添付資料 1

INTERNER BERICHT 04-03

“ Proceedings of a workshop on the release and transport of C-14 in repository environments ”

nagra National Cooperative for the Disposal of Radioactive Waste

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L. H. JOHNSON & B. SCHWYN (eds.)

FEBRUARY 2004

KEYWORDS

carbon-14, C-14, gas transport, gas production, safety assessments

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Preface

Wettingen, Switzerland – Oct. 27-28, 2003

L. Johnson and B. Schwyn (Nagra)
E. Wieland (PSI)

Introduction

On Oct. 27-28, 2003, a Workshop on the Release and Transport of C-14 in Repository Environments was held at the offices of Nagra in Wettingen, Switzerland, organised and hosted by Nagra and RWMC. The purpose of the workshop was to examine the evidence for the chemical state of C-14 in various waste materials (spent fuel, fuel cladding and fuel assembly structural materials, neutron-activated reactor core materials and resins) and to discuss measurements of release, sorption and transport of C-14 in repository environments.

A total of 17 papers were presented at the Workshop and, of these, 15 are included in this proceedings volume. The papers have not been peer reviewed by the organisers of the Workshop. Nonetheless, there is considered to be significant value in quickly publishing, at least informally, the proceedings of the Workshop, as this is a rapidly developing area with a relatively sparse literature. The following provides some summary comments based on our notes, which were taken during the discussion periods. Of necessity, it is biased based on our perceptions of the points discussed, but we nonetheless hope readers find the comments useful. They are not intended to provide a summary of the work presented, but rather a record of some of the most significant issues raised by the participants during the discussion periods. It is hoped that the points raised will encourage further work that will address some of the most important remaining uncertainties.

Summary of Main Discussion Issues

The papers presented covered a wide range of areas, including calculation and measurement of inventories of C-14 in many types of waste, speciation of released C-14, sorption of various chemical forms of released C-14, and modelling of transport of C-14 in the context of repository safety assessment, including transport in both aqueous and gas phases. Some key points include the following:

- Discussions on the issue of the C-14 concentration in various waste materials highlighted the need for careful assessment of the different routes of C-14 production in neutron-activated materials, as well as the need for more direct measurements of inventories and chemical forms of C-14 in some types of waste.
- It is clear from various studies of the release of C-14 by anaerobic corrosion of metals that release rates are very low under anaerobic conditions, thus explicit consideration of such low rates in assessment models will lead to decay of much of the inventory of C-14 before release can occur. Careful determination of such rates thus appears worthwhile, as opposed to adopting excessively conservative rates in performance assessment.
- One of the most significant developments with respect to the issue of the chemical form of C-14 released from various activated metals and other ILW is the finding that a high

proportion of organic C-14 vs. inorganic C-14 is released upon corrosion of activated metals. The finding that small organic molecules such as short-chain carboxylic acids, alcohols and aldehydes are dominant species raises many questions regarding the ultimate fate of such molecules. Whether their sorption chemistry should be assessed, for input to repository safety assessment models, or whether their ultimate fate is likely to be oxidation to CO_2 or reduction to CH_4 via microbiological activity was a key point of discussion. In the former case, small organic molecules exhibit significant sorption, leading to significant decay during transport. In the latter case, C-14 may be effectively retarded in alkaline systems due to precipitation of calcite, whereas reduction to methane may lead to more rapid transport, although the likelihood of oxidation to CO_2 by microbes in the surface environment should also be considered. Further examination of how to treat C-14 transport in safety assessment in a realistic fashion, including how to obtain evidence to support such models, is clearly warranted.

