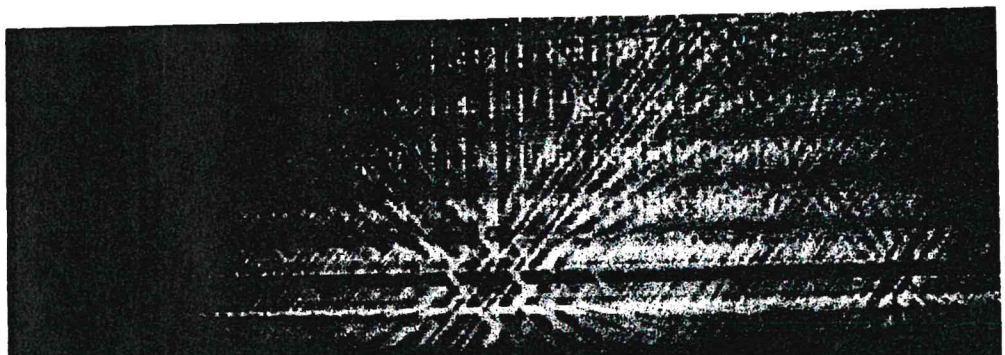

TECHNICAL REPORTS SERIES NO. 421

Management of Waste Containing Tritium and Carbon-14

IAEA

MANAGEMENT OF WASTE CONTAINING TRITIUM AND CARBON-14

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FOREWORD

Carbon-14 and tritium are radioisotopes produced as a by-product or special product in various nuclear reactor systems and globally in the atmosphere by cosmic ray interaction with nitrogen and hydrogen, respectively. Owing to their relatively long half-lives, high residence time in the environment, high isotopic exchange rate and ease of assimilation into living matter, it is necessary to control their production at nuclear facilities. There is also a requirement for the proper management of related waste and material, because of the potential impact on human health. The purpose of this report is to review and analyse experience in the application of different organizational and technological approaches to the management of waste containing ^{14}C and tritium. This report also reviews different sources of waste containing ^{14}C and tritium and their characteristics important in the selection of appropriate methods for the processing, storage, disposal and release of this type of waste. It is also intended by the publication of this report to update the information on the management of tritium contaminated waste published by the IAEA in 1981 in Technical Reports Series No. 203, Handling of Tritium-Bearing Wastes, and, in 1991, in Technical Reports Series No. 324, Safe Handling of Tritium: Review of Data and Experience.

This report was prepared by experts from five countries through a series of Consultants Meetings. The IAEA officer responsible for the preparation of this report was V. Efremenkov of the Division of Nuclear Fuel Cycle and Waste Technology. The IAEA is grateful to all experts who contributed to the preparation of this report.

EDITORIAL NOTE

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CONTENTS

3. PRODUCTION AND EMISSION PATHWAYS

3.1. CARBON-14 PRODUCTION AND RELEASE

3.1.1. Natural production in the atmosphere

Natural ^{14}C is produced in the upper atmosphere by the $^{14}N(n,p)^{14}C$ reaction induced by cosmic ray neutrons. The annual production rate by this mechanism is estimated to be 1.4×10^6 GBq (3.8×10^4 Ci), with a total inventory of 1.4×10^8 GBq (3.8×10^6 Ci) in the atmosphere. A much larger quantity of ^{14}C (approximately 1.0×10^{10} GBq) is located in the deep oceans and exchanges with atmospheric carbon [6].

3.1.2. Production in nuclear explosions

Carbon-14 is formed in nuclear explosions as a result of neutron capture on nitrogen and resides in the atmosphere as $^{14}CO_2$ [6]. The amount of ^{14}C added to the atmosphere and labile biosphere by atmospheric nuclear weapon testing in the 1950s and 1960s has been estimated to be 2.2×10^8 GBq (6.0×10^6 Ci) [10]. Figure 1 [11] shows ^{14}C concentrations in the atmosphere between 1955 and 1994. The high concentrations of ^{14}C during the 1960s were the result of atmospheric nuclear weapon testing.

3.1.3. Production in and release from nuclear power reactors

The normal operation of nuclear reactors for the generation of electric power produces various radioisotopes by fission within the fuel or by neutron activation in the structural materials and component systems of the reactor. The escape of these radioisotopes from the reactor and its auxiliary process systems generates a variety of solid, liquid and gaseous radioactive waste. Although the design of the reactor ensures that releases of liquid and airborne waste are minimized, small quantities of radionuclides escape the systems and are continuously discharged in various effluents. Carbon-14 is one of these radionuclides.

