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

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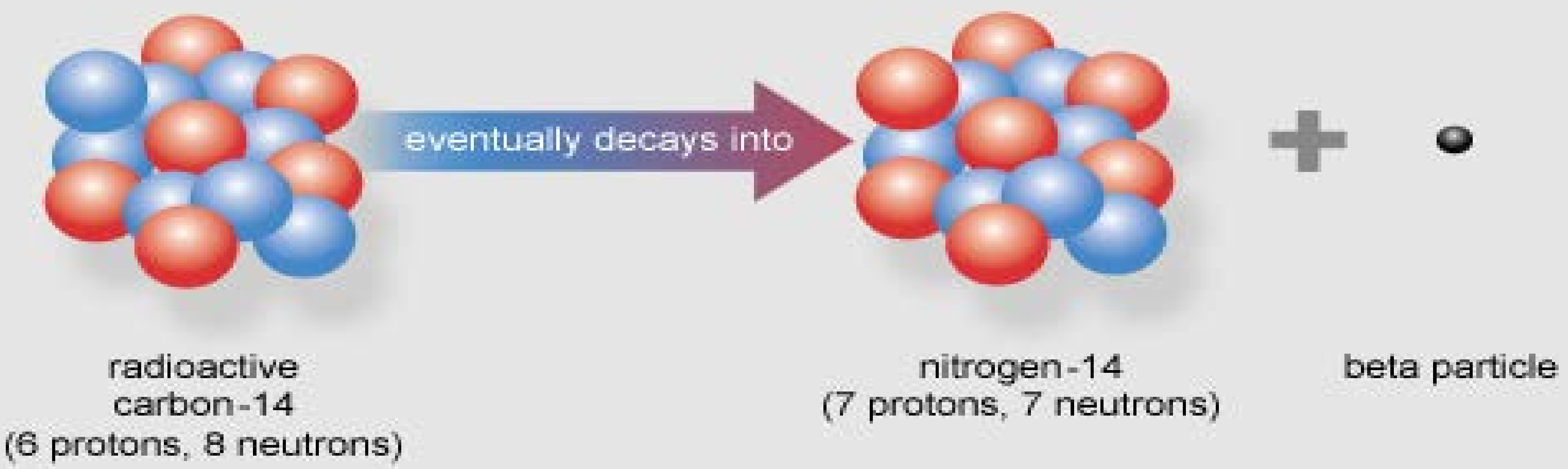


