Titolo

The life cycle of ^{14}C

CAST CArbon-14 Source Term

Kick-off Meeting

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Sommario

14C is a radionuclide of considerable interest in nuclear power production. Its 5730 years of half-life and a big mobility in the environment make it present in all parts of nuclear reactor primary system.
From there it pass to the environment through gaseous and liquid discharges and through the disposal of radioactive waste.
This presentation summarize the life cycle of C14, from the production in various nuclear plants to the management and the disposal into waste typologies.

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Note

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PER LE NUOVE TECNOLOGIE, L'ENERGIA
E LO SVILUPPO ECONOMICO SOSTENIBILE

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The life cycle of ^{14}C

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The life cycle of ^{14}C

$^{14}_{6}C$ β

half – life 5733 years

decay to : $^{14}_{7}N$ β^- (49,5 KeV)

specific activity : 1,6485E+11 Bq/g

CDE (effective dose coefficient) : 4,0000E+07 Sv/Bq for ingestion

ALI (annual limit of Intake) : 5,0000E-10Bq for ingestion

The life cycle of ^{14}C

Global estimates of carbon-14 production rates and reservoirs (Note: 1 PBq = 10^{15} Bq)

Item	Liepins and Thomas (1988)	Choppin et al. (2002)
Natural		
Production in the upper atmosphere, (PBq/a)	1.4	1
Inventories, (PBq)		
Atmospheric	220	140
Terrestrial	11,500	8360
Total natural	11.7×10^3	8.5×10^3
Man-made		
Atmospheric testing, (PBq)	230 (up to 1969)	220 (up to 1990)
Nuclar reactor emissions, (PBq/a)	–	0.3
Total man-made	230	~220

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The life cycle of ^{14}C

in NP $^{14}C_6$ is produced → core structural materials

in NP $^{14}C_6$ is produced → reactor coolant

$$^{14}N_7 + {}^{1}n_0 \longrightarrow {}^{14}C_6 + {}^{1}p_1$$

$$^{13}C_6 + {}^{1}n_0 \longrightarrow {}^{14}C_6 + \gamma$$

$$^{17}O_8 + {}^{1}n_0 \longrightarrow {}^{14}C_6 + {}^{4}\alpha_2$$

Carbon-14 production mechanisms and cross-sections

Target isotope	Mechanism	Thermal cross-section (barns)	Isotopic abundance
^{14}N	$^{14}N(n, p)^{14}C$	1.81	99.6349
^{13}C	$^{13}C(n, \gamma)^{14}C$	0.0009	1.103
^{17}O	$^{17}O(n, \alpha)^{14}C$	0.235	0.0383

Source: (IUPAC, 1984).

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The life cycle of ^{14}C

Formation in LWR (PWR and BWR) is primarily caused by ^{14}N impurities in the fuel, by ^{17}O in UO_2 matrix and in reactor coolant by oxygen atoms, dissolved nitrogen and carbon.

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	

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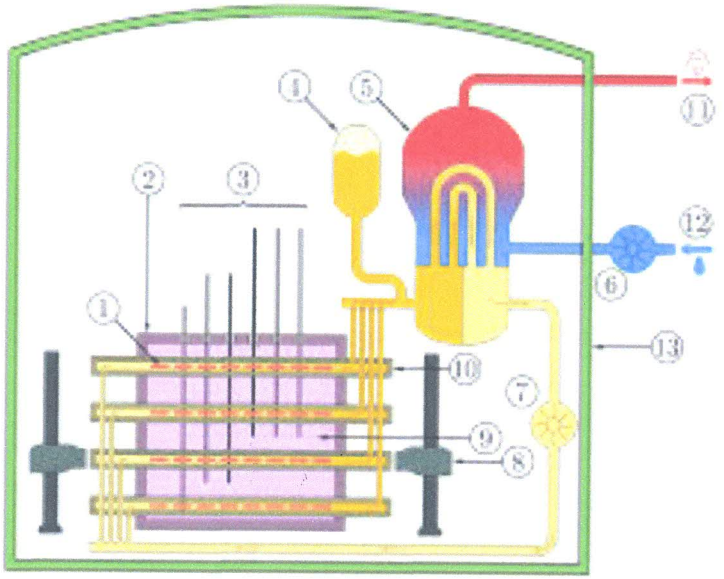
The life cycle of ^{14}C

Production of ^{14}C in HWRs (CANDU type).
In this reactors we have two heavy water circuits in the reactor core: the fuel channels and the calandria. A 55% enrichment of ^{17}O in the heavy water is responsible of high production of ^{14}C. Other contribute of ^{14}C derives from flushed N_2 into calandria, via $^{14}N(n,p)^{14}C$, decreased amount (<1%) from the use of CO_2 in place of N_2.