Workshop on C-14 Release and Transport in Repository Environments
October 27 - 28, 2003
Wettingen, Switzerland

Final programme - Agenda

Monday, Oct 27

08:15	*Pickup at Hotel du Parc*	
08:45	Welcome and introduction of participants	L. Johnson, Nagra
Session I	***Treatment of C-14 in performance assessment***	
09:00	Effect of C-14 in Performance Assessment of Radioactive Waste Disposal	T. Tochiyama, Tohoku University
09:30	C-14 Behaviour in the Opalinus Clay Safety Case	L. Johnson, Nagra
10:00	Treatment of C-14 Release and Transport in the Long-term Safety Assessment in the Final Repository in Morsleben	U. Noseck, GRS, M. Niemeyer, Colenco
10:30	*Coffee Break*	
Session II	***Chemical form of C-14 in wastes***	
11:00	Study on Chemical Forms of C-14 Released from Activated Metals	M. Sasoh, Toshiba
11:30	Methods For Measuring 14-C on Spent Ion Exchange Resins – A Review	K. Stenström, Lund University
12:00	*Lunch*	
13:30	N and C-14 Contents of Spent Fuel	P. Marimbeau, CEA
14:00	Measurement of Organic and Inorganic C-14 in a Graphite Reflector from a Swedish Nuclear Reactor	Å. Magnusson, Lund University
14:30	Study on Photocatalytic Destruction of Organic C-14 in the Waste Package	S. Kaneko, RWMC
15:00	*Coffee*	
Session III	***Behaviour and chemical state of C-14 in the near field***	
15:30	Fundamental Study of C-14 Chemical Form Under Irradiated Condition	K. Noshita, Hitachi
16:00	Interactions of Carbon in Repository Environments	B. Kienzler, FZK-INE
16:30	Study on Chemical Behaviour of Organic C-14 Under Alkaline Condition	M. Sasoh, Toshiba
17:00	*Discussion*	
17:30	*Adjournment*	

19:30	***Workshop dinner – Restaurant Pavillon***	

Tuesday, Oct.28

08:00	*Pickup at Hotel du Parc*	
Session IV	***Transport of C-14***	
08:30	C-14 Carbonate Uptake by Limestone in Concrete Buffer Environments	I. Pointeau, CEA
09:00	Investigations of Distribution Coefficients for C-14 from Activated Metal	M. Sasoh, Toshiba
09:30	C-14 Source Term Characterisation and Migration Behaviour of C-14 Labelled Bicarbonate in Boom Clay	J. Fernandez Lopez, Belgonucleaire, H. Van Humbeeck, NIRAS
10:00	*Coffee break*	
10:30	Migration of C-14 in Activated Metal Under Anaerobic Alkaline Conditions	N. Kogawa, NDC
11:00	Modelling the Partitioning and Transport of C-14 in a Microbially Active LLW Site	J. Small, BNFL
11:30	Application of a New Gas Generation Model to Develop the Source Term of C-14 Bearing Gases in Radioactive Waste Disposal	S. Vines, NIREX
12:00	*discussion*	
12:30	*Close of meeting*	

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Behaviour of ^{14}C in the Safety Assessment of a Repository for Spent Fuel, High-level Waste and Long-lived Intermediate Level Waste in Opalinus Clay

L. Johnson and B. Schwyn
Nagra, Hardstrasse 73, Wettingen Switzerland

Introduction

Nagra has been developing the concept of a repository for spent fuel (SF), high-level waste from reprocessing (HLW) and long-lived intermediate-level waste (ILW) in the Opalinus Clay for over ten years. A fully integrated study incorporating three main aspects of (i) geological understanding, (ii) repository design and (iii) long-term safety assessment has now been completed. The study provides a demonstration of siting feasibility for the selected host rock in the region of the Zürcher Weinland, where detailed site investigations have been performed. The results of calculations of radiological consequences, which constitute one of several lines of argument making up the safety case for the selected disposal system, indicate that disposal is feasible from a safety point of view (Nagra 2002a).

Radiological calculations have been performed following the methodology described in Nagra (2002a). In this study, based on a qualitative and quantitative analysis of the evolution of the disposal system, a Reference Scenario and a Reference Case are defined, together with a range of alternative cases that explore other possible paths for the evolution of the disposal system. The Reference Scenario represents the expected behaviour of the disposal system, being based on the assumption that the engineered barriers perform as designed and that the Opalinus Clay is a medium in which transport is dominated by diffusion, as indicated by hydrogeological and geochemical studies. The biosphere, which is not considered part of the disposal system, is based mainly on present-day conditions, with conservative assumptions regarding human behaviour and diet. In the Reference Case (i.e. the Reference Scenario, implemented with additional more specific conceptual assumptions and parameter values), the carbon steel canisters for SF/HLW have a lifetime of 10,000 years and groundwater and radionuclide transport after canister breaching is dominated by aqueous diffusion in the near field and by aqueous diffusion/advection in the Opalinus Clay.

The annual individual doses calculated as a function of time for the Reference Case for each of the three waste types are shown in Fig. 1. It can be seen that ^{14}C is one of the most important radionuclides in the reference case (although doses are at levels several orders of magnitude below the regulatory limit). Its importance in the assessment arises from specific assumptions made regarding the rate of release, speciation upon release and mobility of the different forms of carbon. Furthermore, assessment of conceptual model uncertainties in the Opalinus Clay disposal system gives rise to alternative assessment cases that consider co-transport of volatile ^{14}C along with hydrogen produced by anaerobic metal corrosion. These aspects are discussed in detail below, along with the underlying data and the associated uncertainties.

Behaviour of ^{14}C in the Reference Case

As seen in Fig. 1, the doses from ^{14}C in the case of SF and ILW occur earlier than doses from other radionuclides and arise from organic ^{14}C. There is no dose contribution due to ^{14}C in the case of HLW. The reasons for these results are discussed below, in the context of brief explanations of the evidence and assumptions regarding ^{14}C inventories in the various wastes and the release and transport models.

Inventories of ^{14}C in the various waste types

SF and SF assembly materials

In the case of SF, ^{14}C is present after irradiation in the fuel matrix, Zircaloy cladding and stainless steel alloy assembly components principally as a result of the reaction ^{14}N (n,p) ^{14}C. A small contribution also arises from the reaction ^{17}O (n,α) ^{14}C in the case of the UO_2 fuel matrix. The assumed impurity levels of nitrogen in UO_2, Zircaloy and stainless steels prior to irradiation are 25, 80 and up to 800 ppm, respectively, based on critical review of data from a number of studies. The chemical state of ^{14}C in these materials is not known with certainty. In the case of SF itself, the chemical form of ^{14}C is assumed to be inorganic (i.e. released as CO_3^{2-}) based on the limited studies of release published (see Stroes-Gascoyne et al. 1994). For Zircaloy and steel alloys, there is evidence of release of organic ^{14}C from irradiated Zircaloy (Yamaguchi et al. 1999) and from unirradiated carbon steel (Deng et al. 1997). This is consistent with the expectation that ^{14}C arising from nitrogen is likely to be present in the form of carbide in various metals. Based on these assumptions and the average burnup of the fuel, the inventories of ^{14}C were calculated using the BOXER code (McGinnes 2002). Approximately equal amounts of organic and inorganic ^{14}C are projected to be present in typical spent fuel assemblies. The inventories of organic and inorganic ^{14}C in the fuel and assembly materials are given in Nagra (2002a).

HLW

The ^{14}C present in vitrified HLW is assumed to be inorganic and present at three orders of magnitude lower levels per canister than for spent fuel, based on the consideration that almost all of the ^{14}C is volatilised during reprocessing operations, captured from the gaseous waste stream and incorporated into various solidified ILW products.

ILW

Various ILW products arise from reprocessing operations, as discussed in Nagra (2002a). The major source of inorganic ^{14}C is barium carbonate incorporated into cementitious waste. Organic ^{14}C is associated entirely with fuel hulls and ends recovered from reprocessing. The inventories of organic and inorganic ^{14}C are roughly equal.

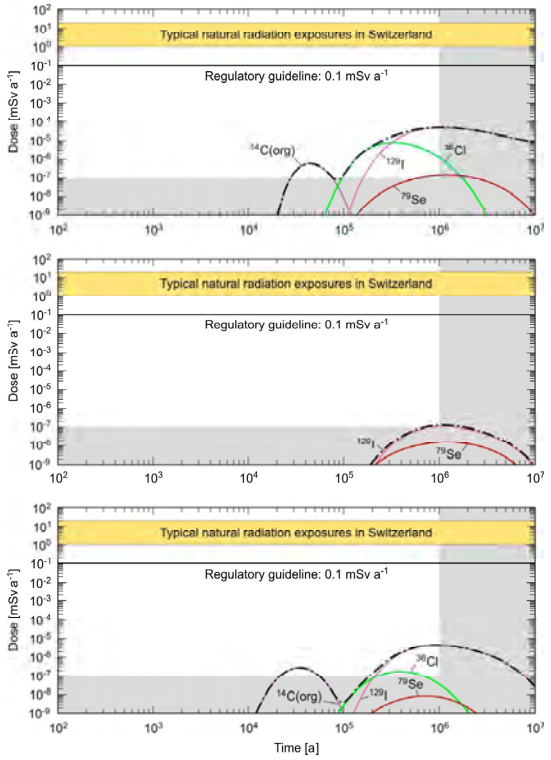

Fig. 1: Doses for the Reference Case for a repository in Opalinus Clay

Upper figure: SF, middle figure: HLW, lower figure: ILW.

Eventually, transport of volatile ^{14}C takes place from the Wedelsandstein formation by gas diffusion through the low-permeability upper confining units to the Malm aquifer where complete gas dissolution is assumed to occur. Radionuclide transport through the Malm aquifer to the biosphere is assumed to be instantaneous. The dissolved radioactive volatile species are diluted in the flowing groundwater of the Quaternary aquifer. Degassing of volatile species is pessimistically assumed not to occur. The calculated summed dose maxima of the present scenario are compared in Fig. 2 with the doses for the reference case.

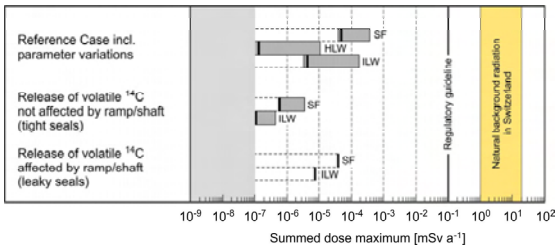

Fig. 2: Dose maxima for conceptualisations for the scenario considering release of volatile ^{14}C along gas pathways through the host rock only ("tight seals") and through the access tunnel system ("leaky seals")

The contribution of doses due to other pathways are not included (Base Cases marked by bold lines). Results for the reference case including parameter variations are also shown.

In the case of "tight seals", slow breakthrough to and accumulation in the Wedelsandstein formation leads to significant decay of ^{14}C, thus doses are lower than in the reference case. For transport of volatile ^{14}C in the ramp/shaft system ("leaky seals"), doses are similar to the total for all radionuclides in the reference case.

Release of ^{14}C from SF and ILW

For SF, 10 % of the ^{14}C is assumed to be released from the oxide matrix during irradiation. This material is considered to be released in inorganic form immediately upon breaching of the SF canister (Johnson and McGinnes 2002), with no containment credit assumed for Zircaloy. The Zircaloy itself is assumed to release 20 % of its ^{14}C inventory in organic form upon canister breaching, associated with material in the oxide film, based on results of Yamaguchi et al. (1999). The remaining ^{14}C is assumed to be released in organic form from Zircaloy slowly as a result of corrosion at a rate of 10 nm a^{-1}.

For ILW, all radionuclides are assumed to be released into the pore water in the cementitious near field from all types of ILW types 100 years after repository closure. This also applies to the ^{14}C present in Zircaloy, which is assumed to be released in organic form. The assumption of 100 % immediate release from Zircaloy is clearly conservative, given the very low corrosion rate of Zircaloy (i.e. it would be justifiable to use a corrosion-based release model, as discussed above for the SF case). The present model is adopted strictly to simplify the modelling of the ILW near field.