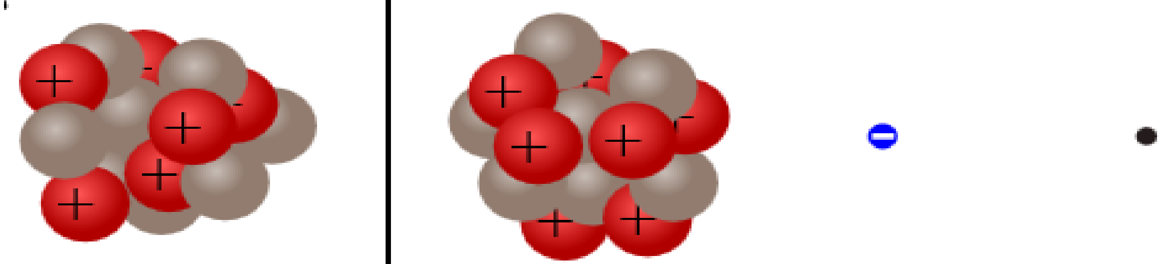
Content

- **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



$$^{14}_{6}C \rightarrow\ ^{14}_{7}N + \,^{0}_{-1}e + \bar{\nu}$$

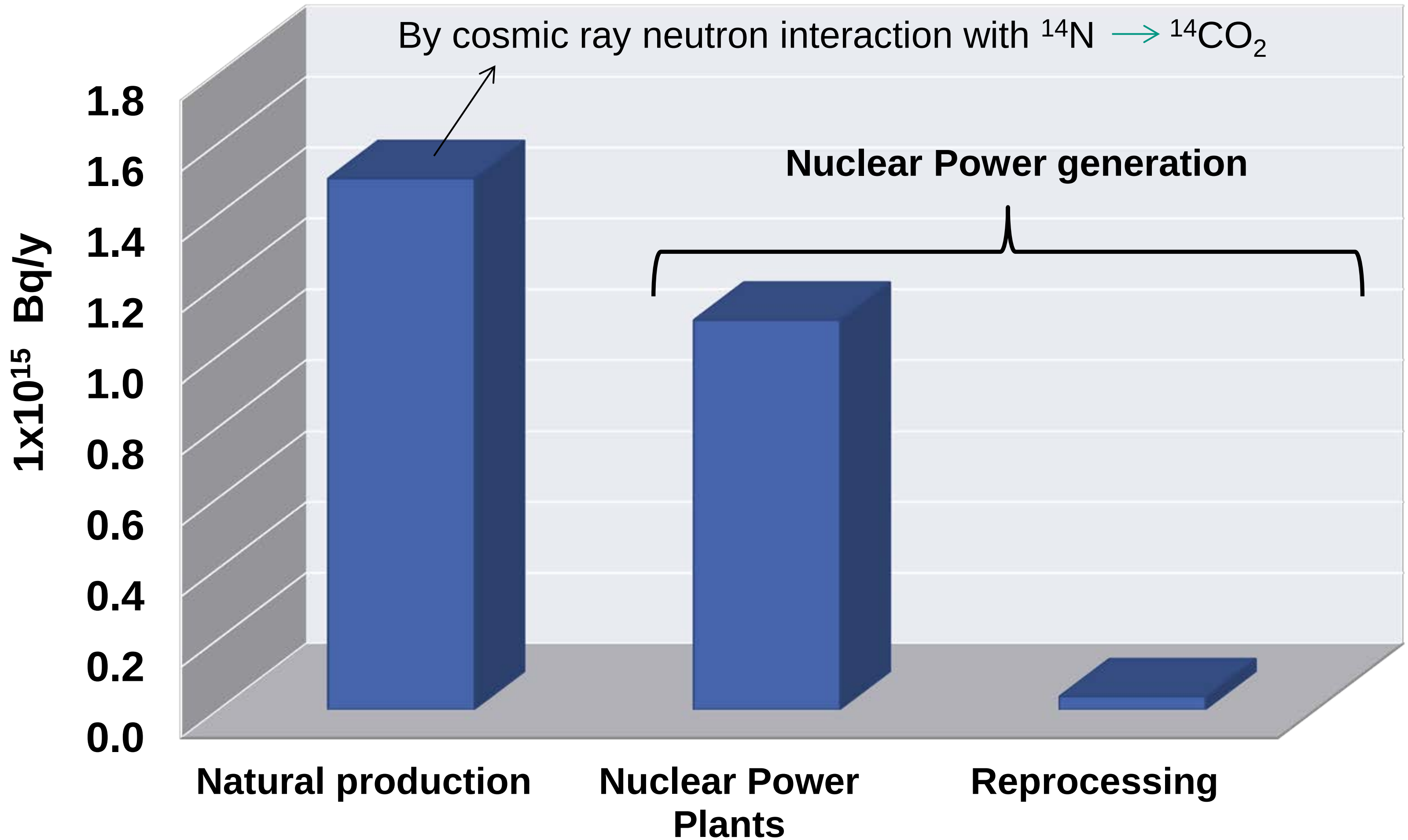
β decay

- 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

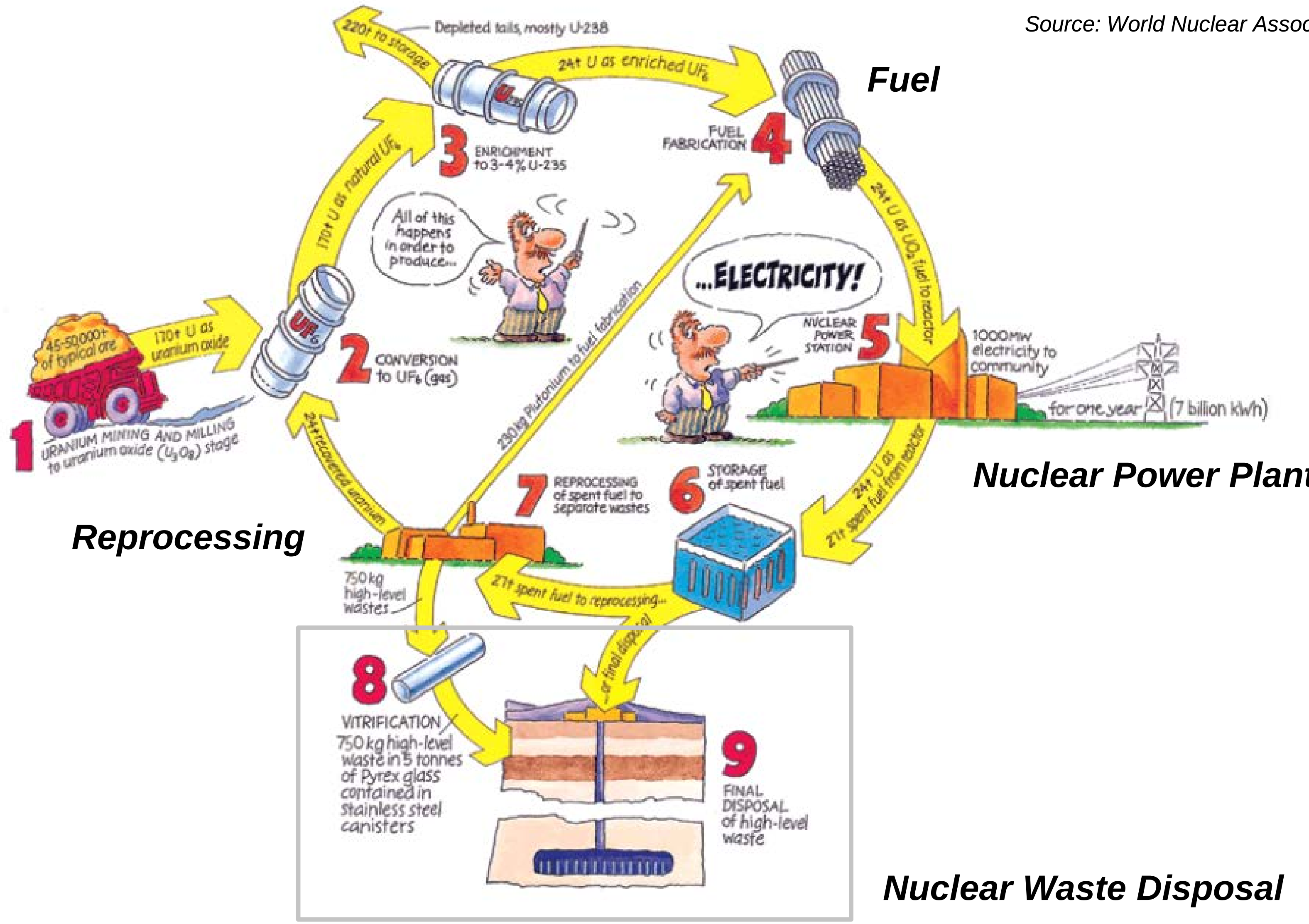
Nuclear weapon testing
(not anymore)