Item	Production (90% capacity factor)[a]		Normalized production[b]		Dominant mechanism
	Ci/a	TBq/a	Ci/GWe-a	TBq/GWe-a	
Fuel					
^{17}O in UO_2	16	0.59	26	0.96	$^{17}O(n,\alpha)^{14}C$
^{14}N impurities[c]	64	2.4	100	3.8	$^{14}N(n,p)^{14}C$
Coolant	8.6	0.3	10	0.38	$^{17}O(n,\alpha)^{14}C$
Moderator	486	18	680	27	$^{17}O(n,\alpha)^{14}C$
Annular gas	1.4	0.05	1.0	0.038	$^{14}N(n,p)^{14}C$

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The life cycle of ^{14}C

Gas cooled Reactors (HTGR).
The fuel of these reactors consists of Uranium particles distributed through a graphite matrix.
The fuel contains N_2 as an impurity, ^{13}C in the graphite and ^{17}O in UO_2 .
The important production of ^{14}C in this reactor are $^{14}N(n,p)^{14}C$ and $^{13}C(n,\gamma)^{14}C$ reactions.
In a CO_2 cooled gas reactor (e.g. Magnox and advanced gas cooled reactor (AGR), instead of helium, additional production of ^{14}C occurs in coolant.

Estimated ^{14}C production rates from gas-cooled reactors (Braun, et al., 1983)

	Production rates (TBq/GWe-y)			Dominant mec
	Magnox	AGR	HTGR	
Coolant	0.27	0.26	0.0007	$^{14}N(n, p)^{14}C$
	0.04	0.04	~0	$^{17}O(n, \alpha)^{14}C$
Fuel	4.8	0.48	0.12	$^{14}N(n, p)^{14}C$
	0.004	0.12	0.06	$^{17}O(n, \alpha)^{14}C$
Fuel Cladding	1.3	1.2	N/A	$^{14}N(n, p)^{14}C$
Graphite moderator	4.1	1.3	1.2	$^{13}C(n, \gamma)^{14}C$
	6.7	2.2	2.0	$^{14}N(n, p)^{14}C$
Total	17.2	5.6	3.4	

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The life cycle of ^{14}C

LWR (PWR and BWR) – Distribution of ^{14}C in reactors and its release.

Most of the ^{14}C produced will remain in the reactor system until these items are removed. Release of ^{14}C from structural activated materials is a concern in the LLWs disposal.

The major chemical form of ^{14}C in ion exchange resin is as $[H^{14}CO_3]^-$.

In a coolant of LWRs and HWRs, and principally in the moderator of HWRs, ^{14}C production is removed by ion exchange resin in a purification system.

Distribution of ^{14}C in LWRs

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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

The life cycle of ^{14}C

HWR (CANDU-type) - 93% of ^{14}C produced is present in cooler and moderator resins, ~4% has been released; the rest ~3% associated in the fuel, is not available for release (ACRP, 1995).

Gas cooled reactors (GCR) – The release of ^{14}C principally occurs by fuel and graphite moderator.
In CO_2 cooled reactors (Magnox, AGR), the ^{14}C release is higher because comes from the purification of the CO_2 coolant circuits and from the isotopic exchange between the moderator and the CO_2 circuit.

Assuming that HTGR fuel is reprocessed, graphite matrix is to be incinerated in oxygen: all particles are dissolved, releasing all of the ^{14}C in the fuel (~ 133 TBq/year is the expected amount assuming a plant reprocessing 40,000 Mwe fuel per year)

The life cycle of ^{14}C

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

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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).

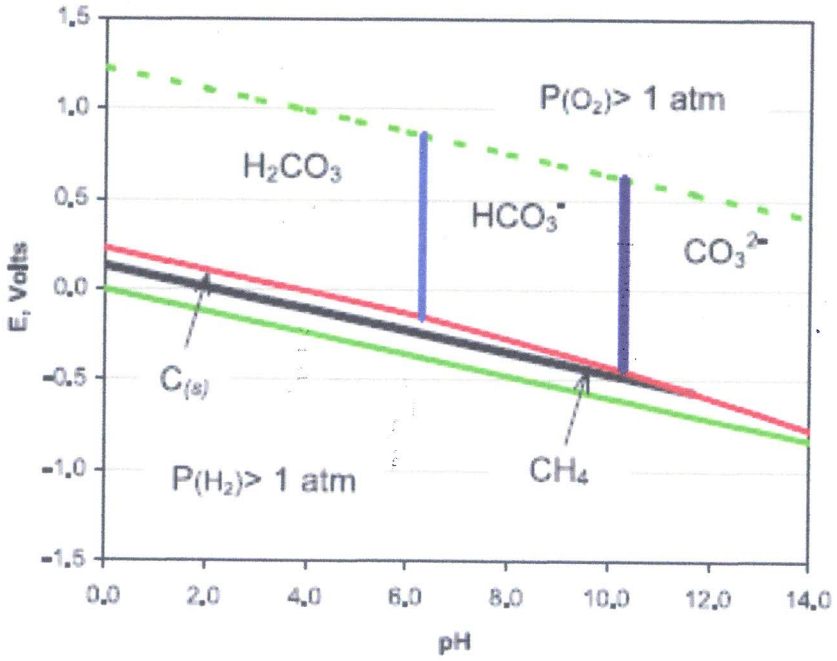
[a] PWR and BWR updated values, based on Van Konynenburg (1994)—see text.

The life cycle of ^{14}C

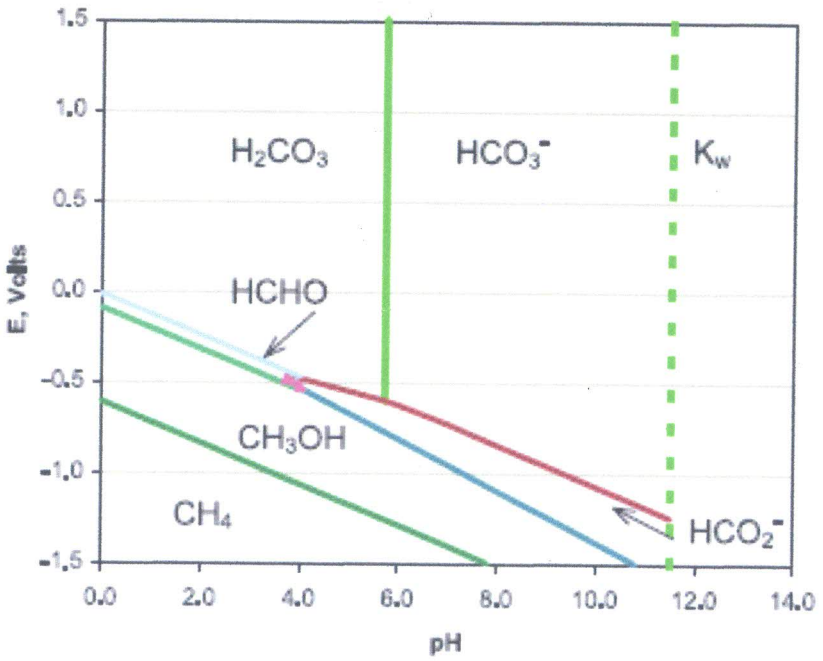
C exist in three oxidation states:

- +IV → CO_2
- 0 → C (graphite)
- -IV → CH_4

Pourbaix diagram - C system (25 °C)



Pourbaix diagram - C system (300 °C)



The life cycle of ^{14}C

BWRs e PWRs – The chemical environment of PWR primary system is reducing because [H_2] dissolved: ^{14}C will be present as organic carbon (acetaldehyde, methyl alcohol, ethyl alcohol, acetone). In BWR the environment is oxidizing: C is present as inorganic form (CO_2 and e carbonate).

HWRs (CANDU-type) – The primary coolant is heavy water contained in a HT loop: it supports the formation of elemental or organic C. Nevertheless, $[^{14}CO_3]^{2-}$ predominate due to the high pH condition.
Organic C is gaseous and it is released in the environment.
The moderator is high purity de-ionized heavy water.
Inorganic C (as CO_2) predominate and its level is controlled with ion exchange resins.

Gas cooled reactors – In the HTGR core ^{14}C is retained as elemental C in the graphite.
On surface it is possible to find ^{14}C associated with O_2, with which reacted.
In CO_2 cooled reactor will have a lot of ^{14}C as $^{14}CO_2$ in the cooler, available for the release.

The life cycle of ^{14}C

^{14}C —(few years / or decades)→ **final disposal as LLW**

in a plant ^{14}C is formed at HT (~300°C) and HP(70-155 bar)
In filters and ionic exchange resins is fixed at ambient T → oxidation and ^{14}C in inorganic form $[HCO_3]^-$ $[CO_3]^{2-}$

Resins polymers C) → suffer thermal damages, oxidative degradation by peroxide and microbial, radiolysis → ino. and organic form ^{14}C decreased retention capacity

Inorganic ^{14}C form in resins increases its mobility and possibility of release.

Anion formation by microbes (exudates, metabolites) can increase ^{14}C mobility.

The effect is reduced with the application of moderators (scrubbers).