The major ^{14}C producing neutron activation reactions in nuclear power reactors are:

(a) The $^{14}N(n,p)^{14}C$ reaction with a very high thermal neutron capture cross-section (1.82 barn (1 barn = 10^{-24} cm^2));

(b) The $^{17}O(n,\alpha)^{14}C$ reaction with a high thermal neutron capture cross-section (0.24 barn);
(c) The $^{13}C(n,\gamma)^{14}C$ reaction with a low cross-section (0.9×10^{-3} barn);
(d) The $^{15}N(n,d)^{14}C$ reaction with a very low cross-section (2.5×10^{-7} barn);
(e) The $^{16}O(n,^{3}He)^{14}C$ reaction with a very low cross-section (5.0×10^{-8} barn).

In general, ^{14}C is produced in nuclear power reactors by $^{14}N(n,p)^{14}C$ reactions with nitrogen in fuels, moderators and coolants as a primary impurity, by $^{17}O(n,\alpha)^{14}C$ reactions in oxide fuels, moderators and coolants, and by $^{13}C(n,\gamma)^{14}C$ reactions in graphite moderators. Reactions (a), (b) and (c) are the most important contributors to ^{14}C production. Reactions (d) and (e) are unimportant in thermal reactors. Carbon-14 is also a ternary fission product, but the amount produced in this way is negligible.

The substrate atoms for the activation reactions (i.e. nitrogen, oxygen and carbon) occur widely in fuel, and in cladding, moderator, coolant or structural material, either as major constituents or as impurities. In consequence, ^{14}C produced in a nuclear power reactor can be released directly to the environment from the coolant and/or moderator in a gaseous form or in much

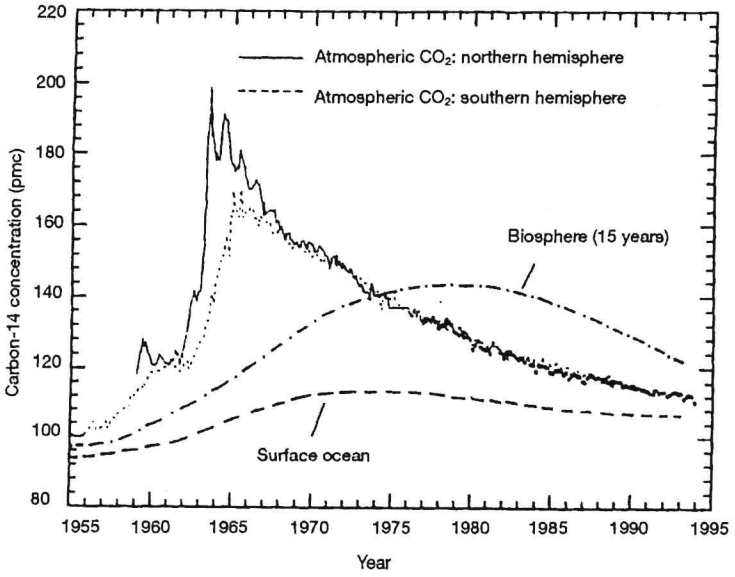

FIG. 1. Carbon-14 concentration in the atmosphere: 1955–1994.

smaller quantities as liquid effluents. Carbon-14 can remain in the reactor core until a reactor is decommissioned (e.g. in the graphite moderator of advanced gas cooled reactors (AGR) and Magnox reactors) or it can pass to a fuel reprocessing plant in the spent fuel and other fuel element components. The ^{14}C from the fuel will be released at the reprocessing plant into the off-gases at the dissolution stage, and the cladding will constitute a separate solid waste arising. Both the amounts of ^{14}C produced and the chemical forms of ^{14}C present depend on the details of the reactor system, as does the subsequent behaviour of the ^{14}C and the pathways by which it can be released to the environment [12].

The amounts of ^{14}C produced by the various types of reactor vary considerably, depending on the fuel enrichment, temperature and relative masses of the fuel, moderator and coolant, and on the concentrations of nitrogen impurities in these systems. The production rate of ^{14}C in a reactor can be calculated from [13]:

$$A = \frac{dN}{dt} = N\sigma\phi - N\sigma\phi e^{-\lambda t_i} = \frac{fmL}{M}\sigma\phi\left(1 - e^{-\lambda t_i}\right)$$

where

A is the activity produced (disintegrations per second);
f is the fractional isotopic abundance of the target element (i.e. the substrate element);
L is Avogadro's number (6.025×10^{23} mol^{-1});
σ is the thermal neutron cross-section in barns (10^{-24} cm^2);
ϕ is the neutron flux in n·cm^{-2}·s^{-1};
λ is the decay constant of ^{14}C per second (ln 2/half-life);
t_i is the irradiation time in seconds;
N is the number of target atoms;
m is the mass of the target element in grams;
M is the atomic weight of the target element in g/mol.