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

Nuclear Power generation

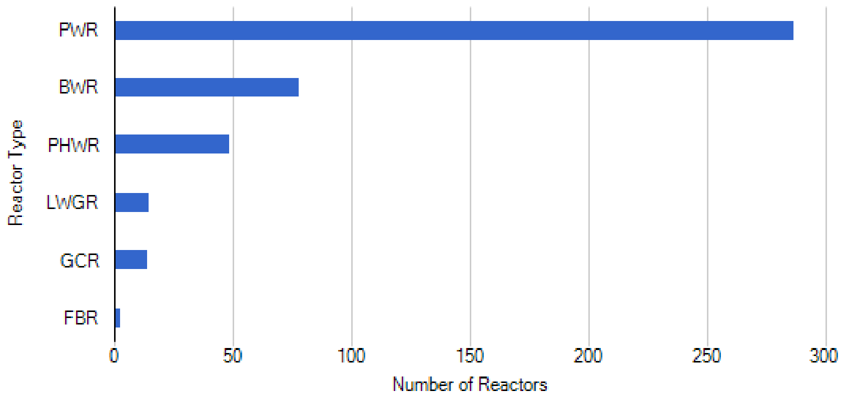
Source: World Nuclear Association



Nuclear Power Plant

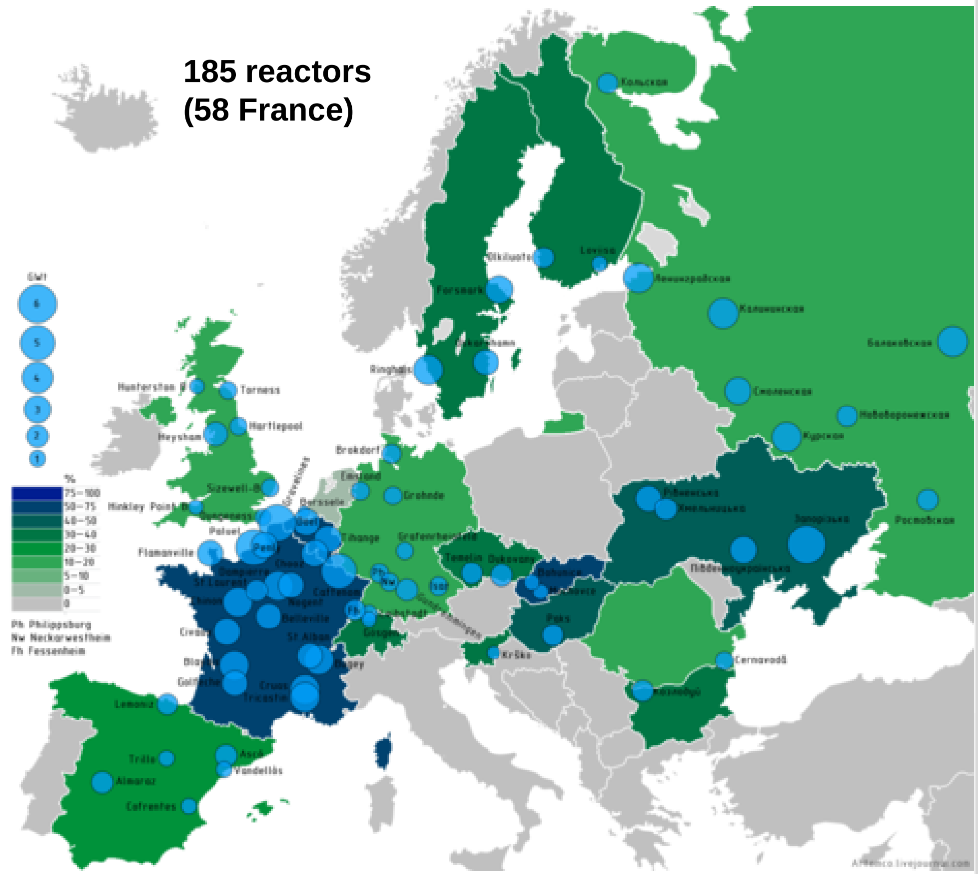
C-14 world inventory

444 reactors in operation*



287 PWR + 78 BWR

Research reactors are not included

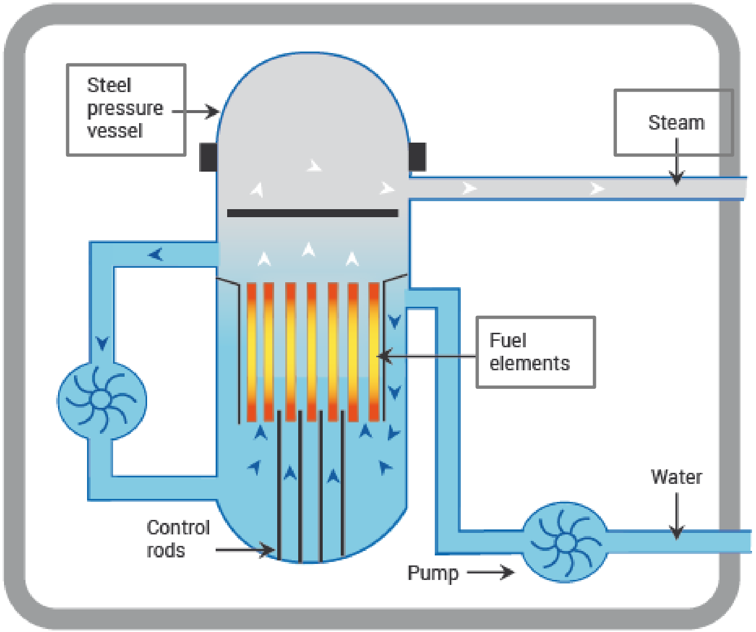


*Data from June 2016 (IAEA)

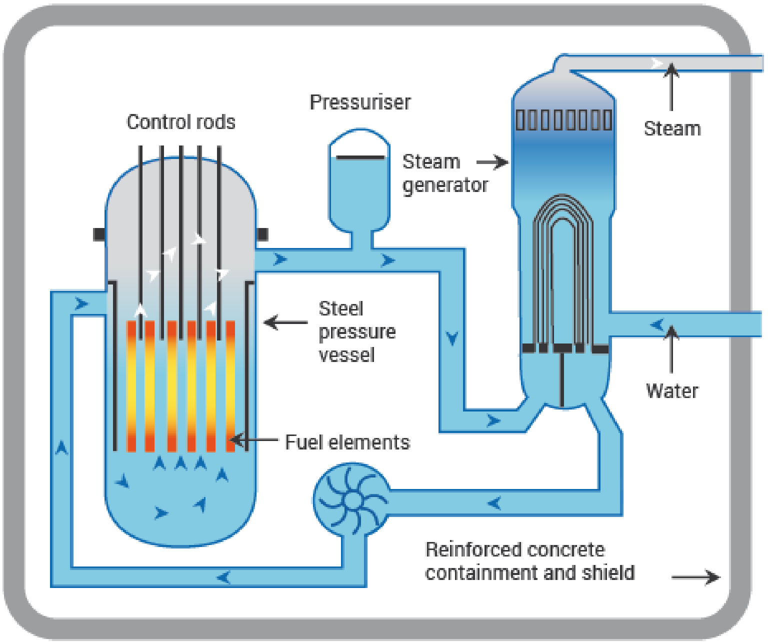
Nuclear Power Plant

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).

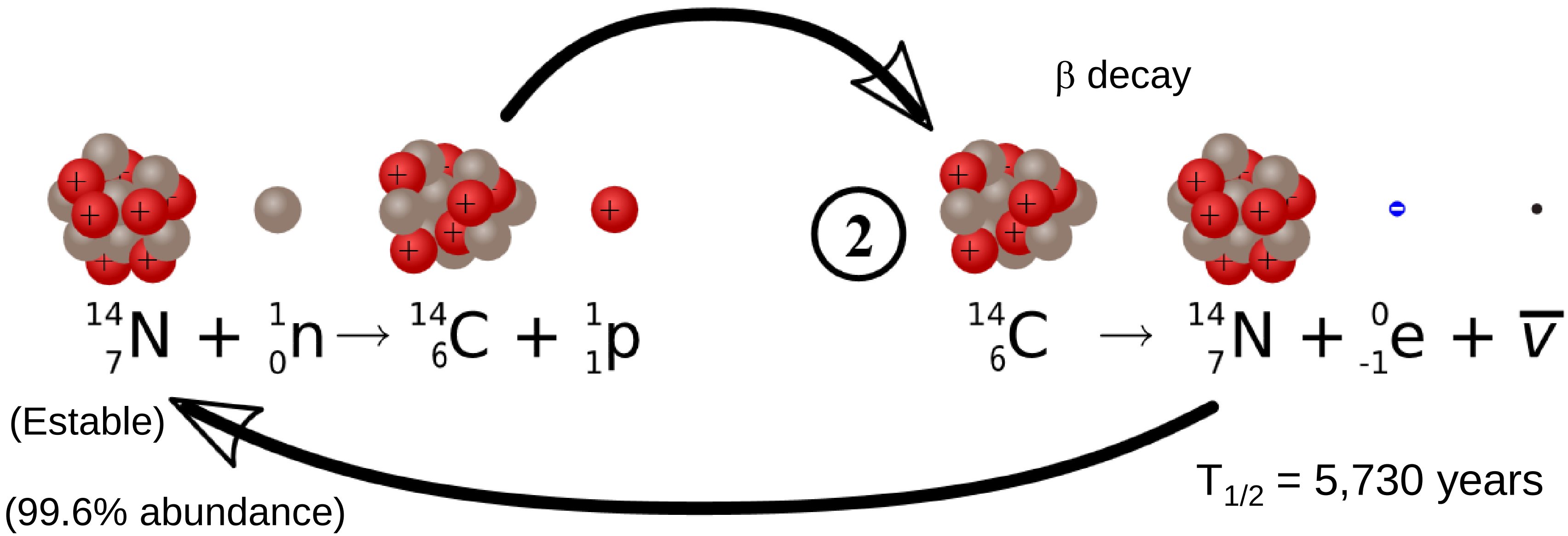
[a] PWR and BWR updated values, based on Van Konynenburg (1994)—see text.

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

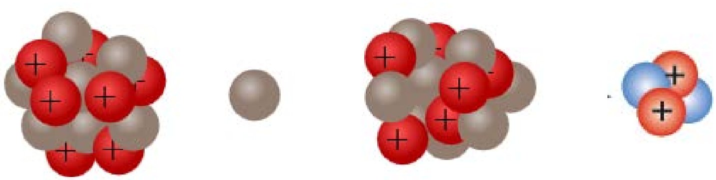
$$^{13}_{8}C + ^{1}_{0}n \rightarrow ^{14}_{6}C + \gamma$$

(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					
^{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[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	

[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).

