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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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1. INTRODUCTION

1.1. BACKGROUND

Carbon-14 and tritium are naturally occurring radioisotopes produced continuously in the atmosphere by cosmic ray neutron interaction with nitrogen and hydrogen, respectively, and are also produced as a by-product or special product in nuclear reactor systems. Carbon-14 and tritium have rather long half-lives (tritium = 12.3 a and ^{14}C = 5730 a) and residence times in the atmosphere and hydrosphere sufficient for transport processes to distribute them worldwide. Their radiological impact is therefore not limited to the region of release, and they may be distributed globally in a nearly uniform manner. Carbon-14 and tritium are weak beta emitters and do not present an external radiation hazard. Owing to their long half-lives, high isotopic exchange rates and ease of incorporation into living organisms, however, it is important to control their release from nuclear facilities and waste management sites to the environment by the use of appropriate waste management strategies and practices.

Carbon-14 in the nuclear fuel cycle is produced by neutron interaction with ^{13}C, ^{14}N, ^{15}N, ^{16}O and ^{17}O, which may be present in the nuclear fuels and the moderator and primary coolant systems of nuclear reactors. Tritium is produced in nuclear power reactors during the fission of heavy nuclei and by neutron interaction with coolants, moderators and some light elements, such as lithium, beryllium and boron. The rates of production of ^{14}C and tritium are dependent on the type of the reactor and its capacity.

The amounts of ^{14}C and tritium in waste generated by the nuclear industry vary as a function of, for example, reactor type, plant operation, the method of fuel reprocessing and the radioisotope production process. One common property of both is that they are difficult to assay, since they are weak beta emitters and do not emit gamma radiation. These factors and some other properties mean that, in the context of the management of radioactive waste, ^{14}C and tritium are considered to be problematic and that their properties need to be specifically considered when selecting methods for the treatment, conditioning and packaging of waste containing ^{14}C and tritium and when establishing release limits and waste acceptance requirements (WARs) for these particular radioisotopes.

1.2. OBJECTIVES AND SCOPE

The primary objective of this report is to provide Member States and responsible organizations with information on the organizational principles and technical options for the management of radioactive waste and effluents containing ^{14}C and tritium, including waste collection, separation, treatment, conditioning, and storage and/or disposal. A subsidiary objective of this report is to identify areas in which a lack of knowledge or proven technology limits achievement of the primary objective. These objectives are achieved by reviewing the different sources and characteristics of waste streams containing ^{14}C and tritium and by analysing methods for the processing, storage and/or disposal of these types of waste, both well proven methods and those at an advanced stage of development.

This report should aid the reader in the selection of an appropriate management strategy for waste and effluents containing ^{14}C and tritium, taking into account the special requirements and limitations associated with the disposal of this type of waste and the release of these radioisotopes. To address the identified objectives, this report:

(a) Overviews some existing regulations for emissions of ^{14}C and tritium and the storage and/or disposal of waste containing these radioisotopes.
(b) Identifies the nature and magnitude of the problems pertaining to waste containing ^{14}C and tritium by analysing sources, production rates and potential emission pathways to the environment of these radioisotopes in various nuclear operations, such as reactor operations and spent nuclear fuel reprocessing.
(c) Identifies and describes the characteristics, physical and chemical forms, and properties of waste containing ^{14}C and tritium produced by nuclear facilities.
(d) Analyses approaches applied for the reduction and/or minimization of ^{14}C and tritium production in nuclear operations; this should be achieved by analysing the different factors influencing the generation of these radionuclides and by taking into account the process chemistry and mechanism of their release.
(e) Reviews technologies for the removal of ^{14}C and tritium from liquid and gaseous waste streams and for concentrating the levels of ^{14}C and tritium in such streams, and discusses their merits and limitations.
(f) Reviews sampling methods, procedures, analytical techniques and equipment for analysing and monitoring these radioisotopes in waste streams and effluents.

(g) Reviews options and specific technologies for the immobilization and/or stabilization of waste containing ^{14}C and tritium, and discusses the aspects of waste form evaluation in respect of the safety requirements, the characteristics of the waste forms and regulatory, administrative and technological issues.
(h) Discusses specific requirements and practices for the storage and/or disposal of waste containing ^{14}C and tritium based on existing national and international regulations.
(i) Analyses trends in the development and application of novel technical approaches in the management of waste containing ^{14}C and tritium.

2. ENVIRONMENTAL AND REGULATORY ISSUES

2.1. PROBLEMS ASSOCIATED WITH ^{14}C AND TRITIUM IN WASTE

Carbon-14 is a radioactive isotope of carbon and is a pure beta emitter with a half-life of 5730 years; it decays to ^{14}N by emitting low energy beta radiation with an average energy of 49.5 keV and a maximum energy of 156 keV. Carbon-14 is easily transferred during biological processes and soil–plant interactions involving carbon compounds. The metabolism and kinetics of ^{14}C in the human body follow those of ordinary carbon. Inhaled $^{14}CO_2$ rapidly equilibrates with the air in the lungs and enters many components of body tissue. The biological half-life of ^{14}C is approximately 40 days. It has been found that accumulation of ^{14}C in the human body via respiration is insignificant compared with that from ingestion of contaminated food. In addition, ^{14}C can be easily concentrated in the food chain. Studies have shown concentration factors of 5000 for fish and molluscs and 2000 for soil sediments.

Tritium is a radioactive isotope of hydrogen and has a half-life of 12.3 years; it decays to ^{3}He by emitting low energy beta radiation with an average energy of 5.7 keV and a maximum energy of 18.6 keV. Transfer of environmental tritium oxide (or tritiated water) (HTO) to humans takes place via inhalation, diffusion through the skin and ingestion. Inhalation is the only meaningful pathway of tritium gas (containing both hydrogen and tritium HT) to humans.

Radioactive waste containing ^{14}C and tritium is continuously generated by the nuclear industry in, for example, nuclear reactor operations, spent fuel reprocessing and radioisotope production, and in medical research. Both ^{14}C

and tritium are considered to be mobile in the environment, and specific considerations are therefore required for the management of waste containing these radioisotopes; for example, the disposal of waste containing significant amounts of ^{14}C will be more difficult than that of waste containing only short lived nuclides, owing to the stringent WARs for ^{14}C. The minimization and segregation of waste containing long lived nuclides (e.g. ^{14}C) are therefore important factors for an effective waste management approach.

2.2. REGULATORY ISSUES

The objective of the management of waste containing ^{14}C and tritium is to protect human health and the environment from the harm associated with these contaminants due to direct exposure and bioaccumulation in the food chain. Environmental protection includes the protection of living organisms other than humans and the protection of natural resources, including land, forests, water and raw materials, together with a consideration of non-radiological environmental impacts.

In assessing the impact of ^{14}C and tritium releases, the possible exposure of an individual in the immediate vicinity outside an exclusion boundary area, and of the public at large, should be considered. Appropriate programmes on effluent and environmental monitoring are therefore required for each nuclear facility to ensure protection of the public from radioactive discharges.

In general, the owners or operators of nuclear facilities are responsible for setting up and implementing the technical and organizational measures necessary for ensuring protection of the public from radioactive discharges. In particular, they are responsible for implementing any conditions or limitations specified by the regulatory body in an authorization [1]. This authorization can be in the form of a registration (for practices with low to moderate associated risks to the public), a licence (for practices with high potential risks to the public) or a similar document.

The application for an authorization such as a licence should contain the following information:

(a) An appropriate safety assessment, including an explanation of how radiological protection has been optimized;
(b) An assessment of the nature, magnitude and likelihood of exposures attributed to the discharges.

In addition, the application should also address the issues of waste generation and management interdependences. In general, discharge limits for the radionuclides concerned would be included in, or would accompany, a licence issued by the regulatory body that allows the operation of the facility.

Authorized discharge limits are set by the regulatory body. The discharge limits discussed in this report are restricted to discharges to the environment of radioactive substances (i.e. ^{14}C and tritium) in the form of airborne (gases and aerosols) or liquid (to surface water bodies only) effluents from the normal operation of practices and sources within practices. The sources considered range from radionuclides used for medical and research purposes to nuclear reactors and spent fuel reprocessing facilities.

General principles for setting limits for the release of radionuclides from nuclear facilities have been provided by the IAEA in several publications [1–3]. The discharge limits should satisfy the requirements for the optimization of protection and the condition that doses to the critical group should not exceed the appropriate dose constraints. They should also reflect the requirements of a well designed and well managed practice and should provide a margin for operational flexibility and variability [1].

Discharge limits are usually attached to or incorporated into the facility licence and become the legal limits with which the operator or licensee should comply. Discharge authorizations are normally set in terms of annual limits. While these are the primary limits, shorter term limits can be set in order to trigger investigations and ensure that the procedure used and the associated conditions and assumptions used to estimate dose limits remain valid (e.g. to prevent significantly higher doses being received due to higher than normal discharges in conditions of poor dispersal in the environment) [1].

In order to evaluate releases of ^{14}C from nuclear facilities, a background activity of 250 Bq of ^{14}C per kilogram of stable carbon has been used by regulatory bodies such as the Institut de protection et de sûreté nucléaire in France, the National Radiological Protection Board in the United Kingdom and safety authorities in Switzerland. Any ^{14}C level above this background level, other than from the normal production of ^{14}C by cosmic ray neutron interaction with nitrogen in the atmosphere, will be considered to be pollution.

Discharge limits for radioisotopes are established in most countries in accordance with the recommendations of the International Commission on Radiological Protection (ICRP) [4]. These limits differ from one site to another depending on assumptions made on the nature of the effluent and on the environment into which the discharges are made. Some examples of the approaches used in various countries to determine the discharge limits for ^{14}C and tritium are summarized in Sections 2.2.1–2.2.6.

2.2.1. Argentina

The regulatory authorities in Argentina have specified two dose constraints on releases of radioactive material from nuclear power plants to the environment [5]. These are that the:

(a) Individual annual dose in the critical group resulting from the release shall not exceed 0.3 mSv/a;
(b) Collective dose commitment per unit of practice shall not exceed 1.5×10^{-2} Sv·MW(e)$^{-1}$·a^{-1} of electric energy generated by the plant.

For example, the derived release limits (DRLs) for airborne and waterborne tritium from the Embalse nuclear power plant (a CANDU heavy water reactor (HWR)) are 3.7×10^4 TBq/a and 3.7×10^3 TBq/a, respectively. These DRLs result in a 0.3 mSv/a dose to a member of the public critical group.

2.2.2. Canada

DRLs for the release of radionuclides from nuclear facilities in Canada are set to ensure that the committed dose to a critical group from one year's release does not exceed the limit of the annual dose to a member of the public set by the Canadian Nuclear Safety Commission (formerly the Atomic Energy Control Board) [6]. The DRL is defined as the radioactive release over a year that would expose members of the critical group to the regulatory dose limit. In general, nuclear power plants set their operating targets for releases of each radionuclide below 1% of the DRL. The annual and weekly DRLs for airborne ^{14}C and tritium releases from two CANDU 600 MW(e) nuclear power plants in Canada are shown in Table 1 [6].

The large variations in the calculated DRLs based on a public dose limit of 5 mSv/a for various sites arise primarily owing to the location of the nuclear reactor site and the proximity of a local population outside the exclusion boundary area. The Gentilly 2 site is located near to a farm and it is considered that a member of the critical group consumes water from the St. Lawrence River 3 km downstream of the station. In contrast, the Point Lepreau nuclear power plant is located in a relatively remote area. As a result, the DRLs for airborne releases from the Point Lepreau nuclear power plant tend to be higher than those from Gentilly 2.

TABLE 1. DRLs FOR AIRBORNE TRITIUM AND ^{14}C DISCHARGES FROM CANDU 600 MW(e) NUCLEAR POWER PLANTS IN CANADA

	DRLs for airborne tritium discharges		DRLs for airborne ^{14}C discharges	
	TBq/week	TBq/a	TBq/week	TBq/a
Point Lepreau	3.00×10^4	1.56×10^6	3.00×10^2	1.56×10^4
Gentilly 2	8.50×10^3	4.42×10^5	1.70×10^1	8.84×10^2

2.2.3. France

In France the limits to discharges of gaseous and liquid effluents from nuclear power plants (mainly pressurized water reactor (PWR) plants) and fuel reprocessing plants imposed by the regulatory authority are relevant for emissions of aerosols, halogens and gross beta–gamma activities; for example, the discharge limits of tritium in gaseous and liquid effluents are 5.6 TBq/a (150 Ci/a) and 56 TBq/a (1500 Ci/a), respectively, from two nuclear power units with a 900 MW(e) capacity each. The discharge limits of tritium from the La Hague reprocessing plant, which consists of two units (UP2 and UP3) with a total processing capacity of 1700 t of heavy metal per year, are 2200 TBq/a (59 460 Ci/a) and 37 000 TBq/a (1 000 000 Ci/a) for gaseous and liquid effluents, respectively.

In general, the average annual emissions of tritium from nuclear power plants are approximately 40% of the airborne discharge limit and 35% of the waterborne discharge limit set by the regulatory authority. For the La Hague reprocessing plant, about 4% and 37% of the discharge limits for gaseous and liquid effluents, respectively, are released per year.

At present in France there are no specific limits set for the release of ^{14}C from nuclear facilities, except the discharge limits for gross beta–gamma emissions, although such discharge limits are likely to be imposed in the near future.

2.2.4. Russian Federation

Standards on radiological protection in the Russian Federation are essentially based on the International Basic Safety Standards for Protection against Ionizing Radiation and for the Safety of Radiation Sources [3] and on the recommendations of the ICRP [4].

According to the Russian radiation safety standards [7], the committed effective dose incurred by any member of the public should not exceed

1 mSv/a, and that for a worker during one year's performance of a practice (e.g. reactor operation) is 20 mSv. The permissible intake values and corresponding concentrations of ^{14}C and tritium to ensure adequate human radiological protection, based on the assumptions that a man (operator) breathes on average 1.2 m^3 of air in an hour and a member of the public consumes 2 kg of water per day, are presented in Tables 2 and 3.

The discharge limits for ^{14}C and tritium are established taking into account the combined effect of all radionuclides present in released gas and/or liquid effluents. A safety factor as high as five is ordinarily used in setting discharge limits for operating existing nuclear power plants, while for newly designed nuclear power plants a safety factor of 25 is usually employed.

2.2.5. United Kingdom

The Environment Agency in the UK has revised the discharge limits for gaseous emissions from Magnox nuclear power plants operated by British Nuclear Fuels (BNFL) in accordance with the present status of the plant (i.e. in operation or in a decommissioning phase). Table 4 shows the existing and drafted revised emission limits for ^{14}C and tritium at various Magnox nuclear power plants in the UK [8].

The revised limits are determined based on the dose uptake by the critical group. All dose limits are set much lower than the recommended maximal limits defined in ICRP 60 [4] for the public of 1 mSv/a. It should be noted that the dose limit set for the Trawsfynnyd plant is relatively low because the plant is in the decommissioning phase.

2.2.6. United States of America

The Nuclear Regulatory Commission (NRC) and the United States Department of Energy (USDOE) have the primary responsibility in the USA for regulating nuclear facilities. The NRC regulates and licenses nuclear power reactors, non-power research reactors and nuclear material (including related waste). There are 32 states that have formal agreements with the NRC by which those states have assumed regulatory responsibility over certain by-product, source and small quantities of special nuclear material. The USDOE oversees and monitors contractors that operate federally owned facilities that produce or process nuclear material and nuclear waste. Both NRC and USDOE regulated facilities are typically subject to all federal regulations governing nuclear facilities.

The Environmental Protection Agency (EPA) defines national policies, goals and regulations concerning the environment. The National Emission

TABLE 2. LIMITATIONS ON TRITIUM AND ^{14}C INTAKE FOR NUCLEAR OPERATORS (RUSSIAN FEDERATION)

	Type of inhaled nuclide (chemical form)	Dose coefficient (Sv/Bq)	Upper annual intake limit (Bq/a)	Permissible specific activity (Bq/m^3)
Tritium	HTO vapour	1.8×10^{-11}	1.1×10^{9}	4.4×10^{5}
Tritium	Gaseous tritium	1.8×10^{-15}	1.1×10^{13}	4.4×10^{9}
Tritium	Tritiated methane	1.8×10^{-13}	1.1×10^{11}	4.4×10^{7}
^{14}C	Elementary carbon	5.8×10^{-10}	3.4×10^{7}	1.4×10^{4}
^{14}C	CO_2	6.2×10^{-12}	3.2×10^{9}	6.2×10^{6}
^{14}C	CO	8.0×10^{-13}	2.5×10^{10}	1.0×10^{7}

TABLE 3. LIMITATIONS ON TRITIUM AND ^{14}C INTAKE FOR THE GENERAL PUBLIC (RUSSIAN FEDERATION)

	Type of inhaled nuclide (chemical form)	Dose coefficient (Sv/Bq)	Upper annual intake limit (Bq/a)	Permissible specific activity (Bq/m^3)
		Intake with air		
Tritium	All types	2.7×10^{-10}	3.7×10^{6}	1.9×10^{3}
		Intake with water and food		
Tritium	Inorganic compounds	4.8×10^{-11}	2.1×10^{7}	7.7×10^{3}
Tritium	Organic compounds	1.2×10^{-10}	8.3×10^{6}	3.3×10^{3}
		Intake with air		
^{14}C	All types	2.5×10^{-9}	4.0×10^{5}	5.5×10^{1}
		Intake with water and food		
^{14}C	All types	1.6×10^{-9}	6.3×10^{5}	2.4×10^{2}

Standards for Hazardous Air Pollutants (NESHAPS) require that the off-site dose from airborne effluents be less than 100 μSv/a (10 mrem/a) for all radionuclides combined.

TABLE 4. AIRBORNE TRITIUM AND ^{14}C DISCHARGE LIMITS AT VARIOUS MAGNOX NUCLEAR POWER PLANTS IN THE UK

	Bradwell	Dungeness A	Hinkley Point A	Oldbury	Wylfa	Sizewell A	Trawsfynnyd
			Tritium				
Existing limit (TBq/a)	3	25	5	7	73.5	10	20
Limit in the draft authorization (TBq/a)	1.5	2.6	5	9	18	3.5	0.75
Critical group dose from the draft authorization limit (μSv/a)	0.26	0.14	0.48	1.2	1	0.51	0.066
			^{14}C				
Existing limit (TBq/a)	5	4	6	1.5	24.7	5	2.4
Limit in the draft authorization (TBq/a)	0.6	5	4	5	2.3	2	0.01
Critical group dose from the draft authorization limit (μSv/a)	14	12	50	86	17	38	0.15
Total dose to the critical group (μSv/a)	80	165	116	191	64	174	0.22

For beta–gamma emitters in water, the standard is derived from average annual concentrations calculated to produce a total body or organ dose of 40 μSv/a (4 mrem/a). The EPA safe drinking water standard for ^{14}C is 74 Bq/L (2000 pCi/L) and that for tritium is 740 Bq/L (20 000 pCi/L). Note that these are standards for drinking water and not discharge limits, but they may be used by the EPA, other federal regulators and state regulators in setting specific discharge limits [9].

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

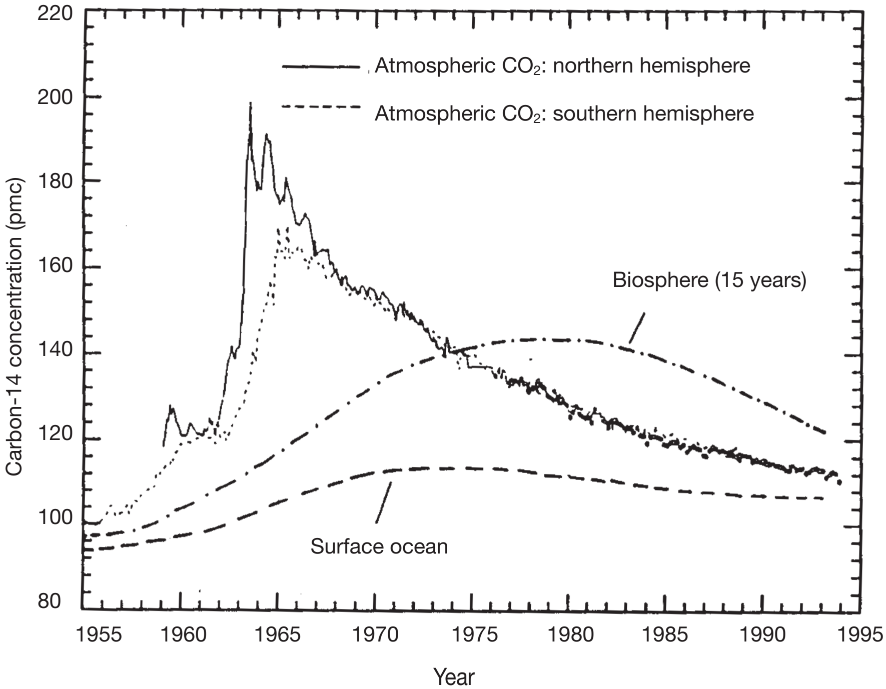

FIG. 1. Carbon-14 concentration in the atmosphere: 1955–1994.

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]:

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

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 ($GBq \cdot GW(e)^{-1} \cdot a^{-1}$) 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].

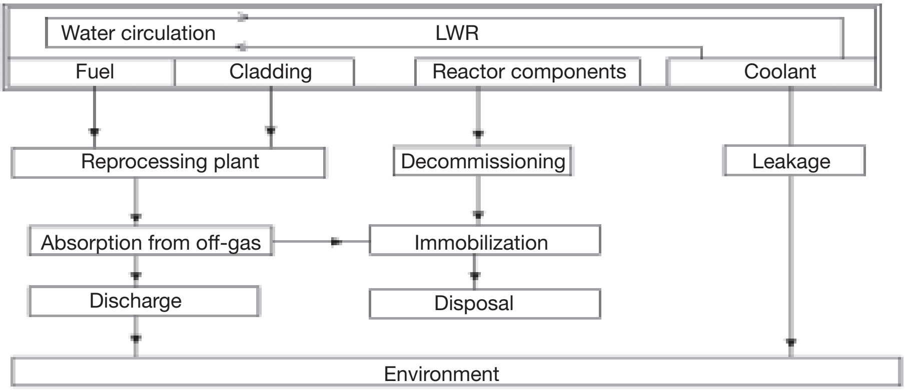

FIG. 2. Simplified diagram of ^{14}C flows in an LWR reactor and at the fuel reprocessing stage.