The study on some decades (average half-life of a plant) gives data non comparable with ^{14}C normal release during normal operation.

The life cycle of ^{14}C

Release of ^{14}C from LLW	type of waste behaviour durability of the waste containers

if LLW is in cementitious waste, the chemical of ^{14}C will be affected by strongly alkaline environment → ^{14}C, in inorganic form, is released as calcite ($CaCO_3$)

^{14}C in LLW as contaminated gas is formed by microbial degradation → the release occurs by air and/or aqueous, through groundwater pathway

The life cycle of ^{14}C

Release of ^{14}C nearby a site LLW (Chalk River- Canada) working from the years '40 → 2 – 3 times in the plant, due to environment
8 - 300 times in waste management area WMA-C (90.000 m^3 LLW)

WMA-C is placed in unlined trenches in a sand dune; has trenches 3 metres deep, up 6 metres deep, covered with overburden after filling, one covered with an impermeable cover. Two contaminant plumes have developed from WMA-C, one in a nearby swamp, 200 metres downstream, the second one in atmosphere.

% release of ^{14}C → 95% as $^{14}CO_2$ in atmosphere
5% as $[HCO_3]^-$ in groundwater

In terms of performance assessment of a LLW site, WMA-C is a good test for ^{14}C release. For ^{14}C dose consequence for inhalation is much less that for ingestion; high ^{14}C amount degassing from LLW site is a lower potential dose to a hypothetical nearby individual.

The life cycle of ^{14}C

Management of ^{14}C wastes

In the US remain three LLW sites operating. All sites are based on shallow land burial.

In Canada there are no operational disposal sites: a lot of LLW sits a Chalk River, new generated LLW remain at their waste management sites.

Nuclear Waste Management Organization (NWMO) — disposal of SF (no L&ILW) → at-site storage / in a central storage / in a deep geologic disposal

The decision, came in 2012, proposed L&ILW disposal at the Bruce site (Ontario)

Ion exchange resins are stored in tank at station, in wet environment, submerged in water or are partially de-watered and placed in liners to ship in structures at a licensed waste management site.

The life cycle of ^{14}C

^{14}C release in atmosphere from LWRs

^{14}C present in the coolant H_2O is released to the atmosphere as gaseous waste
about 10 Ci (0.37 TBq) per year.

→ in BWRs ^{14}C is released from the condenser steam jet air ejector

→ in PWRs ~70% of ^{14}C is released by off-gas vent, the rest by building ventilation system.

^{14}C release in atmosphere from HWRs

^{14}C emission is controlled by ion exchange resins of the moderator system in 6 step:
radiolysis of heavy water → H_2O_2 attacks the ion exchange resin → resins degrade releasing degradation products, C based, that can return to the calandria → the organic C will be converted in CO_2 in calandria → raise the $[HCO_3]^-$ that overload the resins → ^{14}C could be released to the atmosphere via system leaks, venting and purging.

Carbon separation and fixation

was suggested ^{14}C separation and fixation from plant release of $^{14}CO_2$, to avoid dispersion of ^{14}C; techniques propose decomposition of CO_2 by microwave and isotope separation by plasma chemical reactions.

The life cycle of ^{14}C

management and disposal of ^{14}C loaded in ion exchange resins

anion-exchange resin to remove ^{14}C from nuclear plant waste stream → stored in reactor site
degradation by microbial action
displacement of

alternative methods: ^{14}C immobilization in cement matrixes → requires separation ^{14}C because anion exchange resin is not compatible with cement matrix

^{14}C separation into H_2O solution → convert CO_2 or $[HCO_3]^-$ in carbonate
($CaCO_3$ – $BaCO_3$) → cleaned from secondary contaminants → placement within engineered barriers

secondary radionuclide separation is controlled avoiding use of strong acids into solution. Collection of gaseous ^{14}C is necessary: it depends upon the ultimate waste form selected for immobilization.

The life cycle of ^{14}C

^{14}C management in graphite waste from gas cooled reactors

graphite from HTGRs is classified as LLW.
retrieval from the core could be challenging due to the high level of contaminants ^{3}H, ^{14}C, ^{152}Eu, ^{137}Cs.

Wigner energy
graphite dust encapsulation
graphite floating within the wasteform
galvanic corrosion (steel and graphite)
anaerobic condition within the package

shallow land disposal as LLW
geologic disposal
incineration
recycling
recovery/enrichment ^{14}C

option for the disposal of graphite

from deep geological disposal correspond lowest collective dose to human
in HTGRs ^{14}C exceed the total radiological capacity of a LLW facility
incineration reduce 40 times volumes, problem due to milling effort, dust and furnace design. Production of gaseous ^{14}C is not avoid.