A summary of typical ^{14}C production rates in various types of reactor is given in Table 5 [10].

Limited data on ^{14}C emissions from nuclear power reactors have been published. The release levels of ^{14}C from nuclear reactors depend mainly on the reactor type, its design and the site specific effluent treatment programmes in place for the plant; for example, in light water reactors (LWRs) the ^{14}C produced in the moderators and coolants can be assumed to be essentially released from the reactor to the environment. However, in HWRs more than

TABLE 5. CALCULATED ^{14}C PRODUCTION RATES (GBq·GW(e)$^{-1}$·a^{-1}) FOR VARIOUS TYPES OF REACTOR

	Fuel	Fuel cladding	Coolant and moderator	Graphite moderator	Total
LWR–PWR	480	740	260	—	1 480
LWR–BWR	470	630	190	—	1 290
HWR	1 465	1 260	7 400	—	10 125
GCR–MGR	4 835	1 300	310	10 730	17 175
GCR–AGR	620	1 180	300	3 480	5 580
GCR–HTGR	190	—	1	3 180	3 371
FBR	200	300	—	—	500

Note: LWR: light water reactor; PWR: pressurized water reactor; BWR: boiling water reactor; HWR: heavy water reactor; GCR: gas cooled reactor; MGR: Magnox reactor; AGR: advanced gas cooled reactor; HTGR: high temperature gas cooled reactor; FBR: fast breeder reactor.

half the ^{14}C produced in the moderators and coolants is retained on system purification ion exchange resins. Table 6 shows the estimated net release rates of various types of reactor and reprocessing plants in 1998 [14]. The majority of ^{14}C released from reactors and fuel reprocessing plants is contained in airborne effluents, and only a small amount is in the form of liquid effluents from nuclear facilities.

For all types of reactor except PWRs, ^{14}C is emitted mainly as CO_2. For boiling water reactors (BWRs) 80–95% of the released ^{14}C appears to be CO_2 and 5–20% hydrocarbons. For HWRs approximately 80% and 20% of the total ^{14}C released are CO_2 and hydrocarbons, respectively. In comparison, the airborne ^{14}C released from PWRs is predominantly hydrocarbons (75–95%), mainly methane, with only a small fraction in the form of CO_2 (Table 7).

The mechanisms of ^{14}C production and ^{14}C release pathways in various types of reactor are summarized in Sections 3.1.3.1–3.1.3.5.

3.1.3.1. Light water reactors

LWRs are widely used throughout the world and hence have a significant effect on overall ^{14}C emissions. Production of ^{14}C depends on the enrichment of the fuel, the relative mass of the fuel and moderator, the concentrations of nitrogen impurities in the fuel and structural materials, and the temperatures of

TABLE 6. ESTIMATED ^{14}C ANNUAL RELEASE RATES IN THE ABSENCE OF CONTROL FROM REACTORS AND REPROCESSING PLANTS

	Number of units	Estimated ^{14}C release rate (GBq/a)	Total (GBq/a)
PWR	207	185	38 295
BWR	93	295	27 435
HWR (CANDU)	35	2 590	90 650
Graphite reactor	35	555	19 425
RBMK reactor	14	1 850	25 900
WWER reactor	47	1 850	86 950
Subtotal	431		288 655
Reprocessing plants[a]	3	18 500	55 500
Total			344 155

Note: RBMK: high power channel type reactor; WWER: water cooled, water moderated power reactor.

[a] The reprocessing plants taken into account are La Hague (COGEMA, France), Sellafield (BNFL, UK) and Chelyabinsk (Russian Federation).

TABLE 7. COMPARISON OF THE CHEMICAL FORMS (RELATIVE PERCENTAGE OF EACH SPECIES) OF ^{14}C IN AIRBORNE RELEASES FROM VARIOUS TYPES OF REACTOR

	$^{14}CO_2$	^{14}CO	^{14}C hydrocarbons
HWR (Bruce unit 7, Canada)[a]	65.5–72.8	0.2–3.7	26.7–34.4
HWR (Gentilly 2, Canada)[b]	77.9–97.5	0.01–0.09	25.0–22.0
PWR (USA and Europe)	5–25	—	75–95 (CH_4 and C_2H_6)
BWR (USA and Europe)	80–95	—	5–20

[a] Data were measured by Atomic Energy of Canada Limited in November 1994.