Fuel

Coolant

Presure

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

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

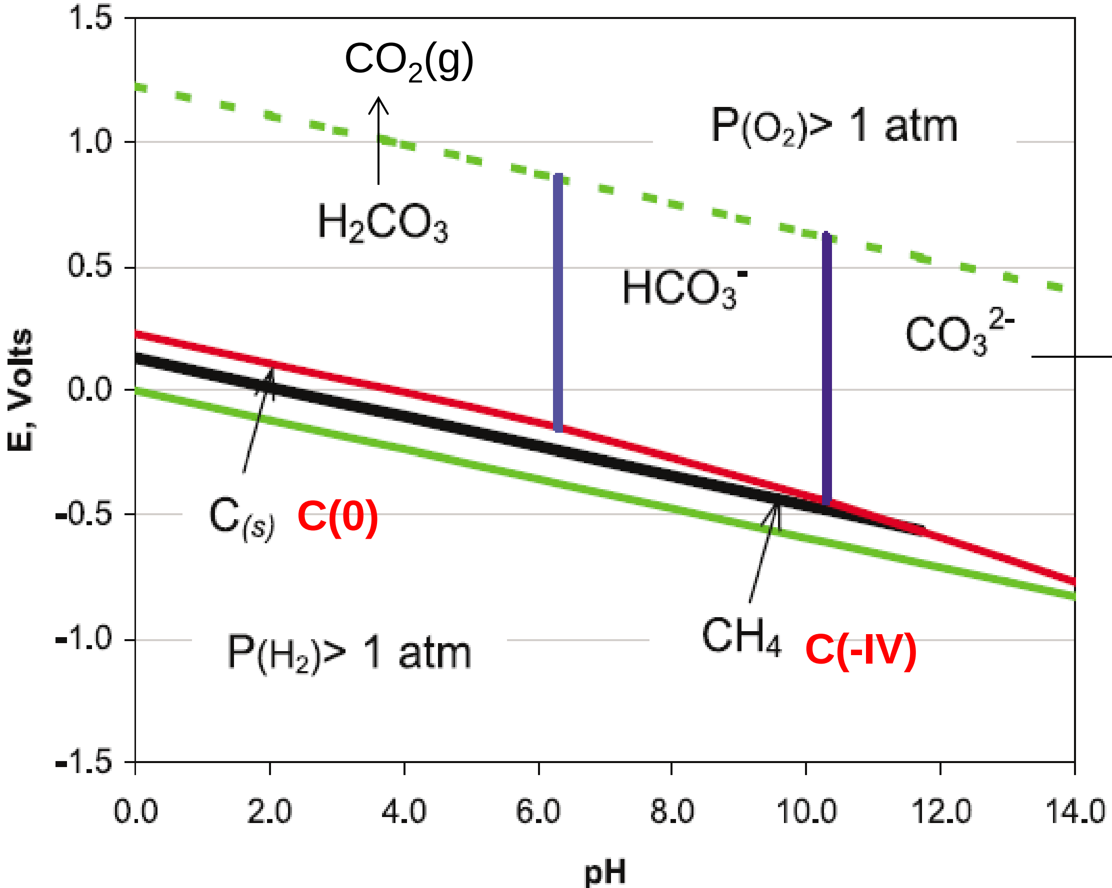
^{17}O in H_2O

$^{13}CO_2$ 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:

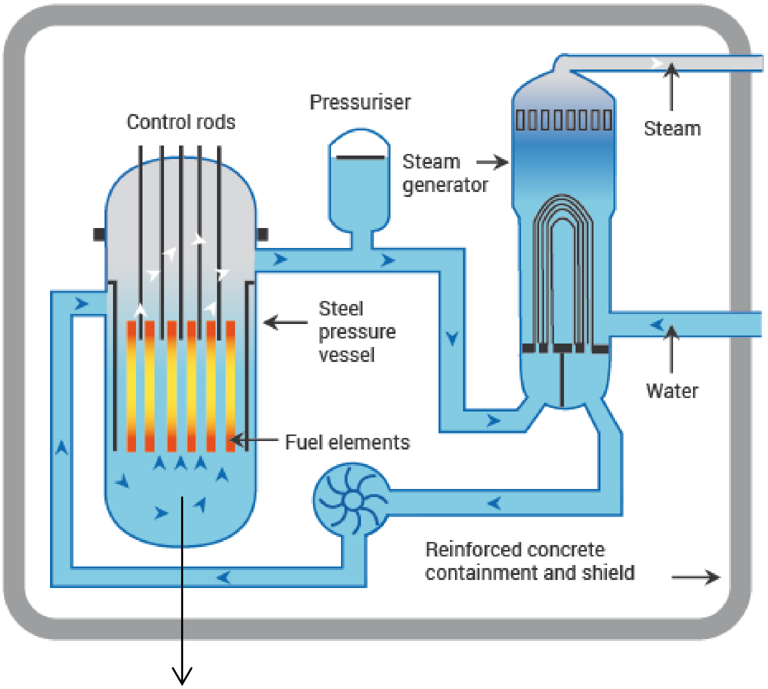
- Eh
- pH
- Temperature

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

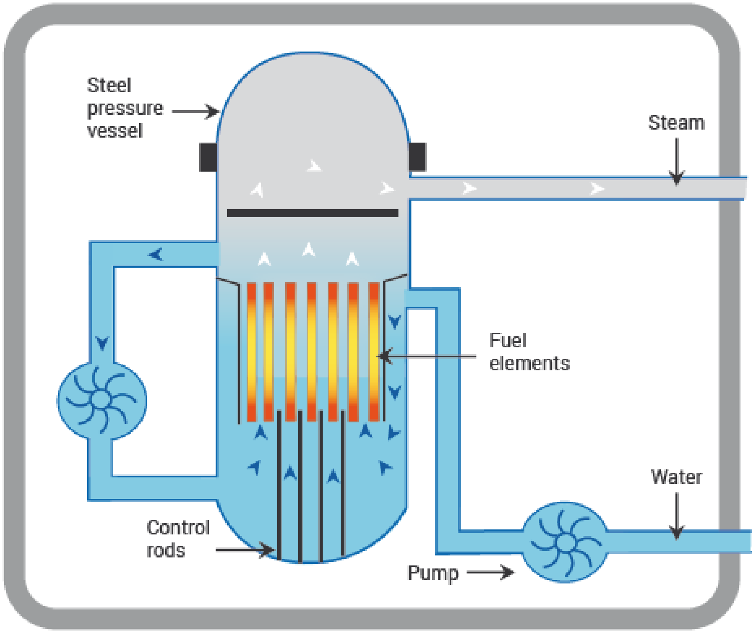
$({}^{14}H_2CO)$ $({}^{14}CH_3OH)$

Coolant system = 58 – 95 % organics

The chemistry of C-14

Chemical conditions in LWR

Boiling water reactor (BWR)



↓

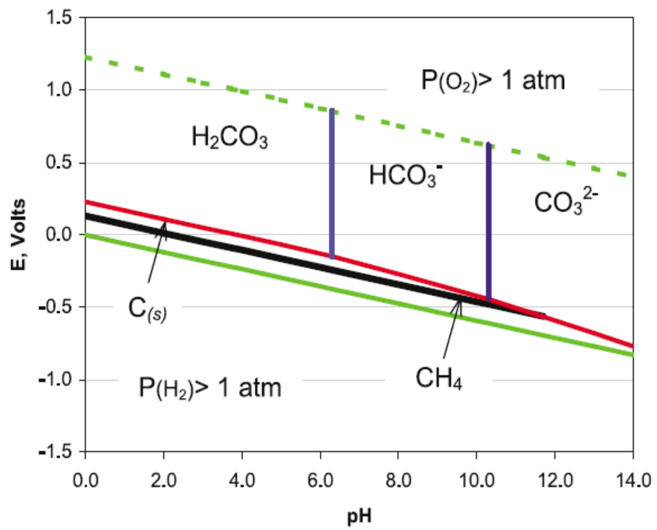
Oxidizing conditions

300°C and 72 bar

Vance et al. 1995, TR-105717. EPRI

Oxidizing conditions

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

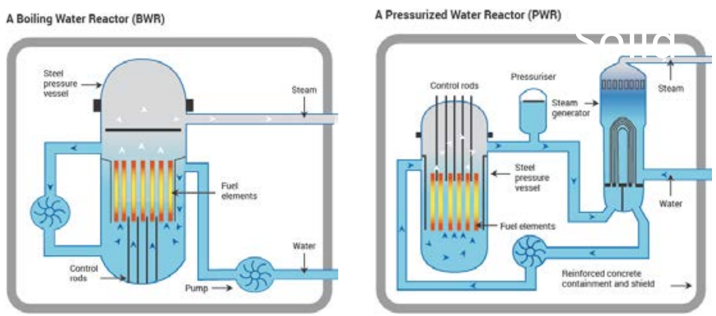


Coolant system = HCO_3^-

The chemistry of C-14

Karlsruhe Institute of Technology

Chemical conditions in LWR and forms of waste



Gas production

$^{14}CO_2$
$^{14}CH_4$,…

Treatment in the NPP

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

Solid phase

Spent Fuel
Zircaloy

Structural fuel material

Steel (metals)

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

Aqueous (coolant)

$H^{14}CO_3^-$
^{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
Solidifed 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

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

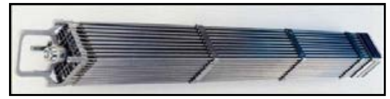
Filter Media (3.6) ← Reactor coolant Cleanup filters.