TABLE 8. RANGES OF CALCULATED ^{14}C PRODUCTION RATES (GBq·GW(e)$^{-1}$·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·GW(e)$^{-1}$·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]:

(a) Primary off-gas treatment vents;
(b) The steam generator blowdown tank vent exhaust;
(c) The turbine gland seal condenser exhaust;
(d) The fuel handling building ventilation exhaust;
(e) The containment ventilation system exhaust;
(f) The auxiliary building ventilation system exhaust;
(g) The turbine building ventilation system exhaust.

The most significant element contributing to ^{14}C release is the off-gas stream from the primary off-gas treatment system, which accounts for approximately 70% of the total release.

The average normalized ^{14}C releases from PWRs and BWRs are summarized in Table 10. The typical average ^{14}C release rate from an LWR is approximately 185–370 GBq/a [11].

The total environmental release of ^{14}C from the reactor, expressed as a function of the production rate, is on average about 50% in BWRs and 30% in PWRs [15].

3.1.3.2. Heavy water reactors

Carbon-14 in HWRs is produced mainly in four systems [15]:

(a) The moderator system;
(b) The heat transport (coolant) system;
(c) Fuel elements;
(d) The annulus gas system.

In general, ^{14}C production in HWRs will be higher than in LWRs, owing to the large quantity of heavy water (with ^{17}O) in the moderator system. Table 11 gives a breakdown of ^{14}C production by a typical CANDU 600 MW(e) nuclear reactor [6]. The majority of the ^{14}C is produced in the heavy water moderator.

The results of ^{14}C distribution within a reactor system, modelled for the CANDU system, are summarized in Table 12 [6]. The model predicts that 3.9% of total ^{14}C production is released into the atmosphere from the moderator cover gas and the annulus gas systems. Approximately 3.4% of the ^{14}C remains in the fuel and 92.7% is removed by ion exchange resins from moderator and primary heat transport purification systems. These resins are in temporary storage, either at the plant of origin or at the designated radioactive waste management sites.

TABLE 10. AVERAGE NORMALIZED AIRBORNE ^{14}C RELEASES[a] ($GBq \cdot GW(e)^{-1} \cdot a^{-1}$) FROM PWRs AND BWRs

	1975–1979	1980–1984	1985–1989
PWR	222	345	120
BWR	518	330	450

[a] Values are averages of all reported data and are taken from the 1982, 1988 and 1993 United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) reports [16–18].

Spent ion exchange resin from water purification systems at HWRs (e.g. CANDU reactors) is a unique waste, owing to its relatively high ^{14}C content (as compared with that produced by LWRs). Typical specific activities of ^{14}C on resins of moderator purification systems are in the range 1.7–7.9 TBq/m^3. Carbon-14 activities on resins of heat transport purification systems range from 0.01 to 0.2 TBq/m^3. Considerable quantities of these resins will be accumulated at the end of a reactor's lifetime.

Figure 3 shows the flows of ^{14}C in an HWR. Annual ^{14}C releases from two Canadian CANDU (600 MW(e)) stations from 1991 to 1998 are shown in Table 13.

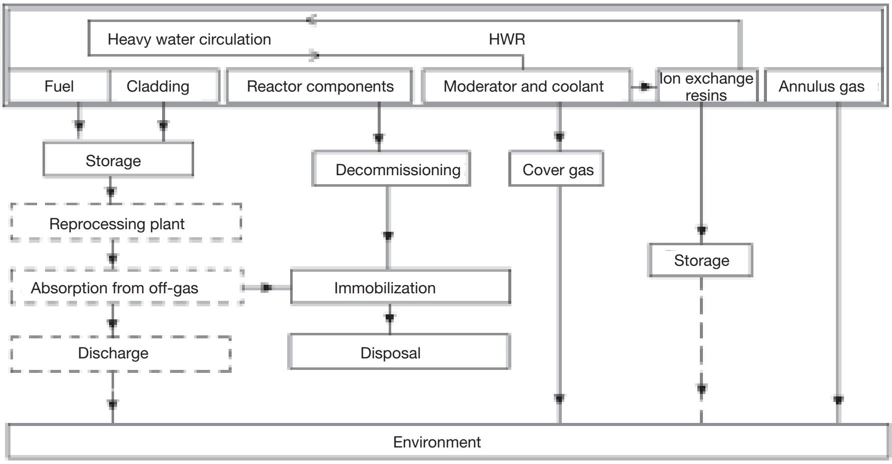

FIG. 3. Simplified diagram of ^{14}C flows in an HWR and at the fuel reprocessing stage.

TABLE 11. PRODUCTION OF ^{14}C ($GBq \cdot GW(e)^{-1} \cdot a^{-1}$) IN CANDU 600 MW(e) REACTORS

Moderator	27 000
Primary heat transport	380
Fuel	960
Annulus gas (with CO_2)	38

TABLE 12. ESTIMATED ^{14}C DISTRIBUTION FOR CANDU 600 MW(e) REACTORS

	Total ^{14}C production (%)	Emitted ^{14}C (%)	^{14}C on ion exchange resins (%)
Moderator	95.2	3.77	91.43
Primary heat transport	1.3	0	1.3
Fuel	3.37	0	0
Annulus gas	0.13	0.13	0

TABLE 13. ANNUAL AIRBORNE ^{14}C RELEASES (GBq/a) FROM TWO CANADIAN CANDU 600 MW(e) REACTORS

	Point Lepreau	Gentilly 2
1991	350	450
1992	720	—
1993	590	480
1994	200	2920
1995	142	1650
1996	121	—
1997	150	500
1998	320	277

3.1.3.3. Magnox reactors and advanced gas cooled reactors

Magnox reactors and AGRs have been the basis of the British nuclear programme. Arisings of ^{14}C in these reactors are dominated by the contribution of the graphite moderator due to $^{13}C(n,\gamma)^{14}C$ and $^{14}N(n,p)^{14}C$ reactions; for example, approximately 1.85 TBq (50 Ci) of ^{14}C is generated per year in a 250 MW(e) gas cooled graphite moderated reactor: about 60% is produced by interaction with nitrogen impurities in the graphite and 40% by interaction with ^{13}C contained in the graphite pile [11].

Most of the graphite moderator remains in the reactor core in both Magnox reactors and AGRs and will constitute a solid waste arising at the decommissioning stage. However, the graphite sleeves of AGRs are removed with the fuel and pass to the reprocessing plant, where they become a separate solid waste arising. Bush et al. [12] calculated ^{14}C production rates for Magnox reactors and AGRs; the results are shown in Table 14.

An example of the total radionuclide inventory in a graphite moderator is given in Table 15 [11].

The graphite becomes corroded during reactor operation by a radiolytic reaction in the presence of the CO_2 coolant. The rate of the reaction depends on the irradiation level, the coolant composition and the pore structure of the graphite. The reaction can be inhibited by adjustment of the coolant composition, but is still significant.

A large portion of the ^{14}C gaseous releases from gas cooled reactors comes from the purification of the CO_2 circuits used to cool the reactor and from isotopic exchange between the moderator and the CO_2 circuit.

The estimated quantity of ^{14}C released from the graphite moderator into the coolant for Magnox reactors and for AGRs is provided in Table 16 [12].

Carbon-14 production within the coolant depends on the nitrogen impurity level present. A level of 100 ppmv was used in Table 16, and the ^{14}N activation reaction accounts for 65% of the total ^{14}C production in the coolant.

The total ^{14}C inventory in the coolant is discharged into the atmosphere, either by leakage or by a periodic routine purge. The remaining ^{14}C, in the fuel and its cladding, will pass to the reprocessing plant. Figures 4 and 5 show the flows of ^{14}C in Magnox reactors and AGR reactors, respectively. The fraction released from the reactor is about 3% for Magnox reactors and about 6% for AGRs of the total production of ^{14}C in the reactors [15]. The emission level of ^{14}C from the RBMK type reactor in the Russian Federation has been estimated to be 1000 ± 300 GBq·GW(e)$^{-1}$·a^{-1} [19]. In France the activity of ^{14}C released from the Chinon A2 reactor (a 200 MW(e) reactor) is reported to be about 370 GBq/a, which is the same as from Saint Laurent A (a 450 MW(e) reactor) [11].

TABLE 14. CALCULATED ^{14}C PRODUCTION RATES ($GBq \cdot GW(e)^{-1} \cdot a^{-1}$) IN MAGNOX REACTORS AND AGRs

	Fuel	Cladding	Coolant	Moderator	Total
Magnox	3 740	295	405	9 550	13 990
AGR	295	1 810	220	5 700	8 025

TABLE 15. TYPICAL RADIONUCLIDE INVENTORY (TBq) IN A GRAPHITE MODERATOR AFTER 10 YEARS OF DECAY

	Half-life (a)	Marcoule G2 reactor (1300 t)	Chinon A2 reactor (1700 t)
Tritium	12.33	200	400
^{14}C	5 730	28	37
^{36}Cl	300 000	0.9	0.4
^{55}Fe	2.63	3	20
^{60}Co	5.33	9	13
^{63}Ni	92	18	23
^{93m}Nb	16	0.5	0.7
^{137}Cs	30	0.6	0.15
$^{154}Eu/^{155}Eu$	8.6/5	0.9	0.07

TABLE 16. CARBON-14 ARISINGS ($GBq \cdot GW(e)^{-1} \cdot a^{-1}$) IN THE COOLANT OF MAGNOX REACTORS AND AGRs

	Magnox	AGR
Total production in graphite	9550	5700
Of which released to coolant	700	330
Production in coolant	405	220
Total present in coolant	1105	550

3.1.3.4. High temperature gas cooled reactors

High temperature gas cooled reactors (HTGRs) were the subject of research and development work in Germany (in the former Federal Republic of Germany) and in the USA. They present special problems in the field of the management of waste containing ^{14}C for the following reasons:

(a) Releases of ^{14}C to the environment from the HTGR fuel cycle per unit of electricity generated will be much greater than for other types of reactor.

(b) Owing to the structure of the fuel elements, much, or all, of the graphite moderator will have to be removed as the first step in fuel reprocessing. Most of the ^{14}C will therefore be released, together with a large amount of CO_2 from the combustion of the graphite moderator, at the reprocessing plant.

The ^{14}C production rate in an HTGR reactor is highly dependent on the nitrogen level in the graphite moderator. In general, HTGRs could give rise to 3700–7400 GBq·GW(e)$^{-1}$·a^{-1} of ^{14}C, eventually all of which will pass to the reprocessing plant.

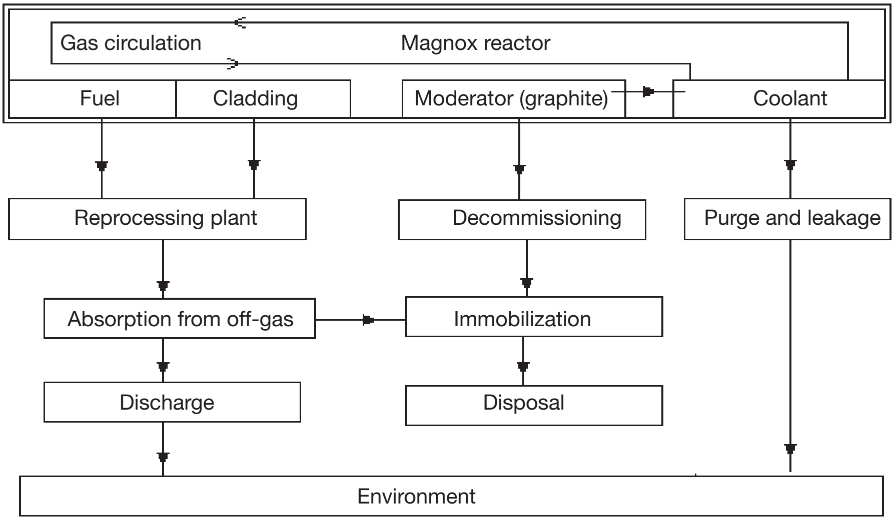

FIG. 4. Simplified diagram of ^{14}C flows in a Magnox reactor and at the fuel reprocessing stage.

3.1.3.5. *Fast breeder reactors*

There is no moderator in a fast breeder reactor (FBR), although the coolant and other core components do have some moderating effect. The coolant is liquid sodium. The significant sources of ^{14}C would therefore be oxygen in the fuel and nitrogen impurities in the fuel and cladding. Nitrogen levels in the coolant will be very low, and releases of ^{14}C from reactors will not be significant. Essentially all the ^{14}C inventory will pass to reprocessing plants in the fuel elements.

Table 17 shows the typical ranges of ^{14}C production rates in the fuel and cladding of FBRs, based on data published in Ref. [12].

3.1.3.6. *Summary of waste containing ^{14}C produced by reactor operation*

It can be summarized, based on the discussion in this section, that the predominant quantity of ^{14}C from nuclear power reactors occurs in the following waste streams:

(a) Reactor off-gases: the ^{14}C is mainly produced in the moderator and coolant during reactor operation. The chemical form of ^{14}C is predominantly CO_2 for HWRs, BWRs, AGRs and Magnox reactors, but predominantly hydrocarbons for PWRs.

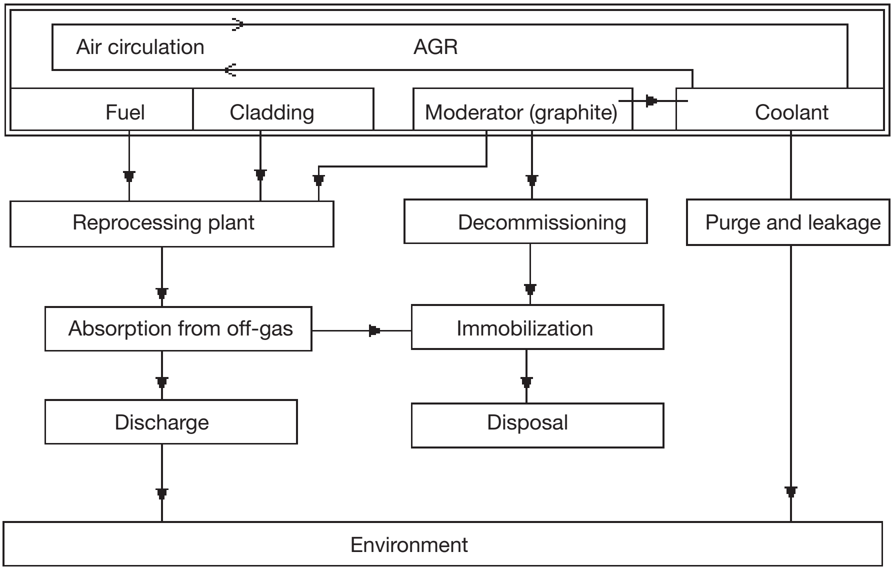

FIG. 5. Simplified diagram of ^{14}C flows in an AGR and at the fuel reprocessing stage.

TABLE 17. CALCULATED ^{14}C PRODUCTION RATES ($GBq\cdot GW(e)^{-1}\cdot a^{-1}$) IN FBRs

Fuel	200–230
Cladding	295–475
Total	495–705

TABLE 18. ARISINGS AND RELEASES OF ^{14}C FROM VARIOUS TYPES OF REACTOR

	Installed capacity (MW(e))	Gaseous waste (GBq/a)	Liquid effluent (GBq/a)	Solid waste (decommissioning) (GBq/a)
LWR–PWR	1000	129.5	1.3	647.5
LWR–BWR	1000	259.0	1.3	1165.5
HWR	600	3108	Small	703[a]
GCR–MGR	480	373.7	Small	2982.2
GCR–AGR	660	255.3	Small	2479
GCR–HTGR	600	14.8	Small	Small
FBR	1250	0.65	Small	Small

[a] Value taken from Dubourg [11].

(b) Solid waste: this includes the graphite moderator in AGRs and Magnox reactors, ion exchange resins in other types of reactor and structural materials in the reactor core of all types of reactor.

In general, a small quantity of ^{14}C is released into liquid effluents from nuclear reactors. Estimated arisings and releases of ^{14}C for various types of reactor are summarized in Table 18 [12].

3.1.4. Release during spent fuel reprocessing

In reprocessing plants a significant part (e.g. typically 40–50% for LWR fuel) of ^{14}C is released from spent fuel into the off-gas at the dissolution stage, so measures should be taken for off-gas cleaning. The remaining ^{14}C is retained with insoluble cladding, which is further managed as solid waste.

The ^{14}C behaviour and the possible pathways to the environment in a spent fuel reprocessing plant are briefly discussed below, based on metal clad

LWR fuels. A typical flow diagram of an LWR fuel reprocessing plant is shown in Fig. 6.

Spent fuel is placed upon arrival at a reprocessing plant in the fuel receiving and storage pool. In general, no significant quantity of the ^{14}C arriving at the reprocessing facility is expected to escape to the fuel storage pool, even in the case of defective fuels.

The first step in reprocessing metal clad fuels is shearing the fuel rods. Fuel elements are mechanically transferred from the storage pool to the remote process cell, in which shearing (chopping) occurs. Any ^{14}C present in the gas space inside the rods will be released into the shear cell off-gases at this stage. Studies have shown that only a very small fraction of the total ^{14}C inventory in the fuel is released in this way [12].

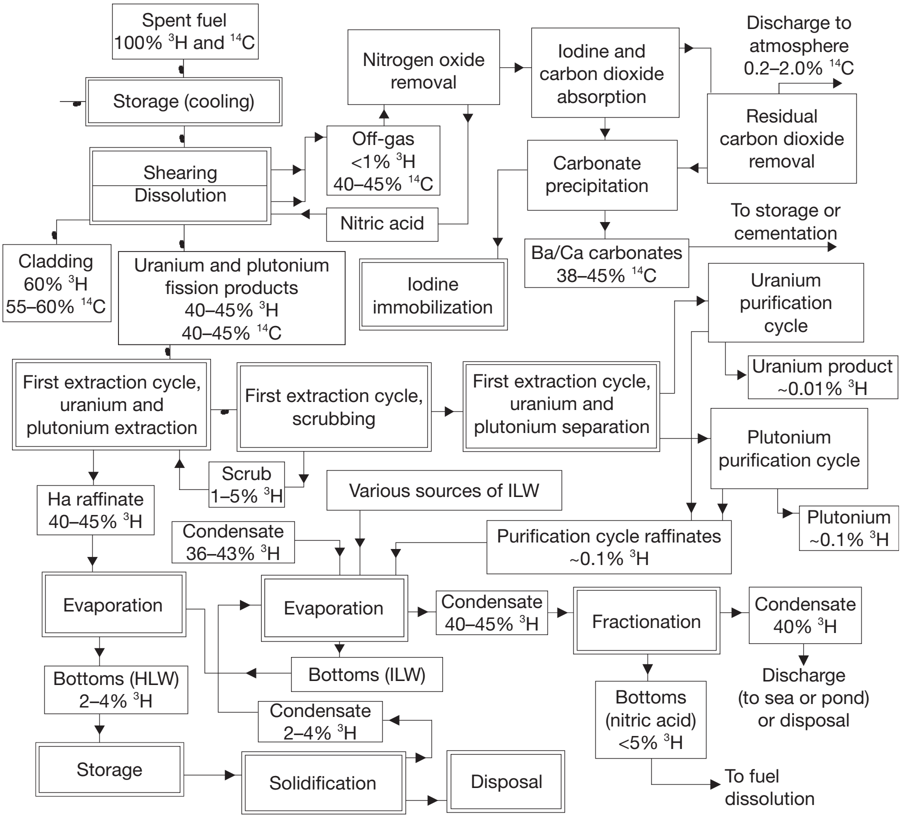

FIG. 6. Simplified flow diagram for a typical plant for LWR fuel reprocessing (the tritium and ^{14}C contents in the process products are expressed as a percentage of their amounts in spent fuel).

The fuel sheared into segments containing hulls and oxide pellets is then transferred to the dissolver, where the pellets react with nitric acid. Studies have indicated that under dissolution conditions essentially all the ^{14}C from the dissolver liquor is evolved into the gas phase. This is an important result, because any ^{14}C compounds retained in the dissolver solution might be extracted in the subsequent solvent extraction process, and might then build up in the recycling solvent. Under the oxidizing conditions in the dissolution step, carbon is almost completely oxidized to CO_2, which is liberated into the dissolver off-gases. The ^{14}C content in dissolver liquor is insignificant compared with the amounts in dissolver off-gases and in the fuel cladding.

Depending on the design and efficiency of the gas cleaning system, ^{14}C is either separated from the dissolver off-gases and converted to solids for disposal (as shown in Fig. 6) or discharged into the atmosphere.

Studies have shown that essentially all the ^{14}C in dissolver off-gases is present in the dioxide form [12]. In particular, the predominance of CO_2 as the ^{14}C species present in the off-gases of a reprocessing plant is confirmed by measurements of emissions at the Karlsruhe plant in Germany. Emissions of ^{14}C as CO_2 when reprocessing PWR and BWR fuels were 459 $GBq \cdot GW(e)^{-1} \cdot a^{-1}$ and 640 $GBq \cdot GW(e)^{-1} \cdot a^{-1}$, respectively, being in good agreement with the expected production in these fuels [12].

Studies of emissions during the reprocessing of fuel from the experimental HWR at Karlsruhe gave similar results to those for LWR fuel. Dubourg [11] has estimated that the ^{14}C activity released from reprocessing the fuels from the Chinon A2 reactor (with a 200 MW(e) capacity) is about 555 GBq/a and that from Saint Laurent A (with a 450 MW(e) capacity) is 1110 GBq/a. No data are available on the behaviour of ^{14}C present in FBR fuel (U/Pu oxide), but similar behaviour to that in LWR fuel can probably be expected [13]. Most of the ^{14}C from HTGRs will be released during the reprocessing of spent fuel.

Table 19 [14] shows estimates of ^{14}C emissions and inventories in solid waste for various reactor systems and reprocessing plants.

It can be concluded from the above information that most ^{14}C will occur in the following waste streams at fuel reprocessing plants:

(a) Off-gases released during fuel dissolution: these will generally contain the ^{14}C originally generated and collected in the fuel. This could either be released as CO_2 gas, scrubbed out and discharged as a liquid, or converted to a solid.

(b) Burner off-gases at HTGR fuel reprocessing plants: these will contain the significant ^{14}C content of the graphite moderator (integral with the fuel elements) in a gas stream rich in CO_2.

(c) Solid waste: the fuel cladding.