[b] Data were measured by Atomic Energy of Canada Limited in September and October 1995.

the fuel and moderator. Since there are considerable variations in design, very precise calculations of ^{14}C production in LWRs are probably not justified.

Calculations of ^{14}C production rates in the fuel and coolant and/or moderator of LWRs have been reported. The calculated values were highly dependent on the assumptions made for the nitrogen impurities and ^{17}O levels in the fuel and the coolant and/or moderator. The ranges of calculated ^{14}C production rates in LWRs based on 25 ppm of nitrogen impurity in the fuel are summarized in Table 8, and those in the cladding and structural materials are given in Table 9 [12].

It can be assumed that most stainless steel structural materials remain inside the reactor when fuel elements are removed and constitute a decommissioning waste. In an LWR the zircaloy cladding is the dominant source of ^{14}C, and contains approximately 50–60% of its total.

Carbon-14 is produced in the fuel and coolant and is distributed wherever gas or fluid streams flow in the power plant. Leakage of plant systems allows for eventual release to the environment, so the partitioning of original ^{14}C in various pathways is an important guide to the establishment of control measures. A simplified diagram of flows of ^{14}C in an LWR is shown in Fig. 2.

Carbon-14 is always carried by stable carbon compounds. In a BWR the air entrained in the coolant is ejected from the main condenser. This off-gas is fundamentally air, and therefore carbon, as CO_2, exists in the similar ratio to other constituents as it does in air. A very small amount of the stable carbon remains in the coolant; this level is probably controlled by coolant chemistry. A part of the ^{14}C remains dissolved in the primary water purification and treatment systems, causing smaller sources of release, for example in the auxiliary building and finally in the active liquid waste processing system [15].

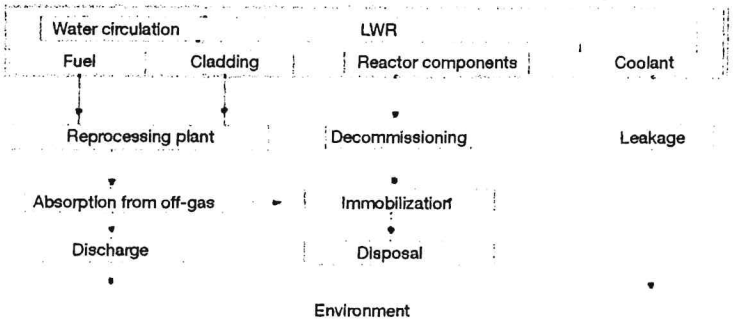

FIG. 2. Simplified diagram of ^{14}C flows in an LWR reactor and at the fuel reprocessing stage.

TABLE 8. RANGES OF CALCULATED ^{14}C PRODUCTION RATES ($GBq \cdot GW(e)^{-1} \cdot a^{-1}$) IN LWRs BASED ON 25 ppm OF NITROGEN IMPURITY IN THE FUEL

	Fuel	Coolant	Total
BWR	600–2340	190–420	790–2760
PWR	600–900	110–230	710–1130

TABLE 9. CALCULATED ^{14}C PRODUCTION RATES ($GBq \cdot GW(e)^{-1} \cdot a^{-1}$) IN THE CLADDING AND STRUCTURAL MATERIALS OF LWRs

	304 stainless steel	302 stainless steel	Zircaloy 2	Nicobraze 50	Total
BWR	1280–2040	—	630	—	1910–2670
PWR	695–1110	77–125	350–740	4	1126–1979

The following systems have been considered to be release pathways for gaseous ^{14}C from a BWR [13]:

(a) The condenser steam jet air ejector;
(b) The turbine gland seal condenser exhaust;
(c) The reactor building purge exhaust;
(d) The turbine building ventilation system exhaust;
(e) The radioactive waste building ventilation system exhaust.

The condenser steam jet air ejector is expected to be the most significant release point (>99% of total ^{14}C release).

In a PWR a portion of CO_2 remains dissolved in the coolant, while most leaks to the airspace in the reactor, where it is diluted in nitrogen. Dilution in the off-gas streams is great enough to ensure an air-like composition with respect to CO_2. Owing to boric acid addition and buffering, a small amount of CO_2 is expected to remain in the primary coolant. A part of the ^{14}C compounds remains dissolved in the water and is released at different steps of the active liquid waste treatment. Corrosion control for the secondary systems maintains a low CO_2 level, causing most to be released as gas in the air ejector. The following systems in a PWR have been considered to be release pathways for gaseous ^{14}C [13]: