Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Progress in Nuclear Energy 48 (2006) 2–36

PROGRESS IN NUCLEAR ENERGY

An International Review Journal

www.elsevier.com/locate/pnucene

Review

Life cycle and management of carbon-14 from nuclear power generation

Man-Sung Yim[a,*], François Caron[b]

[a]Department of Nuclear Engineering, North Carolina State University, Campus Box 7909, Raleigh, NC 27695-7909, USA
[b]Department of Chemistry and Biochemistry, Laurentian University, Sudbury, Ont., Canada P3E 2C6

Received 13 July 2004; received in revised form 21 April 2005; accepted 21 April 2005

Abstract

With its long half-life (5730 years) and high mobility in the environment, ^{14}C is a radionuclide of considerable interest in nuclear power production. Carbon-14 is present in virtually all parts of nuclear reactor primary system and has a high production rate. It is released to the environment through gaseous and liquid discharges and though the disposal of solid radioactive waste. This paper summarizes existing scientific understanding of ^{14}C issues surrounding nuclear power production. Two main purposes of the paper are: (1) To provide the basic/up-to-date understanding of the life cycle of ^{14}C, starting from its production in reactors, to eventually its transport and its potential incorporation in natural cycles; (2) To present the technical issues in current ^{14}C waste management. The emphasis of the paper is on Light Water Reactors (LWRs, which include Pressured Water Reactors-PWRs, and Boiling Water Reactors-BWRs) and Heavy Water Reactors (HWRs-CANDU type reactors). Major issues with ^{14}C in HTGR are also addressed.

1. Introduction

Carbon-14 is a radionuclide of considerable interest in nuclear power production. Carbon-14 is present in virtually all parts of nuclear reactor primary system and has a high production rate. It is released to the environment through gaseous and liquid discharges and through the disposal of solid radioactive waste. With its long half-life (5730 years) and high mobility in the environment, ^{14}C can be a nuclide of major concern after mixing with stable $^{12+13}C$ followed by the biological incorporation into biota, as carbon is the fabric of life.

Naturally occurring carbon comprises 3 isotopes: mass 12 (^{12}C), 13 (^{13}C) and 14 (^{14}C). The isotopes ^{12}C and ^{13}C are stable, with natural occurrences of approximately 98.89 and 1.11%, respectively. The isotope ^{14}C, a radioactive one, is produced in the upper atmosphere by the irradiation of ^{14}N by neutrons of cosmic ray origin. This imparts a natural radioactivity to the carbon present in the atmosphere and the recent biosphere (e.g. the living material), due to mixing with the other stable isotopes. On an atom basis, the current ^{14}C levels of 250 Bq $(kgC)^{-1}$ correspond to approximately 1 atom of ^{14}C to $\sim 7\times 10^{11}$ atoms of stable carbon, or $\sim 1.5\times 10^{-10}\%$ of all carbon present.

Human activities over the past few decades have increased the levels of ^{14}C in the atmosphere through nuclear weapons tests and nuclear reactors. At present, nuclear reactors constitute the only major source of anthropogenic ^{14}C, because atmospheric nuclear weapons tests have been banned. The additional man-made radiocarbon eventually enters the natural cycle and mix with the stable carbon ($^{12+13}C$) to become part of the food chain, which would give

---

[*] Corresponding author. Tel.: +1 919 515 1466; fax: +1 919 515 5115.
E-mail address: yim@ncsu.edu (M.-S. Yim).

0149-1970/$ - see front matter
doi:10.1016/j.pnucene.2005.04.002

a radioactive dose to biota and humans alike. Not all the ^{14}C produced by reactors has the potential to become bioavailable, and for the portion available for release, engineered structures are in place to minimize releases to the environment. Although relatively only small amounts of ^{14}C make it to the environment, the overall inventory of this radioisotope continues to grow as the need for power production increases, and eventually, long-term options are needed for its management.

In the development of Low-Level Waste (LLW) facilities in the U.S., ^{14}C is one of the inventory limiting nuclides, and also a major player in demonstrating regulatory compliance with NRC's 10CFR61 (US NRC, 1982). In nuclear power plants, a large inventory of ^{14}C is captured in ion-exchange resin. These resins are stored sometimes for extended periods of time, without special engineering treatment. There is potential for ^{14}C in resins to be mobilized during storage through resin degradation, and the resulting contaminant could be released to the environment. Handling and disposal of these degraded resins could be a concern. Recently, some PWR stations have reported relatively high concentrations of ^{14}C in reactor coolant system cleanup filters (Miller, 2000), and these concentrations have sometimes exceeded the Class C waste category, which precludes their disposal in commercial LLW sites. This increased loading of ^{14}C has been linked to the use of sub-micron size filters, which is driven by the plant dose reduction efforts (NCRP, 1994). Exact causes of this increased ^{14}C loading with the sub-micron filters have not been identified. In the development of the proposed high-level waste repository at Yucca Mountain in Nevada, ^{14}C was the only radionuclide which exceeded the original release limit in the EPA's 40CFR191 standards (US EPA, 1994). However, this has become a no-issue as the standards for Yucca Mountain were newly revised to a dose-based one [10CFR63 (US NRC, 2001) and 40CFR197 (US EPA, 2001)].

For the situation in Canada, it is generally recognized that domestic CANDU reactors, on an unit basis, produce more ^{14}C than other types of reactors (Liepins and Thomas, 1988). Most of this ^{14}C sits on ion exchange resins, and this ^{14}C is considered available for release to the atmosphere (Boss and Allsop, 1995; ACRP, 1995). This radionuclide is also potentially inventory limiting in Canada, with respect to a projected LLW disposal concept (Dolinar et al., 1996). Plans or proposed disposal concepts are not definitive for spent resins, which contain the majority of the ^{14}C inventory. At present, these wastes sit in station tanks and in dedicated waste holding facilities, for long-term storage.

Use of high-temperature gas cooled reactor (HTGR) has gained significant interest in recent years in the U.S. and abroad. HTGR provides the benefit of passive safety, good economics, and deep burn capability with its TRISO-coated-particles-based fuel. HTGR also provides high temperature process heat which can be applied to hydrogen generation. Pebble-bed reactors, the Gas turbine-modular helium reactors, and very high temperature gas reactors (VHTR) are all under consideration as part of the U.S. DOE's Nuclear Hydrogen Initiative. All HTGR design uses a graphite moderator/reflector and either graphite composite fuel or fuel pebbles, thereby contributing significantly to the total quantity of irradiated graphite, eventually requiring disposal (Wickham and Neighbour, 1999). This is one of the concerns with the use of HTGR. The activity levels of ^{14}C in graphite from HTGR are high enough for the waste not amenable to direct disposal. Proper management of graphite waste from HTGR asks for careful management of ^{14}C.

There have been a large number of scientific investigations in the past regarding ^{14}C waste management and public health concerns over the release of ^{14}C from nuclear power plants. These investigations include characterizing ^{14}C inventory in plant systems and in plant waste streams, characterizing the amount and chemical forms of ^{14}C release to the environment, understanding the fate and transport of ^{14}C in the environment, applying necessary processing and treatment of ^{14}C waste, finding appropriate waste forms for ^{14}C immobilization and isolation, etc. Many of these investigations were performed in the 80 and 90 s. Presently, there are virtually no continuing scientific studies on ^{14}C waste management in the U.S. This lack of current research activities in the U.S. is in part due to the changes in the regulatory practices and requirements. However, if, in the future, the existing LLW disposal facilities reach their capacity limit, or if construction of HTGRs is realized in the U.S., needs for scientific investigations surrounding ^{14}C issues may be renewed.

This paper intends to provide a bridge between the past and the future by summarizing existing scientific understanding of ^{14}C issues surrounding nuclear power production. In this context, this paper has two major purposes: (1) To provide the up-to-date understanding of the life cycle of ^{14}C, starting from its production in reactors, to eventually its transport and its potential incorporation in natural cycles; (2) To present the technical issues in current ^{14}C waste management. The emphasis of the paper is on Light Water Reactors (LWRs, which include Pressured Water Reactors-PWRs, and Boiling Water Reactors-BWRs) and Heavy Water Reactors (HWRs-CANDU type reactors). Major issues with ^{14}C in HTGR are also addressed given the recent interest in the U.S.

2. The life cycle of ^{14}C

2.1. General aspects of ^{14}C cycling

2.1.1. Carbon-14 in nature

Carbon-14 is produced naturally by the stratospheric irradiation of atmospheric nitrogen from the $^{14}N(n, p)^{14}C$ reaction. It is readily converted to $^{14}CO_2$, which then becomes available for incorporation in the food chain via photosynthesis. The current atmospheric and biotic mass activities of ^{14}C in nature are expected to be ~250 Bq/kg C (McNeely, 1994). This level is close to the levels prior to atmospheric nuclear weapons testing. Given that ^{14}C is in the proportion of 1 atom for $\sim 7\times 10^{11}$ atoms of total carbon, or $\sim 1.5\times 10^{-10\%}$ of all carbon present, there is a tremendous dilution of naturally produced ^{14}C in the various pools of C in nature.

Starting the natural cycle of carbon from its production in the atmosphere, the ^{14}C produced in the upper atmosphere readily mixes with $^{12+13}$C. The atmospheric half-life of $^{14}CO_2$ is ~12–16 years in the Northern hemisphere (McNeely, 1994; Kotzer and Watson, 1999), which is short compared to the half-life of radiocarbon. Incorporation of natural ^{14}C in organic matter takes place via photosynthesis, whereby CO_2 is assimilated by plant material. In land areas, carbon is sequestered in plant material and other biota, while organic deposits in litter, soils, sediments, peat bogs, etc, become part of the land cycling (see Swift et al. (1979); Morel and Herig, (2000) for a general discussion). In oceanic areas, atmospheric CO_2 transfers to shallow ocean waters, where some of this carbon is utilized by biota (photosynthesis and organic matter decay). A significant portion of C is held in deep ocean waters as bicarbonate, with a limited mixing between the deep and shallow ocean waters in upwelling and downwelling areas. Some of this dissolved bicarbonate is immobilized as carbonates (e.g. calcite, $CaCO_3$) in limestone deposits. Order of magnitude estimates of the sizes of reservoirs and production rates are given in Table 1.

Over geological times, organic materials have accumulated to make important fossil deposits. The carbon in these deposits is sufficiently old that naturally produced ^{14}C has decayed, and it is often called 'dead' carbon. In the last century or so, these deposits have been used extensively as fossil fuel, which contributed to the atmospheric load of CO_2 as stable carbon. Similarly, the carbon sequestered in oceanic deposits (e.g. limestone) is considered unavailable for cycling. It is true that in a steady-state cycling of the earth's crust and the mantle, the removal of C from deposits is counterbalanced by gaseous releases from volcanic activities. This cycling of deposits is very slow for the geological time scale, hence it can be considered that the ^{14}C removed by oceanic deposits is unavailable for cycling. It is generally accepted that the ^{14}C present in the atmosphere is mixed, is in balance with living biota, and is at least partially mixed in shallow waters (including some freshwaters), and in recent soil materials as organic matter and perhaps associated with carbonate soil minerals.

Apart from CO_2, organic forms of volatile carbon are also emitted to the atmosphere, such as methane. Methane production takes place in sediments, peat bogs, etc., which are generally waterlogged, and provide conditions for the breakdown of organic materials by bacterial action. Once released to the atmosphere, slow oxidation to CO_2 will take place. For methane, the mean atmospheric residence time was estimated to range from 0.7 to 6 years (Ehalt, 1973). Carbon eventually can re-enter the food chain as the CO_2-bound component. These cycles provide an opportunity for ^{14}C to mix with the stable carbon. This mixing will go along with the natural variations, for example, the ambient

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

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

concentration of CO_2 varies in diurnal and seasonal cycles. This is also locally influenced by industrial CO_2 sources of fossil origins. Reduction in the concentration of ^{14}C activity in the atmosphere by the injection of stable carbon is known as the Suess effect (Suess, 1955). Eventually, with mixing processes, the ^{14}C that enters the food chain will be cycled in biota. Exposure of humans to ^{14}C will take place via direct consumption of plant matter, meat or dairy products from animals that have fed on plant matter containing the ^{14}C. It has been estimated (UNSCEAR, 2000) that a natural production rate of 1 PBq a^{-1} would lead to an individual effective dose rate of 12 μSv a^{-1} and a collective effective dose commitment of 120,000 man Sv PBq^{-1} (assuming the world population of 10^{10} at equilibrium).

2.1.2. Carbon-14 from human activities

Human activities have increased the production of ^{14}C in the environment through nuclear reactors (research and power production) and atmospheric nuclear weapons testing (Table 1). Atmospheric nuclear weapons tests have been banned decades ago, and current atmospheric levels are close to pre-testing levels (McNeely, 1994; Kotzer and Watson, 1999). The majority of ^{14}C produced in reactors is either still contained in reactor facilities (trapped in fuel, structural materials, graphite moderator, in-house waste holding structures), or in licensed waste management sites.

Releases of ^{14}C from nuclear reactors take place as operational gaseous or as liquid-borne emissions: for example, releases from LWRs as CO_2, methane, ethane, and other hydrocarbons are known to take place. In HWRs, ^{14}C releases also take place, mostly as $^{14}CO_2$ gas, with small proportions of light hydrocarbons (Rao, 1997). Release of ^{14}C from gas-cooled reactors are mostly as CO_2. Releases of ^{14}C from waste storage sites depend upon several factors, namely the original chemical form of the element, plus other biogeochemical factors contributing to the mobilization and mixing of the radioisotope with $^{12+13}C$ in nature. Table 1 indicates that the contribution from the nuclear power industry to global ^{14}C inventory is negligible.

In its path from nuclear reactors (source) to the environment (end), a good understanding of the major factors affecting production, storage, release, mixing, etc., needs to be developed for containing ^{14}C-bearing material. This understanding is important to minimize unnecessary increases of the environmental inventory of ^{14}C and keep low dose consequences to biota and human populations.

2.2. Sources and production of ^{14}C in nuclear power plants

In nuclear power plants, ^{14}C is produced in the fuel, from core structural materials, and in reactor coolant, due to the presence of the (stable) parent isotopes ^{14}N, ^{17}O and ^{13}C. These stable isotopes are present as major components or impurities. These parent isotopes are involved in the three major types of reactions to produce ^{14}C, as listed in Table 2. Specifics are discussed separately for LWRs, HWRs, and HTGRs.

2.2.1. Production in LWR (PWR and BWR)

Formation of ^{14}C in nuclear fuel is primarily caused by nitrogen impurities contained in the fuel (by the $^{14}N(n,p)^{14}C$ reaction) and the ^{17}O in UO_2 matrix (by $^{17}O(n,\alpha)^{14}C$). Production rates of ^{14}C in typical LWRs are about a factor of four higher for the nitrogen reaction, compared to the oxygen reaction (see Table 3).

Carbon-14 is also produced in reactor coolant from reactions with: (a) oxygen atoms in the water molecules by $^{17}O(n,\alpha)^{14}C$; (b) nitrogen dissolved in the water by $^{14}N(n,p)^{14}C$, and; (c) dissolved carbon, as carbon dioxide and organic compounds in the water, by $^{13}C(n,\gamma)^{14}C$.

Oxygen is abundant in the reactor coolant system, whereas nitrogen is present in a small concentration. Due to its low cross-section and small concentration in the coolant, generation of ^{14}C from ^{13}C is several orders of magnitude lower than the former two. Production estimates (Table 3) suggest that oxygen reaction is the dominant ^{14}C

Table 2
Carbon-14 production mechanisms and cross-sections

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

Source: (IUPAC, 1984).

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

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

[a] Based on median values of Tables 2.2 and 2.3 in (Bush et al., 1984); normalized for 20 ppm nitrogen impurities in fuel.

[b] Based on calculations by Van Konynenburg (1994) using 25 ppm nitrogen impurities.

[c] Values of (Bonka et al., 1974) (**op. cit.), updated by (Vance et al., 1995).

production mechanism in the coolant, whereas the nitrogen reaction is marginally smaller, depending upon the reactor practice. Operating PWRs add both Hydrogen and Nitrogen to the primary systems to control the pressure in the Volume Control Tank (VCT) (Vance et al., 1995). Under these conditions, and upon addition of makeup water, dissolved nitrogen will be present, whose concentration depends upon the partial pressure in the system. For example, the water equilibrated with air in a tank contains 13 ppm of dissolved N_2, whereas a tank pressurized at 20 psig (140 kPa) will contain 40 ppm of dissolved N_2. Bounding estimates using updated numbers (Vance et al., 1995) suggest that ^{14}C production in the coolant is ~2–3 times lower in PWRs compared to BWRs, but in both cases, they are similar or slightly lower than the ^{14}C production in the fuel.

The lower values in BWRs are caused in part by lower concentrations of nitrogen in the makeup water. The makeup water for the reactor steam loop is from the condensate storage tanks that have normal air cover at atmospheric pressure, and would be equilibrated with dissolved oxygen and nitrogen. The makeup is supplied via the control rod drive pumps and the main condenser hotwell. In the hotwell, dissolved gases would be largely removed along with the other non-condensibles in the hotwell water. Hence, the dissolved oxygen and nitrogen contributions to reactor coolant are small. The makeup water supplied via the control rod drive pumps will contain a nitrogen concentration of 13 ppm if the condensate storage tank is exposed to air. However, because of direct steaming configuration of a BWR, the nitrogen concentration in coolant should be small, and production from nitrogen should not be a significant source of ^{14}C in a BWR.

Production of ^{14}C from fuel and fuel assembly materials is due to the presence of ^{17}O in UO_2 and ^{14}N impurities in UO_2, stainless steel, zircaloy cladding, and nickel alloys used in fuel assembly and support hardware. The estimated production rates are presented in Table 3. These results indicate that the previously reported values of ~50–70 Ci/GWe-a (1.9–2.6 TBq/GWe-a) in Bush et al. (1984); Liepins and Thomas (1988) are an overestimate.

2.2.2. HWRs (CANDU type)

HWRs of the CANDU type have two heavy water circuits going through the reactor core, the fuel channels and the calandria. This constitutes a major difference compared to other water reactor types. The coolant, or heat transport system, goes through the fuel channels, and contacts the fuel to transport the heat to the heat exchangers. The other circuit, the moderator, fills the calandria, surrounding the fuel channels. Most of the moderator heavy water inventory is located in the calandria, whereas in most of the heat transport system heavy water sits outside the core. Consequently, the ^{14}C production rate is comparatively high in the moderator because of the higher number of targets (^{17}O) in the heavy water. An additional and unique feature of these reactors is the presence of an annular space between the calandria tubes and the pressure tubes. This annular space is flushed with CO_2 gas.

Table 4
Annual normalized ^{14}C production rates for the HWRs-generic CANDU-6 reactor

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

[a] (Boss and Allsop, 1995); (Rao, 1997).
[b] (ACRP, 1995), normalized to 100% capacity.
[c] This work, assumed for 20 ppm impurity in the fuel (see text).

Table 4 lists the production rates for each major compartment of the HWR reactor. As discussed, production in the moderator is the major source in HWRs. A 55% enrichment of ^{17}O in the heavy water was assumed in the calculations. This enrichment is expected to vary from reactor to reactor, because of operational requirements, heavy water upgrading needs and the quantities of make-up water used. Estimates of ^{14}C production from UO_2 (via the $^{17}O(n, \alpha)^{14}C$ mechanism) are comparable to the LWRs, however, production through the $^{14}N(n, p)^{14}C$ are not known nor available. Based on Bush et al. (1984), it is reasonable to assume a higher ^{14}C production from nitrogen impurities, compared to that from ^{17}O production, by a factor of 3–4. Our estimate is based on a realistic level of N_2 impurities, and likely represents the upperbound for HWRs. Actual values or better estimates are currently unknown or unavailable.

Annular gas production of ^{14}C is mostly by the $^{14}N(n, p)^{14}C$, calculated using the upper operating limit of 5000 ppm of N_2 impurity in the CO_2 gas (Rao, 1997). The practice has changed in the 1980 s and 90 s, from the use of nitrogen gas or air to CO_2. Finally, the impact of nitrate additions is small, e.g, primarily from $Gd(NO_3)_3$ used for reactivity control; this constitutes $<1\%$ of production (Boss and Allsop, 1995; Rao, 1997). This is a transient addition, mostly at start-up following a shutdown, and ion exchange resins remove this salt.

2.2.3. Gas cooled reactors

The fuel of the HTGR consists of uranium particles distributed through a graphite matrix. The fuel contains nitrogen as an impurity and ^{13}C in graphite and ^{17}O in UO_2. Besides pebble bed reactors, graphite is also used as fuel element blocks. In moderator/reflector, ^{13}C exists as a major constituent of the structure as graphite piles along with nitrogen impurities. The important ^{14}C producing reactions in this reactor are $^{14}N(n,p)$ and $^{13}C(n,\gamma)$. Estimated production rates of ^{14}C in HTGR (Braun et al., 1983) are shown in Table 5.

In a CO_2 cooled gas cooled reactor (e.g. Magnox and advanced gas cooled reactor (AGR), as opposed to the use of helium gas in HTGR, additional production of ^{14}C occurs in coolant.

In the moderator graphite, over 60% of ^{14}C is produced by interaction with nitrogen impurities in the graphite and 40% by interaction with the ^{13}C contained in the graphite pile. The concentration of ^{14}C in the moderator graphite is estimated to be between 6.5×10^{-4} Ci/kg (2.4×10^{4} Bq/g) and 1.8×10^{-3} Ci/kg (6.7×10^{4} Bq/g) (Guiroy, 1995).

Table 5
Estimated ^{14}C production rates from gas-cooled reactors (Braun, et al., 1983)

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

N/A: Not available.

2.3. Distribution of ^{14}C in reactor systems and forms available for release

Once ^{14}C is generated, it can remain in the structural/fuel materials, in the coolant and the moderator (HWRs), on ion exchange resins used in purification, or it can be released to the atmosphere as gaseous form. Cycling of ^{14}C in the environment depends upon its potential for release from its origin or its containment. Most of the ^{14}C produced in the structural and fuel materials will remain in reactor systems until these items are removed. Release of ^{14}C from these materials could be realized during the long-term disposal phase. Gaseous release of ^{14}C from spent fuel has been the focus of extensive investigations in the 1990 s in the context of disposal into the hot, unsaturated Yucca Mountain repository. The dose to the population of the world due to ^{14}C releases from the proposed Yucca Mountain repository was predicted to be large in comparison to the EPA's limit on the 'collective dose', even though the dose per person was miniscule. However, with the changes toward the individual dose-based standards, ^{14}C release (with very small individual dose resulting from gaseous release) from spent fuel has become a non-issue and thus will not be further discussed in this paper. In the context of HWRs fuel disposal, dose estimates due to ^{14}C (assuming an ingestion scenario) are projected to be orders of magnitude lower than other radioisotopes in spent fuel (AECL, 1994). Carbon-14 release from structural activated materials is potentially a concern in the LLW disposal. However, its dose impact compared to other ^{14}C containing waste materials has been projected to be small.

The major chemical form of ^{14}C available for release is as bicarbonate on ion exchange resins ($H^{14}CO_3^-$). Production in the coolant of all types of LWRs and HWRs, and especially in the moderator of HWRs, is removed by ion exchange resins in a purification system. After the service life in the reactor, the resins are discarded into storage tanks, whether these tanks are inside reactor buildings or in licensed sites for long-term storage. The chemical form on the resins is still bicarbonate. This anion can still be chemically displaced by other anions present in natural waters, hence, it is considered as available.

2.3.1. LWR (PWR and BWR)

The ^{14}C produced in the coolant system can remain in the reactor coolant, in solid or liquid wastes from the processing of reactor coolant (includes spent ion exchange resins). For the ^{14}C in the coolant system, about 95% is expected to be available for gaseous release, with the remaining 5% becoming mostly part of the LLW. Typical annual releases of ^{14}C are 10–20 Ci (0.37–0.74 TBq) via gaseous release (NCRP, 1985; Fowler and Nelson, 1981; Kunz, 1985). Most of the ^{14}C produced in fuel in LWRs is not available for release and remains in the fuel/structural materials.

For solid waste streams, major low level wastes for ^{14}C include ion-exchange resins, irradiated hardware, evaporator bottoms, filter sludges, cartridge filters, and trash. These solid LLWs are stored at the plants until they are

Table 6
Distribution of ^{14}C in LWRs

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

shipped to disposal facilities. Annual average quantities of ^{14}C shipped in low-level solid radioactive wastes for nuclear power plants, excluding the irradiated hardware, is 1.9 and 1.23 Ci/GW(e)-yr (0.07–0.046 TBq/GW(e)-y) for PWRs and BWRs on a reactor year basis, respectively (Vance et al., 1995).

Table 6 shows the distribution of radionuclide inventory in various LLW streams and forms (Yim and Simson, 1999). The estimates are based on the Barnwell LLW site data between 1989 and 1994 (Dames and Moore, 1995a). The ^{14}C activity was mainly in dewatered ion-exchange resins (48.8%), activated hardware (24.1%), and the mixed DAW (13.6%). The solidified waste represents only 7.2% of the ^{14}C inventory.

2.3.2. HWR (CANDU-type)

Most of the ^{14}C inventory in HWRs is present on resins, with comparatively small fractions present at its production place (fuel and irradiated components). In terms of the total ^{14}C production, approximately 93% of the production remains on resins (coolant and moderator resins), ~4% has been released. The rest, ~3% associated with fuel (includes defected fuel elements), is not available for release (ACRP, 1995). The inventory in the moderator/coolant can be available for release even when the activity is captured in resins as resins go through degradation and ^{14}C partitions out of the system. Spent resin wastes are usually kept in storage tanks inside the reactor service building, while at some stations, the practice is to transfer these resin wastes at a licensed wastes site outside the station, for long-term storage.

Approximately ~5% of the non-fuel associated ^{14}C activity in HWRs is actually released to the atmosphere, which amounts to ~10–15 Ci/yr (0.37–0.56 TBq/yr) for a typical reactor (Boss and Allsop, 1995, for 90% capacity). Most of this comes from venting and purging the moderator cover gas from normal reactor operations, and small leaks from the moderator components. The storage tanks at the stations containing spent resins potentially release small amounts of ^{14}C through the stacks.

It is safe to assume that ^{14}C releases from the fuel are negligible, for the planned life of a station or the interim storage period (assuming a period of less than 50 years altogether). The chemical form of the ^{14}C in the fuel is mostly carbide, oxycarbide or elemental C (Stroes-Gascoyne and West 1994). These forms are unlikely to be released as gaseous form. Even the fuel defect proportion (typically <0.1% (AECL, 1994)) constitutes a negligible potential for gaseous releases.

2.3.3. Gas cooled reactors (GCR)

Release of ^{14}C from HTGR is relatively small as most of ^{14}C production is in fuel and moderator graphite. In the absence of ^{14}C control, the predicted ^{14}C release from a 1000 MWe plant per year is about 0.04 TBq (Braun et al., 1983). For a CO_2 cooled reactors (e.g. Magnox and AGR), the ^{14}C release is higher as a large portion of gaseous ^{14}C release comes from the purification of the CO_2 coolant circuits and from the isotopic exchange between the moderator and the CO_2 circuit (DuBourg, 1995). The amount of ^{14}C release from the CO_2 cooled reactors is expected to be about 0.37 TBq per year (10 Ci/yr) per 1000 MWe plant.

Also, if the HTGR fuel is reprocessed, the graphite matrix is to be incinerated in oxygen, requiring the fuel particles to be dissolved, thus releasing all of the ^{14}C in the fuel. The amount of ^{14}C release from this is estimated at 133 TBq per year assuming a plant reprocessing 40,000 MWe fuel per year (Braun et al., 1983).

2.4. Inventory and emissions estimates

Estimation of worldwide ^{14}C inventories and potential emissions (i.e. available for release) by reactor types have been made to compare the production numbers with natural cycles. These are presented in Table 7. There were 436 reactors in operation at the end of 2003 (WNA, 2004). Of these, the combined total of LWRs was 356 (264 and 92 for PWR and BWR, respectively), followed by HWRs (39), GCR (Magnox, ACR, GCR, total of 22) and LGR (Light Water Cooled - Graphite Moderated Reactor) (17).

Other types (e.g. FBRs) are in small numbers and not discussed. Research reactors (~280), reactors in submarines and vessels (~220) and old shutdown reactors (112) are not discussed, because of their anticipated small figures, compared to power production reactors. One notable exception is the 6 reactors currently not in operation, of which 5 are PHWR (CANDU-type) and are anticipated to return to service; these 5 reactors are included in our estimates.

For these figures, the production estimate, in activity units per energy produced (e.g. TBq/GWe-y) were multiplied by the total cumulative generating capacity (GWe-y or equivalent), compiled from available data (WNA, 2004;

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

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

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

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

ACRP, 1995). The percentage of world generating capacity by the different types of reactors was obtained from the literature (Liepins and Thomas, 1988; Choppin et al., 2002; WNA, 2004). This distribution has remained relatively constant since ~1976. Before 1975, the total generated capacity was small (<5% of the total historic production), so this percent distribution is accurate within a percent or two.

The reactor-made production rate is in the same range as the natural production in the atmosphere, while the total cumulated ^{14}C produced by reactors is quite small compared to the atmospheric inventory. Although the presence of ^{14}C inventory does not necessarily constitute an environmental problem, this nevertheless constitutes a liability requiring appropriate characterization of the impact of the release.

3. The chemistry of ^{14}C in the reactor systems

3.1. General aspects of carbon chemistry

Carbon has one of the most elaborate chemistry among the elements. As for all elements, the chemical form of ^{14}C is controlled by the redox potential, the pH and the temperature of the system. Carbon can exist in various oxidation states, from its +IV state (as CO_2, including the carbonic acid species) to its -IV state (as methane), while its elemental state at 0 is solid carbon ('graphite'). Several intermediate states exist, in inorganic and organic forms.

Looking strictly at the redox behaviour of carbon, thermodynamics dictate that CO_2 and CH_4 are the most stable species under acidic standard ambient conditions of 25 °C, while the fully dissociated carbonate is most stable under alkaline conditions. Pourbaix diagrams (i.e. E_H-pH diagrams) show a large predominance field for all the carbonate species for most redox conditions under standard conditions (Fig. 1a). The presence of a narrow field is generally accepted for elemental C ('graphite') to pH ~ 11 under mildly reducing conditions, although this has been questioned (Rosset and Desbarres, 1993). The stability field of small organic molecules (e.g. formaldehyde, formic acid, etc.) would be very close to that of elemental carbon (Brookins, 1988). Under strongly reducing conditions, methane is stable for the full pH range; Rosset and Desbarres (1993) have also predicted the presence of methanol (CH_3OH) as an intermediate reduced species under strongly reducing conditions.

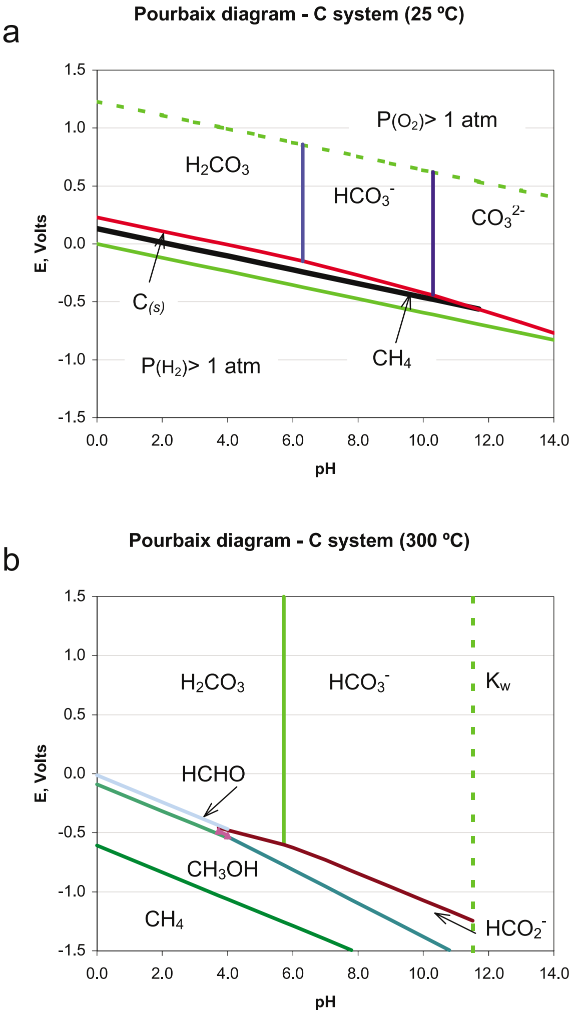

Fig. 1. Pourbaix diagrams of the major carbon species (modified, using the approach of Rosset and Desbarres, 1993); (a), 25 °C and standard conditions; (b), 300 °C.

Under high temperatures (~300 °C) close to reactor conditions, carbon can exist in a greater variety of chemical forms (Rosset and Desbarres, 1993). The predicted forms include CO_2 (plus carbonic acid and bicarbonate), and simple organic carbon compounds of mixed oxidation states. Elemental C ('graphite') would not be stable under these high temperature conditions. The other dominant forms include a narrow formaldehyde field at low pH, and a larger stability field for formic acid at high pH (~4–11), both under mildly reducing conditions. The reduced field is dominated by CH_3OH, while the CH_4 field is present under strongly reducing potential.

It should be mentioned that Pourbaix diagrams are useful, but oversimplifications were necessary, e.g. equilibrium conditions, Standard States (1 atm, temperature of 25 °C or 298 K, 1 mol/L solutions) were assumed for Fig. 1a.

Along with the difficulty of predicting the correct concentrations of C in coolant, kinetics, which are difficult to predict, could keep species outside their stability field before equilibrium could take place. Likewise, species formed under specific conditions (e.g. reactor environment at high temperature) might not be stable under ambient conditions (e.g. for sampling or analysis), or conditions expected in a disposal vault. In other words, if a species is detected and reported in a study, it does not necessarily mean that it existed in the very environment where it was formed, unless sampling was done specifically for it. The reverse is also true.

3.2. BWRs and PWRs

The chemical environment of PWR primary system is reducing because the concentrations of dissolved hydrogen (caused by maintaining an overpressure in the gas space of the Volume Control Tank) are high enough to consume radiolytically generated oxygen species (Wood, 1995). The concentration of dissolved hydrogen is sufficient to combine with ^{14}C to create organic compounds. Under this environment, the $^{14}CO_2$ will be reduced to carbon, methane, or other organic compounds such as formaldehyde or methanol. In contrast, the chemistry environment of BWR coolant systems is oxidizing. Under this environment, the ^{14}C will be present as $^{14}CO_2$ and carbonic acid species.

The presence of other chemical species such as corrosion products or various anions in the coolant systems also affects the fate of ^{14}C activity: most anions originate from ion exchange resin debris released from the degradation of the ion exchange resins in the column. The debris range from dissolved polymer segments to particulates small enough to pass through the filter pores. If the coolant system to which these anions are introduced is oxidizing, oxidation of the species to bicarbonate is continued.

Experimental investigations have showed that ^{14}C exists in PWR coolant systems mainly as organic carbons (58–95%) (Vance et al., 1995). In contrast, the ^{14}C in the BWR primary coolant was shown to be predominately inorganic, such as bicarbonate. The organic carbon content in BWRs ranged from 13 to 48%. The attachment mode of these organic species of ^{14}C on the resin was unknown, and an alternate sorption mechanism, rather than a classical ion exchange, was assumed for this (Vance et al., 1995). Another independent investigation showed that the major forms of organic carbons in PWR coolant systems were acetaldehyde, methyl alcohol, ethyl alcohol and acetone (Matsumoto et al., 1995). The presence of large inventory of solid carbon in PWRs was also noted based on the observations made with the filters drawn from the coolant system (Miller, 2000).

It was speculated that large fractions of the ^{14}C (in PWR stations) rapidly associates with the hydrogen or trace quantities of organic matter present in the reactor coolant, once the ^{14}C is formed in the coolant. As mentioned before, the dissolved hydrogen concentration is sufficient to combine with ^{14}C to create organic compounds. One can also speculate, as mentioned before, that the conditions (temperature, pressure) are different in the place where the ^{14}C is formed, as opposed to the ion exchange resin columns, where it was observed, and transformations in the carbon species might have occurred.

3.3. HWRs (CANDU-type)

A wide variety of carbon species can form in the primary coolant (heat transport system) of HWRs. The coolant is heavy water contained in a high temperature loop, with the potential to make elemental or organic C forms. Sampling has shown that, although organic species were observed, dissolved $^{14}CO_2$ ($14CO_3^{2-}$ to be exact) predominate due to the high pH conditions ($\sim$10.5 or above; Rao (1997)). According to that same work, the exact chemical forms of C in this loop are unknown. The ^{14}C is controlled to some extent with ion exchange resins, hence a significant portion of the ^{14}C from the heat transport system is considered to be on resin wastes in anionic form. The ^{14}C produced in the fuel, likely present as carbide, oxycarbide and elemental C, would be released to the heat transport system only under rare and occasional fuel failures. For waste management purposes, the organic forms of ^{14}C could be gaseous, and they are available for release to the environment, rather than being confined within resins.

The moderator consists of high purity de-ionized heavy water in a closed-circuit loop. It is kept under oxidizing conditions with excess O_2, which is used to recombine hydrogen gas (as D_2) produced by radiolysis. The recombined D_2O will return to the moderator loop. As a result, the inorganic carbonate species are the dominant form of ^{14}C, as $^{14}CO_2$ in the gas phase, and the dissolved forms of carbonic acid in the water. The levels of ^{14}C in the moderator are controlled with ion exchange resins in a purification system.

Finally, in the annulus gas, the major form of ^{14}C is $^{14}CO_2$, as the CO_2 purge annular gas is doped with $\sim$2–3% of O_2 to keep oxidizing conditions (Rao, 1997). Currently this gas is released, but its chemical form makes it easy to isolate, if needed.

3.4. Gas cooled reactors

In the HTGR core, ^{14}C is retained in graphite primarily as elemental carbon. On surfaces, some oxygen will be associated with it. ^{14}C produced in reactions other than from ^{13}C (i.e. ^{14}N or ^{17}O) is likely to be present in surface oxide and in the carbonaceous deposits (C/H/O compounds of high molecular weights) (Wickham, et al., 1995). In a CO_2 cooled reactor, a large amount of ^{14}C is produced as $^{14}CO_2$ in the coolant. This form is available for release.

4. Issues in short-term management of Carbon-14 at stations

Carbon-14 generated in reactors will undergo phase and/or chemical transformations related to changes in the immediate environment, and other external changes, such as microbial degradation, ingress or contact with other chemicals, etc. It is not unusual that the period between production and removal from reactors for disposal takes several years to decades. During this period, transformations can take place, similarly to an early disposal period in a waste site, with the difference that engineered controls and monitoring are generally more extensive at a reactor site than in a disposal facility. Some considerations may be needed to help decide when or if ^{14}C should become an operational consideration or a long-term dose contributor, if long-term storage is necessary.

4.1. Chemical transformations of ^{14}C during storage

The chemical forms of ^{14}C in the material that will eventually become LLW will be different from those existing at the source (e.g. coolant/moderator system), as the temperature and redox potential of the system environment change. During a water-reactor operation, the coolant temperature is on the order of 300 °C, and pressures are high (155 bar for PWR; 72 bar for BWR; 89 bar for CANDU). The condition for filters and ion exchange resins represent what is closer to ambient conditions. As the temperature of the system is lowered and the system becomes more oxidizing by being exposed to the ambient atmosphere, the ^{14}C could experience a series of oxidation processes. This implies that ^{14}C inventory in LLW may be more in inorganic form such as the insoluble reduced forms of carbon (elemental C) and the aqueous species carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-). Presence of organic ^{14}C is still possible. The ^{14}C on ion exchange resins is mostly as bicarbonate, which is stable under the near-atmospheric conditions for storage tanks. This is in agreement with the chemical species that are most commonly found in the natural environment and typical waste (Krupka and Serne, 1998; Dayal and Reardon, 1992; Jeffries, 1990; Gruhlke et al., 1986; Kunz, 1985; Martin, 1986; Cline et al., 1985; Impell Corporation, 1985). The fraction of inorganic vs organic ^{14}C is significant in that it factors into the solubilities, distribution coefficients, and microbial activity models.

Although it is expected that the ^{14}C produced in the fuel will remain trapped, the ^{14}C produced by irradiation of nitrogen impurities in the cladding and supporting hardware can be released in spent fuel pools. The mechanism by which this can take place is unclear, whether it is surface leaching, minute corrosion, etc. (see the discussion by Van Konynenburg, (1994)). Eventually, the ^{14}C can find its way into the ventilation system and it is potentially exhausted out through the building stack, and not in wastes.

4.2. External transformations affecting ^{14}C chemistry during storage

There is potential for transformations of the ^{14}C on spent resins, during the interim storage period at the stations, resulting in expedited ^{14}C release to the environment. Resins generally consist of a carbon-based polymer, which can undergo damage during service, such as thermal damage (Simister et al., in press), oxidative degradation by peroxide, radiolysis, or a combination of all the above. The resin damage potentially affects the ion exchange capacity and the potential for the resin to retain the radiocontaminants.

Other factors, such as ion ingress and microbial degradation in storage tanks, affect the equilibrium of resins by changing the following set of equilibria (the superscript ‘14’ is omitted for simplicity):

$$R^{(+)}OH^{(-)} + HCO_3^- \leftrightarrow R^{(+)} - HCO_3^{(-)} + OH^- \quad (1)$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \quad (2)$$

$$HCO_3^- + H^+ \leftrightarrow H_2CO_3 \quad (3)$$

$$H_2CO_3 \leftrightarrow H_2O + CO_2(\text{gas}) \quad (4)$$

For example, Eq. (1) represents a ‘fresh’ resin (R) with its associated counter ion hydroxide (OH^-), as $R^{(+)}OH^{(-)}$, which is displaced by the bicarbonate ion (HCO_3^-). Eqs. (2)–(4) represent the dissociation of carbonic acid in water. During storage, any factor affecting the bicarbonate-resin (Eq. (1)) and acid-base equilibria (Eqs. (2) and (3)) could increase the volatility of carbonic acid (Eq. (4)). The latter equilibrium is bi-directional, which means that changes in the CO_2 partial pressure affects the equilibrium (Eq. (1)), while changes in the isotopic content of the overlaying CO_2 ($^{14}CO_2 + {}^{12}CO_2$) is a mechanism of isotopic exchange:

$$R^{(+)}O_3{}^{14}CH^{(-)} + H^{12}CO_3^- \leftrightarrow R^{(+)}O_3{}^{12}CH^{(-)} + H^{14}CO_3^- \qquad (5)$$

This does not significantly affect resin equilibrium (Eq. (1)). Equilibria (3) and (4) are involved with isotopic exchange. Exposure to the atmosphere follows this mechanism; upon removal of $^{14}CO_2$-rich air overlaying the solution contacting the resin, resins can become depleted in ^{14}C. This exchange is slow but it does take place.

Other exchange with foreign ions like nitrate can also occur:

$$R^{(+)}O_3CH^{(-)} + NO_3^- \leftrightarrow R^{(+)}O_3N^{(-)} + HCO_3^- \qquad (6)$$

This also affects the potential for resins R to retain bicarbonate, thus affecting ^{14}C release to the environment. Nitrate is of particular interest in HWRs because Gadolinium nitrate is used for reactivity control. If ingress of water takes place in a tank, other common ions (Cl^-, SO_4^{2-}, etc.) have the same effect, but to different extents. This extent depends upon the general selectivity of strong-base anion resins for the ions (Bio-Rad, 1987). The selectivity of strong-base anion resins for the ions is compared as the following:

$$OH^- < \text{Acetate} < HCO_3^- < Cl^- < NO_3^- < HSO_4^- < \text{citrate} \qquad (7)$$

This list indicates that the hydroxyl ion (OH^-) is the least strongly held anion on resins, followed by acetate, etc. This order also means that common ions (Cl^-, NO_3^-) can easily displace bicarbonate (HCO_3^-) from the exchange sites on spent resins in waste tanks. This is true, especially when ingress of foreign ions takes place on discarded resins that have been in extended service, with exhausted capacity, or if resin damage occurred, affecting the capacity.

The effect of service temperature and strong oxidants on resin equilibrium and capacity (in isolation or combination) is not well addressed in the literature. Similarly, the effect of bacterial growth is not well known. One would expect the effect of bacterial growth to be twofold: (1) It can potentially convert some inorganic C into organic forms and enhance ^{14}C cycling; and (2) Production of anions from microbes (exudates or metabolites), which can displace the ^{14}C from resins; this includes acetate and other citrate-like organic anions.

These issues are recognized at some plant stations, and at present, engineered solutions, such as use of scrubbers, can mitigate against emissions from storage tanks. Long-term effects on the scale of a few decades (the assumed projected life of a station) are not well known, but in general, these are small, compared to the normal operating releases from the stations.

5. Carbon-14 in low-level waste management facilities

There are at present several commercial near-surface LLW facilities in both the U.S. and Canada, some of which are in operation, while others are no longer in operation. All of the commercial LLW facilities in the U.S. are disposal sites. In Canada, near-surface LLW facilities are considered long-term storage, and not for disposal.

The discussion focuses here on specific situations or wastes sites. The processes taking place and described within are sufficiently well known to apply to other sites that have similar physical, hydraulic and climatic characteristics.

5.1. Modeling the behavior of ^{14}C wastes within LLW facilities

The release of ^{14}C and other radionuclides from LLW materials depends on the type, behavior and durability of the waste forms and containers in which the radiocontaminants are disposed of. The ^{14}C in U.S. LLW is mostly associated with ion exchange resins, irradiated hardware, dry active waste, and filters (Yim and Simonson, 1999). Most of these waste forms, except the irradiated hardware, will be susceptible to degradation during the extended periods of storage. If the activity is retained at the surface of the waste material through adhesion, sorption, or ion exchange, the radionuclides can be easily released through surface-wash by water. The activity immobilized in a solidified matrix

Table 8
C-14 K_d Values in cemetitious environments

Study (K_d values in ml/g)	K_d Value (mL/g)	Environment	Nature of data
NAGRA study (Allard, 1985)	5000		Best estimate from experiments
UK DOE study (Nacarrow, et al., 1988)	10,000	Not specified	
NIREX study (Ewart, et al., 1989)	2000	Reducing	Best estimate
SKB study (Wilborgh and Lindgreen, 1987)	1000	Fresh concrete	Lowest experimental value found in the literature
GSF study (Buhmann et al., 1991)	0.4		Best estimate

(such as in cement or polymer) would be released through migration in the pore waters of the solidified waste form. In this case, release of radionuclides takes place by diffusion through the pore water in the waste form. If the radionuclides are bound or are part of the matrix material (e.g., irradiated hardware), they can only be released congruently when the matrix material is corroded or dissolved.

The process of surface wash is typically modeled with the assumption of equilibrium partitioning (of radionuclides) between the waste form and the contacting solution (Sullivan and Suen, 1989; Yim and Simonson, 2000). Experimental values of K_d to represent equilibrium partitioning of ^{14}C surface wash release in the LLW are not available. Instead, the values of K_d[1] expected in the soils for ^{14}C are used for the K_d in the waste. Typically, the K_d value used in the LLW source term modeling ranges between 0.01 and 1 mL/g. When site-specific data are not available, a value of 0.01 mL/g is commonly used (US NRC, 1993; Looney et al., 1987; US EPA, 1988a,b).

If the LLW is immobilized in cementitious waste form or backfill, the geochemical behavior of ^{14}C will be significantly affected by the strongly alkaline environment. Under this condition, ^{14}C will transform into inorganic form (calcite) through carbonation process. The mineralogic changes with carbonation of cementitious materials also induce changes in permeability and porosity of the waste form. Release of ^{14}C as calcite is mainly controlled by solubility and dissolution kinetics of calcite under varying flow rates. Under relatively stagnant flow conditions, ^{14}C release is solubility-limited as calcite does not undergo dissolution at high pH conditions. However, if high flow conditions exist, hence, lowering the pH, calcite will exhibit some degree of dissolution, resulting in release of ^{14}C by diffusing through the waste form matrix.

The process of diffusion in a waste form is dependent on the effective diffusion coefficient in the material and the boundary conditions by which the concentration gradient is determined. The effective diffusion coefficient is a function of processes such as diffusion, dissolution kinetics effect, sorption/desorption, and the matrix properties such as porosity and tortuosity. However, given the long half-life of ^{14}C, the effectiveness of the cement waste form as diffusion barrier is a very short-term one.

Although the durability or integrity of the cementitious waste form is not maintained for long enough time periods to prevent fluid flow for the long-lived ^{14}C, the chemical interactions and reaction-induced chemical conditions are likely to last very long periods to make it an effective long-term chemical barrier for the immobilization of ^{14}C (Dayal, 1995a,b). In cement, the SiO_2 is originally negatively charged, but through the interaction with CaO, becomes positively charged. These positive sites on the SiO_2 surface adsorb inorganic ^{14}C by an electrostatic force. The increased sorption capacity (Noshita et al., 1996) can significantly reduce ^{14}C release. Table 8 gives the examples of data for ^{14}C K_d in cementitious environments. Most of these data reflect conditions expected after significant degradation since it is based on studies of sorption of pulverized concretes and cements (Dames and Moore, 1995b).

Finally, corrosion rates are often used to model the process of dissolution release, based on the assumption that the radionuclide is released congruently with the matrix (Sullivan and Suen, 1989). The release rate is typically assumed to be constant in time. For carbon steels, the mean value of corrosion rate in soils was estimated at $1.8 \pm 1.5 \times 10^{-10}$ cm/s (Romanoff, 1957).

---

[1] K_d is defined as the ratio of the amount of a contaminant sorbed on a solid to the amount of the same contaminant in a liquid phase, equilibrated together. A low K_d value means low affinity for the solid phase, compared to the liquid. The references quoted here should be consulted for more details.

5.2. Generation and release rates of ^{14}C gases from LLW

Carbon-14 contaminated gases, methane and CO_2, can be generated from LLW through microbial degradation of organic materials in the waste. Gas phase ^{14}C may be available for release at rates greater than would normally be experienced through the liquid (groundwater) pathway. At the same time, if significant amounts of gaseous ^{14}C activity are released through the air pathway, this will deplete the inventory of ^{14}C available for release through the groundwater pathway.

Microorganisms play a significant role in the generation of ^{14}C gases, either directly through their metabolic activity (assimilatory carbon), or by displacement of the ^{14}C by $^{12+13}C$ from respiration (CO_2 from respiration, acetate generation, etc.). Both processes could lead to converting solid substrates, or displacing substrates (e.g. $H^{14}CO_3^-$ on resins) from solids, into gaseous end products. The gases produced will depend on the evolution of the oxidation potential of the environment and the particular organisms present. Under aerobic conditions, organic substrates decompose and consume oxygen to produce CO_2. Under anaerobic conditions, methanogenic bacteria use hydrogen and carbon to produce methane and CO_2. On the longer-term, the degradation processes (including microbial) will control the redox potential of the system (Caron, 1996).

The long-term behavior of ^{14}C from a source in a degrading matrix, which contains mostly stable carbon ($^{12+13}C$), has to involve the simultaneous measurements and prediction of the behaviour of both ^{14}C and ^{12}C (‘total’). To determine the generation of ^{14}C-contaminated gases, LLW streams need to be characterized in terms of the ^{14}C contaminated organic carbon inventory and their biodegradation characteristics. The organic fraction of LLW will have the potential to degrade by microbially mediated processes. Various LLW streams in the form of metals and inorganic substances do not contribute to the organic carbon inventory. These waste streams include equipment, solid non-combustibles, non-cartridge type filter media or incinerator ash. Besides these, many compounds in non-utility waste streams are varieties of organic radiocarbon compounds, depending on the type of waste stream. They decompose at various rates when exposed to hydrolysis and microbial action. Among the total ^{14}C activity in organic compounds, the fraction in a cement waste form in which the pH will remain high is not generally available for microbial degradation. Excluding this fraction, about 40% to 60% of the total ^{14}C activity is estimated to have the potential for gas-phase release through microbial attack for the LLW disposed of in the U.S. (Yim, 1994).

According to the studies done at the Chalk River site in Canada in a long-term storage LLW area, the amount of wastes available for microbial degradation could be higher than above. Approximately ~80% of the LLW received at the Chalk River Laboratories are diverted to low-level trenches, while ~92% of the LLW intended for disposal in a projected near-surface site consist of waste bales (Dolinar et al., 1996). These wastes are the most susceptible to biodegradation.

Biodegradation of organic waste is critically dependent on the hydrolysis characteristics of the wastes. Based on appropriate rate constants, ^{14}C contaminated gases generation by microbial activity can be modeled using a chemical kinetic description of aerobic and anaerobic decomposition, along with modeling of oxygen transport in the waste (Yim, 1994). A LLW waste degradation model has been modified to predict future trends of waste degradation (Caron, 1996; Caron et al., 1998b). The model follows the stoichiometry of sugar degradation, under both aerobic and anaerobic conditions (Pirt, 1978):

$$\text{Aerobic}: \ C_6H_{12}O_6(\text{"cellulose"}) + O_2 \rightarrow H_2O + CO_2(g) + \text{biomass} + \text{energy} \tag{8}$$

$$\text{Anaerobic}: \ C_6H_{12}O_6(\text{"cellulose"}) + O_2 \rightarrow CH_4O + CO_2(g) + \text{biomass} + \text{energy} \tag{9}$$

These degradation reactions generally follow a first-order rate (Jenkinson and Rayner, 1979; Swift et al., 1979). These reactions and the accompanying kinetics also apply to municipal landfills (Ehrig, 1983; Findikakis et al., 1988). The model is based on the amount of C left in a closed system at time t, using the basic relationship:

$$C_t = C_0 e^{-k\,t} \tag{10}$$

Where

C_t Amount of C left in the system at time t (mass units)

C_0 Amount of C in the system at time $t=0$ (same units as above)

k First order rate constant, or hydrolysis rate constant (time^{-1})
t Time (reciprocal units to k).

Wastes contain various substrates available for microbial degradation, which have their own biodegradation potential. For example, in sanitary landfills, food and yard wastes decay much faster than polymers such as plastic bags. LLW are generally similar to ordinary landfills, with the major difference that yard and food wastes are not permitted in radioactive wastes. Without this type of C source, Caron (1996); Caron et al. (1998)) have suggested their model with different types of carbon source:

$$C_t = \sum_{i=1}^{n} C_{0(i)} e^{-k_i t} \tag{11}$$

The different carbon sources i have different biodegradation rates k_i and different initial quantities $C_{0(i)}$. The number of categories n depends upon the number of categories of biodegradation rates that are identified. For the degradation rates of wastes from a near-surface LLW burial site such as WMA-C (waste management area, 'C', see later section for further details), three categories of organic C have been created ($n=3$ for Eq. (11)). Subscripts 1 and 2 for the Carbon types refer to biodegradable material, and subscript 3 refers to the non-decomposable or recalcitrant type of organic C. The choice of rate constants is based on the following:

Type #1 Paper and cellulosic material: paper, cardboard, textiles, mop heads, etc., which is slowly biodegradable (SB). Caron et al. (1998a,b), after a literature review, proposed a degradation rate $k_1=1.87\times10^{-2}\ \text{a}^{-1}$, corrected to $9\times10^{-3}\ \text{a}^{-1}$ using the Arrhenius relationship, for the temperature of 8 °C expected in a waste repository. The value of $C_{0(1)}$, the initial amount of SB Carbon, depends upon the relative quantity of wastes containing the carbon of this type. Various estimates, based on literature values and macroscopic evaluations of LLW, are given in Caron et al. (1998a,b).

Type #2 Plastics and artificial polymers: packaging material, plastic bags, tyvek suits, etc. These are considered as Moderately Slowly Biodegradable (MSB). Caron et al. (1998b) have proposed the rate constant $k_2=9\times10^{-4}\ \text{a}^{-1}$, which is 10 times lower than for the SB material. The value for $C_{0(2)}$ is also based on literature values and macroscopic evaluations of LLW (Caron et al., 1998b).

Type #3 This type of organic C is the non-biodegradable components, or *recalcitrant material* (RM). This is the portion of the organic C from the types above that is not significantly decomposable. Its half-life was set to the same degradation rate as the RM of Jenkinson and Rayner, (1979), $k=3.5\times10^{-4}\ \text{a}^{-1}$, or $t_{1/2}=2000$ a., while $C_{0(3)}$ is the difference of biodegradable and non-biodegradable material from above (Caron et al., 1998b).

This simulation provides useful estimates of the degradation behaviour of wastes containing organic Carbon, and the source term of gases generated by waste burial sites. Although this has been modeled extensively for municipal landfills (see, e.g. Ehrig (1983); Findikakis et al. (1988)), estimates for nuclear wastes are scarce (Yim et al., 1996; Caron, 1996; Caron et al., 1998b). The simulation is plotted in Fig. 2 for wastes representative of WMA-C, according to different scenarios of initial content biodegradability, and different carbon contents waste contents. The single point for WMA-C is based on the field data in a 1997 study where the average age of the waste was 17 years.

Although these estimates can be done for long-term degradation of carbon, it should be pointed out, again, that gaseous releases originating from the degradation of (primarily stable) $^{12+13}$C are not necessarily similar to gaseous releases of ^{14}C. Both isotopes (^{14}C and ^{12}C) are not necessarily mixed, because the isotopes are most likely locked up in different original species: ^{12}C is primarily in organic forms, while ^{14}C is more likely present in inorganic C, such as ^{14}C bound to resins by ion exchange; a small portion is as organic ^{14}C (Rao and Killey, 1994). Realistic long-term predictions, not available at this stage for LLW, should focus on determining long-term washout rates of ^{14}C. A situation close to this is based on lysimeter studies (Sheppard et al., 1994) which is still a short-term experiment.

The key finding of gaseous release on performance assessments has been through the reduction of inventory of ^{14}C available for transport in ground water. Fig. 3 illustrates the reduction observed in the overall LLW inventory in a typical U.S. disposal facility through airborne releases of ^{14}C. The figure compares the reduction of ^{14}C inventory due to radioactive decay only with that combined with depletion by biodegradation. The result was obtained by using

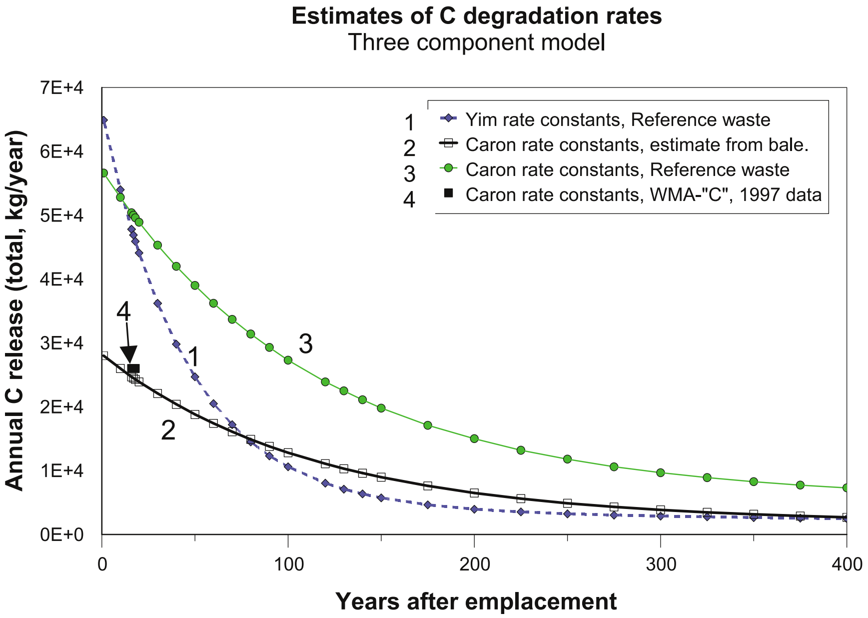

Fig. 2. Simulations of organic carbon degradation from a near-surface LLW site (Caron et al., 1998b). The best estimate is for curve No. 2 (assuming the average C inventory of baled wastes is representative of the wastes). Curve 1 stands for the reference wastes from Chalk River, assuming different rate constants taken from Yim et al. (1996), while curve 3 uses the rate constants of the current work, with a C inventory calculated for the Reference wastes. Point #4 stands for the field work at WMA-C in Caron et al. (1998b).

the standard mix of LLW in the U.S. and the corresponding biodegradation rates for different waste forms, taking into account the degree of water saturation in each waste (Yim et al., 1996). The result indicates the potential for significant depletion of the ^{14}C inventory via gas-phase release. This generally translates into an overall equivalent reduction in release compared to the benchmark performance assessment case, which typically does not take into account the gas pathway.

5.3. Release and cycling of ^{14}C in the vicinity of a LLW site

Studies on the release/cycling of ^{14}C have been done at several of the Canadian sites (Milton, 1993; Milton, 1996; Caron and Milton, 1998). These studies deal with environments typical of the Canadian boreal forest, which hosts the Chalk River site (Ontario, Canada, approximately 180 km west of Ottawa). This site has been the focus of nuclear research since the 1940's, and it hosts several waste management areas.

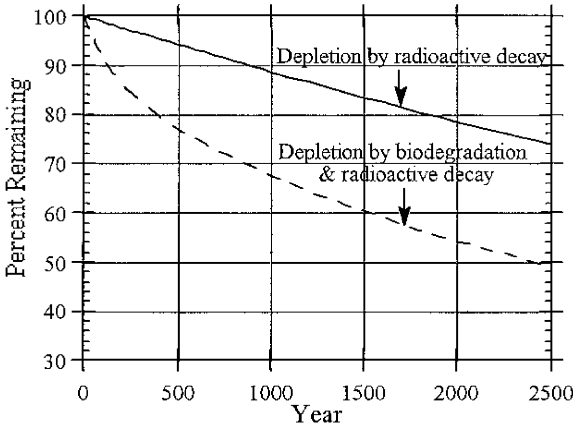

Fig. 3. Depletion of ^{14}C Inventory from a LLW burial site by radioactive decay and biodegradation.

A general survey of atmospherically dispersed ^{14}C levels has been done around the Chalk River site, in air and in plant material (Milton et al., 1996). Carbon-14 levels in plant materials were routinely found at about 2–3 times the natural levels around the site, while the enrichment was ~8–300 times in or around waste management areas. The highest levels of the survey were found near Waste Management Area 'C' (WMA-C), and in a nearby swamp, downstream from the site. This has sparked a series of ^{14}C cycling work that perhaps constitute the most unique set of studies available (Rao and Killey, 1994; Killey et al., 1998; Evenden et al., 1998; Milton et al., 1998; Caron et al., 1998a,b; Link et al., 1999). Summary highlights of these studies and implications are given here.

WMA-C is a major site used for the long-term storage of low-level wastes. It hosts approximately 90 000 m^3 of LLW, which were placed in unlined trenches, from 1963 to approximately 2000. The site is located in a sand dune, and the trenches are generally 3 m deep, with some that are up to 6 m-deep. The trenches were covered with overburden after filling, except for a large trench, which was covered with an impermeable cover in 1983. The wastes are exposed to infiltrating water except under the cover, but they are not submerged. Two contaminant plumes have developed from WMA-C, one of which emerges at a nearby swamp (Duke swamp), ~200 m downstream. The studies of Caron et al. (1998a,b) have revealed that most of the ^{14}C (~95% or more) is released from WMA-C to the atmosphere as $^{14}CO_2$, while the smaller portion is as ^{14}C-bicarbonate in groundwater. Methane is likely generated in the wastes, but it was not detected near WMA-C, as it is readily converted to CO_2 in the unsaturated, well-aerated sand surrounding the trenches. Rao and Killey (1994) have measured organic ^{14}C in contaminated groundwater, but it was not clear whether this material was originally present in the wastes as an organic ^{14}C form, or if it originated from microbial conversion. Their study also suggested that most of the ^{14}C leaving WMA-C is inorganic.

The main contaminant plume from WMA-C emerges and degasses at a nearby swamp (Killey et al., 1998). The majority of the ^{14}C coming from subsurface flow to the swamp is released to the atmosphere (~95%) via degassing from the plume at the resurgence point, leaving only a small portion in the water (stream and baseflow). The latter leaves the site through a surface stream. The swamp is a few hectares in area, and other studies of ^{14}C cycling in plants have been done (King et al., 1998; Evenden et al., 1998; Link et al., 1999). The uniqueness of these studies at Duke swamp relate to the area size of the source of ^{14}C, which is of the scale expected for disposal sites.

If the release from WMA-C was representative of a source term for LLW safety assessment, a significant portion of the initial inventory is lost through degassing. This is a significant finding from the perspective of performance assessment. Given that dose consequence from inhalation is much less than what is from ingestion for ^{14}C (see **Section 2.8), the significant amount of degassing means a lower potential dose to a hypothetical individual in a nearby dwelling. Field surveys have been performed to obtain mass balances (for ^{14}C and ^{12}C) from WMA-C, to obtain current release rates.

5.4. Movement of ^{14}C in the environment

5.4.1. Migration studies in groundwaters and soils

Transport of ^{14}C from an underground burial ground to a receptor location will be controlled by the movement of groundwater, the amount of water available for transport, the direction and speed of groundwater movement. Any physical phenomena affecting the dilution and dispersion of the contaminant will be important in this regard. The transport should also take into consideration of geochemical factors, such as immobilization (precipitation), sorption during the transport, matrix diffusion and isotope exchange with the more abundant stable C in soils. Bidirectional gaseous exchange may take place as well (this is discussed later). While precipitation depends largely upon other ions in solution and the pH, the mobility of ^{14}C in the soils/underground is typically represented by the sorption or partition coefficient K_d. Both aspects have to be considered on a case-by-case basis.

The K_d values of ^{14}C in different soil types have been complied by Sheppard and Thibault (1990) based on the literature. These values (in mL/g) are 5 (sand), 20 (loam), 1 (clay), and 70 (organic soil) as geometric means. Examples of ^{14}C K_d in different types of soil based on experiments are given in Table 9. Although most of the data are for the inorganic form of carbon, some are for the organic forms.

Examples of ^{14}C K_d values used for performance assessment are shown in Table 10. These represent estimates of ^{14}C K_d, based on a critical examination of original published data (such as those in Table 7), and other expert judgment on the geochemistry for the various types of soils and other conditions in the soils, sediments, or rocks. These values are used for modeling purposes by a number of government agencies in U.S., Canada, the United Kingdom, Switzerland, Germany, and Finland (McKinley and Sholtis, 1993). The values are primarily for the

Table 9
Measured data for the characterization of C-14 K_d in the soils

EPRI C-14 Study (Vance et al., 1995)		AECL Study (Evenden et al., 1998)	
K_d Value (mL/g)	Environment	K_d Value (mL/g)	Environment
3	Bicarbonate in sands,	85	Synthetic calcite
0	Bicarbonate in sediment	8–50	Natural calcite (different sizes)
57	Citric acid in sands	0	Montmorillonite
6	Citric acid in soil	30	Manitoba soil (inorganic ^{14}C)
7	Palmitic acid in sands	1	Manitoba soil (organic ^{14}C)
0	Palmitic acid in soil	76	Soil, calcite amended (inorg. ^{14}C)
		2	Soil, calcite amended (org. ^{14}C)

inorganic form of carbon. Note that the data from these two Tables differ from Table 8, which was strictly for the ^{14}C K_d in the near-field of a cementitious repository.

5.4.2. Fate of ^{14}C in the groundwater: groundwater-soil gas interface

It is important to understand the processes of soil-groundwater exchange to properly assess the migration of ^{14}C at this interface. This exchange of inorganic ^{14}C takes place through a complex mass transfer process. The rate of ^{14}C release as gas from groundwater depends on the speciation of the ^{14}C (pH-dependent) and the structure of the soil gas interface.

The dynamics of ^{14}C transfer in soils has been covered by Johnston (1990), who looked at the effect of soil porosity (inert silica sand) and the exchange between the soil water and soil gas. In dry soils, CO_2 migrates by diffusion, but the water in aerated soils (i.e. the vadose zone) can provide some retardation. Diffusion of $^{14}CO_2$ in soil is fast when the moisture content is small and CO_2 equilibration is fast (in the matter of minutes), but it is slow when the water content is high, due to a combination of a slower exchange rate and gas pore restriction.

Table 10
Examples of soil C-14 K_d values for performance assessment

Study (K_d values in ml/g)	K_d Value mL/g	Environment	Nature of data
Sandia/US NRC study (Beyeler, et al., 1999)	1.89	Soil	Estimated from database ('mean')
UK DOE study (Nacarrow, et al., 1988)	2	Clay	Best estimate
UK Nirex (Lever and Woodwark, 1990)	1	Clay mudstone	Best estimate
Swiss, NAGRA (McKinley and Hadermann, 1985)	50	Soil/surface sediment	Estimated from database
Swiss, NAGRA (McKinley and Hadermann, 1985)	5	Bentonite	Best estimate
Swiss, NAGRA (NAGRA, 1985)	1	Soil/surface sediment	Estimated from database
Swiss, NAGRA (McKinley and Hadermann, 1985)	5	Granite	Best estimate
Swiss, NAGRA (NAGRA, 1988)	50	Clay	Best estimate
German PSE study (Butow, et al., 1985)	0	Sediment	Best estimate
AECL LLW study (Guvanasen, 1985)	2	Soil/surface sediment	Estimated from database ('conservative)
RIVM study (Glasbergen, et al., 1989)	2	Sand clay	Best estimate
GSF study (Buhmann et al., 1991)	5	Sediment	Best estimate
Finnish TVO study (Peltonen et al., 1985)	6	Crystalline rock/reducing	Best estimate
Finnish TVO study (Vieno and Nordman, 1991)	1	Crystalline rock	Best estimate

The mass transfer coefficient of CO_2 between soil gas and a simulated groundwater was measured in static soil columns (Caron et al., 1994), and later in a pilot-scale experiment with a moving aquifer (Caron 1996; Caron et al., 1998c). These studies have revealed that the transfer of CO_2 between soil gas and groundwater (which is bi-directional) is much slower than through a quiescent liquid, because of the structure of the capillary fringe. In other words, the soil-gas interface is broken up and offers a resistance to gaseous exchange. This exchange was slower (than through a quiescent liquid) by a factor of ~20–55 in sand columns (Caron et al., 1994) and by a factor of ~15–25 in the pilot-scale experiment (Caron et al., 1998a). The transfer rate is pH-dependent, especially at mid pHs, because of the first ionization constant of carbonic acid (Eq. (3), at pH 6.3), and because of the interface condition. A high pH solution in an open system has a high holding capacity for carbonic acids, hence affecting the gradient and the mass transfer rate (Caron et al., 1994; 1998a).

These experiments were validated in the field near WMA-C (Caron et al., 1998a). A comparison between experimental and calculated mass transfer rates has revealed that $^{14}CO_2$ and $^{12}CO_2$ behave differently in the field. This is not an isotopic effect, but rather, is likely the effect of a different source of carbon: there is an overwhelming quantity of organic ^{12}C in the soil column, while ^{14}C is mostly inorganic (Rao and Killey, 1994; Caron et al., 1998b). Most of the organic ^{12}C in the soil column is converted to inorganic CO_2 and its carbonic acid species by microbial degradation and/or root respiration. In contrast, ^{14}C is likely inorganic, originating from the wastes or by groundwater degassing. As the $^{14}CO_2$ is released in the soil, it readily mixes with the dominant $^{12}CO_2$, produced in the soil column. These studies confirmed the findings of Thorstenson et al. (1983); Striegl and Healy (1990) on the difference of behavior in soils between $^{12}CO_2$ and $^{14}CO_2$.

Once the $^{14}CO_2$ is in groundwater as $H^{14}CO_3^-$, transfer to the soil water is slow, and it can be further reduced by incoming rainwater that provides a layer of ‘virgin’ water and ‘cap’ a moving groundwater (Killey et al., 1998). Only a small amount of soil CO_2 is brought to groundwater by infiltrating rainwater (Caron et al., 1998a), just by equilibration with soil CO_2. Infiltrating rainwater removes porosity from the soil, resulting in a net flux of pore gas to the atmosphere. The effect of barometric pumping increases isotope mixing in soil gas, but may not play a major role in the soil-groundwater gas transfer. The impact of these effects need to be determined for closing the loop on the air-soil-gas-groundwater continuum, but on an annual basis, these mechanism are likely to be small.

5.4.3. Terrestrial behavior of ^{14}C

The main source of carbon in humans is from ingestion of crops and vegetation, either directly or indirectly through animal products (Sheppard et al., 1990). Thus, understanding ^{14}C uptake by crops and vegetation is critical for the environmental pathway modeling for ^{14}C from groundwater.

Carbon-14 concentrations in crops/vegetables are due primarily to uptake through photosynthesis. A minor fraction of ^{14}C can also be from root-uptake. The ^{14}C concentration in crops due to photosynthesis is a function of the concentration in the air, the fraction of carbon in plants that is derived from this photosynthesis, and the ratio of the concentration of stable carbon in plants to stable carbon in air (Rautenstrauch et al., 2003). Similarly, the concentration of ^{14}C in crops from root uptake is calculated as a function of the fraction of concentration in soil, the fraction of soil-derived carbon in plants, and the ratio of the concentration of stable carbon in plants to stable carbon in soil. This represents a major shift from the earlier approach in modeling ^{14}C transfer from the soil to plants which was solely based on the use of soil-to-plant transfer factors (Sheppard et al., 1990).

The soil-to-plant transfer factor, defined as the ratio of radioactivity per mass of vegetation to radioactivity per mass of soil ($Bq/kg_{(Plant)}/Bq/kg_{(Soil)}$), was to describe direct uptake of ^{14}C by the roots and gaseous uptake by the leaves of the ^{14}C that was volatilized from the local soil. Recent studies on ^{14}C uptake by plants (Milton et al., 1998; Evenden et al., 1998; Link et al., 1999) showed that vegetation incorporates most of its carbon from atmosphere through photosynthesis and that plant carbon content is unrelated to soil carbon content.

Studies near the resurgence area at Duke Swamp (Chalk River) have provided important data for the issue. These Duke swamp studies have shown a fast decrease of ^{14}C activity with height in the vegetation, with low translocation within higher plants. Only the small plants (shrubs, ferns, lower branches of trees), which have their photosynthetic activity close to the soil (the source of contaminated material), showed elevated ^{14}C. While the groundwater contained both ^3H (as tritiated water) and ^{14}C (as inorganic C), there was no vertical ^3H gradient to the top of trees (~11 m), in comparison to an apparent vertical gradient of ^{14}C (Evenden et al., 1998). The conclusion was that both radioisotopes are absorbed differently by vegetation, and the soil-atmosphere-leaf pathway appeared a dominant path for ^{14}C uptake. Milton et al. (1998); Link et al. (1999) have complemented this work by suggesting that $<2\%$ of the

^{14}C came from roots (soil-root-leaf path), which means the soil-atmosphere-leaf path was dominant. It was estimated that $<5\%$ of the ^{14}C inventory on vegetation originated from degassing of the groundwater plume. This figure is low because of the high atmospheric dispersion, which caused ^{14}C levels in plants to be difficult to measure, just a few tens of meters away from the resurgence area. This estimate ($<5\%$, above) should be interpreted very carefully, as a large portion of the biomass is in trees; smaller plants at the ground levels within the resurgence area could show high levels of ^{14}C (~ 300 times background, as stated earlier).

5.5. ^{14}C Dose response

The food-chain transfer begins by the incorporation of ^{14}C by plants through photosynthesis. Carbon-14 is unavailable for photosynthetic uptake in the food chain until oxidation to CO_2 occurs, unless the material is already present as CO_2-bound components. Scoping calculations have suggested the main pathway for ^{14}C intake by humans from the disposed LLW is food ingestion mediated by groundwater transport. There may be some contribution of ^{14}C release to the atmosphere through gas generation. Ingestion of fish can also be significant, if a dwelling scenario near a lake is to be employed.

Dose modeling involved with ^{14}C in the biosphere typically uses specific activity model (Till and Meyer, 1983; Amiro, 1995). The specific activity model assumes that ^{14}C will behave in the same manner as the stable carbon (e.g. there is no difference in chemical speciation or diffusion characteristics between them), and that they are well mixed. Thus the ratio of ^{14}C/^{12}C is the same in all parts of the biosphere. Thus, the ingested food is contaminated to the same specific activity as the contaminated groundwater entering the biosphere. This implies a limit to biosphere contamination (i.e. ^{14}C activity in food and irrigation water cannot exceed that in well water). In reality, the biosphere will be less contaminated than this limit because of additional isotopic dilution by stable carbon in the biosphere.

Use of specific activity model requires estimates of concentrations of stable carbon in groundwater. Gascoyne (1992) indicates that groundwater concentrations of carbon (as carbonate) range between 0.02 and 0.068 kg/m^3, or 1.7 and 5.7 mol/m^3. Thus the resulting dose rate would also vary within this range. However, the representativeness of these data (obtained from measurements at the Whiteshell Research Area) in describing the spatial variability expected at other sites is unknown.

After the intake of ^{14}C into human body, the metabolism and kinetics of ^{14}C follow those of ordinary carbon in the human body. Essentially all ingested carbon is absorbed into the body. Most of this is metabolized into CO_2, urea, or other metabolites, and either exhaled or excreted within the next few hours. While a fraction of the ^{14}C introduced into the body is retained as protein, fat, carbohydrate and other cellular components (NCRP, 1985), only a small fraction is retained on a long-term basis. In the case of a relatively rapidly growing 8-year old child, the retained portion accounts for about 1% of that ingested. The biological half-life of ^{14}C in human body ranges from a fraction of an hour to several years with the whole body as the target organ for ^{14}C. A biological half-life of 40 days has been suggested as a conservative value (ICRP, 1968) for dosimetric purposes. It has been shown that the mass ratio of $^{12+13}$C to ^{14}C in the soft tissues of the body lags in the troposphere by about one or two years (Nydal et al., 1971). Since some body tissues and compartments have long turnover times, it may require decades for the total carbon in these portions of the body of an adult to approach equilibrium following a significant change in the intake mass ratio of $^{12+13}$C to ^{14}C (NCRP, 1985). The magnitude of this lag represents a significant source of conservatism in dose rate estimates for ingested ^{14}C.

Carbon-14 decays to ^{14}N by emission of an electron with a maximum energy of 0.156 MeV and an average energy of 0.045 MeV. The range (average distance traveled before being stopped) of these electrons is about 1 ft (30 cm) in the air, and 0.029 cm in water. Therefore, the electrons from the decay of ^{14}C will be stopped at the skin dead-layer or basal cells of the epidermis underneath dead layer of skin. Dose rate to basal cells of epidermis from 1 μCi of ^{14}C per cm^2 area (37 kBq/cm^2) is about 1400 mrad per hour (14 Gy/h) (Healy, 1971). At the same time, the electrons emitted from the decay of ^{14}C in the human body will deposit all of their energy in local tissues. As these electrons travel at low energy, the linear energy transfer (LET) will be higher than the electrons at higher energy. The LET of electrons from ^{14}C is about 0.7 keV/μm in water, compared to 0.19 keV/μm for electrons from ^{32}P or ^{90}Sr decay. Therefore the dose delivery from ^{14}C is more localized than from ^{32}P or ^{90}Sr. The dose from internally deposited ^{14}C through inhalation and ingestion and its retention in the body is a key component in the determination of potential health effects of ^{14}C.

The dose conversion factor for unit intake of ^{14}C into human body is 6.36×10^{-12} (for CO_2) and 5.64×10^{-10} Sv/Bq for inhalation and ingestion, respectively (US EPA, 1988a). These dose conversion factors are

Table 11
Dose conversion factors for key radionuclides in LLW performance assessment (US EPA, 1988a)

Nuclide	Ingestion (Sv/Bq)	Inhalation (Sv/Bq)
^{3}H	1.73×10^{-11}	1.73×10^{-11}
^{14}C	5.64×10^{-10}	6.36×10^{-12}
^{36}Cl	8.18×10^{-10}	5.93×10^{-9}
^{99}Tc	3.95×10^{-10}	2.25×10^{-9}
^{129}I	7.46×10^{-8}	4.69×10^{-8}
^{226}Ra	3.58×10^{-7}	2.32×10^{-6}
^{232}Th	7.38×10^{-7}	4.43×10^{-4}
^{238}U	6.88×10^{-8}	3.20×10^{-5}
^{239}Pu	9.56×10^{-7}	1.16×10^{-4}

compared to those of the key radionuclides in LLW performance assessment (US NRC, 1993, 1994) in Table 11, including US NRC's big four nuclides (^{3}H, ^{14}C, ^{99}Tc, ^{129}I) in the draft Environmental Impact Statement on 10CFR Part 61 (US NRC, 1981). The table indicates that ^{14}C dose conversion factor for ingestion, which is the main exposure pathway for LLW, is on the same order of magnitude with ^{36}Cl and ^{99}Tc and is approximately two or three orders of magnitude lower than that for ^{129}I, ^{226}Ra, ^{232}Th, ^{238}U, and ^{239}Pu. Its long half-life, biomobility, and incorporation into tissue make it a potentially significant contributor to dose among various nuclides of concern in LLW.

6. Management of carbon-14 wastes

This section gives an overview of the current situation on how ^{14}C is managed in reactors and in wastes sites. We also outline issues for the perspective of waste management.

6.1. Status on long-term storage and disposal

In the United States, most of the ^{14}C containing low level wastes are in permanent disposal sites. Extended storage of LLW has been practiced in the U.S. whenever there was a problem with site accessibility due to conflicts in interstate compacts. There have been a total of seven commercial disposal sites in U.S. LLW management history of which three remain operating. All of these sites are based on shallow land burial. The operating sites include the Barnwell site in South Carolina, the Richland site in Washington, and the Envirocare site in Utah. The Envirocare site currently accepts only Class A (low activity) LLW. Carbon-14 is expected to be the inventory limiting nuclide at the Barnwell site.

In Canada, there are no operational disposal sites, but the situation may change within a few years (Government of Canada, 2002). A substantial portion of LLW sits at Chalk River, while LLWs generated at the stations remain at their waste management sites. Wastes are segregated according to different classes. At present, concepts for HLW and LLW disposal facilities are at an advanced stage (AECL, 2002). This may or may not be the final decision, as public consultation is taking place, as part of the mandate of the Nuclear Waste Management Organization. Three options are considered: at-site storage, central storage, and deep geological disposal (NWMO, 2003). It should be noted that this consultation is for spent fuel, and the scope of the NWMO does not include L&ILW.

Current storage practice for spent fuel consists of storage in pools, in stations, while some 'cooled down' fuel sits in dry storage structures, within the fenced area at the stations. The pools are monitored, and the small amount of failed fuel is placed in separate canisters (also in pools) to minimize the spread of contamination. Ion exchange resins are either stored in tanks at stations, or placed in shipping liners and placed in structures at a licensed waste management site, for long-term storage (Holtorp, 1996). The resins are in wet environment: they are submerged in water (tanks), or they are partially de-watered by displacement in the liners, prior to shipping [ibid].

6.2. Control of ^{14}C release from nuclear power plants to the atmosphere

Atmospheric release of ^{14}C could be potentially a concern if a large amount of ^{14}C was produced in a plant. This was possibly a case with HWRs (CANDU-type) (see Tables 3 and 4). Hypothetically, if the full ^{14}C production were released from individual HWRs, doses would still be within the risk-based release limits. This scenario is unlikely and it is nevertheless desirable to keep emissions to a low level, because it is part of good engineering practice.

6.2.1. LWRs

The ^{14}C present in the coolant water is available for release to the atmosphere as gaseous waste. In BWRs, virtually all the ^{14}C is released from the condenser steam jet air ejector. In PWRs, the off-gas treatment vents are the largest source ($\sim$70%) followed by the building ventilation systems. Typical levels of ^{14}C release from LWRs are about 10 Ci (0.37 TBq) or less per year.

US EPA (Fowler and Nelson, 1981) has assessed the health impact of ^{14}C emissions from typical LWRs. The assumed annual release rates of ^{14}C were 9 Ci/yr (0.33 TBq/yr) and 5 Ci/yr (0.185 TBq/yr) for BWR and PWR, respectively. Representing a Midwestern site in the Unites States, with food production and consumption pattern for a rural setting, maximum individual effective dose rates (503 m downwind) were estimated at 4.1×10^{-3} mSv/yr (0.41 mrem/yr) (BWR) and 2.3×10^{-3} mSv/yr (0.23 mrem/yr) (PWR). These estimates correspond to the fatal cancer risk level in the order of 10^{-7} per year. This is three orders of magnitude lower than the risk from natural background radiation ($\sim10^{-4}$ per year) and is a very small fraction of regulatory dose limit for the public. Presently, control of ^{14}C release is not exercised in LWRs.

6.2.2. HWRs

There have been significant improvements in the understanding of the chemistry of HWRs (CANDU-type) related to the ^{14}C production and its management. It has been found that ^{14}C emissions can effectively be controlled by appropriate management of ion exchange resins of the moderator system. A 6-step mechanism was proposed to come to this conclusion (Torok and Caron, 2000; Caron and Torok, 2000):

1. Peroxide is produced in the calandria, due to radiolysis of the heavy water;
2. Peroxide attacks the ion exchange resins. This is especially important when, or if some metals (e.g. Fe) are already present on the resins (impurity or picked up during service);
3. The resins degrade, releasing resin degradation products to the moderator (resins are C-based polymers), which eventually return to the calandria;
4. The organic C from resins will also be converted to CO_2 (and bicarbonate) in the calandria;
5. This will eventually raise the bicarbonate concentration and prematurely overload the resins;
6. Because of the higher bicarbonate levels (^{14}C and ^{12}C), ^{14}C could be released to the atmosphere via system leaks, plus venting and purging; the latter are part of normal reactor operation.

The major recommendation based on the above mechanisms pertains to limiting the service time of the ion exchange resins. The ^{14}C emissions have decreased by a factor of $\sim$6 for two CANDU-6 stations during the course of the investigation (Torok and Caron, 2000; Caron and Torok, 2000). Low emissions at CANDU-6 reactors (Rao, 1997; Torok and Caron, 2000) have continued for several years, are typically in the range of 200–400 GBq/a (5.5–11 Ci/a). These emissions are small compared to the production (Table 4) and are in the same range as LWRs (see above). The link between resin degradation and poor moderator quality has been reported at the Fugen reactor in Japan (Kitabata and Sakurai, 1988). This reactor has a configuration similar to that of the CANDU reactor. The recent work took this further in demonstrating that resin degradation and performance for the moderator purification can be linked to ^{14}C emissions.

6.2.3. Carbon separation and fixation

Several researchers have suggested separation and fixation of ^{14}C from plant's operational release of $^{14}CO_2$ to avoid ^{14}C discharge to the environment. Techniques explored for the separation of ^{14}C from $^{14}CO_2$ include decomposition of CO_2 by microwave discharge (Sakurai and Yokoyama, 2000) and isotope separation by plasma chemical reactions (Mori et al., 2001). Once successfully separated, it is envisioned to store the ^{14}C activity as elemental carbon. These techniques are still at the early stage of development.

6.3. Management and disposal of ^{14}C loaded ion exchange resins

Anion-exchange resins are well known to be efficient at removing ^{14}C from nuclear plant waste streams. Presumably various forms of ^{14}C adhere to the resins through the ion-exchange process for ionic forms, and physical adsorption or microfiltration for organic or colloidal forms. As shown in Table 1, ion-exchange resins are one of the largest sources of ^{14}C activity among different waste forms in LLW.

Most of these ion-exchange resins are either stored at a reactor site or disposed as dewatered resins (in a high-integrity container or in shipping liners). Processes taking place during long-term storage or disposal period include direct resin degradation by microbial actions, displacement of ^{14}C-bicarbonate by foreign ions (microbial action, groundwater infiltration), and isotope exchange (exchange with atmospheric CO_2). Release of ^{14}C activity through aqueous leaching is expected to be diffusion- or chemical reaction-controlled. Modeling for these processes has been discussed elsewhere (Su and Yim, 2000). Currently, effects of resins degradation on ^{14}C leaching behaviours are not fully addressed.

Storage of ^{14}C resins for extended periods of time before the permanent disposal has been also practiced in the industry. This practice was necessary, mainly due to the lack of access to the disposal sites. This, however, raises the concern for the stability of the waste materials and the ^{14}C release to the environment through the gaseous and aqueous pathways.

Alternative methods of ^{14}C management for these resins include separation of ^{14}C from the resins and immobilizing them into a stable waste form or immobilization of ^{14}C into a waste form without the separation of ^{14}C (Yim, 1998). Cement encapsulation, as one of the major alternatives for ^{14}C immobilization, requires the separation of ^{14}C prior to immobilization as cement is not compatible with IX resin.

Demonstrated technologies used to separate/release ^{14}C from resins include gas-phase stripping of resins (Buckley et al., 1985) and acid leaching (Chang et al., 1990; Chang and Krochmalnek, 1992). Recent advancements have shown the potential to clean up spent resins using supercritical fluid extraction, using CO_2 as cleaning fluid. This technology is well known in the food industry. It was used in a demonstration for lowering the content of residual organics prior to service (Dias and Shapka, 2000). Since the fluid is CO_2, the potential exists for removing the ^{14}C from resin, which is present on resins as bicarbonate/carbonate (see prior discussion). The technology is sufficiently advanced for its implementation at the industrial scale. Major obstacles are, among others, financial and priorities in waste management strategies.

Once separated from the waste, ^{14}C can be captured through carbonate precipitation. The processing steps to take the evolved ^{14}C from the waste to a $CaCO_3$ precipitate (for disposal) can be summarized as:

(1) Separation into an aqueous solution;
(2) Convert CO_2 or HCO_3^- into a carbonate;
(3) Consolidation into a waste form or matrix (often as $CaCO_3$ or $BaCO_3$);
(4) Cleanup of any secondary contamination or wastes during the process, and;
(5) Placement within engineered barriers.

This process uses a $Ca(OH)_2$/methanol trap, which is a proven method in chemical processing industry. If ^{14}C exists as carbonate or bicarbonate in solution, $CaCO_3$ can be precipitated through reaction with CaF_2 or $CaCl_2$ in an alkaline solution. Generation of secondary wastes is a concern with the approach. Use of strong acids should be avoided, as they are likely to release many secondary radionuclides from the resin into solution. The type and quantity of secondary wastes generated during $CaCO_3$ processing depends on the details of chemical processing steps.

Collection of gaseous ^{14}C from any of these separation techniques is also necessary. The collection technique will depend upon the ultimate waste form selected for immobilization. For example, $^{14}CO_2$ can be collected as a $CaCO_3$ precipitate in a $Ca(OH)_2$/methanol trap. The carbonate precipitate must be immobilized for disposal. This may involve processing into cement or another matrix material, or perhaps processing into solid pellets of calcite.

In cases where ^{14}C is in organic form in the waste (e.g. acetic acid, acetaldehyde), oxidation of organic ^{14}C species into $^{14}CO_2$ or $^{14}CO_3^{2-}$ and subsequent capture as carbonate can be done.

6.4. ^{14}C Management in graphite waste from gas cooled reactors

Graphite from gas-cooled reactors is classified as LLW. Retrieval of graphite from the reactor core could be challenging due to the high levels of contamination (dominated by ^{3}H, ^{14}C, ^{152}Eu, ^{137}Cs, etc.). This will be more so with significant fuel failures.

Regarding the packaging of graphite for disposal, technical issues to be addressed include control of Wigner energy in irradiated graphite, graphite dust encapsulation and immobilization, and preventing graphite flotation within the wasteform, and preventing galvanic corrosion (between steel and graphite) of the waste package by maintaining the anaerobic conditions within the package (Wise, 2001). Wigner energy is the potential energy of the unstable carbon atom by being out of position when the carbon atom is pushed out from its original position by the neutrons in the graphite lattice (Wise, 2001). When the carbon atom has enough thermal energy, i.e. it is hot enough, it is able to return to its position. Since the energy required to initiate a return to position is less than the stored energy, the excess is released as heat. A finite amount of Wigner energy can be released by heating the piece of graphite above a certain temperature. If too much energy is released at one time or the heat is not carried away from the system a self-sustaining release can occur and the system will get hotter and hotter even though no further heat is being put into the system. Slow heating of graphite has been used to release Wigner energy. Graphite dust generated from the removal of graphite from the reactor needs to be effectively immobilized. Intimate immobilization would be achieved by the encapsulation of graphite dust typically in a cementitious matrix aided by some form of wetting agent. Graphite flotation could occur during grouting because the irradiated graphite has a lower density (1.6 g/cm^{3}) than the typical grout density of 1.8 g/cm3. The flotation can be overcome by the use of an antiflotation device to withstand the uplift forces caused by the graphite.

Options considered for the disposal of graphite waste include shallow land disposal as LLW, deep geological disposal, incineration, and recycling. Lowest collective dose to humans will results from deep geological disposal. However, with the difficulty in developing a deep geological disposal site and the known premium for the space, disposal of bulk graphite in deep geological repository is unlikely unless a new regulatory scheme is in place. Due to high mobility and long-half life, ^{14}C is typically one of the inventory limiting nuclides for shallow land disposal facilities for LLW. Considering the total ^{14}C content of the graphite in a typical gas cooled reactors, disposal of graphite pile as LLW is expected to exceed the total radiological capacity of a LLW facility for ^{14}C. Thus direct disposal of the bulk reactor graphite in a LLW facility is unlikely to happen (Wise, 2001).

Incineration of graphite waste provides the advantages of complete Wigner energy removal and significant volume reduction. The 1400 m^{3} of graphite waste could be reduced to as little as 35m^{3} of cemented ash products and filters (Wise, 2001). Candidate methods of incineration include burning in a conventional incinerator, fluidized bed incineration, and power laser driven incineration (Wise, 2001). Conventional burning involves controlled combustion of the graphite in a furnace where it is subject to a blast of air at about 1000 °C after crushing the graphite into pieces of typical dimension of 2.5 cm. The disadvantages of this process are the milling effort required, the production of active dust, and the difficulties of the incinerator design. In fluidized bed incineration, the graphite would have to be ground to a powder (possibly down to 30 μm) to provide enough surface area for reaction with oxygen at incineration temperatures. The milling would produce dust, requiring containment. The irradiated graphite can be very hard making milling more difficult. This process could lead to ignition if significant stored Wigner energy and air were present.

Power laser driven incineration does not require prior milling or crushing of the graphite. The bricks can be loaded straight from the reactor core. The laser beam heats the graphite surface to about 1500 °C (Wise, 2001) and rapid combustion can take place when oxygen is supplied. The laser itself can be outside the furnace area, thus handling in a radiation area is not required. As high temperatures are limited to one side of a single block, control of laser beam may not be complicated. Continued research and development are expected to prove this technology at a larger scale.

Main concerns with graphite incineration are gaseous emissions of ^{14}C, generation of secondary wastes, and the issue of public perception and acceptability. Recovery of $^{14}CO_2$ through ^{14}C-enrichment process has also been proposed to address the issue. The recovery/enrichment is based on CO_2/carbamate chemical exchange process (Takeshita, et al., 2002) from which the concentration of ^{14}C in the depleted flow is reduced to less than the specified environmental release standard. The depleted $^{14}CO_2$ would then be released to the atmosphere. The enriched flow would be transferred to the immobilization stage, where CO_2 is converted to carbonate and then subsequently immobilized in a waste form (e.g. cement).

6.5. Waste forms for ^{14}C

Using a highly durable waste form ensures the long-term stability and isolation of radioactive material within the waste during interim storage and permanent disposal. The waste form, as the first and foremost barrier to the release of radionuclides from nuclear waste, provides functions such as: (1) Providing physically, chemically, thermally stable form, (2) Immobilizing the radioactive materials (slow release when contacted with water), and (3) Resisting leaching, powdering, cracking and other modes of degradation. Because ^{14}C is generally highly mobile once released to the environment, using proper waste form is important for ^{14}C. Incorporating ^{14}C into a durable waste form (e.g. immobilizing into cement) could significantly reduce the peak release from the waste form in performance assessment.

6.5.1. Cement (with the use of carbonate minerals)

Cement was one of the first materials used as a low-level radioactive waste solidification agent (Morghissi, 1986). In fact, most of the efforts for ^{14}C waste form have been focused on cement. Cement provides natural advantage for ^{14}C immobilization due to its specific chemical features and solidifies the waste by forming a crystalline matrix. Solids in the waste may be incorporated by being physically trapped in the matrix, or by reacting chemically to become part of the crystal. Cement's advantage includes ready availability, low cost, ability to solidify a wide variety of wastes, long shelf life, being relatively safe and easy to handle, tolerance of variations in the waste chemistry, and acceptance at the commercial radioactive waste burial sites (Moghissi et al., 1986). Drawbacks of cement include increased volume of the encapsulated waste, the fact that cement cannot be directly used for the immobilization of resins, and a potential concern for structural durability.

As the wastes are solidified in cementitious grout, the environment surrounding the wastes becomes highly basic/akaline. These high pH conditions fall outside the stability field of organic C, into the oxidized (carbonate) field (Rosset and Desbarres, 1993). This is true to both oxidizing and mildly reducing conditions at different temperatures of interest (25, 300 °C; see Fig. 1). This implies that regardless of the original chemical forms of ^{14}C in waste, the ^{14}C will tend to transform into inorganic forms in the cement encapsulated waste form, likely as carbonate.

Calcite (calcium carbonate, or generically limestone) is a widely distributed form of carbon in the natural environment, and generally has low solubility and good chemical and thermal stability. It has also a lower solubility over the largest range of naturally occurring waters and low leaching rates (Scheele and Burger, 1982). Possible concerns with $CaCO_3$ include:

- The leach rate is high during the first several days of water contact.
- Dissolved carbon dioxide in the system could have a deleterious effect of increasing carbonate leaching (Bush et al., 1984).
- $CaCO_3$ has low solubility in most natural water systems. However, in non-alkaline solutions, the solubility will increase.

The fact that the solubility of $CaCO_3$ increases significantly when pH is less than ~11 limits the use of calcite in the alkaline environment. See, for example, Fig. 4, which shows the potential Ca^{2+} solubility and calcite precipitation field, for a total Calcium concentration of 10^{-3} mol/L (40 ppm). Using calcite in a cemented environment meets this requirement (Dayal and Reardon, 1992; Dayal, 1995a,b; Krupka et al., 1995). In this regard, incorporating ^{14}C into calcite along with cement encapsulation will be suitable for ^{14}C immobilization.

At pH above 12, calcite is more insoluble than portlandite in the cement and any carbonate ions present in the solution will combine with the enriched calcium from the dissolution of portlandite to form a carbonate precipitate (Krupka and Serne, 1998). Thus, the carbonate/bicarbonate ions that contain ^{14}C in the waste are expected to be exchanged with hydroxyl ions in the cement slurry, followed by localized precipitation of solid calcium carbonate in the waste/cement interface (Dayal and Reardon, 1992). Almost complete incorporation of ^{14}C in the aqueous solutions into the cementitious material is expected by the precipitation of calcite ($CaCO_3$) within the pores of the cement (Serne et al., 1992; Allard et al., 1981; Dayal and Klein, 1987; Hietanen et al., 1985; Bayliss et al., 1988). As long as the high pH conditions are maintained, cement is an effective a long-term chemical barrier for the immobilization of ^{14}C (Dayal, 1995a,b).

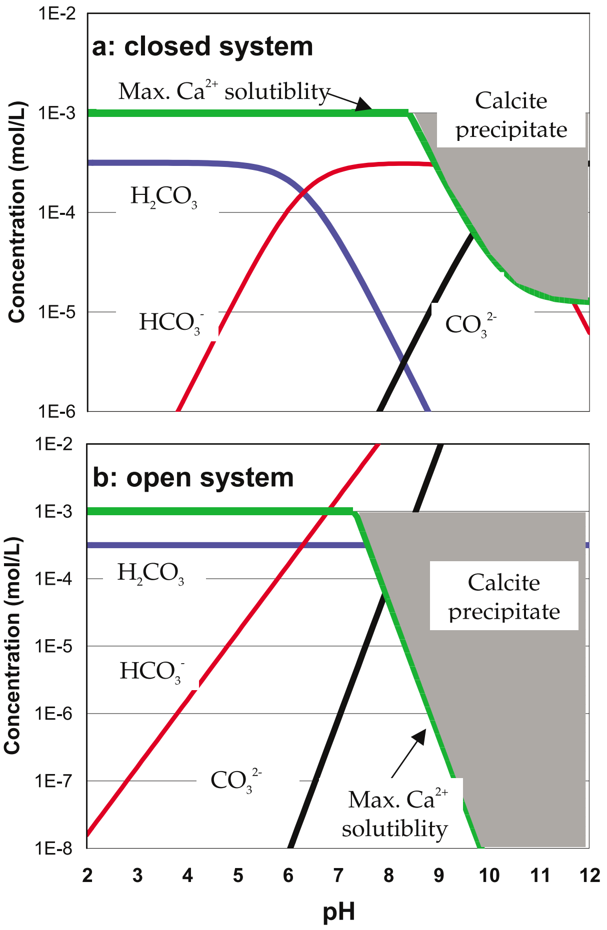

Fig. 4. Distribution of carbonate species as a function of pH, also featuring the potential for calcite ($CaCO_3$) Precipitation. a: closed system (no gaseous exchange); b: open system (assumed $P_{CO2} = 10^{-2}$ atm). Only H_2CO_3 exchanges with the gas phase, below pH 6.3 (see Eq. (4) in the text). Calcite precipitate can form where carbonate (CO_3^{2-}) is significant compared to Ca^{2+} (see shaded part). Assumed concentrations: total $C = 10^{-3.5}$ mol/L (a), total $Ca = 10^{-3}$ mol/L (both).

At present, cement is the preferred waste form of choice for ^{14}C fixation. However, due to the volume increase with cement encapsulation, alternative waste form could be needed if volume reduction becomes a major requirement. Considerations for possible alternative waste forms for ^{14}C are given in the following.

6.5.2. Synthetic polymers

Synthetic polymers include a broad range of possible organic compounds (polyethylene, rubber, polystyrene, bitumen, etc.). Desirability of these materials depends on the ease or difficulty in the synthesis of ^{14}C into the structure and the final chemical stability. Various synthetic organic polymers have been investigated as an encapsulating matrix material for low level or mixed waste solidification (Moghissi et al., 1986). These include polyethylene, epoxy polymers, unsaturated polyesters, and urea-formaldehyde. Use of urea-formaldehyde produces very acidic conditions in pore waters which may convert ^{14}C into $^{14}CO_2$ thus is not desirable. Polyethylene as matrix material requires heating above 120 °C, suggesting likely loss of ^{14}C through volatilization.

Vinyl esters, a class of unsaturated polyesters, are a feasible option for ^{14}C solidification. Vinyl-esters are a subclass of polyesters in which double carbon-carbon bonds are introduced by using an unsaturated acid monomer (IAEA, 1991). Vinyl-esters are used as proprietary formulations in which a pre-polymer is dissolved in styrene as a suitable solvent. This solvent takes part in the polymerization process by modifying the repeating structural unit or altering the degree of cross-linking. The vinyl ester monomer is diluted to about 45–50 wt% in styrene to form a low viscosity liquid which is polymerized through free radical initiators to form a three-dimensional network.

The solidification of aqueous wastes with vinyl ester-styrene binder requires high shear-mixing to promote the formation of a waste water-monomer emulsion (Moghissi et al., 1986). Advantages of vinyl-esters over other polyesters are increased chemical resistance and better performance in the presence of water (IAEA, 1991). Vinyl esters are less polar than polyesters and thus are less prone to the effects of water when cured by organic peroxides (Franz et al., 1994).

A potential drawback with the use of styrene is the health and fire risk concerns during the handling of the material. The long-term chemical and radiation stability of epoxy polymers and vinyl esters have not been fully demonstrated.

6.5.3. Glassy carbon

Glassy carbon (carbon allotropes) is an amorphous, gas-impermeable form of carbon with the appearance and fracture characteristics of glass (McKee, 1973). Glassy carbon could potentially offer a unique approach to waste disposal, as an intrinsic waste form because its durability does not depend upon maintaining a protective oxide film as is required for glass. It may also be less susceptible to non-uniform modes of attack for the same reason.

Glassy carbon is manufactured by the solid-phase pyrolysis and heat treatment of certain thermosetting polymers, typically phenolic resins. Glassy carbon has high temperature structural stability, chemical inertness, low gas permeability, high thermal shock resistance, and is electrically conductive and thermally insulating. The formation of glassy carbon involves the slow carbonation of nonmelting cross-linked polymers, with or without applied pressure. In determining the morphology of the product, the chemical nature of the precursor is less important than the condition of pyrolysis. Similar products can be prepared from a variety of starting materials, including phenolic resins, acetone-furfural resin, etc. (McKee, 1973). For glassy carbon to be a candidate ^{14}C waste form, a method would have to be developed to incorporate ^{14}C into one of these starting materials. This would generally involve a reduction step to form a ^{14}C hydrocarbon. Methods to convert from CO_2 to CH_4 and other hydrocarbons have been identified (Calvin, et al., 1949), but the feasibility and practicality has not been fully assessed.

An alternative approach would be the capture of ^{14}C from water after leaching from the ion-exchange resins into phenolic ion-exchange resins. The efficiency of this process is expected to be high. The resulting phenolic resins can be processed by slow pyrolysis above 1000 °C and be converted to glassy carbon. The maximum process temperature is dependent on the required level of environmental durability and will be an important parameter for the feasibility of using glassy carbon as a waste form.

Based on a process by Fitzer (Fitzer and Schafer, 1979), total carbon yield of the final product is estimated to be between 80 and 85% with about 15–20% of initial carbon content expected to be released during the process. Therefore, the issue of secondary waste generation needs to be addressed as well.

6.5.4. Silicon carbide

Silicon Carbide (formula SiC), which is known as carborundum (artificially-produced) or moissanite (naturally occurring), is a very hard material, non-toxic, whose properties are close to those of the Carbon allotrope diamond. Silicon makes bonds of the same tetrahedral arrangement as carbon-carbon bonds in diamond. The potential for silicon carbide for encapsulating radioactive wastes is known (see e.g. Angelini et al., 1984). Silicon carbide is the outer coating material for high-temperature gas cooled reactor fuels. Use of it as a coating for encapsulating transmutation by-products following controlled burnups has been proposed (Rodriguez and Baxter, 2000). A demonstration to include ^{14}C wastes as part of the carbide ($Si^{14}C$) has also been done (Torok et al., 1990). The latter approach has the advantage that ^{14}C is chemically bound to Si and it is part of the fabric of this stable mineral. Use of silicon carbide requires that ^{14}C is removed from the wastes (adding a purification step and potentially creating other secondary wastes). The resulting carbide may include other impurities if spent resins are used as starting material. In addition, costs and technology may not be ready for the large-scale transformation of ^{14}C wastes into this waste form. Silicon carbide is among new materials used in several expanding applications and this technology could become economically feasible in the future.

6.5.5. Graphite

Graphite is a hexagonally crystallized allotrope of carbon that is widely used as a high-temperature refractory because of its thermal stability. It is one of the materials most resistant to attack by the natural environment (Gray, 1980; Gray, 1982). Graphite, as in the case of glassy carbon, does not depend upon maintaining a protective oxide film for its environmental durability. It is also less susceptible to non-uniform modes of attack for this same reason. In the presence of a high-intensity gamma-radiation field, radiolysis of the water is enhanced by the presence of graphite. But no measurable effect on the reaction rate of graphite was detected (Gray, 1982). Graphite is also very insoluble in most acids and alkalis.

Processing of ^{14}C waste into graphite waste form presents challenges due to the high temperature processing required. Nonetheless, graphite has been proposed as a waste form for the fixation of ^{14}C from the spent coated-particle fuels from HTGR (Forsberg et al., 2003).

6.5.6. Use of special waste containers

The waste form/barrier includes those various components for disposal, i.e. the chemical form of the radionuclide, the solidification matrix, and the container. To establish the necessary level of performance, the waste form must be viewed as part of the entire waste disposal system, which includes components such as engineered structure, the container, the geochemistry, and hydrogeology of the site and its climate.

In this regard, using a very highly durable waste container is a feasible alternative to immobilizing ^{14}C. Although high integrity containers (HICs) are currently employed for this purpose, the lifetime of HICs is expected to be between 300 and 1000 years. Compared to the 5730 years of half-life of ^{14}C, HICs' lifetime is not long enough to effectively control the potential hazard of ^{14}C. Alternative approaches to HICs could include application of special coating technologies to existing metallic waste containers or using a material of superior durability (e.g. graphite, glassy carbon) for the container. Application of special coating over metallic surfaces appears feasible with the recent advancement in coating technologies. The coating layers can include various ceramic oxide, metal carbide or nitride.

A major remaining challenge to the use of special waste containers is the development of a long-term data to justify the extended lifetime of the containers for licensing purposes.

6.6. Management and disposal of ^{14}C GTCC

Spent cartridge filters have recently emerged as a very important radioactive waste stream for ^{14}C. They are extensively used in PWRs to remove insoluble materials in the coolant. BWRs often use cartridge filters in the processing of reactor cavity liquids and for spent fuel pool vacuuming (EPRI, 1996). As part of the nuclear industry's plant dose reduction efforts (NCRP, 1994; Yim and Ocken, 2001), submicron size filters have been adopted in nuclear power plant systems. Experiences with these submicron size cartridge filters (Miller, 2000) showed that the concentrations of ^{14}C are much higher in these filters than what would normally be expected. The conventional cartridge filters are currently disposed of after dewatering in poly HICs (without any immobilization). In some cases the higher ^{14}C concentration has resulted in the cartridge being 'Greater-than-Class C' by more than a factor of ten. Such cartridges cannot be disposed of as low-level waste unless they are encapsulated and concentration averaging includes the encapsulating agent.

This issue was discussed in a EPRI report (Yim, 2001) where cement and polymer waste forms were compared for the purpose of concentration averaging. A cemented waste form provides a good encapsulation medium for ^{14}C filters with the benefits of reducing ^{14}C release by the reduction in permeability/porosity, precipitation in the form of calcite with reduced solubility, and with increased sorption capacity for ^{14}C. As disadvantages with cement, worker radiation exposure can be a concern depending upon the amount of cleanup efforts needed after the solidification process. A vinyl ester styrene (VES) waste form provides a rigid, cross-linked, impermeable mass transport barrier for ^{14}C leaching. It also provides possibility of co-disposal of IX resins and filters. The potential concern for cracking with VES encapsulation of waste can be minimized by adding bead resins and by controlling the polymerization reaction. NRC has approved the VES method with addition of bead resins in the polymerization as encapsulation medium for filters. There is less worker radiation exposure during cleanup operations. However, the VES solidification processes have to be closely controlled. VES option is more expensive than cement. The shelf life of VES binder is rather short (about 6 months).

7. Conclusions and future directions

This paper reviewed the anthropogenic production of ^{14}C, emissions potential from nuclear power plants, types of wastes and waste forms, the potential of this radionuclide for migration in the environment, and other environmental aspects of ^{14}C. Our intention is to provide a bridge between the past and the future by summarizing existing scientific understanding of ^{14}C issues.

Although ^{14}C in the environment is not at a level to pose threat to public health, ^{14}C features characteristics to be a concern if appropriate measures are not enforced. The current inventory continues to grow annually due to nuclear power production. The natural levels of ^{14}C are close to the disposal limits (based on an individual 10^{-6} risk factor). The inventory of ^{14}C in the environment will increase as the release/disposal of ^{14}C waste continues. If long-term storage strategy is adopted, wastes will accumulate in storage facilities, along with the associated potential for emissions. This may points to the need to build engineered controls for ^{14}C. Should an effective disposal strategy be implemented, issues of capacity, costs, pre-processing, waste forms, containment, etc., will need to be addressed. The balancing act, at present, is the balance between priorities, costs, and benefits to society and the environment.

Some general directions and/or issues that need attention to better manage ^{14}C were identified in this paper. These are summarized below.

The data to characterize ^{14}C production in fuel, coolant/moderator are old in particular with LWRs. The situation appears to be better for HWRs. Some of the estimates from Table 3 originate from surveys from the mid-1970 s, particularly for the production in fuel. A substantial amount of data for HWRs is of proprietary nature and cannot be disclosed at present. This practice may need to change. Either obtaining new data or verifying the accuracy of the old data would be necessary for reliable risk management and for public support.

It would be necessary to develop and/or share databases to show recent trends in ^{14}C emissions (from nuclear reactors and waste storage sites). Any progress in using relevant engineering approaches to reduce ^{14}C emissions should be noted and shared. The authors believe that recent trends and engineered controls have progressed and it is important to share these findings to the Scientific Community and the Public.

Additional data to better understand the behavior of ^{14}C in the environment is needed to improve the scientific basis. These data needs may become practically important in the future, depending upon the evolution of the regulatory and public perspective on LLW site performance assessment. The data needs include (1) Quantitative data on isotope mixing-for the inorganic components of soils, (2) Quantitative data on conversion from inorganic to organic C (and vice-versa as applicable); (3) Groundwater/gas transfer factor for ^{14}C using field-based data covering the field scale for waste management areas, and; (4) Updated data for terrestrial transport of ^{14}C for relevant environmental assessments covering the height effect of ^{14}C transfer for different plants/vegetation.

With regards to modeling the behavior of ^{14}C in the waste, two areas of research needs are noted. These are: (1) Leaching studies on ion exchange resins, especially on the effect of biodegradation. Ion exchange resins are a major source of ^{14}C, and although leaching models and protocols have been developed, specific mechanisms need to be better characterized (effects of ion competition, the effect of bacterial decay, etc.). (2) Given the widespread use of K_d-based leach modeling for a wide variety of ^{14}C wastes (resins, filters, and various solid wastes), validating the current practice along with development of appropriate data could be necessary. On a practical standpoint, leaching studies, K_d's, effective diffusivities can be readily incorporated in prediction models. The drawback is that these parameters lump together several geochemical processes together. It is important to identify these limitations, such that the actual mechanisms are known and they are controlled during the period of interest.

One major related issue is the handling and disposal of ion exchange resins: If long-term storage of resins is necessary, what should be planned, and what type of processing should be done, if at all? Would it be necessary to segregate and re-route the wastes in dedicated facilities? Included in this should be cost/benefit analysis of separating the ^{14}C from resins (to place ^{14}C in stable chemical form such as carbonate minerals, separated from extracted resins), resin encapsulation in stable materials, or other technologies. The option of ^{14}C separation and incorporation into cement waste form needs to be compared with the alternatives using new waste form materials.

Developing knowledge on new ^{14}C waste forms deserves further consideration if the affected LLW volume becomes a concern. The resulting new waste forms would be useful for the disposal of other major long-lived radionucldies. Thus use of a specific waste form and its pros and cons should be evaluated not only for ^{14}C but also for other major long-lived radionuclides present in the waste. New technologies should be considered in the future (e.g. extraction, encapsulation, incorporation into new materials), especially if they are becoming available and economically feasible.

Acknowledgements

The authors are grateful for the valuable comments provided by the anonymous reviewers and Dr Dade Moeller of Harvard University.

References

ACRP, 1995. The management of Carbon-14 in Canadian Nuclear Facilities, ACRP-14. Advisory Committee on Radiological Protection (committee of the Atomic Energy Control Board of Canada), Ottawa, Ontario.

AECL, 1994. Environmental Impact Statement on the concept for disposal of Canada's nuclear fuel waste, AECL-10711, COG-93-1. Atomic Energy of Canada Limited, Chalk River, Ont.

AECL, 2002. New Opportunities for Atomic Energy of Canada Limited (AECL). http://www.cna.ca/english/speeches.asp.

Allard, B., 1985. Radionuclide sorption on concrete. Nagra NTB 85-21, Nagra, Baden/Swtizerland.

Allard, B., Torstenfelt, B., Anderson, K., 1981. Sorption studies of $H^{14}CO3$ on some geologic media and concrete. Scientific Basis for Nuclear Waste management III, MRS Symposium Proceedings 3, 465–472.

Amiro, B.D., 1995. Some simplified radiological dose estimates using isotopic dilution in the biosphere for the disposal of Canada's nuclear fuel waste. Atomic Energy of Canada Limited Technical Record, TR-693, COG-95-286, Chalk River, Ontario.

Angelini, P., DeVore, C.E., Lackey, W.J., Blanco, R.E., Stinson, D.P., 1984. Method of Deposition of Silicon Carbide Layers on Substrates and Product. U.S. Patent No. 4,459,338.

Bayliss, S., Ewart, F.T., Howse, R.M., Smith-Briggs, J.L., Thomason, H.P., Wilmott, H.A., 1988. The solubility and sorption of Lead-210 and Carbon-14 in a near-field environment. Scientific Basis for Nuclear Waste Management XI, MRS Symposium Process 112, 33–42.

Beyeler, W.E., Brown, T.J., Hareland, W.A., Conrad, S., Olague, N., Brosseau, D., Kalinina, E., Gallegos, D.P., Davis, P.A., 1999. Residual Radioactive Contamination from Decommissioning: Parameter Analysis. NUREG/CR-5512, SAND99-2148, Vol. 3, Sandia National Laboratories.

Bio-Rad, 1987. Guide to ion exchange, Catalog Number 140-9997, Richmond, CA: Bio-Rad Laboratories.

Bonka, K.H., Brussermann, G., Schwarz, 1974. Umweitbelatung durch Radiokolenstolf aus Kerntechnichen Analgen, Reactortagung, Berlin.

Boss, C.R., Allsop, P.J., 1995. Radioactive Effluents from CANDU 6 Reactors During Normal Operations, AECL-11506. Atomic Energy of Canada Limited, Chalk River, Ont..

Braun, H., Gutowski, H., Bonka, H., Grundlen D., 1983. Plant for Retention of 14C in Reprocessing Plants for LWR Fuel Elements, in Proc. 17th DOE Nuclear Air Cleaning Conference, CONF-820833, pp. 381–399.

Brookins, D.G., 1988. Eh-pH Diagrams for Geochemistry. Springer, Berlin.

Buckley, L.P., Woods, B.L., Ward, W.J., 1985. A method for removing Carbon-14 from particulate, ion exchange resins. Canadian Patent No. CA 1250378, Canadian Intellectual Property Office, http://patents1.ic.gc.ca.

Buhmann, D., Nies, A., Storck, R., 1991. Systemanalyse Mischkonzept, Technischer Anhang 7. KWA Nr.5702A. GSF, Braunschweig, Federal Republic of Germany.

Bush, R.P., Smith, G.M., White, I.F., 1984. Carbon-14 Waste Management, EUR-8749 EN. Commission of the European Communities, Luxembourg.

Butow, E., et al., 1985. Modellrechnungen zur Ausbreitung von Radionukliden im Deckgebirge. Projekt Sicherheitsstudien Entsorgung (PSE). Fachband, 18, BFT, Berlin.

Calvin, M., Heidelberger, C., Reid, J.C., Tolbert, B.M., Yankwich, P.F., 1949. Isotopic Carbon. Wiley, NY.

Caron, F., 1996. Overview and dynamics of organic carbon in a low-level radioactive waste degradation experiment. In: Waste Management'96, Eds., Post, R.G., Wacksno M.E. AECL report RC-M-20. Tucson, AZ: WM'97 Symposia Inc.

Caron, F., Milton, G.M., 1998. Preface to papers on carbon cycling in mid-latitudes. Applied Geochemistry 13, 1–2.

Caron, F., Torok, J., 2000. Ion exchange resin degradation and Carbon-14 emission control in CANDU moderator system. Eight International Conference of Water Chemistry of Nuclear Reactor Systems, Bournemouth UK, Oct. 22–26, 2000. Water chemistry of nuclear reactor systems 8, British Nuclear Energy Society, Thomas Telford, ISBN 0-7277-2958-6, pp. 241–243.

Caron, F., Wilkinson, S.R., Torok, J., Haas, M.K., Selander, W.N., 1994. CO_2 transport through the capillary fringe in sand. Waste Management 14, 421–434.

Caron, F., Manni, G., Workman, W.J.G., Haas, M.K., 1998a. Soil CO_2 Gas-groundwater Exchange and Migration Near Waste Management Area C, Chalk River, Ontario, RC-2121, COG 98 253-I. Atomic Energy of Canada Limited, Chalk River Laboratories, Chalk River, Ont..

Caron, F., Sutton, J., Recoskie, C.L., Haas, M.K., scoping, A., 1998b. A Scoping Study of C-14 Gaseous Emissions from Waste Management Area C, Chalk River Laboratories. RC-2113. Atomic Energy of Canada Limited, Chalk River, Ontario.

Caron, F., Manni, G., Workman, W.J.G., 1998c. A large-scale laboratory experiment to determine the mass transfer of CO2 from a sandy soil to moving groundwater. Journal of Geochemistry Explor. 64, 111–125.

Chang, F.H., Krochmalnek, L.S., 1992. Method for separating Carbon-14 from particulate ion-exchange resins. Canadian Intellectual Property Office, Application CA 2023729. http://patents1.ic.gc.ca.

Chang, F.H., Krochmalnek, L.S., Vogy, H.K., Sood, S.K., Bartoszek, F.E., Robins, J.R., Woodall, K.B., 1990. Canadian Intellectual Property Office, Application CA 2061307. http://patents1.ic.gc.ca.

Choppin, G.R., Liljenzin, J.-O., 2002. Radiochemistry and Nuclear Chemistry, third ed. Butterworth-Heinemann, Woburn, MA.

Cline, J.E., Noyce, J.R., Coe, L.F., Wright, K.W., 1985. Assay of Long-Lived Radionuclides in Low-Level Wastes from Power Reactors. NUREG/CR-4101. U.S. Nuclear Regulatory Commission.

Dames and Moore, 1995. Waste Inventory Revision 3, North Carolina Low-Level Radioactive Waste Disposal Facility Project, DM/DR-002, prepared for Chem-Nuclear Systems, Inc.

Dames and Moore, 1995. Literature Review of Sorption Coefficients for Radionuclides in Cementitious Environments, Revision 1, Prepared for Chem-Nuclear Systems, Inc.

Dayal, R., 1995a. The Role of Cementitious Materials in Carbon-14 Waste Disposal, Proceedings of Conference, Radioactive Waste Management and Environmental Remediation, American Society of Mechanical Engineers 1995.

Dayal, R., 1995b. The Role of Cementitious Materials in Carbon-14 Waste Disposal, Proceedings of the 5th International Conference on Radioactive Waste Management and Environmental Remediation. American Society of Mechanical Engineers pp. 1009–1013.

Dayal, R., Reardon, E.J., 1992. Cement-based engineered barriers for Carbon-14 isolation. Waste Management 12, 189–200.

Dayal, R., Klein, R., 1987. Evaluation of Cement-Based Backfill Materials. Report No. 87-223-K, Ontario Hydro Research Division, Toronto, Canada.

Dias, S.A., Shapka, W., 2000. Supercritical carbon dioxide extraction of contaminants from ion exchange resins. Canadian Patent CA 2348521, Canadian Intellectual Property Office, http://patents1.ic.gc.ca.

Dolinar, G.M., Rowat, J.H., Stephens, M.E., Lange, B.A., Killey, R.W.D., Rattan, D.S., Wilkinson, S.R., Walker, J.R., Jategaonkar, R.P., 1996. Preliminary Safety Analysis Report (PSAR) for the Intrusion Resistant Undergound Structure (IRUS), AECL-MISC-295 (Rev. 4). Atomic Energy of Canada Limited, Chalk River Laboratories, Chalk River, Ont..

DuBourg, M., 1995. The Carbon 14 Cycle, IAEA-TECDOC-901, pp233-237, Graphite Moderator Lifecycle Behaviour, Proceedings of a specialist meeting, Bath, UK, 24–27 September, 1995, IAEA.

Ehalt, D.H., 1973. Methane in the Atmosphere. In: Woodwell, G.M., Pecan, E.V. (Eds.), Carbon and the Biosphere, Proceedings of the 24th Brookhaven Symposium in Biology, Upton, N.Y., May 16–18 1972 AEC Symposium Series, CONF-720510. U.S. Atomic Energy Commission, Washington, D.C..

Ehrig, H.-J., 1983. Quality and quantity of sanitary landfill leachate. Waste Management and Research 1, 53–68.

EPRI, 1996. Level Waste Characterization Guidelines. Electric Power Research Institute.

Evenden, W.G., Sheppard, S.C., Killey, R.W.D., 1998. Carbon-14 and tritium in plants of a wetland containing contaminated groundwater. Applied Geochemistry 13, 17–21.

Ewart, F.T., Pugh, S.Y.R., Wisbey, S.J., Woodwark, D.R., 1989. Chemical and Microbiological Effects in the Near-Field-Current Status 1989, NSS/G111, Nirex, Harwell/UK.

Findikakis, A.N., Papelis, C., Halvakadis, C.P., Leckie, J.O., 1988. Modelling gas production in managed sanitary landfills. Waste Management and Research 6, 115–123.

Fitzer, E., Schafer, W., 1979. The effect of crosslinking on the formation of glasslike carbons from thermosetting resins. Carbon 8, 353–364.

Forsberg, C.W., Del Cul, G.D., Spencer, B.B., Collins, E.D., 2003. A New Repository Waste Form: Graphite–Carbon High-Level Waste. Proc. 2003 International HLW Management Conference, Las Vegas, NVm March 30–April 2.

Fowler, T.W., Nelson, C.B., 1981. Health Impact Assessment of Carbon-14 Emissions from Normal Operations of Uranium Fuel Cycle Facilities. EPA 520/5-80-004. Environmental Protection Agency, Washington, DC.

Franz, E., Fuhrmann, M., Bowerman, B., Bates, S., Peters, R., 1994. Proposed Waste Form Performance Criteria and Testing Methods for Low-Level Mixed Waste. BNL-52436, DOE/MWIP-30, Brookhaven National Laboratory.

Gascoyne, M., 1992. Concentrations of C in groundwater for the geosphere model. Atomic Energy of Canada Limited Technical Record, TR-567, COG-92-27. Chalk River, Ontario.

Government of Canada, 2002. An act respecting the long-term management of nuclear fuel waste, House of Commons of Canada, Bill C-27, Ottawa, Ontario.

Glasbergen, P., Englend-Boroviec, G., Nijhoff-Pan, I., Slot, A.F.M., 1989. Transport van radionukliden door de ondergrond. RIVM (Rijksinst. Milieuonderzoek), Bilthoven, Rep. 728513010.

Gray, W.J., 1980. Reaction of graphite with water and its implications for radioactive waste storage. Radioactive Waste Management 1 (1), 105–109.

Gray, W.J., 1982. A study of the oxidation of graphite in liquid water for radioactive waste storage applications. Radioactive Waste Management and the Nuclear Fuel Cycle 3 (2), 137–149.

Gruhlke, J.M., Neiheisel, J., Battist, L., 1986. Estimates of the Quantities, Form and Transport of Carbon-14 in Low Level Radioactive Waste. EPA 520/1-86-019, US Environmental Protection Agency.

Guiroy, J.-J., 1995. Graphite Waste Incineration in a Fluidized Bed, IAEA-TECDOC-901, pp. 193–203, Graphite Moderator Lifecycle Behaviour, Proceedings of a specialist meeting, Bath, UK, 24–27, 1995, IAEA.

Guvanasen, V.M., 1985. Preliminary Assessment for the Disposal of Intermediate-Level Reactor Waste, AECL TR-293. Atomic Energy Canada Ltd, Pinawa, Man..

Hietanen, R.T., Kaakkola, Miettinen, J., 1985. Sorption of cesium, strontium, iodine, and carbon in concrete and sand. Scientific Basis for Nuclear Waste Management VIII, MRS Symposium Process 44, 891–898.

Healy, J.W., 1971. Surface Contamination: Decision Levels. LA-4558-MS. Los Alamos National Laboratories.

Holtorp, J., 1996. A Strategy for the Management of Carbon-14 at OHN's Nuclear Facilities, N-REP-03467-0138 Rev 0. Ontario Hydro Nuclear, Toronto, Ont..

IAEA (International Atomic Energy Agency), 1991. Conditioning of Alpha Bearing Waste. Technical Report Series No. 326, Vienna.

ICRP, 1968. Report of Committee IV on Evaluation of Radiation Doses to Body Tissues from Internal Contamination due to Occupational Exposures. ICRP Publication 10. Pergamon Press, New York, NY.

Impell Corporation, 1985. Radionuclide Correlations in Low-Level Radwastes. EPRI NP-4-37, Electric Power Research Institute.

IUPAC, 1984. Element by element review of their atomic weights. Pure and Applied Chemistry 56, 695–768.

Jefferies, N., 1990. The Evolution of Carbon-14 and Tritium Containing Gases in a Radioactive Waste Repository. Report NSS/R198, Nirex Ltd., Harwell, UK.

Jenkinson, Rayner, 1979. Decomposition in terrestrial ecosystems. In: Swift, M.J., Heal, O.W., Anderson, J.M. (Eds.), Vol. Studies in Ecology, vol. 5. University of California Press, Berkely, CA (USA), pp. 119–219 (Chapter 4 and 5).

Johnston, H.M., 1990. Laboratory studies of the transport of Carbon-14 in Unsaturated Geologic Materials. University of Waterloo. Also available as Ontario Hydro Report 90-142-K, Toronto, ON.

Killey, R.W.D., Rao, R.R., Eyvindson, S., 1998. Radiocarbon speciation and distribution in an aquifer plume and groundwater discharge area, Chalk River, Ontario. Applied Geochemistry 13, 3–16.

King, K.J., Kramer, S.J., Repta, C., 1998. Measurements of CANDU ^{14}C Emissions from Tree Rings, COG-98-251-I. Atomic Energy of Canada Limited, Chalk River, Ont..

Kitabata, T., Sakurai, N., 1988. Experience of water chemistry control in Fugen NWR. Second International Topical Meeting on Nuclear Power Plant Thermal Hydraulics and Operations. 11-47-11-55.

Kotzer, T.G., Watson, W.L., 1999. Spatial and Temporal Distribution of C14 in Cellulose in Tree Rings in Central and Eastern Canada: Comparison with Long-term Atmospheric and Environmental Data, AECL-12002. Atomic Energy of Canada Limited, Chalk River, Ont..

Krupka, K.M., Serne, R.J., 1998. Effects on Radionuclide Concentrations by Cement/Ground-Water Interactions in Support of Performance Assessment of Low-Level radioactive Waste Disposal Facilities. NUREG/CR-6377, PNNL-11408, U.S. Nuclear Regulatory Commission.

Krupka, K.M., Serne, R.J., Jenne, E.A., 1995. Geochemical Effects on the Behavior of Low-level Waste Radionuclides in Soil/Groundwater Environments. 17th. U.S. DOE LLW Management conference, Phoenix, AZ, December 12–14.

Kunz, C., 1985. Carbon-14 discharge at three light-water reactors. Health Physics 49, 25–35.

Lever, D.A., Woodwark, D.R., 1989. Radionuclide Transport by Groundwater Flow Through the Geosphere-Current Status 1989. NSS/G113. Nirex Ltd, Harwell, UK.

Liepins, L.Z., Thomas, K.W., 1988. Survey of ^{14}C literature relevant to a geologic nuclear waste repository. Rad. Waste Management Nuclear Fuel Cycle 10, 357–380.

Link, S.O., King, K.J., Benz, M.L., Evenden, W.G., Robertson, D.E., 1999. Environmental Dynamics of Carbon-14 Near a Low-Level Radioactive Waste Burial Ground. U.S. Nuclear Regulatory Commission, Washington, DC.

Looney, B.B., Grant, M.W., King, C.M., 1987. Estimation of Geochemical Parameters for Assessing Subsurface Transport at the Savannah River Plant. DPST-85-904. Savannah River Laboratory, Aiken, SC.

Martin, J.E., 1986. Carbon-14 in low-level radioactive waste from two nuclear power plants. Health Physics 50, 57–64.

Matsumoto, J., Banba, T., Muraoka, S., 1995. Adsorption of Carbon-14 on mortar. Mater Research Society Symposium Process 353, 1029–1035.

McKee, D.W., 1973. Carbon and graphite science. Annual Review of Materials Science 3, 195–231.

McKinley, I.G., Hadermann, J., 1985. Radionuclide Sorption Database for Swiss Safety Assessment. NTB 84-40, NAGRA (National Coop. For Storage of Radioactive Waste), Baden.

McKinley, I.G., Sholtis, A., 1993. A comparison of radionuclide sorption databases used in recent performance assessments. Journal of Contaminant Hydrology 13, 347–363.

McNeely, R., 1994. Long-term environmental monitoring of ^{14}C levels in the Ottawa region. Environment International 20, 675–679.

Miller, C.C., 2000. Personal Communications. Pacific Gas and Electric Company, Avila Beach, CA.

Milton, G.M., 1993. Workshop on the Environmental Behaviour of C-14, RC-1009; COG-93-209. Atomic Energy of Canada, Ltd, Chalk River, Ont..

Milton, G.M., 1996. Workshop on Carbon cycling in Mid-latitudes: Field and tracer studies. RC-1570. Atomic Energy of Canada Limited, Chalk River Laboratories, Chalk River, Ont..

Milton, G.M., Brown, R.M., Repta, C.J.W., Selkirk, C.J., 1996. Atmospherically Dispersed Radiocarbon at the Chalk River Laboratories, AECL-11421. Atomic Energy of Canada Limited, Chalk River Laboratories, Chalk River, Ont.

Milton, G.M., King, K.J., Sutton, J., Enright, S., 1998. Tracer studies of carbon source utilization in a wetland on the Canadian shield. Applied Geochemistry 13, 23–30.

Moghissi, A.A., Godbee, H.W., Hobart, S.A., 1986. Radioactive Waste Technology. The American Society of Mechanical Engineers.

Morel, F.M.M., Herig, J.G., 2000. Principles and Applications of Aquatic Chemistry. Wiley-Interscience, New York.

Mori, S., Akatsuka, H., Suzuki, M., 2001. Carbon and oxygen isotope separation by plasma chemical reactions in carbon monoxide glow discharge. Journal of Nuclear Science and Technology 38 (109), 850–858.

Nacarrow, D.J., Summerling, T.J., Ashton, J., 1988. Preliminary Radiological Assessments of Low-Level Waste Repositories. DOE/RW/88.084, Department of Environment, London, United Kingdom.

NAGRA (Swiss National Cooperation for Storage of Radioactive Waste). 1985. Project Gewahr, Project Summary Report, NGB 85-09, 8 vol., NAGRA, Baden, Switzerland.

NAGRA (Swiss National Cooperation for Storage of Radioactive Waste). 1988. Sediment Study-Intermediate Report, NGB 88-25E (English executive summary), NAGRA, Baden, Switzerland.

NCRP, 1994. Dose Control at Nuclear Power Plants. NCRP Report No. 120, National Council on Radiation Protection and Measurements, Bethesda, MD.

NCRP, 1985. Carbon-14 in the Environment. NCRP Report 81, National Council on Radiation Protection and Measurements, Bethesda, MD.

Noshita, K., Nishi, T., Matsuda, M., Izumida, T., 1996. Sorption Mechanism of Carbon-14 by Hardened Cement Paste. Scientific Basis for Nuclear Waste Management Mat. Res. Soc. Symp. Proc., vol. 412. Materials Research Society.

NWMO, 2003. Nuclear Waste Management Organization, http://www.nwmo.ca/.

Nydal, R., Loveseth, K., Syrstad, O., 1971. Bomb 14C in the human population. Nature 232, 418.

Peltonen, E., Vuori, S., Anttilla, M., Hillebrand, K., Meling, K., Rasilainen, K., Salminen, P., Suolanen, V., Winberg, M., 1985. Safety Analysis of Disposal of Spent Nuclear Fuel-Normal and Disturbed Evolution Scenarios. Report YJT-85-22, Nuclear Waste Commission of Finnish Power Companies, Helsinki, Finland.

Pirt, S.J., 1978. Aerobic and anaerobic microbial digestion in waste reclamation. Journal of Applied Chemistry Biotechnology 28, 232–236.

Rao, R.R., 1997. Tritium and Carbon-14 in CANDU Reactors: Comparison of their Production and Release Rates with Those from Other Types of Reactors, COG-97-463-I. Atomic Energy of Canada Limited, Chalk River, Ont..

Rao, R.R., Killey, R.W.D., 1994. Quantitative separation and determination of inorganic and organic forms of total carbon and radiocarbon in natural waters and application at a radioactive waste management site. Radiochima Acta 65, 63–74.

Rautenstrauch, K.R., Smith, A.J., Andrews, R., 2003. Technical Basis Document No. 12: Biosphere Transport, Revision 1, Bechtel SAIC Company, LLC, Las Vegas, Nevada.

Rodriguez, C., Baxter, A., 2000. Transmutation of nuclear waste using gas-cooled reactor technologies. 8th International Conference on Nuclear Engineering (ICONE 8), Apr. 2–6, 2000, Baltimore, MD.

Romanoff, M., 1957. Underground corrosion. National Bureau of Standards Circular, 579.

Rosset, R., Desbarres, J., 1993. Propriétés rédox de 14C, Report Submitted to Electricite De France.

Sakurai, T., Yokoyama, A., 2000. Decomposition of carbon dioxide, carbon monoxide and gaseous water by microwave discharge. Journal of Nuclear Science and Technology 37 (9), 814–820.

Scheele, R.D., Burger, L.L., 1982. Selection of Carbon-14 Fixation Form. PNL-4447, Pacific Northwest Laboratory.

Serne, R.J., Lokken, R.O., Criscenti, L.J., 1992. Characterization of grouted low-level waste to support performance assessment. Waste Management 12, 271–287.

Sheppard, M.I., Thibault, D.H., 1990. Default soil solid/liquid partition coefficients, K_ds, for four major soil types: a compendium. Health Physics 59, 471–482.

Sheppard, M.I., Sheppard, S.C., Amiro, B.D., Schwartz, W.J., Hawkins, J.L., Thibault, D.H., 1990. Soil-to-plant transfer factor of carbon-14 for environmental assessment of radioactive waste repositories. EPRI NP-6946, Electric Power Research Institute, Palo Alto, CA.

Sheppard, S.C., Amiro, B.D., Sheppard, M.I., Stephenson, M., Zach, R., Bird, G.A., 1994. Carbon-14 in the biosphere: modelling and supporting research for the canadian nuclear fuel waste management program. Waste Management 14, 445–456.

Simister, C., Caron, F., Gedye, R., in press. Determination of the thermal degradation rate of polystyrene–divinyl benzene ion exchange resins in ultra-pure water at ambient and service temperature. J. Radioanal. Nucl. Chem.

Striegl, R.G., Healy, R.W., 1990. Transport of $^{14}CO_2$ in Unsaturated Glacial and Eolian Sediments. In: Melchior, D.C., Bassett, R.L. (Eds.), Chemical Modeling of Aqueous Systems II, no. ACS Symp. Ser. 416. ACS, Washington DC.

Stroes-Gascoyne, S., West, J.M., 1994. Microbial Issues Pertaining to the Canadian Concept for the Disposal of Nuclear Fuel Waste, AECL-10808; COG-93-54. Atomic Energy of Canada, Ltd., Pinawa, Man. (Canada).

Su, S.-I., Yim, M.-S., 2000. Analysis of radionuclide release from spent ion-exchange resins. Nuclear Technology 130, 71–88.

Suess, H.E., 1955. Radiation concentration in modern wood. Science 122 (3166), 414–417.

Sullivan, T.M., Suen, C.J., 1989. Low-Level Waste Shallow Land Disposal Source Term Model: Data Input Guide. NUREG/CR-5387, BNL-NUREG-52206, Brookhaven National Laboratory, Upton, NY.

Swift, M.J., Heal, O.W., Anderson, J.M., 1979. Decomposition in Terrestrial Ecosystems, Vol. Studies in Ecology, vol. 5. University of California Press, Berkely, CA (USA) (pp. 119–219, Chapters 4 and 5).

Takeshita, K., Nakano, Y., Shimizu, M., Fujii, Y., 2002. Recovery of ^{14}C from graphite moderator of gas-cooled reactor. Journal of Nuclear Science and Technology 39 (11), 1207–1212.

Thorstenson, D.C., Weeks, E.P., Haas, H., Fisher, D.W., 1983. Distribution of gaseous $^{12}CO_2$, $^{13}CO_2$, and $^{14}CO_2$ in the sub-soil unsaturated zone of the western US great plains. Radiocarbon 25, 315–346.

Till, J.E., Meyer, H.R., 1983. Radiological Assessment, A Textbook on Environmental Dose Analysis. NUREG/CR-3332, ORNL-5968, U.S. Nuclear Regulatory Commission.

Torok, J., Caron, F., 2000. Carbon-14 chemistry in CANDU moderator system. 21st Canadian Nuclear Society meeting, Toronto, ON, June 11–14, 2000. Canadian Nuclear Society, Toronto, ON.

Torok, J., Lovasic, Z., Haas, M.K. 1990. Unpublished internal AECL report.

UNSCEAR, 2000. Limiting. EPA-520/1-88-020, Office of Radiation Programs, Environmental Protection Agency, Washington, DC.

US EPA, 1988. Limiting Values of Radionuclide Intake and Air Concentration and Dose Conversion Factors for Inhalation, Submersion, and Ingestion. EPA-520/1-88-020, Office of Radiation Programs, Environmental Protection Agency, Washington, DC.

US EPA, 1988. Low-Level and NARM Radioactive Wastes, Draft Environmental Impact Statement for Proposed Rules, Volume 1, Background Information Document, EPA 520/1-87-012-1, Office of Radiation Programs, Environmental Protection Agency, Washington, DC.

US EPA. 1994. Code of Federal Regulations, Title 40, Chapter 1, Part 191, Environmental Radiation Protection Standards for Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes. Federal Register.

US EPA. 2001. 40 CFR Part. 197. Public Health and Environmental Radiation Protection Standards for Yucca Mountain. Nevada, June 13.

U. S. NRC. 1981. Draft Environmental Impact Statement on 10CFR Part 61. NUREG-0782, Vol. 4, U.S. Nuclear Regulatory Commission.

US NRC., 1982. Code of Federal Regulations, Title 10, Chapter 1, Part 61, Licensing Requirements for Land Disposal of Radioactive Waste. Federal Register. 47, 57446.

US NRC, 1993. Source Term Implementation for Initial Performance Assessment Calculation. Technical Review of Performance Assessment Modeling Strategy, Rockville, MD, July 12–13, Nuclear Regulatory Commission.

US NRC, 1994. Overview of NRC Staff LLWPA Modeling Efforts. Low-Level Waste Performance Assessment Workshop, Rockville, MD, November 17, Nuclear Regulatory Commission.

US NRC. 2001. 10 CFR Part. 63, Disposal of High-Level Radioactive Waste in a Geologic Repository at Yucca Mountain. Nevada, November, 2.

Van Konynenburg, R.A., 1994. Behavior of Carbon-14 in waste packages for spent fuel in a tuff repository. Waste Management 14, 363–383.

Vance, J.N., Cline, J.E., Robertson, D.E., 1995. Characterization of Carbon-14 generated by the Nuclear Power industry, TR-105715. EPRI, Palo Alto, California, Electric Power Research Institute.

Vieno, T., Nordman, H., 1991. Safety Analysis of the VLJ Repository. Report YJT-91-12, Nuclear Waste Commission of Finnish Power Companies, Helsinki, Finland.

Wickham, A.J., Marsden, B.J., Sellers, R.M., Pilkington N.J., 1995. Graphite Core Stability During Care and Maintenance and Safe Storage, IAEA-TECDOC-901, pp. 225–232, Graphite Moderator Lifecycle Behaviour, Proceedings of a specialist meeting, Bath, UK, 24–27 September, 1995, IAEA.

Wickham, A.J., Neighbour, G.B., Dubourg, 2001. The Uncertain Future for Nuclear Graphite Disposal: Crisis or Opportunity? Proceedings of Technical Committee Meeting, Nuclear Graphite Waste Management. Manchester, UK, October 18–20, 1999, International Atomic Energy Agency, Vienna, Austria.

Wilborgh, M., Lindgree, M., 1987. SKA Progress Report, SFR 87-09, SKB, Stockholm, Sweden.

Wise, M., 2001. Management of UKAEA Graphite Liabilities, Proceedings of Technical Committee Meeting, Nuclear Graphite Waste Management. Manchester, UK, October 18–20, 1999, International Atomic Energy Agency, Vienna, Austria.

WNA, 2004. World Nuclear Association web site, http://www.world-nuclear.org/, accessed October to December 2004.

Wood, C.J., 1995. Dose Reduction Methods. In: Maletskos, C.J. (Ed.), Dose Reduction Methods: Chemical and Physical, in Radiation Protection at Nuclear Reactors. Medical Physics Publishing, Madison, WI.

Yim, M.-S., 1994. Gas-Phase Release of Radionuclides from Low-Level Radioactive Waste Disposal Facilities. Sc.D. Thesis, Harvard University School of Public Health, Boston, MA.

Yim, M.-S., 1998. Evaluation of Waste Forms for Immobilization of ^{14}C and ^{129}I. EPRI TR-110096, Final Report, Electric Power Research Institute.

Yim, M.-S., 2001. Investigation of Alternative Waste Forms for GTCC 14C Filters. Report 1003066, EPRI, Palo Alto, CA.

Yim, M.-S., Simonson, S.A., 1999. Carbon-14 in Low-Level Waste. TR-107957, EPRI, Palo Alto, CA.

Yim, M.-S., Simonson, S.A., 2000. Performance assessment models for low level radioactive waste disposal facilities: a review. Progress in Nuclear Energy 36 (1), 1–38.

Yim, M.-S., Ocken, H., 2001. Radiation dose management in nuclear power plants. Progress in Nuclear Energy 39 (1), 31–51.

Yim, M.-S., Simonson, S.A., Sullivan, T.M., 1996. Investigation of C-14 release from a generic LLW disposal facility. Nuclear Technology 114 (2), 254–271.