TABLE 19. ESTIMATED ^{14}C EMISSIONS AND INVENTORIES IN SOLID WASTE FOR VARIOUS REACTOR SYSTEMS

			Reactor		Reprocessing plant	
	Power (MW(e))	Estimated ^{14}C production (GBq/a)	Airborne ^{14}C emission (GBq/a)	Solid waste (GBq/a)	Airborne ^{14}C emission (GBq/a)	Solid waste (GBq/a)
PWR	900	1850	148	666	518	518
PWR	1300	2590	185	925	740	740
BWR	1000	3515	296	1295	962	962
Graphite reactor[a]	200	2849	370	1850	555	74
Graphite reactor[b]	450	4255	370	2664	1110	266
AGR	600	4070	296	2664	185	925
HWR	600	5550	4070	—	814	703

Note: The calculations were based on 7000 operating hours per year.

[a] Chinon nuclear power plant (1700 t graphite moderator) in France.

[b] Saint Laurent A2 nuclear power plant (2440 t graphite moderator) in France.

Table 20 summarizes the expected specific quantities of ^{14}C in gaseous and solid waste for the types of reactor considered and for corresponding reprocessing plants [12].

3.2. TRITIUM PRODUCTION AND RELEASE

Tritium is produced by nuclear reactions that occur naturally in the environment, in nuclear weapon testing and in nuclear reactors. It is continuously generated by the interaction of high energy cosmic rays with oxygen and nitrogen atoms in the upper atmosphere. These processes produce most of the world's natural tritium. Tritium converts into water and reaches the Earth's surface as rain. An estimated production rate of 1.48×10^8 GBq/a results in a world steady state natural inventory of 2.59×10^9 GBq [20].

Atmospheric nuclear test explosions from 1945 to 1975 added about 2.96×10^{11} GBq of tritium to the environment, much of which has since decayed. However, about 1.85×10^{10} GBq (5×10^8 Ci) remains in the environment,

TABLE 20. EXPECTED NORMALIZED ^{14}C DISTRIBUTION ($GBq \cdot GW(e)^{-1} \cdot a^{-1}$) IN WASTE AT NUCLEAR FACILITIES

		Gaseous waste[a]		Solid waste	
	Total produced	Reactor	Reprocessing plant	Reactor[b]	Reprocessing plant
LWR–PWR	2 590	185	740	925	740
LWR–BWR	3 515	370	740	1 665	740
HWR	10 175	7 400	1 480	NR	1 295
GCR–MGR	14 060	1 110	3 700	8 880	370
CGR–AGR	8 140	555	370	5 365	1 850
CGR–HTGR	5 587	37	5 550	Small	Small
FBR	925	0.74	185	NR	740

[a] This waste could be discharged as gases, transferred to liquid effluents or converted to solids for disposal.

[b] Decommissioning waste.

NR: no data have been reported.

mostly diluted in the oceans. Underground nuclear tests appear to add little tritium into the atmosphere [20].

3.2.1. Production and release in nuclear power reactors

Production processes, which are described in detail in Refs [21–23], and mechanisms for the generation of tritium at nuclear reactor facilities have not fundamentally changed in the past decade. Tritium is produced in reactors by neutron activation of ^{2}H, ^{3}He, ^{6}Li and ^{10}B, and is thus formed in the following reactor components [24]:

(a) The water coolant–moderator (LWRs);
(b) The heavy water coolant and moderator (HWRs);
(c) The helium coolant (HTRs);
(d) The boron control rods (many types of reactor);
(e) The dissolved boric acid in the moderator (PWRs, HTRs);
(f) The graphite moderator (lithium impurity: gas cooled reactors (GCRs), HTGRs);
(g) The UO_2/PuO_2 core and UO_2 breeder fuel (lithium and boron impurities: FBRs).

TABLE 21. ESTIMATED TRITIUM PRODUCTION RATES ($GBq \cdot GW(e)^{-1} \cdot a^{-1}$) IN VARIOUS TYPES OF REACTOR

	Fuel	Coolant	Moderator	Total
LWR–PWR	5.18×10^5	3.70×10^4	NA	5.55×10^5
LWR–BWR	5.18×10^5	Low	NA	5.18×10^5
HWR	5.18×10^5	1.85×10^6	5.18×10^7	5.42×10^7
GCR	5.18×10^5	Low	$(0–1.85) \times 10^5$	$(5.18–7.03) \times 10^5$
GCR–HTGR	5.18×10^5	1.85×10^5	$(0.18–7.40) \times 10^4$	$(5.2–5.9) \times 10^5$
FBR	7.40×10^5	7.40×10^4	NA	8.14×10^5

NA: data not available.

The estimated tritium production rates in various types of reactor are reported in Ref. [25] and summarized in Table 21.

Most of the fission product tritium produced in fuel rods is usually retained within the fuel and is not released to the environment at the reactor site; it is released only during fuel reprocessing, if fuel reprocessing is carried out.

Tritium in reactor core materials may remain where it is formed and be accumulated until the reactor is decommissioned. The quantities of tritium in various reactor components were estimated in Ref. [25] and are shown in Table 22.

The most important movement of tritium in the reactor is diffusion of a portion of tritium from the fuel either into the zircaloy cladding, where it is trapped (most water cooled reactors), or through stainless steel cladding into the coolant (AGRs, FBRs). Only a small quantity of tritium escapes from Magnox fuel elements. The portion of tritium trapped in zircaloy cladding is typically 15–60%, while about 30% passes into the GCR coolant and >95% into the FBR (sodium) coolant [25]. A further transfer of tritium from the graphite moderator of GCRs to the coolant may occur due to corrosion of the moderator.

The activity produced in the coolant is partly or entirely released in the effluent streams, depending on the waste management practices at the plant. Releases to the environment are mainly in the form of HTO in reactors that use water as the primary coolant. The typical discharge rates of tritium from various types of reactor are summarized in Table 23 [25].

TABLE 22. ACCUMULATION OF TRITIUM (GBq/kW(e)) IN VARIOUS REACTOR COMPONENTS

Heavy water coolant–moderator (HWRs)	7.40×10^8
Graphite moderator (GCRs, HTRs)	3.70×10^4
Boron control rods	1.85×10^6
Cold traps for sodium purification (FBRs)	1.11×10^7 [a]

[a] Transfer from fuel.

3.2.1.1. Light water reactors

The main source of tritium in LWRs is ternary fission, which produces (5.55–7.40) × 10^5 GBq·GW(e)$^{-1}$·a^{-1} [23]. This tritium is partly transferred with the fuel to the reprocessing plant. The amount of tritium produced through neutron reactions in the coolant–moderator is small, less than 3.70 × 10^4 GBq·GW(e)$^{-1}$·a^{-1} [26]. The formation of tritium by activation reactions in PWRs is considered to be mainly from boron in the coolant water, which is used for reactivity control. In BWRs the contribution of tritium by activation reactions is mainly from boron in the control rods. The tritiated effluents from light water (the coolant–moderator of LWRs) can be released directly to the environment without additional processing, owing to the very low concentrations of tritium.

The average normalized tritium releases from PWRs and BWRs between 1975 and 1989 are summarized in Table 24. It can be noticed that tritium releases from PWRs gradually decreased by almost a factor of three between 1975–1979 and 1985–1989. This decrease is the result of better maintenance and management of the reactor component systems.

Tritium activities discharged from BWRs to the environment are lower than those of PWRs because less tritium is produced in or diffuses into the primary coolant.

3.2.1.2. Heavy water reactors

The amount of tritium generated in fuel by ternary fission is approximately the same in HWRs as in LWRs. However, a relatively large amount of tritium is produced in the D_2O coolant and moderator (approximately 8.9 × 10^7 GBq·GW(e)$^{-1}$·a^{-1}, primarily in the operation of the moderator system [26].

In a CANDU 600 MW(e) HWR most of the tritium is formed in the thermal neutron capture reaction, $^2H(n,\gamma)^3H$. The reaction occurs in the heavy

TABLE 23. TYPICAL TRITIUM DISCHARGE RATES ($GBq\cdot GW(e)^{-1}\cdot a^{-1}$) FROM VARIOUS TYPES OF REACTOR

	Gaseous effluent	Liquid effluent
PWR (zircaloy cladding)	3.70×10^3	2.59×10^4
BWR	1.85×10^3	3.70×10^3
HWR	7.40×10^5	1.85×10^5
GCR	7.40×10^3	1.11×10^4

water of both the moderator and coolant systems. The mass of heavy water in the high flux zones of the fuel channels is small compared with the mass of moderator heavy water in the reactor core. In addition, the average thermal neutron flux inside the fuel channels is slightly lower than that in the moderator. As a result, the rate of tritium formation is much higher in the moderator than in the coolant system. This production of tritium results in a steady rise of tritium concentration in the heavy water inside the moderator; for example, the calculated concentration of tritium in the moderator heavy water is 3640 GBq/kg after 40 years, while in the coolant heavy water it is only 81 GBq/kg, for the same operation time, based on a capacity factor of 90% [27].

Leakage of water from the moderator and coolant systems gives rise to tritium release to the reactor building. In general, most of the heavy water leakage is recovered, for economic and radiological reasons, so that tritium emissions to the environment by way of airborne and water emissions are kept very low. A portion of the heavy water from the coolant and moderator systems of HWRs may also be withdrawn for detritiation before it is returned to the reactor, and some tritium may escape during this process; for example, the average annual airborne tritium emission from a CANDU 600 MW(e) reactor (Point Lepreau nuclear power plant, Canada, 1984–1994) was 2.68×10^5 GBq/a. The average annual aqueous emission was 1.85×10^5 GBq/a [27].

3.2.1.3. Other types of reactor

In GCRs the contribution of tritium is from lithium impurities in the graphite moderator and from the presence of water vapour in the core. In Magnox reactors CO_2 in the coolant circuit is continually dried to remove water vapour, and hence tritium produced in the core finds its way primarily into the liquid effluent removed by the dryers.

The five year average normalized airborne tritium releases from various types of reactor are compared in Table 25; as expected, HWRs release more

TABLE 24. AVERAGE NORMALIZED AIRBORNE TRITIUM RELEASES[a] ($GBq \cdot MW(e)^{-1} \cdot a^{-1}$) FROM PWRs AND BWRs

	1975–1979	1980–1984	1985–1989
PWR	7.8	5.9	2.8
BWR	3.4	3.4	2.5

[a] Values are averages of all reported data taken from the 1982, 1988 and 1993 UNSCEAR reports [16–18].

airborne tritium than the other types of reactor. It should be noted that the use of large amounts of heavy water as a moderator and coolant is one of the major design features of HWRs for improved neutron efficiency, which inherently causes a higher production and release of tritium.

3.2.2. Release during spent fuel reprocessing

The amount of tritium in the fuel that passes to a reprocessing plant depends on the type of reactor and on the fuel cladding material. Most of the tritium released from the fuel during dissolution appears in the liquid waste streams, while some is found in the dissolver off-gas stream and a portion is immobilized as a solid zirconium compound in the cladding. Fuel with stainless steel cladding may lose up to 50% of the tritium produced in the fuel because of diffusion and permeation through the cladding. In AGRs and FBRs with stainless steel clad fuel, only small amounts of tritium are expected to be passed to the reprocessing plant. Zircaloy clad fuel, the fuel of most LWRs, retains essentially all the tritium through the formation of zirconium tritide. For an LWR fuel reprocessing plant, with a capacity of 1400 t/a of heavy metal serving 50 GW(e) of electric production capacity, the tritium release rate was estimated to be $(1.85–3.70) \times 10^7$ GBq/a (0.5–1.0 mCi/a) [26].

In an LWR fuel reprocessing plant using the Purex process (a typical flow diagram of an LWR fuel reprocessing plant is shown in Fig. 6), after chopping the fuel elements and fuel dissolution in nitric acid, about 60% of the total amount of tritium is retained in zircaloy cladding [28]. The bulk of the remainder is in the form of HTO and nitric acid, which is distributed through the various streams in the process. A simplified distribution of tritium in a conventional fuel reprocessing plant is shown in Table 26 [26].

As fresh water and nitric acid are added to the process, the tritium becomes progressively more diluted, so large volumes of tritiated aqueous effluents, of the order of 100 m^3/t of heavy metal, can be produced. In reproc-

TABLE 25. AVERAGE NORMALIZED AIRBORNE TRITIUM RELEASES[a] (GBq·MW(e)$^{-1}$·a^{-1}) FROM VARIOUS TYPES OF REACTOR

	1975–1979	1980–1984	1985–1989
PWR	7.8	5.9	2.8
BWR	3.4	3.4	2.5
HWR	540	670	480
GCR	—	5.4	9.02
FBR	—	—	96
Light water cooled graphite moderated reactor	—	—	26

[a] Values are averages of all reported data taken from the 1982, 1988 and 1993 UNSCEAR reports [16–18].

essing plants at coastal sites these large volume effluents are discharged directly into the sea, in which there is an enormous additional dilution effect. Solar evaporation of HTO is used in India, while long term storage in open ponds is used in the Russian Federation.

Table 27 provides typical annual amounts of tritium (per a unit of electric power) in waste streams and process products from an LWR reprocessing plant.

Concepts for concentrating tritium into smaller volumes of water have been developed for locations where access to the sea is limited or discharge is otherwise prohibited. Effluent volumes can be reduced to the order of 1 m^3/t of heavy metal by means of partial recycling of the water and nitric acid, along with segregation of tritium in the first extraction cycle of the Purex process.

Use of the voloxidation process (see Section 5) as an alternative head end process (dissolution of fuel in nitric acid) could further reduce the volume of tritiated wastewater to the range of 2 to 20 L/t of heavy metal, with a tritium concentration in the range 370–3700 GBq/L (10–100 Ci/L) [26]. This highly tritiated water can be then converted into the less toxic HT form by electrolysis and discharged into the atmosphere. However, for reasons of cost and owing to some technological drawbacks, the voloxidation process has not been employed in operating reprocessing plants.

TABLE 26. SIMPLIFIED DISTRIBUTION SCHEME OF TRITIUM IN A CONVENTIONAL FUEL REPROCESSING PLANT

Operation	Process stream	Fraction of tritium in the process stream (per cent of inventory)
Chopping	Fuel element	100[a]
	Fuel element pieces	>99.99
	Off-gas	<0.001
Dissolution	Aqueous phase	~40
	Cladding	~60[b]
	Off-gas	<0.5
Extraction	Aqueous phase	>35
	Organic phase	<5
Re-extraction	Aqueous phase	<4.9
	Organic phase	~0.01
	Plutonium product	~0.1
	Uranium product	~0.01

[a] Corresponding to 350–700 Ci/t at 30 $GW(e)\cdot d\cdot t^{-1}$.

[b] Depends on local fuel rod temperatures.

TABLE 27. TYPICAL TRITIUM DISTRIBUTION ($GBq\cdot GW(e)^{-1}\cdot a^{-1}$) AMONG LWR REPROCESSING PLANT WASTE STREAMS AND PROCESS PRODUCTS

Solid waste (zircaloy cladding)	3.3×10^5
Liquid waste (aqueous)	$\sim 2.2 \times 10^5$
Liquid waste (spent solvent)	<55
Gaseous waste	2.8×10^3
Plutonium product	5.5×10^2
Uranium product	55
Total	5.5×10^5

3.3. CATEGORIES OF WASTE CONTAINING ^{14}C AND TRITIUM

3.3.1. Reactor operation and fuel cycle waste

Most of the human-made ^{14}C and tritium will continue to be produced in nuclear power reactors. The fate of these contaminants depends highly on the reactor type and on its design and operation. Typical production rates for various types of reactor are shown in Table 5. Fractions of these radioisotopes will go into different waste streams produced in the nuclear fuel cycle. In general, the following waste streams that contain ^{14}C and tritium will be generated routinely by reactor operations:

(a) Reactor coolant water (liquid);
(b) Spent ion exchange resins (solid);
(c) Spent filter cartridges (solid);
(d) Radioactive refuse (solid);
(e) Reactor off-gases (gas);
(f) Condensates from off-gas systems (liquid);
(g) Coolant (CO_2) of Magnox reactors and AGRs (gas);
(h) Highly irradiated steel structures and components (solid, decommissioning waste);
(i) Graphite moderators, mainly from graphite reactors (solid, decommissioning waste).

There are a number of waste streams containing ^{14}C and tritium associated with the reprocessing of spent nuclear fuel, which include:

(i) Fuel cooling storage basin water (liquid);
(ii) Spent fuel washing solutions and condensates from head end fuel treatments (liquid);
(iii) Dissolver off-gases from the gas cleaning system (gas);
(iv) Off-gas scrubber solutions, which are partially recycled (liquid);
(v) Condensates from off-gas systems (liquid);
(vi) Highly active raffinate from the first extraction cycle of uranium and plutonium decontamination after it is concentrated by evaporation (liquid);
(vii) Recovered nitric acid that is recycled for fuel dissolution (liquid);
(viii) Recovered water (condensate) from the nitric acid regeneration process (liquid);
(ix) Refuse from the plant's operation (solid).

3.3.2. Other waste

Waste containing ^{14}C and tritium is also generated by radioisotope producers, hospitals, medical schools, universities and colleges. Such waste can be in the form of refuse, liquid scintillation vials, absorbed aqueous and organic liquids, discard sealed sources and biological waste.

The inventories of ^{14}C and tritium, and volumes of the waste generated, in radioisotope production for industrial uses and medical and research activities are much smaller than those generated by reactor and fuel reprocessing operations. Treatment of this waste by the technologies discussed in the following sections may not be required.

Waste generated in research activities such as accelerator operations will contain tritium and/or ^{14}C. However, the total volume of this waste is likely to be small.

There are a number of historical waste streams (e.g. equipment related to nuclear testing programmes) around the world that may contain ^{14}C and tritium. In particular, in the past a large quantity of tritium was used in the production of luminous materials, electrostatic neutralizers, etc. While ^{14}C and tritium are not necessarily the most significant radionuclides in this type of waste, they may need to be considered in its treatment and disposal.

4. REDUCTION OF PRODUCTION AND RELEASE

4.1. REDUCTION OF ^{14}C PRODUCTION AND RELEASE

It has been suggested that some ^{14}C production sources may be controlled by limiting the amounts of parent substances subject to irradiation. Such control would also reduce releases of ^{14}C from nuclear reactors [13].

In general, two neutron activation reactions dominate the production of ^{14}C: $^{17}O(n,\alpha)^{14}C$ and $^{14}N(n,p)^{14}C$, which, respectively, have a cross-section of 0.24 barn and 1.82 barn. Most of the ^{14}C produced in fuel will pass to the reprocessing plant and will be released with the dissolver off-gases. It is therefore useful to consider the possibility of reducing the initial nitrogen and ^{17}O contents in the fuel.

Calculations indicate that approximately 0.15 $TBq\cdot GW(e)^{-1}\cdot a^{-1}$ of ^{14}C is produced by the activation of ^{17}O in LWR fuel. This represents an irreducible minimum, since the amount of oxygen present in the fuel is somewhat inflexible to adjustment. However, the nitrogen impurities in the fuel may be controlled during fuel fabrication. Bush [29] indicated that a modest reduction (by at most a factor of about five) in ^{14}C production could be achieved by a reduction in the level of nitrogen impurity in the fuel; for example, at a level of 25 ppm of nitrogen in the fuel, nitrogen contributes 0.55–0.74 $TBq \cdot GW(e)^{-1} \cdot a^{-1}$ of ^{14}C. Reduction of this level to 5 ppm (a level frequently found in some fuels) gives a contribution from nitrogen about equal to that from ^{17}O.

The materials of core structures contain certain amounts of nitrogen (e.g. the nitrogen contents in stainless steel range from 0.04% to 0.08%). However, nitrogen levels in many reactor materials are not known with certainty, and it is therefore difficult to estimate what reduction might be possible. The costs of decreasing the nitrogen levels in reactor core materials should be balanced against the benefit of a better mechanical property and corrosion resistance and the reduction in collective doses to humans thereby achieved. The total cost of reducing nitrogen levels plus that of the remaining dose detriment should be minimized in accordance with the ALARA (as low as reasonable achievable) principle.

Gaseous ^{14}C is produced in LWRs mainly by activation of nitrogen entering the primary coolant, and is released in gaseous effluents. The average PWR release rate is about 185–370 GBq of gaseous ^{14}C per year. In order to minimize the presence of nitrogen in the primary coolant, the cover gas of water storage tanks has been switched from nitrogen to argon, so as to prevent the dissolution of nitrogen gas in the primary coolant. Recently, operating experience of HWRs in the Republic of Korea has indicated that controlling the nitrogen level in the moderator cover gas may lead to lower ^{14}C emissions.

Moreover, the pH control of the primary coolant in Western PWRs is carried out by depleted ^{6}Li, lithium hydroxide, instead of hydrazine (NH_2–NH_2), to prevent the formation of ^{14}C. Better control of the chemicals used in the operation of reactors is one means of reducing ^{14}C production.

Air ingress, especially in the moderator and primary coolant systems, has been found to be one of the sources of ^{14}C production during reactor operation. Improving the system design to minimize the potential for air ingress will therefore reduce ^{14}C production and release.

It is interesting to note that the old style CANDU reactors (using nitrogen as the annular gas), WWER reactors and RBMK reactors released large quantities of ^{14}C in gaseous effluents, owing to the extensive use of nitrogen blanketing inside the reactor. The current CANDU reactors, using CO_2 as the annular gas, have shown a significant reduction in ^{14}C production in the annular gas system. Avoiding the use of chemicals that could produce ^{14}C during reactor operations is a viable approach to reducing ^{14}C production.

In general, HWRs produce relatively large quantities of ^{14}C as compared with LWRs; this is because:

(a) The quantities of water exposed to neutron irradiation are much larger than in LWRs;
(b) The heavy water contains more ^{17}O (about 55% above the natural level), since enrichment of ^{17}O occurs during the production of heavy water.

Reduction of ^{17}O to less than the normal level of 0.038% is likely to be uneconomic, but restoring the oxygen in heavy water to the natural concentration could be a practicable proposition. Again, the ALARA principle should be applied to balance the costs of reducing the ^{17}O levels in the heavy water against the benefit of the reduction in collective doses to humans.

One of the pathways for ^{14}C emissions from HWRs is venting and purging the moderator cover gas and the heat transport system. The frequency of venting and purging can be reduced by improving reactor operation practice, which will reduce the release of ^{14}C to the environment.

4.2. REDUCTION OF TRITIUM PRODUCTION AND RELEASE

Tritium is produced in all nuclear reactors as a by-product of ternary fission, which is the largest source of tritium production in power reactors. Tritium is also formed as a product of other reactions, such as reactions with ^{2}H, ^{3}He, ^{6}Li and ^{10}B.

As the largest source of tritium production is within the fuel itself, which typically comprises uranium, plutonium or thorium, it is desirable to keep the tritium produced in close proximity to this source. One way to lower the tritium released into the reactor coolant, and hence the amount of tritium that may be discharged to the environment, is to provide a means within each fuel rod to store the tritium produced.

It has been found that tritium diffuses through stainless steel in a reactor environment at a high rate, the rate being significantly higher than tritium diffusion through zirconium alloys. Tritium also reacts with the zirconium alloy cladding to form a hydride, lessening the release of tritium to the reactor coolant. An apparatus [30] has been developed to remove and store tritium from a gaseous medium; this apparatus can be incorporated in a fuel rod to retain tritium and to minimize the release of tritium to the reactor coolant. The apparatus consists of an internal core of zirconium or zirconium alloy, which retains tritium, and an adherent nickel outer layer, which acts as a protective and selective window for the passage of the tritium.

Increased production of tritium in LWRs has been associated with the presence of deposits known as crud (the word originated as an acronym for Chalk River unidentified deposits). It was initially observed as a black deposit on the first naval nuclear fuel test rod tested in the NRX reactor at Chalk River, Canada. Crud has now become a standard nuclear industry term that refers to minute, solid, corrosion products that become highly radioactive and plate out on reactor rods, components and piping. The actual composition of crud is unique to the water chemistry and fuel failure history of each reactor [31].

Crud deposits consist mainly of iron oxides with high porosities. Uranium from failed fuel elements (tramp fuel), boron and lithium are deposited or trapped in the crud. These materials are concentrated on the surface of the fuel rods, increasing the probability of neutron interactions, which result in an increase in the production of tritium, fission products and activated corrosion products.

In order to minimize the production of tritium and release into the primary coolant of reactors, it is important to:

(a) Improve fuel rod fabrication and the quality of the fuel rods, in order to avoid fuel cladding failure.
(b) Use zircaloy cladding instead of stainless steel cladding, where possible (PWRs, BWRs).
(c) Use enriched (99%) ^{7}Li as lithium hydroxide for pH control in PWRs; it should be noted that the predominant neutron activation reaction in LWRs is $^{6}\mathrm{Li}(n,\alpha)^{3}\mathrm{H}$, with a cross-section of 942 barn.
(d) Isolate as soon as possible defect fuel assemblies in leaktight canisters, in order to avoid polluting spent fuel pools.
(e) Control the coolant chemistry, in order to minimize the deposit of crud on the fuel rods.

In order to prevent the spread of tritium contamination, it is advisable to monitor nuclear sites with tritium measurement systems in several locations, to use impermeable layers under the reactor units to prevent dispersal of tritium in the aquifer, and to allow for the possibility of collecting contaminated water in separate tanks.

5. TECHNOLOGIES TO CAPTURE ^{14}C AND TRITIUM FROM EMISSION STREAMS

One of the objectives of radioactive waste management is to minimize or eliminate releases of contaminants to the environment and to reduce the final waste volume for storage and/or disposal. In general, waste can be housed in containers that provide containment for minimizing the release of contaminants (e.g. tritium and ^{14}C), and volume reduction can be achieved through processes such as compaction or incineration.

Since contaminants in liquid or gaseous waste are mobile and easily migrate to the environment, methods are required to remove these contaminants from the waste streams and to convert the contaminants into a stable waste form (e.g. a solid matrix) for storage and/or disposal. The following sections review technologies for the removal of ^{14}C and tritium from gaseous and liquid waste streams.

5.1. REMOVAL OF ^{14}C FROM GAS STREAMS

For physical and chemical reasons, CO_2 is the carbon compound that can most easily be separated from other gases. It is therefore prudent to oxidize other ^{14}C compounds into $^{14}CO_2$ before its removal [32]. The treatment processes discussed below focus on the removal of CO_2 from gas streams.

The selection of a specific process for the capture and retention of CO_2 from a gaseous stream depends on the volume of gas to be treated, the concentration of CO_2 in the gas stream, the composition of the gas stream and the desired final waste form. Some of the criteria used in the selection of removal technology options include:

(a) Cost considerations;
(b) Simplicity of implementation;
(c) Worker safety.

Various methods for $^{12}CO_2/^{14}CO_2$ removal from gas streams have been studied and have undergone different levels of development. Detailed reviews are made in Refs [10, 12, 33], which examine proven and potential $^{12}CO_2/^{14}CO_2$ removal processes in fuel reprocessing facilities, nuclear power plants and industrial chemical separation plants that handle CO_2. Methods for the removal of $^{12}CO_2/^{14}CO_2$ from gaseous effluents can be broadly divided into four major categories:

(i) A single-step chemical reaction involving absorption in an alkaline earth hydroxide slurry or a solid (e.g. an agitated slurry scrubber or a packed bed column);
(ii) A two-step chemical reaction involving sodium hydroxide and lime slurry (e.g. a double alkali process);
(iii) Physical absorption (e.g. absorption in water, absorption in methanol or absorption in a fluorocarbon solvent);
(iv) Physical adsorption on an active surface (e.g. a molecular sieve process).

5.1.1. Single-step chemical reaction involving absorption in an alkaline earth hydroxide slurry or solid

Two processes in which CO_2 is removed by absorption in an alkaline earth hydroxide medium have been studied extensively and have advanced to a stage ready for demonstration. One process is based on an agitated slurry scrubber configuration and the other is based on a solid packed bed column design. Brief descriptions of these two processes are given below.

5.1.1.1. Alkaline slurry scrubber

Essentially a complete removal of $^{12}CO_2/^{14}CO_2$ from gas streams can be accomplished by reaction with agitated alkaline slurries. The carbonate product is very stable and satisfies many long term storage and/or disposal requirements. The feasibility of CO_2 removal by contacting CO_2 with $Ca(OH)_2$ or $Ba(OH)_2$ slurries in an agitated gas–liquid contactor has been the subject of several studies [34–37]. Agitated slurry scrubbers are often preferred to gas–liquid contacting because of the high interfacial area available for mass transfer (30 m^2/m^3) as compared with other processes, such as packed beds (0.5–3.0 m^2/m^3) [10].

In general, a slurry scrubber consists of a variable-speed agitation system, a gas distribution system and a stirring tank. The slurry concentrations range from 10 wt% to 20 wt%, depending on the application.

Holladay [35] studied the removal of CO_2 with lime slurry in a stirred tank reactor (0.196 m internal diameter and 0.33 m high) and reported that the rate of reaction was fast and that a virtually complete removal of CO_2 could be achieved. The decontamination factor was >100 in a single stage reactor for CO_2 concentrations ranging from 5% to 100% (pure CO_2). The reaction rate was constant up to a 90% utilization of the lime and then rapidly decreased, as did the pH for the remainder of the reaction. Patch et al. [37] studied the removal of CO_2 from an air stream in a continuously sparged, agitated slurry carbonation reactor (0.273 m internal diameter and 0.35 m high). Experimental results indicated that the decontamination factor ranged from 3 to 1200 for $Ca(OH)_2$ slurries and from 60 to 2100 for $Ba(OH)_2$ slurries. For both slurries low values of decontamination factor were observed at higher gas flow rates and lower impeller speeds.

Atomic Energy of Canada Limited (AECL) has recently developed a prototype lime slurry scrubber for the removal of $^{14}CO_2$ from the moderator cover gas in the CANDU system. The scrubber was tested for more than 450 h at various operating conditions using a specially designed helium recycle loop. The results indicated that the slurry scrubber could remove low concentrations of CO_2 (0.04–1000 ppmv of $^{14}CO_2 + {}^{12}CO_2$) from gas streams with a high single pass removal efficiency, high reagent utilization, relatively low system pressure drop and phase entrainment.

5.1.1.2. Alkaline packed bed column

Absorption of CO_2 in solid absorbents (e.g. alkaline earth hydroxides) is another CO_2 removal process. The absorbent is usually arranged in a fixed bed configuration with the gas stream passing through the bed: the gas stream enters the bed, CO_2 is absorbed by the absorbent and the gas stream exits, leaving CO_2 behind.

A number of absorbents, belonging to the group I (alkali metal) and group II (alkaline earth) hydroxides, can remove CO_2 effectively from gas streams; they include ascarite (NaOH on asbestos), $LiOH{\cdot}H_2O$, $Ca(OH)_2$, $Ba(OH)_2$, soda lime ($NaOH–Ca(OH)_2$ mixtures) and baralyme ($Ca(OH)_2–Ba(OH)_2$ mixtures). However, some absorbents are not suitable for $^{14}CO_2$ removal, owing to poor reactant utilization or a lack of a stable final product for storage and disposal (e.g. ascarite, $LiOH{\cdot}H_2O$).

A number of feasibility studies for the removal of CO_2 by $Ca(OH)_2$ [38–42] and $Ba(OH)_2$ [36, 43–45] in a fixed bed configuration have been reported. The studies found that the efficiency of this process is closely related to the amount of excess water in the influent gas.

Researchers at Ontario Hydro (now Ontario Power Generation) developed a process for ^{14}C removal based on the $CO_2–Ca(OH)_2$ reaction. The process was designed for the removal of $^{14}CO_2$ from the moderator cover gas of CANDU reactors [40]. Over 1000 h of pilot scale testing were performed and the test results showed that CO_2 could be effectively removed by $Ca(OH)_2$ at ambient temperature, but a high utilization of absorbent could only be achieved at relatively high humidity (80–100% relative humidity). The process was further developed to remove ^{14}C from the extremely dry nitrogen annulus gas of CANDU nuclear power plants [46].

A demonstration unit based on the solid $Ca(OH)_2$ fixed bed configuration has been built and successfully demonstrated for $^{12}CO_2/^{14}CO_2$ removal from the moderator cover gas in the Nuclear Power Demonstration reactor in Canada [47]. The unit was operated from 27 April to 22 May 1987 for a total of 612 h. No CO_2 was detected downstream of the unit, and a total of 234 g of $^{14}CO_2$ and $^{12}CO_2$ was captured during the demonstration.

A subsequent demonstration of a modified solid $Ca(OH)_2$ fixed bed scrubber for $^{12}CO_2/^{14}CO_2$ removal from the annulus gas system was carried out in 1989 at Pickering generation station (unit 3) in Canada. During the demonstration period a total of 0.56 TBq of $^{14}CO_2$ from the inventory, in addition to 0.17 TBq produced in seven days, was removed by the scrubber. The test results indicated that no $^{14}CO_2$ was detected downstream of the scrubber [47].

A process utilizing fixed bed canisters of $Ba(OH)_2{\cdot}8H_2O$ has been developed at the Oak Ridge National Laboratory (ORNL), Tennessee, USA [43–45]. The study at the ORNL was designed for the treatment of air based (~350 ppmv CO_2) gas streams, such as those potentially present in LWRs. The CO_2 removal systems (0.102 m internal diameter and 0.305 m internal diameter) were tested over 18 000 h at isothermal conditions and over 2100 h at near adiabatic conditions. The researchers at the ORNL concluded that the $Ba(OH)_2{\cdot}8H_2O$ process is capable of high CO_2 removal efficiencies and high reactant utilization, and has acceptable operational characteristics at near ambient conditions.

Recently, AECL has developed a prototype dry bed ^{14}C removal system. The system consists of layers of commercially available absorbent to capture $^{14}CO_2$. The ^{14}C removal system was tested for more than 200 h at various operating conditions. The test results showed that the dry scrubber could remove low concentrations of CO_2 (0.04–1000 ppmv of $^{14}CO_2$ + $^{12}CO_2$) from gas streams with a high single pass removal efficiency, low system pressure drop and phase entrainment.

5.1.2. Two-step chemical reaction involving sodium hydroxide and lime slurry

Scrubbing is a popular commercial method for the removal of one or more constituents from a gaseous stream and involves absorbing into a liquid stream the gaseous constituent to be removed by passing the gaseous stream through the liquid.

5.1.2.1. Double alkali process

Absorption of CO_2 by scrubbing with a caustic aqueous solution is a familiar industrial process. The double alkali process involves scrubbing the gas stream with an aqueous solution of sodium hydroxide in a packed column. The CO_2 is stripped from the gas by the following chemical reaction:

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

The bulk of the treated gas is filtered by roughing and by high efficiency particulate air filters before being released to the environment.

At appropriate intervals the spent scrubbing solution containing mainly Na_2CO_3 is removed from the column to a mixing tank in which calcium hydroxide is added to the solution, causing the carbonate to precipitate as calcium carbonate:

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$$

The solution and precipitate are then pumped to a filtration system, where they are separated. The sodium hydroxide filtrate is cycled back to the absorption column, while the calcium carbonate cake is removed for final disposal as solid radioactive waste by incorporation into cement. The amount of $Ca(OH)_2$ used to precipitate the $CaCO_3$ may have to be metered very carefully to avoid any excess, which would cause saturation of the filtrate with $Ca(OH)_2$. The calcium hydroxide would in turn react in the packed column to form $CaCO_3$, which could plug the packing.

Removal of CO_2 by caustic scrubbing involves absorption accompanied by a chemical reaction. Experience indicates that the use of a 2M sodium hydroxide solution and maintenance of a CO_2 to carbonate conversion of 15–25% will generally yield an optimum absorption of CO_2 [13].

5.1.3. Physical absorption

5.1.3.1. Gas absorption by wet scrubbing

Carbon dioxide can be removed from a gas stream by contacting the stream with water in a counter-current flow packed column. The process depends on normal gas absorption principles.

By studying the solubility of CO_2 in water in conjunction with the design procedure for packed columns, it has been found that a large column is needed to attain almost complete removal of the CO_2. Space limitations in nuclear power plants and reprocessing facilities make this method less feasible than other methods.

5.1.3.2. Ethanolamine scrubbing

Gas scrubbing with ethanolamine ($HOCH_2CH_2NH_2$) is one method for the removal of CO_2 from gaseous streams and involves absorbing the CO_2 into an ethanolamine solution at ambient temperatures in a scrubbing tower; the solute is then steam stripped back out of the scrubbing solution in a second contactor. Such a process removes CO_2 from one gas stream and produces another gas stream somewhat richer in CO_2.

The particular operating problem of ethanolamine is its oxidation to corrosive oxalic acid and glycine, which has been experienced in the gas industry. This would possibly be amplified in a radiochemical application. A product solidification technique would be required in addition to the ethanolamine scrubbing.

5.1.3.3. Absorption in a fluorocarbon solvent

Carbon-14 as CO_2 is quite soluble in liquid refrigerant-12 (R-12), dichlorodifluoromethane. Krypton, xenon and CO_2 are considerably more soluble than other volatile gases that may be in the gaseous effluent stream from a nuclear power reactor, and are favourably temperature sensitive relative to the others. Differences in relative solubility make gas separation possible. Since lower temperatures increase the extraction efficiency, systems are designed to operate at low temperatures (e.g. –17°C).

Two such processes have been developed for spent fuel reprocessing plant off-gases: one at the ORNL and one at the Kernforschungszentrum Karlsruhe, Germany [12]. Both processes are intended for the retention of ^{85}Kr. However, the solubility of CO_2 in R-12 is greater than that of krypton, and the possibility therefore arises of removing ^{14}C from the off-gas stream in the same plant as used for krypton removal.

The ORNL design originally consisted of an absorber, fractionator and stripper, and was later modified into a single column operation containing the three process operations. The product from the stripper column is a krypton–xenon–CO_2 mixture, and further separation is possible by cold traps. When operating in the single column mode, concentration peaks for the various components were observed at various locations along the column, and selective removal of the enriched fluids was deemed possible.

The process developed at Karlsruhe used only two columns, each consisting of absorbing, fractionating and stripping sections. Xenon and CO_2

removal and enrichment are accomplished in the first column, and krypton removal and enrichment in the second column [10]. However, CO_2 removal from a krypton–CO_2 gas mixture may result in contamination of the CO_2 fixation product by ^{85}Kr and may therefore complicate waste disposal.

5.1.4. Physical adsorption on an active surface

The capture of CO_2 by fixed bed adsorption using molecular sieves would require a pre-absorption step to dry the feed gas, removing essentially all the water. A widely used molecular sieve that effectively removes CO_2 is sodium zeolite. The bed being loaded would have to be maintained between –75 and –78°C to achieve good adsorption. Bed temperature is the most important parameter for loading considerations.

The regeneration of a loaded bed is accomplished by heating it to a temperature between 150 and 350°C, then passing a purge gas through the bed at the elevated temperature to remove CO_2. The purge gas would have to be passed through the double alkali process to convert the ^{14}C to a stable waste form for storage and eventual disposal.

The type 13X molecular sieve is one of several types that can be used to remove CO_2. With proper bed regeneration, extremely high removal efficiencies with decontamination factors greater than 100 are possible [10].

Mineo et al. [48] studied the performance of natural mordenite, hydrogenated mordenite and modified hydrogenated mordenite for the removal of $^{14}CO_2$ from dissolver off-gases. They concluded that the modification of hydrogenated mordenite by NaOH resulted in a larger adsorption capacity compared with the other adsorbents. The capacity was found to decrease in the presence of 1% NO_x.

5.1.5. Other methods

It has been suggested that the reaction of CO_2 with magnesium at 600°C could be used for ^{14}C fixation [12]:

$$^{14}CO_2 + 2Mg \rightarrow 2MgO + {}^{14}C$$

The solid carbon product is expected to be stable and suitable for direct immobilization and disposal.

Sakurai et al. [49] used a dry method to decompose $^{14}CO_2$ into elemental ^{14}C through its reaction with H_2 using microwave discharge. The reaction produces CO as an intermediate, and proceeds in two steps:

$$\begin{aligned}&CO_2 + H_2 \rightarrow CO + H_2O\\&CO + H_2 + C_n \rightarrow C_{n+1} + H_2O\end{aligned}$$

where C_n denotes the carbon already deposited on the wall of the discharge tube. The results showed that microwave discharge for a CO_2–H_2 mixture in reduced pressures (~0.67 kPa) reduced CO_2 into carbon. The reduction of CO_2 into CO proceeded fast, and there was a low rate of conversion of CO into carbon.

The recovery of ^{14}C from an irradiated graphite moderator of a decommissioned Calder Hall type power reactor has been studied in Japan [50]. The recovery process consists of three main steps: graphite combustion, ^{14}C enrichment and $^{14}CO_2$ immobilization (Fig. 7). Carbon isotope exchange between CO_2 and carbamate was employed for the ^{14}C enrichment. The process can be described by the following isotope exchange reactions:

$$\begin{aligned}&^{14}CO_2 + R_2N^{12}CO_2^{-1} \leftrightarrow {}^{12}CO_2 + R_2N^{14}CO_2^{-1}\\&^{14}CO_2 + R_2NH^{12}CO_2^{-1} \leftrightarrow {}^{12}CO_2 + R_2NH^{14}CO_2^{-1}\end{aligned}$$

The performance of ^{14}C separation was calculated under the conditions that the concentration of $^{14}CO_2$ in the stripped flow is less than the environ-

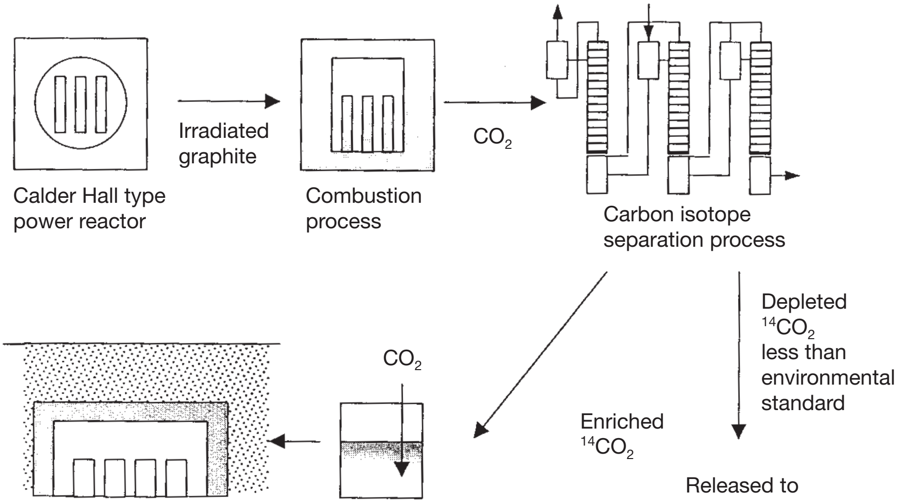

FIG. 7. Carbon-14 recovery process from irradiated graphite.

mental standard (3 Bq/cm^3) and that the stripped flow corresponding to 99% of the feed CO_2 is released into the atmosphere. The process dimensions, which were calculated for the recovery of ^{14}C from 1600 t of graphite used in the Japanese Calder Hall type reactor Tokai 1 (166 MW(e)), are estimated to be 5.2 m in diameter and 16 m in height for continuous operation when using the conventional dibutylamine (DBA) octane solution system. If diethylamine (DEA) octane is used as a working fluid and the process is operated at higher pressures (0.2 MPa), the column dimensions can be decreased to 3.2 m in diameter and 5.7 m in height. If, however, the process is operated at 0.3 MPa with 4M of DEA, then the exchange column can be designed compactly with dimensions of 3.3 m in diameter and 6.7 m in height. For this compact design, the process can be operated batchwise at the rate of four batches per month. These results suggest that the CO_2 carbamater method is applicable for the recovery of ^{14}C from irradiated graphite. In particular, the batch operation, in which the exchange column can be operated simply in a total reflux mode, is an attractive option.

A sophisticated off-gas treatment system has been proposed to enrich $^{14}CO_2$ from graphite incinerator off-gas (Fig. 8). This system, which is based on the separation nozzle process (i.e. the Helicon process), has been used in the past for uranium enrichment and the separation of gaseous isotopes. The treatment system consists of a primary separator for the separation of light gases such as nitrogen, oxygen and steam from the relatively heavy gases $^{12}CO_2$ and $^{14}CO_2$, and a secondary separator to separate $^{14}CO_2$ from $^{12}CO_2$, based on their density difference (i.e. the density of $^{14}CO_2$ is 2.05 g/L and of $^{12}CO_2$ is 1.96 g/L). The enriched stream is expected to contain approximately 80% of the $^{14}CO_2$ of the feed stream. This enriched stream will be neutralized by barium hydroxide to form insoluble barium carbonate [11].

In general, ^{14}C separation methods are costly and require a high energy consumption. Applications of these separation technologies may therefore be limited by their high cost.

