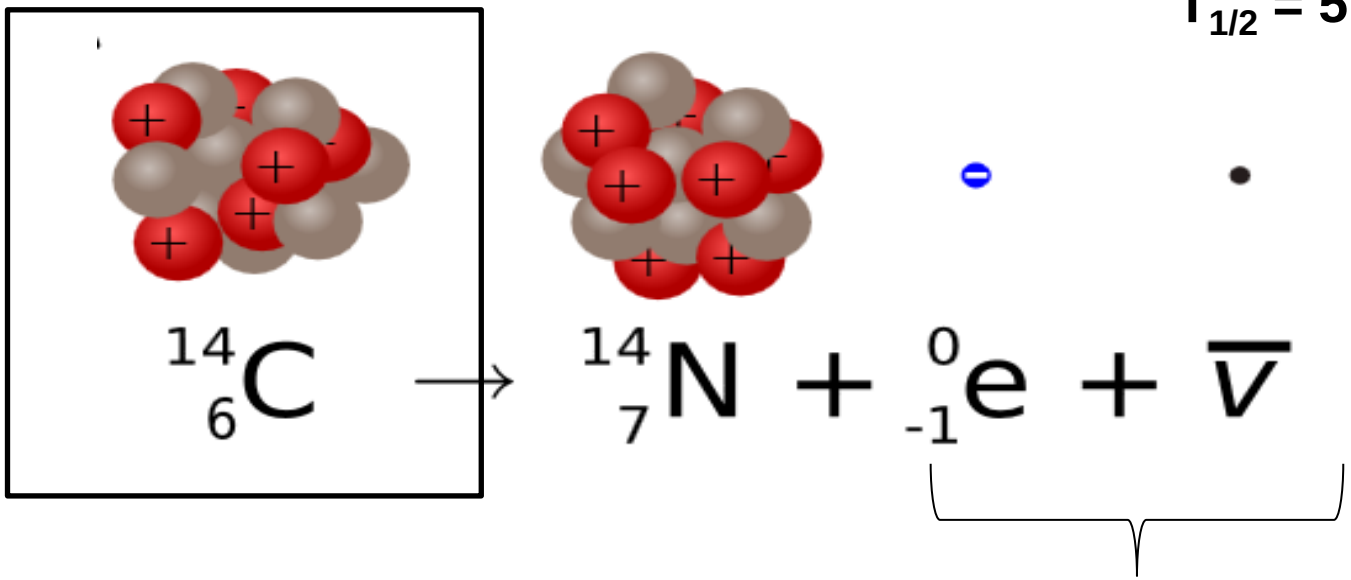
Content

- **General Aspects of C-14**
  - C-14 in the nature
  - C-14 from human activities
- **Source of C-14 in Nuclear Power generation (LWR)**
- **Transformation of C-14 during storage and disposal**

Carbon – 14

Radionuclide: β emitter

$T_{1/2}$ = 5,730 years



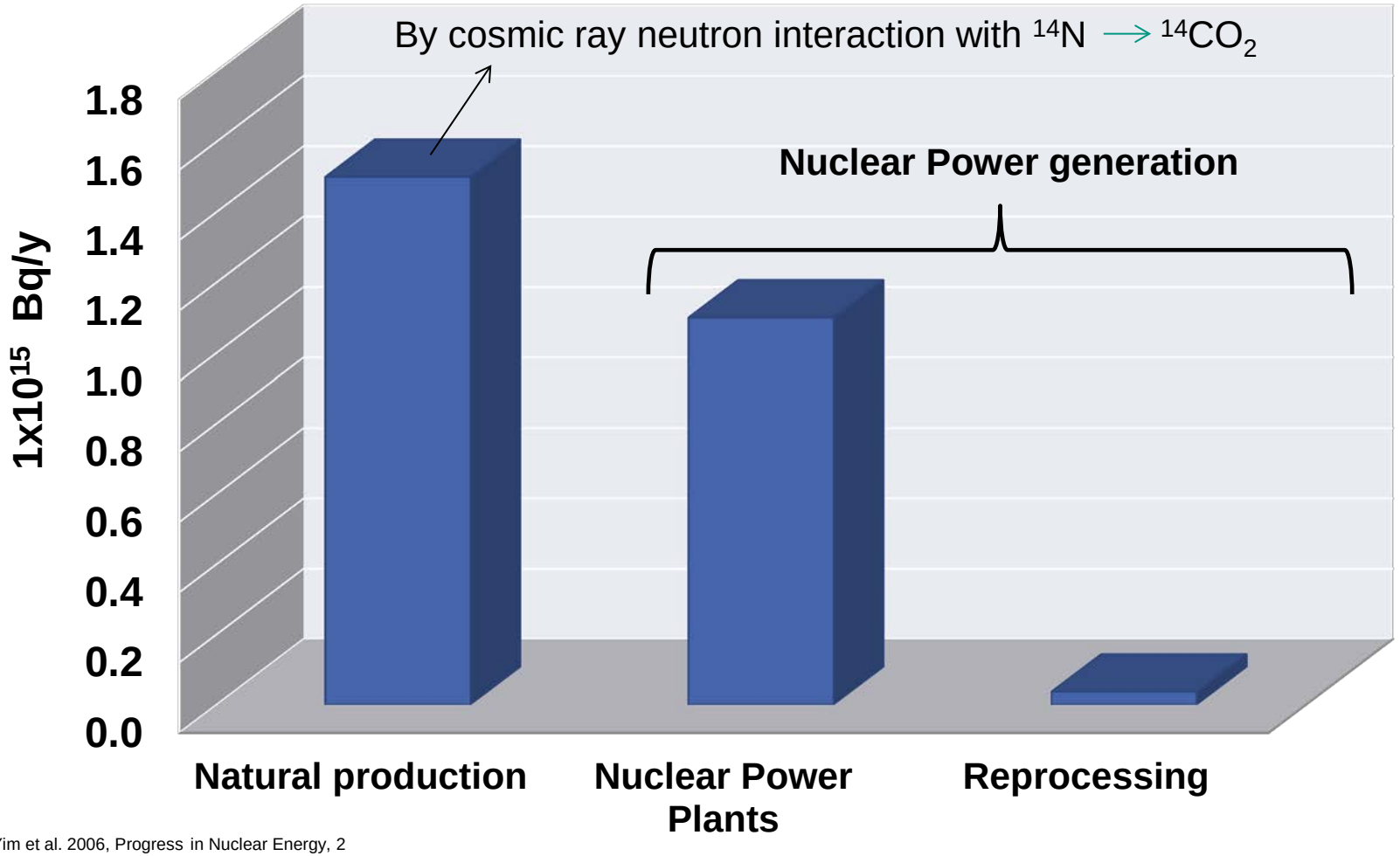
β decay

- Weak beta emitters
- Long half-live
- High isotopic exchange (^{12}C and ^{13}C)
- Incorporation into living organisms

Carbon – 14

Production and release of C-14

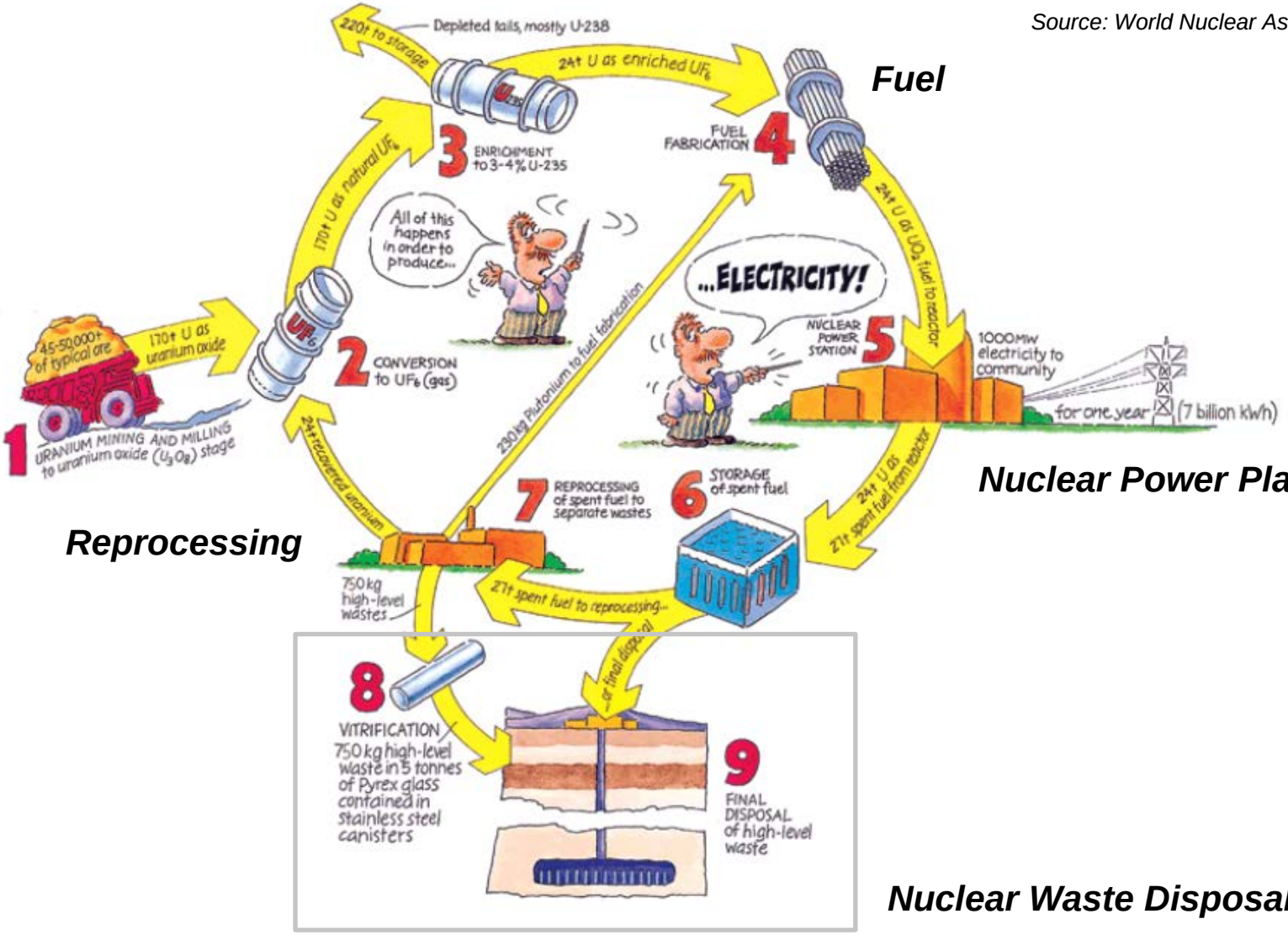
Nuclear weapon testing
(not anymore)



Yim et al. 2006, Progress in Nuclear Energy, 2

Nuclear Power generation

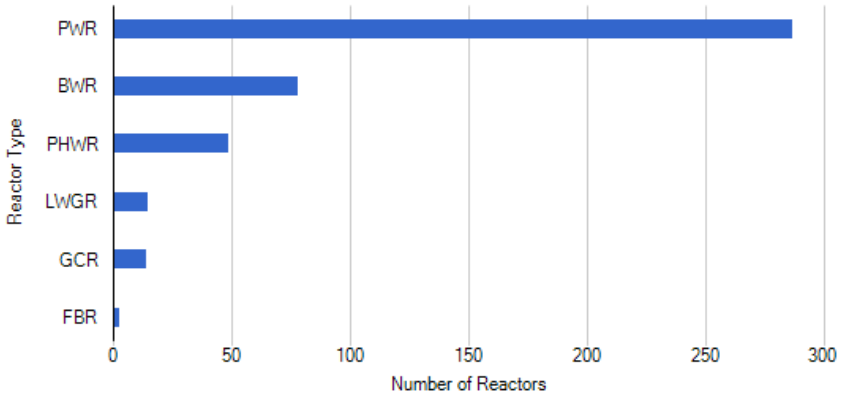
Source: World Nuclear Association



Nuclear Power Plant

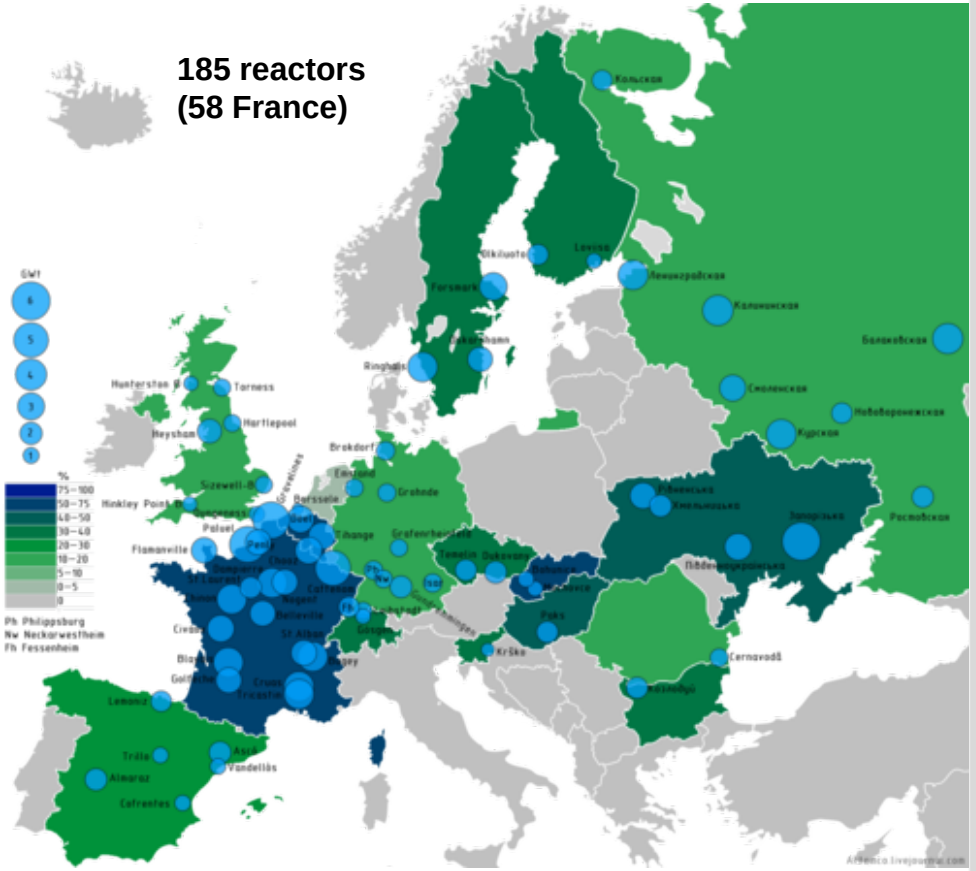
C-14 world inventory

444 reactors in operation*



287 PWR + 78 BWR

Research reactors are not included

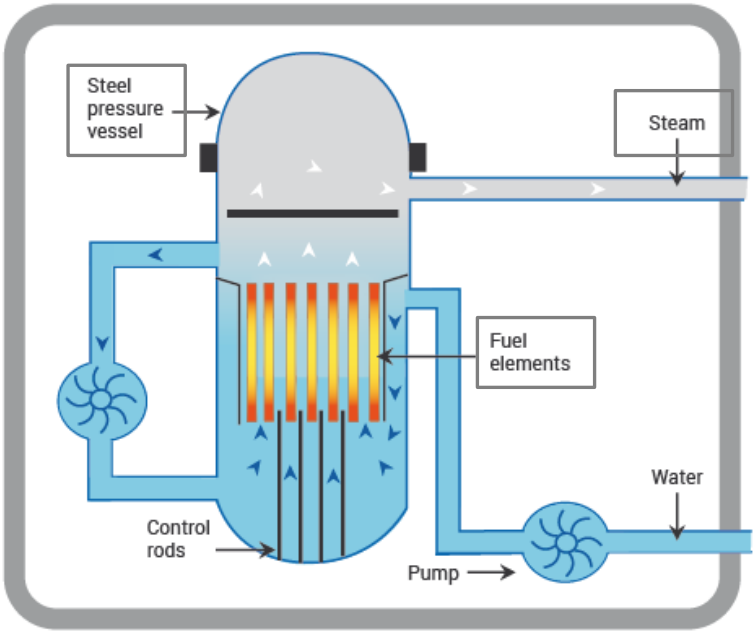


*Data from June 2016 (IAEA)

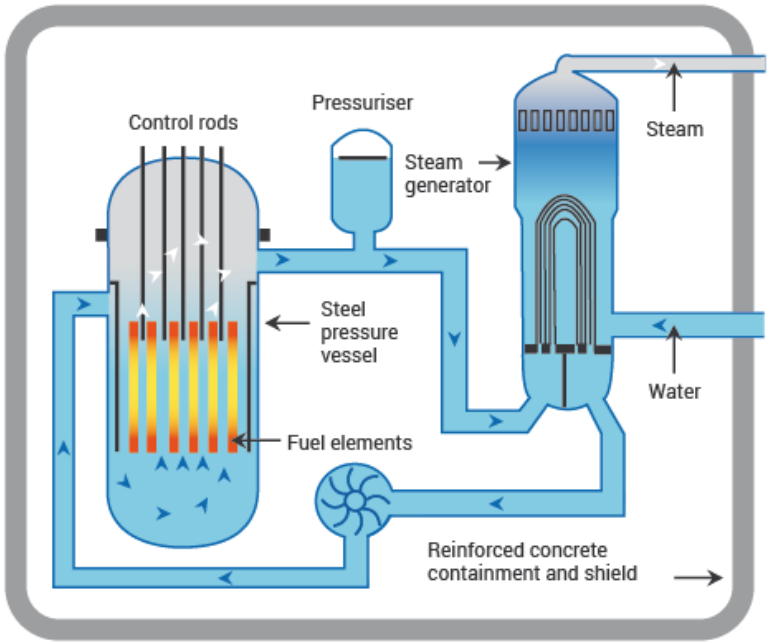
Nuclear Power Plant

Type of Nuclear reactors: Light Water Reactors

A Boiling Water Reactor (BWR)



A Pressurized Water Reactor (PWR)



Moderator = coolant = Water

Slows down the neutrons released from fission

To transfer the heat

Nuclear reactor primary system

Nuclear Power Plant

Type of Nuclear reactors: Light Water Reactors

Table 7
Global estimate of ^{14}C production, by reactor type

Reactor type	Component	Production estimate TBq/GWe-y	% of world generating capacity	Cumulated production to date (to the end of 2003)	
				Estimated cumulative ^{14}C production PBq	Available for release PBq
PWR	Fuel	0.72	65	2.6	
	Coolant	0.30		1.1	1.1
	Zircaloy+hardware[a]	0.38		1.4	
BWR	Fuel	0.73	23	0.9	
	Coolant	0.59		0.8	0.8
	Zircaloy+hardware[a]	0.51		0.7	
PHWR	Fuel	3.76	5	1.1	
	Coolant	0.38		0.1	0.1
	Moderator	27.0		7.6	7.6
Gas cooled	Fuel (Magnox/AGR/HTR)	6.1/1.8/0.17	7	1.0	
	Coolant (")	0.31/0.3/~0		0.06	0.06
	Moderator (")	10.8/3.4/3.1		3.8	
Grand total-reactors worldwide				21.1	9.6

PHWR: fuel includes our proposed value which includes production due to nitrogen impurities in fuel. Gas-cooled, given in the order of (Magnox/AGR/HTR). Values taken from (Liepins and Thomas, 1988) and (Braun et al., 1983).

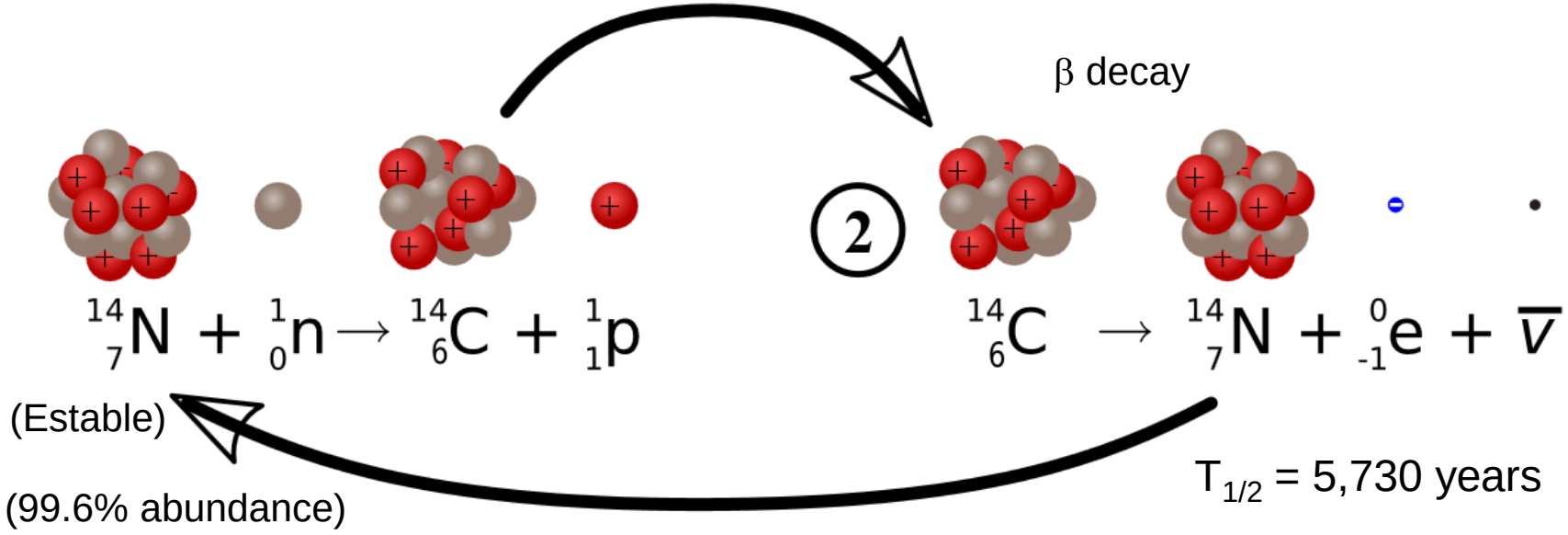
[a] PWR and BWR updated values, based on Van Konynenburg (1994)—see text.

Nuclear Power Plant

Source of C-14

From ^{14}Nitrogen + neutrons

Component or impurity in **fuels** (cladding), **moderators**, **coolants**, **structural hardware** (metals).



Nuclear Power Plant

Source of C-14

From ^{13}Carbon + neutrons

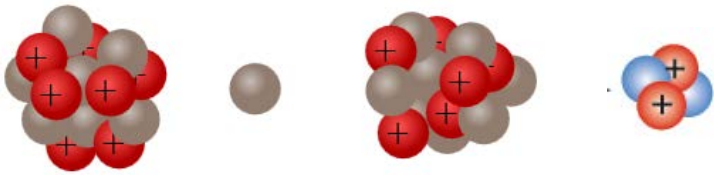
$$^{13}_{8}C + {}^{1}_{0}n \rightarrow {}^{14}_{6}C + \gamma$$

(1.1% abundance)

Graphite moderators

(Not relevant for LW Reactors)

From ^{17}Oxygen + neutrons



$$^{17}_{8}O + {}^{1}_{0}n \rightarrow {}^{14}_{6}C + {}^{2}_{2}\alpha$$

(0.038 % abundance)

Oxide fuels, moderators = coolants (**Water**)

Nuclear Power Plant

Source of C-14

Table 3
Annual normalized ^{14}C production rates for the LWRs

	Item	Production-BWRs		Production-PWRs		Dominant mechanism
		Ci/GWe-a	TBq/GWe-a	Ci/GWe-a	TBq/GWe-a	
Fuel	*Fuel*					
	^{17}O in UO_2	4.0	0.15	3.9	0.14	$^{17}O(n, \alpha)^{14}C$
	^{14}N impurities in UO_2[a]	15.6	0.58	15.4	0.57	$^{14}N(n, p)^{14}C$
	^{14}N impurities in zircaloy and fuel assemblies[b]	13.8	0.51	10.3	0.38	$^{14}N(n, p)^{14}C$
Coolant	*Coolant*[c]					
	^{17}O in H_2O	14.5	0.54	6.0	0.22	$^{17}O(n, \alpha)^{14}C$
	Dissolved N_2-bounding estimates (10–40 ppm)	2.9–11.6	0.11–0.43	1.2–5.0	0.04–0.19	$^{14}N(n, p)^{14}C$
	Total	45–54	1.7–2.0	36–40	1.3–1.5	^{17}O in H_2O

^{14}N impurities zircaloy/UO_2 **BWR**

^{14}N impurities UO_2 **PWR**

Presure

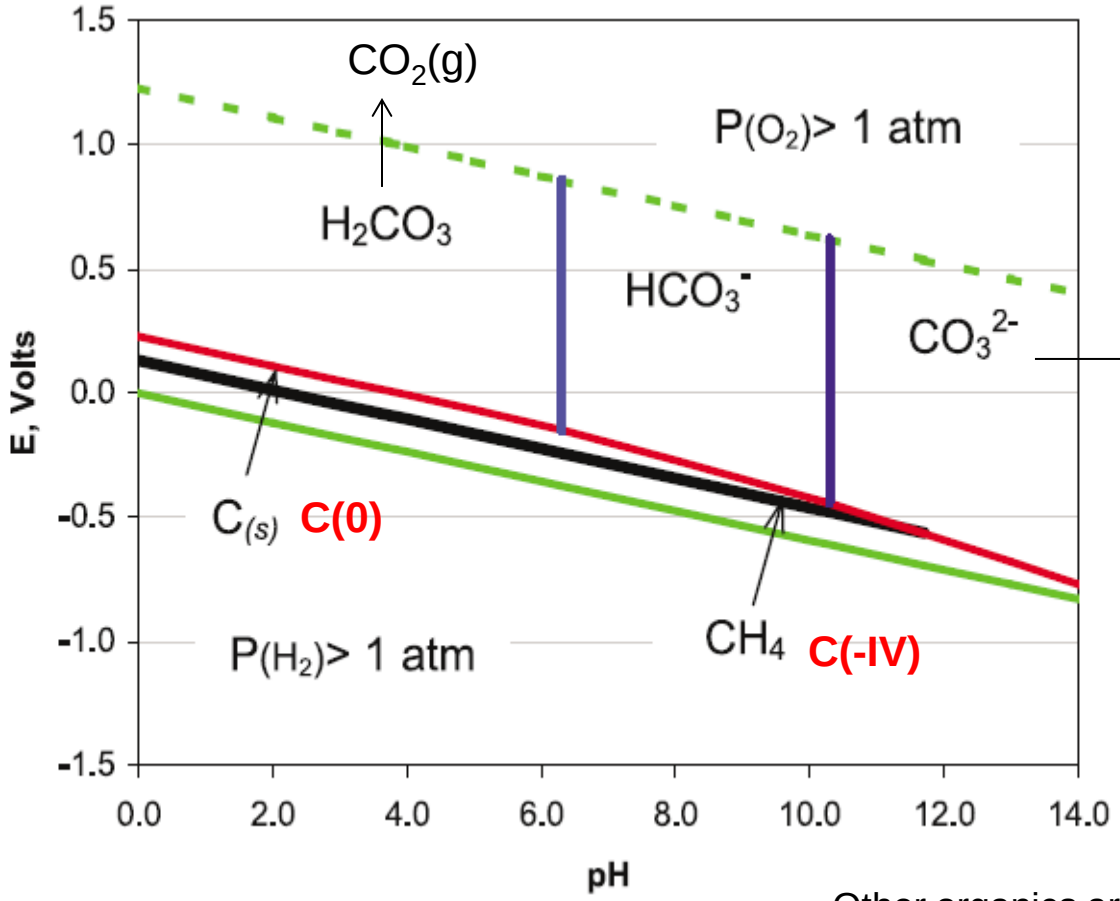
[a] Based on median values of Tables 2.2 and 2.3 in (Bush et al., 1984); normalized for 20 ppm nitrogen impurities in fuel.
[b] Based on calculations by Van Konynenburg (1994) using 25 ppm nitrogen impurities.
[c] Values of (Bonka et al., 1974) (**op. cit.), updated by (Vance et al., 1995).

$^{13}CO_2$ dissolved is negligible

1TBq = 10^{12} Bq

The chemistry of C-14

C-14 chemical system at 25°C



C(+IV)

Kinetics can play a role

Speciation depends on:

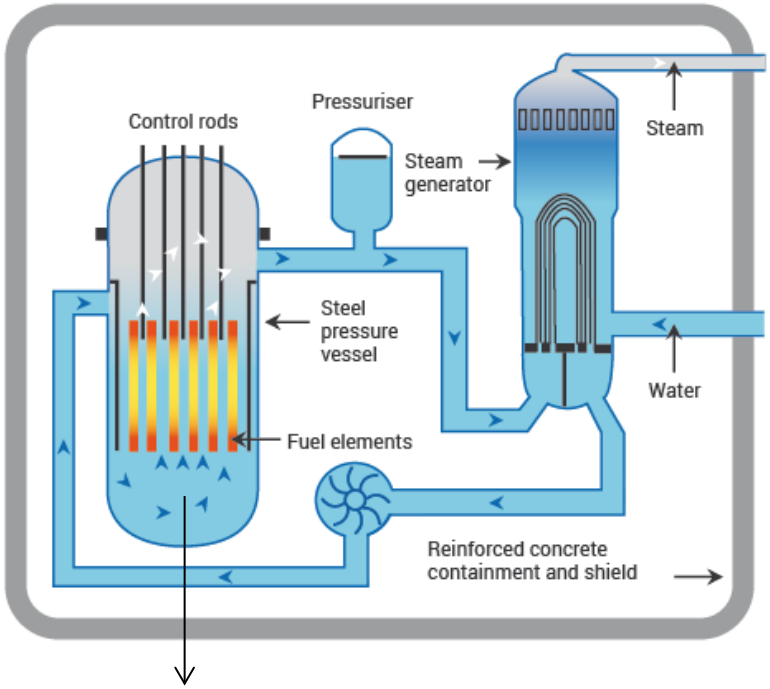
- Eh
- pH
- Temperature

Other organics are not included (mixed oxidation states)

The chemistry of C-14

Chemical conditions in LWR

Pressurized water reactor (PWR)



Reducing conditions (high P ~ 155 bar)

- H_2 **300°C**

Reducing conditions

$H_2 + {}^{14}C\ ? \longrightarrow {}^{14}C$ - organics

${}^{14}CO_2 \longrightarrow {}^{14}C$ (s)
${}^{14}CH_4$ (g)
${}^{14}C$ - organics

organics = formaldehyde + methanol

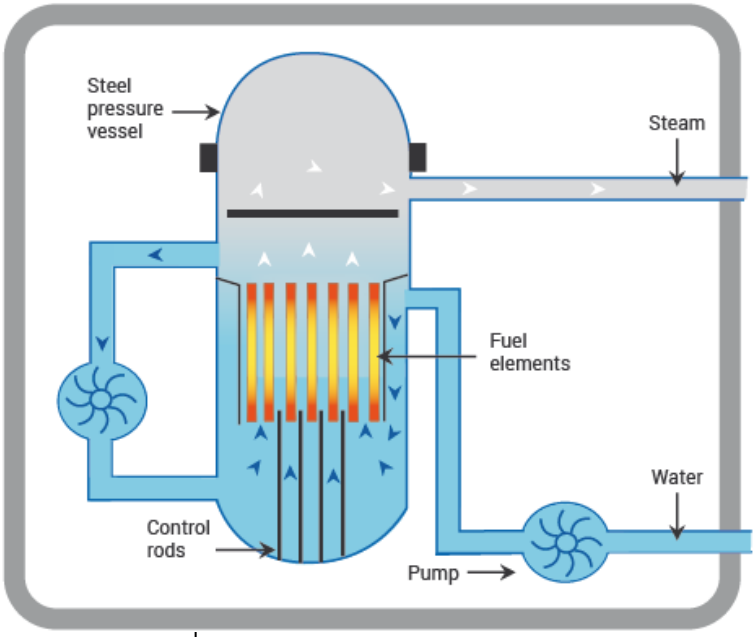
$({}^{14}H_2CO)$ $({}^{14}CH_3OH)$

Coolant system = 58 – 95 % organics

The chemistry of C-14

Chemical conditions in LWR

Boiling water reactor (BWR)



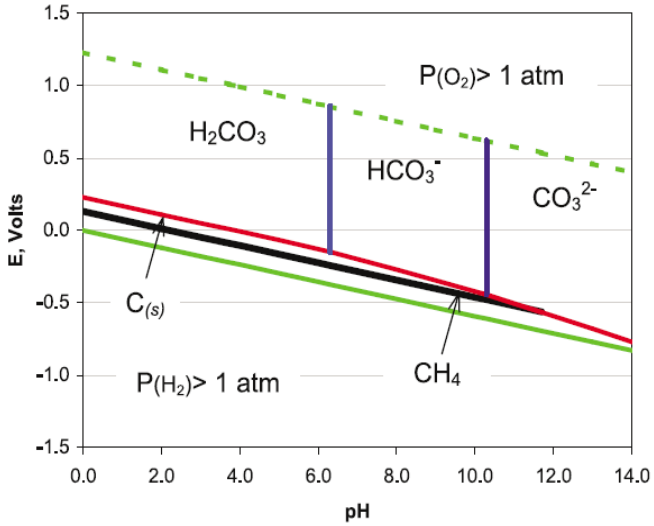
Oxidizing conditions

300°C and 72 bar

Vance et al. 1995, TR-105717. EPRI

Oxidizing conditions

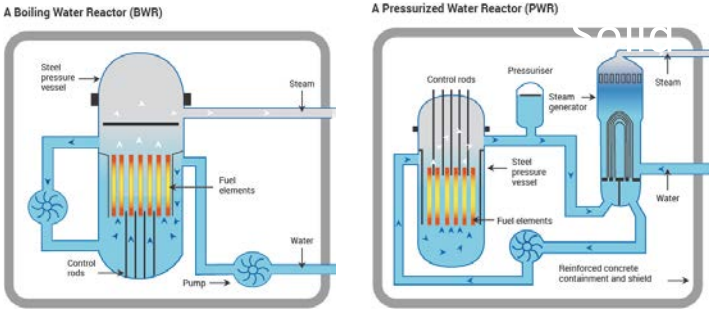
$$^{14}C \longrightarrow {}^{14}CO_2\ (g)$$
$$H^{14}CO_3^-$$



Coolant system = HCO_3^-

The chemistry of C-14

Chemical conditions in LWR and forms of waste



Gas production

$^{14}CO_2$
$^{14}CH_4$,…

Solid phase

Spent Fuel Zircaloy — **Structural fuel material**

Steel (metals)

Aqueous (coolant)

$H^{14}CO_3^-$
^{14}C –organics (colloids)

Treatment in the NPP

< 3 x 10^{11} Bq/y
(3 order of magnitude lower than natural background)

Resins (ion exchange)
$H^{14}CO_3^-$
^{14}C –organics (colloids)

Yim et al. 2006, Progress in Nuclear Energy, 2

Form of waste in LLW

Initial inventory of ^{14}C

Table 6
Distribution of ^{14}C in LWRs

Waste form description (as stated in Manifest)	Distribution (%)
Ion Exchange Resins	48.8
Irradiated Hardware	24.1
Mixed DAW	13.6
Solidified Liquids	4.4
Filter Media	3.6
Cartridge Filters	2.7
Solid Non-combustibles	1.2
Incinerator Ash	1.2
Air Filters	0.15
Biological Wastes	0.15
Cement	7.2
Sorbent	
None	
Total	99.9
Class	
A	31.3
B	15.6
C	53.1

Dry radioactive waste: plastic, textiles and cellulose, in the form of protective clothing, rags, paper etc.

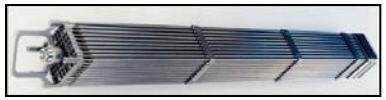
Reactor coolant Cleanup filters.

(Recently increase due to the use of **sub-micron size filters**).

Yim et al. 2006, Progress in Nuclear Energy, 2

Radioactive waste

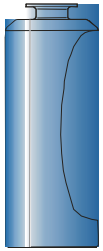
Irradiated Nuclear fuel



Intermediate storage

Repository for **heat generating** radioactive waste

Waste from reprocessing (i.e vitrified)

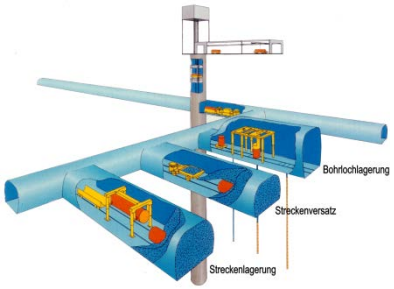


(NPP operational waste and decommissioning)

Intermediate storage

Repository for radioactive waste with **negligible heat generation**

Final disposal

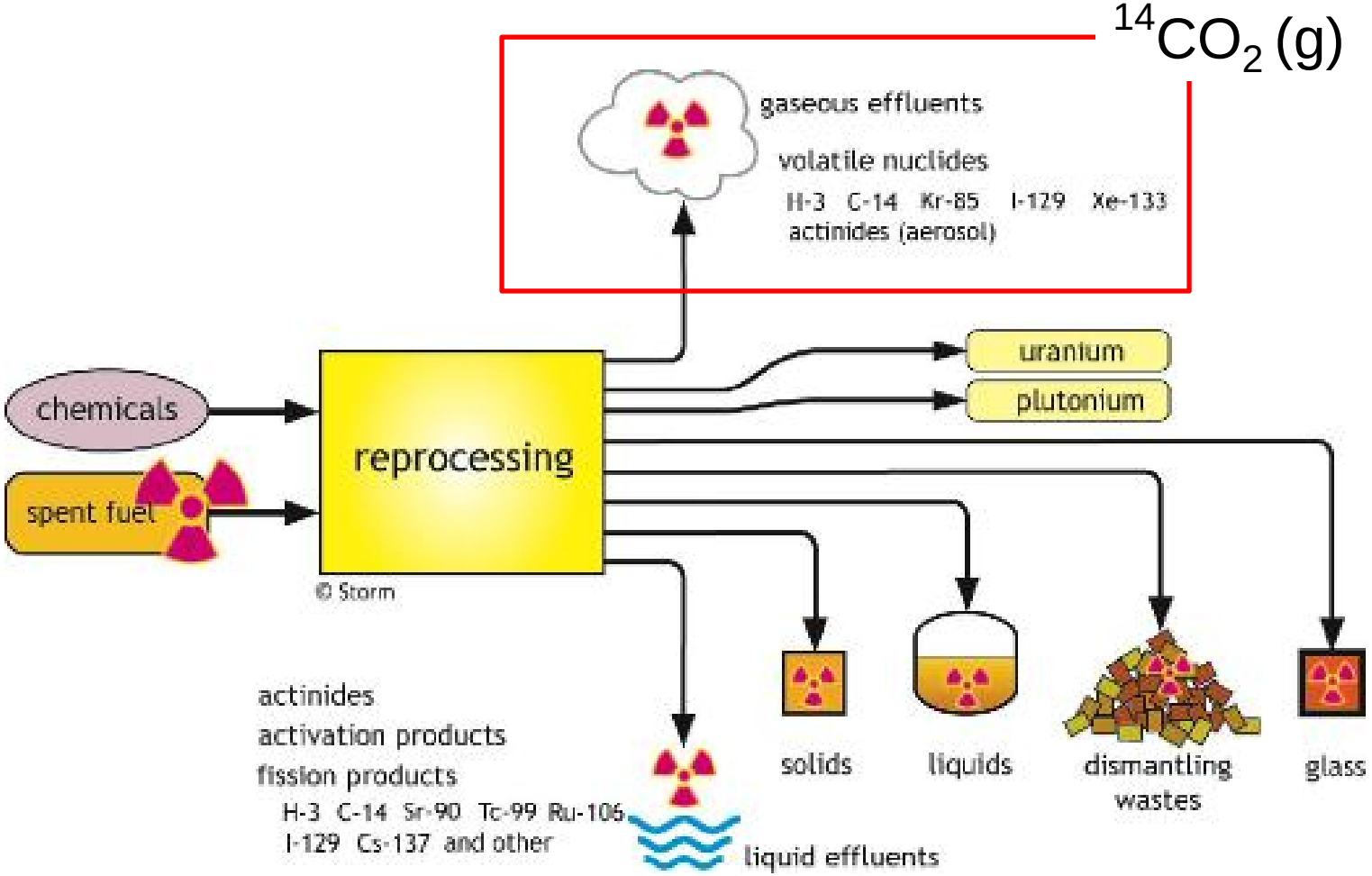


Heat generating radioactive waste

Negligible heat generating waste

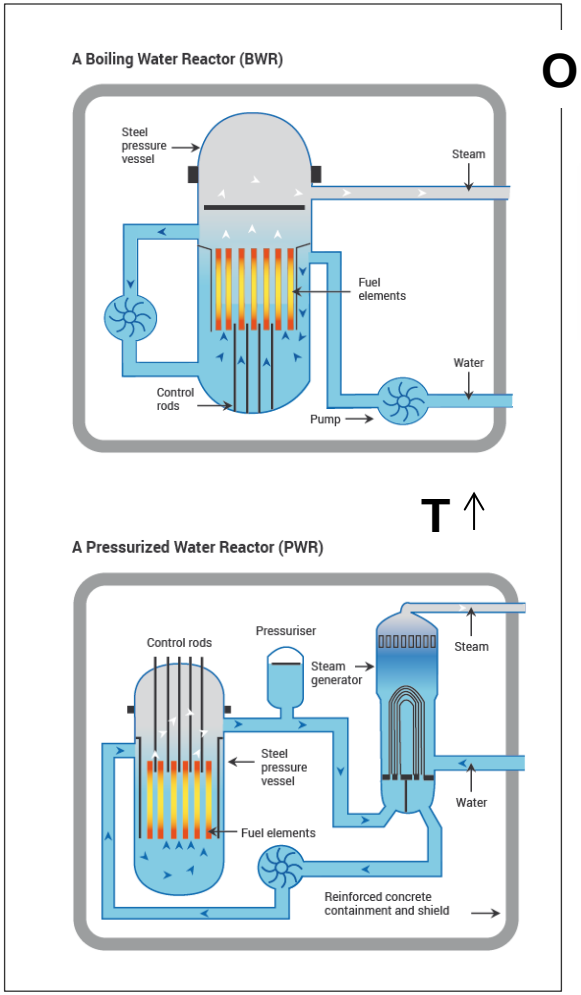
Radioactive waste

Reprocessing

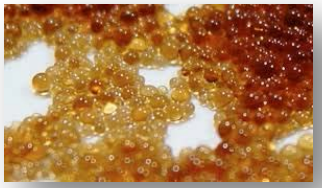


Intermediate storage

LLW



Operational waste (effluent treatment, circuit, etc)



Resins

T ↓

Chemical transformation

Temperature
Redox conditions (O_2)
Microbial activity
Degradation
Contact with chemicals

$H^{14}CO_3^-$

^{14}C - organics

Intermediate storage

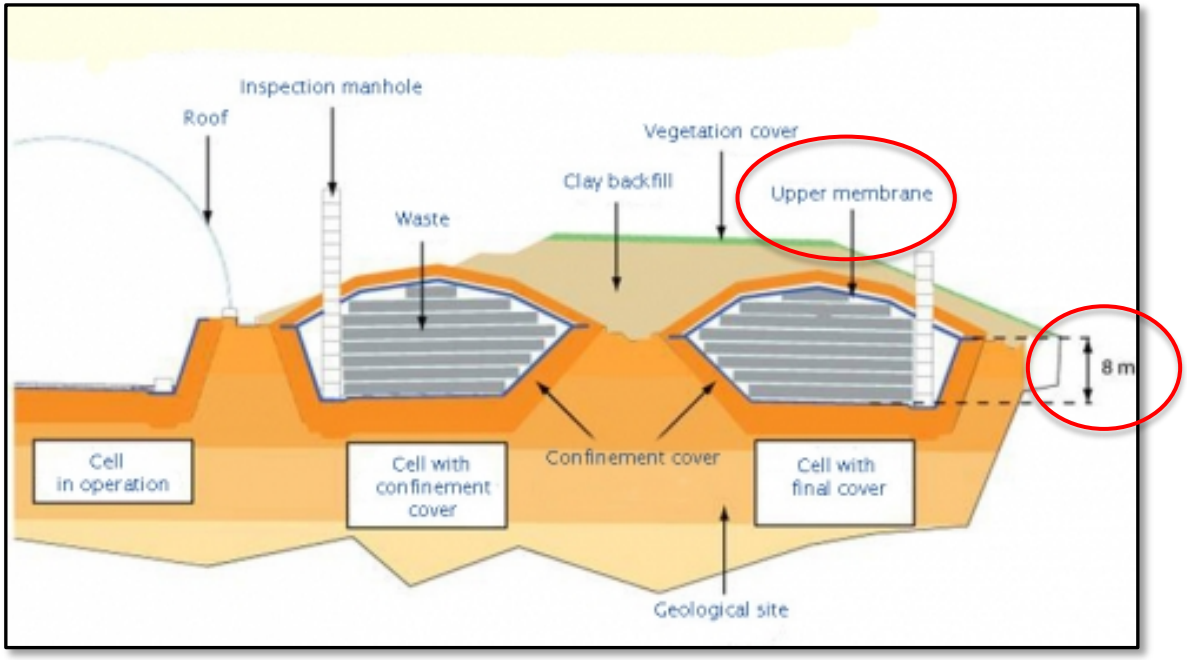
HCO_3^-, C(s), ?

^{14}C - organics

$^{14}CO_2(g)$

Final storage

LLW - near surface disposal at ground level



Schematic diagram of a disposal cell (ANDRA-France)

Final storage

LLW - near surface disposal at ground level

LLW Drigg, Cumbria (NDA-UK)

LLW-ILW El Cabril (ENRESA-Spain)

LLW Rokkasho-Mura (JNFL-Japan)

LLW Texas Compact (WCS-USA)

Final disposal

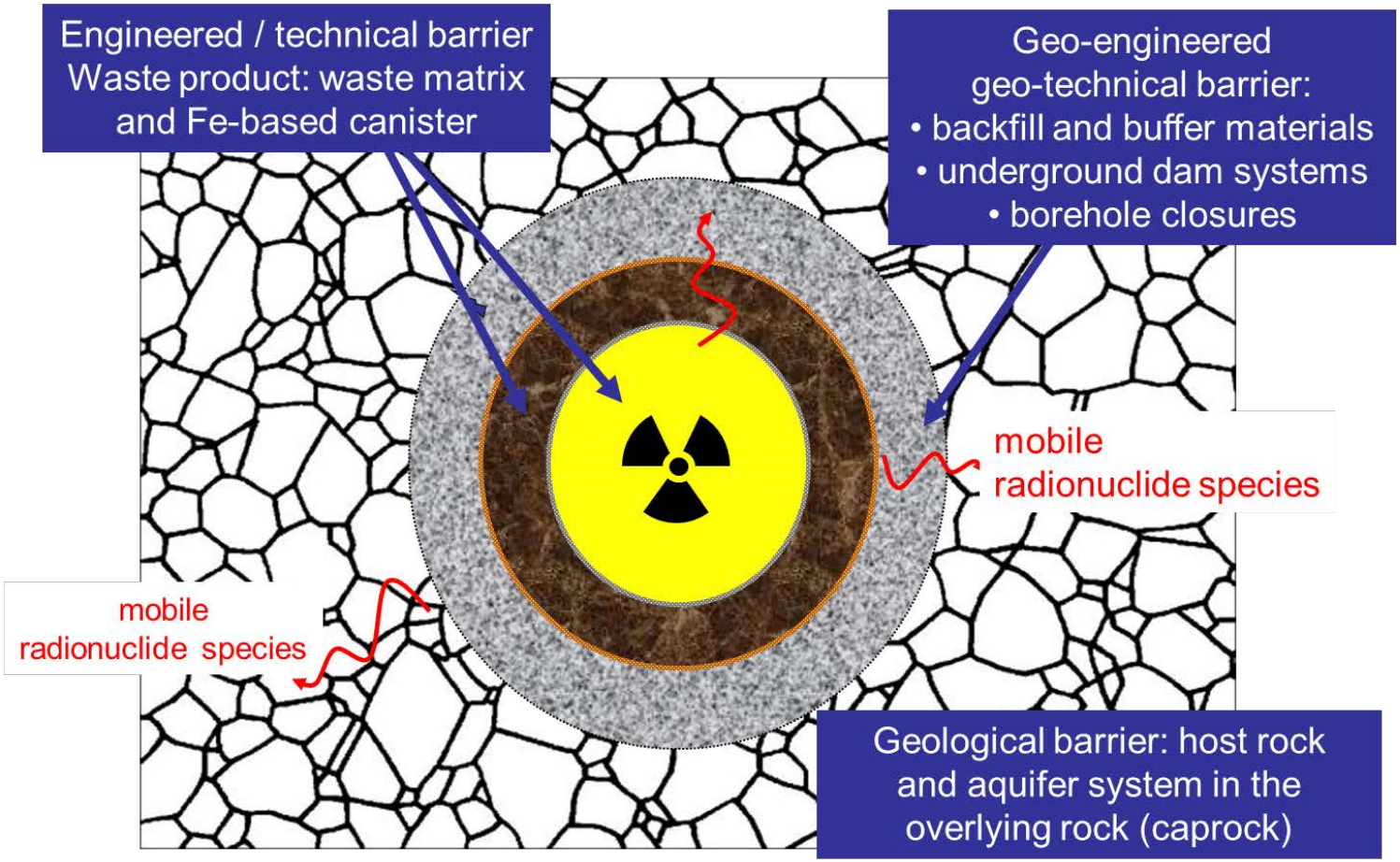
LLW/ILW - near surface disposal below ground level

short-lived radioactive waste

SFR, Forsmark (SKB-Sweden)

Final disposal

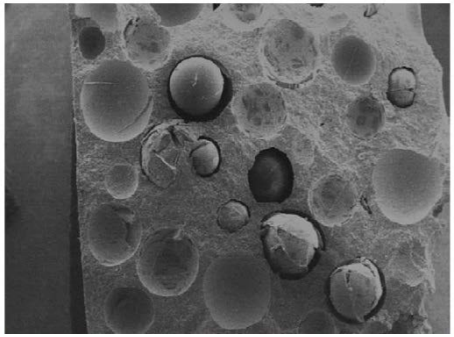
Multibarrier system



Multibarrier system

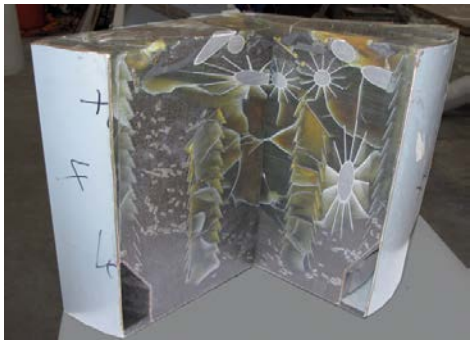
Waste matrix and waste container

Cement matrix



High pH porewater (> 12)
Low porosity, permeability

Synthetic polymers

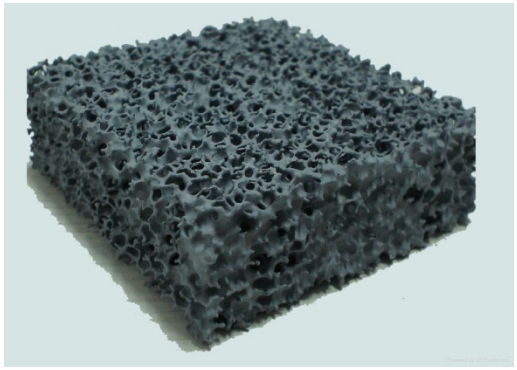


Organic compounds
Polyethylene, bitumen

Glassy carbon

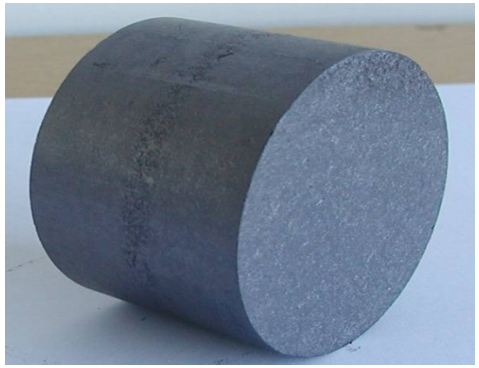
Low porosity, permeability
High temperature stability

Silicon carbide matrix



Properties close to diamond
(expensive)

Graphite matrix



(Very resistant to attack by
natural environment)

Waste container

Highly durable waste container
(metallic, High integry containers)

Management of ^{14}C in LLW

Spent Ion exchange resins

Waste (NPP) | **Interim storage** | **Final disposal**

Resins with ^{14}C

$H^{14}CO_3^-$

^{14}C - organics

Change enviroment

Degradation of the resins with ^{14}C (SIER)

Microbial actions (gas production)
Groundwater infiltration
....

Treatment of the resins

Separation Resin / ^{14}C

^{14}C
(solid matrix)

Management of ^{14}C in LLW

Irradiated steel

Waste (NPP) | **Interim storage** | **Final disposal**

Steel

NPP structures
Nuclear fuel assemblies
- C-steel
- Stainless steel
- Ni-alloys

(Decommissioning)

Cemented waste

Corrosion

?

Release of ^{14}C by corrosion

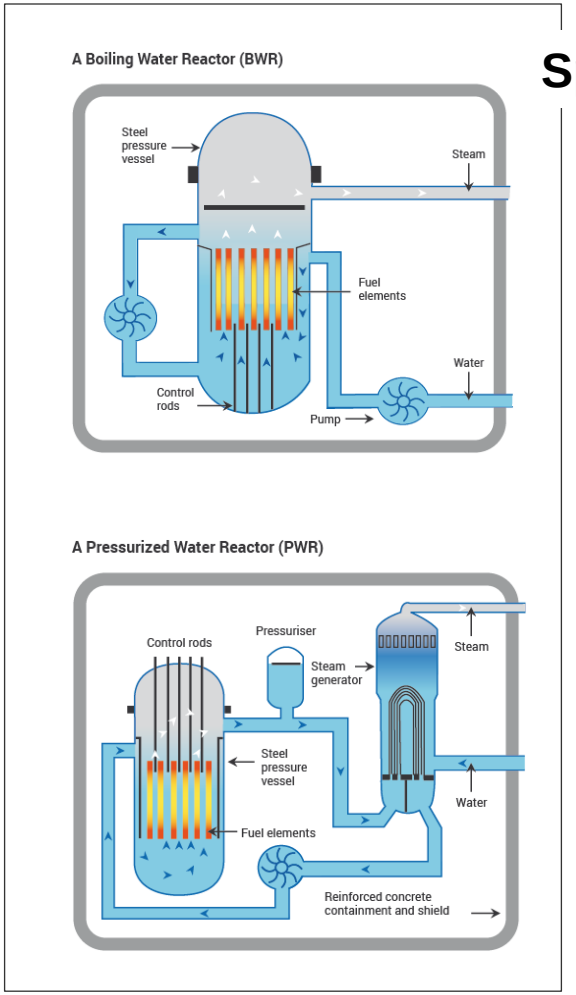
Aerobic
Anaerobic conditions
....

HCO_3^-, alcohols?

Carbides ($M_{n-1}C_{2*x}$) (covalent, ionic) + H_2O $\longrightarrow$ CH_4 + hydrocarbons

Intermediate storage

HLW including Spent Fuel



Spent Fuel

UO_2 pellets

~95 wt% UO_2 matrix

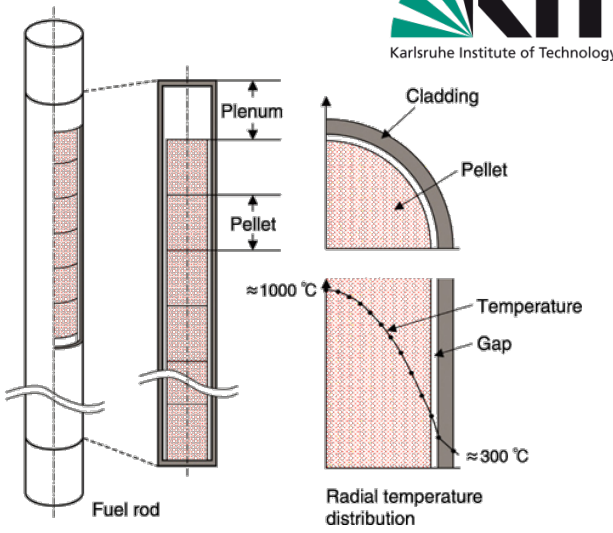
↓

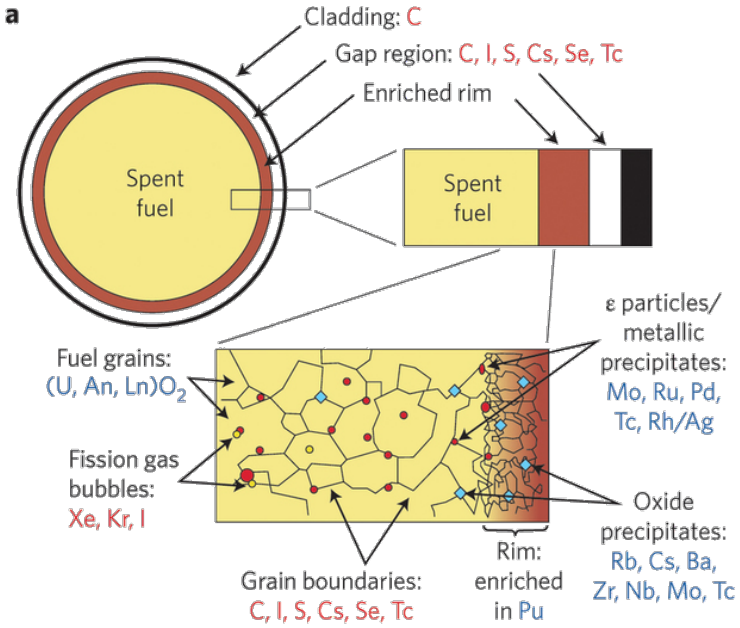
^{14}N impurities

$U^{17}O_2$ matrix

↓ + *n*

^{14}C (especiation?)

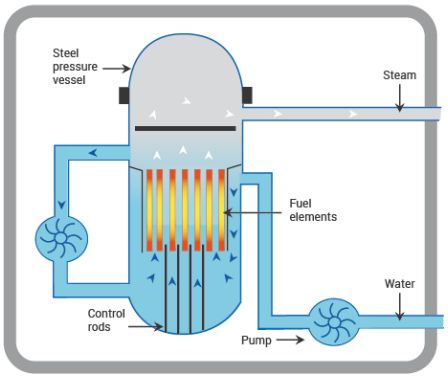




Intermediate storage

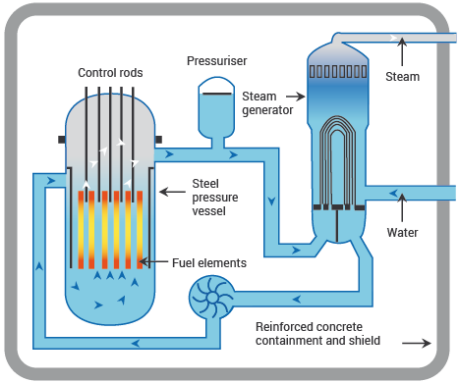
HLW including Spent Fuel

A Boiling Water Reactor (BWR)



T ↑

A Pressurized Water Reactor (PWR)



Spent Fuel

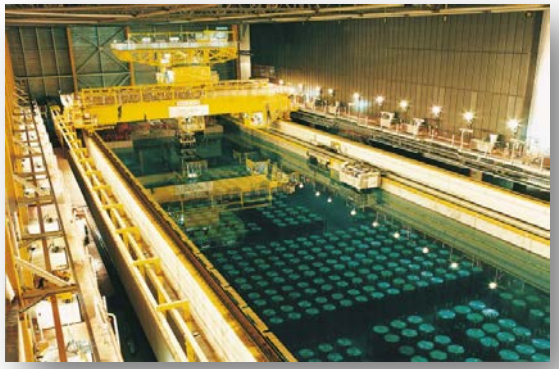
$H^{14}CO_3^-$

^{14}C (especiation?)

Intermediate storage

(dry cask)

(pools)



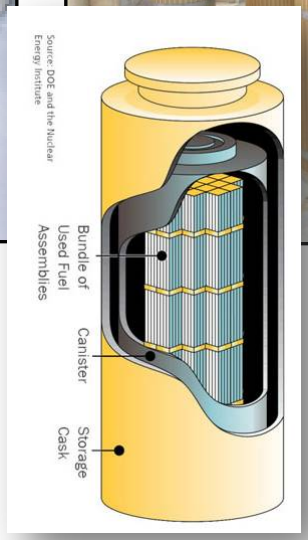
Pools are monitored and cleaned (filters)

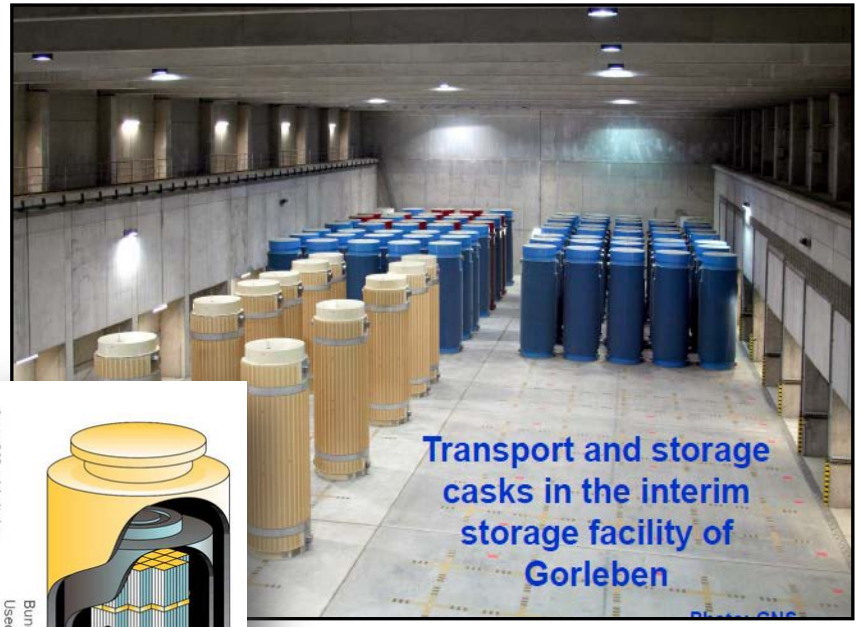
Intermediate storage

HLW including Spent Fuel

(dry cask)

Zwilag´s ZZL (Switzerland)





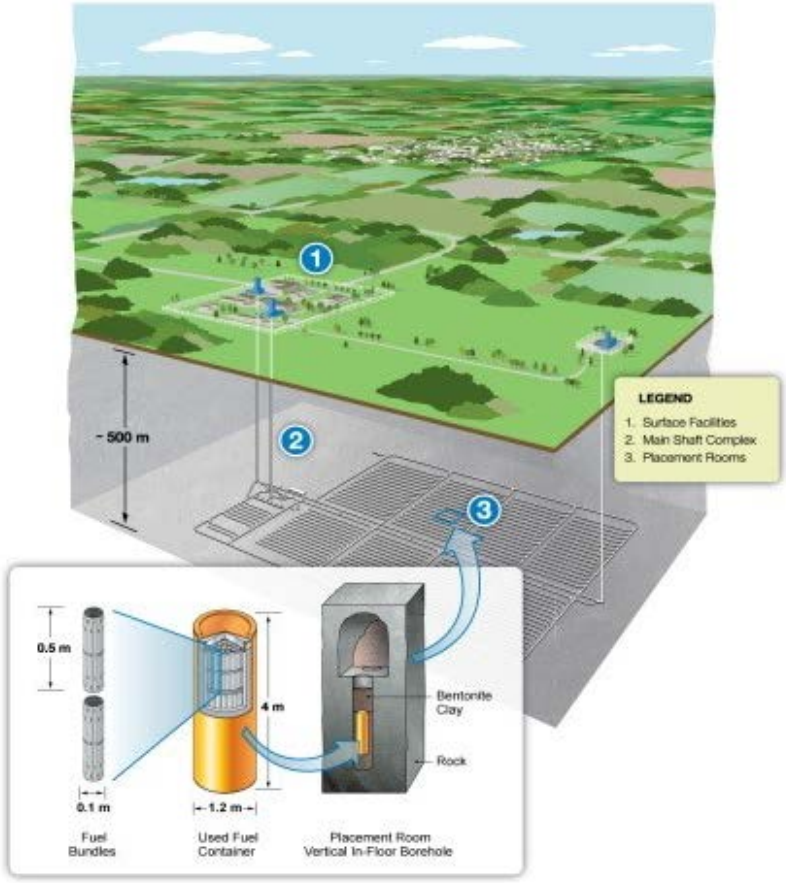
Gorleben (Germany)

Final disposal

HLW including Spent Fuel

Isolation is provided by a combination of engineered and natural barriers **(rock, salt, clay)** and no obligation to actively maintain the facility is passed on to future generations.

A multi-barrier concept, with the waste packaging, the engineered repository and the geology all providing barriers to prevent the radionuclides from **reaching humans and the environment.**

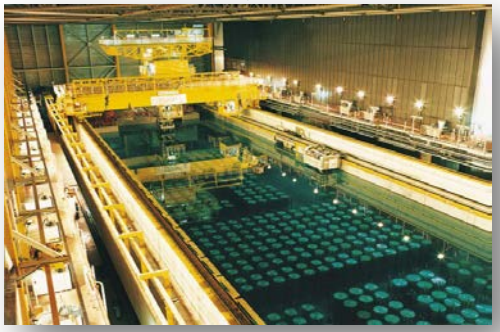


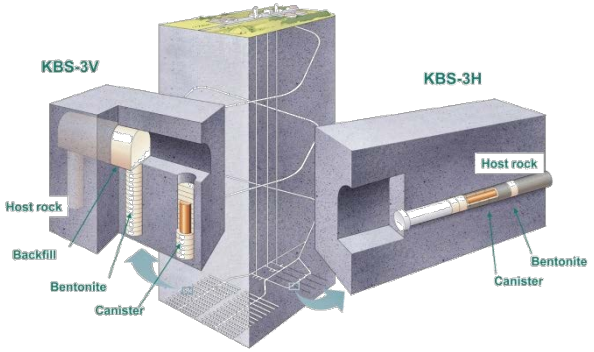
Management of ^{14}C in HLW

Spent Fuel

Waste (NPP)	Interim storage	Final disposal

Spent Fuel (including zircaloy)





Corrosion

Release from SF?
(Matrix dissolution, IRF)

Release of ^{14}C by corrosion

Aerobic
Anaerobic conditions
….

Dose of ^{14}C in spent fuel very small compared with other radionuclides

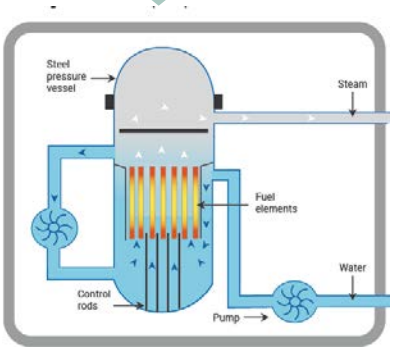
Presentation E. Gonzalez-Robles

What have we learnt?

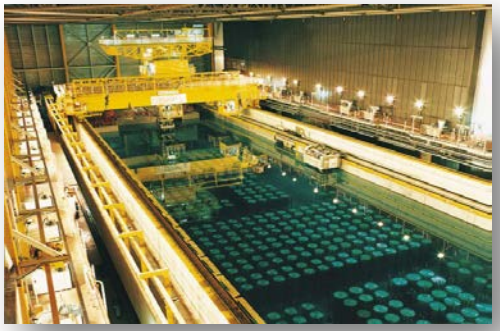
- **Production of C-14**
  - C-14 in the nature
  - C-14 from human activities (Nuclear Energy production)
- **Source of C-14 in Nuclear Power generation (LWR)**
- **Transformation of C-14 during storage and disposal**

What have we learnt?

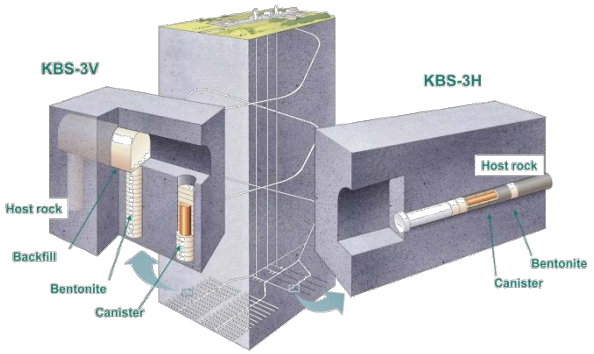
Nuclear PP



Interim storage



Final disposal



Source of ^{14}C

Spent Fuel
Metallic Structures
Ion exchange resins

$H^{14}CO_3^-$ (inorganic)

^{14}C - organics

Transformation

Temperature
Redox conditions (O_2)
Microbial activity
Degradation
Contact with chemicals
Corrosion

^{14}C waste

$H^{14}CO_3^-$ (inorganic)

^{14}C - organics

$^{14}CO_2$ (g)

Safety Analysis

Presentation V. Metz tomorrow

^{14}C is a long lived radionuclide

*The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) under grant agreement 604779 (**CAST project**)*

http://www.projectcast.eu/

Karlsruhe Institute of Technology

Production of C-14 in fuel elements of light water reactors – introduction to calculation methods and related NEA databases

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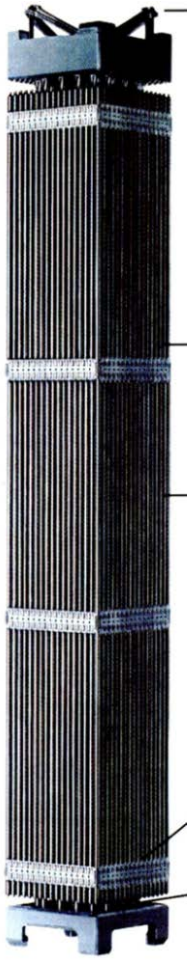
^{14}C Production

- Physical formation of ^{14}C in fuel assemblies by
  - neutron capture reactions
  - ternary fission in the fuel

during reactor operation

$^{14}_{7}\mathrm{N}(\mathrm{n},\mathrm{p})^{14}_{6}\mathrm{C}$	$^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n} \rightarrow \left[^{15}_{7}\mathrm{N}\right]^{*} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p}$
$^{17}_{8}\mathrm{O}(\mathrm{n},\alpha)^{14}_{6}\mathrm{C}$	$^{17}_{8}\mathrm{O} + {}^{1}_{0}\mathrm{n} \rightarrow [^{18}_{8}\mathrm{O}]^{*} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{4}_{2}\mathrm{He}$
$^{13}_{6}\mathrm{C}(\mathrm{n},\gamma)^{14}_{6}\mathrm{C}$	$^{13}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n} \rightarrow [^{14}_{6}\mathrm{C}]^{*} \rightarrow {}^{14}_{6}\mathrm{C} + \gamma$

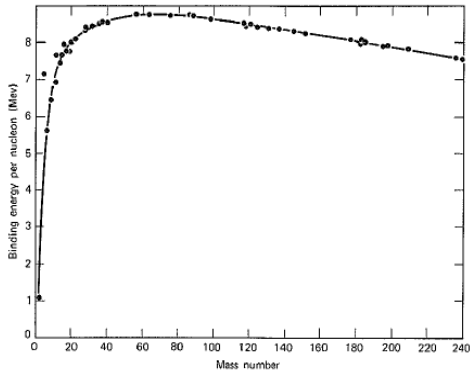
ternary fission in LWR fuel	1.7×10^{-6} per thermal ^{235}U fission [1] 1.8×10^{-6} per thermal ^{239}Pu fission [1]



[[1] Neeb (1997) The radiochemistry of nuclear power plants with light water reactors. de Gruyter, Berlin. // Nucl. Engineering International (2003) vol. 48, no. 590, Fuel design data.

Bethe Weizsaecker- binding energy

- The components of the total energy bindings:
  - Nuclear forces
  - surface effect
  - Coulomb effect
  - Neutron excess
  - Parity of neutron/proton



$$B = \sum_{i=1}^{5} B_i$$

$$B = \Delta m c^2$$

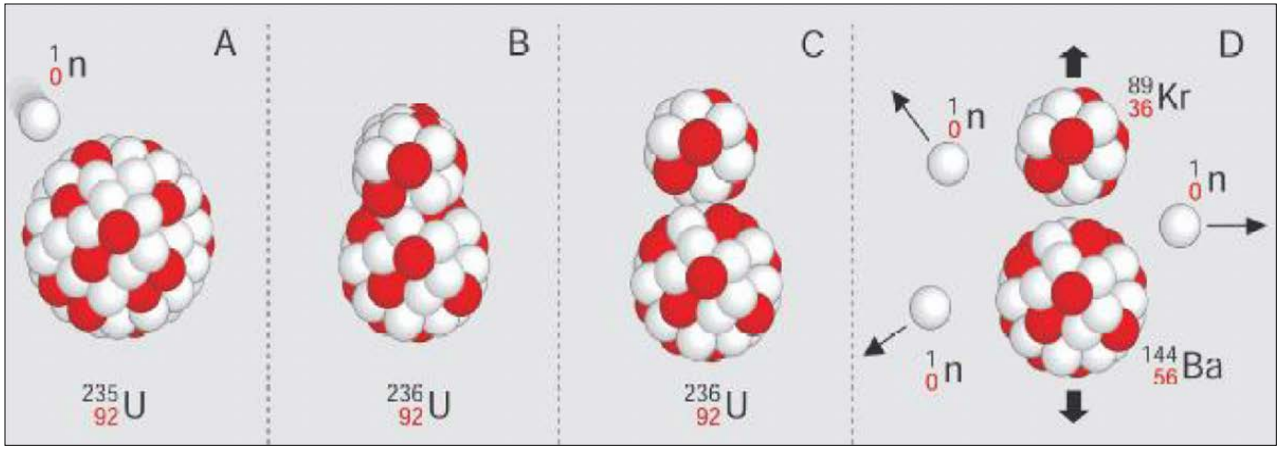
- An expression for the differences between two adjusted Isotopes A and A+1
  - (derivative of the Bethe Weizsaecker Formula-central difference)
  - Basis for the Liquid drop model

$$\Delta(A+1) - \Delta A = a_v - \frac{2}{3} a_s (A+1/2)^{-1/3} + \frac{1}{3} a_c Z^2 (A+1/2)^{-4/3} - a_e \left[1 - \left(\frac{2Z}{A+1/2} \right)^2 \right]$$

$$\pm c(A+1/2)^{-3/4} \quad (+ : A\ odd \quad - : A\ even)$$

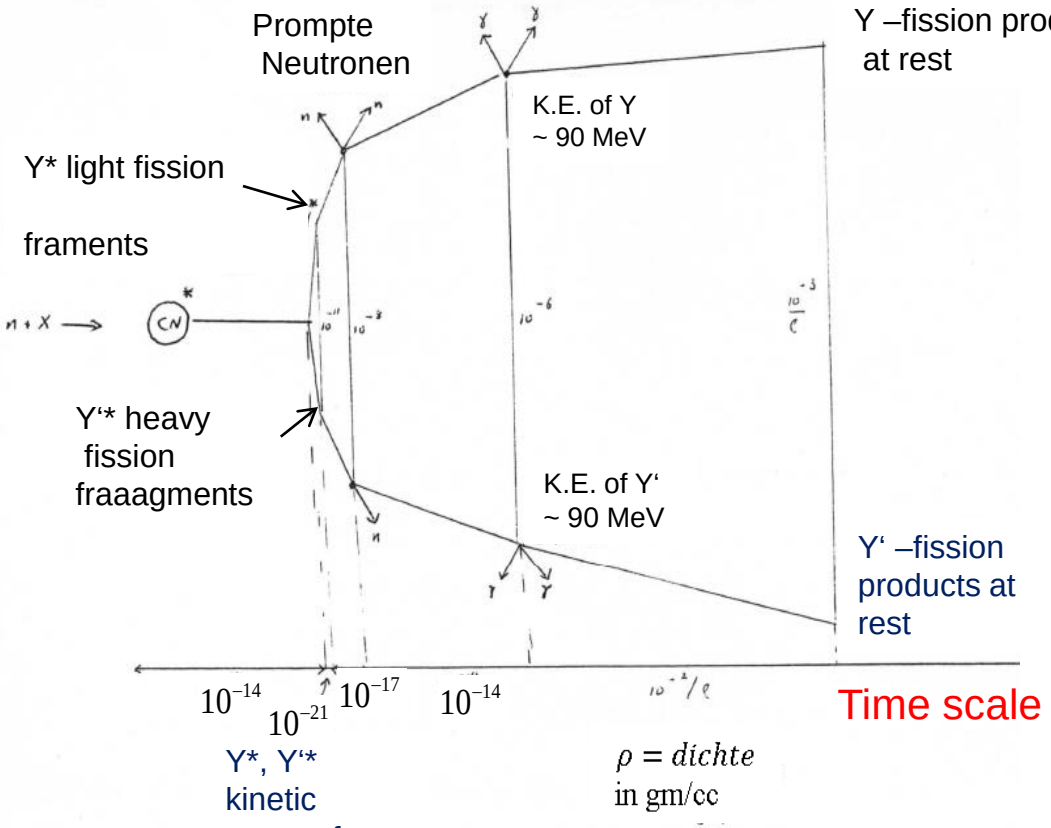
The fission process

Nuclear fission

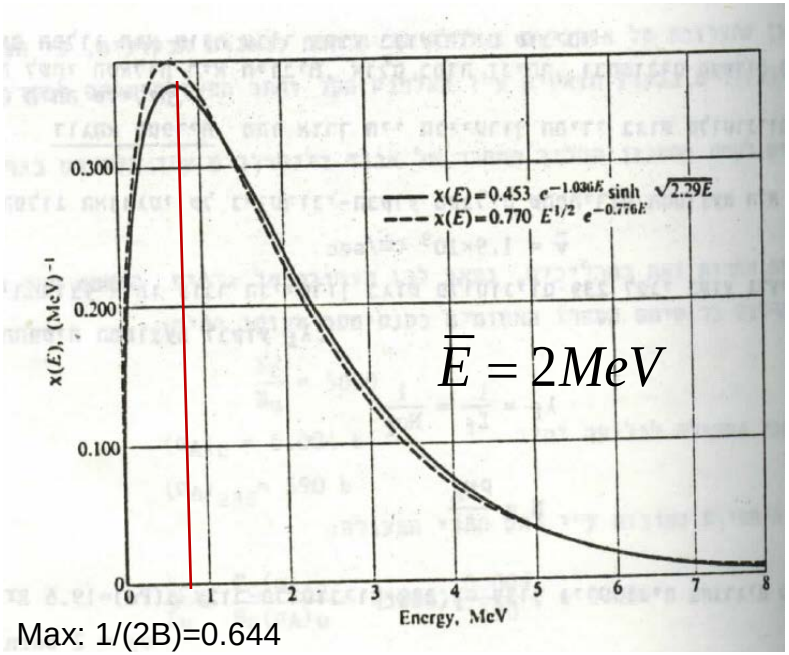


- The fission process is explained by the liquid drop model:
  - A: A drop is round due to the attractive force of the molecules.
  - B: External force leads to deformation
  - C: the force can be large enough to create two new attached drops. The surface energy is larger than the volume energy that held the original drop.
  - D: the new two drops get a spherical shape (also through further decay)

The fission process



The fission spectrum

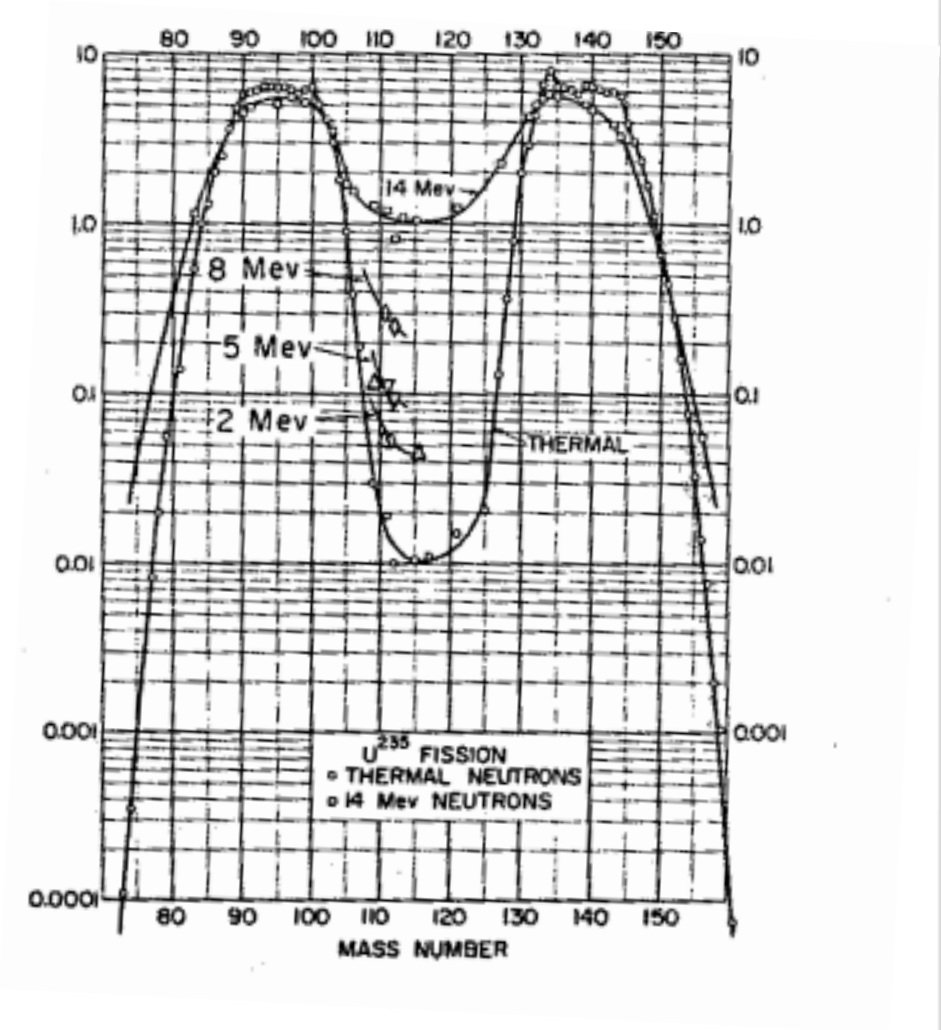


Max: 1/(2B)=0.644

Fission-yield Distribution

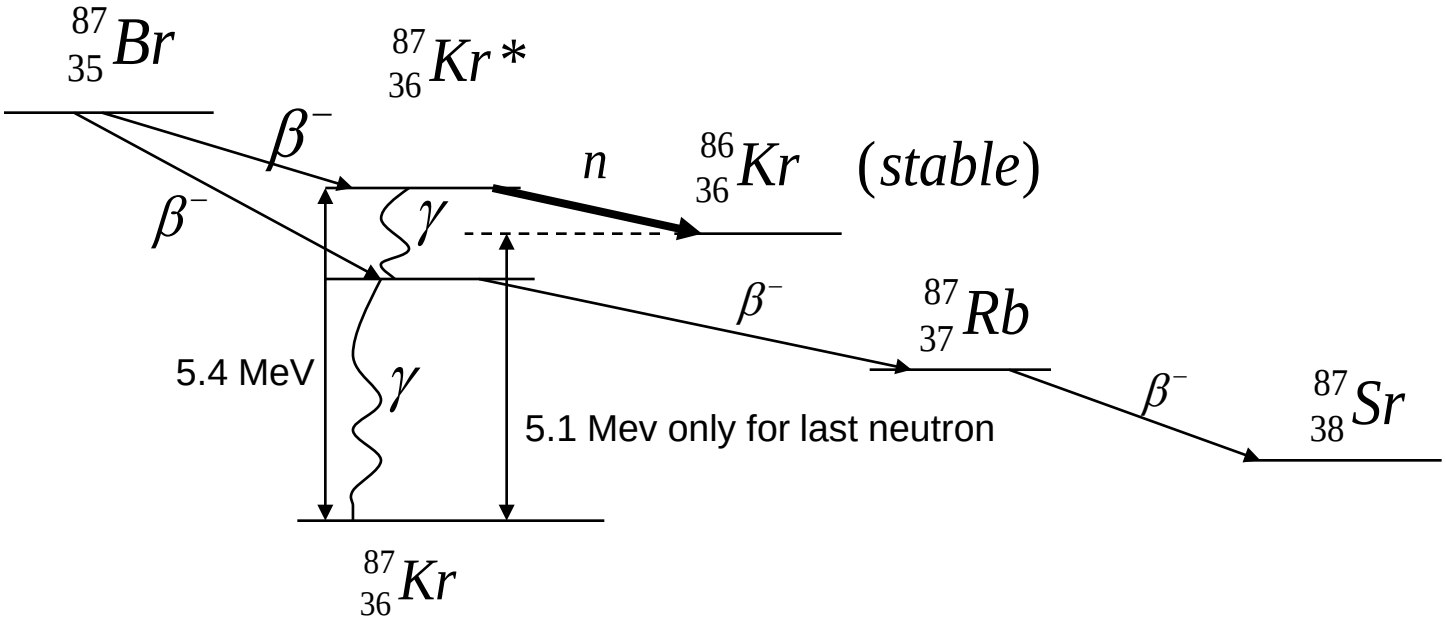
- High energy → Symmetrical distribution

- Corrections are ongoing
  - based on new models
  - (i.e. GEF)



An example for fission product yields and decay : delayed neutrons

$$^{87}_{35}Br \xrightarrow{\beta^- (T_{1/2}=55\text{sec})} {}^{87}_{36}Kr^* \xrightarrow{n} {}^{86}_{36}Kr$$



- $$^{137}_{53}I \xrightarrow{\beta^- (T_{1/2}=22\text{sec})} {}^{137}_{54}Xe^* \xrightarrow{n} {}^{136}_{54}Xe$$

Magic number 82 is obtained

Radioactive Decay I

- Radioactive decay is a spontaneous disintegration of a nucleus. It decays because the nucleus is in a unstable state.
- Law: The probability per unit time of a nucleus to disintegrate is marked by the letter λ and it is time independent. Therefore it is called: Decay constant.
- Remark: The excited state of the nucleus can be expressed in energy term by the Energy Level “Width”
- In this way the Heisenberg uncertainty rule is pronounced.

$$\Gamma = \hbar\lambda \qquad where \;\; \hbar = h/2\pi = 6.62559 * 10^{-17} \; / (2\pi) \; J \cdot \sec$$

$$\Delta t \Delta E \approx h \qquad \Delta E \equiv \Gamma \qquad \Delta E = \frac{\hbar}{\Delta t}$$

Radioactive Decay II: Half Life time

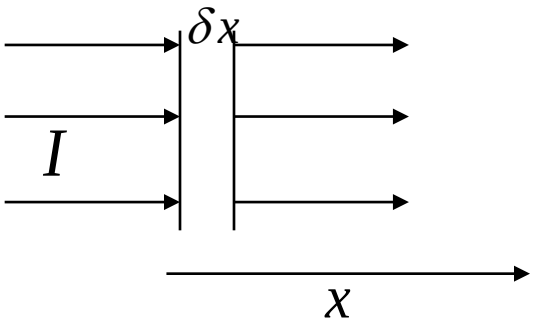
- The uncertainty in time indicates that the full decay time cannot be assessed.
- This calls for the expression: Half Life time

The decay rate per unit time is defined as: $$-\frac{dn(t)}{dt} = \lambda n(t)$$

with the solution: $$n(t) = n_0(t)e^{-\lambda t} \qquad n(0) = n_0$$

We define as half life: $$\frac{n(t)}{n_0} = 0.5 = e^{-\lambda t} \rightarrow \ln 2 = \lambda \rightarrow t = T_{1/2} = \frac{\ln 2}{\lambda}$$

Cross sections : Definition



- Thin target : N (material density (nucleus/cc)
- n: neutron density
- v: neutron velocity
- mono-energetic neutrons
- proportionality constant.
- units: barns (b)=10-24 cm2,
- reaction probability per unit path length
  units: cm-1

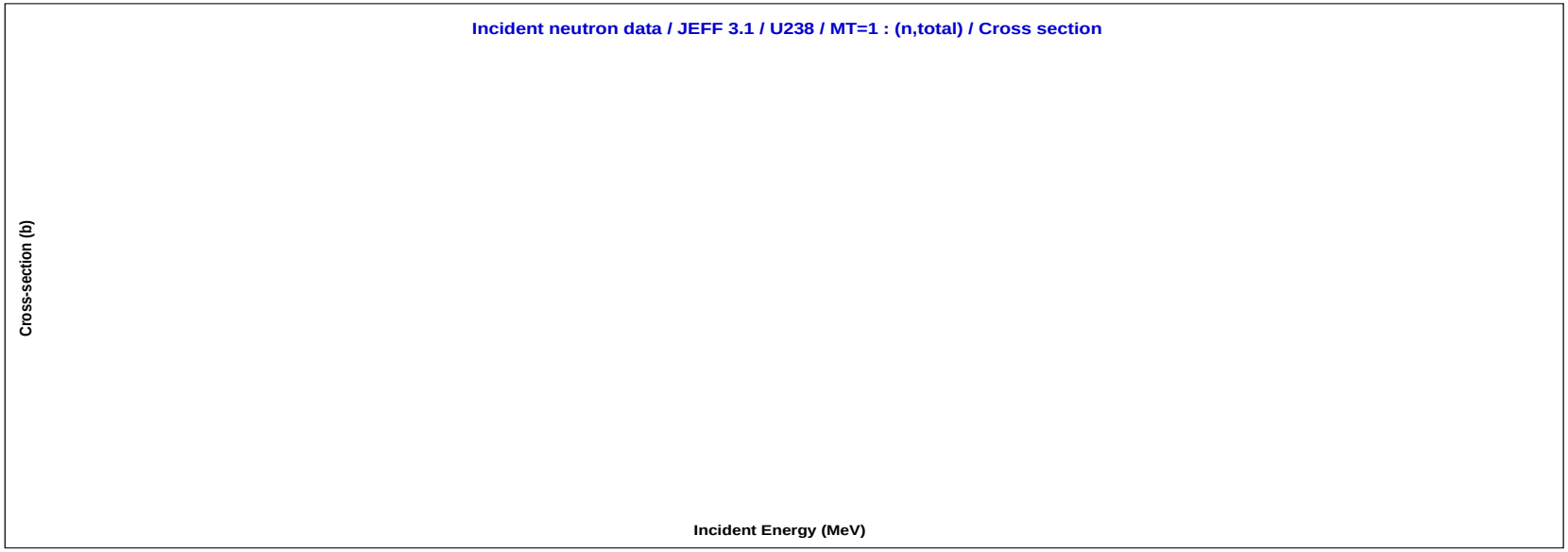
σ - Microscopic cross section Σ - Macroscopic cross section

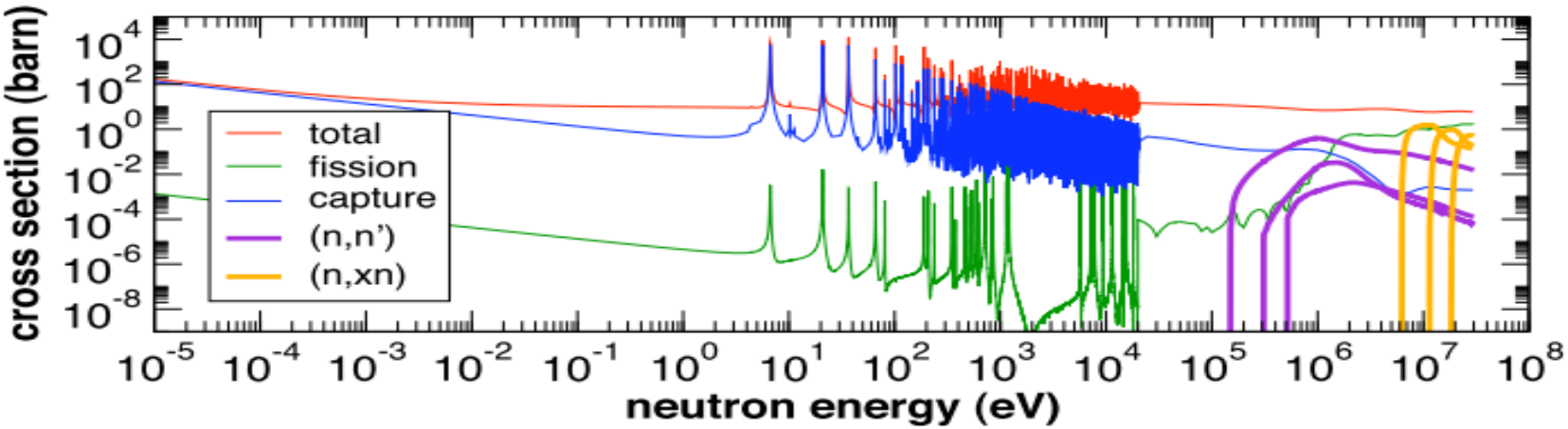
$$R = reaction\ rate = -\frac{\delta I}{\delta x} = \Sigma I = N\sigma nv \longrightarrow \delta I = -N\sigma \delta x I$$

$$[R] = cc^{-1}\sec^{-1}$$

$$-\frac{\delta I}{\delta x\, I} = N\sigma = \Sigma$$

Characteristics of Cross sections





Characteristic of Transuranic isotopes

- Changes in the isotopes are mainly due to (n,γ) reactions

Isotope	$T_{\frac{1}{2}}$ ‡	E_α (MeV)	1-gr. cross section (barn)			Most important sources in a PWR
			$<\sigma_f>$	$<\sigma_c>$	$<\sigma_{n,2n}>$	
U^{234}	2.47 10^5 a	4.7	-	-	-	natural isotope, Pu^{238} decay
U^{235}	-	-	47.5	10.7	4.3 10^{-3}	natural isotope
U^{236}	2.342 10^7 a	4.5	0.19	8.5	4.2 10^{-3}	$U^{235}(n,\gamma)$, Pu^{240} decay
U^{237}	6.75 d	-	-	-	-	U^{238} (n,2n), $U^{236}(n,\gamma)$
U^{238}	-	-	0.01	0.91	7.5 10^{-3}	natural isotope
U^{239}	23.5 m	-	-	-	-	$U^{238}(n,\gamma)$
Np^{236}	22.5 h	-	-	-	-	Np^{237} (n,2n)
Np^{237}	2.14 10^6 a	4.8	0.48	35.4	2.5 10^{-3}	Am^{241} and U^{237} decay
Np^{238}	2.117 d	-	-	-	-	Am^{242m} decay, $Np^{237}(n,\gamma)$
Np^{239}	2.355 d	-	0.58	14.2	1.0 10^{-3}	U^{239} and Am^{243} decay
Pu^{236}	2.851 a	5.8	-	-	-	Np^{236} decay, Pu^{238} (n,3n)
Pu^{238}	87.74 a	5.5	2.45	34.9	2.5 10^{-3}	Pu^{239} (n,2n) Np^{238} and Cm^{242} decay
Pu^{239}	2.411 10^4 a	5.2	119.9	67.7	4.3 10^{-3}	Np^{239} decay, $Pu^{238}(n,\gamma)$
Pu^{240}	6550 a	5.2	0.57	228.9	2.0 10^{-3}	$Pu^{239}(n,\gamma)$, Pu^{241} (n,2n) Cm^{244} decay
Pu^{241}	14.4 a	-	122.2	46.8	9.4 10^{-3}	$Pu^{240}(n,\gamma)$, Pu^{242} (n,2n)
Pu^{242}	3.763 10^5 a	4.9	0.40	30.0	3.5 10^{-3}	$Pu^{241}(n,\gamma)$, Am^{242} decay
Pu^{243}	4.956 h	-	-	-	-	$Pu^{242}(n,\gamma)$
Pu^{244}	8.26 10^7 a	4.6	-	-	-	$Pu^{243}(n,\gamma)$
Am^{241}	432.6 a	5.5	1.35	127.8	2.5 10^{-3}	Pu^{241} decay, $Am^{242}(n,2n)$
Am^{242m}	141 a	-	736.5	149.9	2.5 10^{-3}	$Am^{241}(n,\gamma*)$
Am^{242}	16 h	-	736.5	149.9	2.5 10^{-3}	$Am^{241}(n,\gamma)$, Am^{243} (n,2n)
Am^{243}	7370 a	5.3	0.42	51.0	2.5 10^{-3}	$Am^{242}(n,\gamma)$, Pu^{243} decay
Cm^{242}	162.8 d	6.1	1.19	4.4	0.2 10^{-3}	Am^{242} decay, $Cm^{243}(n,2n)$
Cm^{243}	28.5 a	5.8	-	-	-	$Cm^{242}(n,\gamma)$, Cm^{244} (n,2n)
Cm^{244}	18.11 a	5.8	0.96	15.4	2.5 10^{-3}	$Cm^{243}(n,\gamma)$
Cm^{245}	8500 a	5.4	-	-	-	$Cm^{244}(n,\gamma)$
Cm^{246}	4730 a	5.4	-	-	-	$Cm^{245}(n,\gamma)$
Cm^{247}	1.56 10^7 a	4.9	-	-	-	$Cm^{246}(n,\gamma)$

‡ a years, d days, h hours, m minutes

Reaction Rate

$I = vn(v)dv$ For parallel beam

We define R as reaction rate

$$dR = \Sigma I = \Sigma(v)vn(v)dv = \Sigma(v)\Phi(v)dv$$

$$R = \int_0^\infty \Sigma(v)\Phi(v)dv$$

In reactor physics we deal with FLUX in term of energies. :

Note: $E = \frac{mv^2}{2}$

We define $\Phi(v)$ *or* $\phi(E)$

the flux per unit velocity and flux per unit energy respectively

The governing Equations I: The transport equation

$$\frac{1}{v}\frac{\partial f(E,r,\Omega,t)}{\partial t}+\Omega\nabla f(E,r,\Omega,t)+\left[\Sigma_s(E)+\Sigma_a(E)\right]f(E,r,\Omega,t)=$$

$$=\int_{\Omega'}\int_0^\infty \Sigma(E'\to E;\Omega'\to\Omega)\,f(E',r,\Omega',t)\,d\Omega'\,dE'+S(E,r,\Omega,t)$$

The Transport equation is a balance equation:

- On the left side the loss terms
- On the right side the source terms
- The result is the angular flux (f) which is an input for the reaction rate.

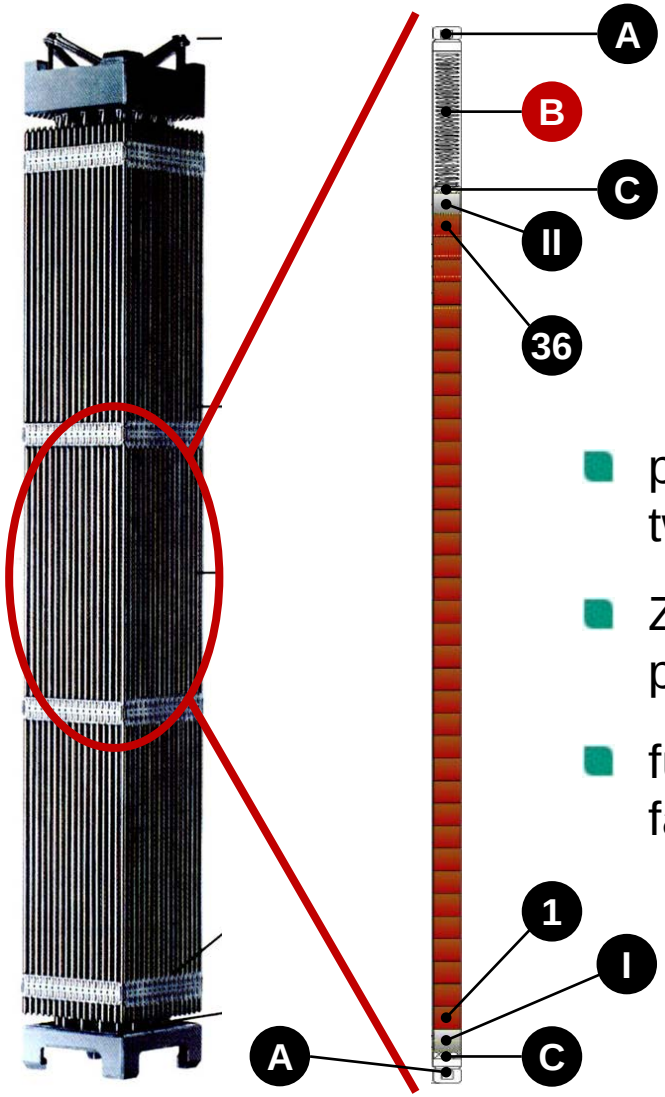
The transport equation gives the flux in greater detail than the diffusion equation. The reason is that one defines a vector flux $f(\vec{\Omega})$ which can evaluate the number of neutrons crossing a unit area perpendicular to a specific direction per second

The governing Equations II: The Bateman Equation

- The reaction rate provides the production of radioactive nuclides either by fission or by absorbing a neutron and creating an unstable nuclide.
- The fission products and the generated unstable nuclides by neutron Absorption (or other relevant reactions) decay according to their decay constant.
- It is clear that the production of one radionuclide depends on the incineration of his precursor. Mathematically speaking it calls for a matrix solution
- Known as the Bate Equation which in its general form is: $\dot{\vec{n}} = A\vec{n}$
- '$\vec{n}$' stand for the material vector . 'A' for the reactions which include the knowledge of the flux ,cross section (reaction rate) and the decay constant λ (decay equation or Activation term)

15

Material: Origin of the used Zircaloy cladding



B **Zircaloy-4 cladding around stainless steel spring**
no contamination of cladding by fuel

- pin KKG–SBS1108 consists of five fuel rod segments + two dummy segments
- Zircaloy-4 cladding specimen are sampled from the plenum of fuel rod segment SBS1108–N0204
- fuel rod segment with UO_2 fuel pellets (3.8 wt.% ^{235}U), fabricated by “Kraftwerk Union AG” (today Areva)

A **end cap**
I + **II** **“natural” UO_2**
C **insulation pellet**
1 … **36** **“enriched” UO_2**

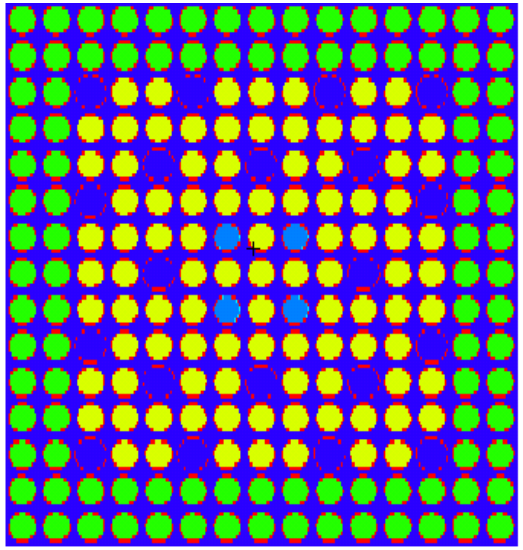
Nucl. Engineering International (2003) vol. 48, no. 590, Fuel design data.

Material: Irradiation characteristics of N0204

- irradiated in the Swiss Gösgen PWR during four cycles (1985–1989)
- 1226 effective full power days
- average burn-up: 50.4 GWd/t_{HM}
- average linear power: 260 W/cm
- max *T*: > 1300°C

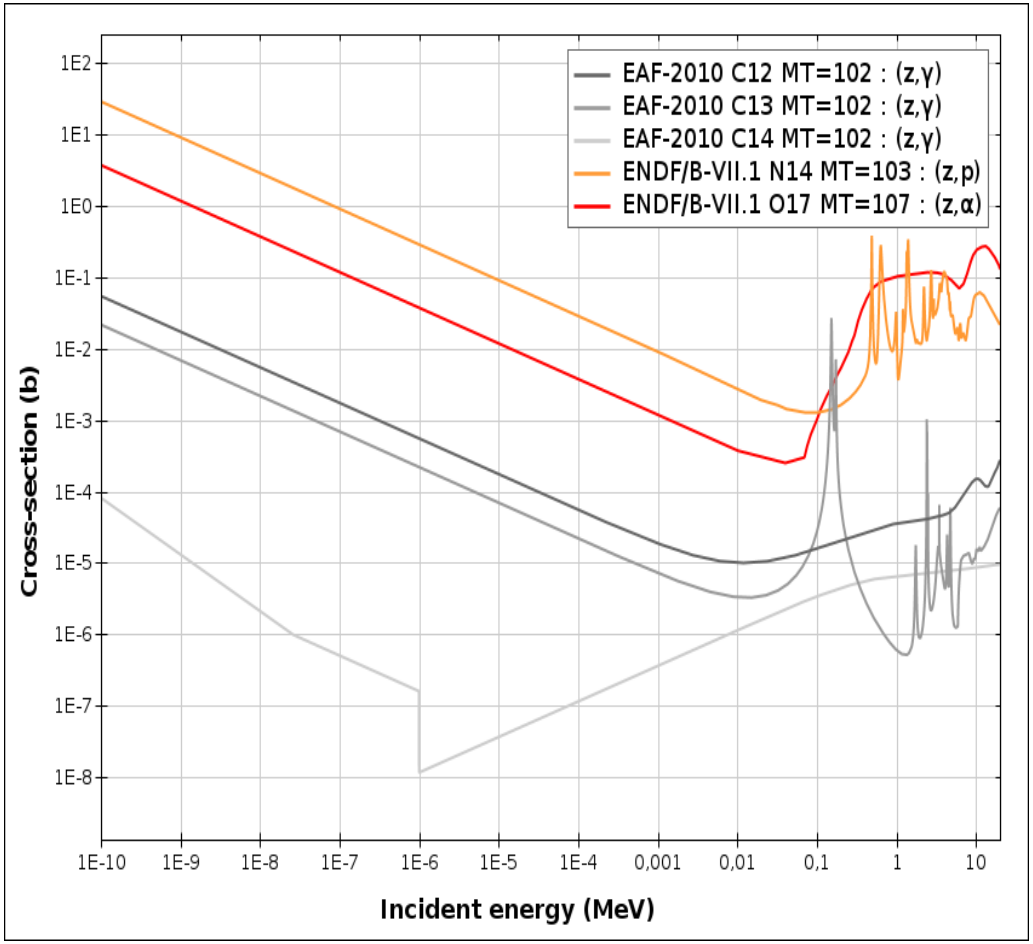
Simulation methodology of the Goesgen Subassembly

- The 4 bright blue fuel elements in the middle depict the investigated fuel segment.
- The water holes are seen as enlarged red cycles
- The green and yellow pins are the rest fuel pins of the subassembly.
- The burn up condition of the fuel rods is adapted in such a manner that the given boundary condition of 50.4 MWD/kg and the irradiation time of 1226 days by ~260 W/cm will be kept



Energy dependent cross section types of nuclides which lead to C14 production

- N14 dominates the production of C14.
- The contribution of O17 seems to be by factor 10 smaller, but the effect at larger energies enhance the importance of O17
- The Production of C14 by C12 and C13 is practically negligible



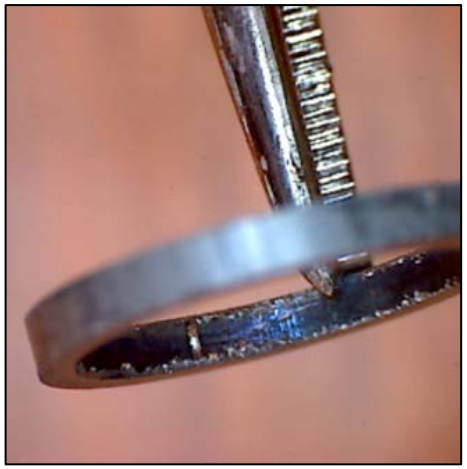
Methods: MCNP inventory calculations

- calculation of the radionuclide inventory were performed by the MCNPX2.7 version which is coupled with the burn up module CINDER
- Several nuclides, in particular C14 have no transport cross-sections data.
  - CINDER uses its own activation data in case of missing transport data
  - Second option: generation of C13 and C14 transport data using different (TENDL) nuclear data library which provides the missing data.
  - Third option: exchanging the missing transport data by “similar” existing nuclides
  - Fourth option: manipulating the MCNP code in such a manner that whenever the transport data of missing nuclides were changes the CINDER module uses its own activation data.
- JEFF and ENDF libraries are different to some extent.

Results: inventory analysis

- experimentally obtained results for ^{14}C, ^{55}Fe and ^{125}Sb are in good agreement with calculations
- The build up of C14 was linear to the N14 concentration about 1000 Bq/gr per 1ppm N14 (different to some extent from [2])
- C/E ^{137}Cs inventory is different by factor 117

  → precipitation of volatile (light blue) ^{137}Cs on inner cladding surface during reactor operation can not be taken into account in the MCNP calculations



radionuclide	**^{14}C**	**^{55}Fe**	**^{137}Cs**	**^{125}Sb**
		[Bq/(g Zyr-4)]		
Experimental	$3.7(\pm0.4)\times10^{4}$	$1.5(\pm0.2)\times10^{5}$	$3.4(\pm0.3)\times10^{6}$	$2.4(\pm0.2)\times10^{5}$
calculated	3.2×10^{4}	1.3×10^{5}	2.9×10^{4}	2.6×10^{5}

Conclusions and outlook

- good agreement of experimental results with calculations for ^{14}C, ^{55}Fe and ^{125}Sb.
- Encouraging the use of simulation for the “missing Cs137”. Combining the calculations with experimental results and by comparing the both , learning what was the migration of Cs137 within the fuel rod
- Similar results were obtained with MCNP5 /Monteburns using updated libraries albeit from 1997.
- black/blueish precipitates on inner irradiated Zircaloy-4 cladding surface
  → XAS investigations at INE-Beamline @ ANKA foreseen

EURATOM Collaborative Project CAST (CArbon-14 Source Term)

Release of radionuclides from SNF under deep geological repository conditions

E. González-Robles

Karlsruhe Institute of Technology – Institute for Nuclear Waste Disposal (KIT-INE)

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

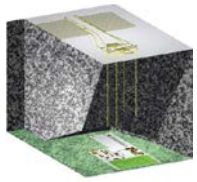
Pu

Reprocessing Plant

CLOSED CYCLE

Reactor

Glass



Geological disposal

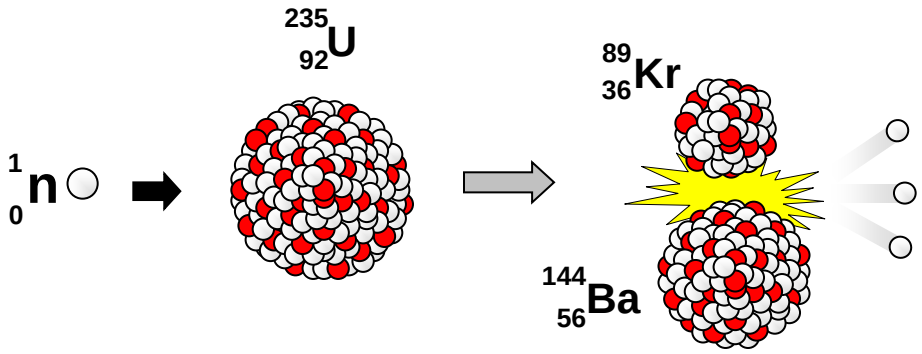
Interim Dry Storage

Pools

OPEN CYCLE

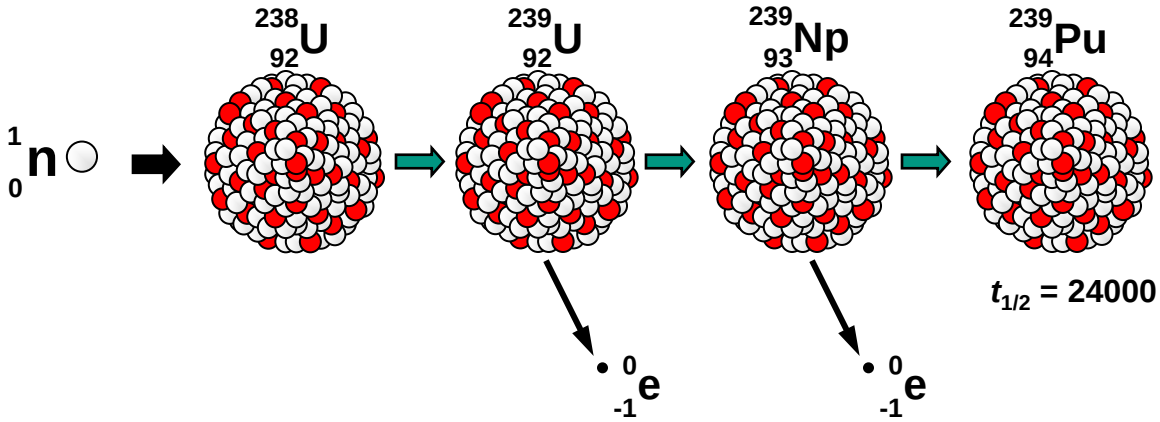
In reactor behavior

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):

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

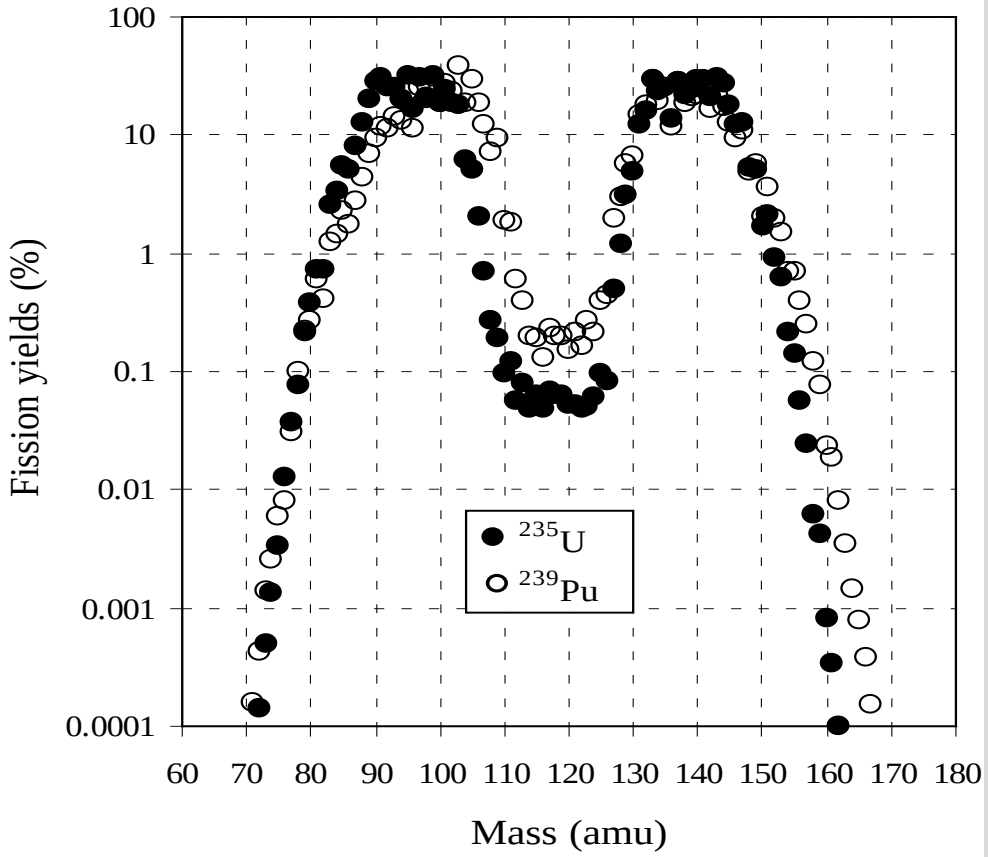
  - Energy produced per unit mass of initial uranium:

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

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

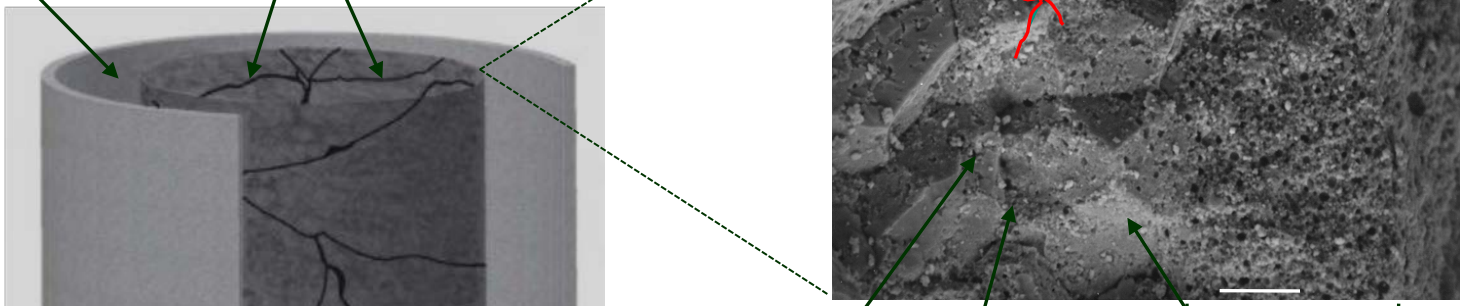
In reactor behaviour

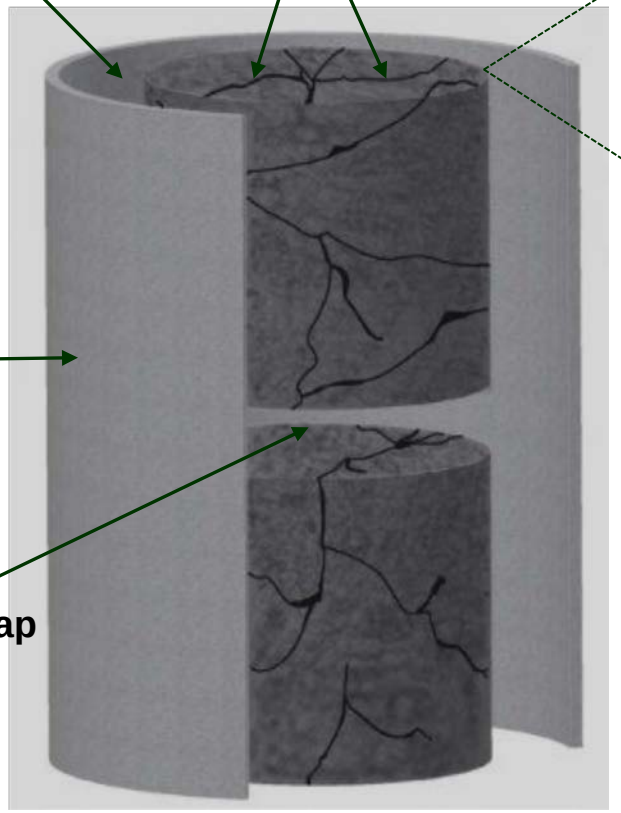
Grains
$(U, An, Ln)O_2$

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

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

Cracks





Cladding
C, Zr

Inter-pellet gap

FG bubbles
Xe, Kr, I

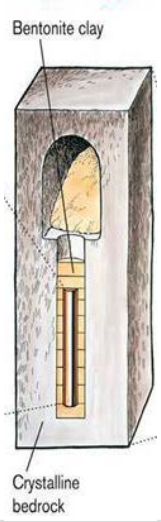
Rim or HBS

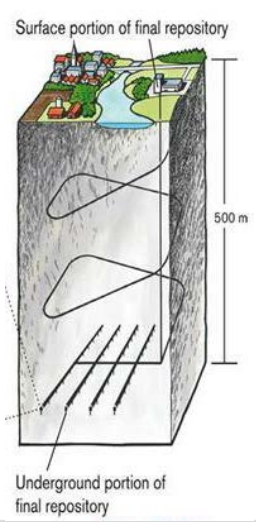
ε-particles/metallic precipitates
Mo, Ru, Rh, Pd, Tc
(Ag, Cd, In, Sn, Sb).

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

Geological disposal

- 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

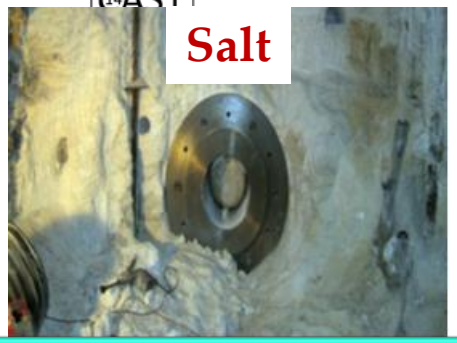
Clay

+ 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

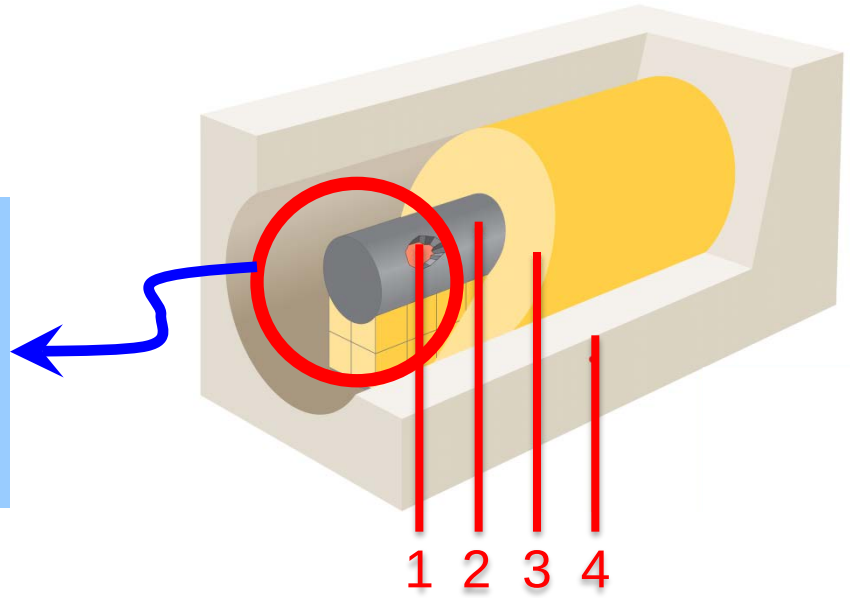
Germany, USA

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

Grains
$(U, An, Ln)O_2$

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

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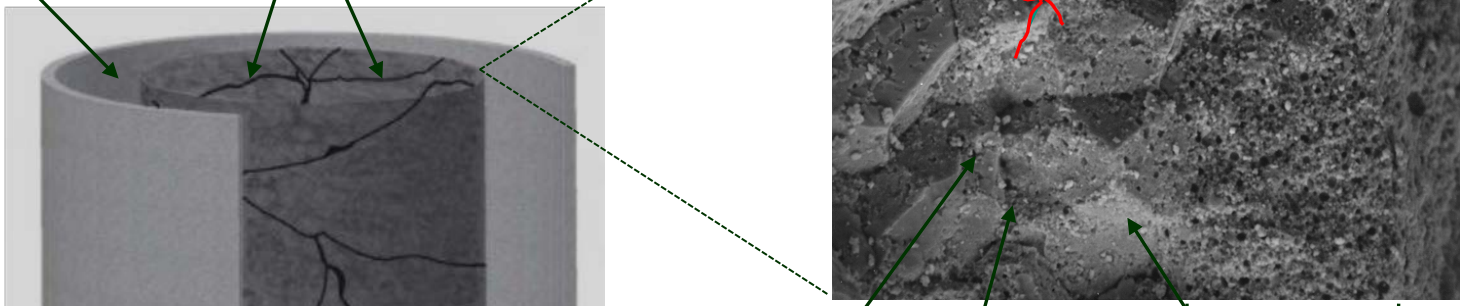

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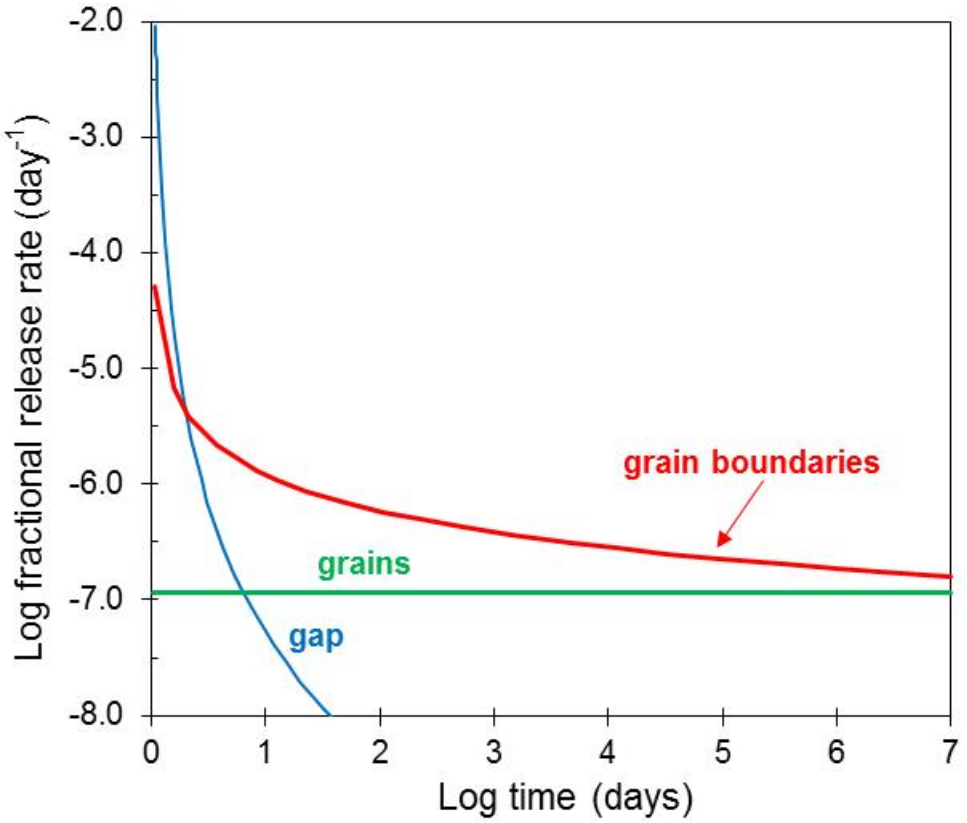
(Ag, Cd, In, Sn, Sb).

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

Geological disposal

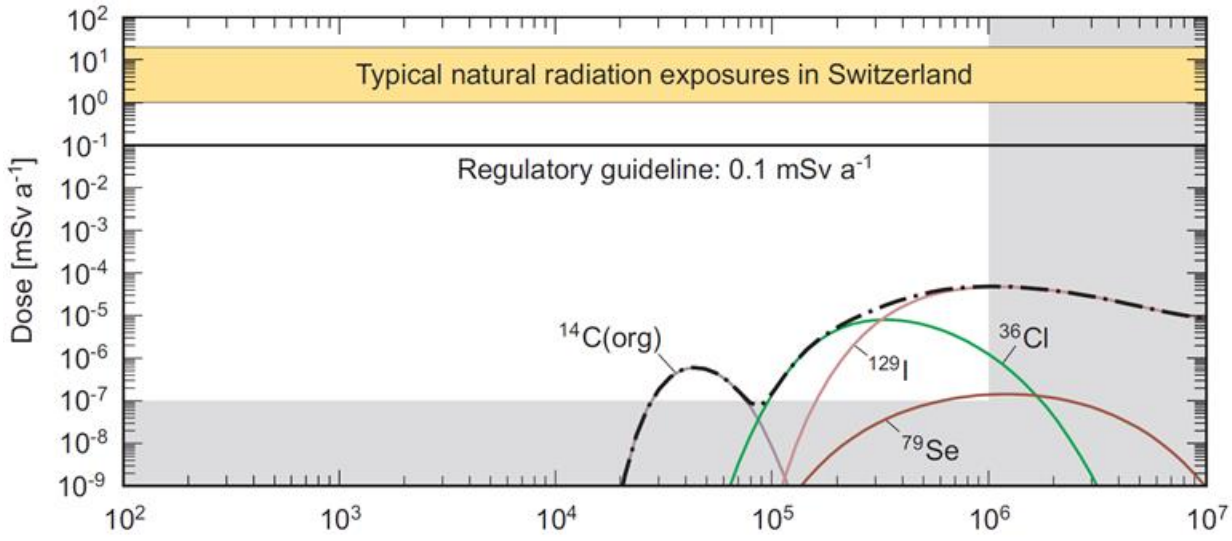
- Radionuclide release can be divided into contributions from the three SNF zones: gap, grain boundary and grain matrix

- 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

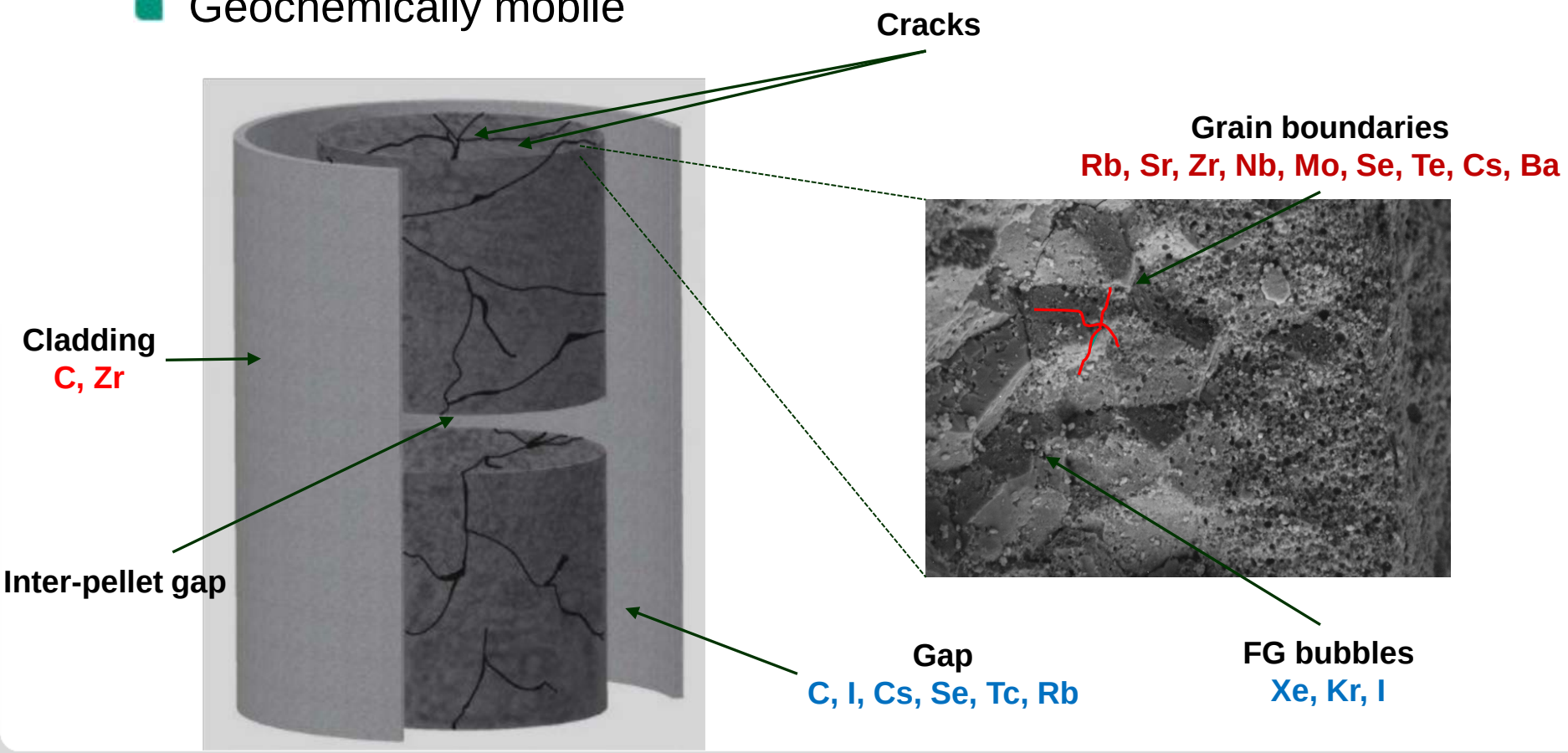
- It is the fraction of the inventory released rapidly when the metal waste package and fuel cladding are first breached
  - Fission gases: Xe and Kr
  - Volatile elements: I, Cs and Cl

- 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



Instant release fraction

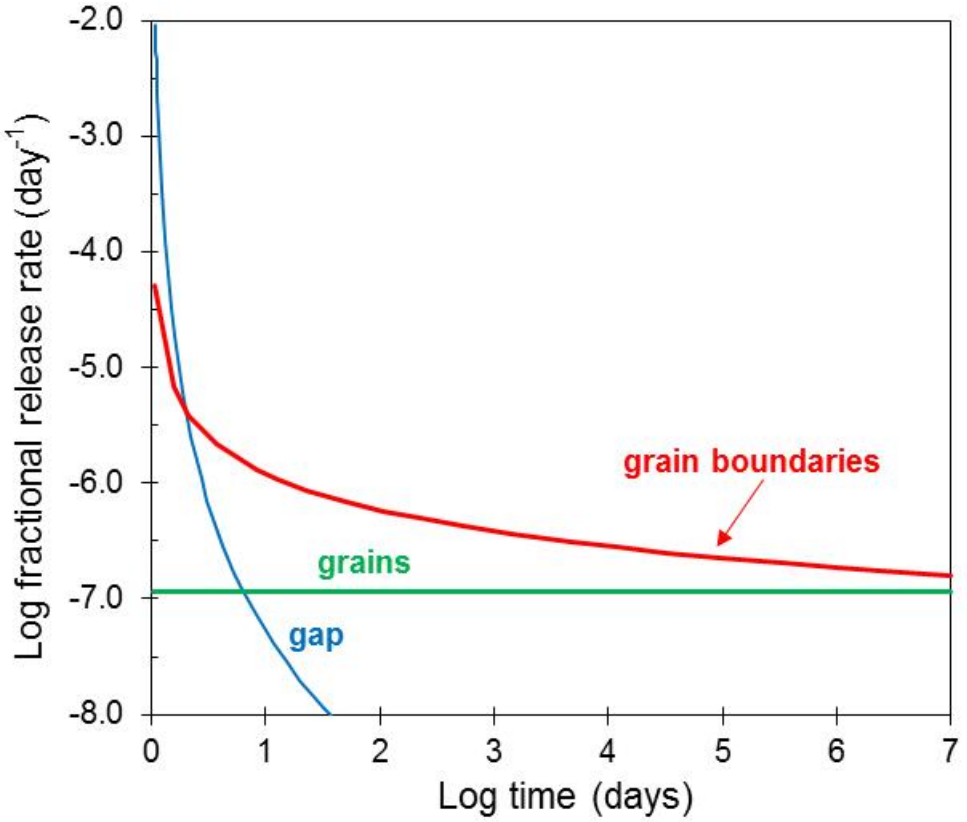
Burn-up (GWd/t_{HM})	48	60	54.4	50.4		54.25		50.5		63
Sample			OS	S	F	S	F	S	OS	F
FGR	2 (4)	4 (8)	2.3	8.5		13.2		14.1		26.7
Cs	2 (4)	4 (8)	1.3	3.9	4.5	6.2	5.0	3.4	3.7	9.2
I	2 (4)	4 (8)	3.2	15.7	16.4	9.0	3.9	10.8	15.6	11.5
Sr	1 (3)	1(5)	0.083	0.002	0.02	na	na	0.2	0.2	na
^{14}C	10	10	na	na	na	na	na	<1.5	<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

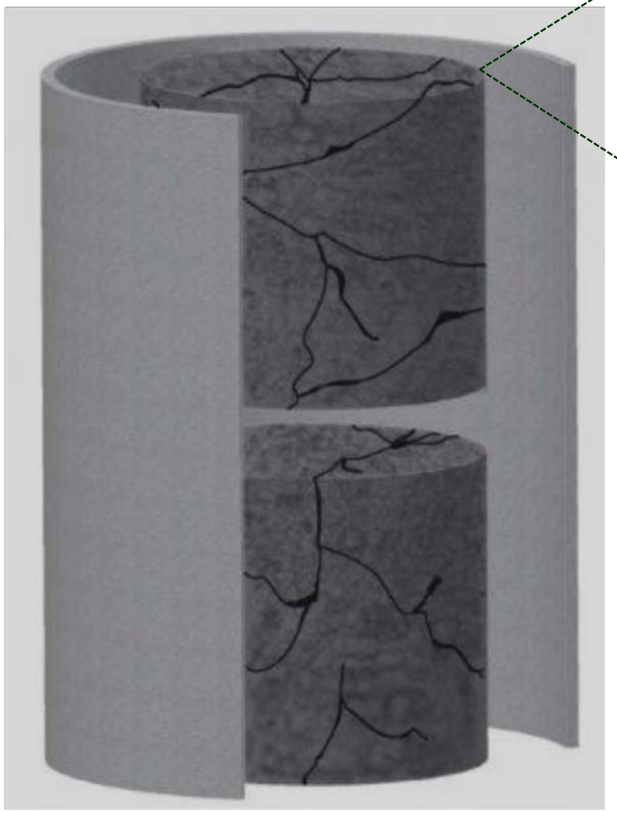
- Radionuclide release can be divided into contributions from the three SNF zones: gap, grain boundary and grain matrix

- Instant Release Fraction (IRF)
  - Gap + fractures
  - Grain boundaries
- Matrix dissolution release:
  - Grains: 90 % of radionuclides

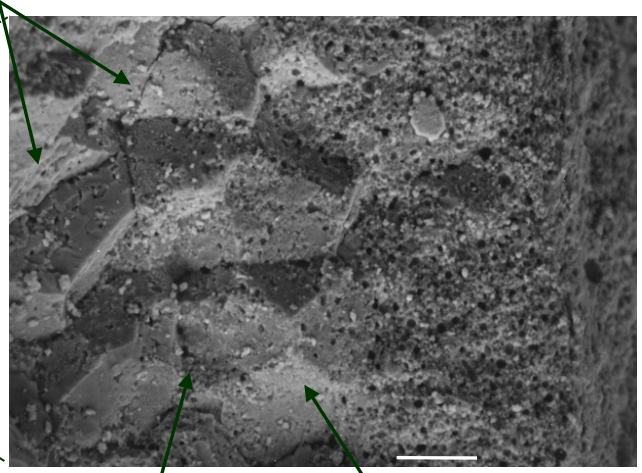


Johnson *et al.*, 1985

Matrix dissolution



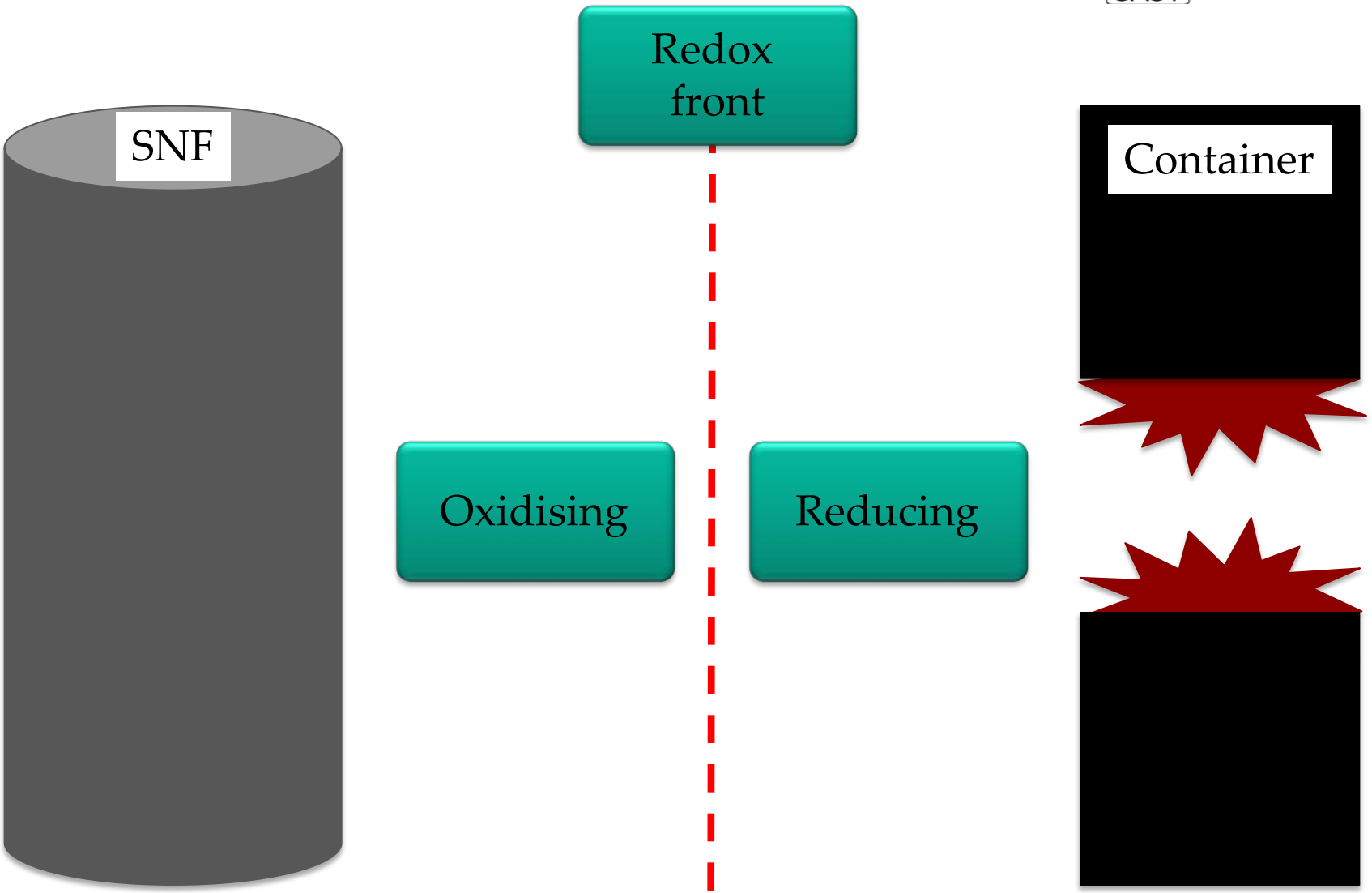
Grains
(U, An, Ln)O_2



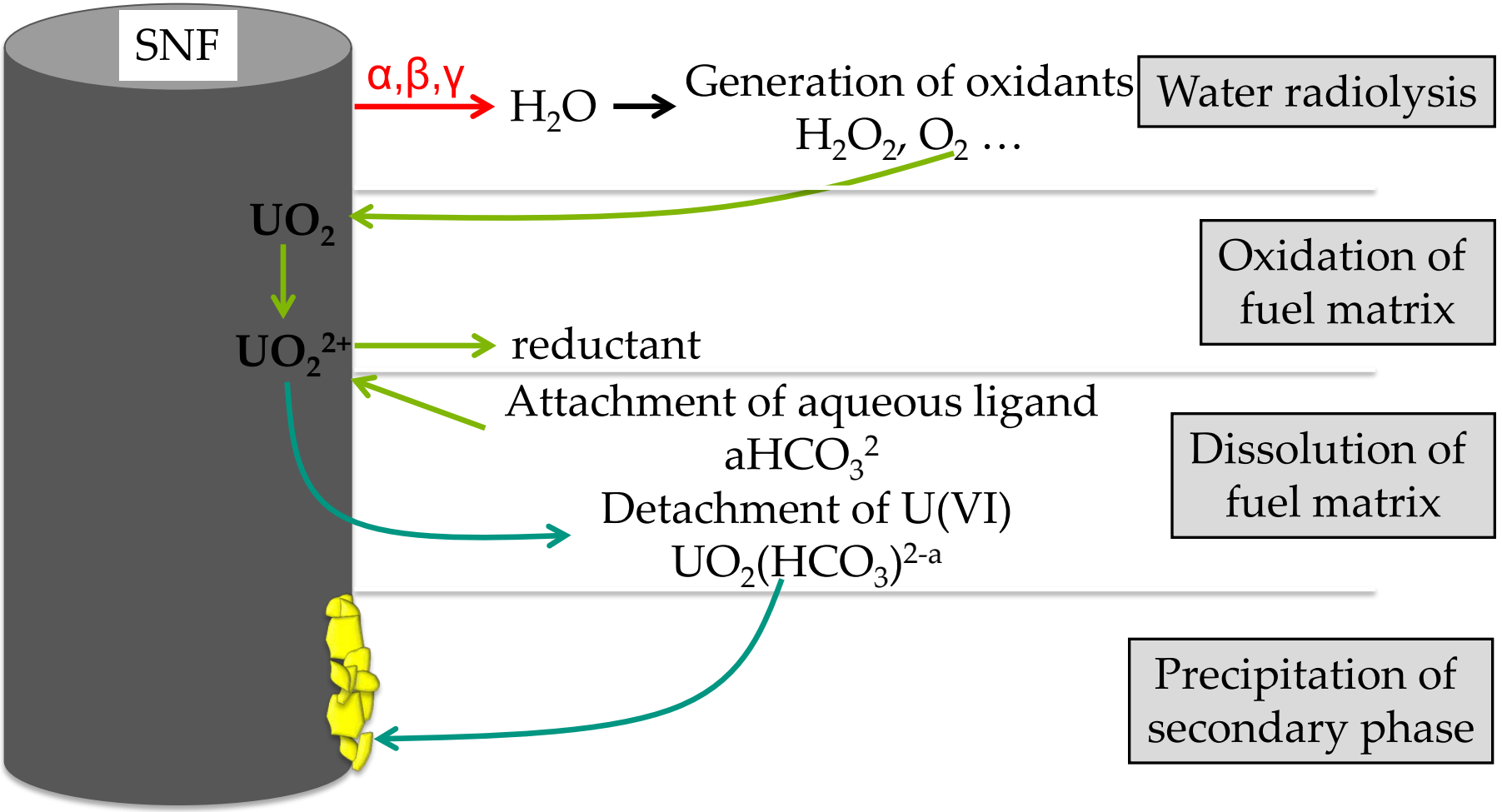
ε-particles/metallic precipitates
Mo, Ru, Rh, Pd, Tc
(Ag, Cd, In, Sn, Sb).

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

Matrix dissolution

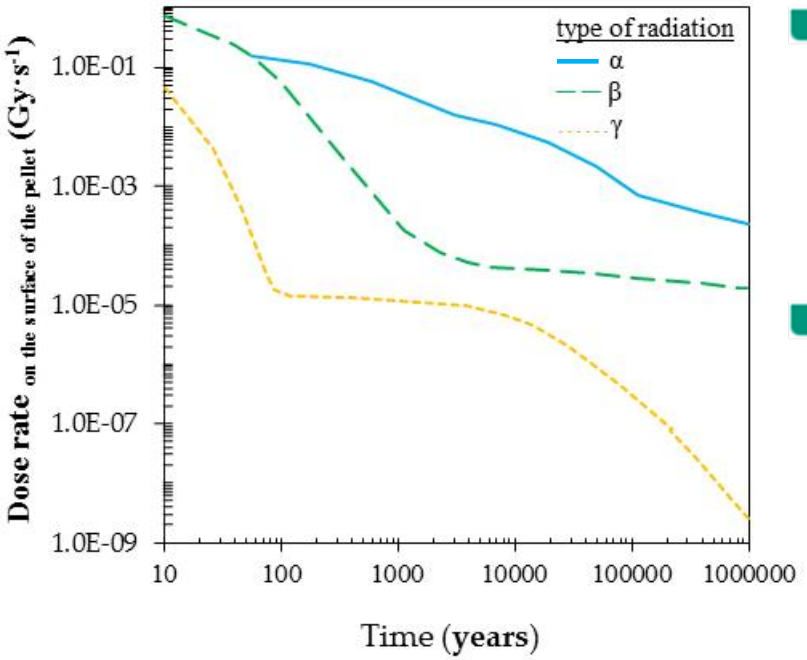


Matrix dissolution



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

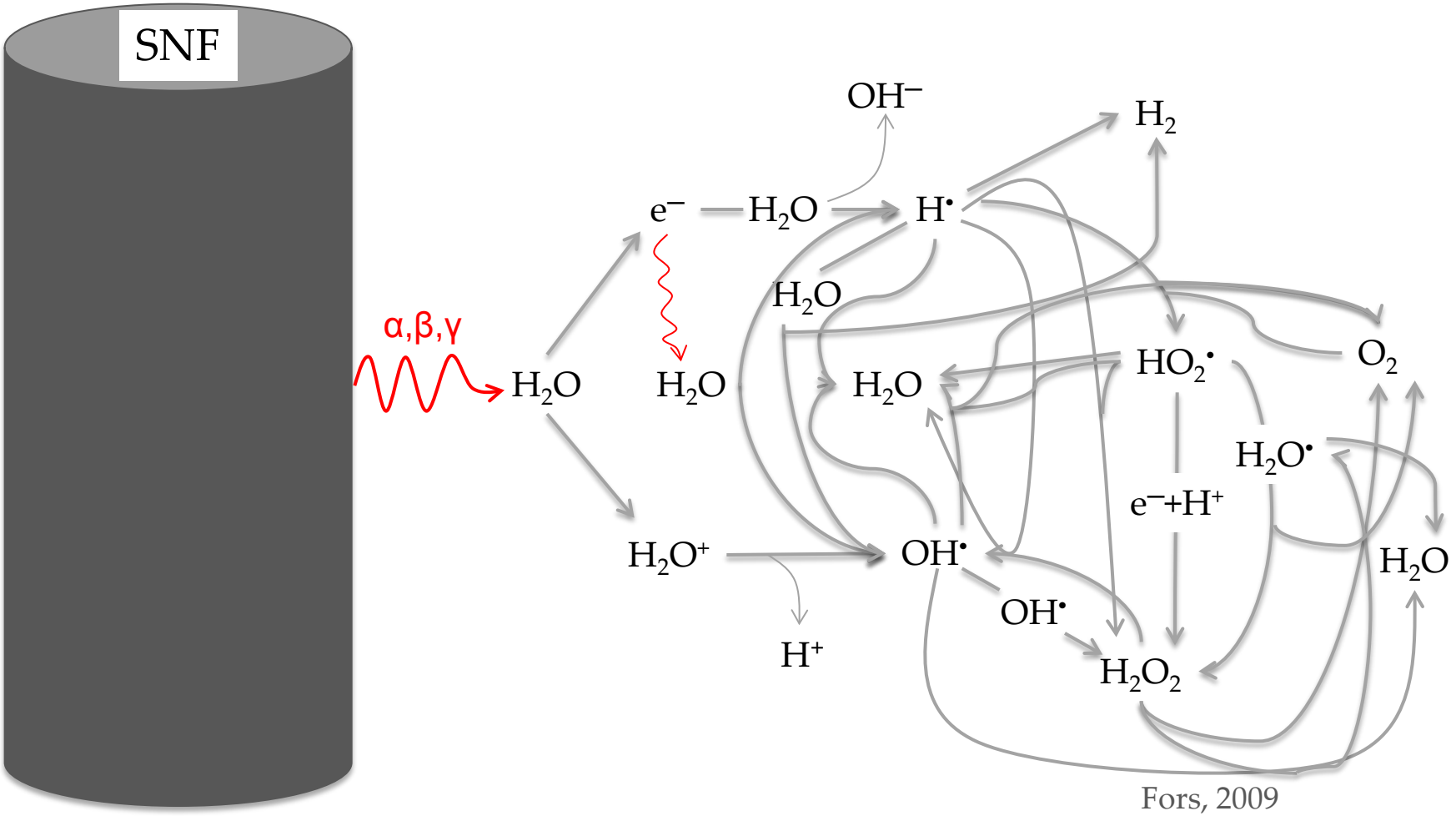
- It will be controlled by water radiolysis
- As a consequence of the water radiolysis:

  - 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



Matrix dissolution

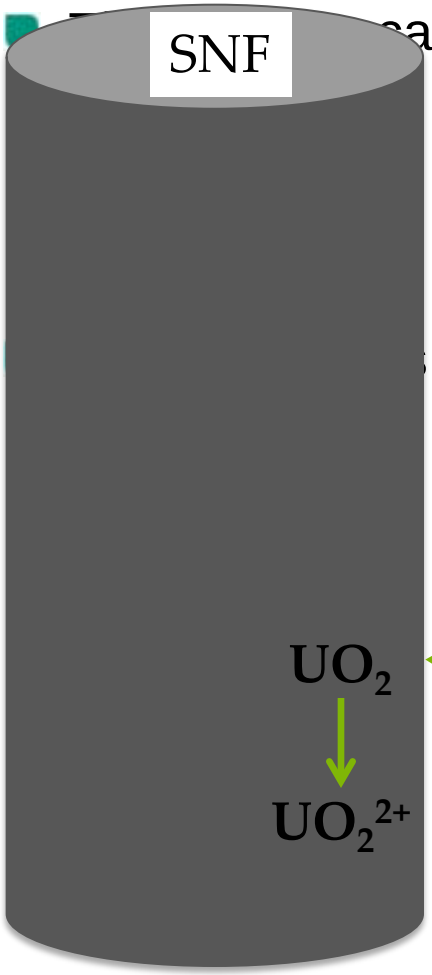
- In deep geological repository the expected conditions are reducing, but the oxidants produced by water radiolysis will lead to oxidising conditions

- 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
- [illegible]an be summarised as:



$$UO_2 \longrightarrow UO_2^{2+} + 2e^-$$

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

- [illegible]s and the environment

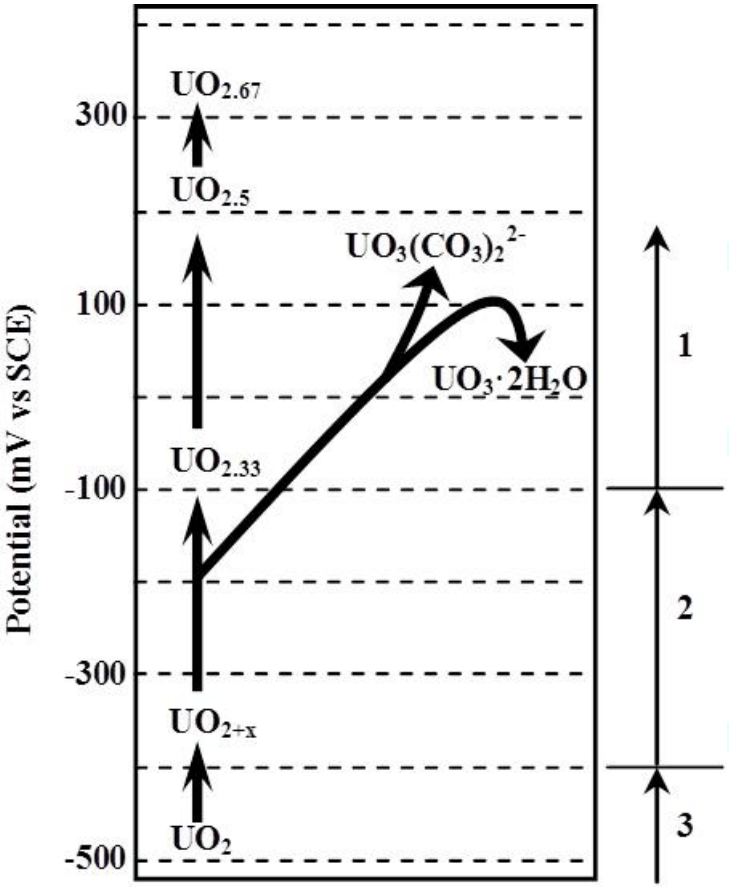
Generation of oxidants by water radiolysis
H_2O_2, O_2 …

Corrosion rate controlled by the slowest reaction

reductant

Matrix dissolution

- Oxidation of fuel matrix



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

Region 2 :

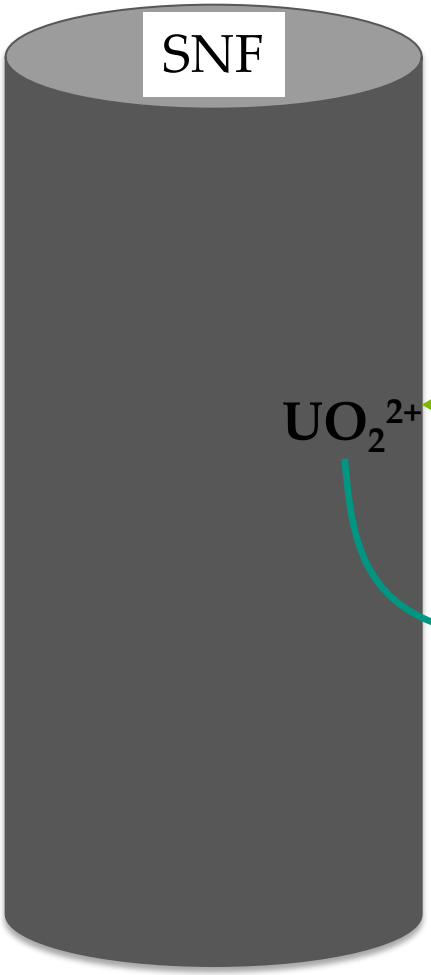
- Irreversible oxidation of UO_2
- Dissolution process starts at -300mV when the UO_2 is oxidised to UO_2^{2+}

Region 3 :

- Small oxidation occurs
- Concentrated to the grain boundaries

Matrix dissolution

- Dissolution of fuel matrix



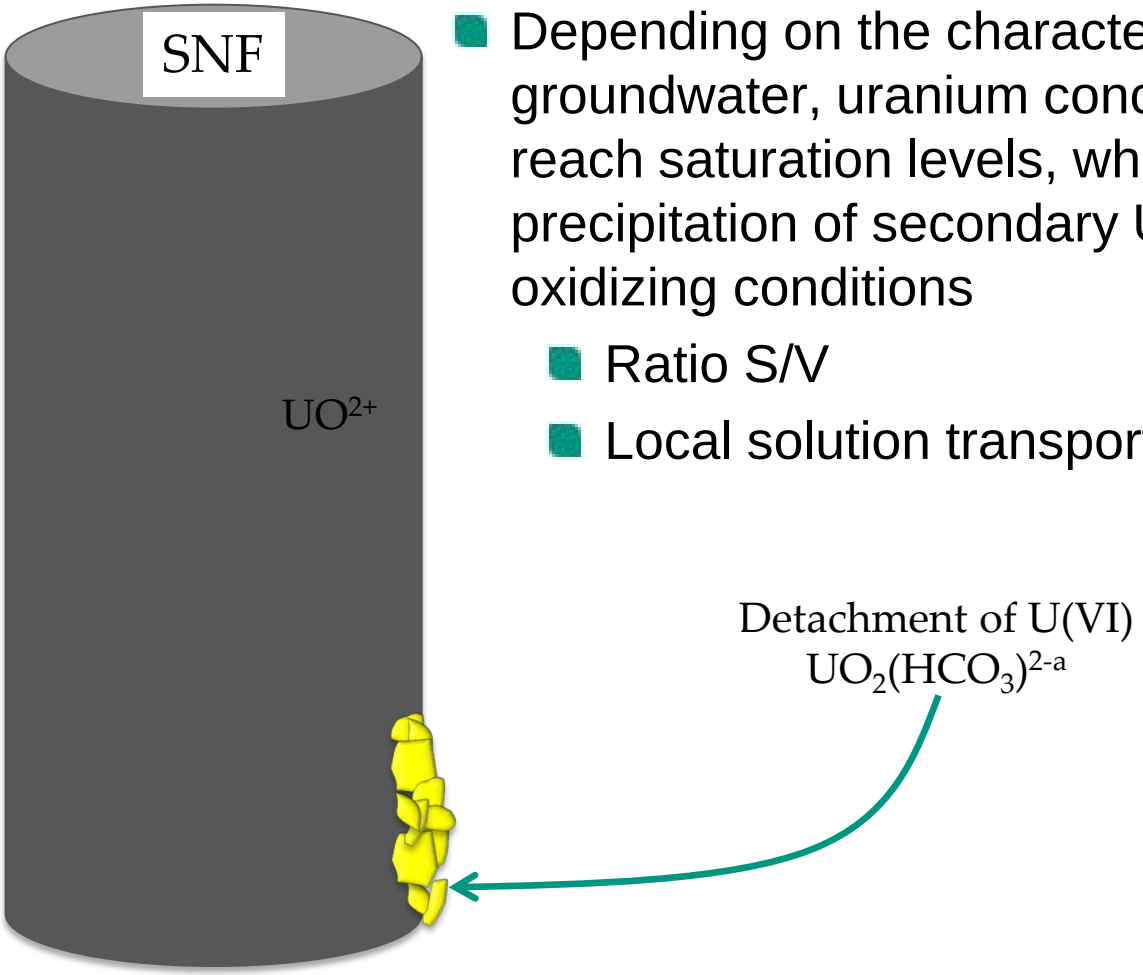
- U(VI) placed at the surface of the SNF is dissolved by complexing ligands
- Depending on characteristics of groundwater

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

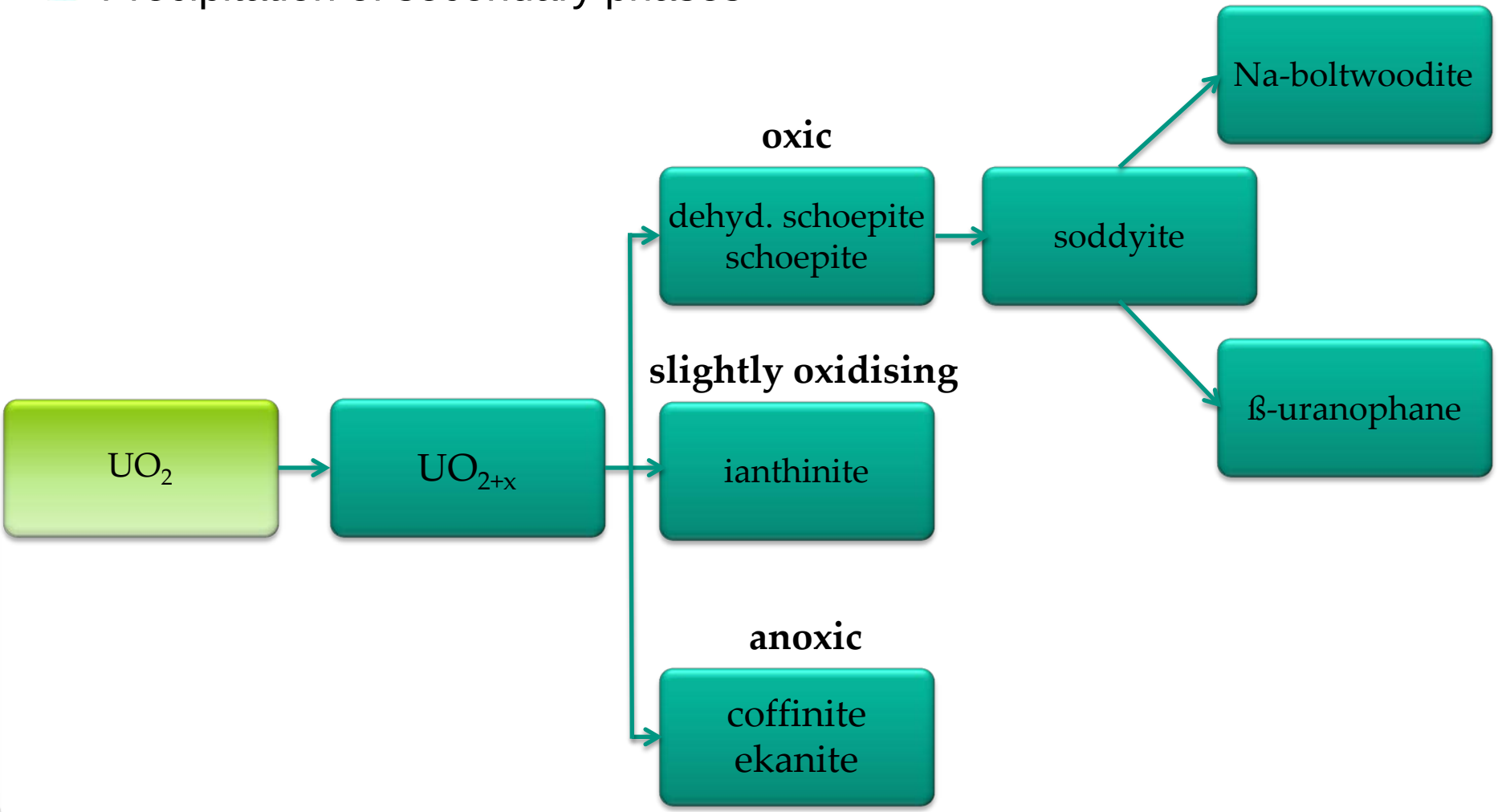
Matrix dissolution

- 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



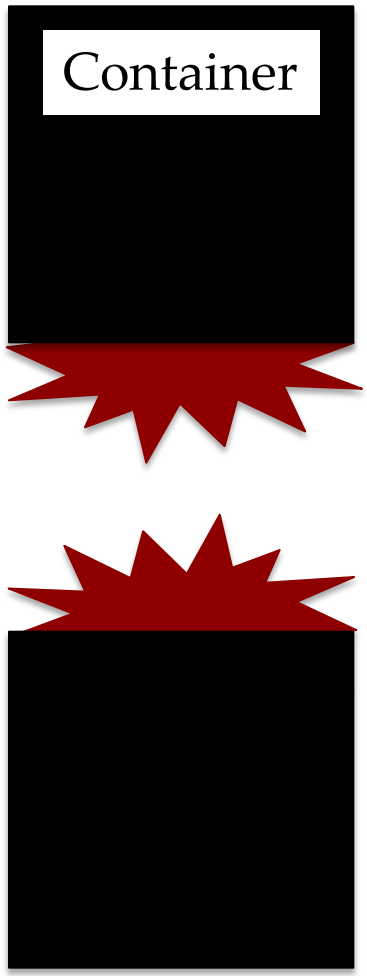
Matrix dissolution

- 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

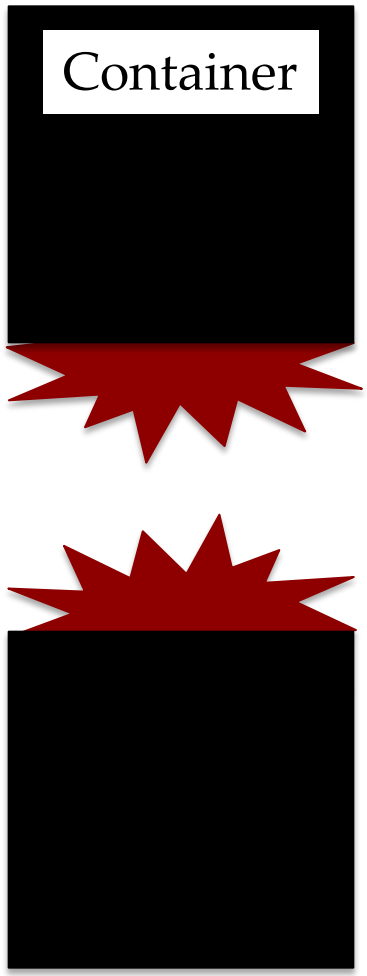
- Accumulation of H_2 in the canister
- Increase of H_2 pressure: formation of gas bubbles
- H_2 pressure ≥ 5MPa remains until α-activity threshold is reached (10000 years)
- Fe and H_2 may react with: radiolytic products and corrosion products from the SNF
- Fuel corrosion in presence of iron:
  - Fenton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

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

  - In presence of H_2:

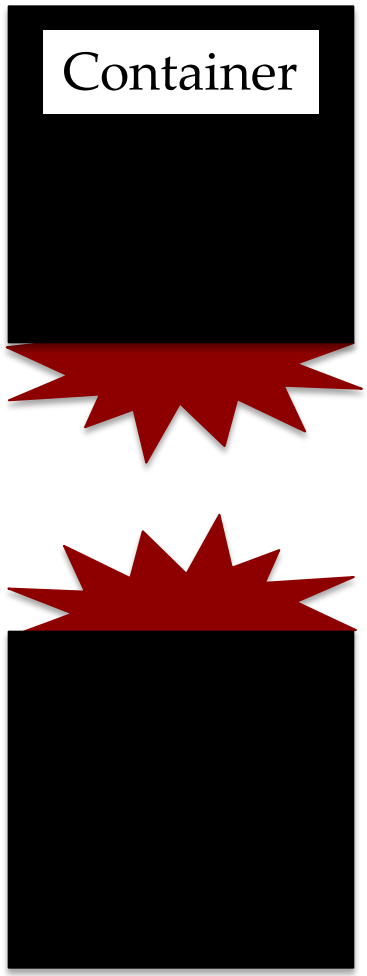
$$Fe^{2+} + OH^{\bullet} \longrightarrow Fe^{3+} + OH^{-}$$

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

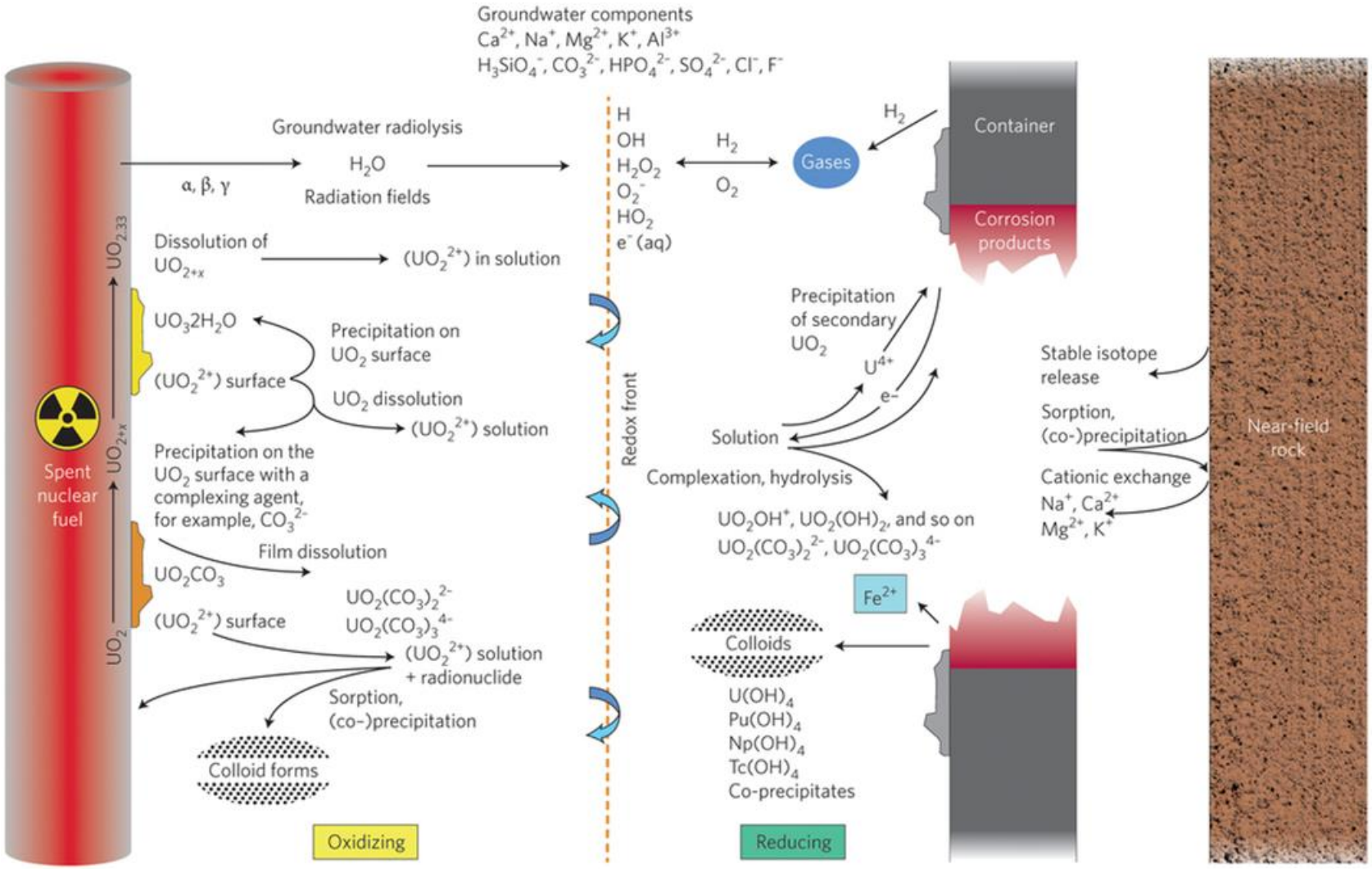


Container corrosion

- 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
$UO_3 2H_2O$
(UO_2^{2+}) surface
Precipitation on UO_2 surface
UO_2 dissolution
(UO_2^{2+}) solution
Precipitation on the UO_2 surface with a complexing agent, for example, CO_3^{2-}
UO_{2+x}
Spent nuclear fuel
Film dissolution
UO_2CO_3
(UO_2^{2+}) surface
$UO_2(CO_3)_2^{2-}$
$UO_2(CO_3)_3^{4-}$
UO_2
(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

Waste Management of LLW / ILW at HDB

EURATOM Collaborative Project CAST

(CArbon-14 Source Term)

Training Course

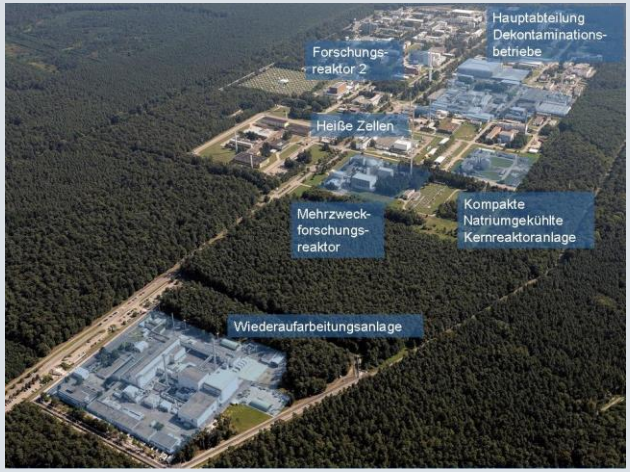
C-14 behaviour under repository conditions

Felix Himmerkus,

Eggenstein-Leopoldshafen, 05.07.2016

Primary assignments of the WAK

- **The WAK is the WAK dismantling and waste management company. Therefore the two major processes of the company is the dismantling of former prototype nuclear installations**



- **and the management of the resulting waste.**

Die HDB der WAK GmbH

The assignment of the HDB is the collection and treatment of radioactive waste:

- Sorting by material and contamination status
- Decontamination and free release
- Incineration of combustible materials
- Concentration of aqueous liquids
- Cementation of concentrates
- Hydraulic compaction of inorganic waste
- Interim storage of waste products

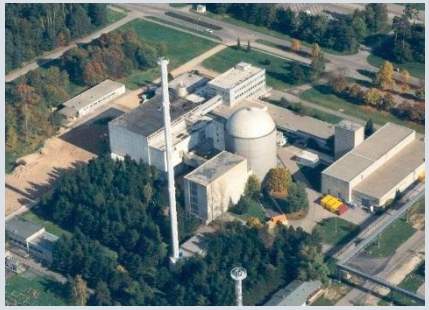
Goal: repository KONRAD in Lower Saxony

In the future the radioactive waste packages will be delivered to the repository KONRAD in Lower Saxony The acceptance will not start before 2022 and will continue for 30 to 40 years.

Critical for project timescale

KIT Campus Nord, ehem. Forschungszentrum Karlsruhe

Decommissioning Projects of the WAK GmbH



Prototype pressurized heavy-water reactor (PHWR)

MZFR

Prototype reprocessing plant

WAK

Prototype for advanced fast reactor cooled with liquid sodium

KNK

Material testing.

Hot Cells

Neutron source heavy-water research reactor

FR2

accelerators

Zyklotron, Van de Graaff-Generator

Prototype and research reactors

Nuklear research and prototype facilities

Waste-Management – in the decomissioning project

Transport of waste materials and components to the HDB

Storage for untreated waste

Hauptabteilung Dekontaminationsbetriebe (HDB)

Aerial view of HDB premises

Tasks of HDB

- Processing of radioactive waste and components
- Decontamination for free release (ca. 70 – 80% of total mass)
- Volume reduction and solidification of radioactive waste for safe final disposal
- Preparation of existing waste for final disposal; Container licensing
- Transport and storage

➡ Permanent staff in total: 169 (12/2015)

History of the HDB

- The Central Decontamination Department was founded in the 1960ies in order to treat and to dispose of the increasing amount of radioactive waste arising from nuclear research at the Karlsruhe site.

- On the Karlsruhe site several research reactors and the reprocessing plant WAK were operated from the 1960ies until today. The resulting process and decommissioning waste is treated by the HDB according to the acceptance criteria of the respective repository.

- The HDB operates the largest interim storage facility for low and intermediate active waste in Germany.

Treatment of waste at HDB

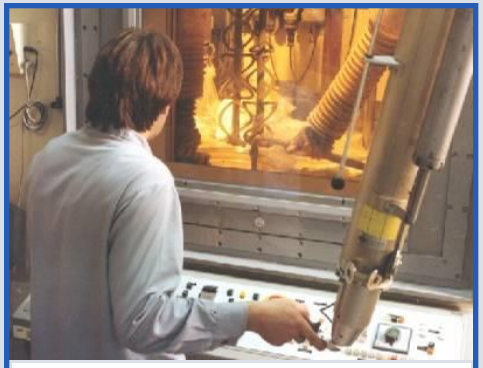
Dekontamination

Disassambling

LAW-scrapping

MAW-Scrapping

Incineration

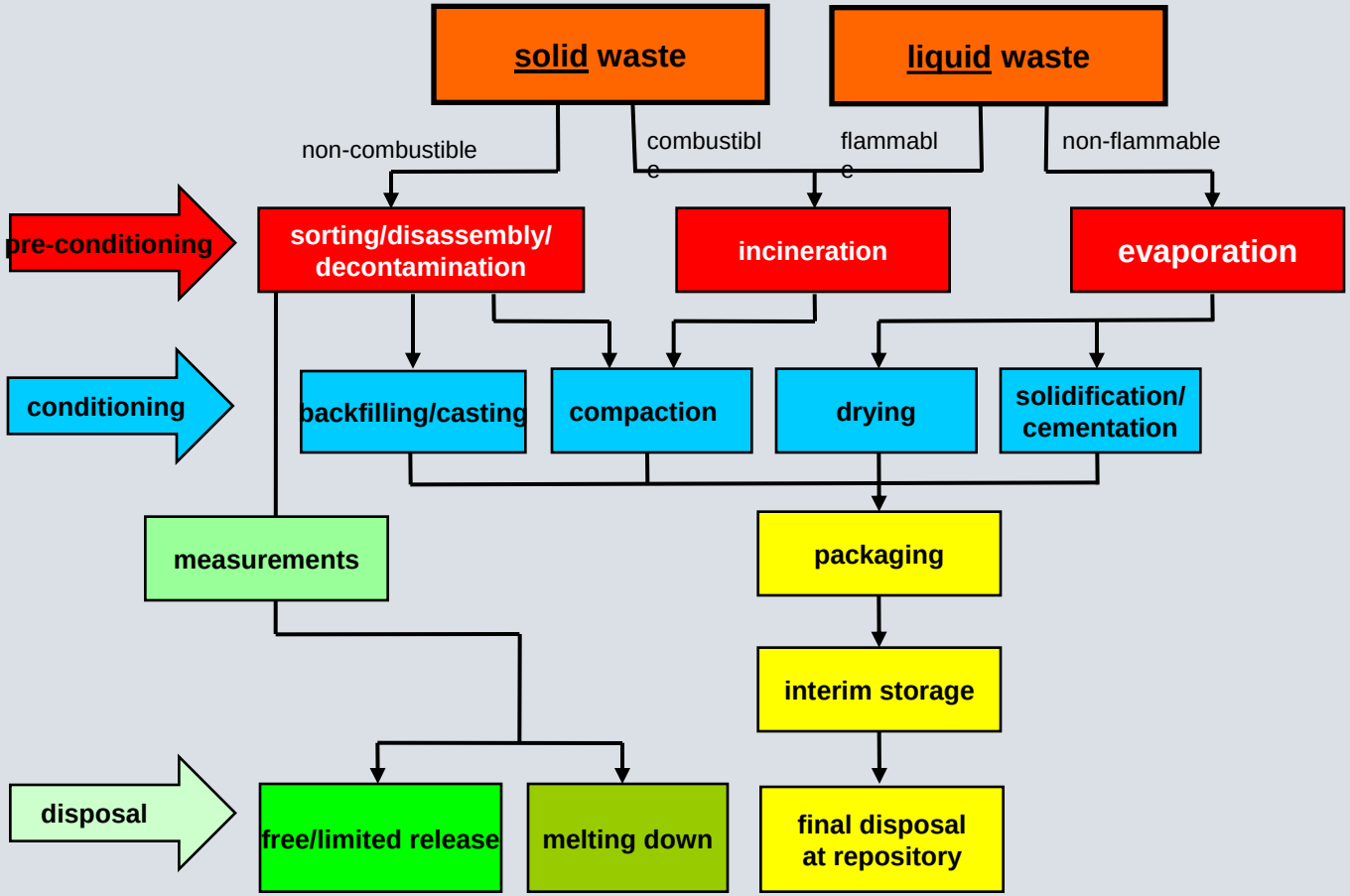


Concentration / Cementation

Origin of radioactive waste

- Operation and decommissioning of WAK (Reprocessing Plant Karlsruhe)
- Operation, decommissioning and deconstruction of research reactors
- European Institute for Transuranium (ITU)
- Federal State Collection Center Baden-Württemberg (incl. KIT institutes)
- External industrial clients and utilities

Pre-conditioning/Conditioning/Disposal



Nuclear Waste Management Division I (ANE I) Decontamination facility

Throughput (on average):
600 Mg/a

10% radioactive waste,
30% waste to melt down,
60% free/limited release

3 caissons,
sandblasting facility,
large component saw,
drying facilities,
backfilling & casting facilities

Nuclear Waste Management Division I (ANE I) Decontamination facility

Nuclear Waste Management Division I (ANE I)

LLW scrapping/compaction

Throughput (on average):
3,000 m³/a

Main tools:
scrapping press
(force 5,000 kN)
4-column press
(force 15,000 kN)

Nuclear Waste Management Division II (ANE II) Incineration of solid and liquid waste

Capacity (on average): 165 Mg/a

Furnace type:

shaft furnace with afterburn - chamber and flue gas scrubber, HEPA filters and dioxin filters

Special attribute: suitable for alpha waste

Nuclear Waste Management Division II (ANE II)

New evaporation facility (circulation evaporator)

2 tanks with 34 m³ usable volume

Evaporation throughput:

200 -250 l / h (depending on solid residues)

Annual throughput (on average):

470 m³ chemical effluents

20 m³ evaporation concentrate

Nuclear Waste Management Division III (ANE III)

ILW scrapping/compaction

Tools:

4-column press (20,000 kN),
hydraulic cutter, hacksaw,
hand and force manipulators,
small tools

Nuclear Waste Management Division III (ANE III)

New solidification facility

Throughput (on average)

approx. 20 m³ evaporation concentrate

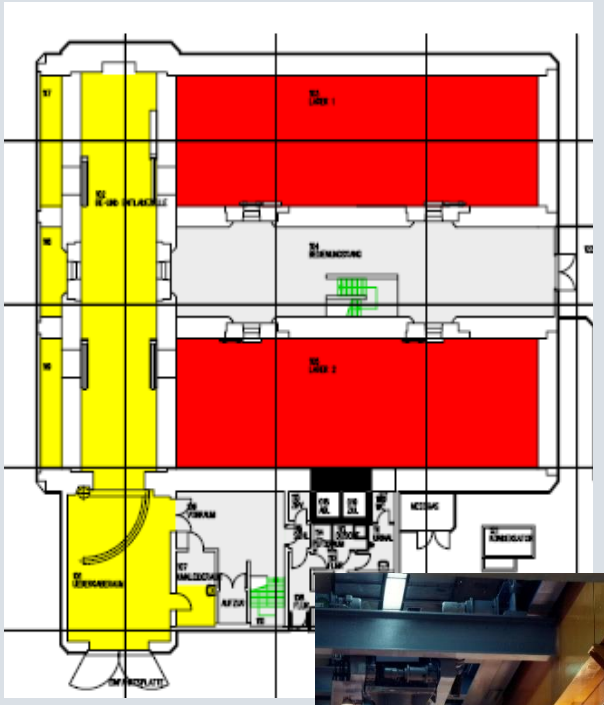
approx. 180 200l drums with solidified/cemented waste

Nuclear Waste Management Division III (ANE III)

Storage for heat-generating waste

Storage building 563 serves as a storage facility for wasteproducts (from decommissioning projects) as well as of raw waste products.

As of December 2014 storage chambers A and B hold 2,424 200l drums with either raw waste or waste products.



In order to maintain the possibility of accepting raw waste with high dose rates from the decommissioning projects of WAK and waste products from the treatment, a new storage has to be build in due time.

Nuclear Waste Management Division IV (ANE IV)

Interim storage for waste with negligible heat generation

Capacity:

77,400 m³ storage space

7,500 Type IV KONRAD containers

Stock:

62,000 m³ occupied

67,400 waste products

6,000 containers

7,000 single-cask shieldings

Storage is allowed only for waste products from FZK, WAK, ITU, the Federal State Collection Center BW, Siemens Hanau and GKN.

Waste products of any other clients can only be stored in preparation for transport.

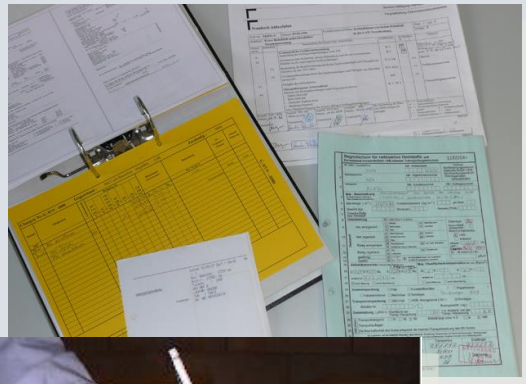
Nuclear Waste Management Division IV (ANE IV)

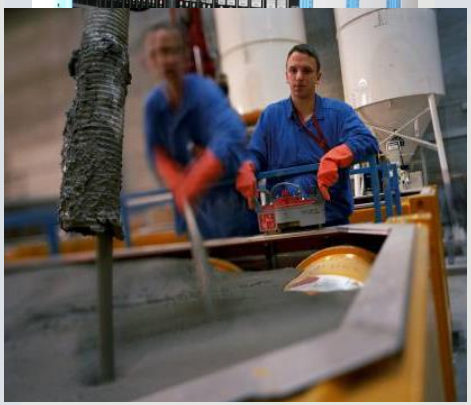
Receiving store and transport

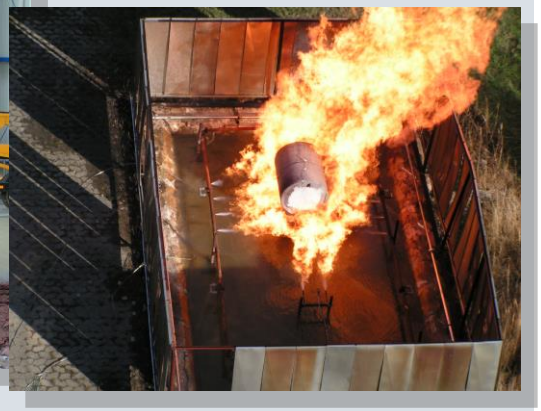
All incoming raw and pre-conditioned waste is stored in the receiving store until processing in one of the HDB facilities is possible.

Staff Division 1 – Final storage/documentation

- Documentation for final repository
- Container licensure
- Operational quality assurance/documentation

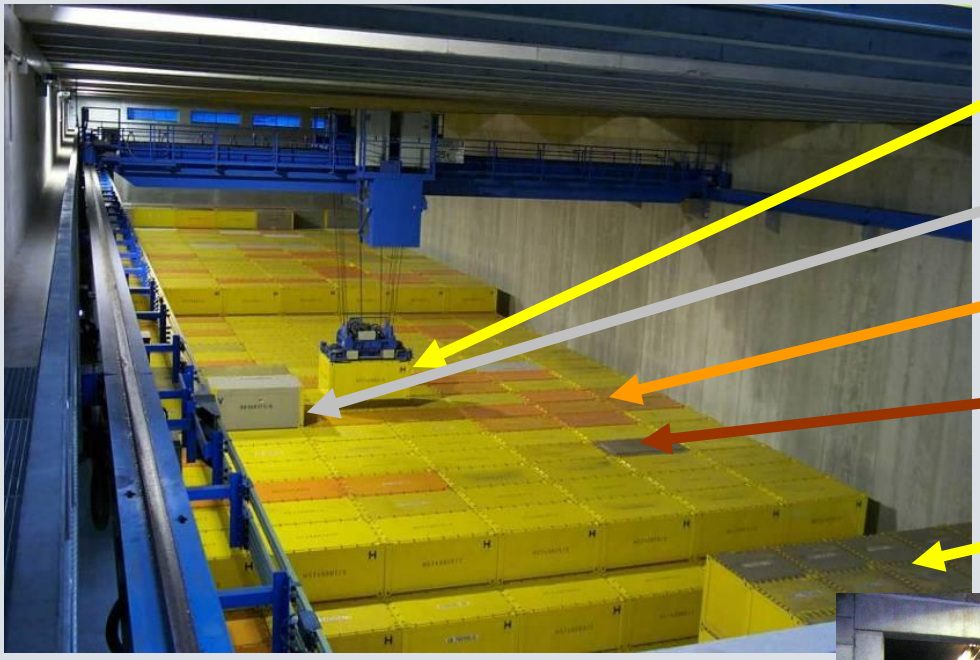


Container Licensing

Approx. 6,000 KONRAD containers and 7,000 single-concrete casks (VBA) without approval for transport and the final repository by BAM or BfS.



approx. 2,750 type IV FSC

approx. 1,000 type IV NBC

approx. 1,100 type IV PSC

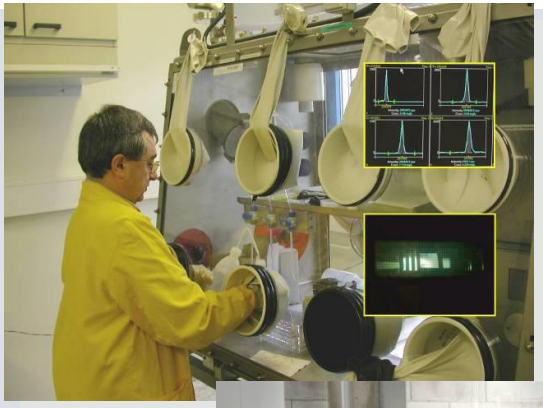
approx. 1,150 type IV SBC

approx. 240 type II PSC

approx. 7,000 type I VBA (NBA/SBA)

Staff Division 2 – Analytics

- Radiochemical laboratory (radioanalysis, elemental analysis)



- Reception and product control (NDA by-γ-Specrometry, dose-rate measurements and neutron counting)

Treatment of radioactive waste at HDB

Objective of waste treatment

1. Reduction of radioactive waste through decontamination and release
2. If this cannot be achieved
   - Reduction of volume (incineration, evaporation, compaction)
   - Compliance with requirements of the repository KONRAD through:
     - Solidification
     - Immobilization of radioactive parts (compaction, cementation)
     - Desiccation

C-14 in the waste streams of WAK GmbH

The waste materials present at HDB contain an overall activity of 1.57E+13 Bq of declared C-14.

The major contributions are:

- Core components from the various reactors
- Casings, hulls and ends from reprocessed nuclear fuel
- Solidified aqueous waste

C-14 in the waste streams of WAK GmbH

In Germany the acceptance criteria of the repository Konrad have the following requirements:

- Declaration of C-14 in terms of mobility (< 1%, 1-10 %, not specified)
- The overall activity of C-14 in Konrad is limited to 4.0E+14 Bq (Mean 1.3E+9Bq/m^3)
- Due to the high limitations generally C-14 is no problematic nuclide

C-14 exceeding the Konrad limitations

In Germany exist a variety of waste-streams containing C-14 beyond the limits of the repository Konrad:

- Core components
- Highly irradiated structural components
- Waste from C-14 production
- Vessel of the prototype reactor AVR

Recent development with regard to C-14

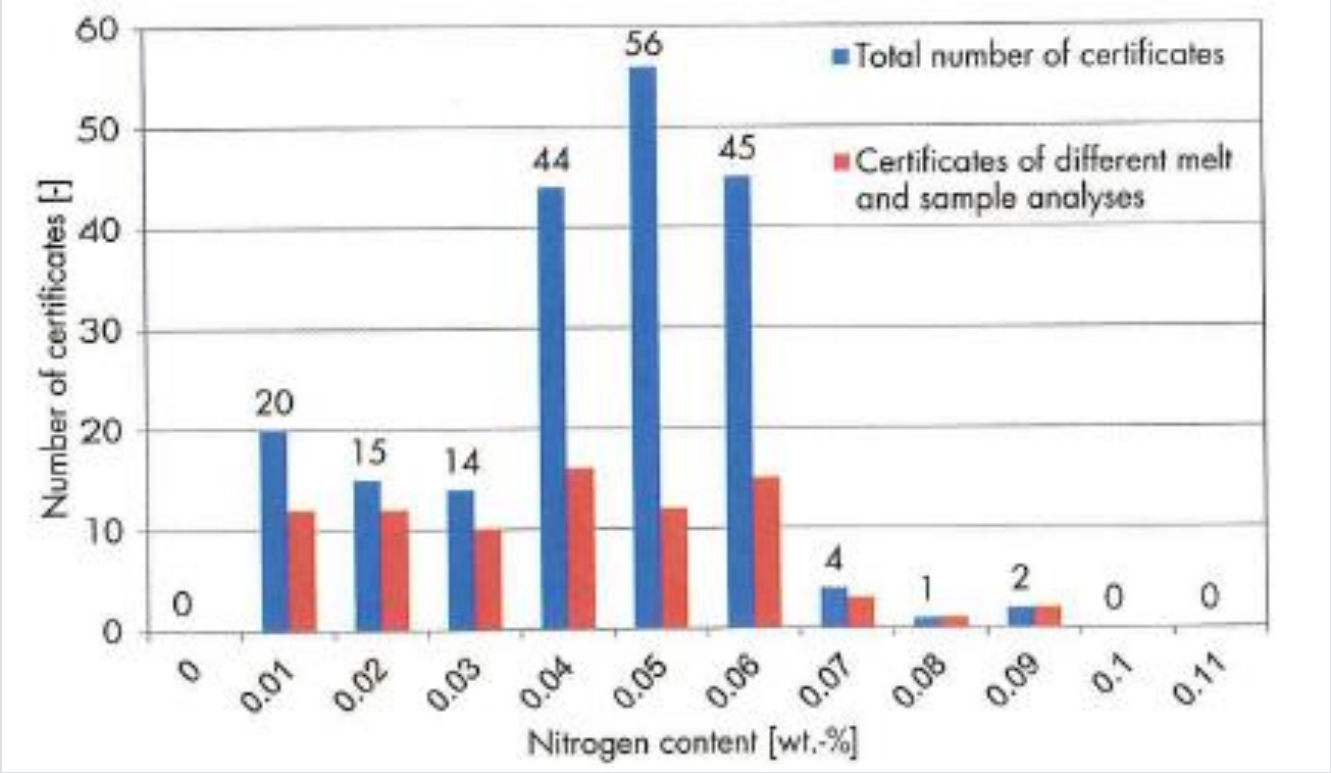
Due to the high uncertainties with regard to the Nitrogen-Content of the various metal types in nuclear reactors especially in the 1970ies and 1980ies GNS and WTI published a recalculation of C-14- in activated core components.

Nitrogen content [wt.-%]	C-14 activities for reference material 1.4550 relative to nominal value Flux factor					
	1	0.1	0.01	0.001	0.0001	0.00001
0.01	9.08 %	0.91 %	0.091 %	0.009 %	0.001 %	0.0001 %
0.03	27 %	2.74 %	0.274 %	0.027 %	0.003 %	0.0003 %
0.05	45 %	4.54 %	0.454 %	0.045 %	0.005 %	0.0005 %
0.07	63 %	6.37 %	0.637 %	0.064 %	0.006 %	0.0006 %
0.09	81 %	8.17 %	0.817 %	0.082 %	0.008 %	0.0008 %
0.11	4.16E+08[1)]	10 %	1 %	0.1 %	0.01 %	0.001 %

Tab. 1.
Calculated C-14 activities depending on the neutron fluence.

Recent development with regard to C-14

Distribution of N in the steel types



Legal requirements

- The acceptance and treatment of radioactive waste requires the compliance with the boundary conditions of:
  - the Atomic Energy Act
  - the Radiation Protection Ordinance
  - the waste acceptance requirements of the respective repository
  - the permission of the HDB.
- The German Radiation Protection Ordinance requires the accounting of radioactive wastes in terms of mass, radiological and physical composition in an electronic database to provide comprehensive information to the appropriate authority upon request.
- The methods of treatment have to be approved by the Bundesamt für Strahlenschutz (BfS, Federal Radiation Protection Authority for this reason treatment methods are regularly defined in tabular qualitie control plans (Ablaufpläne) .

Conditioning of radioactive waste at HDB

Necessary administration:

Transfer of waste to HDB → **Conditioning** → **Documentation** → **Goal: final disposal at KONRAD**

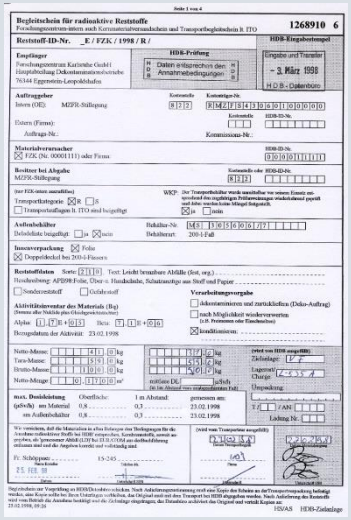
correct declaration of waste

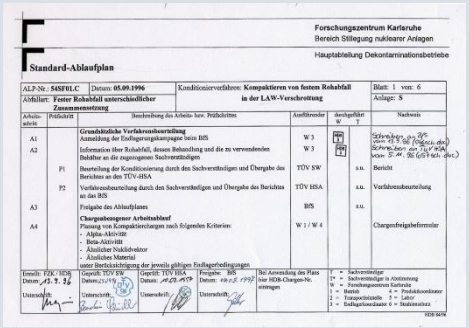
treatment according to process control plan

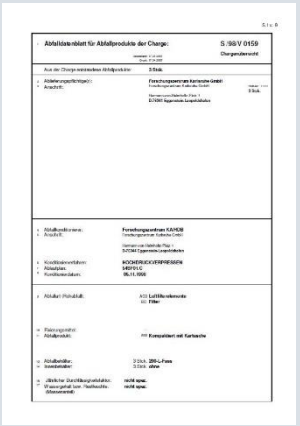
compilation and verification of waste data sheet

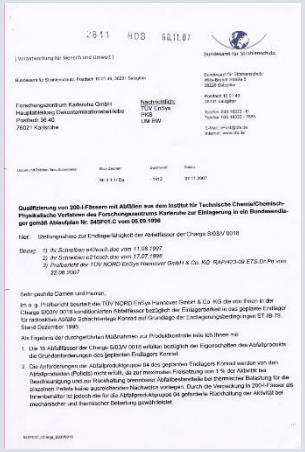
Proof of conducted product control measures

approval by BfS (federal authority) = compliance with KONRAD requirements



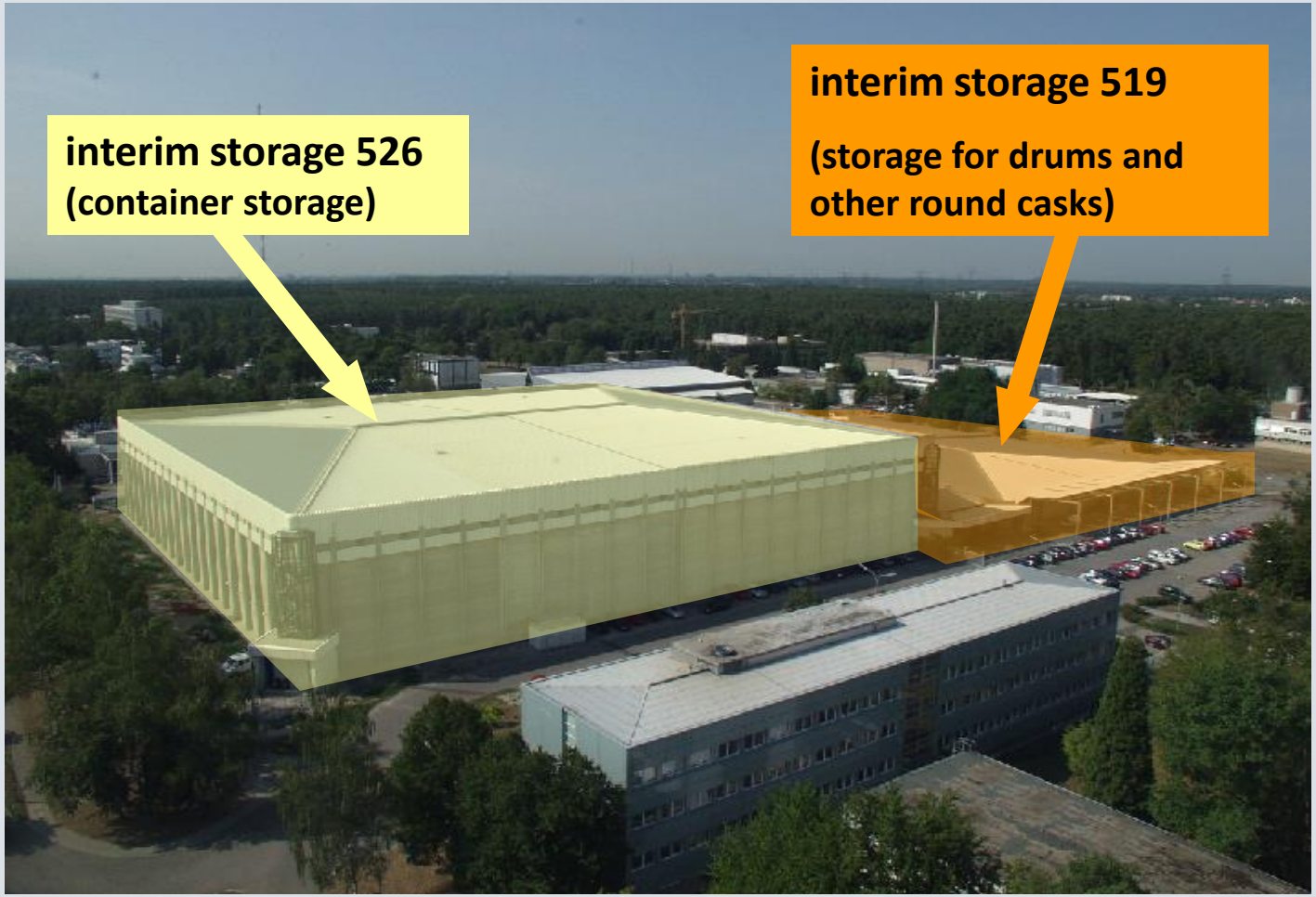






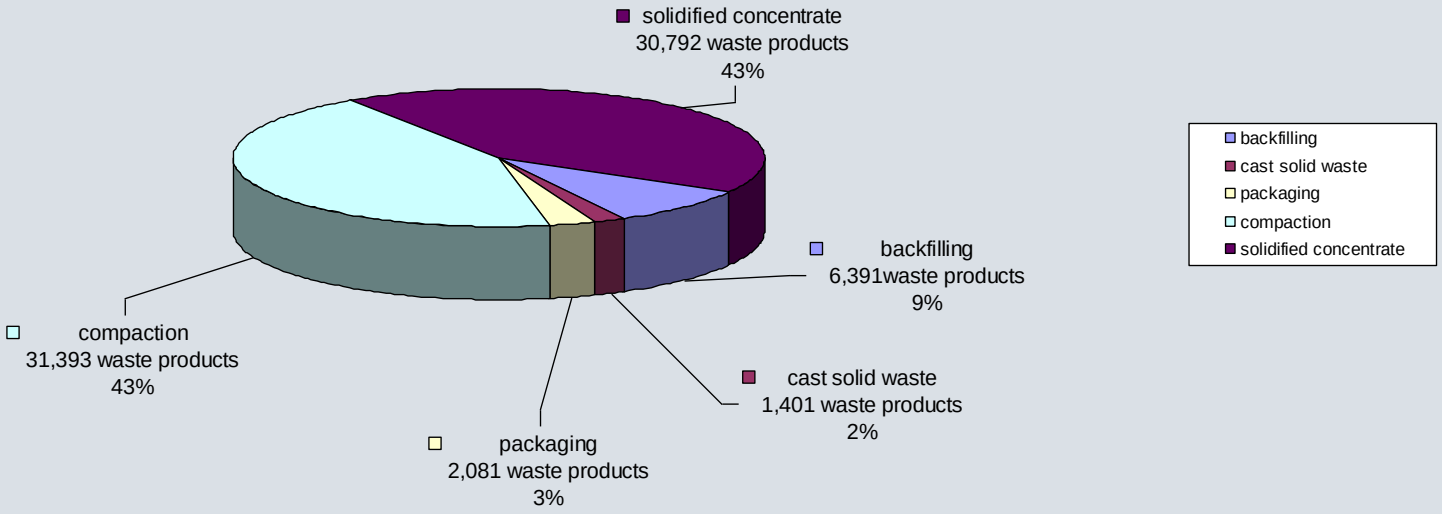
Inventory of radioactive waste

- **HDB interim storage 519/526**



Inventory of radioactive waste

- **Waste distribution at HDB interim storage**
  - **capacity 77,500 m³, approx. 66,000 m³ occupied ≙ approx. 85 %**



Total: 72,058 waste products

Inventory of radioactive waste

- **Interim storage 519**

storage chamber with drums

Cask inventory in L519

approx. 5,500 200-litre drums,
approx. 400 cast-iron casks (SGA, Mosaik) and
approx. 7,000 concrete-shielded casks

storage chamber with concrete-shielded casks

Waste package quality assurance

- **Waste package quality assurance**

unloading of containers

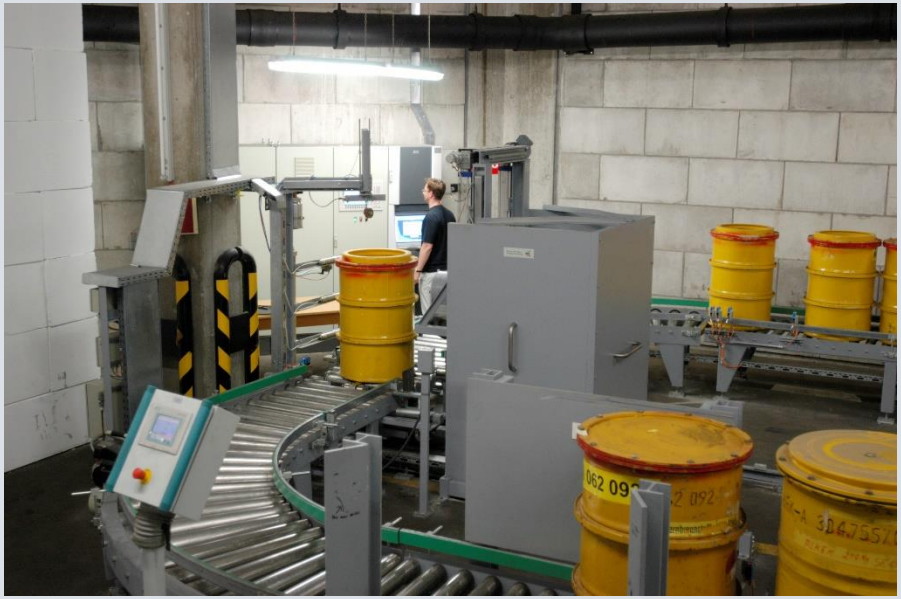
drill line

(placement of pressure relief valves and preparation for gas analysis)

Waste package quality qssurance

- **Waste package quality assurance**

gas sampling



gamma spectrometry

Waste package quality assurance

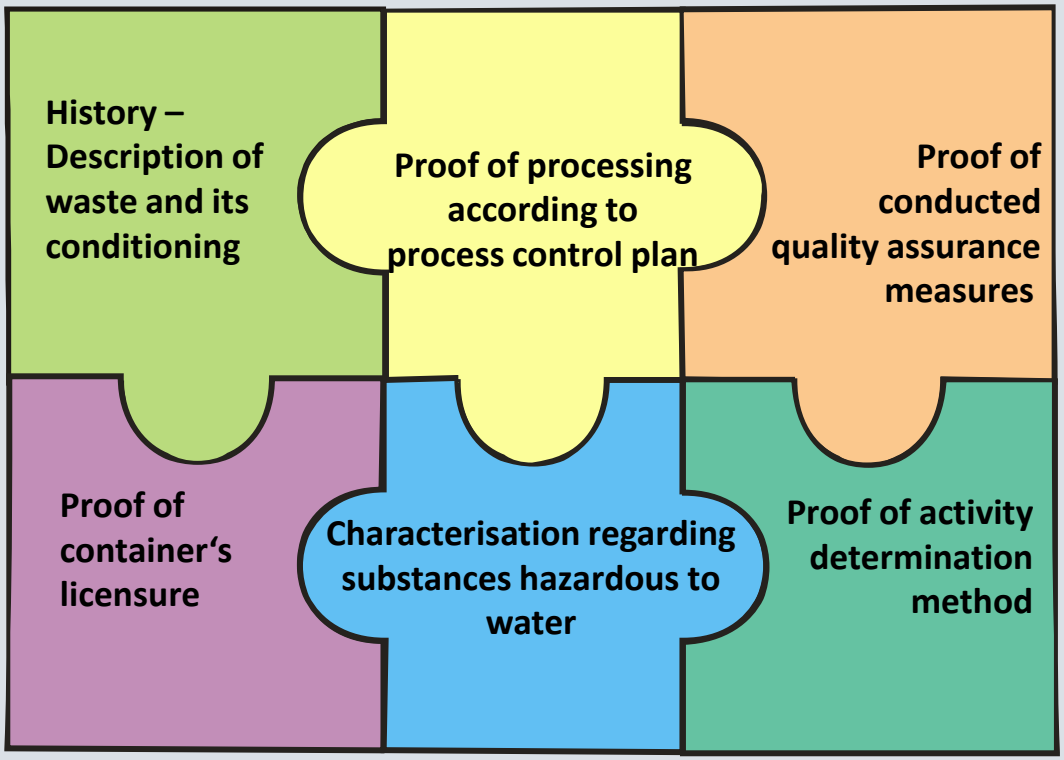
- **Waste package quality assurance**

dose rate measurement, weight check and photo documentation

cementing of containers

Goal: Repository KONRAD

Necessary documentation blocks:



WAK Safety and Responsibility.
For Decades.

CArbon-14 Source Term
CAST

Name: Michel Herm
Organisation: KIT-INE
Date: July 06, 2016

The project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 604779, the CAST project.

Outline

Separation and analysis of gaseous/dissolved C-14 compounds in structural parts of irradiated LWR fuel elements

Training Course
C-14 behaviour under repository conditions

July 05–06, 2016, Karlsruhe, Germany

- Introduction
- Materials and irradiation characteristics
- Preparation of subsamples
- Dissolution experiments involving Zircaloy-4 and stainless steel
- Extraction of ^{14}C from gaseous and aqueous samples
- Methods (LSC, gas-MS, γ-spectroscopy)
- MCNP calculations
- Results

Introduction

- ^{14}C is a key radionuclide in safety assessments of geological disposal systems for nuclear waste
- Chemical form of ^{14}C upon release unknown and $t_{1/2}$ = 5730 a
  → ^{14}CO, $^{14}CO_2$, gaseous/dissolved hydrocarbons
- Speciation crucial to assess mobility/retention of ^{14}C upon release
  → gaseous/dissolved hydrocarbons hardly retained in technical/geo-technical barriers
- Until now: transfer of total ^{14}C inventory to biosphere considered in safety assessments

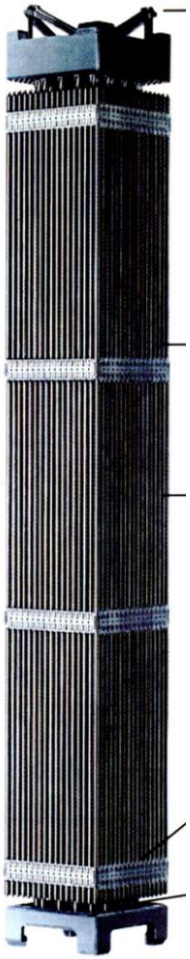
Introduction

- Physical formation of ^{14}C in fuel assemblies by
  - neutron capture reactions
  - ternary fission in the fuel

  during reactor operation

$^{14}_{7}\mathrm{N}(\mathrm{n},\mathrm{p})^{14}_{6}\mathrm{C}$	$^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n} \rightarrow \left[^{15}_{7}\mathrm{N}\right]^{*} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p}$
$^{17}_{8}\mathrm{O}(\mathrm{n},\alpha)^{14}_{6}\mathrm{C}$	$^{17}_{8}\mathrm{O} + {}^{1}_{0}\mathrm{n} \rightarrow [^{18}_{8}\mathrm{O}]^{*} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{4}_{2}\mathrm{He}$
$^{13}_{6}\mathrm{C}(\mathrm{n},\gamma)^{14}_{6}\mathrm{C}$	$^{13}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n} \rightarrow [^{14}_{6}\mathrm{C}]^{*} \rightarrow {}^{14}_{6}\mathrm{C} + \gamma$

ternary fission in LWR fuel	1.7×10^{-6} per thermal ^{235}U fission 1.8×10^{-6} per thermal ^{239}Pu fission



Introduction

- N and C are present as impurities in fuel, Zircaloy cladding and structural parts of LWR fuel assemblies
- ^{17}O is a stable low-abundance, naturally occurring istope
- Exemplary N impurities and calculated ^{14}C inventories of spent PWR fuel assemblies with an average burn-up of about 50 GWd/t_{HM}:

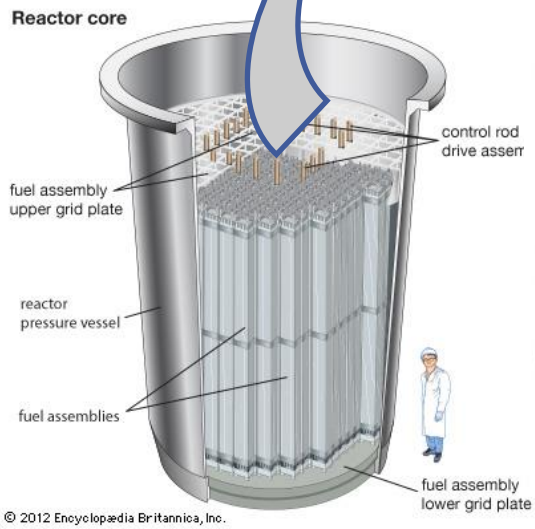
material	N impurity [ppm]	calculated ^{14}C inventory [Bq/g]
PWR SNF	~10	~27200
Zircaloy-4	~40	~30000
stainless steel	~500	~80000

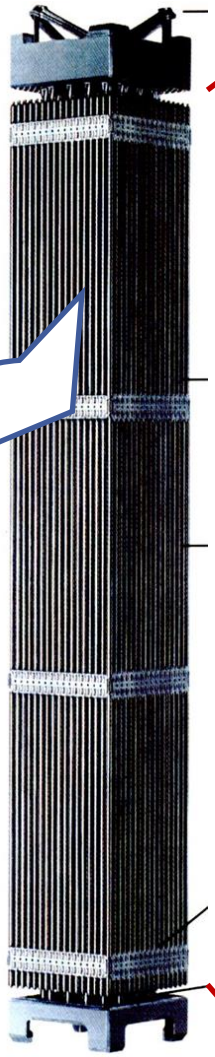
Introduction

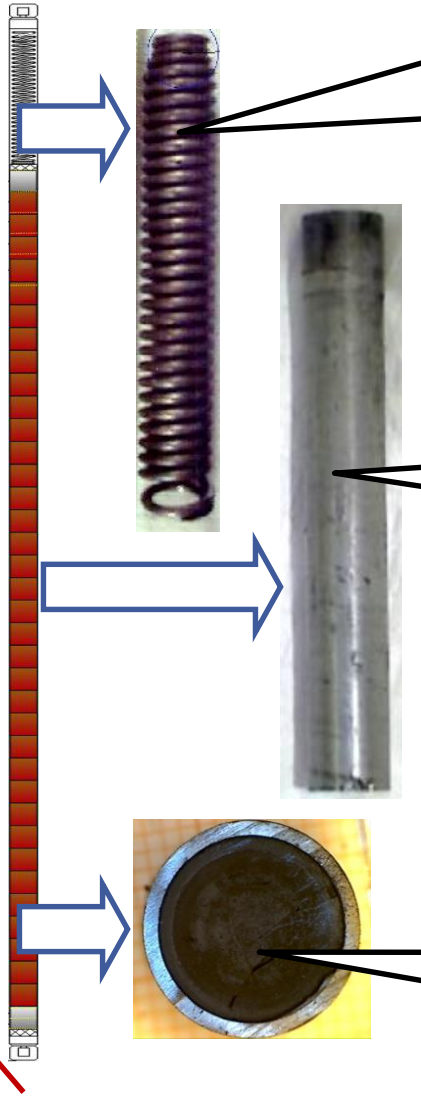
- N, C in Zircaloy / stainless steel **before** irradiation is potentially present as
  - interstitial solid solution
  - N also present as nitrides of alloying metals
  - C also present as metal carbides
  - carbonitrides maybe also form
- ^{14}C is potentially present in Zircaloy / stainless steel **after** irradiation as
  - interstitial ^{14}C from interstitial N
  - carbides / carbonitrides
- Corrosion leads to formation of volatile and/or dissolved compounds
  - hydrocarbons/CO (carbonates from oxides)
- Chemical state of ^{14}C is far from clear in Zircaloy / stainless steel / spent nuclear fuel

LWR fuel assembly parts

Gösgen (CH) PWR core:
- 177 fuel assemblies
- 15×15 lattice
  - 205 fuel rods
  - 20 guide tubes





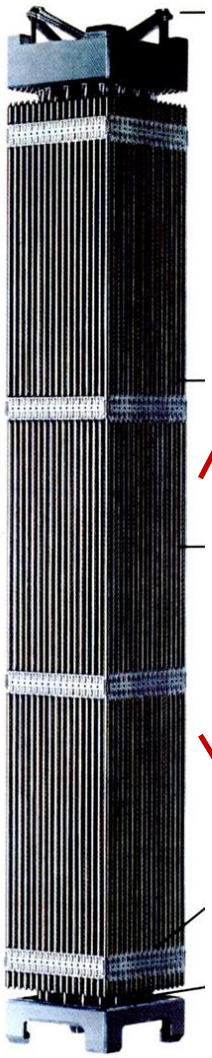


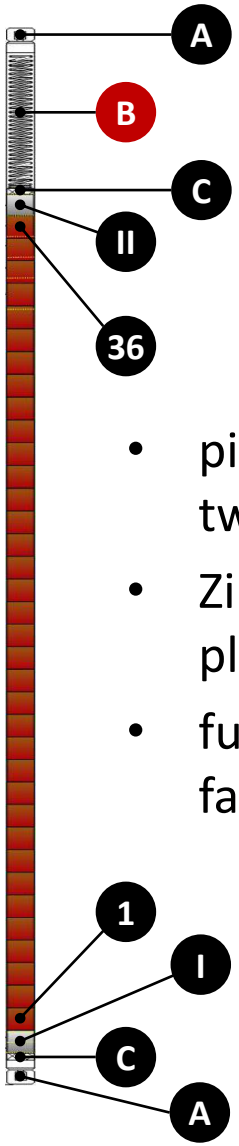
^{60}Co
^{55}Fe
^{63}Ni
^{59}Ni
^{14}C

^{60}Co
^{125}Sb
^{55}Fe
^{14}C
^{137}Cs
^{90}Sr

An (Pu, Np, Am,…)
FP (^{137}Cs, ^{90}Sr, ^{99}Tc, ^{129}I,…)
AP (^{14}C)

Origin of the material used in this study





B **Zircaloy-4 cladding around stainless steel spring**

no contamination of cladding by fuel

- pin KKG–SBS1108 consists of five fuel rod segments + two dummy segments
- Zircaloy-4 cladding specimen are sampled from the plenum of fuel rod segment SBS1108–N0204
- fuel rod segment with UO_2 fuel pellets (3.8 wt.% ^{235}U), fabricated by “Kraftwerk Union AG” (today Areva)

A end cap

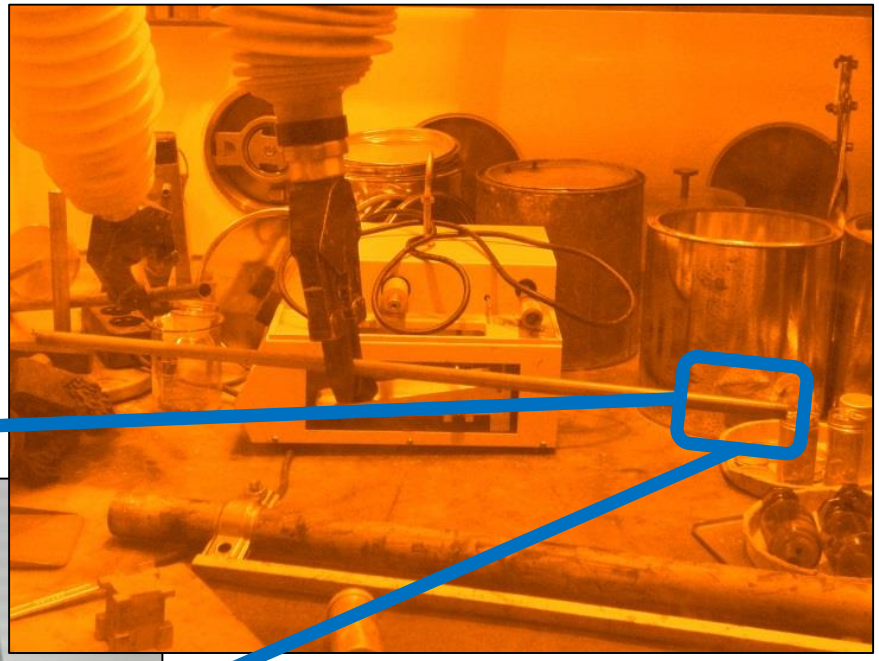
C insulation pellet

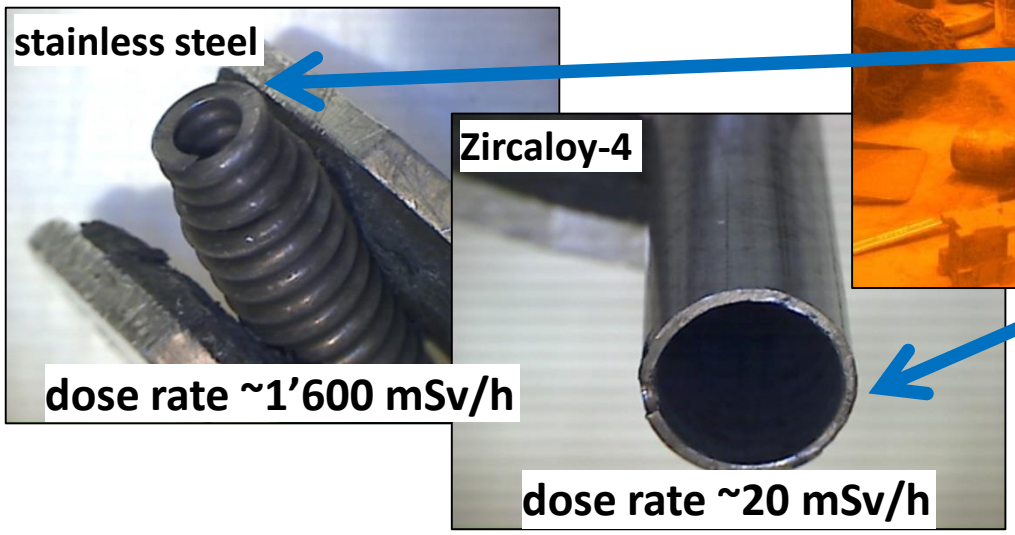
I + **II** “natural” UO_2

1 … **36** “enriched” UO_2

Irradiation characteristics of SBS1108

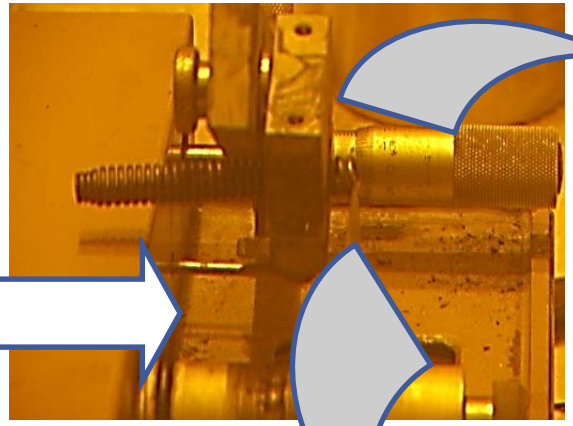
- Irradiated in the Swiss Gösgen PWR during four cycles (1985–1989)
- 1226 effective full power days
- Average burn-up: 50.4 GWd/t_{HM}
- Average linear power: 260 W/cm
- Max *T*: > 1300°C
- Stored gas tight until 2012

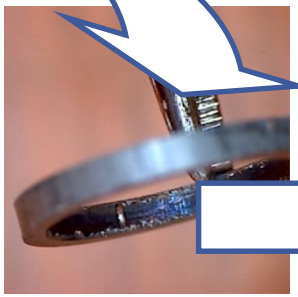




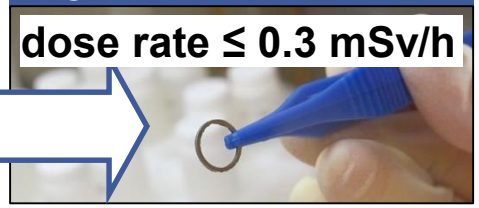
Preparation of subsamples

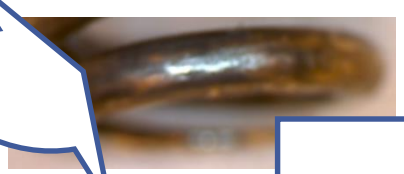
- Preparation of small subsamples by dry cutting in hot cell





dissolution experiments in glove box





dissolution experiments in hot cell

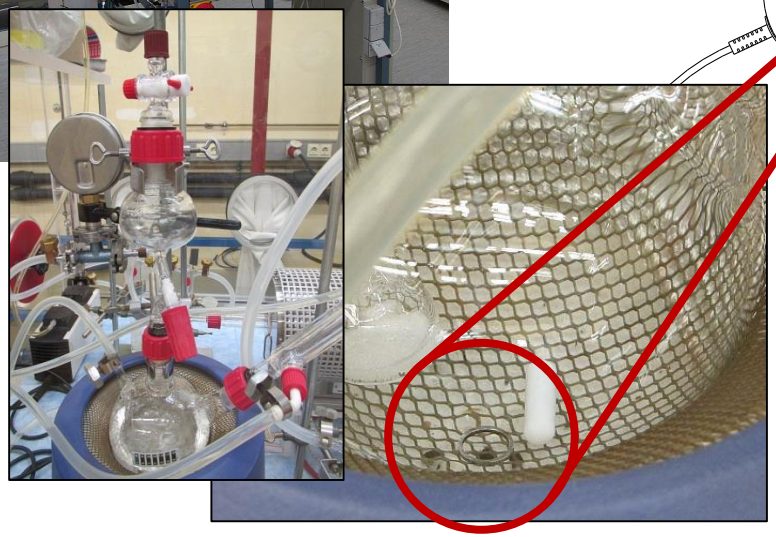
dose rate ≤ 120 mSv/h

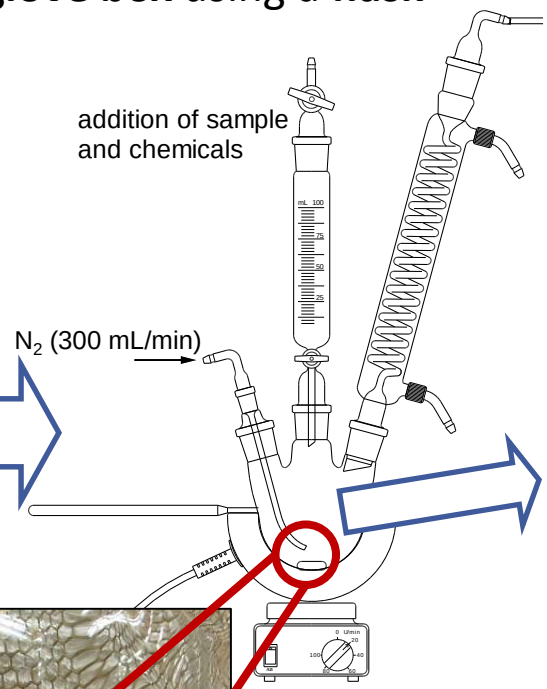
	Zircaloy-4	stainless steel
# of subsamples	6	1
mass [mg]	≤ 189.0	283.0
dose rate [mSv/h]	≤ 0.3	≤ 120

Dissolution experiments in glass reactor

dissolution of Zircaloy-4 subsamples in **glove box** using a **flask**

^{14}C extraction glove





to ^{14}C extraction system

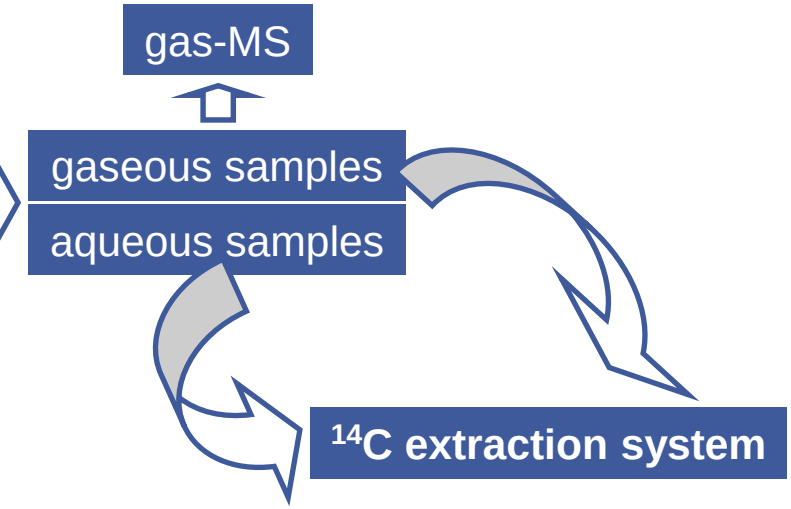
Liquid scintillation counting (LSC) for [^{14}C]

conventional (radio)chemical analyses determining e.g. ^{60}Co, ^{125}Sb, ^{137}Cs, actinides

- cladding sample is placed in a flask
- 100 mL 24% H_2SO_4 added
- 50 mL 10% HF added
- cladding digested within 30 min at RT

Dissolution experiments in autoclave

dissolution of Zircaloy-4 subsamples in **glove box** using an **autoclave**

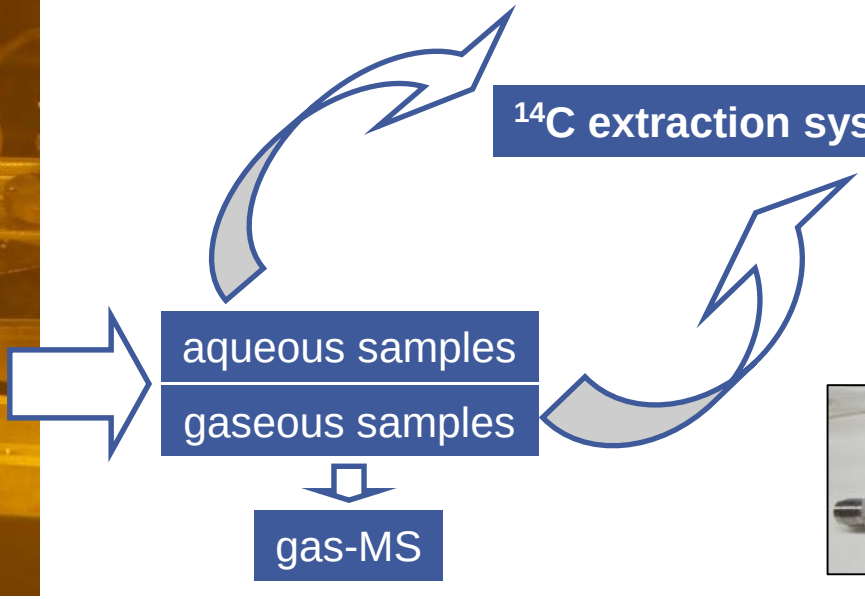


- cladding sample placed in autoclave
- autoclave sealed air tight
- gas collecting cylinder mounted on top
- flushing with Ar or N_2
- 20 mL 16% H_2SO_4 + 3% HF added
- p(autoclave) ~ 1.4 bar

Dissolution experiments in autoclave

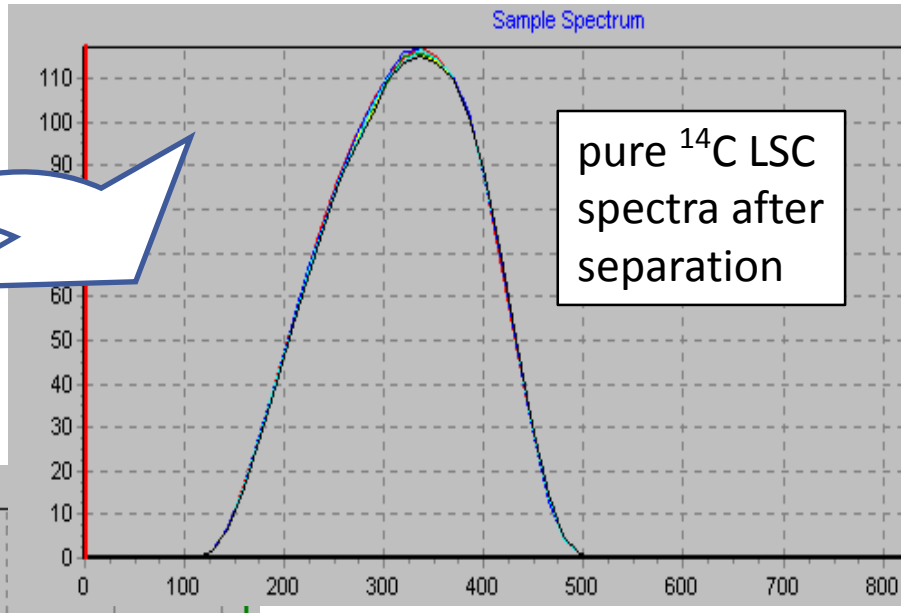
dissolution of stainless steel subsample
in **hot cell** using an **autoclave**

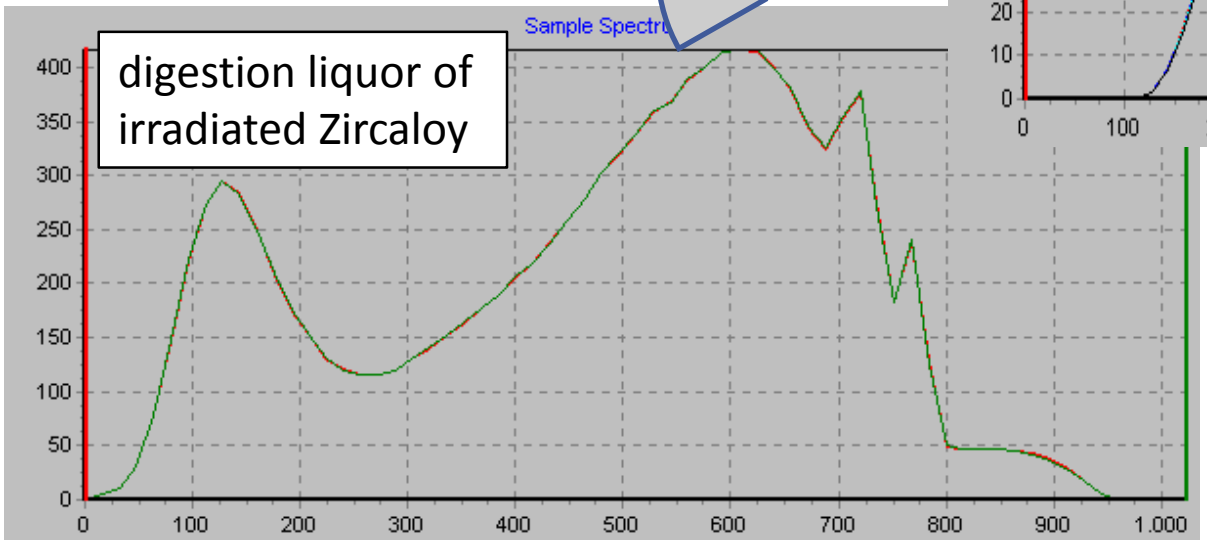
- stainless steel subsample placed in autoclave
- autoclave sealed air tight
- gas collecting cylinder mounted on top
- flushing with Ar
- 150 mL 24% H_2SO_4 + 3% HF added
- digestion of steel sample within a day at RT



Extraction of ^{14}C from digestion liquor

- ^{14}C is a difficult radionuclide to measure: pure soft β^- emitter (no γ-rays)





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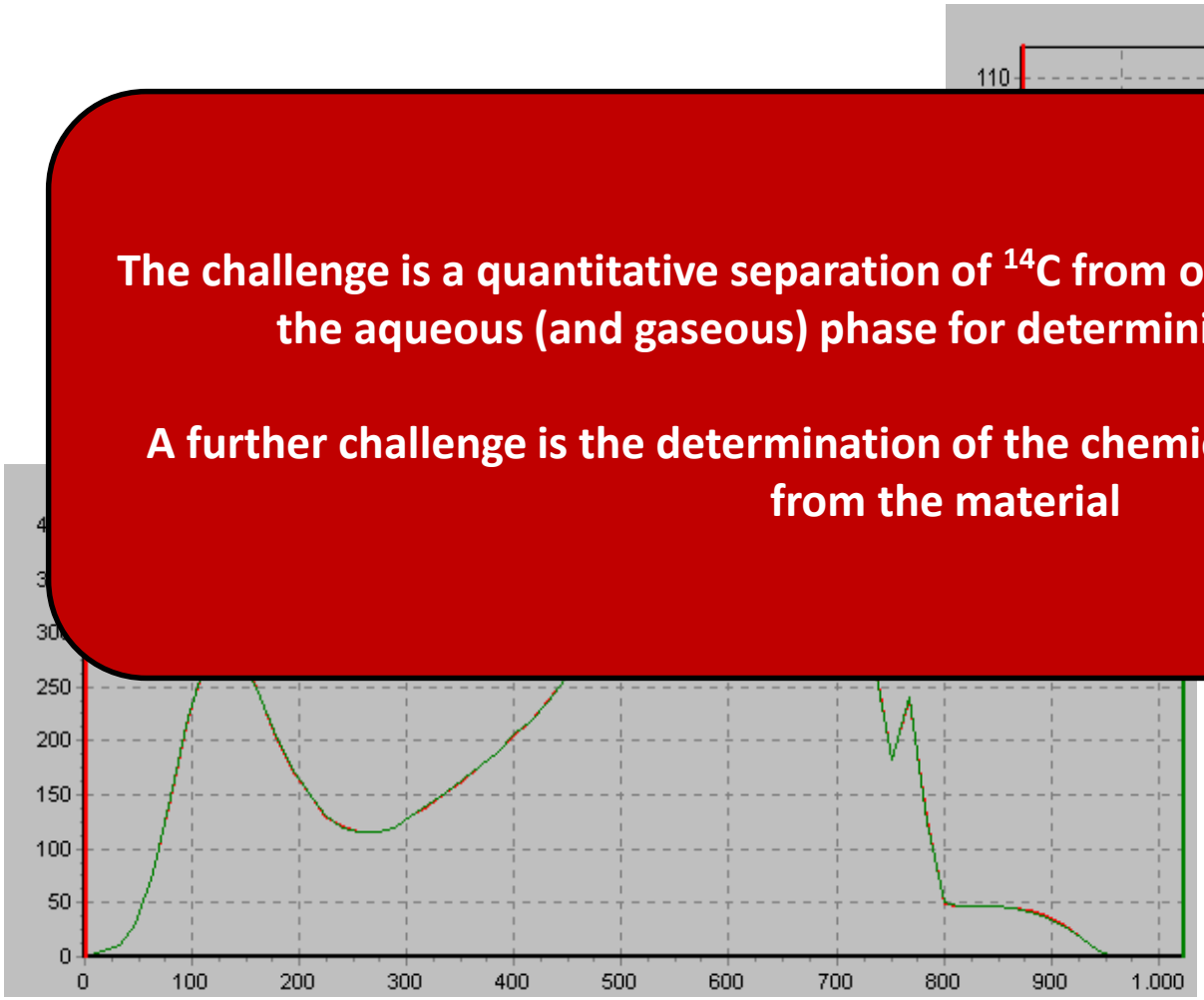

The challenge is a quantitative separation of ^{14}C from other radionuclides present in the aqueous (and gaseous) phase for determining the ^{14}C inventory.

A further challenge is the determination of the chemical form of ^{14}C after release from the material

^{14}C extraction – literature

- Aittola and Olsson (1980)
- Speranzini and Buckley (1981)
- Nott (1982)
- Bleier et al. (1983, 1984, 1987, 1988)
- Salonen and Snellman (1981, 1982, 1985)
- Martin et al. (1986, 1993)
- Moir et al. (1994)
- Stroes-Gascoyne et al. (1994)
- Vance et al. (1995)
- Yamaguchi et al. (1999)
- Magnusson et al. (2005, 2008)
- Schumann et al. (2014)

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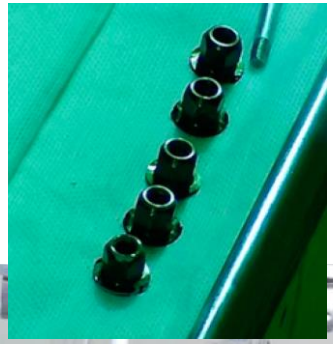
- Moir et al. (1994)
- **Stroes-Gascoyne et al. (1994)** – **^{14}C inventory in used CANDU fuel**
- Vance et al. (1995)
- **Yamaguchi et al. (1999)** – **^{14}C inventory/chemical form in Zircaloy**
- **Magnusson et al. (2005, 2008)** – **^{14}C chemical form in ion exchange resin**
- **Schumann et al. (2014)** – **^{14}C inventory in stainless steel**

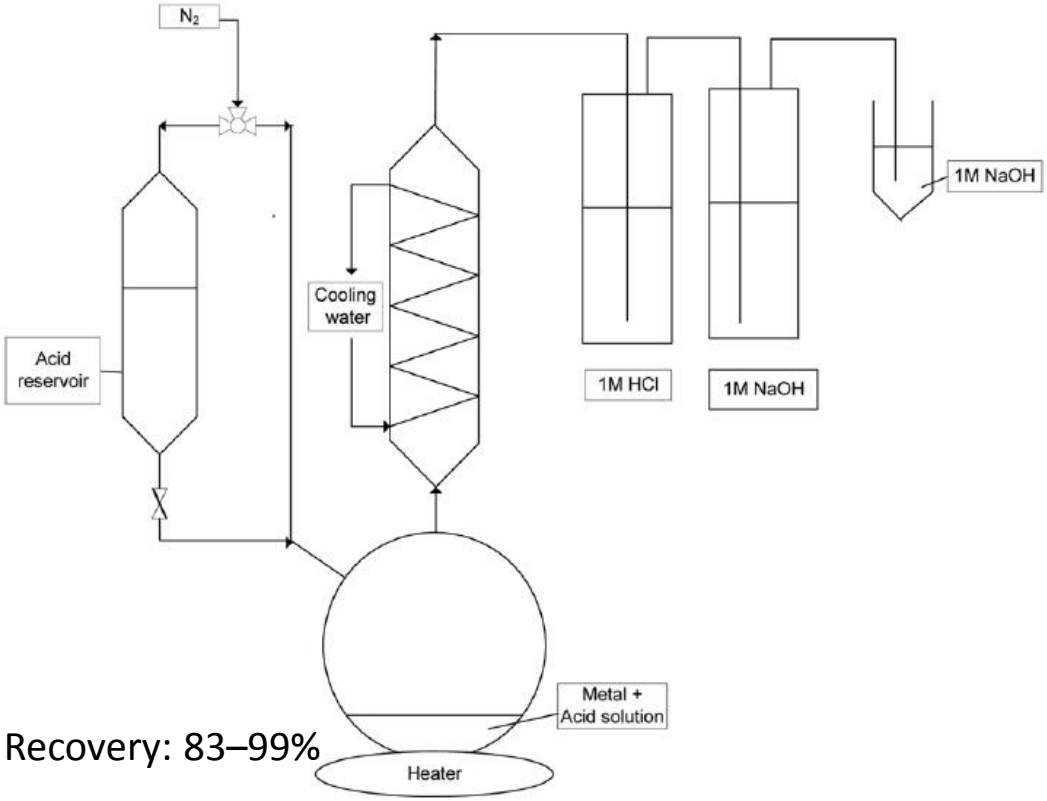
Similarities of methods:

- use of flasks and washing bottles
- alkaline traps → $^{14}CO_2$
- acidic traps → ^{3}H
- furnace (CO, CH_4 → CO_2)
- acid stripping/digestion
- wet oxidation
- carrier gas (N_2)
- vacuum pump
- Liquid scintillation counting

Schumann et al. (2014)

- Fuel assembly guide tube nuts (stainless steel) irradiated in PWR Gösgen (CH)
- Concentrated HNO_3/HCl (aqua regia) + H_2SO_4/$HClO_4$/HNO_3
- ^{14}C inventory determined by liquid scintillation counting (LSC)

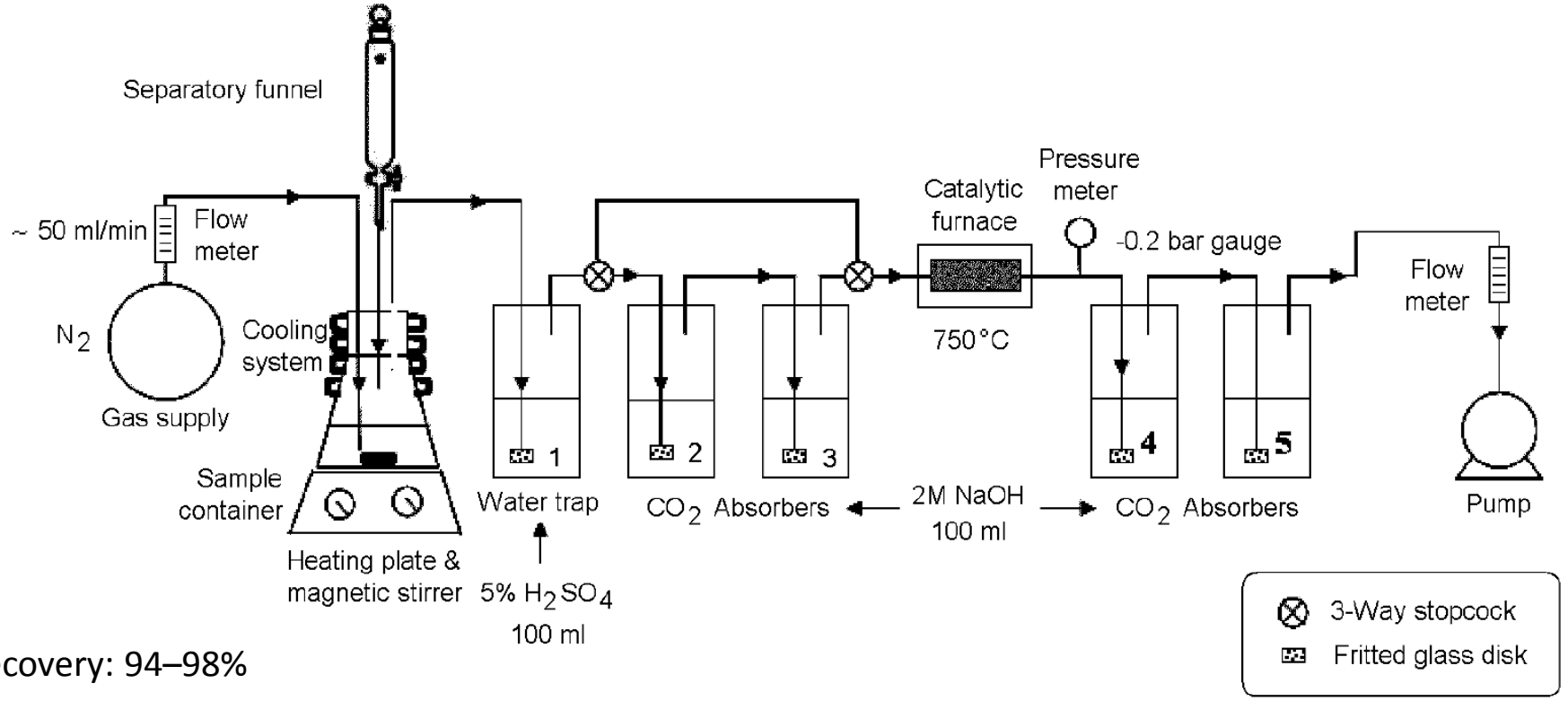




Recovery: 83–99%

Magnusson et al. (2005, 2008)

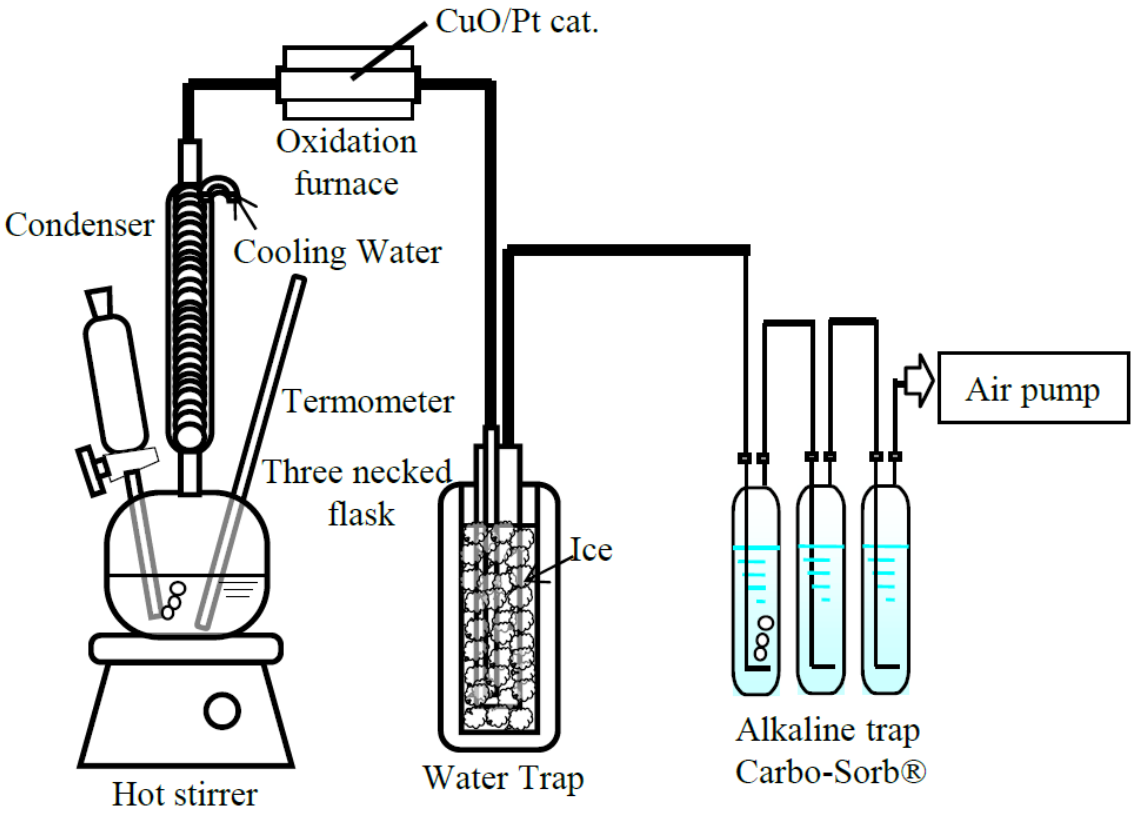
- Spent ion exchange resins and process water from nine PWR and BWR (Sweden)
- 6/8 M H_2SO_4 (acid stripping) + $K_2S_2O_8/AgNO_3$ (wet oxidation)
- ^{14}C inventory and chemical form determined in washing bottles using LSC



Recovery: 94–98%

Yamaguchi et al. (1999)

- Zircaloy-4 with/without oxide layer irradiated in PWR (47.9 GWd/t_{HM})
- HNO_3 + HF
- ^{14}C inventory determined in washing bottles (chemical form of ^{14}C determined in leaching experiments)



Recovery: 80–100%

Stroes-Gascoyne et al. (1994)

- Used CANDU fuels (5.4–15.5 GWd/t_{HM}), one pellet of about 20 g
- Boiled in 50% HNO_3 + 1.6 M $Na_2S_2O_8$, 6 h under refluxing
- ^{14}C inventory determined by LSC

Experimental set-up:

- Flask with cooler and washing bottles
- N_2 as carrier gas
- ^{3}H trap (0.1 M HNO_3)
- ^{14}C trap (0.2 M NaOH)
- furnace (CuO, 500°C)
- activated charcoal filter to remove ^{129}I

Recovery: 87.6 ± 11.9%

^{14}C extraction set-up and procedure

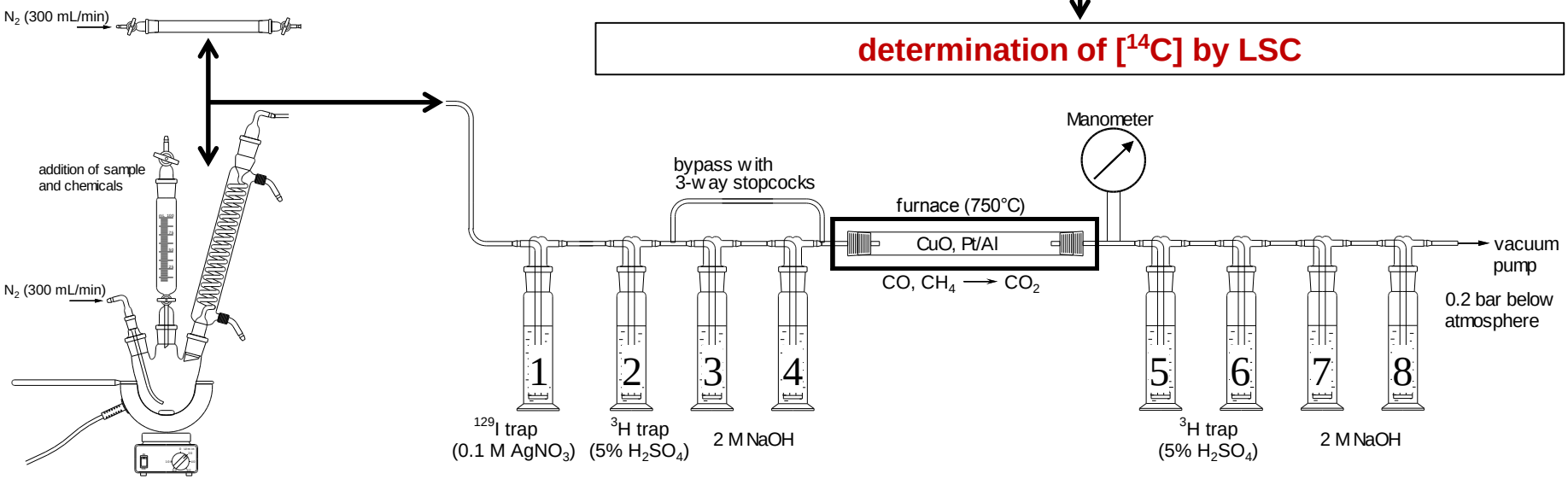
acid digestion in glass reactor

acid digestion in autoclave

gas-MS

absorption of $^{14}CO_2/CO_2$ in various washing bottles

determination of [^{14}C] by LSC



^{14}C extraction set-up and procedure

acid digestion in glass reactor

acid digestion in autoclave

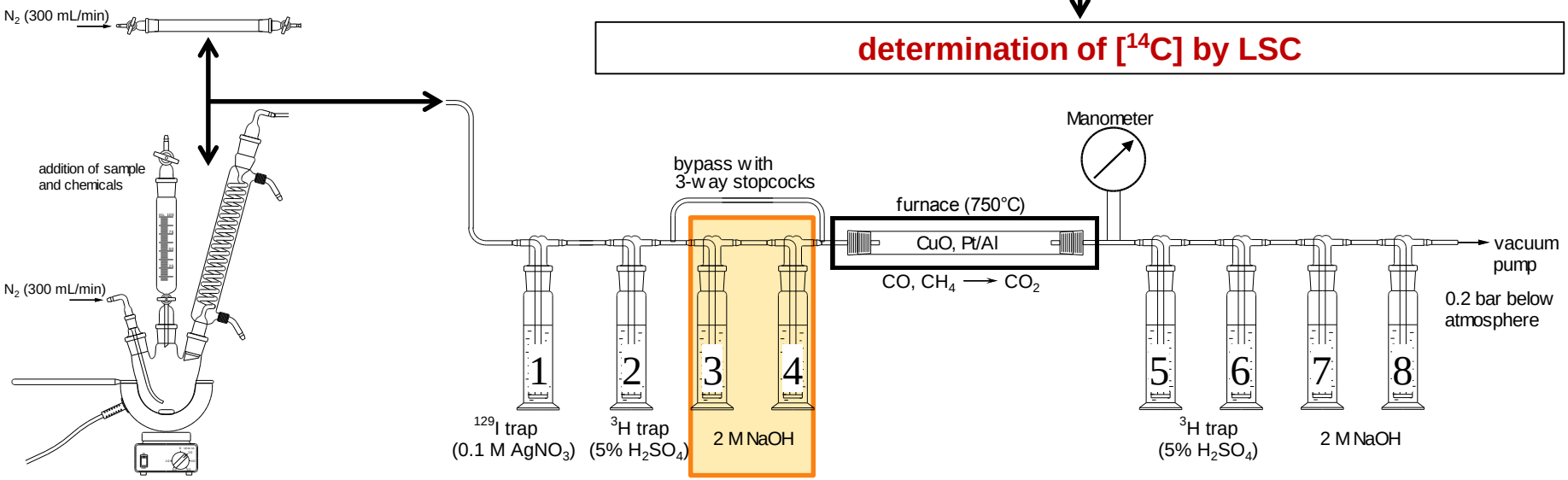
gases released during digestion / gaseous samples

CO_2

gas-MS

absorption of $^{14}CO_2/CO_2$ in various washing bottles

determination of [^{14}C] by LSC



^{14}C extraction set-up and procedure

acid digestion in glass reactor

acid digestion in autoclave

gas-MS

gases released during digestion / gaseous samples

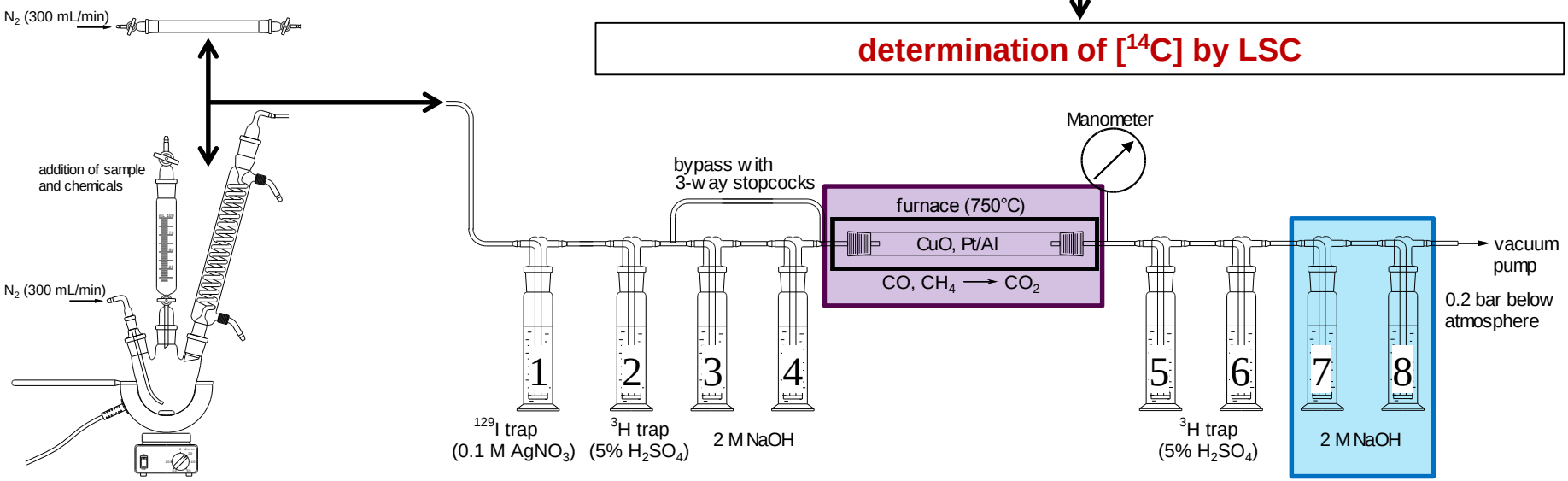
CO, gaseous hydrocarbons

CO_2

catalytic furnace (CuO, Pt/Al, 750°C)

absorption of $^{14}CO_2/CO_2$ in various washing bottles

determination of [^{14}C] by LSC



^{14}C extraction set-up and procedure

acid digestion in glass reactor

acid digestion in autoclave

gas-MS

gases released during digestion / gaseous samples

CO, gaseous hydrocarbons

CO_2

acidic digestion liquor

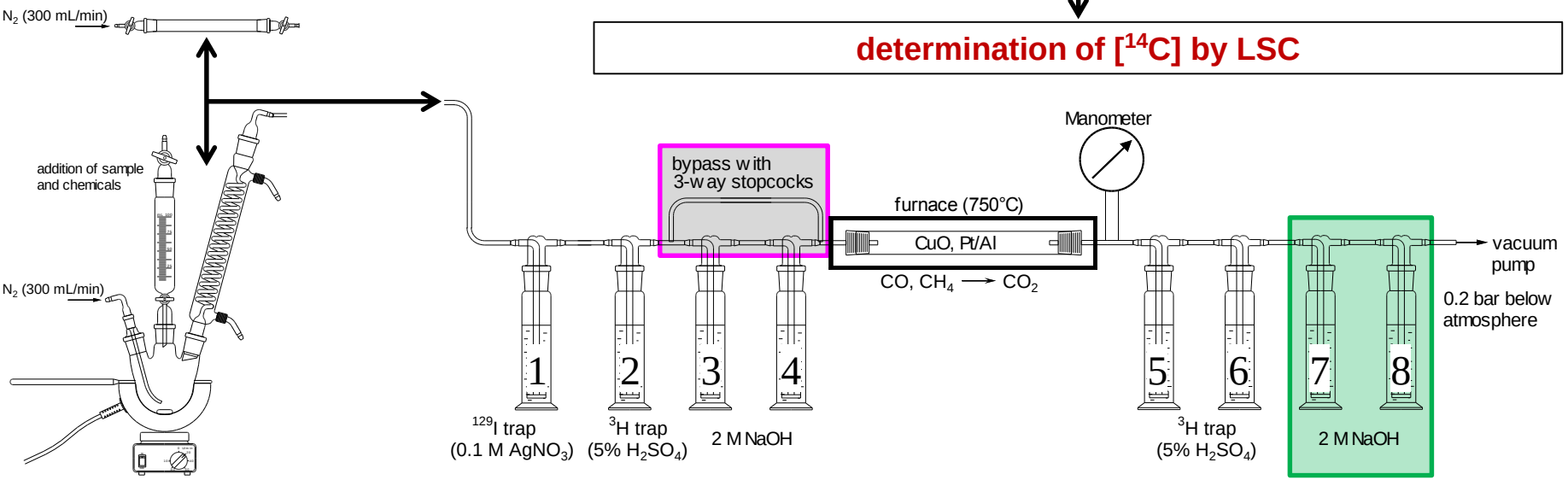
dissolved hydrocarbons

catalytic furnace (CuO, Pt/Al, 750°C)

wet oxidation ($K_2S_2O_8$, $AgNO_3$, 95°C)

absorption of $^{14}CO_2/CO_2$ in various washing bottles

determination of [^{14}C] by LSC



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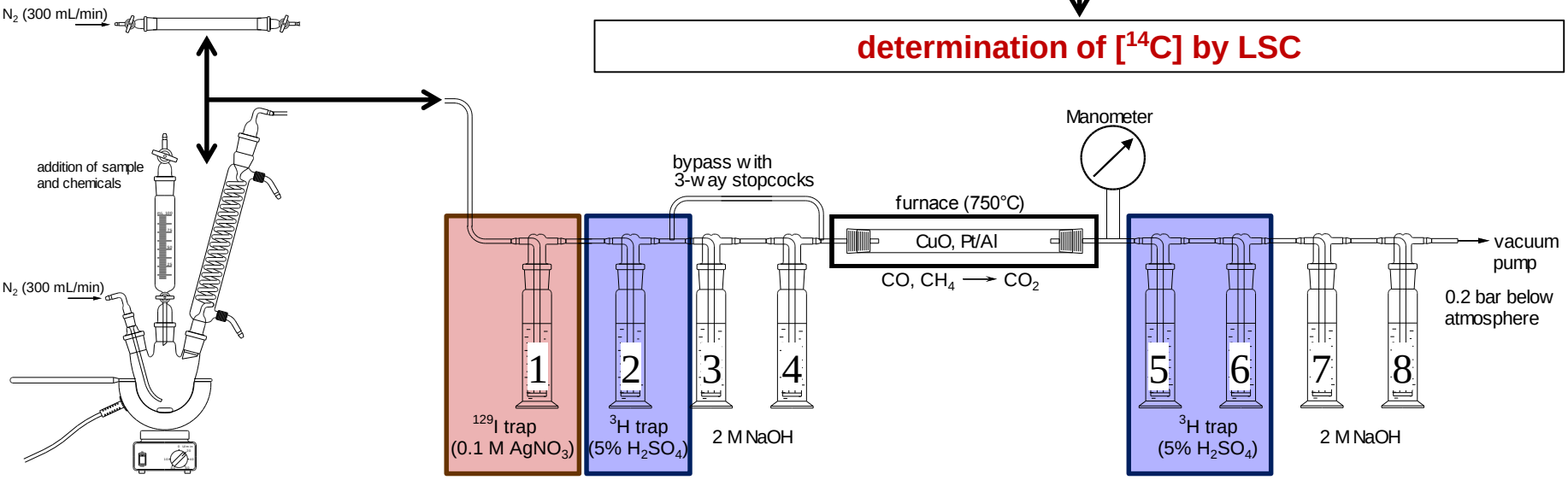
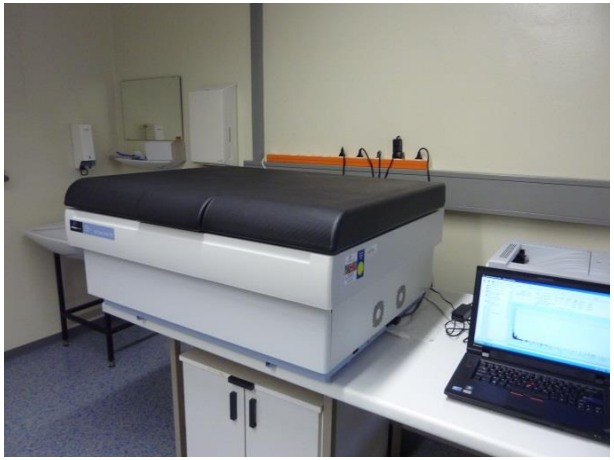


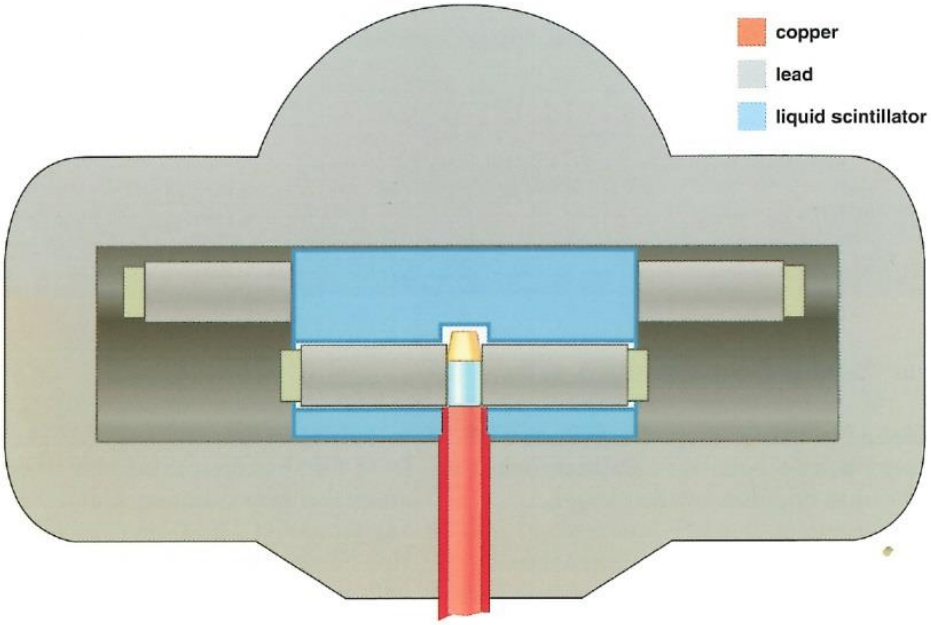
Methods: LSC measurements

- Determining activity of a radioactive sample by mixing the active material with a liquid scintillation cocktail (Toluene, Xylene)
- Radiation emitted by radionuclides transfers energy to solvent molecules
- Excited molecules relax back to ground state by emitting photons
- Photomultiplier converts and multiply light quanta into electrons which are subsequently detected by a semiconductor detector
- Detected light quanta are directly proportional to the decay energy



Methods: LSC measurements

- ultra-low level LSC spectrometer (Quantulus 1220, Wallac Oy, PerkinElmer)
- passive shielding (lead)
- active guard technology (active shielding)
  → remove natural background fluctuations by an anti-coincidence guard counter that detects cosmic and environmental γ radiation

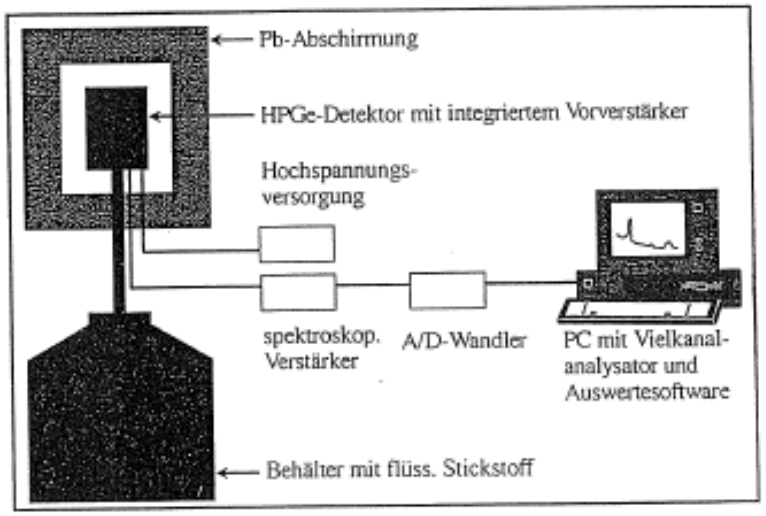


Methods: LSC measurements

- Polyvials used for counting (20 mL, PE, Zinsser Analytic)
- ^{14}C:
  - 3 mL sample solution (NaOH, collected from washing bottles #3, #4, #7, #8)
  - mixed with 18 mL scintillation cocktail (Hionic Fluor, PerkinElmer)
  - measuring time: 3 × 30 min
- ^{55}Fe:
  - separated from other radionuclides present in the digestion liquor by extraction column
  - 1 mL sample (1.5 M HCl) mixed with 10 mL scintillation cocktail (Ultima Gold LLT, PerkinElmer)
  - measuring time: 1 × 30 min

Methods: γ measurements

- Solid-state detectors (semiconductor detectors) e.g. high purity germanium (HPGe) used
- Rely on detection of electron-hole pairs generated by γ-rays in semiconductor material
- Electrons and holes move to respectively charged electrodes due to electric field applied to the detector and create electrical signal



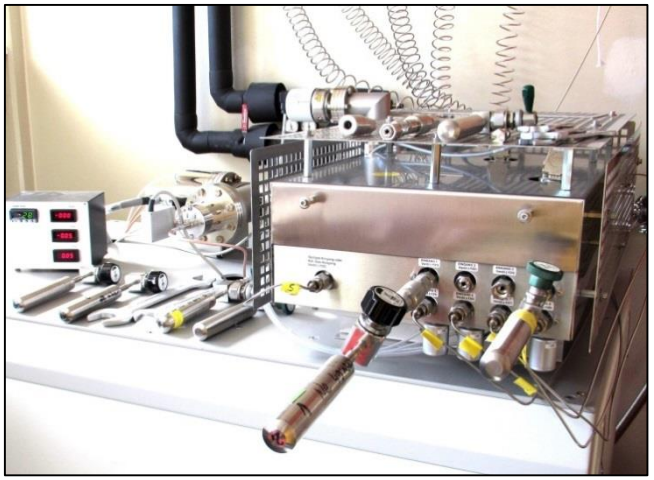
Methods: γ measurements

- Determination of ^{125}Sb and ^{137}Cs
- Extended range coaxial Ge detector (GX3018, Canberra Industries Inc.)
- APEX screw-cap microcentrifuge tubes (2 mL, PP, Alpha Laboratories Ltd.)
- ^{125}Sb and ^{137}Cs:
  - 1 mL aliquot from digestion liquor
  - measuring time: 2–4 h
- ^{125}Sb (after cesium removal to lower background):
  - 2 mL of digestion liquor mixed with 0.1 g AMP*
  - filtration (0.45 µm) of CsAMP suspension
  - 1 mL filtrate used for γ-counting
  - measuring time: 2–4 h

*ammonium molybdophosphate

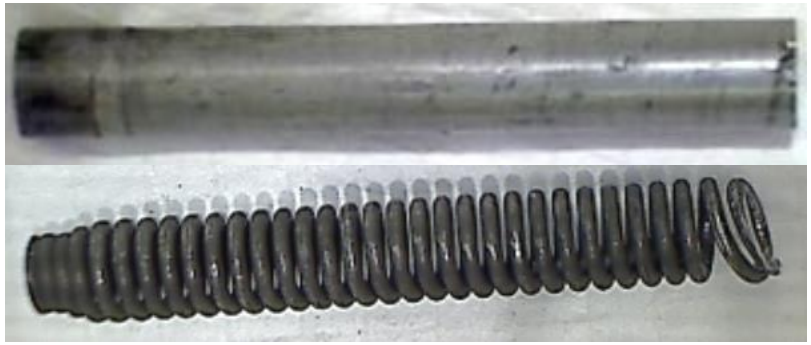
Methods: gas-MS

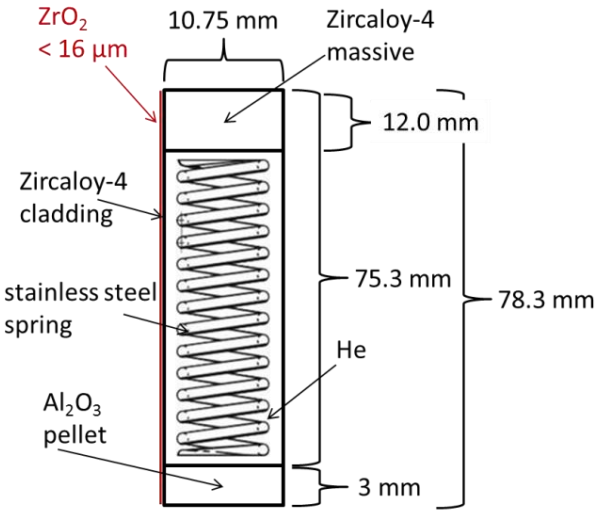
- Analysis for: H_2, N_2, O_2, CO_2, CH_4, Ar,… ([^{14}C-compound] too low for analysis)
- samples are collected in a stainless steel miniature sampling cylinder (V = 50 mL) with two valves (SS-4CS-TW-50, Swagelok)
- quadrupole gas mass spectrometer (GAM400, InProcess Instruments) equipped with secondary electron multiplier (SEM) detector, Faraday cup and batch inlet system
- calibration performed in the same pressure range as samples; 10 measurements are performed with the SEM detector



MCNP inventory calculations

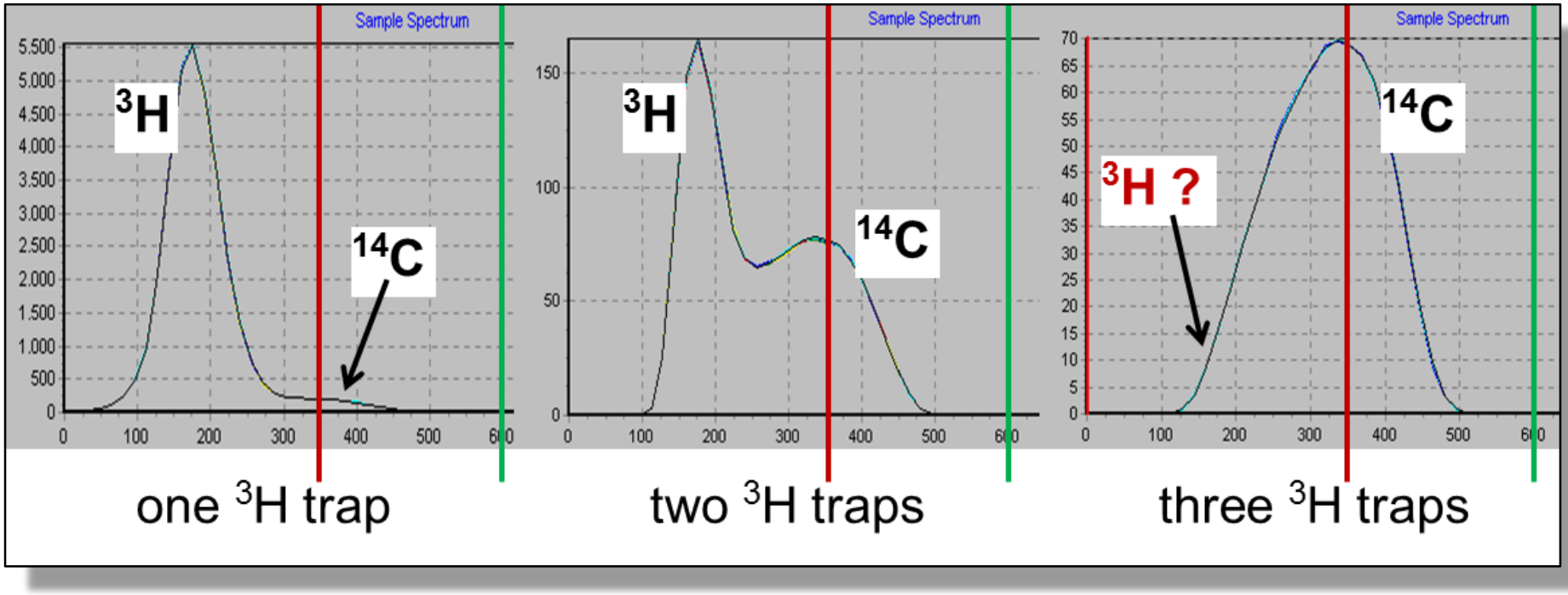
- Calculation of the radionuclide inventory of the irradiated plenum Zircaloy-4 cladding (30 ppm N) and plenum stainless steel spring (80 ppm N)
- Monte Carlo N-Particle transport code (MCNP-X)
  - taking into account nominal composition of unirradiated Zircaloy-4 cladding and stainless steel spring
  - taking into account dimensions, weight and density of the material
  - direct surrounding of the material and (vertical) position in the fuel assembly and nuclear reactor
  - taking into account irradiation characteristics





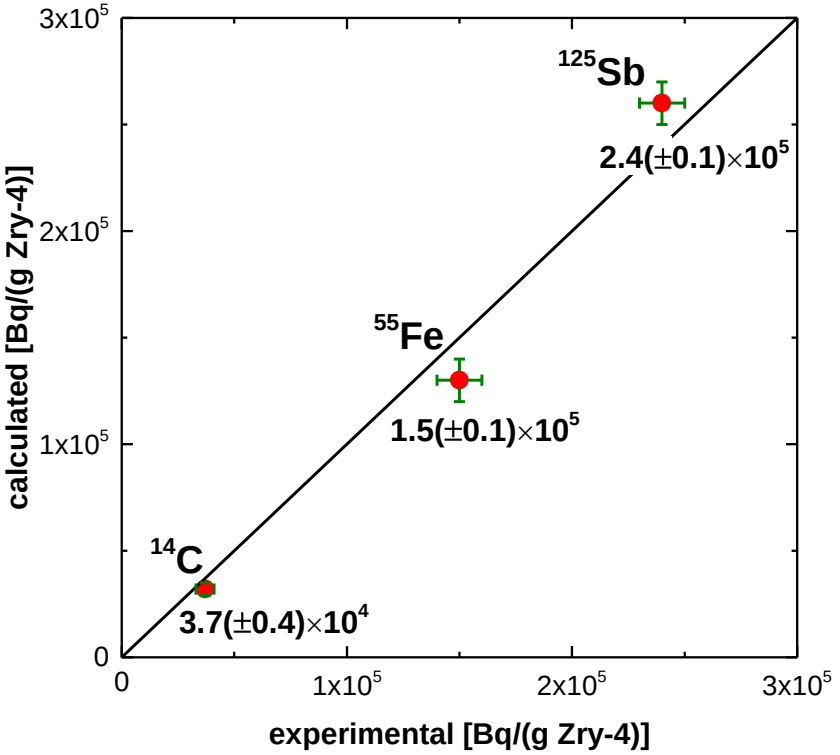
Results – digestion of Zircaloy

- Digestion of irradiated Zircaloy releases quantitatively gaseous ^{1}H–^{3}H (HT)
  → catalytic furnace oxidize HT to HTO, which is absorbed in washing bottles after the furnace



Results – Zircaloy-4

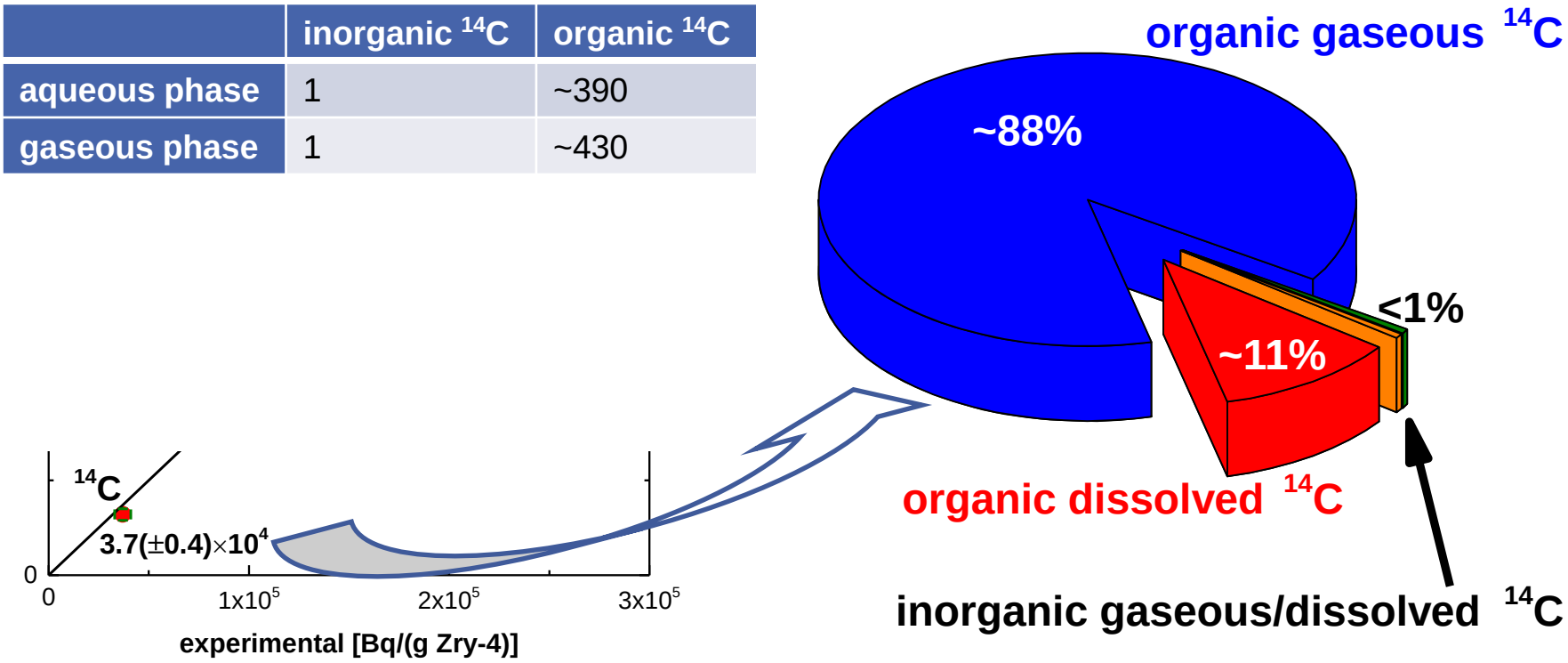
- Experimental and calculated results in good agreement for ^{14}C, ^{55}Fe, ^{125}Sb
- Experimental activities agree, within analytical uncertainty, with calculations
- Experimental ^{137}Cs inventory exceeds calculated by factor 117
  → ^{137}Cs precipitation on inner surface of irradiated Zircaloy cladding



Results – Zircaloy-4

- ~99% of ^{14}C as gaseous/dissolved hydrocarbons or carbon monoxide
- Similar ratio between organic and inorganic ^{14}C bearing compounds in aqueous and gaseous phase

	inorganic ^{14}C	organic ^{14}C
aqueous phase	1	~390
gaseous phase	1	~430

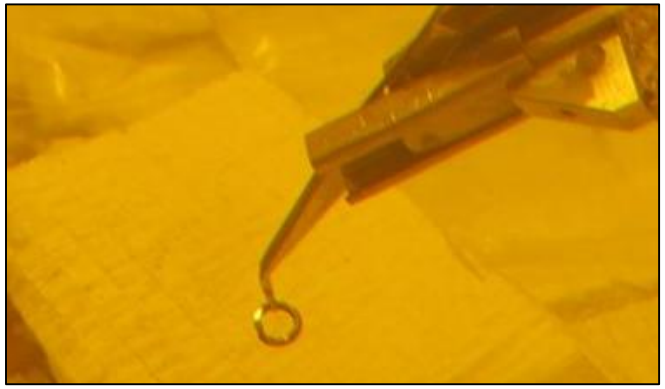


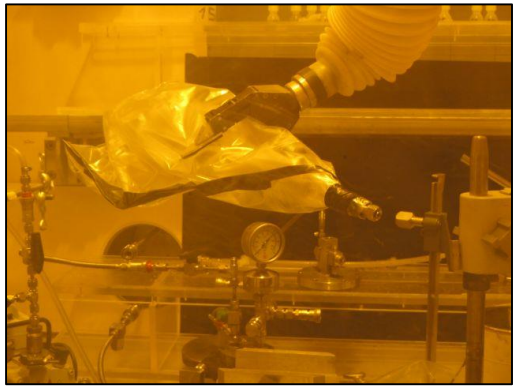
Results – stainless steel

- **Preliminary results:** ^{14}C inventory and chemical form of ^{14}C after release from stainless steel

radionuclide	experimental [Bq/g]	calculated [Bq/g]	factor
^{14}C	$2.7(\pm0.3)\times10^{5}$	$8.5(\pm0.9)\times10^{4}$	3.1

- Experimental and calculated results agree within a factor ~3 for ^{14}C
  → great uncertainty of nitrogen content in stainless steel (0.04–0.1 wt.%)
- ~99% of ^{14}C as gaseous/dissolved hydrocarbons or carbon monoxide





Thank you for your attention!

CArbon-14 Source Term
CAST

^{14}C behaviour under repository conditions – application to geo-chemical based long-term safety analysis for a underground disposal system

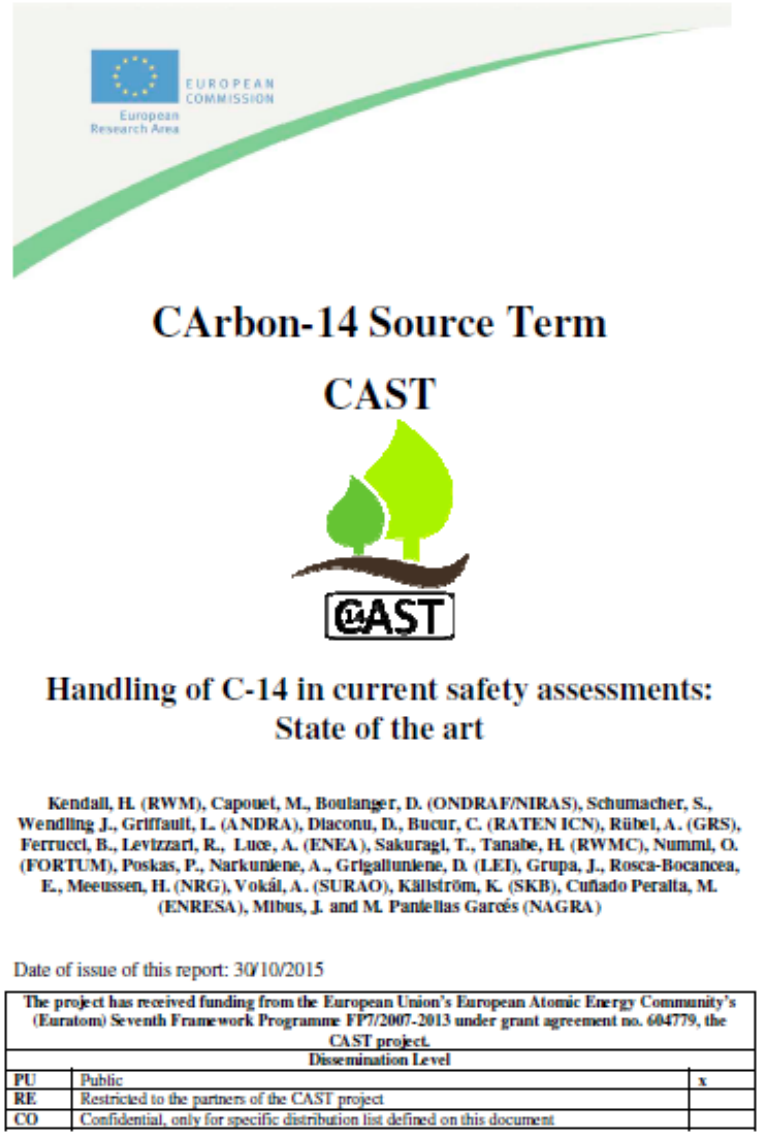
Volker Metz, KIT-INE

The project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 604779, the CAST project.

Kendall, H. (RWM), Capouet, M., Boulanger, D. (ONDRAF/NIRAS), Schumacher, S., Wendling J., Griffault, L. (ANDRA), Diaconu, D., Bucur, C. (RATEN ICN), Rübel, A. (GRS), Ferrucci, B., Levizzari, R., Luce, A. (ENEA), Sakuragi, T., Tanabe, H. (RWMC), Nummi, O.(FORTUM), Poskas, P., Narkuniene, A., Grigaliuniene, D. (LEI), Grupa, J., Rosca-Bocancea, E., Meeussen, H. (NRG), Vokál, A. (SURAO), Källström, K. (SKB), Cuñado Peralta, M. (ENRESA), Mibus, J. and M. Pantelias Garcés (NAGRA)

Handling of C-14 in current safety assessments: State of the art.

CArbon-14 Source Term report CAST-2015-D6.1



EUROPEAN COMMISSION
European Research Area

CArbon-14 Source Term

CAST

Handling of C-14 in current safety assessments: State of the art

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Date of issue of this report: 30/10/2015

The project has received funding from the European Union's European Atomic Energy Community's (Euratom) Seventh Framework Programme FP7/2007-2013 under grant agreement no. 604779, the CAST project.

Dissemination Level		
PU	Public	x
RE	Restricted to the partners of the CAST project	
CO	Confidential, only for specific distribution list defined on this document	

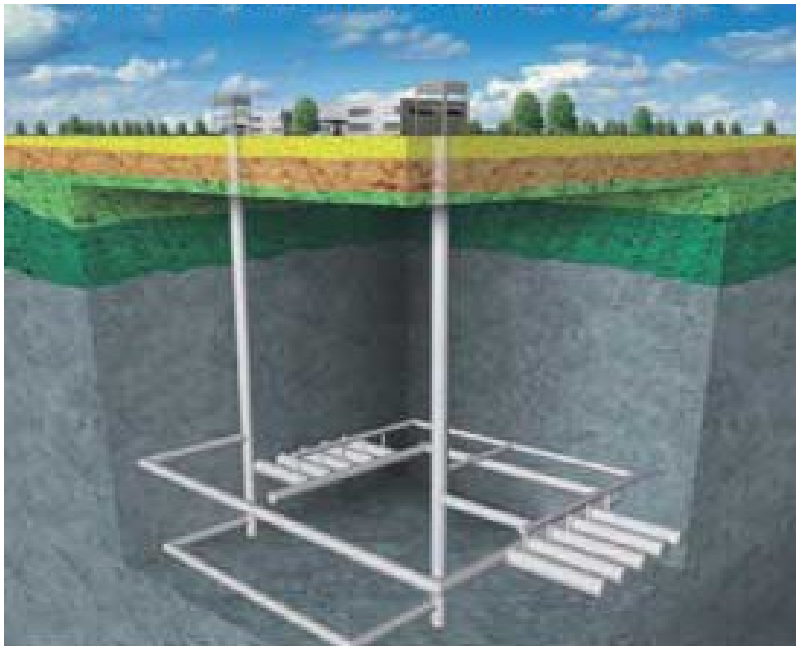
containment and isolation of radioactive waste

→ deep geological multi-barrier systems

European Council Directive 2011/70/EURATOM of 19 July 2011 establishing a Community framework for the responsible and safe management of spent fuel and radioactive waste:

"Radioactive waste, including spent fuel considered as waste, requires containment and isolation from humans and the living environment over the long term. Its specific nature, namely that it contains radionuclides, requires arrangements to protect human health and the environment against dangers arising from ionising radiation, including disposal in appropriate facilities as the end location point. The storage of radioactive waste, including long-term storage, is an interim solution, but not an alternative to disposal. (…)"

There is still no alternative to final disposal in deep multi-barrier systems for the safe management of high-level radioactive waste. Isolating radioactive waste from the biosphere in a geologically stable environment over periods of several hundreds of thousands of years offers maximum safety, which cannot be guaranteed at present by other concepts

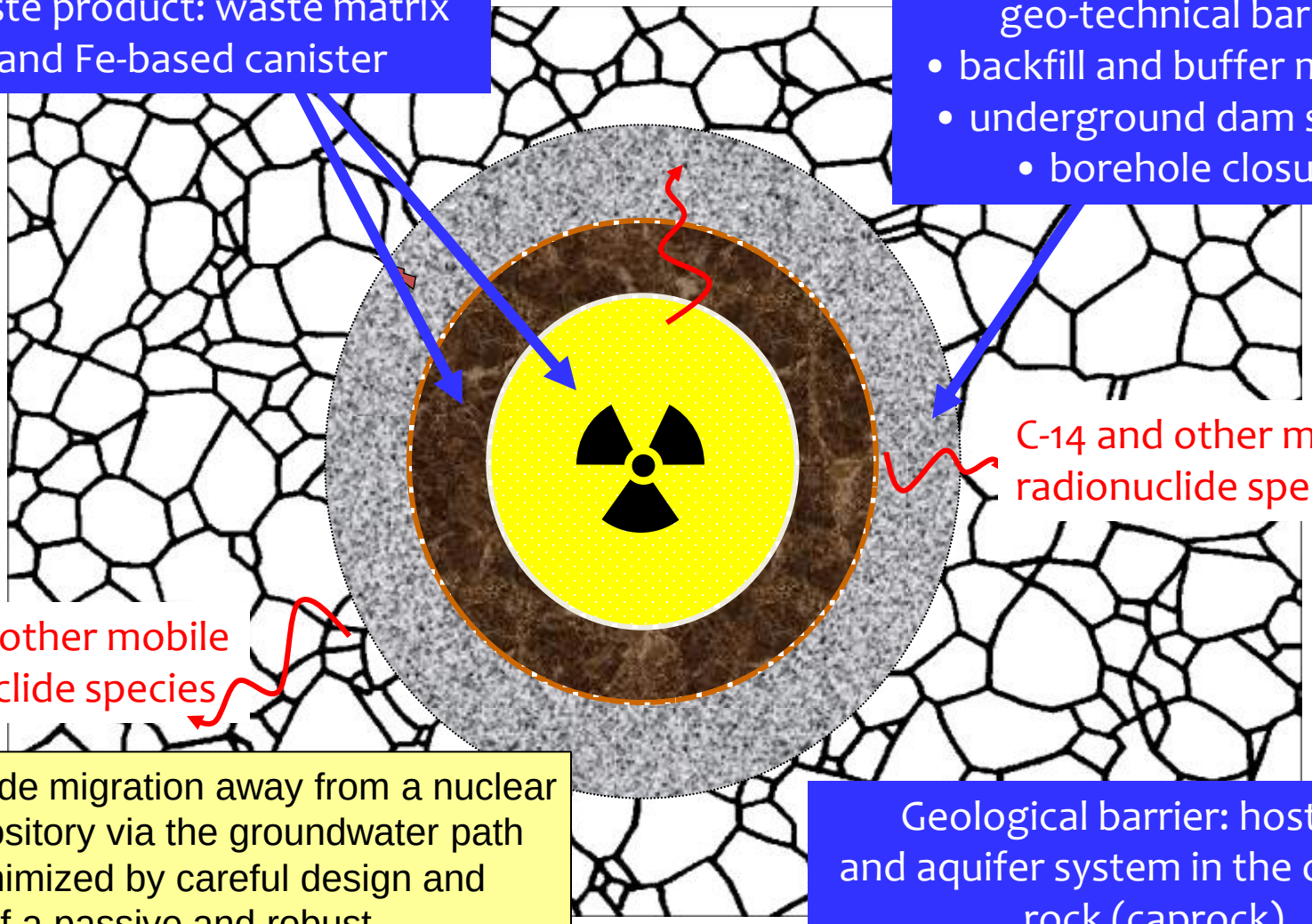


source: Official Journal of the European Union (ABl. L 199, 2. Aug. 2011, p. 48f), http://eur-lex.europa.eu/LexUriServ

Basic concept of multi-barrier disposal systems

Engineered / technical barrier waste product: waste matrix and Fe-based canister

Geo-engineered geo-technical barrier:
- backfill and buffer materials
- underground dam systems
- borehole closures



C-14 and other mobile radionuclide species

C-14 and other mobile radionuclide species

Geological barrier: host rock and aquifer system in the overlying rock (caprock)

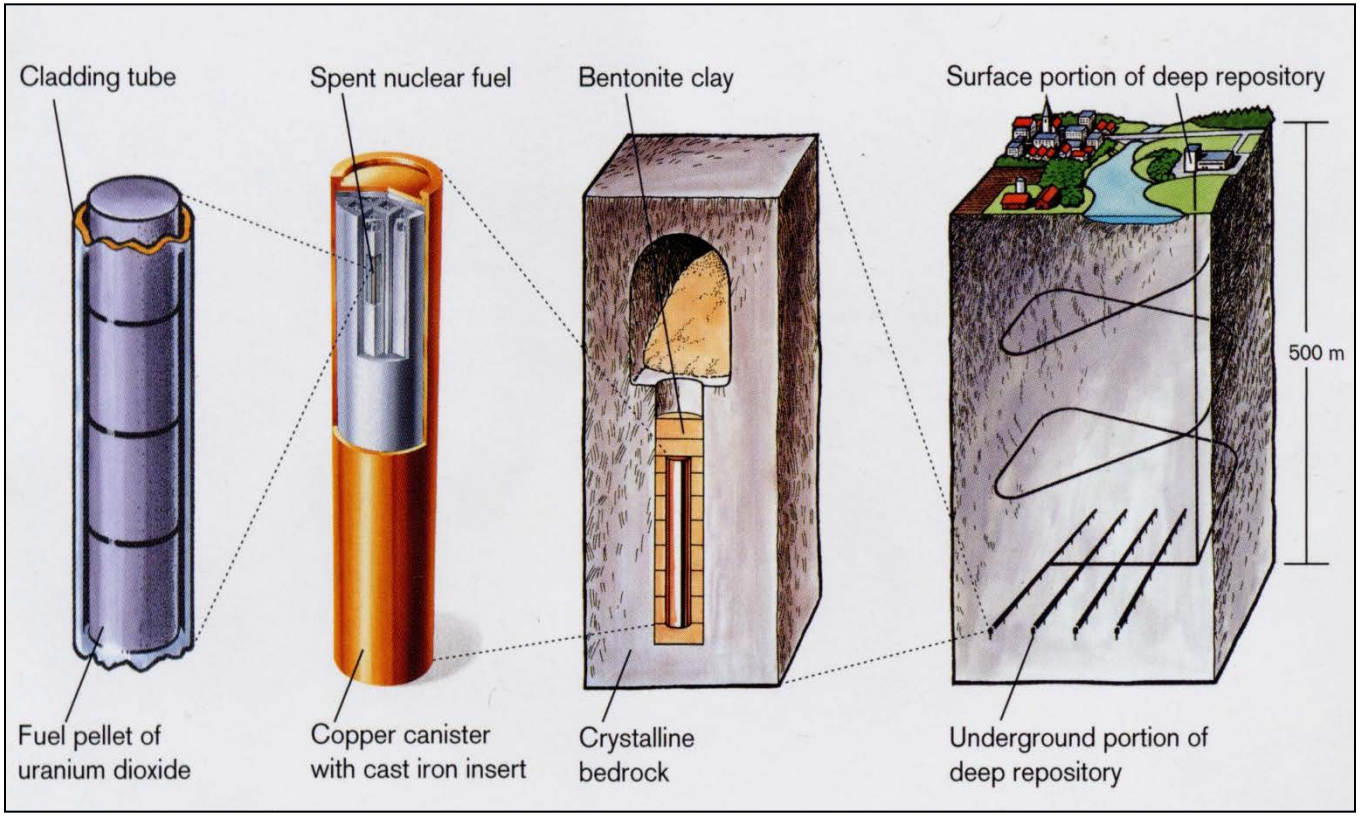
Radionuclide migration away from a nuclear waste repository via the groundwater path can be minimized by careful design and selection of a passive and robust multi-barrier system.

Example : Swedish multi-barrier concept (KBS-3)

Engineered Barrier
- Spent fuel
- HLW-glass
- Container

Geoengineered Barrier
- Drift backfill
- Underground dam systems
- Shaft and borehole seals

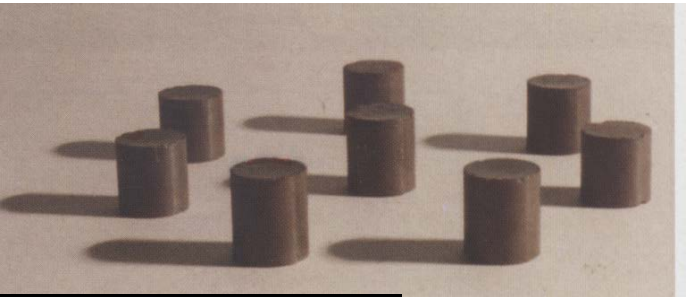
Geological Barrier
- Host rock (crystalline rock)
- Aquifer system in the overlying sediments

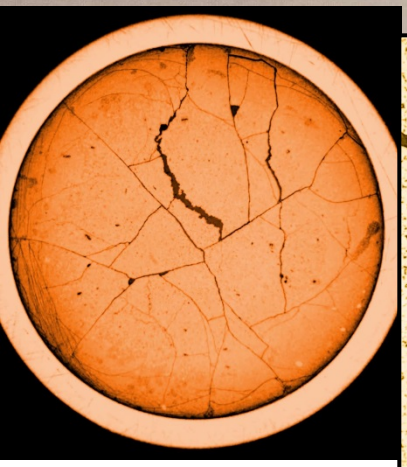


sources: SKB (2006) Long-Term Safety for KBS-3 Repositories at Forsmark and Laxemar – A First Evaluation, Main Report of the SR-Can project, SKB TR 06-09, Swedish Nuclear Fuel and Waste Management Co., Stockholm; Hedin et al. (2007) NEA-RWM report, NEA No. 6362, Nuclear Energy Agency, Paris, pp 45-56

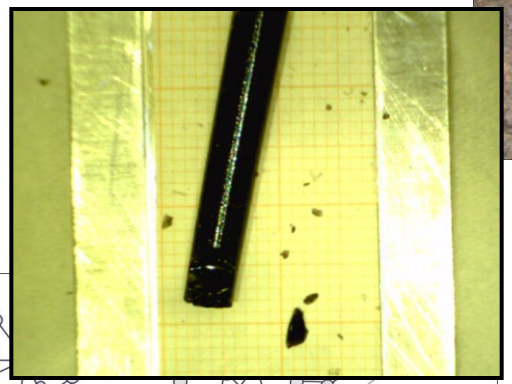
Technical barrier: UO_x / HLW glass / cement matrix

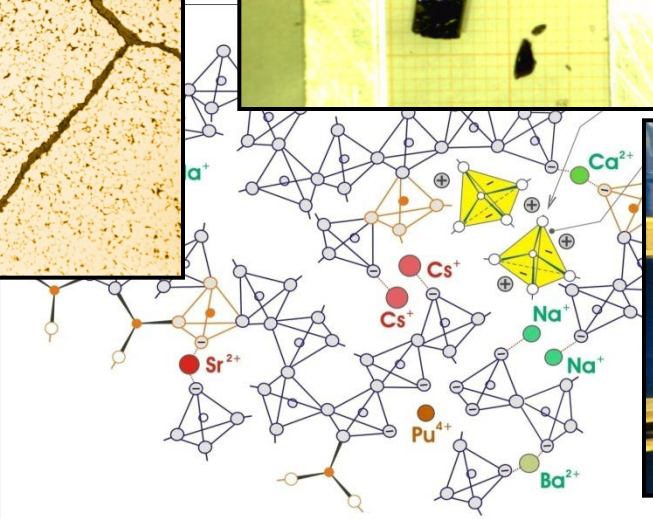
UO_x matrix of spent nuclear fuel (SNF)





HLW glass matrix





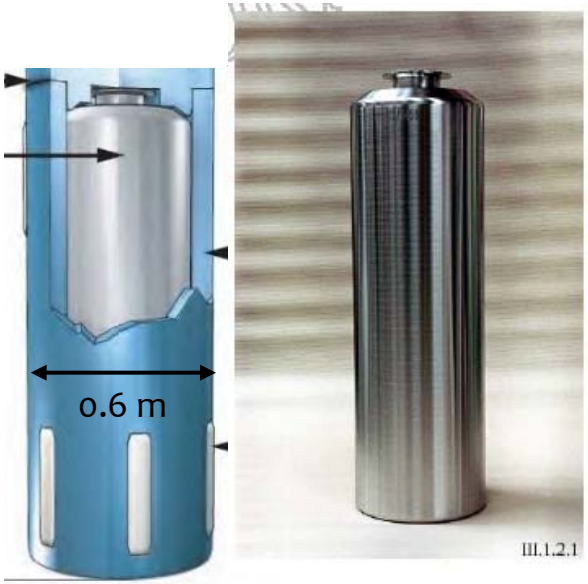
cement matrix of LLW/ILW

Images source: KIT-INE (6), Nuclear Engin. Int'l (2003) vol. 48, no. 590, Fuel design data; GSF / BfS

Engineered barriers: containers for spent nuclear fuel / HLW glass

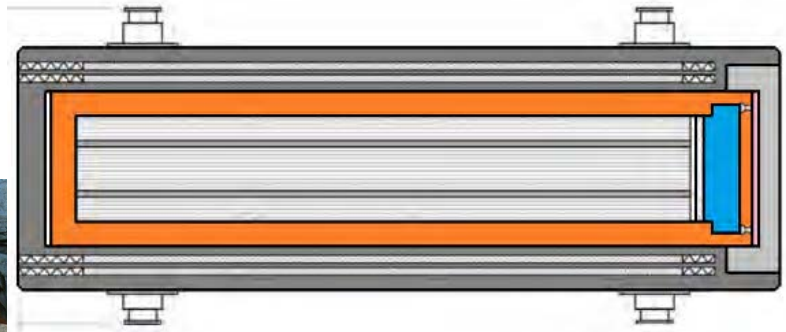
Thin walled iron "CU1"containers for spent MOX fuel elements and iron "C-overpacks" for HLW coquilles for disposal in claystone (France)

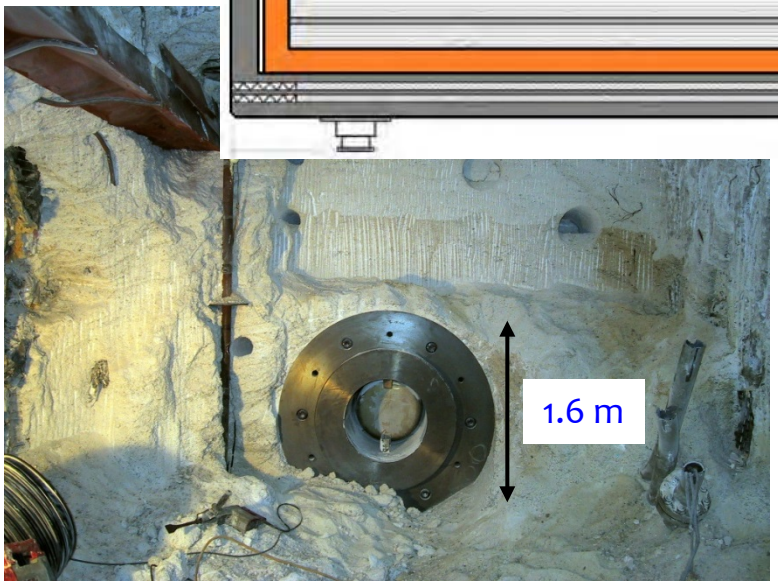
Source: ANDRA 269 VA (Dec 2006): Dossier 2005 Argile, Phenomenological evolution of a geological repository (Dezember 2005), Report Series ; T. Hassel et al. (2014) Behälterdossier, ENTRIA, Leibniz Universität Hannover, Version 0.2



Engineered barriers: containers for spent nuclear fuel / HLW glass

Thick walled cast iron container with inner steel container for spent nuclear fuel elements and HLW coquilles for disposal in rock salt (for example Germany)

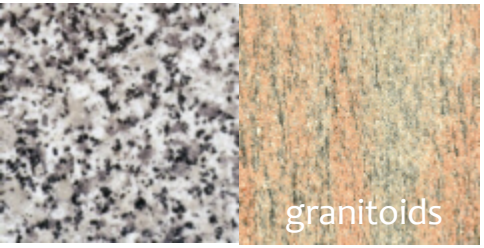




Nodular iron (a kind of cast iron) container with 5 cm thick copper liner as chemical barrier against corrosion for disposal in crystalline rock (for example Sweden and Finland)

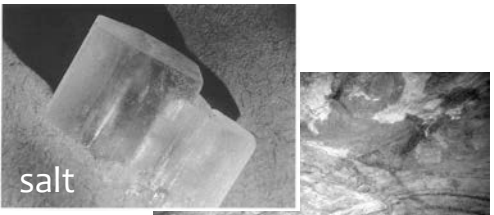
Sources: GRS, Endlagerung wärmeentwickelnder Abfälle in Deutschland, GRS-247, 2008; 9. Projektstatusgespräch BMBF/BMWI-geförderter FE-Vorhaben zu Entsorgung gefährlicher Abfälle in tiefen geol. Formationen, 2010; SKB, Technical Report, TR-01-03, December 2000

International concepts for final disposal of radioactive waste



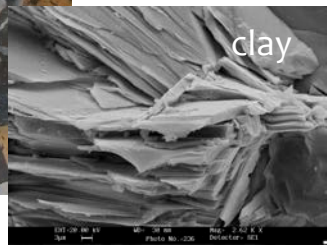
short-lived LLW - shallow land disposal

- at sites with *clay-rich aquicludes* for reasonable protection of groundwater (Czechia, France, Finland, Japan, Sweden, Spain, United Kingdom, USA …)



LLW / ILW – final disposal in deep geological formations

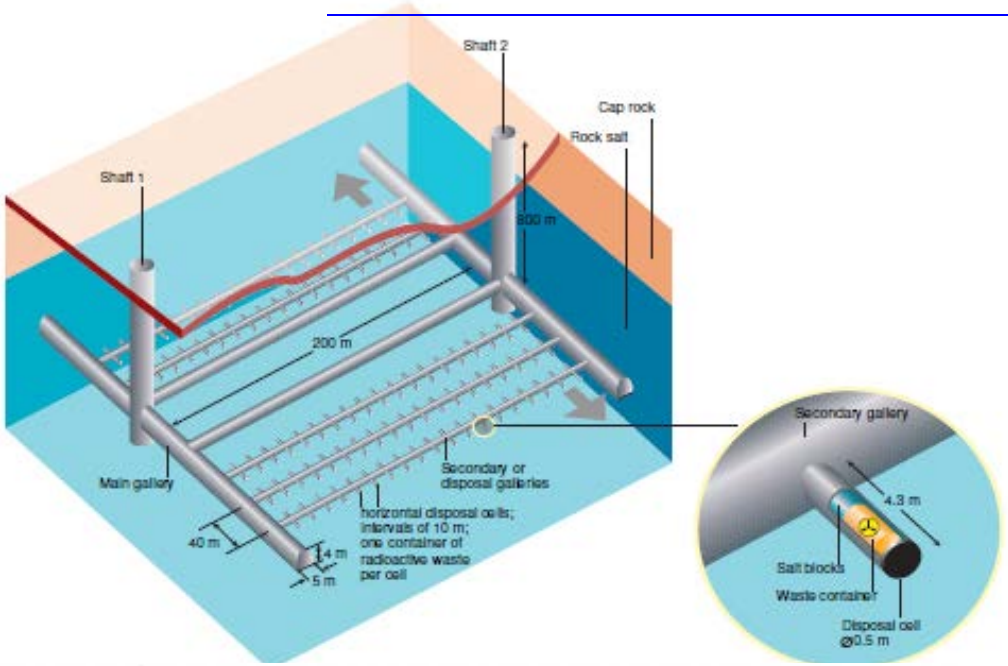
- *rocks with argillaceous overburden* (Canada, Germany)
- *granite* (Hungary)
- *bedded salt formations* (USA)
- *salt diapirs* (Germany)
- *clay rock* or *marl* (Switzerland)

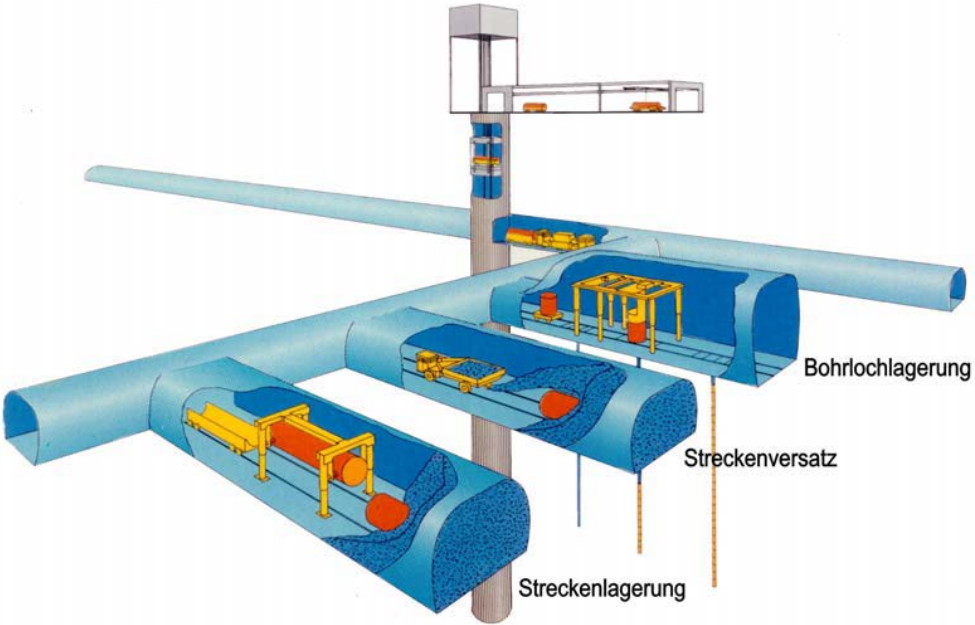


HLW – final disposal in deep geological formations

- *granite / granitoides* (Finland, Sweden, Spain and Argentina, China, Czechia, Hungary, India, Japan, Korea, Lithuania, Russia, Slovakia, South Africa, United Kingdom)
- *salt* (Germany, Lithuania, Netherlands, Romania, Russia, USA)
- *clay rock*, plastic (Belgium , Netherlands)
- *clay rock*, solidified (Argentina, Bulgaria, France, Germany, Hungary, Italy, Japan, Lithuania, Switzerland, Slovenia, Spain, United Kingdom

SNF and HLW-glass disposal in rock salt (Germany, Netherlands)



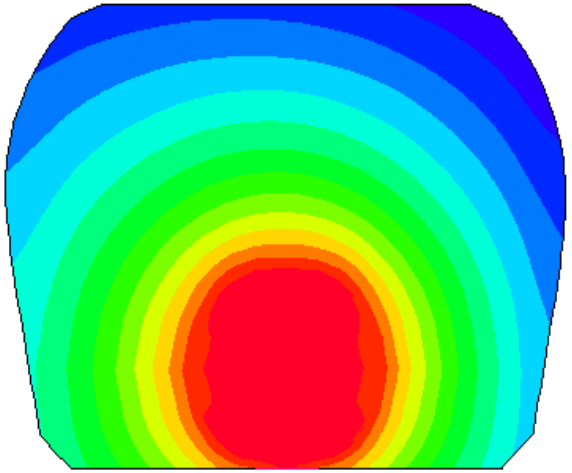


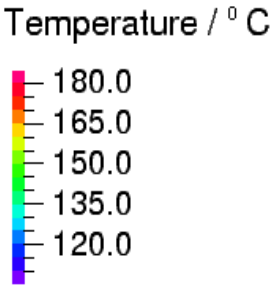
- disposal in depth of 500 to 800 m
- very high plasticity → "complete isolation" possible
- host rock posses extremely low permeability (except anhydrite zones)
- thick-walled cask iron / steel container
- back-filling with crushed rock salt
- reference case: no water access
- less probable scenarios: water access due to failure of shaft sealing etc.

Sources: J. Grupa, E. Rosca-Bocancea & H. Meeussen (2015) NRG contribution to D6.1 in Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term (CAST). Thermal Simulation of Drift Emplacement (TSDE) 1990 – 2000, Asse II, 800 m level; Bollingerfehr, W. et al. (2011) EUGENIA, DBE-Technology, BGR; FKZ 02 E 10346

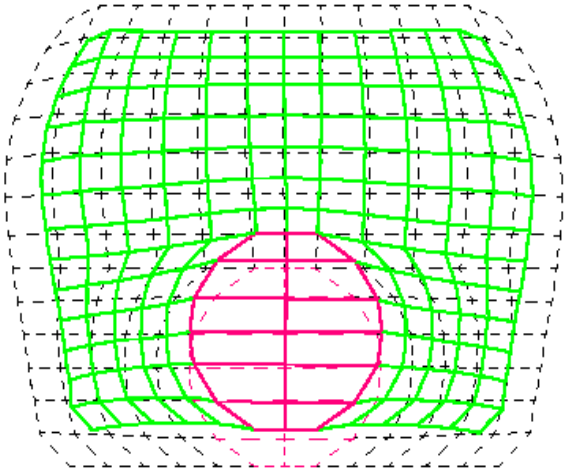
Rock salt : heat conductivity and convergence

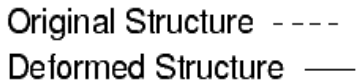
start





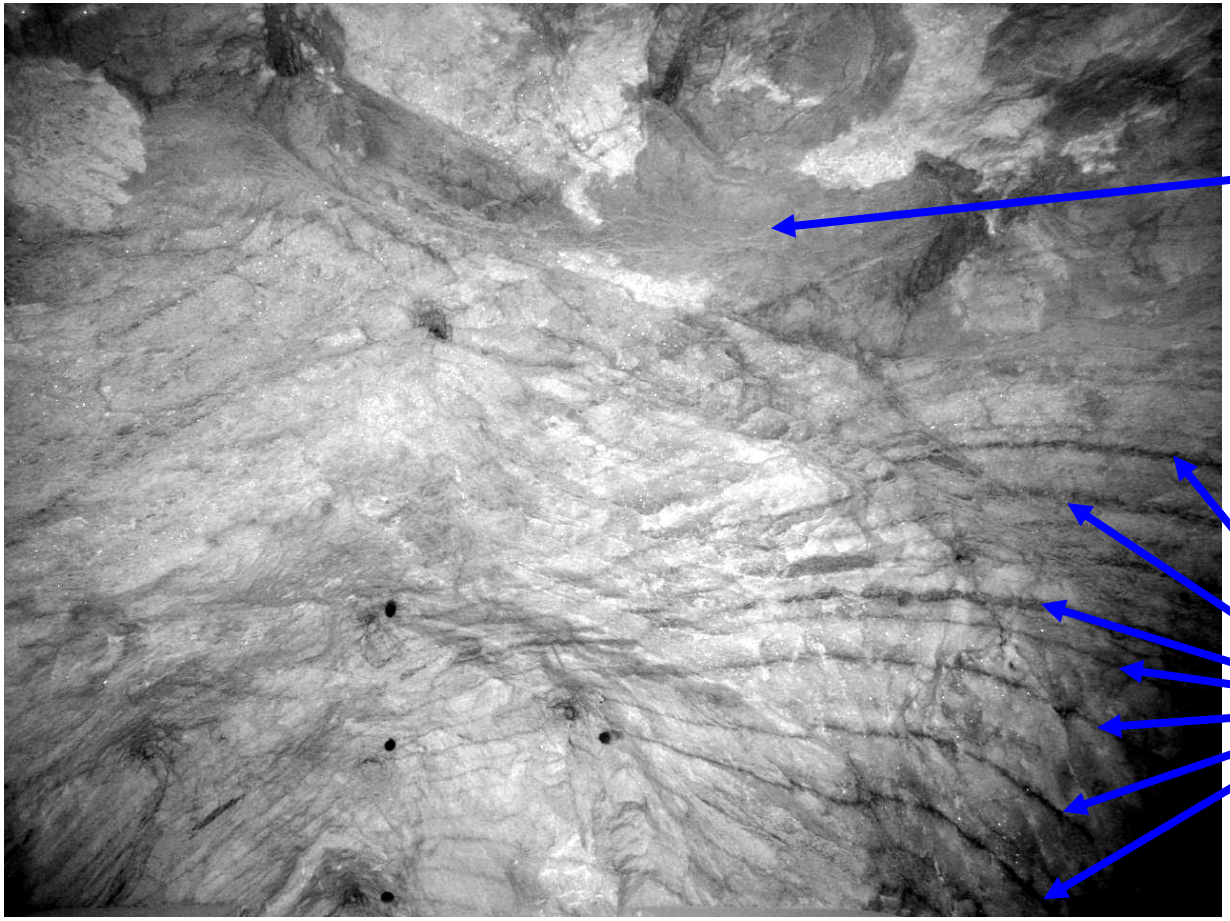
11 years





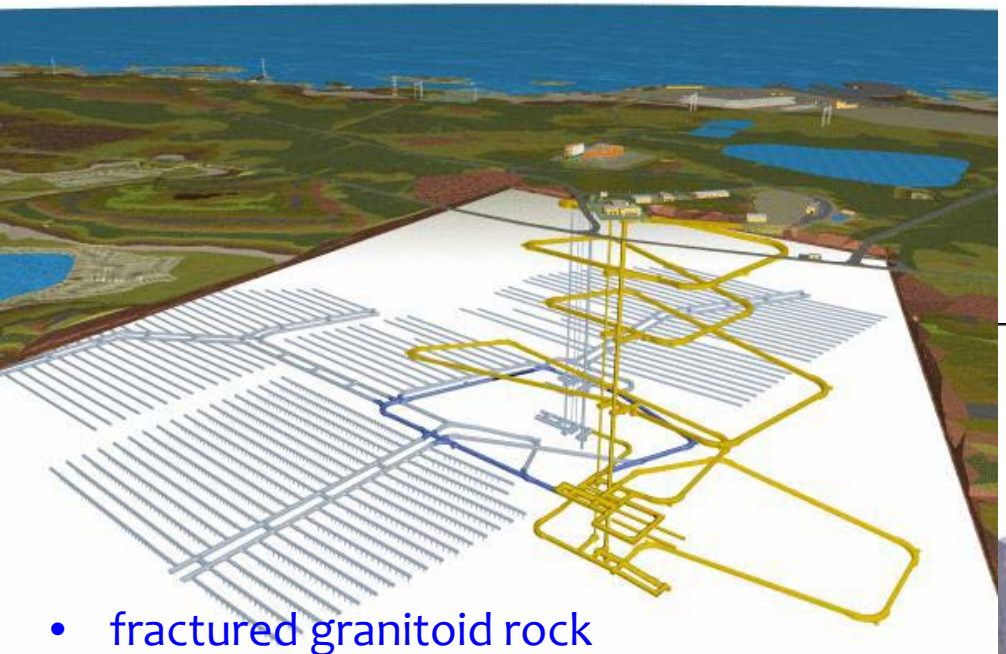
Source: Thermal Simulation of Drift Emplacement (TSDE) 1990 – 2000, Asse II, 800 m level

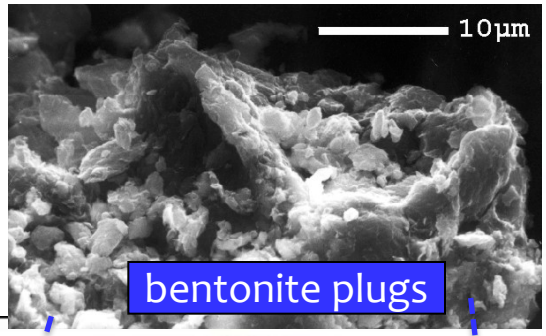
Potential migration paths in rock salt : anhydrite bands

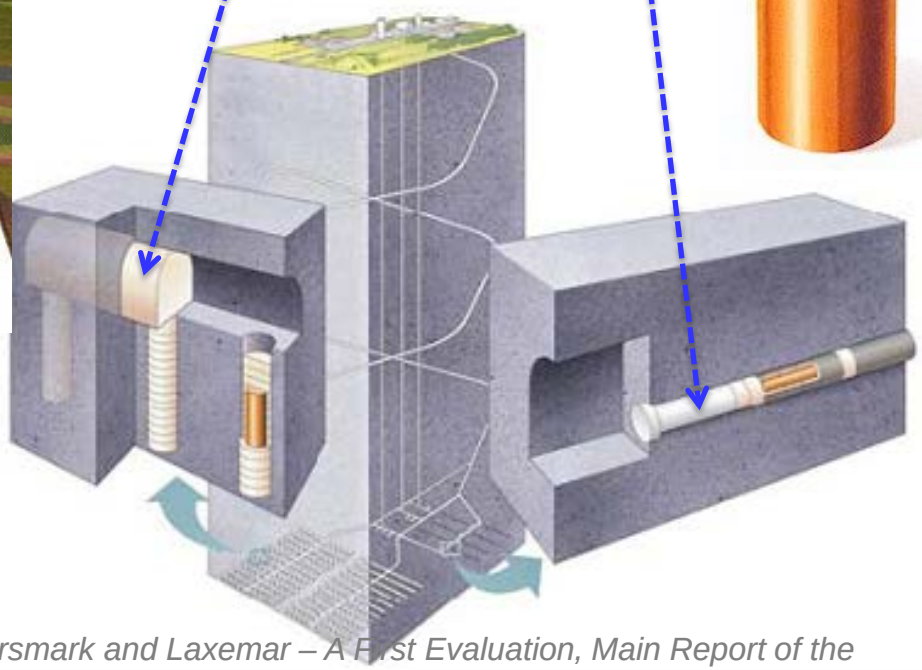


rock salt (Na3) with anhydrite bands,
Schachtanlage Asse II

SNF disposal in crystalline rock (Finland, Sweden, Canada)





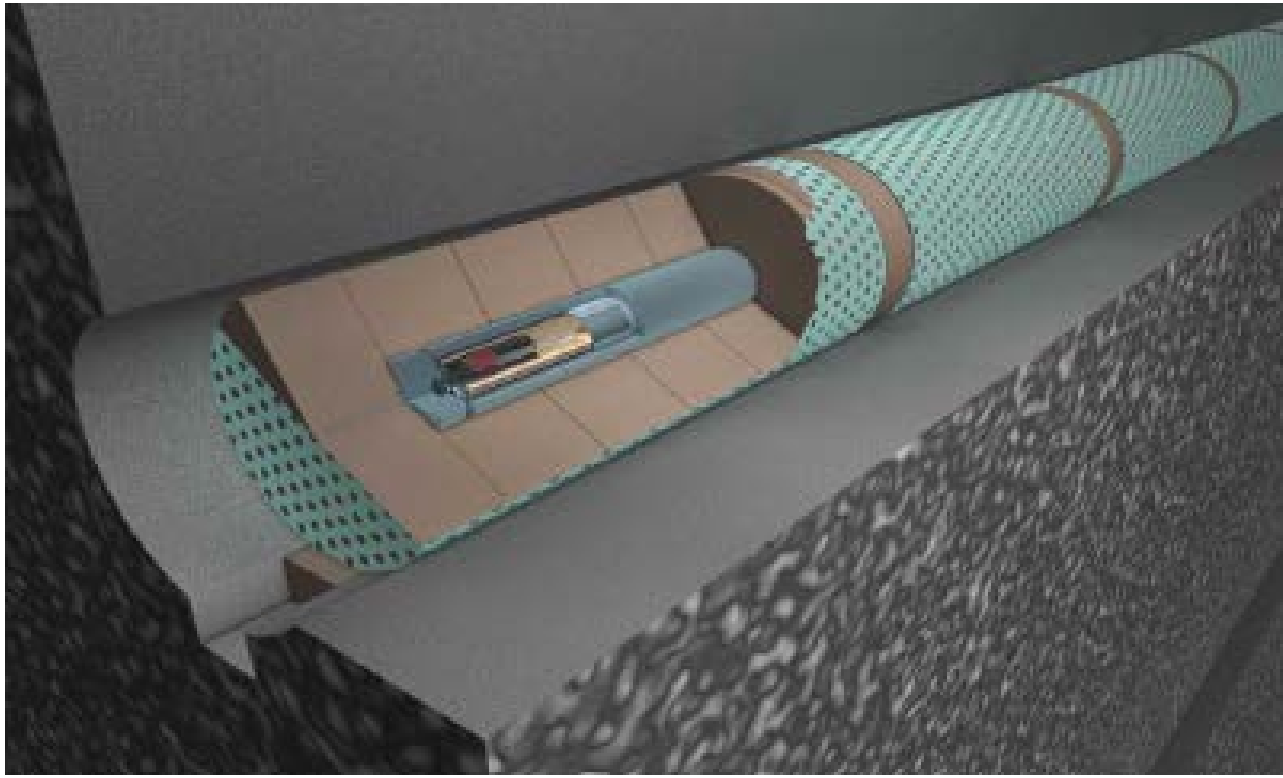


- fractured granitoid rock
- advective water transport → bentonite as barrier against water access and radionuclide migration
- nodular iron with 5 cm thick Cu liner as chemical barrier against corrosion

sources: SKB (2006) Long-Term Safety for KBS-3 Repositories at Forsmark and Laxemar – A First Evaluation, Main Report of the SR-Can project, SKB TR 06-09, Swedish Nuclear Fuel and Waste Management Co., Stockholm; Hedin et al. (2007) NEA-RWM report, NEA No. 6362, Nuclear Energy Agency, Paris, pp 45-56; Pastina, B. & Hellä, P.: Expected evolution of a spent fuel repository in Olkiluoto, Posiva 2006-05, December 2006

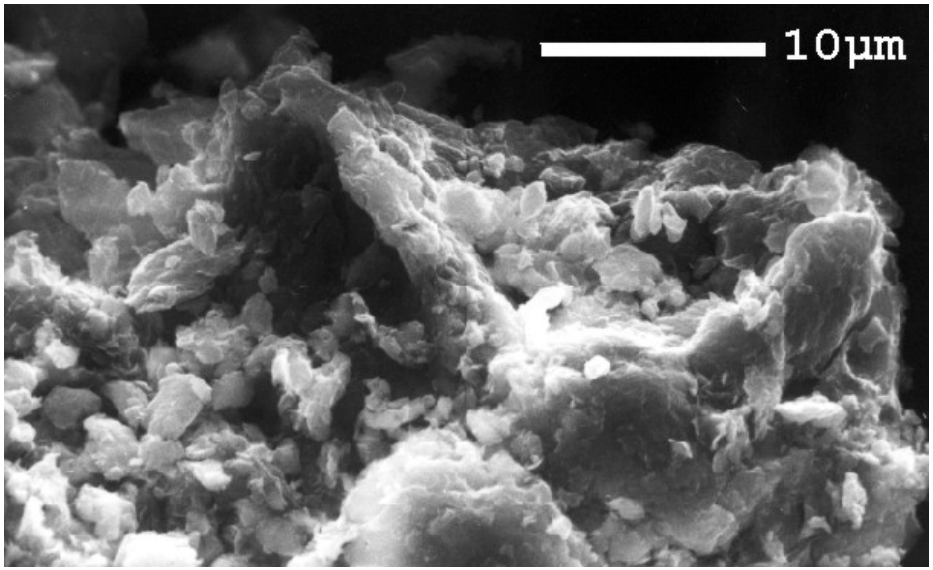
SNF disposal in crystalline rock (Czech Republic)

- fractured granitoid rock with advective water transport → bentonite as barrier against water access and radionuclide migration
- canister consists of an outer layer of carbon steel (which will corrode very slowly under anaerobic conditions) and a second inner layer of stainless steel (which will corrode at an almost negligible general corrosion rate and exhibit a low tendency to local corrosion under anaerobic conditions)



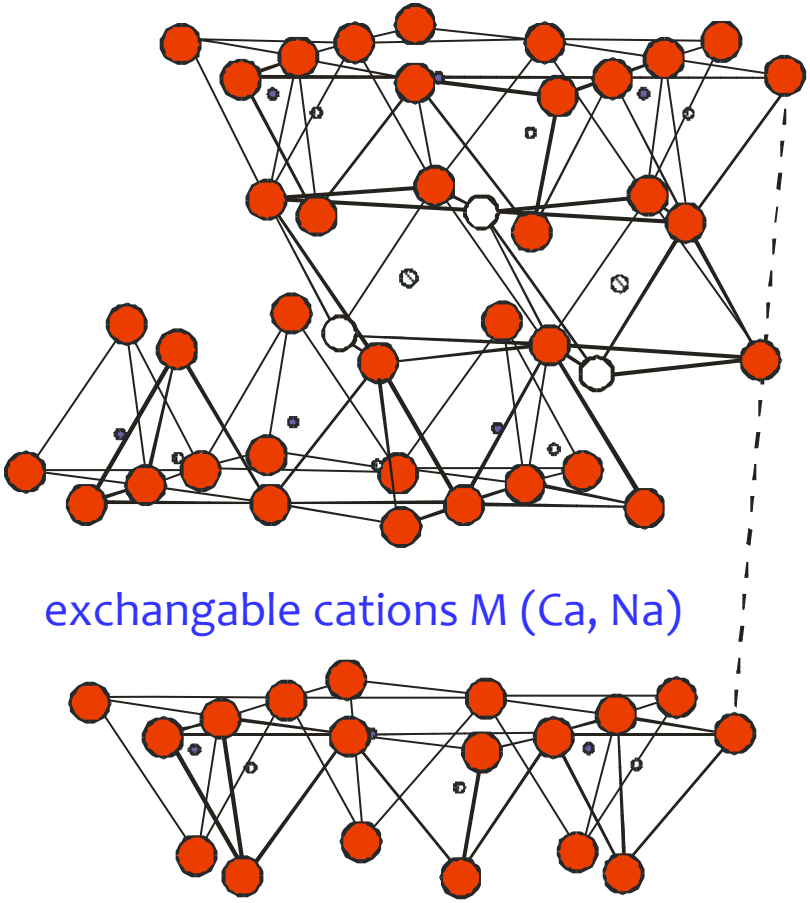
source: Antonín Vokál (2015) SURAO contribution to D6.1 in Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term (CAST)

Montmorillonitic smectite: main constituent of claystone / bentonite



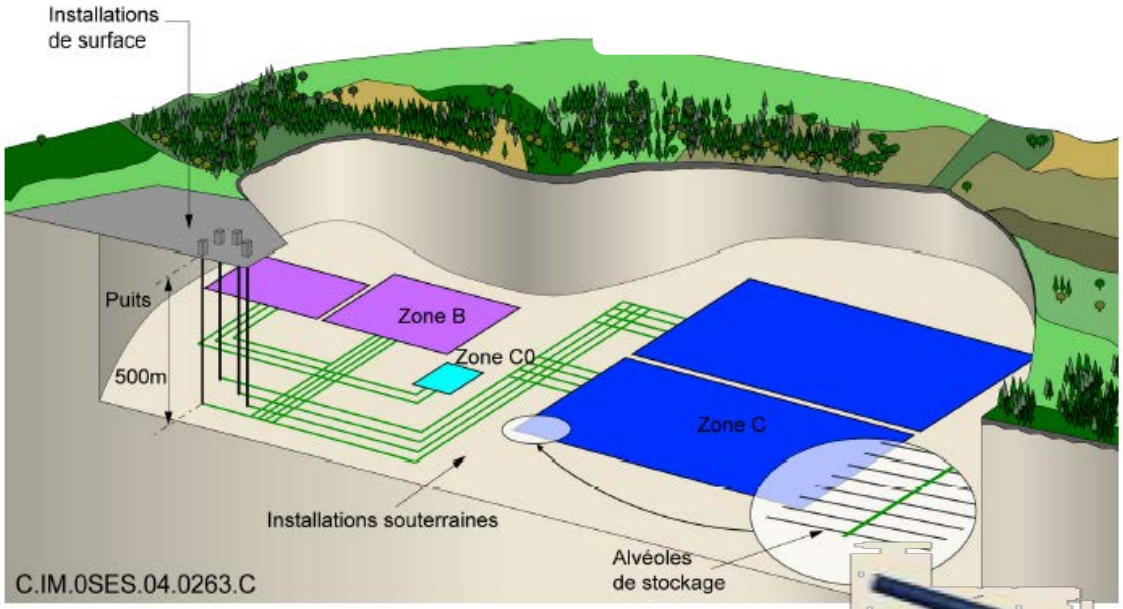
chemical analysis (wt %)	
SiO2	61
Al2O3	20
TiO2	<1
Fe(III) as Fe2O3	3
MnO	<1
MgO	3
CaO	1
Na2O	2
K2O	<1
loss on ignition	11
total	100

$M_{0.66}[Mg_{0.66}Al_{3.34}][Si_8]O_{20}(OH)_4 \cdot (H_2O)_n$

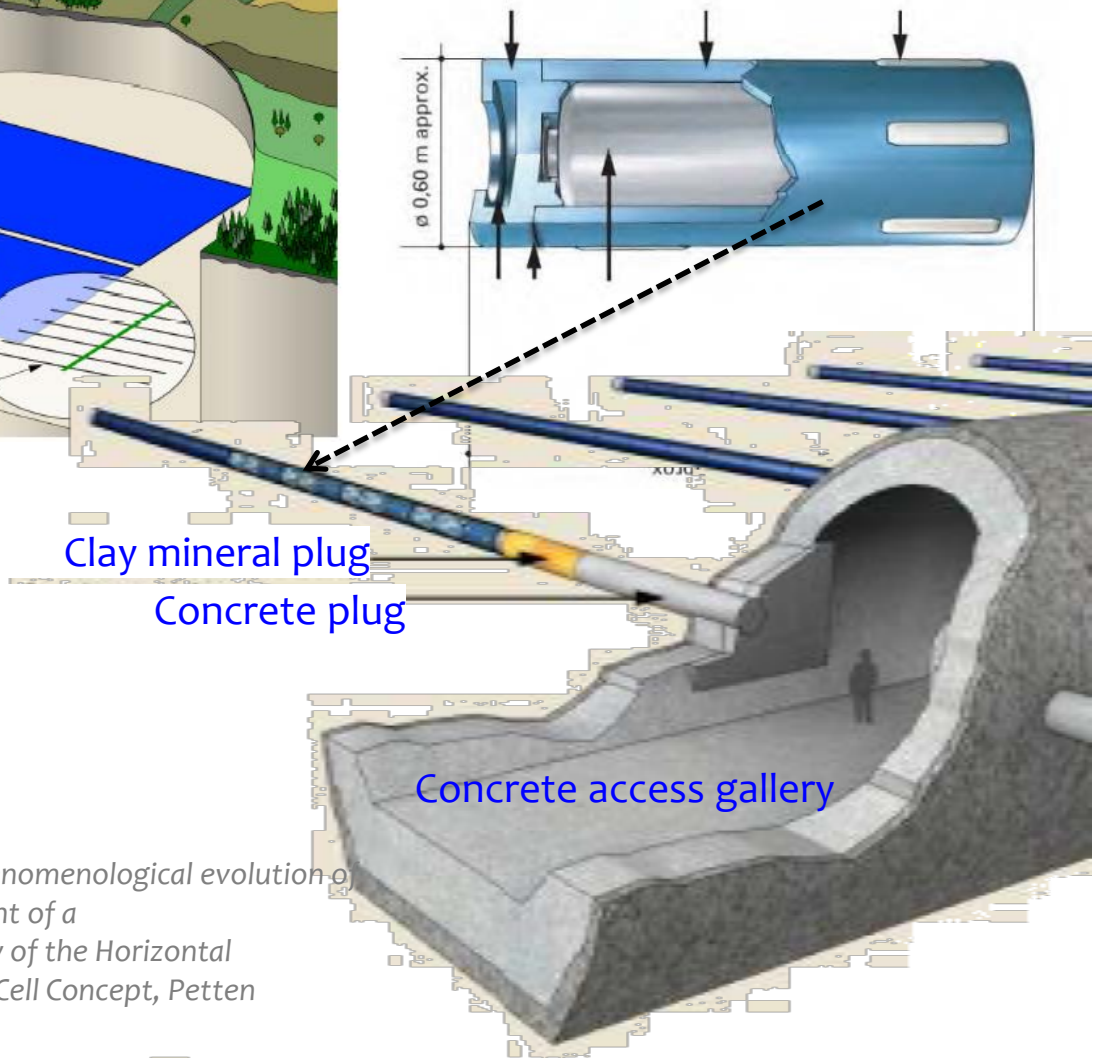


exchangable cations M (Ca, Na)

SNF/HLW and LLW/ILW in Callovo-Oxfordian clay rock (France)

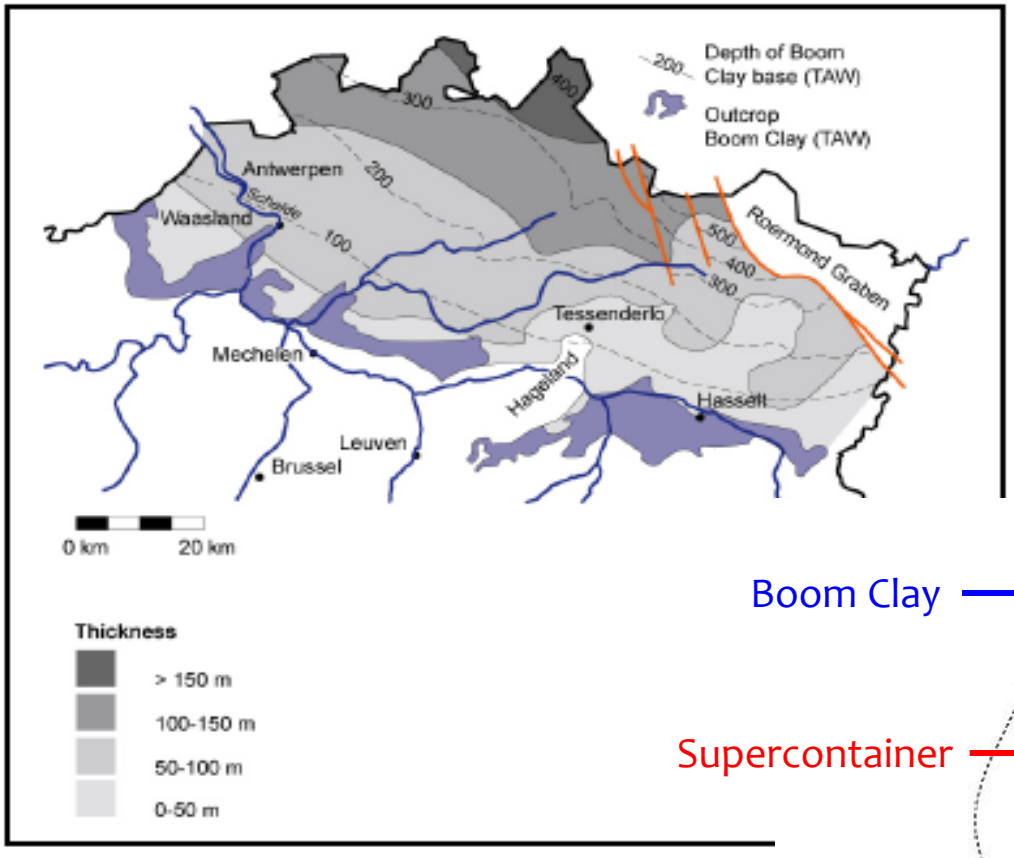


Nanoporous solidified clay rock characterized by high plasticity; only diffusive water transport

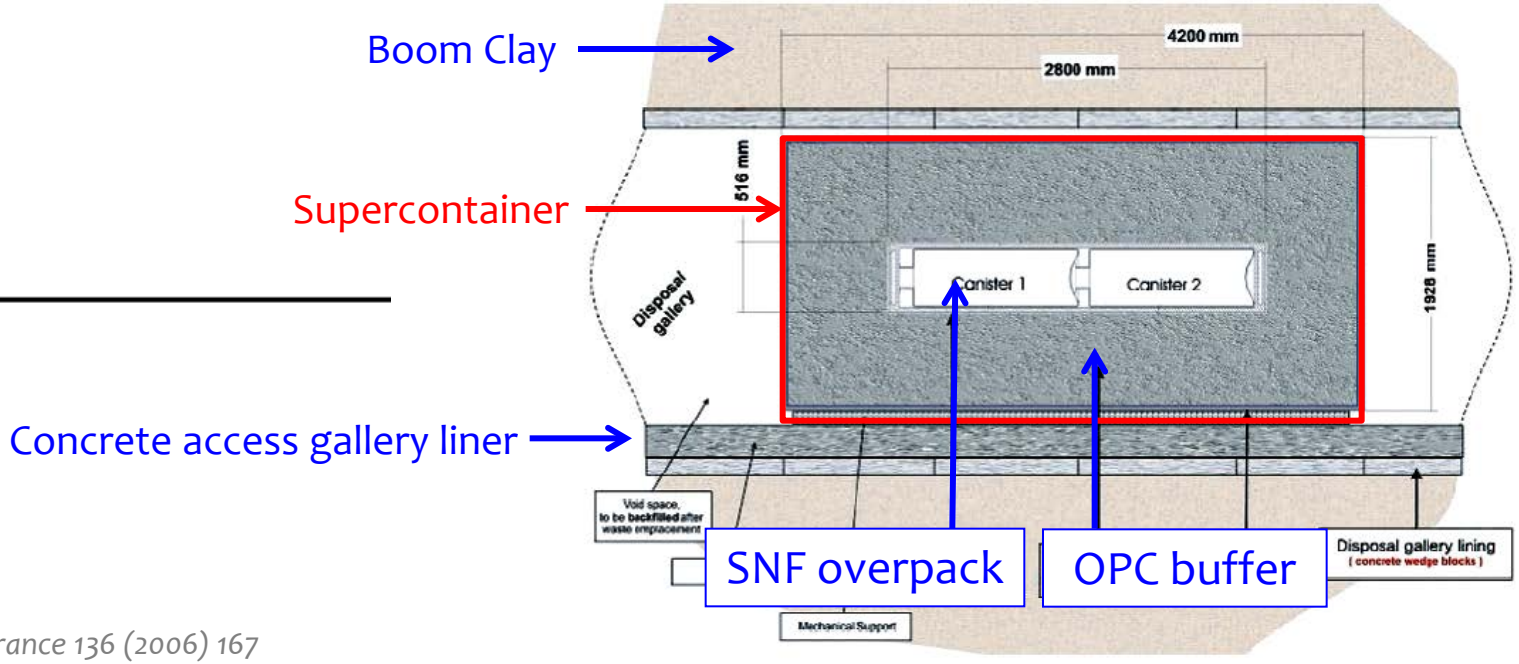


Sources: ANDRA 269 VA (Dec 2006): Dossier 2005 Argile, Phenomenological evolution of a geological repository; Tome: Architecture and management of a geological (Dezember 2005); Haverkate et al. (2006) Review of the Horizontal Emplacement Technique concerning Retrievability Disposal Cell Concept, Petten

SNF disposal in Boom Clay (Belgium, Netherlands)

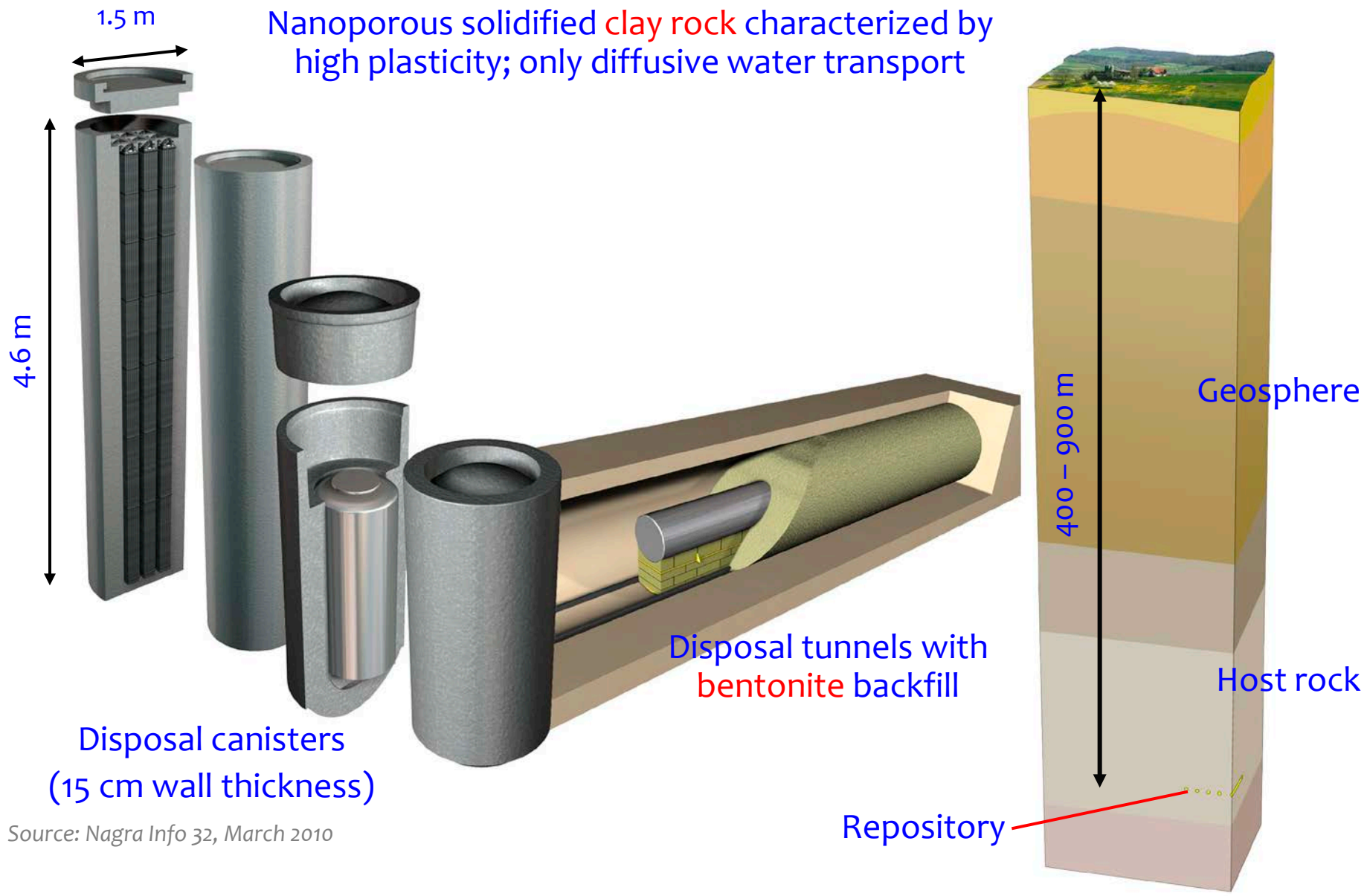


- plastic clay rock
- only diffusive water transport
- *Supercontainer* concept: carbon-steel overpack with SNF within Ordinary Portland Cement (OPC) buffer



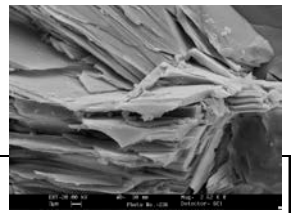
Source: Poyet, J. Phys. IV, France 136 (2006) 167

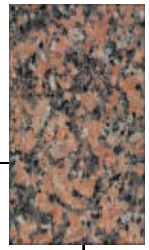
SNF and HLW-glass disposal in Opalinus clay (Switzerland)



Source: Nagra Info 32, March 2010

Properties of rock types





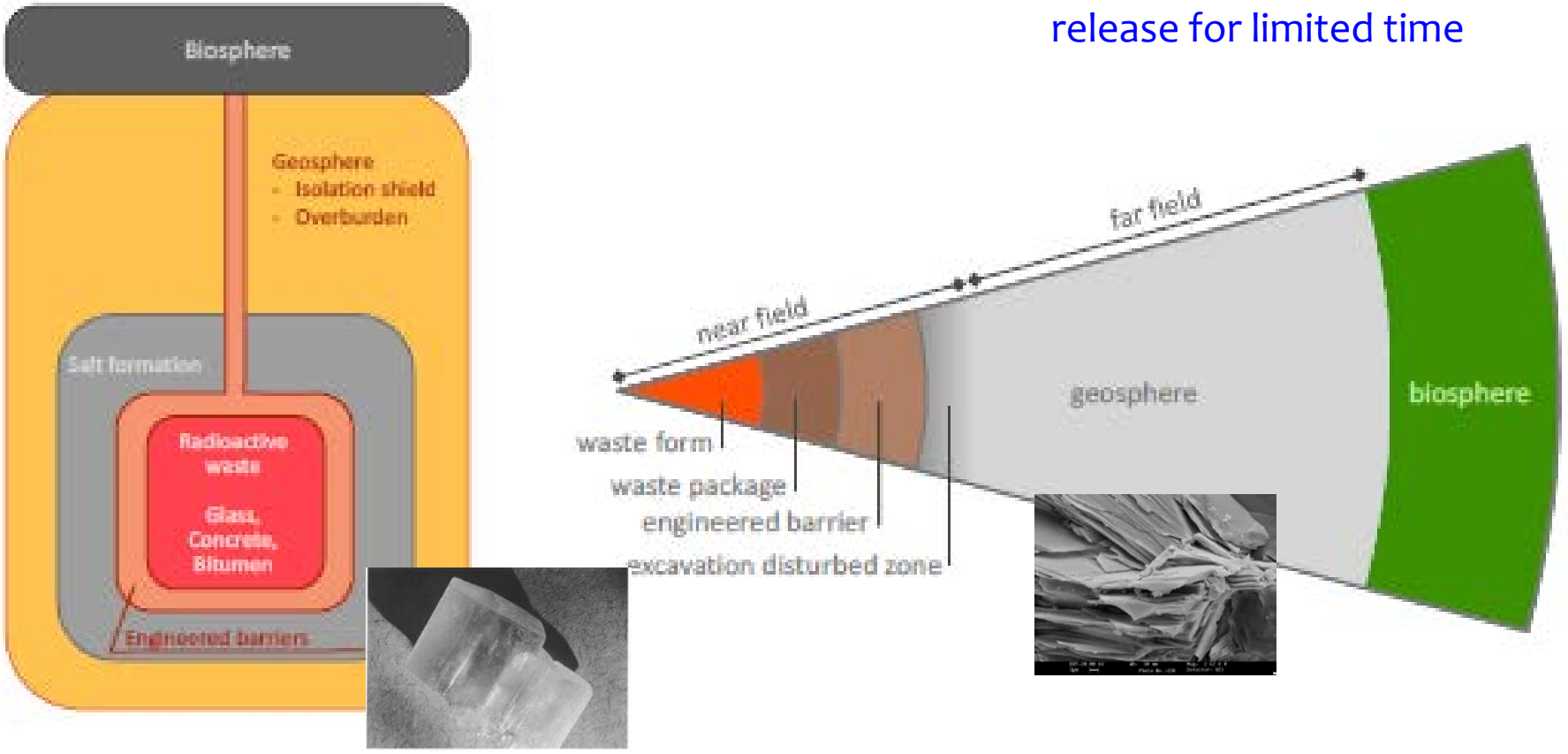
Properties	rock salt	clay / clay rock	crystalline rock
heat conductivity *	high	**low**	**medium**
temperature load *	high	**low**	high
permeability **	impermeable	very low	**permeable**
sorption capacity **	**very low**	very high	**medium**
solubility **	**high**	very low	very low
mechanic stability *	**medium**	**medium**	high
plastic behavior *	viscose	**plastic**	**brittle**
excavation stability *	convergence	**very low**	**low (fractured)**

Source: Table after BGR (2007) „Untersuchung und Bewertung von Regionen mit potenziell geeigneten Wirtsgesteinsformationen“ Hannover / Berlin

Primary safety functions assigned to engineered anthropogenic and natural geogenic parts of the repository system

Rock salt contains waste + canister retains / delays release for limited time

Clay retains / delays radionuclide release + canister retains / delays release for limited time



source: J. Grupa, E. Rosca-Bocancea & H. Meeussen (2015) NRG contribution to D6.1 in Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term (CAST)

Long-term safety analysis as component of safety case

IAEA / OECD-NEA definitions

IAEA
International Atomic Energy Agency

AEN NEA Agence pour l'énergie nucléaire
Nuclear Energy Agency

The safety case is an integration (a synthesis) of evidences, analyses and arguments that describe, quantify and substantiate the safety, and the level of confidence in the safety, of the geological disposal facility

Safety assessment is a crucial part of the safety case. It is the process of systematically analyzing the hazards associated with the facility and the ability of the site and designs to provide the safety functions and meet technical requirements

Safety Analysis Model Chain:

- Container and waste degradation → radionuclide release (leaching, dissolution of waste)
- Near-field source term → including radionuclide retention by engineered barriers
- Transport and retardation in the geosphere
- Biosphere modelling (e.g. dilution in near-surface waters and aquifers, up-take through food chain, exposure) → Annual individual dose mSv/a

Transport processes under repository conditions (near-field)

After breaching of the container, radionuclides may be released from the waste after contact with water

⇩

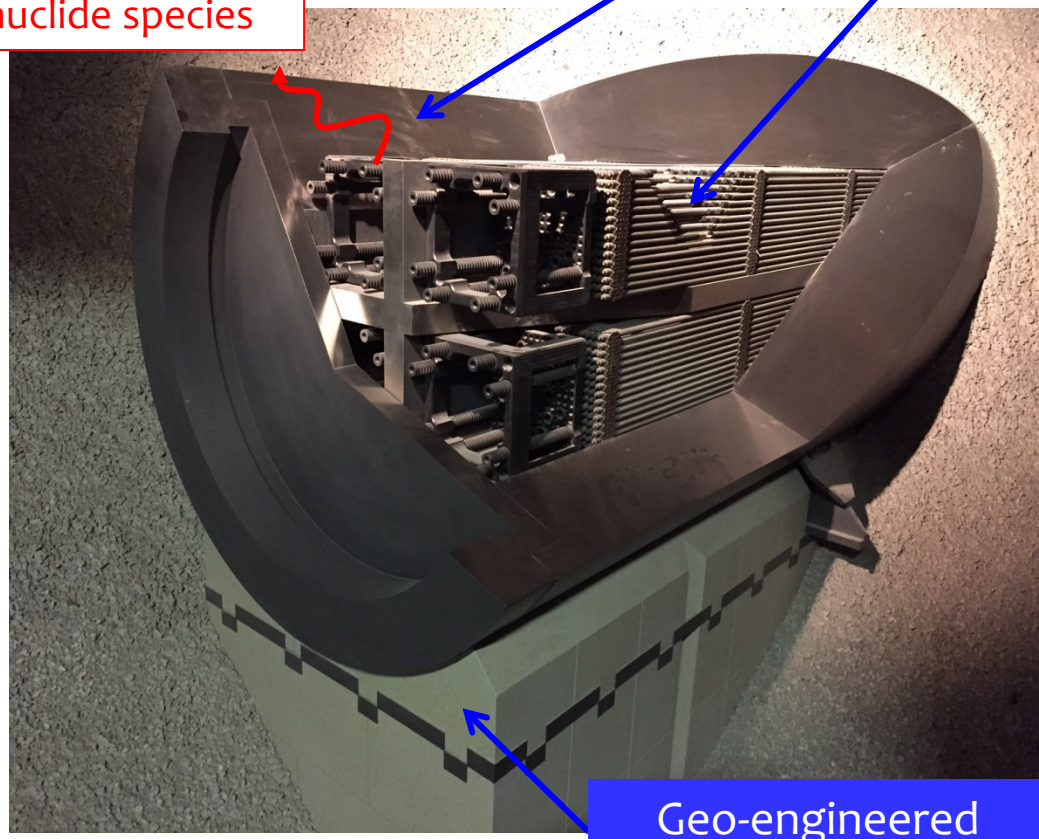
Transport and retardation of radionuclides in the engineered barriers (i.e. corroded container + backfilling)

⇩

Release into geosphere

Radionuclide transport occurs in most cases in aqueous solution (pore and ground water) e.g. dissolved $^{14}CO_3^{2-}$ or $^{14}CH_3COO^-$

In some cases radionuclides are released as gases e.g. $^{14}CH_4$

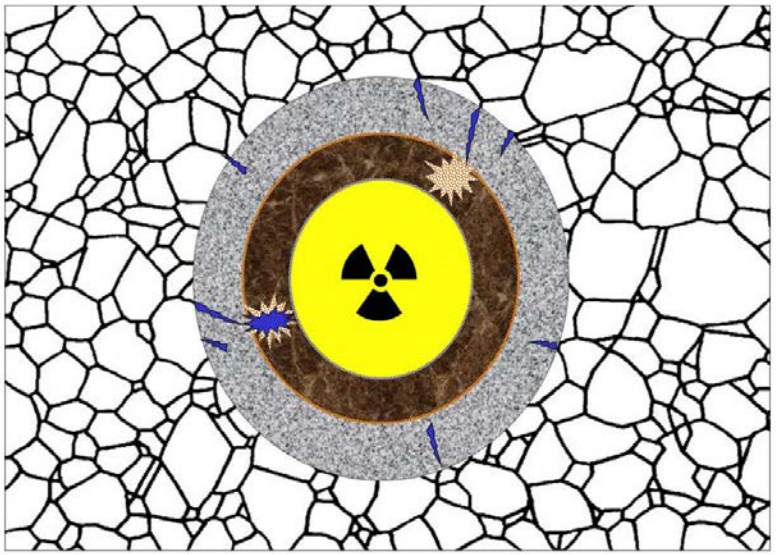


Relevance of ^{14}C in long-term safety analyses

^{14}C is relatively fast released from spent nuclear fuel (^{14}C belongs to Instant Release Fraction) as well as fast released from metallic parts of fuel assemblies

Retention of ^{14}C by container material, geoengineered depends both on chemical speciation of ^{14}C and on geochemical milieu in repository system (i.e. pH, eH, fluid composition, properties of barrier materials)

^{14}C is expected to migrate through multi-barrier system as dissolved species (e.g. $^{14}CO3^{2-}$ or $^{14}CH_3COO^-$) or as gases (e.g. $^{14}CH4$)

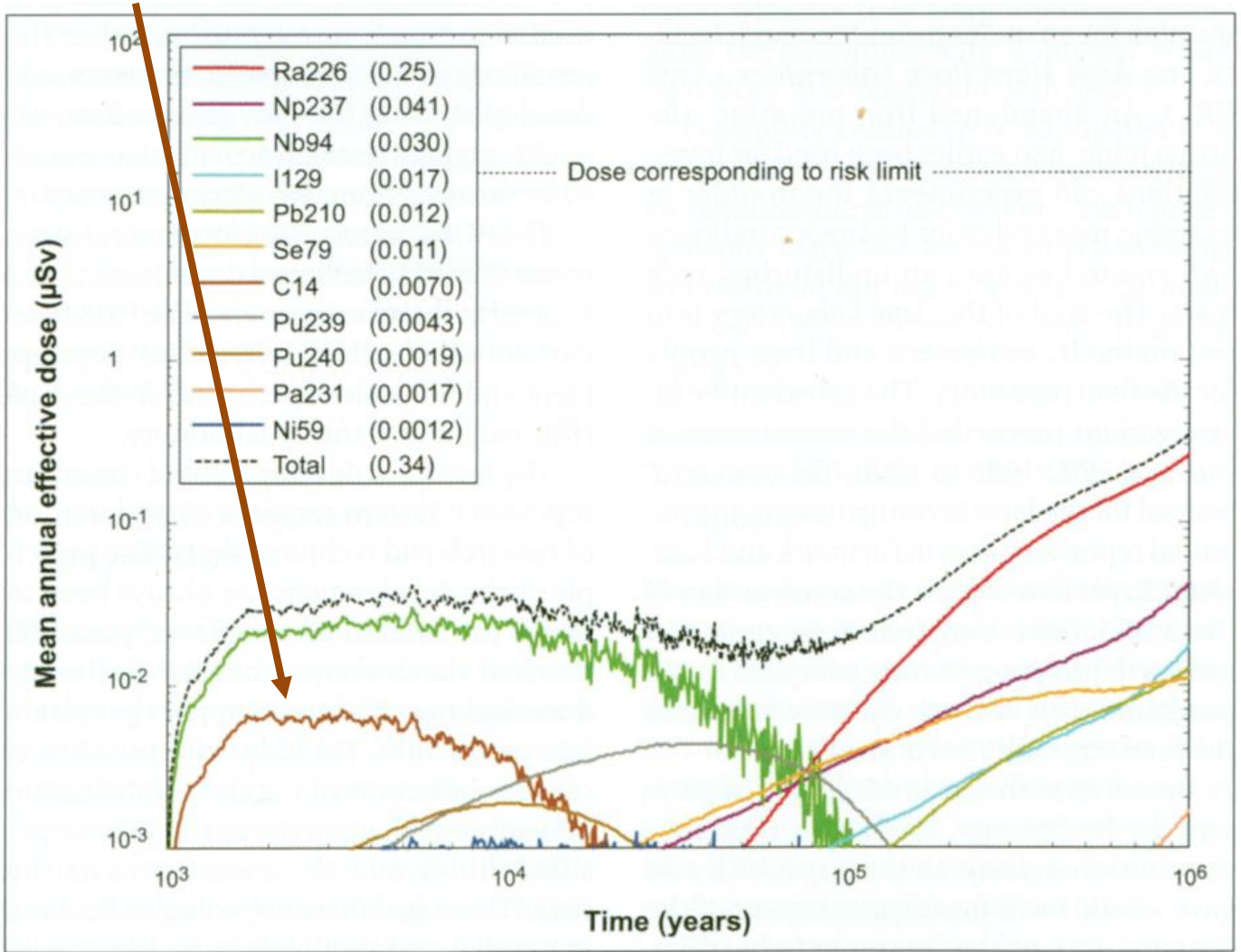


Since knowledge on chemical speciation of ^{14}C and reliable knowledge on retention mechanisms is rather **poor**, a significant ^{14}C release and negligible ^{14}C retention is assumed in most safety assessments →
^{14}C is one of the radionuclides that produces the highest releases from the near field to the geosphere, especially in the first thousands years, according to long-term safety analyses for repositories in clay / clay stone and crystalline rocks

source:
Kendall et al. (2015) Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term. CAST-2015-D6.1

Example: Long-term safety analysis of SKB (Sweden)

Estimate of effective doses with contribution of C-14 in probabilistic calculations for a normal evolution scenario in a SNF repository in granite → calculated dose dominated by long-lived fission, activation and decay products (C-14, Cl-36, I-129, Nb-94, Pb-210, Ra-226, Se-79) and to less extent by actinides

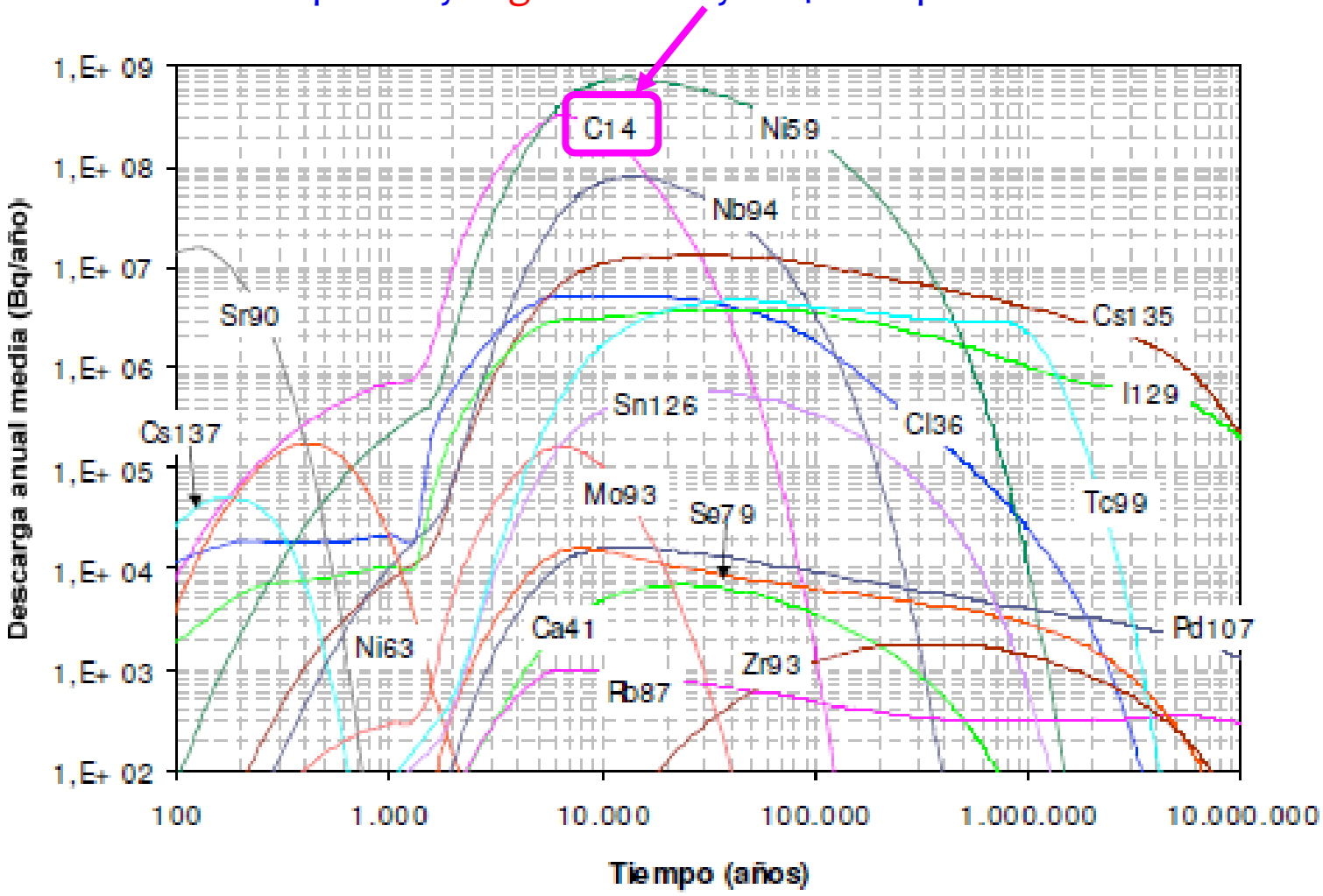


Mean annual effective dose (µSv), i.e. mean effective dose rate (µSv/year)

source: Wikberg (2012) ATW Int'l Journal Nucl Power 57, 102-105

Example: Long-term safety analysis of ENRESA (Spain)

Mean release rates from the near field in probabilistic calculations for a normal evolution scenario in a SNF repository in granite. Only C-14 transport as solute is considered.

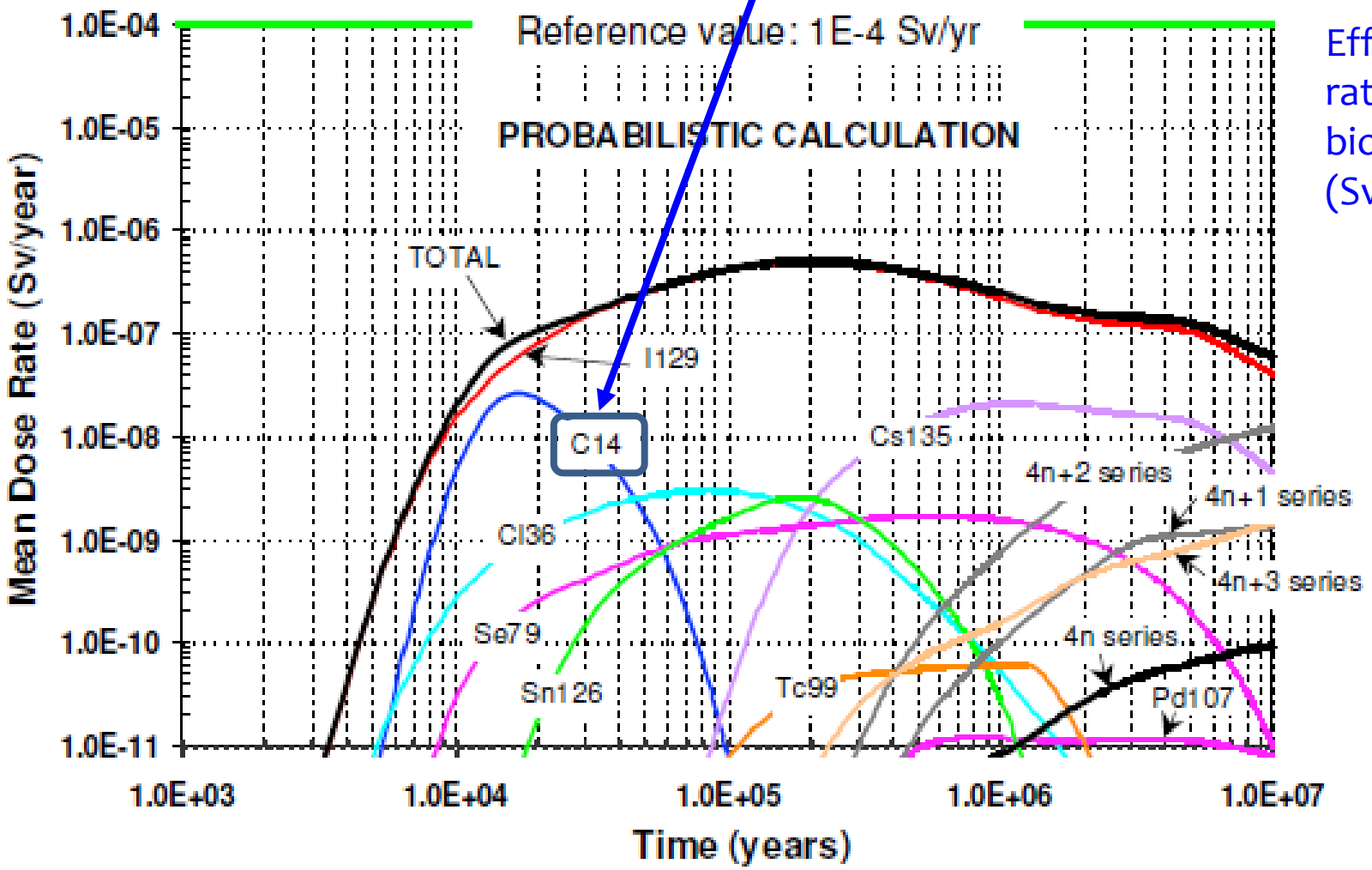


Released activity flux to biosphere (Bq/year)

source: Miguel Cuñado Peralta (2015) ENRESA contribution to D6.1. Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term. CAST-2015-D6.1

Example: Long-term safety analysis of ENRESA (Spain)

Estimate of effective doses with contribution of C-14 in probabilistic calculations for a normal evolution scenario in SNF repository in clay stone. Only C-14 transport as solute is considered.

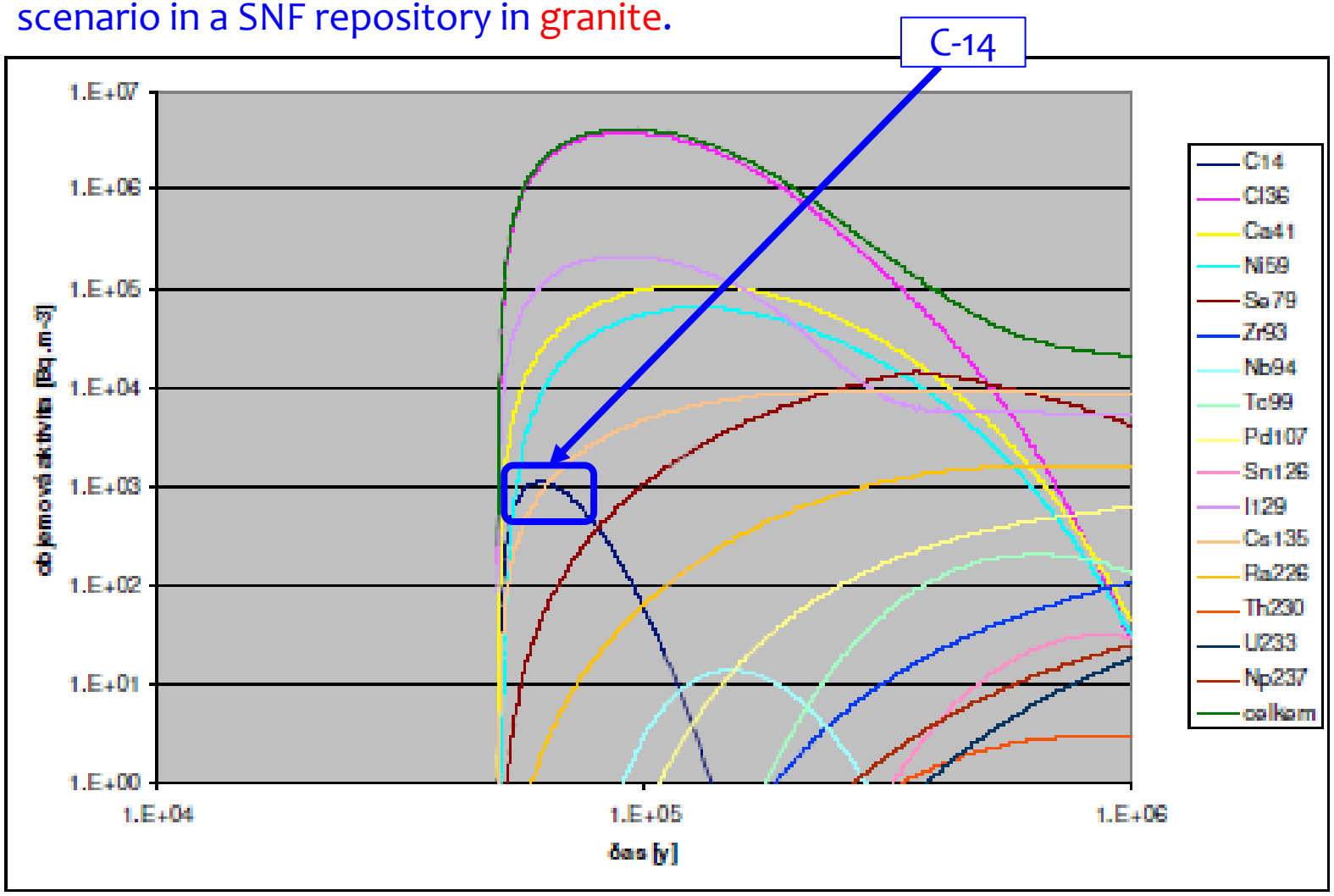


Effective dose rate in biosphere (Sv/year)

source: Miguel Cuñado Peralta (2015) ENRESA contribution to D6.1. Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term. CAST-2015-D6.1

Example: Long-term safety analysis of SURAO (Czech Republic)

Mean release rates from the near field in probabilistic calculations for a normal evolution scenario in a SNF repository in granite.

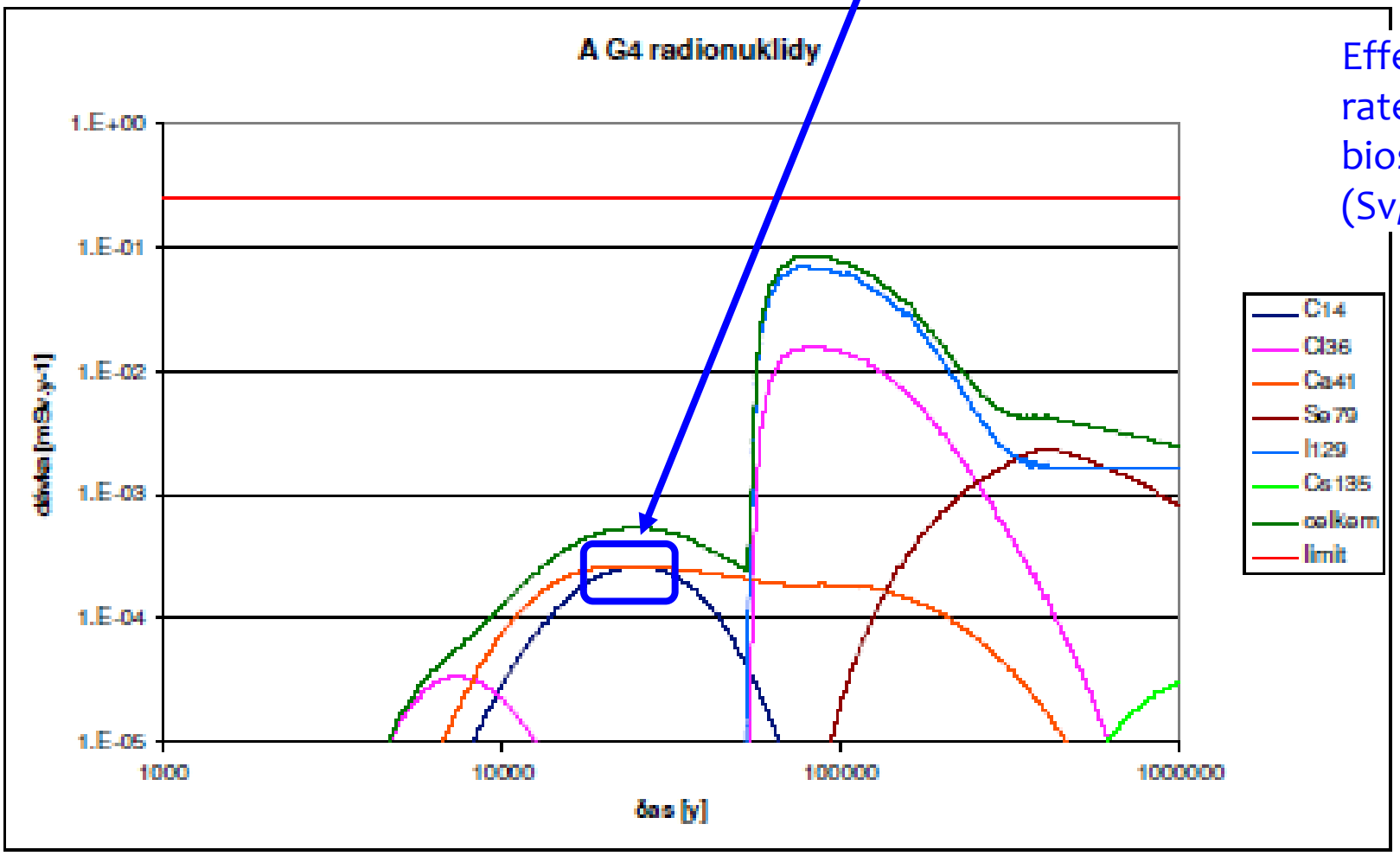


Released activity to biosphere (Bq/m^3)

source: Antonín Vokál (2015) SURAO contribution to D6.1. in Kendall et al., Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term. CAST-2015-D6.1

Example: Long-term safety analysis of SURAO (Czech Republic)

Estimate of effective doses with contribution of C-14 in probabilistic calculations for a normal evolution scenario in a SNF repository in granite.

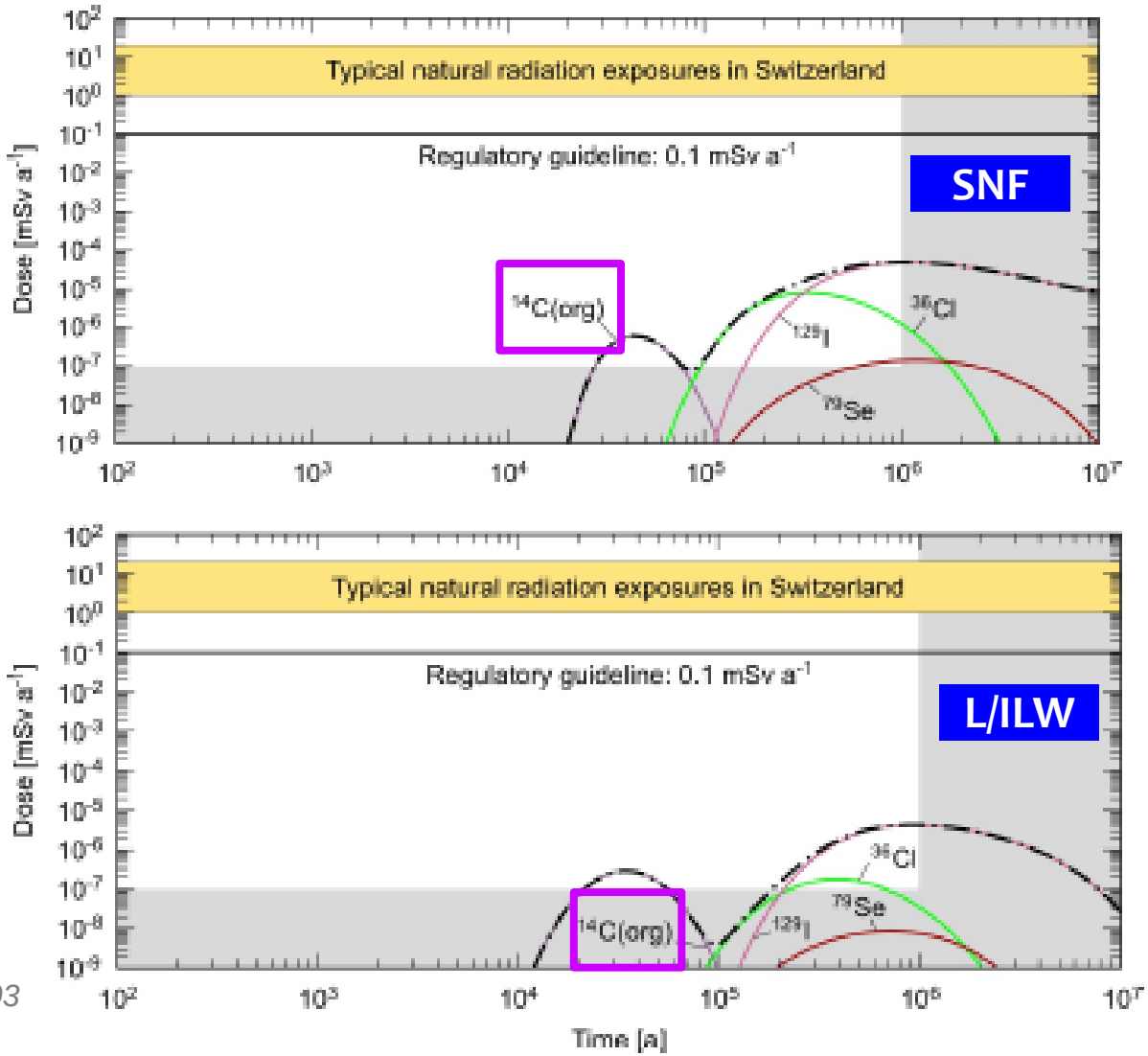


Effective dose rate in biosphere (Sv/year)

source: Antonín Vokál (2015) SURAO contribution to D6.1. in Kendall et al., Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term. CAST-2015-D6.1

Example: Long-term safety analysis of NAGRA (Switzerland)

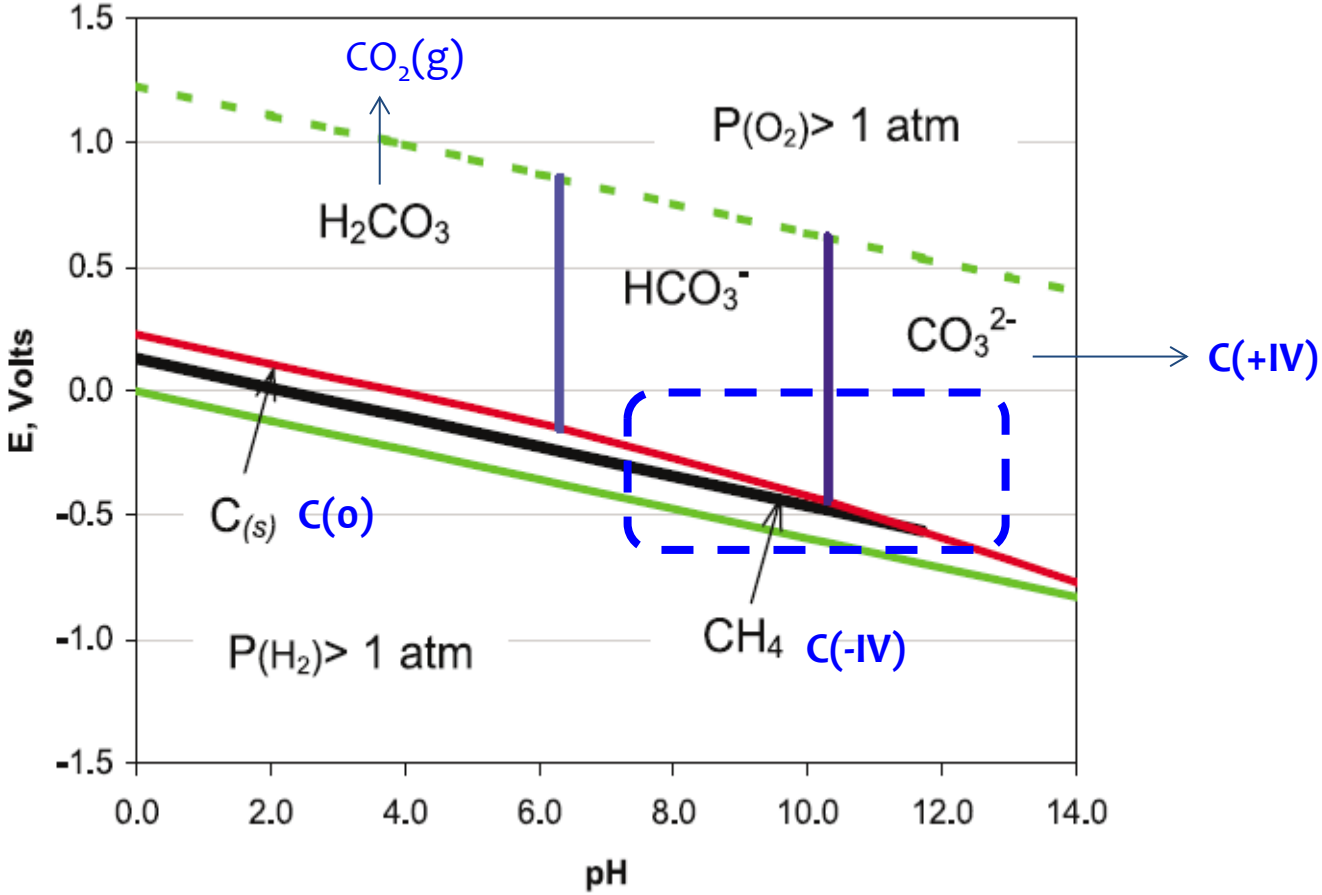
Estimate of effective doses with contribution of C-14 in probabilistic calculations for a normal evolution scenario in a spent nuclear fuel (SNF) repository and low-/intermediate level waste (L/ILW) repository in clay stone.



Effective dose rate in biosphere (Sv/year)

source: Johnson et al. (2004) NAGRA NTB 04-03

Simplified thermodynamic stability fields of ^{14}C compounds at 25°C



$^{14}CO_3^{2-}$, $H^{14}CO_3^-$, $^{14}CH_4$, $^{14}CO_2$

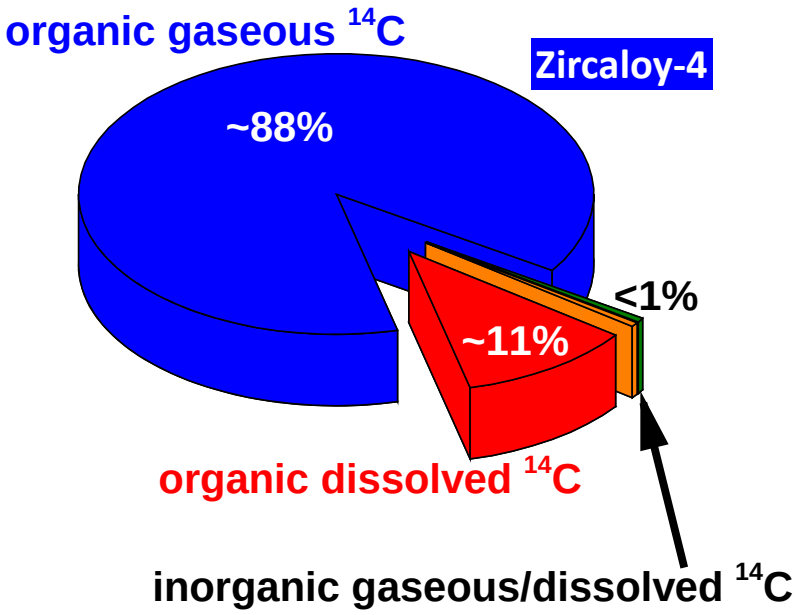
however other organics species are not included (mixed oxidation states)

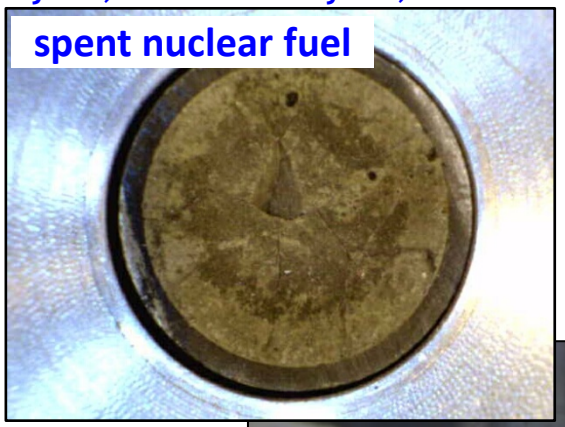
Chemical speciation of released C-14

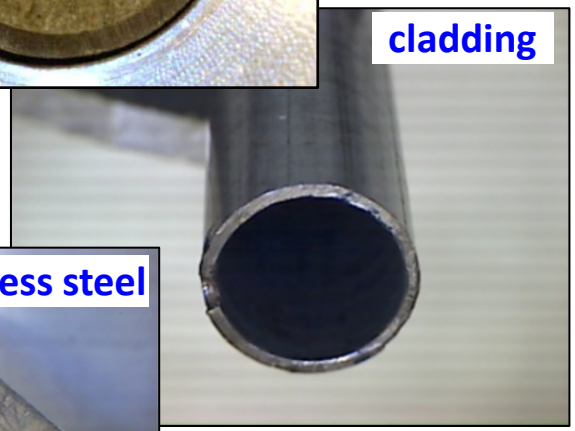
Under repository conditions, ^{14}C is released from spent nuclear fuel, cladding (Zircaloy) and other metallic parts of fuel assemblies as

- organic solutes (e.g. methanol, ethanol, formaldehyde, acetaldehyde, formate, acetate)
- aqueous inorganic species (e.g. $^{14}CO_3^{2-}$, $H^{14}CO_3^-$)
- organic gases (e.g. $^{14}CH_4$)
- inorganic gases (e.g. $^{14}CO_2$)

→ defining the ^{14}C source term







Transport / retardation processes under repository conditions

After breaching of the container, radionuclides may be released from the waste after contact with water

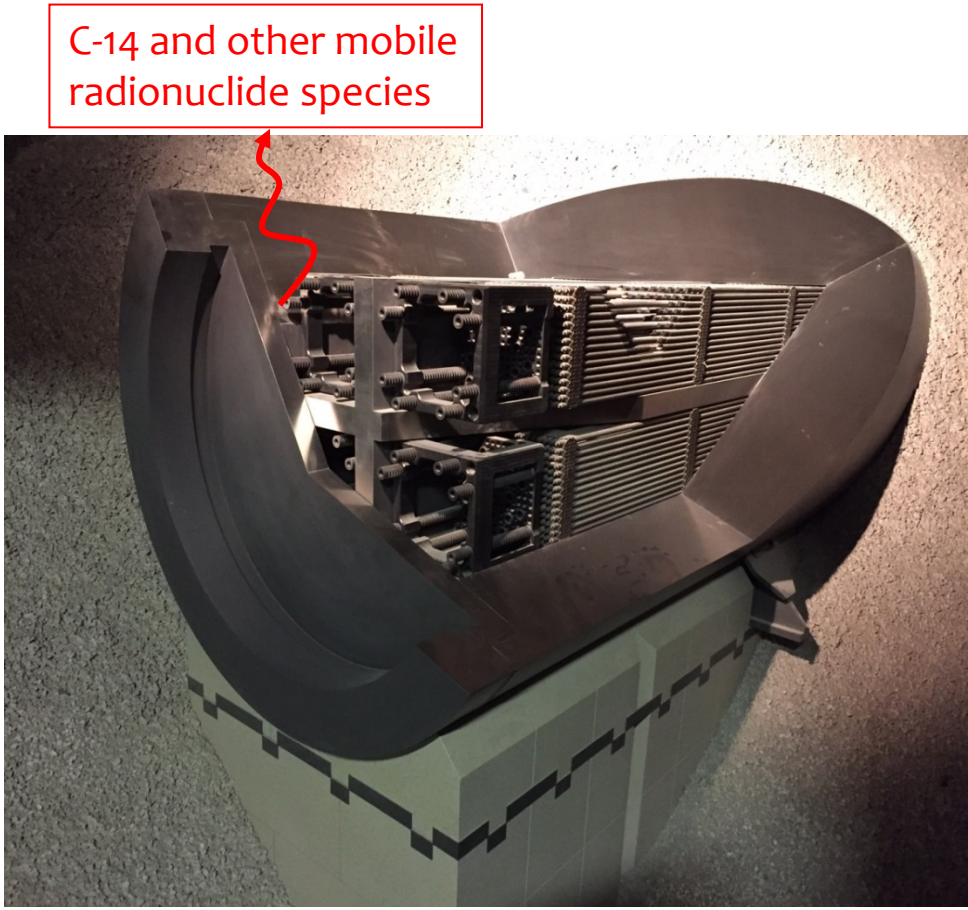
Transport and retardation of radionuclides in the engineered barriers

= chemical interactions with ground-water / porewater (e.g. $Ca^{2+} + {}^{14}CO_3^{2-} \rightarrow$ precipitation of calcite) ruled by solubility phenomena

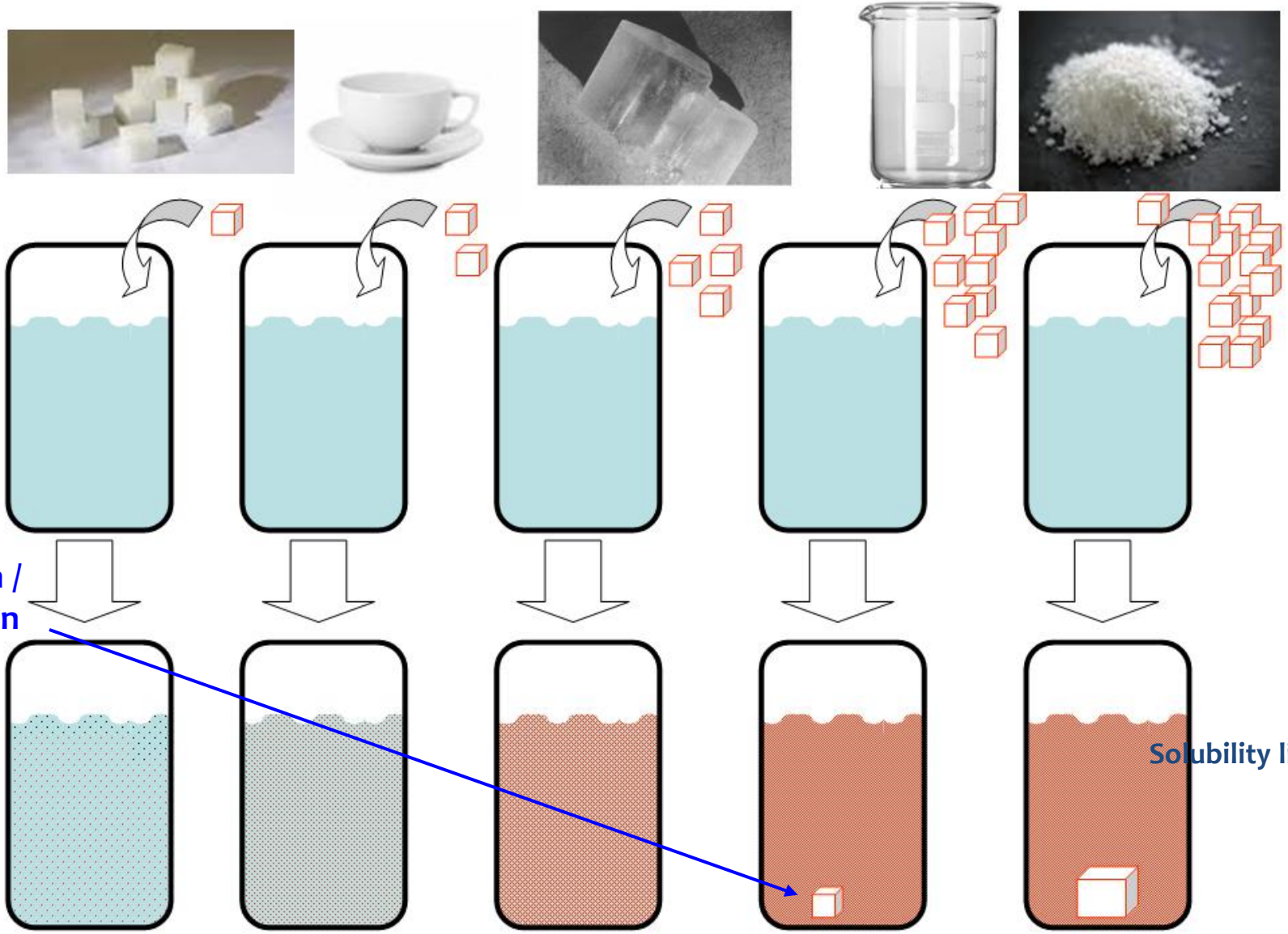
and biotransformation of organic species into $^{14}CH_4$, $^{14}CO_2$

and chemical interactions with solid phases (corroded metal, bentonite, concrete, host rock)

- isotopic dilution,e.g. $Ca^{12}CO_3 \rightarrow Ca^{14}CO_3$
- sorption, surface precipitation, solid solution formation, incorporation

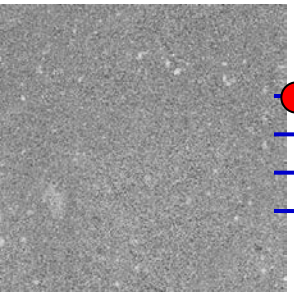


Basic concept for concentration limitation due to solubility phenomena

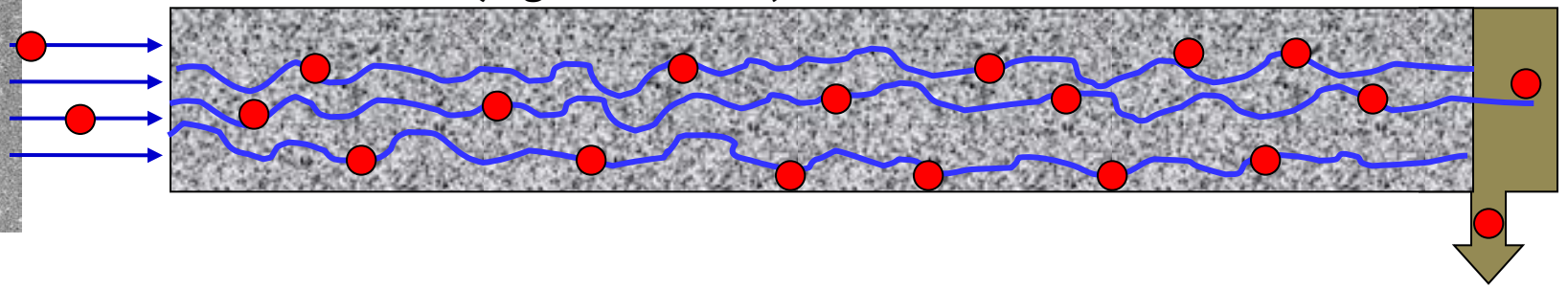


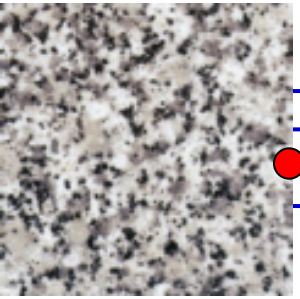
Basic concept for migration and retention in geo-engineered / geological barriers

^{14}C

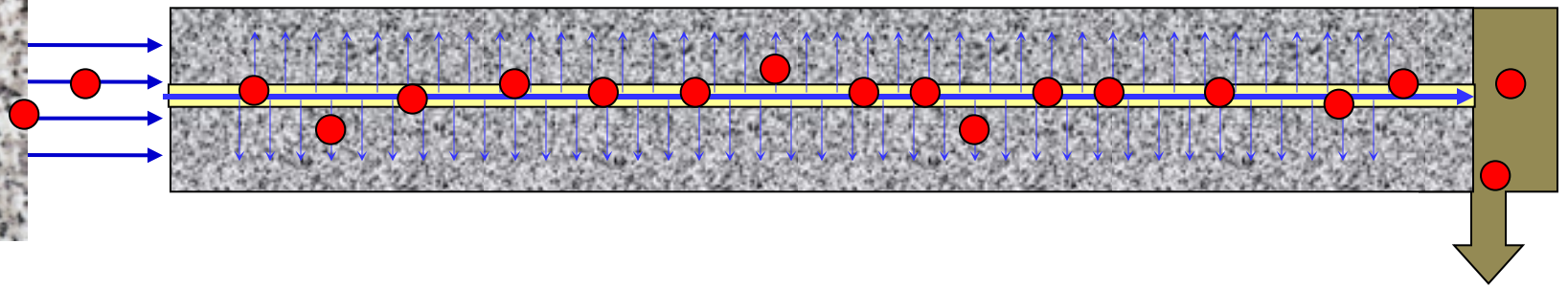


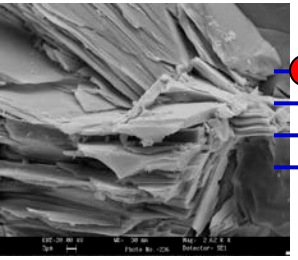
Porous media (e.g. sandstone)



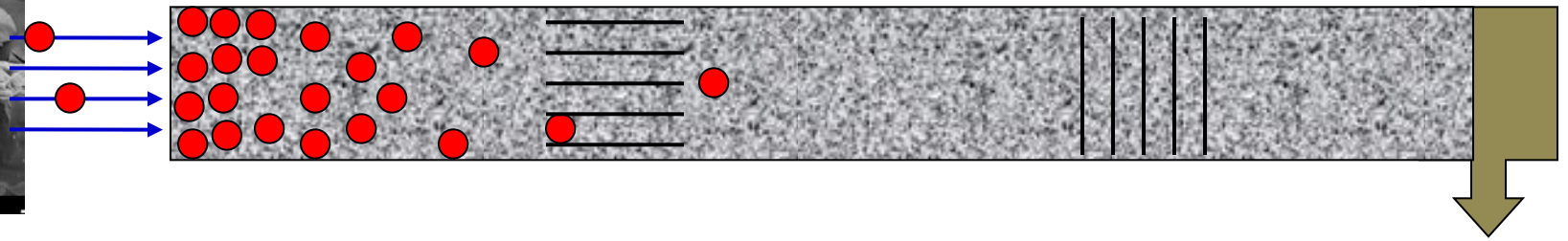


Fractured media (e.g. granite / granodiorite)





Porous media (e.g. bentonite / argillaceous rock)



biotic degradation of organic ^{14}C compounds into $^{14}CH_4$ and $^{14}CO_2$

small organic species (methanol, ethanol, formaldehyde, acetaldehyde, formate, acetate)

biotic degradation

$^{14}CH_4(g)$

$^{14}CO_2(g)$

$^{14}CO3^{2-}$, $H^{14}CO3^-$ (aq)

$^{14}CH_4(g)$

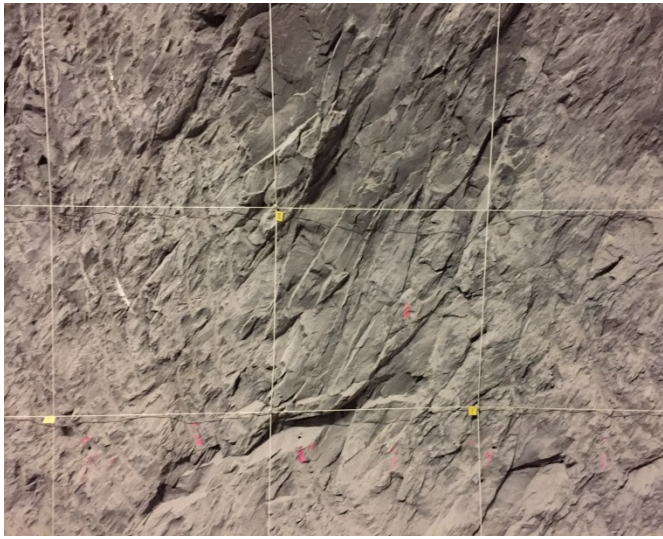
$^{14}CO_2(g)$

aqueous inorganic species partly retained; small organic species sorbed to some extent

$^{14}CH_4(g)$ is highly mobile (hardly any retention in multi-barrier system); $^{14}CO_2(g)$ retained to some extent under alkaline conditions

- aerobe respiration $CH_2O + O_2 = CO_2 + H_2O$
- denitrification $CH_2O + 4/5\ H^+ + 4/5\ NO_3^- = CO_2 + 2/5\ N_2 + 7/5\ H_2O$
- Fe^{3+} reduction $CH_2O + 8\ H^+ + 4\ Fe(OH)_3 = CO_2 + 4\ Fe^{2+} + 11\ H_2O$
- SO_4^{2-} reduction $CH_2O + {}^1/_2\ H^+ + {}^1/_2\ SO_4^{2-} = CO_2 + {}^1/_2\ HS^- + H_2O$
- methanogenesis $C_6H_{10}O_5 + H_2O = 3\ CO_2 + 3\ CH_4$

^{14}C behaviour under repository conditions – application to long-term safety analyses for SNF / HLW repositories in clay / claystone (BE, CH, NL)



Conservative approaches to simulate ^{14}C behaviour:

- ^{14}C released from SNF is assumed to be in organic form; transport in Opalinus Clay and Boom Clay is dominated by diffusion, whereas advective flow and gas transport are considered negligible
- no sorption is considered for organic forms of ^{14}C (NAGRA)
- ^{14}C is assumed to be not retarded at all (ONDRAF-NIRAS)

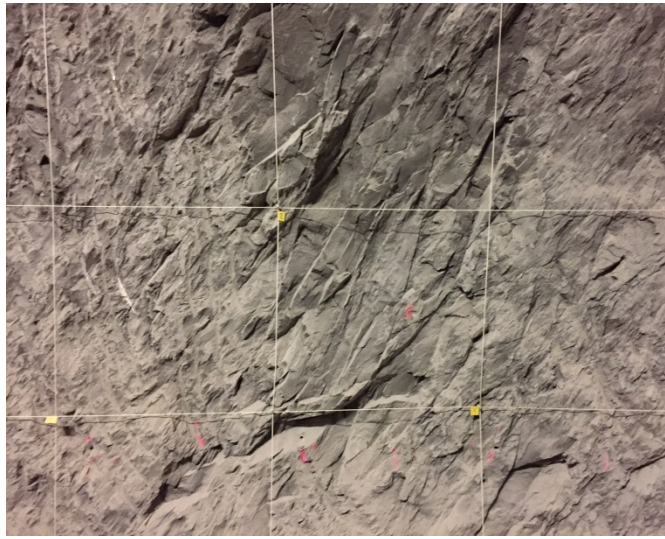
- Still, since diffusion rate is very slow and migration path from deep underground repository to biosphere is rather long, virtually all ^{14}C will decay in Boom Clay host rock (NRG)

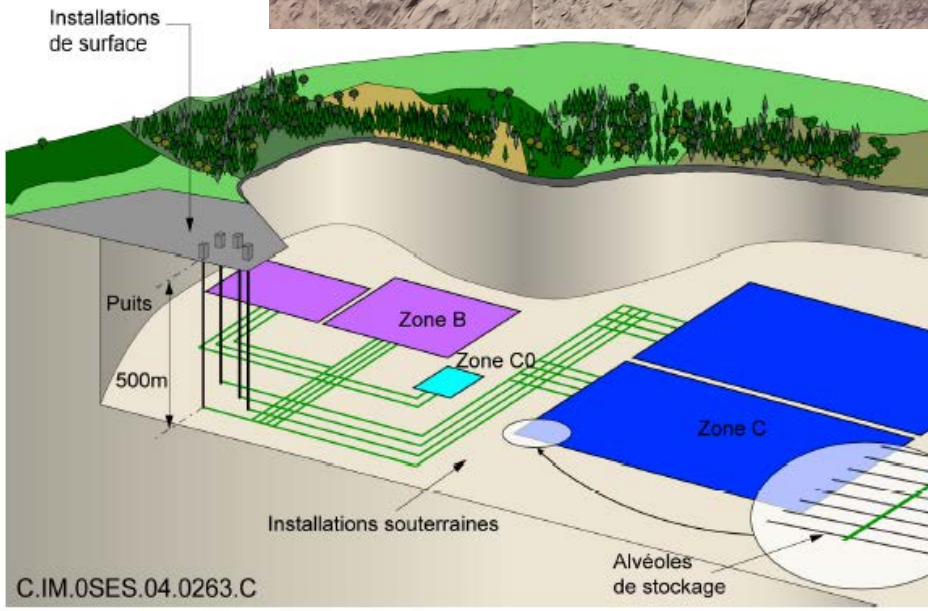
source:
Kendall et al. (2015) Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term. CAST-2015-D6.1

^{14}C behaviour under repository conditions – application to long-term safety analyses for HLW repository in clay stone (FR)

Conservative approach to simulate ^{14}C behaviour:
Migration of complete ^{14}C inventory as gas without any retention; conservative approach chosen by ANDRA due to lack of knowledge on chemical ^{14}C behaviour under repository conditions

Alternative approach to simulate ^{14}C behaviour (ANDRA):
Taking into account migration of complete ^{14}C inventory as dissolved inorganic species; considering migration by diffusion, advection and dispersion and sorption of inorganic ^{14}C species in bentonite, concrete and claystone





source:
Kendall et al. (2015) Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term. CAST-2015-D6.1

14C behaviour under repository conditions – application to long-term safety analyses in crystalline rock (SF, CZ)

Diffusion through bentonite backfilling and advective transport of dissolved species in crystalline bedrock considered

14C speciation may change due to reactions either inside the repository or while migrating along the bedrock fractures

Due to related uncertainties, 14C is conservatively assumed to be released in organic gaseous form in alternative scenario (FORTUM)

Diffusion coefficients for bentonite as well as sorption coefficients for bentonite and granite are estimated (SURAO)

source:
Kendall et al. (2015) Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term. CAST-2015-D6.1

Complete isolation in "normal evolution scenarios" of long-term safety analyses for repositories in rock salt (DE, NL)

"In the case of disposal in rock salt, the waste is completely enclosed by several hundred meters of dry rock salt. Consequently, ***all C-14 will decay in the facility****. The displacement of air from the mine (potentially including C-14), caused by the convergence of the rock salt has not yet been taken into account."* (NRG)

"Crushed salt backfill is expected to be compacted over time by convergence of the host rock to achieve a sufficiently high hydraulic resistance to avoid inflow of brines into the repository. Plugs and seals ***must*** *provide their sealing function during the early post closure phase, until the compaction of the backfill is adequate and the permeability of the backfill is sufficient low. (…) According to the regulations, the waste containers (…)* ***must*** *be designed to avoid the release of radioactive aerosols for a period of 500 years.* ***No dissolved radionuclides are released from the isolating rock zone*** *during the whole reference period."* (GRS)

Different results for less probable scenarios: water access due to failure of shaft sealing etc.

source:
Kendall et al. (2015) Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term. CAST-2015-D6.1

Summary

- ^{14}C is relatively fast released from spent nuclear fuel as well as fast released from metallic parts of fuel assemblies
- Retention of ^{14}C by container material, geo-engineered barriers and geological barriers depends both on chemical speciation of ^{14}C and on geochemical milieu in repository system
- ^{14}C is expected to migrate through multi-barrier system as dissolved species or as gases
- Since knowledge on chemical speciation of ^{14}C and reliable knowledge on retention mechanisms is rather poor, a significant ^{14}C release and negligible ^{14}C retention is assumed in safety assessments for repositories in clay / clay stone and crystalline rock $\rightarrow$ ^{14}C is one of the radionuclides that produces the highest releases
- With respect to "normal evolution scenarios", no 14C release is expected from the near-field of a SNF / HLW repository in rock salt