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

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

Radioactive waste

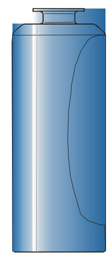
Irradiated Nuclear fuel



Intermediate storage

Repository for **heat generating** radioactive waste

Waste from reprocessing (i.e vitrified)

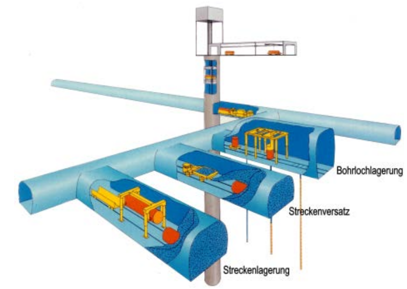


(NPP operational waste and decommissioning)

Intermediate storage

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

Final disposal

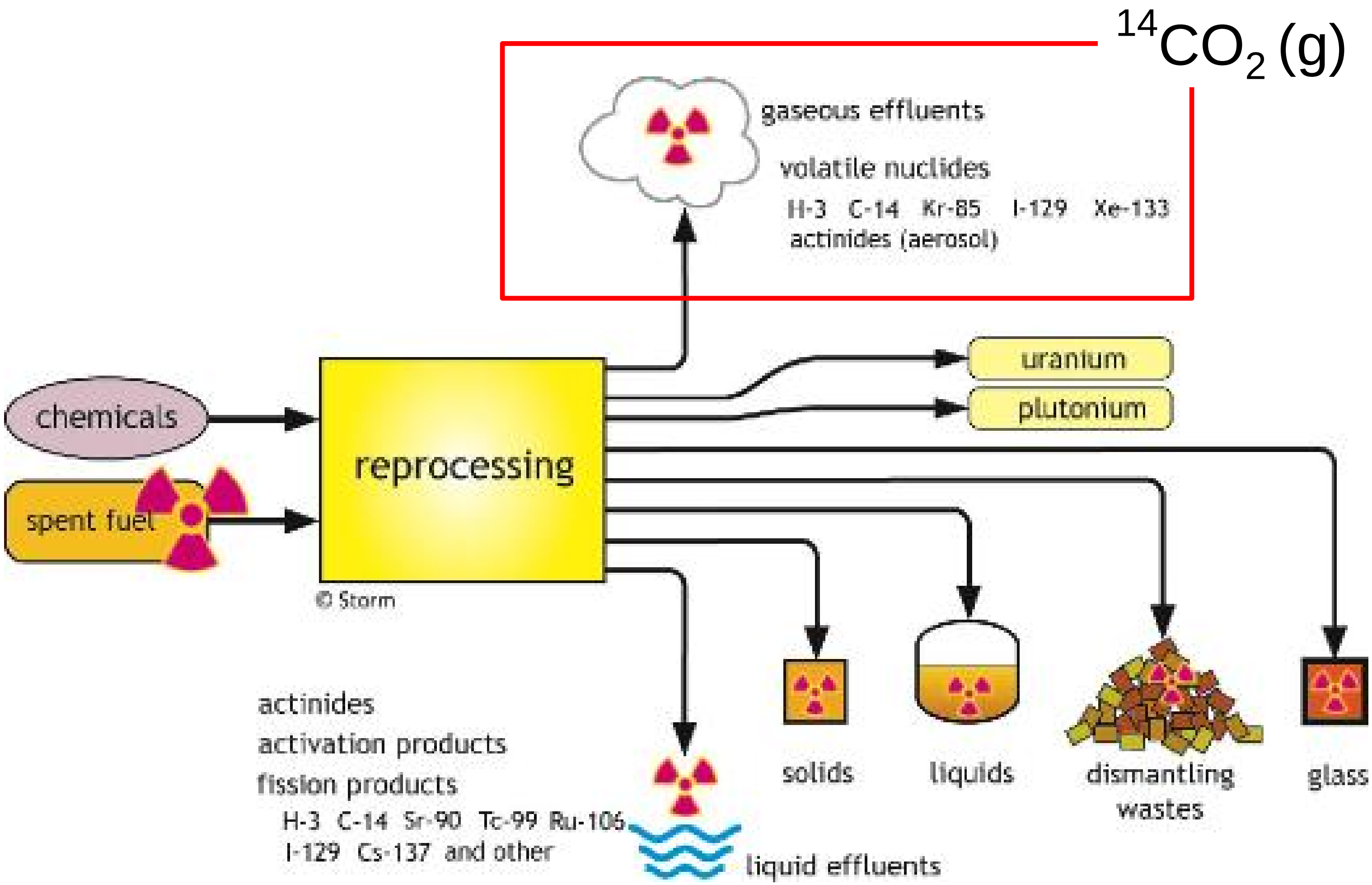


Heat generating radioactive waste

Negligible heat generating waste

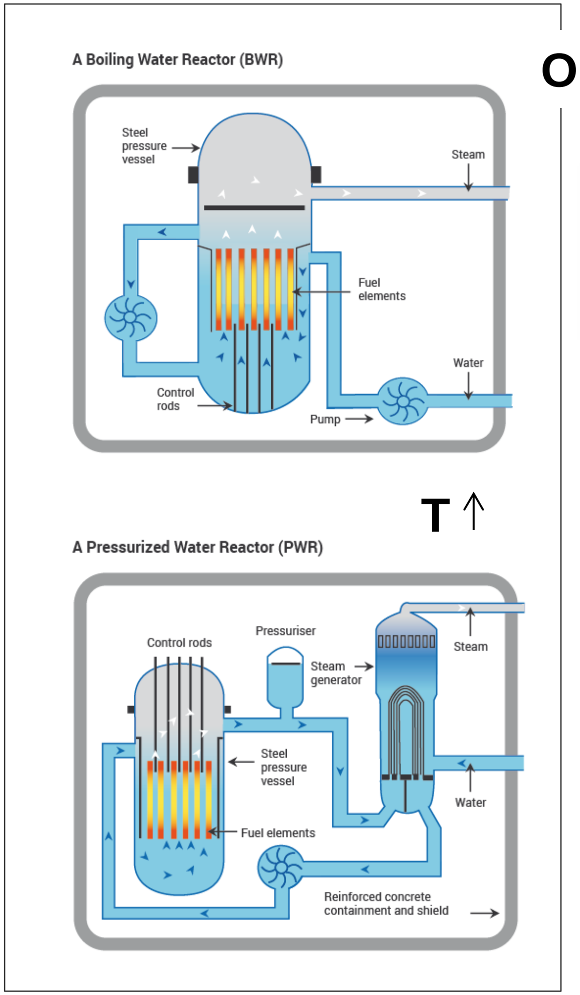
Radioactive waste

Reprocessing



Intermediate storage

LLW



T ↑

Operational waste (effluent treatment, circuit, etc)