5.2. REMOVAL OF ^{14}C FROM LIQUID WASTE

Carbon-14 in aqueous liquid waste is usually in chemical forms of carbonate and/or bicarbonate, depending on the solution pH. Conventional water treatment processes, such as ion exchange, can therefore sufficiently remove ^{14}C as HCO_3^{-1} /CO_3^{-2} from liquid streams.

The amount of ^{14}C in liquid waste produced during reactor operations is relatively small (Table 18). The active liquid waste treatment system installed in a reactor is designed for the removal of other radiochemicals (e.g. ^{60}Co and

^{137}Cs) and some toxic chemicals (e.g. boron, PO_4^{-3} and organics). Carbon-14 in liquid water is expected to be removed by this treatment system. In general, when reporting the discharge water quality from a nuclear facility, ^{14}C is grouped with other beta emitters as gross beta activity in which tritium and ^{90}Sr may be the dominant species.

At fuel reprocessing plants the principal liquid stream containing ^{14}C is the spent caustic solution from the off-gas scrubbing. The ^{14}C (e.g. as Na_2CO_3) can be removed by contacting with compounds of calcium or barium to form more stable carbonate compounds. The solid carbonate is separated from the liquid and is usually solidified by a binding material (e.g. cement) for long term storage and/or disposal.

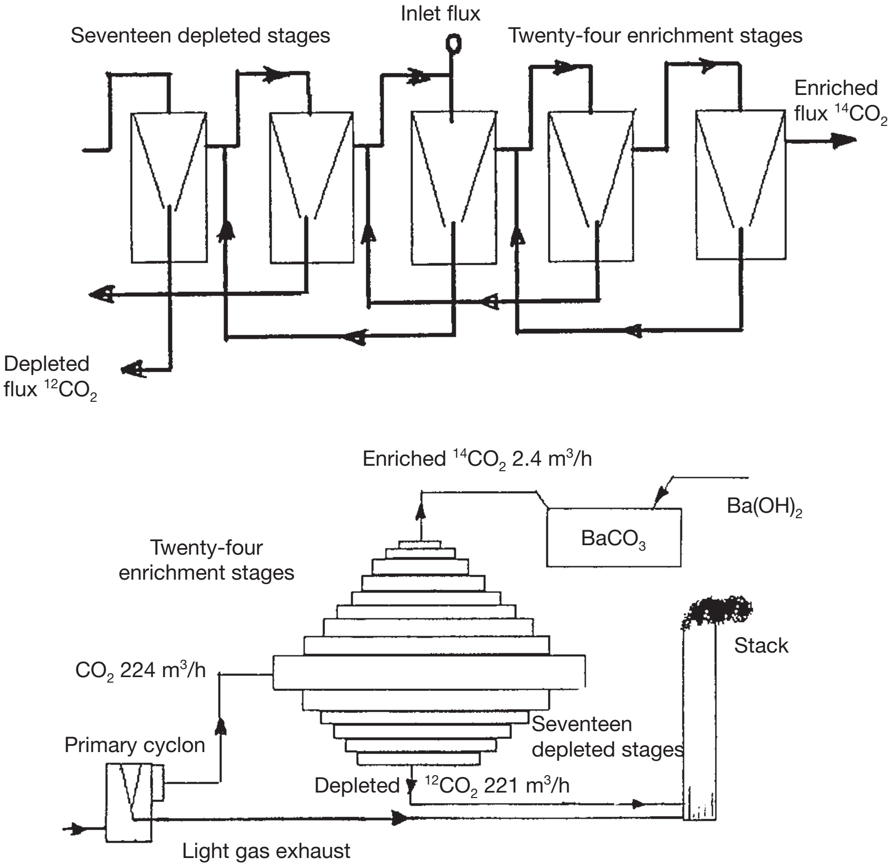

FIG. 8. Processing off-gas from irradiated graphite incineration for ^{14}C recovery.

5.3. SEPARATION OF TRITIUM FROM SPENT FUEL

Tritium removal from gas streams and liquid streams can be uneconomic, especially when the tritium concentration is low. If the goal is the removal or recovery of tritium, it is desirable to apply the removal technologies before additional dilution takes place. However, the common practice in many instances, particularly in reprocessing plants and LWRs, is to allow dilution to take place within the plant processes, followed by further dilution upon release to the environment.

Tritium can be separated from spent fuel prior to the dissolution step in reprocessing plants. The released tritium can then be removed from the evolved gas by means of tritium removal methods. Two technologies have been developed for the separation of tritium as a gas: voloxidation and pyrochemical processing.

5.3.1. Voloxidation

This process was developed as a means of separating tritium from irradiated reactor fuel prior to dissolving the fuel in nitric acid for reprocessing operations. The voloxidation process depends on the oxidation of UO_2 to U_3O_8 in order to break down the crystal lattice and release gases from it. Tritium release efficiencies of greater than 90% are expected from the fuel with this method, which exposes the fuel to 450–500°C for several hours in a rotary kiln. The evolved gas is passed through a catalytic converter to ensure that all the tritium has been converted to HTO, and then it is removed as water in solid absorbents. A large portion of the tritium left in LWR fuel elements is bonded in the zircaloy cladding and will remain with the cladding during fuel dissolution. This process may not work for ThO_2 fuels, since there is no higher oxide of thorium. Metal fuels may also be difficult to treat in this manner because heat generation rates may be difficult to control during oxidation [51].

5.3.2. Pyrochemical processing

Pyrochemical processing involves the application of high temperatures. This approach is considered to be a head end treatment in the reprocessing plant and involves two steps:

(a) Chopping and/or cladding removal;
(b) Treatment of the oxide fuel to effect the release of volatile fission products, including tritium.

Decladding by melting has been studied for stainless steel clad fuels; in principle, it could be used for zirconium clad fuels. Unlike the voloxidation process, in which UO_2 is oxidized to U_3O_8, in this process the second step will normally be a reduction step in which uranium and plutonium metals are produced by reduction in the presence of a molten salt. A mixture of zinc, calcium and magnesium or another reductant alloy and a salt such as calcium chloride is heated with the oxide fuel at about 800–900°C. The principal reaction is:

$$UO_2 + 2Ca \rightarrow 2CaO + U$$

The salt is separated from the metal phase. After distilling the magnesium and zinc for recycling, the uranium and plutonium are sent to the acid dissolver for solvent extraction processing of the aqueous solution [52].

Fission product tritium and noble gases are both released during the decladding and reduction steps and are handled as in the voloxidation process.

5.4. REMOVAL OF TRITIUM FROM GAS STREAMS

In the off-gases from nuclear facilities, tritium can be present as HT or HTO. Removal methods for HT and HTO are briefly discussed below.

5.4.1. Removal of HT

There are non-oxidative processes for the removal of HT that employ hydrogen getters. These getters typically consist of zirconium alloys and compounds. However, the selection of the appropriate getter depends greatly on the other constituents of the gas. The fact that most getters will not tolerate oxygen in the feed stream greatly limits the usefulness of getters for most effluent streams.

5.4.2. Removal of HTO

The typical processes for removing tritium from gas streams involves conversion of HT to HTO followed by the removal of the HTO. A number of methods exist for removing HTO vapour from gaseous streams, depending on the degree of removal required.

5.4.2.1. Molecular sieves

A very high degree of HTO removal can be achieved through the use of molecular sieves. Lakner et al. [53] reported that up to 47 cm^3 of HTO per gram of molecular sieve (at standard temperature and pressure) could be obtained. Absorption on molecular sieves is a reversible process and allows for the regeneration of the molecular sieve and the recovery of the tritium as water vapour by heating to moderate temperatures (e.g. 250°C). In practice, recovery of this tritium is not usually determined to be cost effective. The molecular sieves containing the HTO are typically stored, disposed of as low level waste or the water is transferred to another medium for disposal.

5.4.2.2. Dehumidification

Packed bed or plate columns can be used to counter-currently contact the gas stream with a chilled water stream. The degree of water removal from the system is not great, but the performance may be improved by an exchange of water vapour between the gas and liquid phases. This technique would only be used if the intention is to generate a dilute tritium stream for direct discharge.

5.5. REMOVAL OF TRITIUM FROM LIQUID WASTE

In general, the volumes of liquid waste generated from the fuel cycle can be reduced by recycling; this is true for both reactors and reprocessing plants. This, however, raises the concentration of the tritium in the waste. Methods for removing tritium from liquid waste provide an alternative to the control of tritium emissions and personnel exposure.

The most commonly practised application of tritium removal from liquids is the detritiation of heavy water. In this application, the detritiation and recycling of the heavy water is much more economic than the production of new heavy water.

A number of techniques have been developed, primarily for tritium removal or the detritiation of heavy water (for HWRs). These techniques include electrolysis and catalytic exchange and fractional distillation. Tritium removal from light water, however, requires larger stripping and recovery factors than for heavy water upgrade. To be capable of obtaining the required high recovery, a feasible tritium removal process will require a high isotopic separation factor.

The hydrogen–water chemical exchange process has the required high isotopic separation factor and is suited to a water feed. In addition, the technical feasibility of hydrogen isotopic enrichment through the exchange between hydrogen and water is established.

Previous IAEA reports [23, 54] have described the state of tritium technologies at the time of their publication (1981 and 1984, respectively), whether speculative, in development or in use. Table 28 provides a summary of these technologies and their current status.

5.5.1. Tritium enrichment

The process of detritiating water consists of three main steps [55]:

(a) A front end step that exchanges the tritium to the less toxic hydrogen phase. This can be performed either through chemical exchange in the presence of a platinum based catalyst:

$$HTO + H_2 \leftrightarrow H_2O + HT$$

or through the decomposition of water:

$$2HTO \rightarrow 2HT + O_2$$

(b) A back end process that concentrates the tritium in the hydrogen phase. Cryogenic hydrogen distillation is usually preferred for this step, since other potential processes, such as gas chromatographic methods, are not economic for large scale applications.

(c) A means of stabilizing the concentrated tritium and storing it safety. Uranium metal is used if storage is temporary; titanium is mainly employed for long term storage.

Several technologies exist for the front end step. The most industrially proven process is vapour phase catalytic exchange (VPCE), which was developed and patented by the Commissariat à l’énergie atomique (CEA) in France. The VPCE process normally comprises three to eight stages, each stage consisting of a water evaporator, superheater, catalyst bed and condenser–separator. Since a conventional platinized catalyst is used, superheating is required to minimize steam condensation within the catalyst pores, which would inhibit isotope exchange. Water is fed to the first stage, where it is evaporated and mixed with cold deuterium gas returning from the condenser–separator of the subsequent stage. This gas–vapour mixture is superheated to 200°C prior to entering the catalyst bed, where tritium is exchanged and equilibrated. The deuterium gas, somewhat enriched in tritium, is separated from

TABLE 28. STATUS OF TECHNOLOGIES AND PROGRAMMES DESCRIBED IN PREVIOUS IAEA PUBLICATIONS ON TRITIUM AND TRITIUM WASTE

Process	Technology	Publication	Status in publication	Current status
Heavy water detritiation	Water distillation	TRS[a] 203 [23]	Has been used to remove tritium from D_2O in HWRs at low throughput	Used in ‘upgraders’ at HWRs to remove light water from heavy water
		TRS 234 [54]	Offered as technology that does not require handling of hydrogen gas, but is energy intensive	
	Cryogenic distillation	TRS 203 [23]	Offered as tritium enrichment technology to be used in conjunction with VPCE, LPCE, combined electrolysis and catalyst exchange (CECE) or direct electrolysis	Used in conjunction with LPCE to detritiate heavy water from all operating CANDU reactors in Canada
		TRS 234 [54]	Has operated with a VPCE process in Grenoble, France, since 1972	Continues to operate in Grenoble, France Ontario Hydro built a compact cryogenic distillation system, which operated at the Princeton Plasma Physics Laboratory in the mid-1990s
	Vapour phase catalytic exchange (VPCE)	TRS 203 [23]	Successfully demonstrated with cryogenic distillation in Grenoble, France	Continues to operate in Grenoble, France

TABLE 28. STATUS OF TECHNOLOGIES AND PROGRAMMES DESCRIBED IN PREVIOUS IAEA PUBLICATIONS ON TRITIUM AND TRITIUM WASTE (cont.)

Process	Technology	Publication	Status in publication	Current status
		TRS 234 [54]	Projected to be used by Ontario Hydro in tritium removal systems	Ontario Hydro selected LPCE instead of VPCE for tritium removal
	Liquid phase catalytic exchange (LPCE)	TRS 203 [23]	Proposed as the preferred method for a Canadian detritation process; only demonstrated at the laboratory scale	AECL modified the process at Chalk River Laboratories to use CECE instead of LPCE; it was started up as a demonstration process in 1999
		TRS 234 [54]	Projected to be used by AECL at Chalk River Laboratories	
	Combined electrolysis and catalytic exchange	TRS 203 [23]	Exchange process developed by AECL; one of the candidates for future detritiation systems	CECE system was built at the Mound Facility, Ohio, USA, to detritiate light water from glovebox cleanup operations; it operated in the 1980s
Tritium recovery as gas at fuel reprocessing plants	Volatilization	TRS 203 [23]	Speculative process, not yet developed; drawbacks include high cost and difficulty controlling the exothermic reaction	

TABLE 28. STATUS OF TECHNOLOGIES AND PROGRAMMES DESCRIBED IN PREVIOUS IAEA PUBLICATIONS ON TRITIUM AND TRITIUM WASTE (cont.)

Process	Technology	Publication	Status in publication	Current status
		TRS 234 [54]	Technology not yet fully developed; additional drawback is the behaviour of remaining volatiles (carbon, ruthenium, krypton, iodine)	
Tritium recovery from water at fuel reprocessing plants	Water distillation	TRS 203 [23]	Has been applied at an LWR fuel reprocessing plant	
		TRS 234 [54]	At present there has been no attempt to trap or retain tritium at reprocessing plants	

[a] TRS: Technical Reports Series.

water in the condenser and fed to the back end cryogenic distillation system. The tritium depleted water flows to the evaporator of the subsequent stage.

With the development of a wetproofed catalyst by AECL [56], the catalyst isotopic exchange process can be greatly simplified to a packed catalyst column, with liquid entering from the top and trickling down the column in counter-current contact with deuterium gas that is flowing up. Wetproofing allows the catalyst to operate in liquid or very humid environments. This process, which operates at 50°C, is referred to as liquid phase catalytic exchange (LPCE), and has been patented by AECL. India, the Republic of Korea, the Russian Federation and the USA also report that they have developed a wetproofed catalyst.

A third option for the front end step is combined electrolysis and catalyst exchange (CECE). This process has also been developed and patented by AECL. Unlike the other options, this process performs some pre-enrichment of the tritium stream before sending the deuterium to the cryogenic distillation system. The process consists of LPCE columns and electrolytic cells. The catalyst column is divided into stripping and enriching sections. HTO is fed to the top of the enriching section, in which it picks up tritium from the electrolytic deuterium produced from the water leaving the bottom of the column. A side stream of tritium enriched deuterium gas is taken from the electrolysis cell as feed for the cryogenic distillation system and is returned detritiated higher up in the exchange column. The deuterium gas flowing through the stripping section is stripped of tritium by the detritiated reflux water formed by catalytic recombination with oxygen produced in the electrolytic cells. The detritiated product water is also drawn from the recombiner.

In the late 1980s the USDOE's Mound Facility in Miamisburg, Ohio, USA, also operated a CECE process for light water detritiation.

The last technology option frequently considered for the front end step is electrolysis, in which water is completely electrolysed to hydrogen and oxygen. The hydrogen gas is fed directly to the cryogenic distillation system, where it is detritiated and then sent to a catalytic or frame type recombiner to re-form with the oxygen from the electrolytic cells, to produce the detritiated water product. This option is power intensive and expensive.

5.5.2. Other tritium removal technologies

Other options for tritium phase conversion include water distillation, laser isotope separation and chemical decomposition, but for various reasons none have been considered to be serious contenders [55].

Molecular Separations, Inc., (MSI) [57] has developed a new approach to the separation of diluted HTO from light water. The process uses modified ion exchange resins to selectively adsorb the heavier water molecules, in particular HTO, relative to light water. MSI conducted pilot scale tests using feeds from an operating nuclear power plant and groundwater from USDOE sites. The reported cost of this process is approximately \$2.5/L, with an average of a 70% reduction in tritium content.

Owing to handling and safety considerations, tritiated organic liquid waste is usually converted into HTO and CO_2 prior to further treatment. Catalytic and thermal oxidation are two well established technologies. Other options are wet oxidation based on chemical, electrochemical, biochemical or photochemical principles [58].

Ontario Hydro Technologies has developed a compact, low inventory cryogenic distillation system for use at the Princeton Plasma Physics Laboratory in Princeton, New Jersey, USA. While the system was used for the cleanup of the exhaust from the Tokamak Fusion Test Reactor, the same cryogenic distillation technology is also suitable for the isotope separation step of a tritium recovery process [59].

In 1998 AECL completed a study, commissioned by the USDOE, which examined the detritiation of light water containing very low concentrations of tritium. Of the nine technologies examined, six were judged to be uncompetitive or impractical: water distillation, electrolysis, bithermal ammonia hydrogen, monothermal ammonia hydrogen, laser isotope separation and water permeation. The three leading processes all include chemical exchange: CECE, Girdler sulphide and bithermal hydrogen–water exchange [60].

6. ANALYTICAL AND MONITORING METHODS

Monitoring of ^{14}C and tritium is of key importance to the managers and operators of nuclear facilities. Accurate and reliable methods to measure the concentrations of the contaminants to be released are necessary for proper emission system operation and, more importantly, to demonstrate to the public and regulators that emissions and nuclide concentrations in stored waste are within acceptable limits.

Detection of surface contamination is also of concern for safe plant operation; however, this type of monitoring is more within the scope of radiation protection than waste management and is therefore not covered in this report.

Effluent monitoring systems are intended to measure radionuclides in airborne and liquid effluents before discharge to the environment, while environmental monitoring systems are intended to measure levels of radionuclides in selected environmental media: the two systems are complementary. Effluent monitoring is always required if radiologically significant amounts of radioactive contaminants are being released from a facility or if there is a potential for radiologically significant unplanned releases. Environmental monitoring may also be required if the potential releases of radioactivity could result in a significant dose to critical groups or to the whole population. Environmental monitoring provides a more direct assessment of the levels of radionuclides to which members of the public are exposed. Information on the objectives and design of environmental monitoring programmes and effluent monitoring programmes are given in Refs [61, 62].

6.1. CARBON-14 MONITORING SYSTEMS

6.1.1. Carbon-14 sample collection

6.1.1.1. Air samples

Techniques for sampling $^{14}CO_2$ in air can be either active or passive. Active techniques for air sampling are adapted from the methods developed for sampling and monitoring ^{14}C in reactor stack effluents. In most of these methods air is pulled through a bubbler containing sodium hydroxide or a tube filled with a molecular sieve. The flow rate must be kept low to allow sufficient time for the CO_2 to be trapped. Concentrations of NaOH used for sampling are in the range 0.8–4M.

^{14}CO, $^{14}CH_4$ and other hydrocarbons present in air samples can be measured separately by oxidizing the gas effluent from the first bubbler (to trap $^{14}CO_2$) and capturing the $^{14}CO_2$ produced in a second NaOH bubbler [63–65]. Alternatively, air samples can be oxidized first, in which case they become an integral part of the total $^{14}CO_2$ measured [38, 66]. The different carbon compounds are oxidized under different conditions. CuO [38, 67] and Pd/Pt [63, 68, 69] are the catalysts most commonly used for oxidation processes, at temperatures ranging from 400 to 800°C.

Passive samplers can be liquid or solid. Liquid passive samplers are used at AECL's Chalk River Laboratories. Four-molar NaOH solution is put into plastic trays, covered with nylon mesh and set on stands attached to pointed metal rods, which can be driven into the ground; they are protected from rain and left unattended for one to two weeks [70]. An alternative sampler with filter paper wetted with 0.8M of NaOH solution has been used at AECL's Chalk River Laboratories to absorb $^{14}CO_2$. This system is only good for short term measurements because the NaOH solution would saturate if longer term sampling were attempted. Other passive samplers, such as those used by Otlet et al. [71], use a variant of this passive sampling method.

Solid adsorbents have obvious advantages for handling and transport, and have been used for monitoring reactor stack gases [38, 63]. The use of NaOH pellets as the absorbent in a passive sampler has been examined at AECL's Chalk River Laboratories. A single pellet (100–200 mg) provides more than enough capacity for sampling periods of up to a week.

6.1.1.2. Water samples

Carbon dioxide can be recovered directly from water samples by acidification and purging with an inert gas (e.g. nitrogen or helium) to transfer the gas into a collector. In general, bicarbonate–carbonate in the samples is recovered as barium carbonate on the addition of barium chloride and NaOH to raise the pH to pH10 [70].

Methane in water samples can be recovered by the purging technique. The CO_2 evolved from the samples is captured in liquid nitrogen traps, while the CH_4 proceeds to a furnace, in which it is oxidized to CO_2. This CO_2 is captured in two more traps for later analysis [70].

6.1.1.3. Vegetation and soils

Samples of leaves and needles are collected in new polyethylene bags; these samples are rinsed in distilled water and dried overnight at approximately 80°C prior to storage in glass sealers [70].

Soil samples can be obtained by driving 10 cm lengths of aluminium tubing into the ground. As soon as the core tube is withdrawn, both ends should be capped, to maintain the integrity of the sample until it can be extruded and sliced into sections. A subsample of each section is taken to determine the percentage of water and organic carbon. The remainder of the sample should be stored frozen for later analysis, to prevent bacterial or fungal activity [70].

6.1.2. Carbon-14 sample preparation

Since ^{14}C occurs in both liquid and gaseous streams in reactors and reprocessing plants, analytical methods are required for a variety of sample types. The low energy of the beta radiation and the absence of gamma emissions in ^{14}C decay, plus the fact that other radioactive gases are always present, make it essential to separate the ^{14}C species before any measurement is made [72].

The separation procedure will vary depending on the ^{14}C levels and the impurities expected; for example, Kunz [73] described procedures for separating gases for internal gas proportional counting from various nuclear facilities. The gases separated included argon, krypton, xenon, H_2, CH_4, CO_2 and water vapour.

In reprocessing plants it will be necessary to use more elaborate separation methods than those used for the samples taken from a reactor environment. Braun et al. [32] described a scheme for the separation of ^{14}C as $^{14}CO_2$ from dissolver off-gases. After uranium fuel dissolution, the off-gas comprises air as carrier gas, aerosols, iodine, NO_x, krypton, xenon, CO_2, water and hydrocarbons. The NO_x present in the off-gas sample is extracted by scouring with an aqueous solution to produce HNO_3; the aerosols and iodine are removed by various filtration processes, and any hydrocarbons present are converted to CO_2 by oxidation.

In general, the sample preparation method will depend on the nature and physical state of the sample, and also on the measurement technique adopted. In all cases, however, the ^{14}C in the sample is at some stage converted into CO_2. For air and water samples, CO_2 is released from either NaOH solution or precipitated $BaCO_3$ on neutralization of the sample with acid. Carbon dioxide adsorbed on a molecular sieve is usually removed by heating and eluting with nitrogen or helium gas. Solid samples are usually combusted to CO_2 if they are combustible [70].

Following its release, CO_2 prior to ^{14}C catalysis can be collected as a gas, either in a gas bag or a cold trap, and subsequently:

(a) Purified by capturing on activated charcoal [74];
(b) Absorbed on solid $Ca(OH)_2$ [38];
(c) Converted to CH_4 by catalytic hydrogenation [75];
(d) Converted to C_2H_2 by synthesis of LiC_2 and its subsequent hydrolysis [70];
(e) Converted to benzene by trimerization of C_2H_2 [70, 76];
(f) Absorbed directly into an amine such as Carbo-Sorb [70];
(g) Reduced to graphite with magnesium metal or H_2, using iron or cobalt as a catalyst [77];
(h) Trapped in NaOH [78], followed by precipitation as $BaCO_3$ or $CaCO_3$ or by direct release into a scintillation cocktail for measurement.

6.1.3. Analytical methods for ^{14}C

There have been many reviews of ^{14}C analytical techniques (e.g. Refs [21, 67, 69, 79]). Brief summaries of the available analytical techniques are given in Sections 6.1.3.1–6.1.3.3.

6.1.3.1. Gas counting

Gas proportional counters combine the advantages of high counting efficiency with pulse height discrimination. Proportional tube volumes range from 5 mL to 7.5 L. Methane as the counter filling has been shown to provide better resolution and gas gain stability, whereas CO_2 is easier to prepare and handle but must be purified from the sample [75]. Efficiencies greater than 90% and backgrounds of 0.1 cpm are at present achievable for $^{14}CO_2$ [70].

6.1.3.2. Liquid scintillation counting

As a result of large improvements in performance, liquid scintillation spectrometry is now the measurement technique employed for ^{14}C at most laboratories. Efficiencies of 80% and backgrounds of approximately 5 cpm are possible on a routine basis; backgrounds of less than 0.5 cpm are achievable with anti-coincidence shields. The nature of the scintillation cocktail chosen will depend on the final sample form, vials to be used, etc. Many reviews of this technique can be found [80–82].

6.1.3.3. Accelerator mass spectrometry

Radiocarbon measurement using single atom counting by accelerator mass spectrometry provides high precision measurements with extremely small samples [83]. At AECL's Chalk River Laboratories samples were prepared by reduction of CO_2 to graphite by reacting the gas with red hot magnesium turnings, using iron powder to facilitate packing the purified carbon into the target cones. Current reduction techniques use H_2 with an iron or cobalt catalyst [77]. This method has been used mostly in the dating of very small amounts of material, but the cost per measurement at dedicated accelerator mass spectrometry laboratories is competitive with that of other methods [70].

6.1.4. Carbon-14 monitoring methods

Monitoring systems for ^{14}C used in nuclear facilities have been developed based on the sampling methods discussed above; for example, Kunz [84] developed a continuous sampler to monitor the ^{14}C levels released from an LWR. The system consisted of an oxidizing furnace, solid absorbents for H_2O and CO_2, a metering valve, a flow meter and a pump. The sampled gas was passed at 600°C through a tube furnace containing pellets of palladium on alumina and platinum on alumina to oxidize all carbon species (CH_4, C_2H_6, CO, etc.) to CO_2. From the furnace, the gas flowed through an absorbent to remove water vapour and then through a cartridge containing an absorbent to capture the CO_2. Commercially available solid absorbents were used for both the water vapour (Drierite) and CO_2 (Ascarite). The absorbent cartridges were changed at regular intervals.

To measure the ^{14}C in the sample, CO_2 was evolved from the Ascarite by acidification. A portion of the recovered CO_2 was chromatographically purified, and the ^{14}C concentration was measured in a gas proportional counter.

Kabat [38] developed a similar system, in which the gaseous organic compounds and CO are first oxidized to CO_2 by catalyst (CuO) combustion; CO_2 is then absorbed on solid $Ca(OH)_2$ at elevated temperatures. Subsequently, $^{14}CO_2$ is liberated by thermal decomposition of $Ca^{14}CO_3$ and is scrubbed in an NaOH solution and measured by liquid scintillation counting.

6.2. TRITIUM MONITORING SYSTEMS

6.2.1. Air samples

Tritium may be present in air as tritium gas or as tritium oxide. Tritium gas cannot be trapped as easily as tritium oxide, and it must first be converted into tritium oxide by passing the air stream over heated copper oxide wool [62].

Sampling of air by a tritium sampler and subsequent measurement of the accumulated tritium activity by liquid scintillation counting is a simple, reliable and inexpensive method of monitoring for HTO vapour in air [85]. In most sampling methods air is passed through a bubbler containing water or a tube filled with a molecular sieve or silica gel. Studies (e.g. Ref. [86]) have shown that the collection efficiency of a single water bubbler exceeds 95% for short term sampling (~10 min), even at an air flow rate as high as 10 L/min. An ethylene glycol and water mixture is used in place of water in the bubbler to minimize evaporative losses in longer term sampling or for use under freezing conditions.

Many different types of gas sampler have been developed and used for measuring very small quantities of tritium in very large volumes of gas. These samplers are used to measure quantities of tritium released through a facility's stack and for environmental monitoring at a site. Stack exhaust gas monitoring systems generally use an ionization chamber to measure tritium in stack gases and a gas sampler to measure the extremely low levels of tritium that cannot be measured by an ionization chamber.

Most of the stack gas samplers are of a similar design as the ethylene glycol sampling system developed at Mound Laboratories, Ohio, USA. A commercial version of this system is now available. In this system, a sample of gas from the stack is circulated through six ethylene glycol bubblers in series. The first three bubblers remove tritium in the form of HTO, DTO and T_2O. The gas stream is passed through a heated catalytic reactor, in which tritium in the form of HT, DT, T_2 and CH_xT_y is cracked and oxidized to form water. This sample is then passed through three more ethylene glycol bubblers to remove the tritium gas, which is now in the form of water. After a period of a few hours to days, a sample of the ethylene glycol from each bubbler is removed and counted using a scintillation counter to determine the quantity of tritium in each bubbler. The tritium recovered from the first three bubblers is proportional to the tritium in liquid form contained in the stack gases, and the tritium recovered in the last three bubblers is proportional to the quantity of tritium in gaseous form contained in the exhaust gases.

Owing to the extremely small quantity of tritium contained in the atmospheric gases surrounding a tritium facility, environmental gas samplers use higher flow rate sampler systems than those required for stack monitoring, and, in general, collect the water on molecular sieve traps. The water collected on the molecular sieve traps is then recovered from the trap and the tritium concentration of the gas passing through the trap is calculated from the tritium concentration of the collected water, the gas flow rate through the trap and the sampling time.

The use of solid adsorbents such as a molecular sieve or silica gel is particularly suited to long term sampling to establish long term tritium contamination levels in the workplace. The tritium oxide accumulated in the sampler is extracted by heating and the water collected is analysed for tritium by liquid scintillation counting.

Both the liquid and solid samplers discussed above require the use of an air pump as well as a means of measuring and controlling the sampling flow at a constant rate over the sampling period. A passive diffusion sampler has been developed in Canada [87, 88]. The sampler consists of a standard 20 mL scintillation vial with a vial lid modified to contain a stainless steel insert with an accurate diffusion orifice in the centre. HTO vapour diffuses through the orifice and is trapped by an appropriate HTO sink, such as de-ionized water. The rate at which HTO in air enters the vial is determined by the diffusion rate of the diffusion orifice. At the end of the sampling period, 1 mL of water is added to the vial; after an equilibration period of about 1 min, 15 mL of liquid scintillation cocktail is added and mixed with the contents of the vial, which is then measured for tritium in a liquid scintillation counter. The diffusion sampler is less expensive and easier to service than the active tritium samplers discussed above. In addition, the diffusion sampler does not require an air pump or power supply. These features make diffusion samplers very attractive for routine outdoor tritium in-air sampling. Field evaluations of this passive tritium sampler have been performed at AECL's Chalk River Laboratories and at Ontario Power Generation's nuclear power plants in Canada [89–91]. The results have indicated that the passive sampler can be used to measure HTO vapour in air at concentrations as low as 1 Bq/m^3 over a month.

Since HTO is more toxic than HT (>10 000 times greater), it may be desirable to know the relative amounts of each species. In the case of stack monitoring, discrete samples of the stack effluent should be taken using active samplers such as water bubblers. A technique for differential monitoring uses a desiccant cartridge in the sampling line of an ionization chamber monitor. The result is a measurement of the HT concentration. The total tritium concentration is determined without the cartridge. Subtraction of HT from the total produces the HTO concentration [21].

Another technique uses a semi-permeable membrane tube bundle in the sampling line to separate HTO from HT, which is routed to an HTO monitor. After removing the remaining HTO with another membrane, the sampled air is directed to an HT monitor. This technique is slower than the one using a desiccant cartridge, but it can be adapted to measure tritium in the presence of noble gases or other radioactive gases by adding a catalyst after the HTO dryers, followed by additional membrane dryers for the HTO [21].

6.2.2. Samples of liquids

Tritium in liquid samples (e.g. wastewater and groundwater) is almost universally measured by liquid scintillation counting; however, the liquid must be compatible with the cocktail. Certain chemicals in a liquid sample can degrade the cocktail, others may retain much of the tritium and still others result in a high degree of quenching, therefore the sample should be pretreated prior to the counting. In addition, samples that contain peroxide or that are alkaline may result in chemiluminescence, which can interfere with measurement. Such samples should be neutralized before counting [21].

6.2.3. Tritium analytical methods and monitoring systems

Several different types of instrument can be used to detect and measure tritium in the operation of a facility [9, 62]. Examples and a discussion of such instruments are given in Sections 6.2.3.1–6.2.3.10.

6.2.3.1. Ionization chambers

Fixed ionization chambers are the most widely used instruments for measuring gaseous forms of tritium in laboratories and in process monitoring applications. Such simple devices require only an electrically polarized ionization chamber, suitable electronics and a method for moving the gas sample through the chamber, such as a pump.

Tritium decays to ^{3}He by the ejection of a beta particle. The beta particle generated by the decay of tritium ionizes the surrounding gas. The number of ions produced due to the loss of energy of the beta particle is a function of the type of gas. A sample of gas is collected in the ionization chamber and the ionization current is measured. The resulting chamber ionization current is proportional to the quantity of tritium in the gas. The larger the measuring chamber volume the higher the output current and the easier it is to measure. However, as the volume of the chamber increases, the longer it will take to obtain an accurate measurement. Chamber volumes typically range from a tenth to a few tens of litres, depending on the required sensitivity [21]. Modern electronic systems have solved most of the problems associated with measuring small ionization currents in small volumes, and, as a result, the volume of ionization chambers has been reduced over the years from 50 L down to 1 or 2 L. Most tritium measuring instruments use an ionization chamber.

Although most ionization chambers are the flow-through type that requires a pump to move the gas, a number of facilities use open window or perforated wall chambers. These chambers, which employ a dust cover to protect the chamber from particulates, allow the air or gas to penetrate through the wall to the inside chamber without the need for a pump. These instruments are used as single point monitors to monitor rooms, hoods, gloveboxes and ducts.

6.2.3.2. Proportional counters

Gas proportional counters can be used to measure the amount of tritium contained in a gas. A sample of the gas to be monitored is mixed with a counting gas and passed through a proportional counter tube, in which the pulses caused by the decay of tritium are counted. Proportional counter monitors can be used for most gas monitoring applications and are also used to measure surface contamination.

6.2.3.3. *Scintillation crystal detectors*

Scintillation detector systems are used to measure the total mole per cent of tritium in a sample of gas, independent of the chemical composition of the tritium in the gas (HT, DT, T_2 and CH_xT_y). A sample of the gas is introduced into a measurement chamber at low pressure, generally less than a few torr (approximately 1–5 kPa). The chamber contains a scintillation crystal, which is exposed to the tritium as it decays. The light pulse produced in the scintillation crystal is either counted or is used to produce a current that is proportional to the mole per cent tritium contained in the gas sample. Crystal scintillation detection is generally used to measure the mole per cent of tritium in gases containing high concentrations of tritium.

6.2.3.4. *Mass spectrometers*

Magnetic sector, quadrupole and drift tube mass spectrometers are used as analytical tools to measure the individual components that make up the gas being measured. Mass spectrometers are generally used for assay and accountability or for scientific purposes. A sample of the gas to be measured is introduced at low pressure (approximately 1–5 kPa) into a chamber and ionized. The ions produced are then measured by a means that discriminates on mass. The number of ions produced at each mass is measured and is proportional to the partial pressure of the component in the gas sample. Light isotope, drift tube mass spectrometers require a large capital investment and a skilled staff for operation, and, in some cases, may not be cost effective. Quadrupole mass spectrometers and crystal scintillation detectors are much less expensive, but still require operation by knowledgeable, well trained personnel.

6.2.3.5. *Liquid scintillation counters*

Owing to the need to measure removable tritium on surfaces and in the body water of workers, almost all tritium facilities are equipped with or have access to a liquid scintillation counter. If a scintillation counter is not available on the site, the service can generally be purchased from a local firm. Liquid scintillation counters are used to measure the quantity of tritium on surfaces, in liquids and in dissolved samples. For removable surface contamination measurements, a wipe of the surface to be measured is taken using dry filter paper or a cotton swab. The filter paper or cotton swab is then placed in a scintillation cocktail and the quantity of tritium is measured by counting the light flashes that occur in the scintillation cocktail as the tritium decays. The surface contamination is then calculated in units of dpm (100 cm^2)$^{-1}$. For liquid measurement, a sample of the liquid to be measured is placed in the liquid scintillation cocktail and measured. The tritium concentration of the liquid is calculated in Bq/mL or Ci/mL. For solids measurement, a known weight of a material is dissolved to produce a liquid and then the liquid is sampled and measured in the scintillation counter. The quantity of tritium is then calculated in units of in Bq/g or Ci/g of the original solid.

6.2.3.6. Portable room air monitors

Several hand held portable room air monitors are on the market, and their capabilities and ranges vary as a function of the manufacturer and the purpose for which they were designed. It is convenient in some activities to have the capability to connect a small hose to the monitor so that it may be used to detect tritium leaks around equipment.

6.2.3.7. Fixed station room air monitors

Fixed station monitors are designed to be installed in fixed locations and to be used to monitor the room air tritium concentration. Depending upon the manufacturer, they may have several ranges, may be equipped with one or two alarm set points and may have audible as well as visual alarms.

6.2.3.8. Glovebox atmosphere monitors

Glovebox monitors may be open mesh or closed ionization chambers and are designed to monitor the higher levels of tritium inside glovebox containment systems. Ionization chambers operated in a dry glovebox environment have a tendency to become more contaminated with tritium than those operated in air, which can lead to false high readings and require frequent cleaning or the adjustment of alarm set points. Gold plated and virtual wall ionization chambers have been used to reduce this tendency for monitor contamination.

6.2.3.9. Hood and exhaust duct air monitors

Hood and exhaust duct air monitors are similar to fixed station monitors in range and characteristics.

6.2.3.10. Exhaust stack air monitors

Exhaust stack monitors are similar to fixed station air monitors, except that they generally have larger ionization chambers to increase the sensitivity of the monitor.

6.2.4. Specialized instrumentation

There are many other types of specialized devices and/or instrumentation vendors, and some may be superior to those discussed here. No endorsement of these devices should be inferred by the reader.

6.2.4.1. Remote field tritium analysis system

The Field Deployable Tritium Analysis System (FDTAS) was developed for the remote, in situ analysis of tritium in surface waters and groundwaters. The system uses automated liquid scintillation counting techniques, and in laboratory and field tests has shown sufficient sensitivity to measure tritium in water samples at environmental levels (10 Bq/L (~270 pCi/L) for a 100 min count) on a near real time basis. The prototype FDTAS consists of several major components: a multi-port, fixed volume sampler; an on-line water purification system using single use tritium columns; a tritium detector employing liquid scintillation counting techniques; and serial communications devices. The sampling and water purification system, referred to as the autosampler, is controlled by a logic controller preprogrammed to perform a well defined sampling, purification and flushing protocol. The tritium analyser contains custom software in the local computer for controlling the mixing of the purified sample with a liquid scintillation cocktail, for counting and for flushing the cell. An external standard is used to verify system performance and for quench correction. All operations are initiated and monitored at the remote computer through standard telephone line communications.

6.2.4.2. Surface activity monitor

A new surface activity monitor (SAM) for measuring tritium on metal (electrically conducting) and non-metal (electrically non-conducting) surfaces has been recently developed at Ontario Hydro Technologies. The monitor detects tritium on the surface and in the near surface regions by means of primary ionization in air due to the outward electron flux from the contaminated surface. The resulting ion pairs are measured by imposing an electric field between the contaminated surface and a collector plate. A simple theoretical model relates the total tritium concentration on the surface to the measured current.

Experiments benchmarking the application of the surface activity monitor on metal surfaces against independent measurement techniques of aqueous dissolution and thermal desorption show equivalence in the total tritium activities measured. Comparison of surface activity monitor measurements with the dry polystyrene smear protocol has shown that the two methods are complementary. Smearing measures the activity removed by the smear action, which can be used to infer the total activity on the surface. Surface activity monitor measurements determine the total activity on the surface, which can be used to infer removable activity. Ontario Power Generation has stated that this device is the only surface monitor for tritium that provides an absolute measurement of the total activity on metallic surfaces.

Application of the surface activity monitor on a variety of non-conducting surfaces has been demonstrated. Some of the non-conducting surfaces examined include paper, concrete, granite and wood. Experiments are under way to extend the database of non-conducting materials measured by SAMs and to catalogue the associated collection efficiencies. Currently, the SAM is commercially available in two models, QP100 and QP200, which have measurement ranges of 0–200 nCi/cm^2 and 0–200 µCi/cm^2, respectively.

6.2.4.3. Breathalyser

A device undergoing development in Canada is the Scintrex tritium in breath monitor. It is an automatic monitor dedicated to health physics and radiation biology applications. The tritium in breath monitor measures levels of exhaled tritium within 5 min of sampling, thus saving considerable time and effort in the monitoring process. This rapid assessment has a sensitivity level of 5 µCi/L urine equivalent, which may be sufficient for identifying cautionary levels of in-body tritium. Preliminary development of this equipment was performed at AECL.

7. IMMOBILIZATION AND WASTE FORM EVALUATION

Immobilization is one of the options for dealing with radioactive waste. The objective of immobilization is to convert radioactive waste into a stable form, which minimizes the probability of radionuclide release to the environment during interim storage, transport and final disposal. The immobilized waste leaving the nuclear facility should therefore have such chemical, mechanical, thermal and radiolytic stability that its integrity can be assured over the time required for the contained radionuclides to decay to an acceptable level. Although environmental considerations are paramount, it is also important from an economic point of view that the process cost, as well as the volume and weight of the immobilized waste forms produced, be as low as possible.

Many types of solid and liquid radioactive waste are immobilized by solidification prior to disposal. Solidification includes both fixation (chemical and physical binding of the waste within a solidifying agent) and encapsulation (physically surrounding the waste within an agent). It should be noted that solidification by itself does not result in a volume reduction of the waste, and, in fact, will result in an overall volume increase. However, solidification is quite important in terms of immobilization of the waste for transport, storage or disposal. The process should be reliable, easy to operate and maintain, and should yield a product with the following properties [92]:

(a) A monolith, with no free standing water;
(b) Free standing without an outer container;
(c) Little or no degradation of the product with time;
(d) An acceptable degree of radiation damage over the design storage period;
(e) Compatibility between the matrix material and the solidified waste;
(f) Sufficient mechanical resistance to compression, shock, erosion, etc.;
(g) A low leaching rate;
(h) No detrimental effects when exposed to fire;
(i) Readily reproducible on an industrial scale;
(j) A low overall production cost.

A number of immobilization technologies have been studied and developed for waste containing ^{14}C and tritium. The following sections describe the immobilization techniques that have been developed and used.

7.1. IMMOBILIZATION TECHNOLOGIES FOR WASTE CONTAINING ^{14}C

Cements, bitumen, polymers and ceramics, including glasses and oxide ceramics, play an important role in the immobilization of radioactive waste. However, some of these methods are costly, are difficult to operate and produce products that may be combustible or susceptible to radiation damage.

Among these methods, cementation has the advantage of being a simple, low temperature process utilizing inexpensive raw materials.

7.1.1. Cementation

Carbon-14 is usually removed from gaseous and liquid streams as carbonate $MeCO_3$ (Me = Ca, Sr, Ba), typically calcium carbonate, $CaCO_3$ or barium carbonate, $BaCO_3$, as described in Section 5. However, one disadvantage of $CaCO_3$ and $BaCO_3$ is their high solubility in low pH media [93]. At a given calcium activity, the equilibrium total carbonate concentration in a solution is about 1000 times higher at pH7 than at pH10. The alkalinity and high calcium content of Portland cement help to minimize this problem and make cement an appropriate medium for immobilizing these carbonates [94].

Cement compounds have a low solubility, a good thermal stability and are easy to prepare; for example, slurries of carbonate from the double alkali process can be directly incorporated into cement after settling, without the need to obtain the carbonate in a dry condition. The carbonate products from calcium hydroxide or barium hydroxide processes (e.g. a dry bed column or canister) can be incorporated into a grout to form a stable matrix. Alternatively, a cement or grout-like solution can be pumped into each canister and/or the entire canister can be encapsulated in cement. Various assessment studies have envisaged the use of cement waste forms [95–99].

Leaching data for cement composites of $CaCO_3$, $SrCO_3$, $BaCO_3$, $PbCO_3$ and K_2CO_3 have been reported [99]. Differences in leaching behaviour between these cemented waste forms are relatively small, but $CaCO_3$ appears to perform the best.

Relatively little work has been conducted to assess the proper loading of a cement matrix. Since ^{14}C is a weak beta emitter, the effects of long term exposure to radiation, gas evolution from radiolysis and heat generation on the stability of the concrete matrix will be minimal. Bush et al. [12] suggest a cement loading of 30 wt% for both $BaCO_3$ and $CaCO_3$.

Methods for reducing the leach rate from cement blocks have been investigated. Coating the blocks with bitumen or polymers has been studied, but is not currently used for waste containing ^{14}C [12]. Extensive research into cement chemistry has been carried out in order to improve cement matrix characteristics.

7.1.2. Other methods

Incorporating waste containing ^{14}C into bitumen or into certain proprietary polymers is an alternative to the use of cement. However, the long term stability of an organic matrix is questionable. No studies have been made of these possibilities for carbonate waste, but the alternative materials would have to offer sufficient overall advantages to outweigh the lower cost of cement. Incorporation of carbon instead of carbonate into cement or bitumen is unlikely to present difficulties [12]. Research on more complex carbonates that are less soluble than $MeCO_3$ in near neutral media is ongoing. Four additional candidate phases for ^{14}C immobilization have been proposed by Taylor [93]: bismuthite, $(BiO)_2CO_3$; rhodochrosite, $MnCO_3$; hydrocerussite, $Pb_3(OH)_2(CO_3)_2$; and bastnaesite, $(Ce,La)(CO_3)F$. Bismuthite appears to have the lowest solubility of the four candidate forms.

7.2. IMMOBILIZATION TECHNOLOGIES FOR WASTE CONTAINING TRITIUM

Owing to the relatively short half-life of tritium (12.3 years), it is feasible to store waste containing tritium until the tritium has decayed by a significant amount. This approach would not require immobilization, giving the potential for the waste to be released. However, the risks associated with this method need to be evaluated based on experience gained in nuclear operations.

A number of compounds containing hydrogen can be utilized as immobilization or storage media for tritium, including hydrates, hydroxides, hydrides, organic solids and absorbents. In addition, materials that adsorb compounds containing hydrogen can also be considered [52, 100]. In most cases the immobilization of tritium by a chemical or physical means is not sufficient to meet the WARs for storage, transport or disposal. For long term storage or disposal, the immobilized media must be put into some type of high integrity containment, such as sealed stainless steel vessels. Specific requirements for additional containment will vary with the waste form and the storage or disposal site.

The factors important to the evaluation of tritium immobilization or storage media are complex and must be considered together in determining the economic and environmental consequences of a particular choice. It is unlikely that only one material will best meet all the criteria and requirements, and the particular waste composition may strongly influence the choice of compound.

Heat generation by tritiated waste is of little concern, owing to the low energy associated with tritium decay (18.1 keV), which produces 2.89×10^{-15} W/Bq of tritium. Similarly, the rate of ^3He production is generally small. However, container pressurization due to ^3He production and composite radiolysis should be considered for high level tritiated waste.

7.2.1. Drying agents

Many types of drying agent may be suitable for tritium immobilization or storage, including silica gel, activated alumina, calcium sulphate and molecular sieves. These drying agents are of value for the removal of water vapour from air or other gases, owing to their ability to absorb water rapidly. For long term storage these materials would have to be containerized to prevent contact with water and water vapour, which would result in tritium release. All these drying agents are stable solids, are widely used for commercial applications and their properties have been thoroughly studied. Among these drying agents, silica gel and molecular sieves have been found to have better characteristics than the other agents, but short term tritium exchange rates (with water) are of the order of 10^{-3}–10^{-4} per day.

Silica gel has a high water absorption capacity, being capable of absorbing 40 wt% water; however, it binds water strongly and exhibits low water vapour pressures only at a low loading. Molecular sieves exhibit high water absorption capacities and flatter isotherms than silica gel. Their capacities are typically 10–20%, based on dry weight, and they are resistant to regeneration by heating and to many chemical environments.

The technology of the use of drying agents to remove HTO vapour from a gas stream or a liquid effluent is well developed. Containerization and the encapsulation of loaded drying agents in concrete and polymers is also available.

7.2.2. Hydraulic cements

Hydrated silicates, such as hydraulic cements and clays, also exhibit desirable properties for immobilization or the storage of tritium as HTO. The use of cement to encapsulate $^{3}H_2O$ can be considered to be a suitable option, as cement is widely used for the immobilization of low and intermediate level waste containing a wide range of radionuclides [101]. Portland cement may be the cheapest material that will bind HTO strongly and have a moderately low exchange rate.

The strength and chemical resistance of the hardened cement block is dependent on the amount of water incorporated into the cement. Typical water to cement ratios of 0.3 to 0.5 are used, depending on the type of cement and any additives used. Initial loss of HTO from cement blocks exposed to moisture can be high (up to 25% in the first week), although this reduces with time [102].

Although concrete is a monolithic solid, it is quite porous and thus a gradual release of tritium can be expected. The leaching of tritium from cement blocks in an aqueous environment has been studied. Typically, the fractional release of tritium per day is of the order of 1 × 10^{-2} for the first month, but decreases with time. This rate of tritium release can be decreased by the application of coatings to the cement block or by polymer impregnation [52]. Studies have been carried out to evaluate materials added to, or coated on, cement to improve its tritium retention [26]. An improvement in release rate is shown for epoxy coatings, particularly when used in combination with other materials. Cement coated with coal tar based paint or with paraffin releases significantly less tritium than uncoated cement. In general, incorporation of tritiated water into cement blocks without further encapsulation or additional containerization does not appear to give useful retention times, owing to the high release rate of tritium from a cement matrix.

Encapsulation in cement is also utilized as a means of immobilizing hulls from spent fuel shearing and dissolution processes. These hulls may contain a significant amount of the tritium formed in the reactor, as well as a number of other radionuclides, such as ^{14}C.

7.2.3. Organic agents

Many organic compounds with carbon–tritium bonds exhibit a slow rate of tritium exchange with the hydrogen of water, and thus exposure of the environment may occur without a significant loss of tritium. Polymeric hydrocarbons are of particular interest, owing to their low volatility, chemical stability and hydrophobic nature. Polymeric materials under study for tritium fixation and storage include polyacetylene, Bakelite analogue polymers, polyacrylonitrile, polyacrylate and polystyrene. Owing to their high cost, polymeric materials appear to be best suited to applications involving high level tritiated waste.

7.2.4. Hydrides

Metal hydrides can be formed with a large number of metals, but only certain metals have the necessary properties for the immobilization and long term storage of tritium. The metallic hydrides of zirconium, titanium, hafnium, yttrium, niobium, tantalum and uranium have been considered for tritium fixation and disposal applications. A good candidate hydride must be stable when exposed to water and air and have a low dissociation pressure, which leaves zirconium, titanium, hafnium and yttrium as possible materials. The formation of metal hydrides requires the generation of tritium gas (HT or T_2) to react with the metal. This can be achieved by electrolysis of the HTO.

Hydrides have been used for the temporary storage of concentrated tritium. The use of uranium beds for trapping tritium gas and storage as UH_3 is currently practised. However, the pyrophoric nature of uranium hydride makes it unsuitable for long term storage, and it is unsuitable for permanent disposal. Titanium and zirconium hydrides have been identified as compounds that have properties suitable for tritium immobilization: low dissolution pressures and little reactivity with air and water at normal storage temperatures. Tritium gas can be recovered by heating the hydride. Leach rates of tritium from these metal hydrides have been measured over a period of 600 days [103] and have been shown to be very low, with incremental leach rates in the range of 10^{-6} to 10^{-9} cm/day. The cumulative fractional release was less than 0.05% over 600 days.

Development of this immobilization technology has been carried out to investigate the effect of different metal surface morphologies. The risks of ignition of the hydrides have also been investigated.

7.3. ASSESSMENT OF IMMOBILIZED WASTE FORM AND QUALITY CONTROL

The variations that occur in the physical and chemical properties of the waste mean that the immobilization process must be adjusted in each case to give a satisfactory waste form. The setting of suitability criteria and arrangment of the properties in order of importance are difficult and depend on local circumstances and the methods selected. It should be noted that the performance requirements of the waste form for storage, transport and disposal are likely to be set by the WARs.

Some important specific requirements for the properties of immobilized waste forms and the selection of the immobilization technique are:

(a) Thermal stability: Heat generated from radiation may lead to thermal decomposition of the waste form during storage and disposal.
(b) Oxidative stability: Oxidation is one of the causes of solid matrix destruction and release of radionuclides from the matrix.
(c) Resistance to water: Waste forms may be exposed to leaching by natural waters of various compositions, depending on the storage and disposal strategy adopted. Low solubility, hydrolytic stability and resistance to leaching are important in ensuring the gradual release of radionuclides under such conditions.
(d) Resistance to radiolysis: In principle, radiolysis may lead to gas evolution, swelling or deterioration of the mechanical properties of the waste form.

(e) Mechanical properties: These should be adequate to ensure the integrity of the waste form, especially during transport, storage and the act of disposal.
(f) Specific activity: This is an important determinant of the acceptability for various transport, storage and disposal options.
(g) Other factors: Compactness and low cost are generally desirable features. Ease of preparation and low dose rates to operators are also desirable.

These requirements are general for all waste forms and have been discussed in various publications [101, 102, 104–109].

Once the method of waste immobilization has been selected, an assessment programme must be implemented to ensure that the waste form will meet the criteria for storage, transport and disposal (i.e. will meet the disposal facility WARs). It has to be emphasized that adequate waste form characterizations need to be based on the properties relevant to storage, transport and disposal, and that suitable test standards for such properties must be available. A test programme should include the choice and/or development of acceptable test procedures and the performance of verification tests on the immobilized waste form [104]. A quality assurance programme should accompany the production of waste forms. In addition, this assessment programme should meet the requirements of the International Organization for Standardization (ISO) in ISO 9000 or a local equivalent to facilitate orderly record retention and adherence to the applicable requirements.

While radioisotopes such as ^{14}C and tritium pose specific challenges to the design and selection of the immobilization technology, the elements and scope of the assessment programme measuring the relative effectiveness of such technologies are not directly tied to the contaminant being immobilized. In other words, the assessment of waste forms designed to immobilize ^{14}C and tritium is not fundamentally different from other assessments involving other contaminants.

Waste containing short lived radionuclides such as tritium may be stored until its activity has decayed to an insignificant level. The immobilization methods for tritium discussed in Section 7.2 are suitable for the long term storage of tritium if the immobilized media are contained by high integrity containers such as sealed stainless steel vessels. In most cases this final waste form will meet the criteria for storage, transport and disposal.

7.3.1. Waste form characterization

In general, the final waste form should be properly characterized to ensure that the waste properties meet the identified waste disposal facility

WARs prior to disposal. Waste characteristics can be established using a combination of process knowledge and waste knowledge (i.e. properties of the waste that are known through consideration of the waste generation process or from previous sampling and analysis of the waste), and data can be obtained from a direct sampling and analysis of the waste.

7.3.2. Waste form testing

Different tests for the physical and chemical properties of a waste form are recommended in different regulatory requirements and guidelines. Several test methods for these properties are available, although only a few of them are standardized and fully accepted by many countries. The recommended tests include those for free water content, unconfined compressive strength, freeze–thaw weathering, radiation resistance, biodegradation, wet–dry weathering, hydraulic conductivity, bulk density, acid neutralization capacity and leach resistance [102, 109–112]. Leach tests are now becoming standardized [113–116] and hence a comparison between different waste forms is possible. The results of leach tests are usually presented either as the cumulative fraction released, as a cumulative leach rate or as diffusivities [104].

Tests for the evaluation of the long term effects from ionizing radiation, corrosion by water and soil components inside the repository, and bacterial attack, as well as for thermal conductivities and heat reactions, have not been standardized and are therefore performed in different ways, making comparison difficult. The tests used for the quality control of immobilized waste relevant for processing, storage, transport and disposal are summarized in Table 29 [104].

TABLE 29. TESTS USED FOR THE QUALITY CONTROL OF IMMOBILIZED WASTE RELEVANT FOR PROCESSING, STORAGE, TRANSPORT AND DISPOSAL

Property	Test	Requirement	Remarks
Water resistance	Immersion in distilled water	Not swell Not decompose	Screening test
Leach resistance	Leaching of contaminant		ASTM International standards [113, 114, 117, 118]
Mechanical strength	Compressive strength, tensile strength and hardness	>50 kg/cm	ASTM International standards [119–121]
Fall resistance	Fall from 9–14 m height	Not break (9 m)	IAEA transport requirements [122]
Form stability	Ring ball penetration, cylinder bending and hole migration		ASTM International standards [119–121]
Heat resistance	Control heating	800°C for half an hour	IAEA transport requirements [122]
Flammability	Heating with a flame		ASTM International standards [123–126]
Frost resistance	Storage in freezer, cycling from –40 to +20°C		ASTM International standards [127]
Structure homogeneity	Microscopy X ray diffraction, autoradiography and chemical analysis	Homogeneity > 10%	ISO standard [128]
Long term stability against radiation, chemical and bacterial attack	Structure changes, radiolytic gas evolution and degradation		ISO and ASTM International standards [129, 130]

8. STORAGE AND DISPOSAL

Options for the management of any waste containing ^{14}C and tritium can be divided into two major groups: storage and disposal. The difference between storage and disposal is defined by the intention of the act: there is an option of retrieval in the case of storage, but there is no intention of waste retrieval with the disposal option.

Disposal of radioactive waste can be subdivided into discharge as an effluent, either in an airborne or aqueous form, and disposal in a solid form. Discharges of radioactive substances to the environment in the form of airborne or liquid effluents are regulated by authorized discharge limits, as discussed in Section 2. To meet or exceed the discharge criteria, some effluent streams may require treatment, as discussed in Section 5, prior to discharge.

Waste containing short lived radionuclides such as tritium may be stored until its activity has decayed to a negligible level. However, the half-life of ^{14}C, 5730 years, is much longer than any reasonable surveillance period, and thus storage of waste containing ^{14}C can only be an interim measure prior to disposal. Where disposal is not immediately available, waste is placed in interim storage; for example, graphite moderators from graphite reactors containing significant amounts of ^{14}C are in interim storage, since no disposal strategy has yet been finalized. Waste in interim storage must initially be conditioned to maintain its integrity such that it can be readily retrieved when disposal becomes available and to contain its contaminants.

The main criterion of a waste storage or disposal facility is that of minimizing the potential for the release of contaminants from the waste to the environment and thus minimizing exposure of humans. Each storage or disposal facility has its own WARs for ensuring that the facility meets the requirements of the regulatory bodies.

8.1. WASTE ACCEPTANCE REQUIREMENTS

WARs are requirements relevant to the acceptance of waste packages for handling, processing, storage and disposal. In general, the WARs may vary from site to site. However, they should clearly state:

(a) The acceptable waste forms;
(b) The waste tracking requirements;
(c) The waste segregation requirements;
(d) A list of excluded materials;

(e) The waste package requirements;
(f) The waste characterization requirements;
(g) The limits on radiological and chemical contents.

Waste tracking is the process of identifying and recording where and when waste originates at a facility and its movements until delivery to the storage and/or disposal site. Waste segregation is the activity of separating, or keeping separate, waste according to its radiological, chemical and/or physical properties. A waste package is a combination that includes the waste or waste form and any containers and internal barrier (e.g. a liner) prepared in accordance with the requirements for handling, transport, storage and/or disposal. Waste characterization is the determination of the physical, radiological, chemical and biological properties of the waste to establish the need for further processing and/or to decide on the appropriate method for storage and/or disposal.

Waste may need to be converted into a stable waste form prior to its transport or disposal. The primary criteria for choosing a waste form are stability with respect to the storage and/or disposal conditions, tolerance to self-irradiation and compatibility with the contained waste. The release of contaminants from a storage and/or disposal facility is a function of the performance of the waste form containing the waste and of the performance of the facility itself. The performance requirements of the waste form are likely to be set by the WARs of the available facilities.

The requirements for waste forms adopted for storage, transport and disposal vary significantly from country to country and can have a significant impact on the immobilization techniques adopted. In addition, the requirement to return waste from reprocessing operations to the country of origin means that the requirements of several countries may need to be considered in deciding upon an appropriate waste form and immobilization technology. The waste form requirements and various waste forms have been discussed in detail in various publications [101, 102, 104–108]. The important requirements include:

(a) Thermal stability;
(b) Oxidative stability;
(c) Resistance to water;
(d) Resistance to radiolysis;
(e) Mechanical properties;
(f) Specific activity.

Disposal sites for low and intermediate level radioactive waste currently range from near surface facilities to engineered geological repositories. The radiological content of the waste is one of the main factors in the selection of the waste disposal method (i.e. near surface disposal versus deep geological emplacement). It is obvious that the cost of deep geological disposal is much higher than that of near surface disposal. An overview of the current disposal methods is presented in Ref. [131]. An approach for the derivation of quantitative acceptable criteria for near surface disposal facilities is discussed in Refs [132, 133]. Some examples are given below for the limits of tritium and ^{14}C waste packages for near surface disposal in various countries.

8.1.1. France

Waste management and storage in France is the responsibility of the French radioactive waste organization, Agence nationale pour la gestion des déchets radioactifs (ANDRA). ANDRA defines the waste classification of and WARs for the activity, the nature of the radionuclides, the doses for transport and the final waste form. This classification is not specified by law or regulation. In general, radioactive waste is classified based on the disposal option and the nature of the waste (the activity level, half-life of the main radionuclides, etc.). Table 30 illustrates the correspondence of this classification to the traditional waste classification of low and intermediate level waste (LILW) and high level waste (HLW), considering also the half-life of the waste.

The WARs for shallow land disposal of FMA-VC waste (Table 31) were established in France for radionuclide inventory [134].

Categories FA-VL and MA-VL are waste containing radionuclides with a long half-life, which must be disposed of in a deep geological repository. The first deep geological repository in France is expected to be opened in 2015. Waste such as reprocessing sludge and hulls of fuel element structures falls into this waste category. At present, waste in this category is interim stored at nuclear sites, such as the CEA's and Cogéma's sites.

HA waste is waste containing alpha emitters and waste with heat generation and will be disposed of in a deep geological repository. Waste in this category is mainly vitrified waste generated at reprocessing plants.

In general, most waste containing tritium falls into the TFA category. However, waste containing ^{14}C is usually classified as FA-VC waste, owing to its long half-life.

Since a large amount of graphite waste containing ^{14}C has accumulated in France, a study for a dedicated disposal repository will be carried out in the future. Feasibility studies for using graphite incineration with a fluidized bed combustor with a capacity of 30 kg/h for reducing the amount of graphite waste

TABLE 30. FRENCH WASTE CLASS MATRIX

Waste class	LILW, short lived (%)	LILW, long lived (%)	HLW (%)
TFA	100	0	0
FMA-VC	100	0	0
FA-VL	0	100	0
MA-VL	0	100	0
HA	0	0	100

Note: TFA is waste of very low activity, similar to 'exempt waste'. FMA-VC, FA-VL and MA-VL are LILW with different half-lives. HA corresponds to HLW.

TABLE 31. CRITERIA FOR SHALLOW LAND DISPOSAL IN FRANCE

	Inventory (MBq/kg)	Annual fraction leached
Alpha emitters	<3.7 per package	$<1 \times 10^{-4}$
Tritium		$<5 \times 10^{-2}$
Beta–gamma emitters	3.7 < initial activity < 37	$<1 \times 10^{-1}$

have been carried out in co-operation with CEA, Electricité de France and Framatome.

8.1.2. Japan

Japan Nuclear Fuel Limited (JNFL) operates a shallow land disposal facility for low level radioactive waste at Rokkasho-mura in Aomori prefecture, 700 km north of Tokyo. The disposal facility commenced operation in December 1992. The first phase involves the construction of eight repositories with a total capacity of 40 000 m^3 of waste. Ultimately, the facility's capacity will be expanded to 600 000 m^3.

Based on the performance assessment, total radionuclide inventory in the first phase is limited by both maximum concentrations and total radioactivity; these limits for tritium and ^{14}C are shown in Table 32 [135]. The maximum concentrations allowed for ^{14}C and tritium are 3.07×10^{11} and 8.51×10^{9} Bq/t, respectively.

TABLE 32. MAXIMUM CONCENTRATION OF RADIOACTIVITY IN WASTE AND TOTAL RADIOACTIVITY AT THE ROKKASHO-MURA DISPOSAL FACILITY FOR THE FIRST 40 000 m^3 OF WASTE

	Maximum concentration (Bq/t)	Total radioactivity (Bq)
Tritium	3.07×10^{11}	1.22×10^{14}
^{14}C	8.51×10^{9}	3.37×10^{12}

8.1.3. Spain

The Spanish National Company for Radioactive Waste Management (ENRESA) is responsible for the operation of the El Cabril disposal facility, which started operation in October 1992. Two activity levels are defined for waste packages intended for El Cabril:

(a) Level 1 waste includes waste with sufficient stability and having mass activities below the following limits:
   (i) Total alpha activity: 1.85×10^5 Bq/kg.
   (ii) Individual beta–gamma activity, half-life more than five years: 1.85×10^7 Bq/kg.
   (iii) Total beta–gamma activity, half-life more than five years (except tritium): 7.40×10^7 Bq/kg.
   (iv) Tritium activity: 7.40×10^6 Bq/kg.
(b) Level 2 waste includes waste that must satisfy strict stability requirements and have mass activities equal to or above level 1 but below the following limits:
   (i) Total alpha activity: 3.70×10^6 Bq/kg.
   (ii) ^{60}Co activity: 3.70×10^8 Bq/kg.
   (iii) ^{90}Sr activity: 3.70×10^8 Bq/kg.
   (iv) ^{137}Cs activity: 3.70×10^8 Bq/kg.

The activity limits for a number of other radionuclides not mentioned above are obtained by multiplication of the above ^{60}Co or ^{137}Cs activities by scaling factors [136]. These radionuclide limits are listed in Table 33, together with the maximum permissible radionuclide loading for the El Cabril disposal facility [137].

TABLE 33. MAXIMUM CONCENTRATION OF RADIONUCLIDES IN WASTE AND MAXIMUM PERMISSIBLE ACTIVITY OF RADIONUCLIDES AT THE EL CABRIL DISPOSAL FACILITY

	Maximum concentration (Bq/t)		Total radioactivity (Bq)
	Level 1	Level 2	
Tritium	7.4×10^{9}	—	2.00×10^{14}
^{14}C	—	3.7×10^{9}	2.00×10^{13}
^{59}Ni	—	3.2×10^{9}	2.00×10^{14}
^{60}Co	—	3.7×10^{11}	2.00×10^{16}
^{63}Ni	—	1.3×10^{11}	2.00×10^{15}
^{90}Sr	—	3.7×10^{11}	2.00×10^{15}
^{94}Nb	—	1.3×10^{7}	1.00×10^{12}
^{99}Tc	—	4.4×10^{5}	3.20×10^{12}
^{129}I	—	7.4×10^{4}	1.50×10^{11}
^{137}Cs	—	3.7×10^{11}	3.70×10^{15}
^{241}Pu	—	2.7×10^{10}	1.15×10^{14}
Each beta–gamma (except tritium)	1.85×10^{10}	—	—
Total beta–gamma	7.40×10^{9}	—	—
Total alpha	1.85×10^{8}	—	2.70×10^{13}

8.1.4. United Kingdom

The Drigg near surface disposal site, owned and operated by BNFL, has been the principal national disposal site for low level radioactive waste in the UK. The WARs for Drigg were established by BNFL to ensure that the facility meets the requirements of the UK's regulatory bodies. Based on the safety assessment of the facility, the annual limits for tritium and ^{14}C disposal are 0.05 and 10.0 TBq, respectively [138, 139].

8.1.5. United States of America

In the USA low level radioactive waste is subdivided into class A, B and C waste. This waste is regulated under 10 CFR Part 61, Licensing Requirements for Land Disposal of Radioactive Waste [140]. Regulation 10 CRF Part 61 refers to the disposal of waste in near surface facilities. Class B and C waste forms or their containers are required to retain their gross physical properties and identity for at least 300 years. Waste designated as class C must be located so that the top of the waste is at least 5 m below the surface of the facility.

To determine whether a waste is class A, B or C the concentrations of certain specific radionuclides must be considered. For long lived radionuclides (e.g. ^{14}C), if the waste contains the radionuclides listed in Table 34 and their concentrations do not exceed 0.1 times the values given in the table, then the waste is class A; for example, if the waste contains less than 2.96×10^{10} Bq/m^3 of ^{14}C and negligible amounts of other radiological contaminants, then the waste is class A waste. If the waste contains the radionuclides listed in Table 34 and their concentrations do not exceed the values given in the table (e.g. less than 2.96×10^{11} Bq/m^3 of ^{14}C), then the waste is class C. If the waste contains the radionuclides listed in Table 34 and their concentrations exceed the values given in the table, then the waste is not generally acceptable for near surface disposal.

For short lived radionuclides (e.g. tritium), if the waste contains the radionuclides listed in Table 35 and their concentrations do not exceed the values given in column 1 (e.g. less than 1.48×10^{12} Bq/m^3 of tritium), then the waste is class A. If the concentrations exceed the values given in column 1, but do not exceed the values given in column 2, then the waste is class B. If the concentrations exceed the values given in column 2, but do not exceed the values given in column 3, then the waste is class C. If the concentrations exceed the values given in column 3, then the waste is not generally acceptable for near surface disposal.

If the waste contains more than one of the radionuclides listed in Tables 34 and 35, with concentrations within the prescribed limits, then Regulation 10 CFR Part 61 [140] provides a method for determining the waste classification.

Waste with concentrations greater than those permitted for class C is called ‘greater than class C’ waste. This waste is not acceptable for near surface disposal and must be disposed of in a geological repository.

8.2. STORAGE AND DISPOSAL OPTIONS FOR WASTE CONTAINING ^{14}C AND TRITIUM

8.2.1. Storage options

Waste containing short lived radionuclides such as tritium may be stored until its activity has decayed to a negligible level. However, storage of waste containing ^{14}C can only be an interim measure prior to disposal, owing to its long half-life (5730 years). Waste in interim storage must initially be conditioned to maintain its integrity such that it can be readily retrieved when disposal is available and to contain its contaminants. The storage methods mainly for waste containing tritium are summarized in Sections 8.2.1.1–8.2.1.4.

TABLE 34. LONG LIVED RADIONUCLIDES CITED IN REF. [140]

	Concentration
^{14}C	2.96×10^{11} Bq/m^3
^{14}C in activated metal	2.96×10^{12} Bq/m^3
^{59}Ni in activated metal	8.14×10^{14} Bq/m^3
^{94}Nb in activated metal	7.40×10^{9} Bq/m^3
^{99}Tc	1.11×10^{11} Bq/m^3
^{129}I	2.96×10^{9} Bq/m^3
Alpha emitting transuranic nuclides with half-life greater than five years	3.70×10^{6} Bq/kg
^{241}Pu	1.30×10^{8} Bq/kg
^{242}Cm	7.40×10^{8} Bq/kg

TABLE 35. SHORT LIVED RADIONUCLIDES CITED IN 10 CFR 61 [140]

	Concentration (Bq/m^3)		
	Column 1	Column 2	Column 3
Total of all nuclides with less than a five year half-life	2.59×10^{13}	[a]	[a]
Tritium	1.48×10^{12}	[a]	[a]
^{60}Co	2.59×10^{13}	[a]	[a]
^{63}Ni	1.30×10^{11}	2.59×10^{12}	2.59×10^{13}
^{63}N in activated metal	1.30×10^{12}	2.59×10^{13}	2.59×10^{14}
^{90}Sr	1.48×10^{9}	5.55×10^{12}	2.59×10^{14}
^{137}Cs	3.70×10^{10}	1.63×10^{12}	1.70×10^{14}

[a] No limits are established for these radionuclides in class B or C waste. Practical considerations such as the effects of transport, handling and disposal will limit the concentrations of this waste. This waste shall be class B unless the concentrations of other nuclides in this table determine the waste to be class C, independent of these nuclides.

8.2.1.1. Storage of HTO waste

Storage of HTO in tanks for several decades to allow for decay should be a viable management method. Corrosion may be of concern in the long term storage of tritium due, in part, to the presence of the radiolytic decomposition products of water. It appears reasonable to assume that tank storage is feasible for at least a 40 year period [141]. As a process, it would consist of piping the HTO to corrosion resistant storage tanks for controlled storage. The tanks would be sealed, monitored and, if necessary, provided with recombiners to oxidize back to water any hydrogen produced by radiolysis. As a method, it has application either for interim storage until separation, reuse or fixation can be achieved or for long term storage (i.e. until significant radioactive decay has occurred). Leakage of HTO is the primary hazard. Continuous radiation monitoring will be required.

Tank storage of low specific activity tritiated heavy water has been assumed to be impractical, owing to the economic penalties associated with the loss of use of the deuterium oxide. Long term tank storage of high specific (>40 TBq/m^3) HTO is not recommended, as such concentrations could require double and triple containment in tanks and associated piping because of the increased hazards from leakage.

8.2.1.2. Storage of tritium gas

Storage of tritium gas has been carried out using appropriate gas containers. These containers were principally designed for the transport of tritium, so the tritium can be readily recovered. However, this method may have an increased potential for leakage of the tritium compared with the use of hydrides.

The radioactive decay of tritium to form ^3He causes an increase in pressure within the vessel, which the system needs to be able to cope with. The pressure inside the container will eventually reach twice the initial value. The potential embrittlement of the container caused by the helium is also a potential problem and has been investigated. For an initial T_2 pressure of 1.01×10^4 kPa (100 atmospheres) and a temperature of 200°C, helium embrittlement has been shown not to be a problem [142, 143].

8.2.1.3. Storage in engineered structures

In general, an engineered storage facility consists of steel shafts enclosed within an underground, steel lined, reinforced concrete enclosure. This type of facility has been used for interim (e.g. 20–50 years) storage for short lived, high level radioactive waste and for transuranic waste. Information on various storage facilities can be found in Refs [144, 145].

Large quantities of solid waste containing tritium have been stored in a shallow land disposal facility (Centre Manche near La Hague) in France.

Owing to the degradation of the waste containers, a significant amount of activity has been released from the waste packages (e.g. up to 7400 Bq/L of activity has been found in drainwater samples). By analysing water samples from the facility drainage, it was possible to locate the degraded waste containers (i.e. concrete containers), which contained a total of 2200 TBq of tritium. The waste was retrieved from the shallow land burial, re-conditioned in new containers and put in interim storage. The HTO in the trench containing approximately 4 TBq/m^3 of tritium was pumped and collected in order to minimize contamination of the environment.

It is important to store tritiated waste in leaktight containers, preferably in stainless steel containers having an endurance life of about 100 years, to allow the tritium activity to decay to an insignificant level. A carbon steel container with a typical endurance life of 35 years is not recommended for storing tritiated waste, since the endurance life is not long enough.

The immobilization methods discussed in Section 7.2 can also be used for the long term storage of tritium. However, these methods have the potential for release of tritium and the risks associated with the methods need to be investigated.

8.2.1.4. Storage of irradiated graphite waste

Irradiated graphite moderators from Magnox reactors and AGRs are considered to be problematic waste because they contain large quantities of radionuclides (e.g. up to 1 MBq/g of tritium and 0.2 MBq/g of ^{14}C). It has been found that these contaminants can be released to the environment due to sudden releases of Wigner energy, which will release a large amount of heat and entail a high risk of fire. Wigner energy is the energy accumulated by the graphite during irradiation in the reactor, which can be suddenly released by an increase in temperature. This effect is important when the graphite irradiation is performed at low temperatures (below 150°C). For safety and radiological reasons, unprocessed graphite moderators from decommissioned reactors are in interim storage inside the reactor containment. However, specific measures must be implemented to ensure that no degradation of the waste occurs, including:

(a) The graphite waste should be stored between 10 and 35°C to prevent sudden releases of Wigner energy; storing the waste at low temperatures (i.e. <10°C) will present a high risk of brittle fractures occurring in the metallic structures that support large quantities of graphite (up to 2500 t).
(b) Oxidation of the graphite should be prevented.

(c) The humidity should be kept low.
(d) Gas exchange with the environment should be minimal.
(e) A fire prevention system should be implemented.

Graphite waste in France will be in interim storage for 50 years, allowing a significant activity decay of short lived radionuclides. A storage period of 120 years for graphite waste is employed in the UK.

8.2.2. Disposal options

A variety of concepts for the disposal of radioactive waste have been studied worldwide; these range from near surface disposal to deep geological disposal. The main objective of a waste disposal facility is to minimize the potential for release of contaminants from the waste to the environment. In particular, much of the effort has been focused on long term waste storage and/or disposal of high level and long lived radioactive waste. Some of these concepts may also be suitable for the storage and/or disposal of waste containing ^{14}C and tritium.

8.2.2.1. Near surface disposal

This approach has been routinely used for the disposal of low level and intermediate level radioactive waste for several decades. Near surface disposal in unlined shafts and disposal in concrete lined trenches or caissons have been used. Considerable amounts of waste containing ^{14}C and tritium have been stored and/or disposed of in near surface disposal facilities.

For the near surface disposal of waste containing tritium, the preferred approach is to immobilize the waste in cement and dispose of the immobilized waste in leaktight containers, which allow the tritium activity to decay to an insignificant level (for 50–100 years). The tritiated waste should be disposed of in dry and sealed containers to prevent tritium release.

Seabed disposal was considered by some countries as the preferable option for the ultimate disposal of most nuclear waste other than high level waste. However, major political changes have subsequently taken place, and there is currently a moratorium on the dumping at sea of any radioactive waste. Nevertheless, some experts believe that sea disposal can be the best practical environmental option for the disposal of bulky low level waste arising from decommissioning, as well as for tritiated waste [146]. The principles of stabilizing the waste within containers, eliminating void volumes and establishing a monolithic form would be applied in the sea dumping option.

Reference [147] includes calculations of collective dose commitment arising from marine pathways and finds them to be dominated by ^{14}C.

8.2.2.2. Liquid injection into geological formations

The disposal of liquid radioactive waste by injection into deep geological strata has been studied both for high level radioactive waste and for the disposal of HTO [148]. The major factors determining the safety of the disposal of liquid nuclear waste are the structure and properties of the geological formations containing the collector beds into which the waste is injected, as well as the physicochemical processes that occur in these collector beds and which determine the localization of the waste components within specified boundaries of a selected geological medium. Two principal injection concepts have been proposed: deep well injection and hydrofracturing.

Deep well injection deposits the water through a borehole into a sealed receiving stratum at a depth of 1000 m or more. The receiving stratum must have porosity, an absence of faults and an excess capacity. Sandstone or limestone rocks sealed with layers of clay and shale meet these requirements. Safety requirements include site selection to ensure that the disposal formation does not contain faults that would transmit water to aquifers and proper casing of the injection pipe to avoid leakage into upper groundwater. This technique has been developed and used for non-radioactive waste disposal, so experience exists and extensive development is not required.

For deep well injection, the HTO would be temporarily stored in tanks at the injection site. The HTO would be mixed with cement to form a slurry, which would be pumped into the underground formation, where it would solidify. This method could be used at the nuclear facility site if adequate geological conditions existed there. Deep well injection for the disposal of waste containing tritium has been considered in the Russian Federation, but has not been put into practice [148].

Hydrofracturing involves the injection of liquid or slurry material at high pressures into a geological formation so that the rock material is fractured or shattered, which creates a semiporous region suitable for containing the waste. This technique was studied at the ORNL and has been used for the disposal of intermediate level radioactive waste [149]. Evidence of increased seismic activity resulting from waste injection suggests that there may be long term containment problems associated with this disposal concept.

8.2.2.3. Disposal in geological formations

The placement of radioactive waste into stable geological formations has the potential for isolating the waste from humans for geological time periods (i.e. hundreds of thousands of years). Consequently, this approach has been investigated in several countries for the disposal of radioactive waste, including high level and transuranic waste. As mentioned above, significant quantities of ^{14}C and tritium are captured within fuel elements. If it is assumed that spent fuel will be disposed of in geological formations rather than being reprocessed, a significant removal of the threat to human health that these radionuclides represent will have been achieved.

The principal and most probable pathway that could result in human radiation exposure due to this waste is the contamination of groundwater aquifers following intrusion of water into the repository formation. The estimated time for tritium to reach humans varies considerably with the assumed leachability of the waste material, the migration distance to sources of potable water and the porosity of the formation. Typical values for groundwater velocities in porous aquifers (about 110 m/a) would indicate a delay of only about 200 years following water intrusion into a repository. Carbon-14 may move somewhat slower and be delayed about 1200–1500 years.

The absence of any appreciable radioactive decay of ^{14}C during groundwater transport means that primary reliance must be placed upon maintaining the integrity of the repository formation itself over long time periods. This will require selection of repository formations located in areas of low seismic activity and surrounded by water impervious strata.

Several geological formations have been considered for radioactive waste storage and/or disposal, including salt beds, shale formations and hard bedrocks such as granite and basalt. Salt deposits have been considered for radioactive waste repositories because the existence of the salt deposit itself indicates that there is little groundwater movement in the formation. Salt also has good heat conduction properties and its plasticity makes it self-sealing for several types of deformation.

The storage of pressurized tritium gas cylinders in geological repositories requires further research. Engineered storage facilities may prove to be preferable, particularly in view of the relatively short storage times required for tritium.

8.2.3. Other options

A number of options based on the reduced volume of water from a modified Purex process have been studied, including in situ solidification in underground salt caverns and conversion of HTO to hydrogen followed by either discharge into the atmosphere or transformation to metal hydrides.

The in situ solidification method consists of mixing cement and perhaps other low and intermediate level waste with HTO and pumping it down into a salt dome cavern.

Conversion of HTO to hydrogen and then either direct discharge or fixation on metal hydrides is one option (Section 7.2.4). Discharge of tritiated hydrogen into the atmosphere is uncertain until the fate of the released hydrogen is more fully understood and a reliable dose assessment can be made. Fixation on metal hydrides is expensive unless the volume is small.

8.3. STRATEGY FOR THE MANAGEMENT OF WASTE CONTAINING ^{14}C AND TRITIUM

Waste containing low levels of ^{14}C and tritium that meets the WARs can be disposed of in existing waste disposal facilities (e.g. near surface disposal). However, for waste containing high levels of ^{14}C and tritium, such as spent ion exchange resins from HWRs, that exceeds the WARs for near surface disposal, no disposal facility is available at present. Different waste management practices are therefore required.

Waste containing high concentrations of tritium (with a half-life of 12.3 years) can be stored in high integrity containers (e.g. stainless steel containers with a life of approximately 100 years) until its activity has decayed to a level that meets the WARs for near surface disposal. The waste is then disposed of in the available near surface disposal facilities.

The above storage–decay option is not, however, suitable for waste containing high levels of ^{14}C, owing to its long half-life (5730 years). This waste can only be in interim storage until a suitable disposal facility becomes available.

9. CONCLUSIONS

Carbon-14 and tritium are produced by nuclear reactions that occur naturally in the environment, in nuclear weapon testing and in nuclear reactors. When released to the environment these radioisotopes are distributed globally, owing to their long half-lives and residence times in the atmosphere and hydrosphere. Since both ^{14}C and tritium are mobile in the environment, it is important to control their release from nuclear facilities and waste management sites by means of appropriate operational procedures and waste management strategies and practices.

In assessing the impact of ^{14}C and tritium releases, the consequences of exposures of an individual in the immediate vicinity outside the exclusion boundary area, and of the public at large, should be considered. Appropriate effluent and environmental monitoring programmes (e.g. for ^{14}C and tritium) are therefore required for each nuclear facility to ensure the protection of the public and the environment from radioactive discharges.

Discharge limits for radioisotopes are established in most countries in accordance with the recommendations of the ICRP and by taking into account other country or site specific factors and requirements. These limits differ from one site to another, depending on assumptions on the nature of the effluent and on the environment into which the discharges are made. In an authorization, such as a licence for a nuclear facility, in most cases tritium discharge limits are established independently of other emission limits, such as for halogens, particulates and beta–gamma and alpha emitters, for both gaseous and liquid effluents. Discharge limits for ^{14}C in liquid effluents are not always established independently, and in some countries they are grouped with other beta and gamma emitters as a gross beta–gamma limit.

Most human-made ^{14}C and tritium is produced as a by-product (or as a special product) in nuclear reactor operations. Both the amounts of ^{14}C and tritium produced and their chemical form depend on the reactor design, as does the subsequent behaviour of these nuclides and the pathways by which they can be released to the environment. It has been found that the majority of these radioisotopes are contained in gaseous waste (e.g. reactor off-gases and dissolver off-gases at reprocessing plants) and solid waste (e.g. graphite moderators, fuel cladding, spent ion exchange resins from HWRs and structural materials in the reactor core). Only a small quantity of ^{14}C is released via liquid effluents from nuclear facilities. However, the amounts of tritium in the liquid effluents from some nuclear facilities may be considerable. In general, tritium discharge limits are higher for HWRs than for LWRs.

Large quantities of ^{14}C and tritium are retained in the structural materials of a nuclear facility, which will be handled during the facility's decommissioning phase. The graphite waste from Magnox reactors and AGRs requires specific considerations, since high inventories of ^{14}C and tritium are expected in this type of waste. Currently, this type of waste is in interim storage in France and the UK.

It is important to take into consideration the potential production of ^{14}C and tritium at the design stage of a new type of reactor. To minimize the production of ^{14}C, the following activities have been identified:

(a) Minimizing nitrogen impurities in the fuel, the moderator structures (e.g. the graphite moderator) and the structural materials in the reactor core;
(b) Avoiding the use of chemicals (e.g. nitrogen blanketing) that will promote the production of ^{14}C;
(c) Minimizing or eliminating air ingress, especially in the moderator and primary coolant systems, through better system design.

The following actions have been identified to minimize the production of tritium:

(i) Improving fuel fabrication to avoid occurrences of fuel cladding failures.
(ii) Improving fuel cladding materials, such as the use of zircaloy instead of stainless steel.
(iii) Reducing lithium impurities or contamination in the reactor coolant, the moderator and the core structures. If LiOH is used for pH adjustment in PWR primary coolant, enriched ^{7}Li (99%) for LiOH should be used to minimize tritium production.

Improved operation practices can also reduce ^{14}C and tritium emissions; for example, reducing the frequency of venting and purging of the cover gases (e.g. the moderator or primary coolant) has been shown to decrease ^{14}C and tritium emissions. Separation or removal of ^{14}C and tritium from waste and effluent will be beneficial to their management. Technologies for the separation or removal of these radionuclides from gaseous and liquid effluents are available; some are well proven, but others are in the development stage.

Most of the available techniques for ^{14}C removal from gaseous streams remove ^{14}C as CO_2. The main disadvantage of these methods is that a large amount of secondary waste is generated if the waste stream contains considerable amounts of $^{12}CO_2$. Although methods for the separation of $^{14}CO_2$ and $^{12}CO_2$ are available, they are relatively costly. No specific study has been carried out for the removal of ^{14}C from liquid streams, although most of the conventional liquid treatment methods can remove ^{14}C as bicarbonate and carbonate. Since more stringent environmental regulation can be expected in the future, specific studies for the removal of ^{14}C from liquid waste will be required.

The typical processes for the removal of tritium from gas streams involves converting HT to HTO, followed by removal of the HTO. Most of the proven technologies for tritium removal from liquids are for applications of the detritiation of heavy water. Tritium removal from light water, however, requires larger stripping and recovery factors than water–heavy water upgrade. Several other processes may be suitable for the removal of tritium from liquid water, including CECE, Girdler sulphide and bithermal hydrogen–water exchange. Other techniques have been developed at the laboratory scale and could be used in the future.

Among the various binding materials, cement is the most promising and appropriate for immobilizing waste containing ^{14}C. Various immobilization methods, such as the use of hydrates, hydrides and organic agents, can be used for the long term storage of tritium. However, these immobilization media should be contained in high integrity leaktight containers for storage, in order to allow for the natural decay of the tritium activity for a significant period of time (50–100 years).

Waste containing low levels of ^{14}C and tritium that meets the WARs can be disposed of in existing waste disposal facilities (e.g. near surface disposal facilities). Special attention must be paid to the disposal of tritiated waste, owing to the mobility of tritium. It is recommended to dispose of this waste in leaktight and stable containers that can prevent the dispersal of tritium into water or to an aquifer system. For release and dilution it is preferable to release tritium gas rather than HTO.

For waste containing high levels of ^{14}C and tritium, such as spent ion exchange resins from HWRs, that exceeds the WARs for near surface disposal, no disposal facility is available at present. Waste containing tritium can be stored in high integrity containers (e.g. stainless steel containers with a life of approximately 100 years) until the activity has decayed to a level that meets the WARs for near surface disposal. However, this storage–decay option is not suitable for waste containing high levels of ^{14}C, owing to its long half-life (5730 years). This waste can only be in interim storage until a suitable disposal facility (e.g. deep geological disposal) becomes available. Other disposal alternatives under investigation may be employed in the future.

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