Resins

T ↓

Intermediate storage

Chemical transformation

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

$H^{14}CO_3^-$

^{14}C - organics

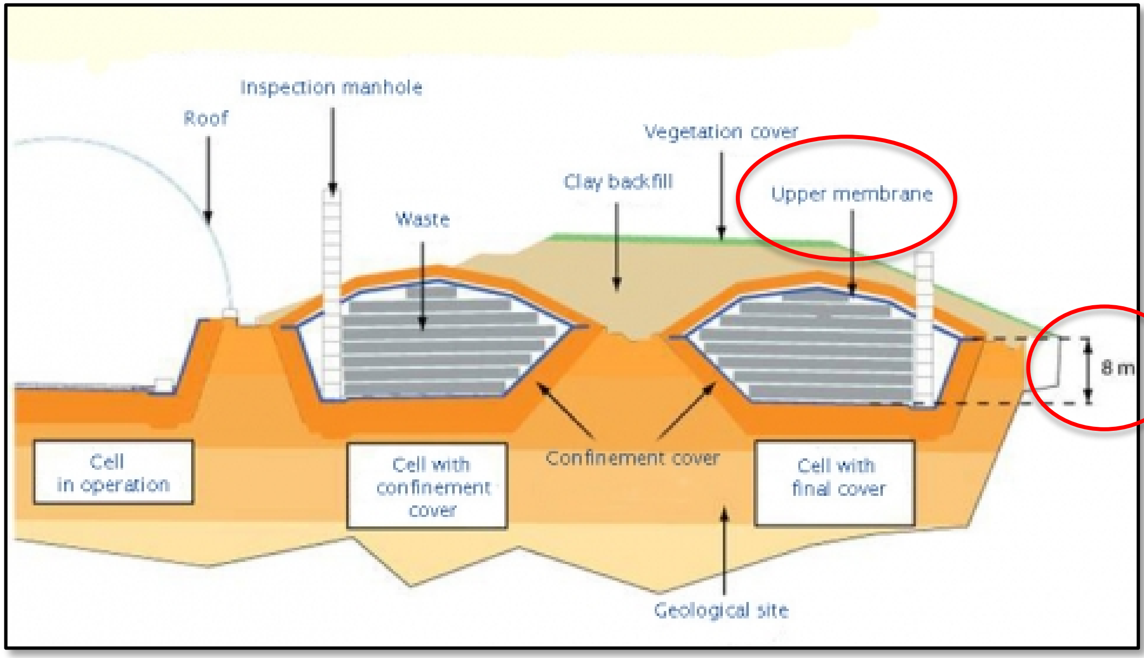
HCO_3^-, C(s), ?

^{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

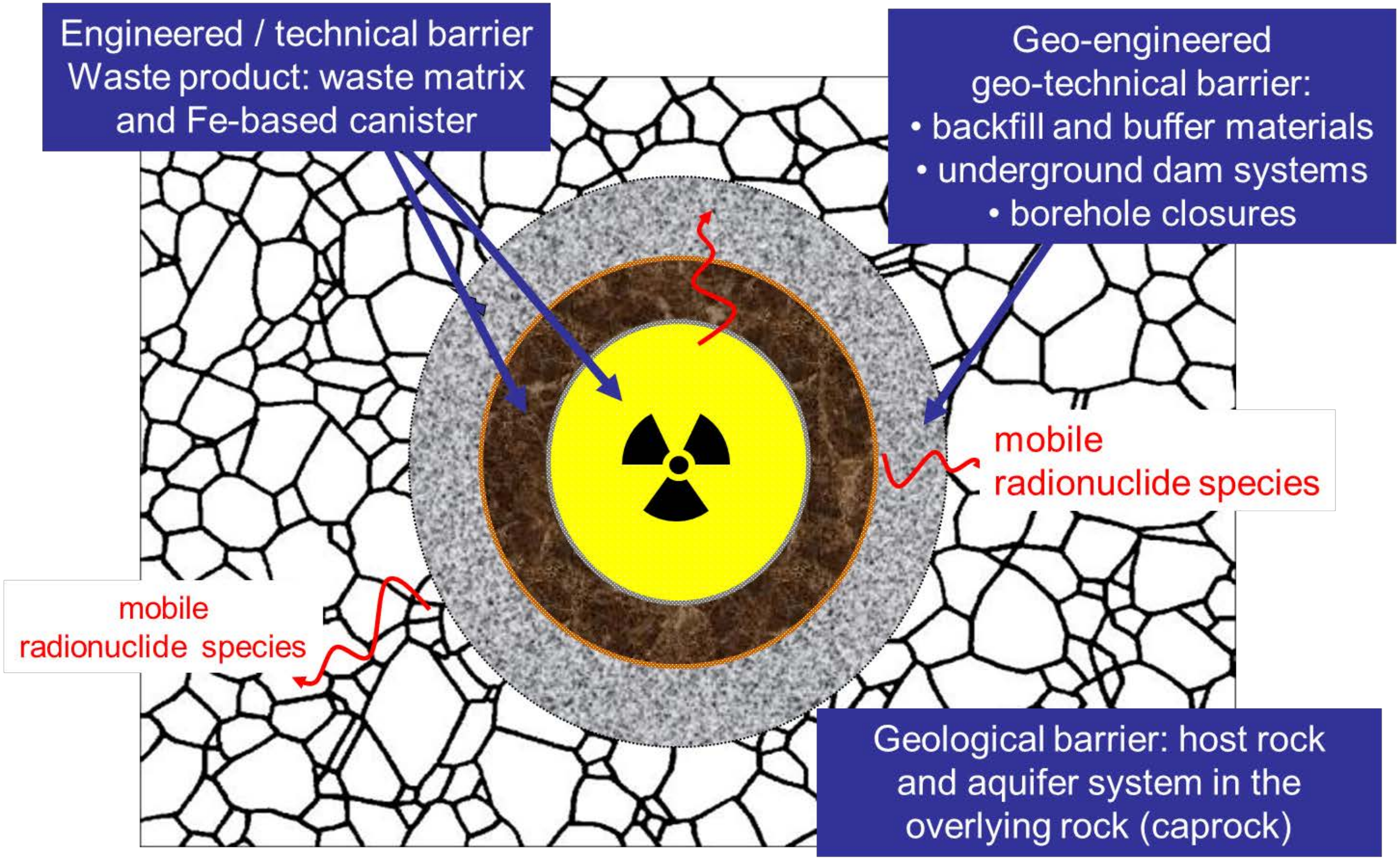
LLW/ILW - near surface disposal below ground level

short-lived radioactive waste

SFR, Forsmark (SKB-Sweden)

Final disposal

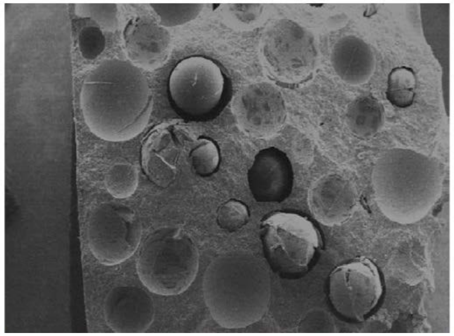
Multibarrier system



Multibarrier system

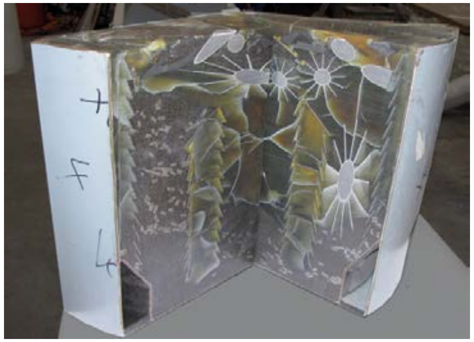
Waste matrix and waste container

Cement matrix



High pH porewater (> 12)
Low porosity, permeability

Synthetic polymers



Organic compounds
Polyethylene, bitumen

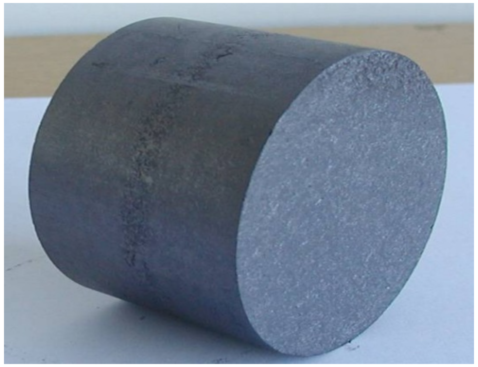
Glassy carbon

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

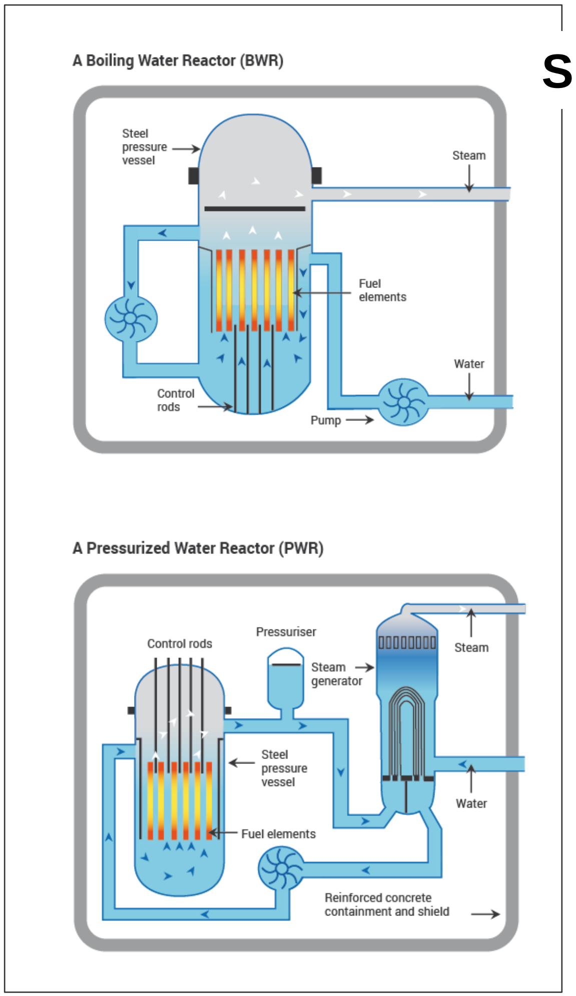
Aerobic
Anaerobic conditions
....

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

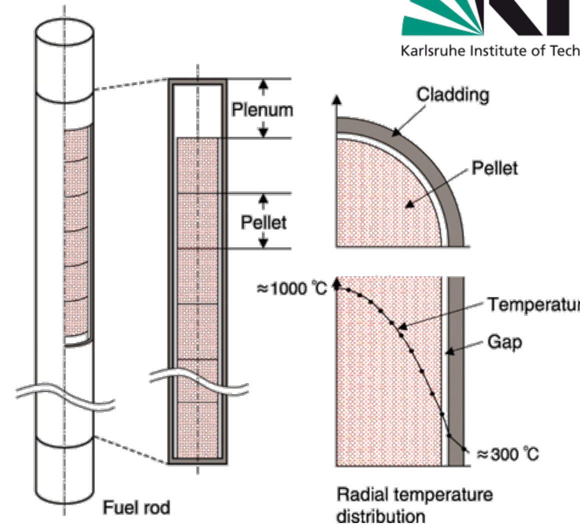
↓

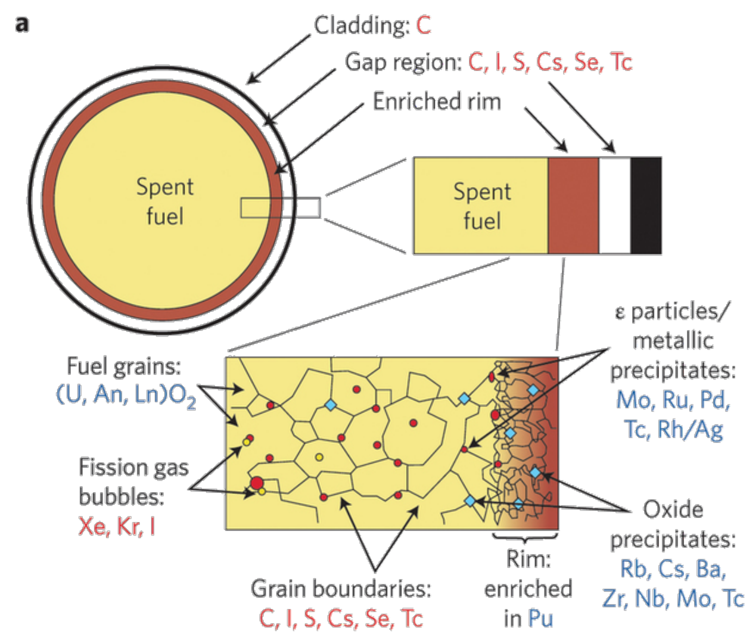
^{14}N impurities

$U^{17}O_2$ matrix

↓ + *n*

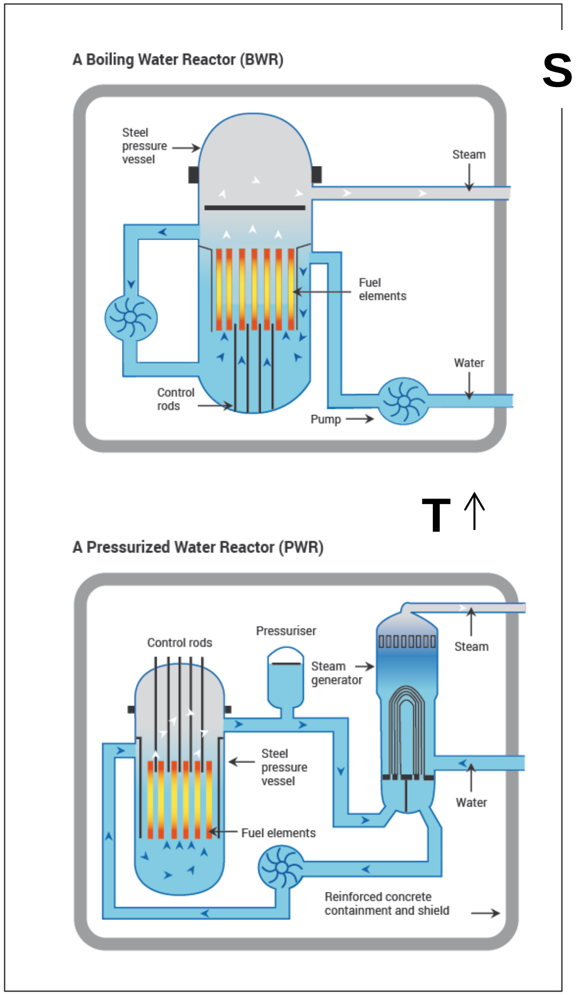
^{14}C (especiation?)





Intermediate storage

HLW including Spent Fuel



Spent Fuel

→

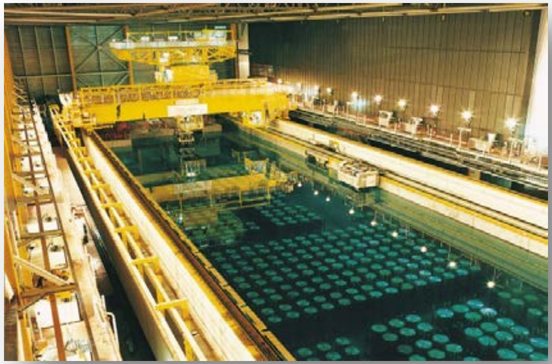
$H^{14}CO_3^-$

^{14}C (especiation?)

Intermediate storage

(dry cask)

(pools)

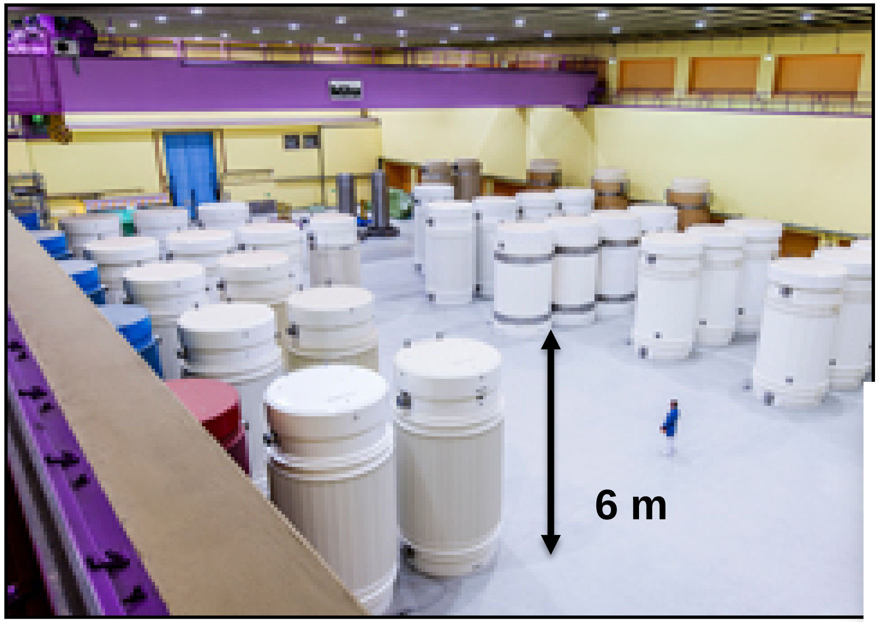


Pools are monitored and cleaned (filters)

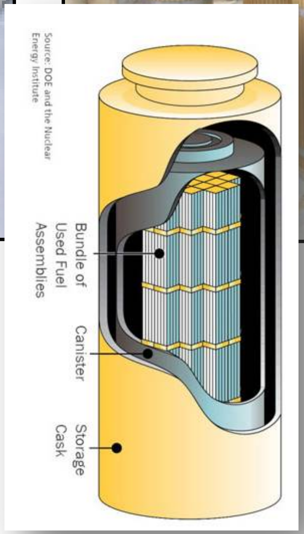
Intermediate storage

HLW including Spent Fuel

(dry cask)



Zwilag´s ZZL (Switzerland)



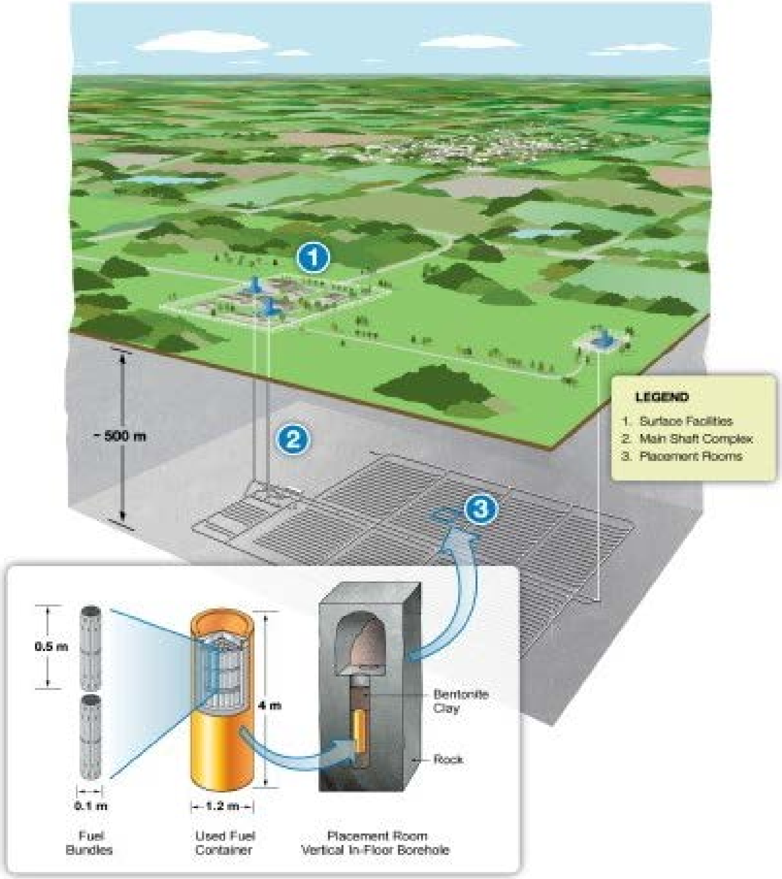
Gorleben (Germany)

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.

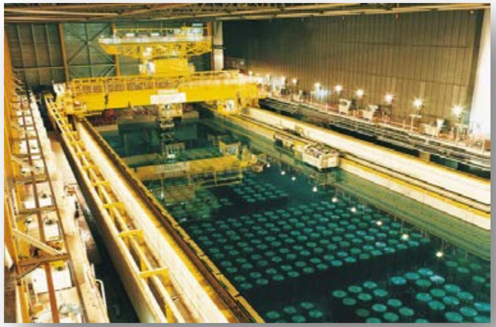
A multi-barrier concept, with the waste packaging, the engineered repository and the geology all providing barriers to prevent the radionuclides from **reaching humans and the environment.**

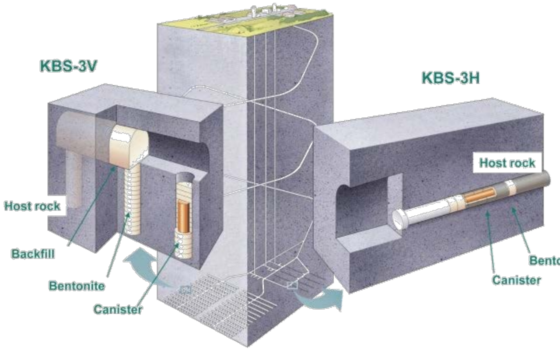


Management of ^{14}C in HLW

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

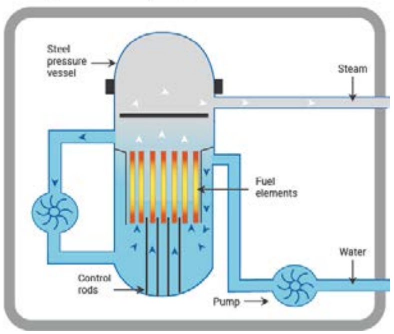
Presentation E. Gonzalez-Robles

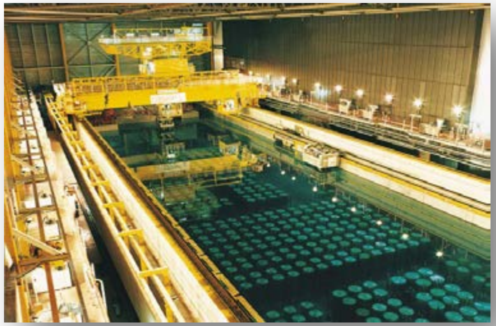
What have we learnt?

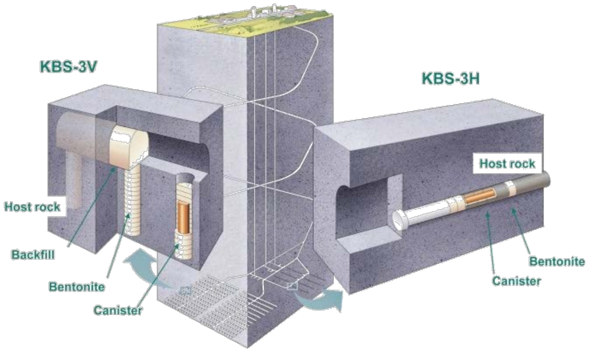
- **Production of C-14**
  - C-14 in the nature
  - C-14 from human activities (Nuclear Energy production)
- **Source of C-14 in Nuclear Power generation (LWR)**
- **Transformation of C-14 during storage and disposal**

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/