Chemical Retention of ^{14}C in the Near Field and Opalinus Clay

For the near field of the SF emplacement tunnels, in which bentonite surrounds the SF canisters, the released ^{14}C is transported through the bentonite buffer and the Opalinus Clay by diffusion. In the case of organic ^{14}C, it is assumed that no sorption occurs on either bentonite or Opalinus Clay. Combined with the assumption noted above of 20 % instant release from Zircaloy cladding, this leads to the dose peak at ~50,000 years in Fig.1. Inorganic ^{14}C, in contrast, experiences some retardation in the bentonite and Opalinus Clay. This retardation originates from an isotopic dilution with the near-surface carbonate of the calcite present in bentonite and Opalinus Clay. In safety assessment calculations the retention is expressed as a sorption coefficient (K_d values of 2×10^{-5} for bentonite and 1×10^{-3} m^3 kg^{-1} for Opalinus Clay, respectively). This rather limited retention in bentonite plays little role in retarding transport through the bentonite, but the somewhat greater retardation in Opalinus Clay, due to the higher calcite content of the latter, ensures virtually complete decay during transit through the host rock.

For ILW, the organic ^{14}C again contributes to doses at about 50,000 years because of the assumption of no sorption, whereas transport of inorganic ^{14}C is significantly retarded. This is also due to the isotopic dilution of inorganic ^{14}C with the calcite in Opalinus Clay, although an additional contribution arises from the coprecipitation of inorganic ^{14}C with inactive carbonate in the alkaline near field pore water (carbonate solubility = 2×10^{-4} mol l^{-1}).

Behaviour of ^{14}C in Alternative Scenarios

Alternative scenarios that explicitly focus on ^{14}C include those that incorporate the assumption that organic ^{14}C is converted to a volatile form (e.g. methane) which is transported with H_2 produced by corrosion of the carbon steel canisters (in the case of SF) or various metals in the ILW. There is no evidence for such a conversion process, but it cannot presently be excluded. In these scenarios, it is assumed that the volatile ^{14}C is transported from the near field via gas pathways through the Opalinus Clay ("tight seals") or through the access tunnel system ("leaky seals") to the overlying Wedelsandstein formation. Gas accumulates in pore spaces in the near field, in and around the gas pathways created in the Opalinus Clay, in the access tunnel system and in the Wedelsandstein formation. Volatile ^{14}C is diluted in the gas-filled pore space with non-radioactive gas generated by anaerobic metal corrosion and microbial degradation.

"What-if?" case considering unretarded transport of ^{14}C as volatile species through the host rock

In the Opalinus Clay safety case, a variety of assessment cases have been developed to address phenomena that are considered to be outside the range of possibilities supported by scientific evidence, but involve assumed perturbations of key properties of the pillars of safety. One of these "what if" cases considers unretarded transport of ^{14}C as volatile species through the host rock. The instantaneous formation of such a gas pathway is not supported by scientific evidence, but would have an impact on the pillars of safety because it involves an instantaneous bypass of the Opalinus Clay. In the conceptualisation, organic ^{14}C is assumed to be volatile and - after the available pore space in the near field has been filled with gas - to escape rapidly to the overlying Wedelsandstein formation, due to the postulated existence of a continuous gas pathway leading to instantaneous release through the Opalinus Clay. Retention in the Wedelsandstein formation is taken into account. Details of the calculation model are given in Nagra (2002b).

In all calculations, a steel corrosion rate of 1 µm a^{-1} is assumed. The gas permeability in the Opalinus Clay is varied, reflecting uncertainty in the gas transport properties of Opalinus Clay. In all of these cases, only the dose contribution of volatile ^{14}C is taken into account.

In all cases, the summed drinking water dose maxima for the conceptualisation "unretarded transport of ^{14}C as volatile species through Opalinus Clay" are approximately the same as the doses calculated for the Reference case for both SF and ILW (see Fig. 1), although the dose peak occurs at an earlier time of about 10,000 years.

Conclusions

Assessment calculations for a repository for SF, HLW and ILW in Opalinus Clay indicate that ^{14}C is a significant contributors to dose, although the doses are several orders of magnitude below the dose limit. Some significant uncertainties remain with respect to speciation of ^{14}C (inorganic vs. organic), as well as the nature of the organic ^{14}C. In addition, some pessimistic assumptions have been made for organic ^{14}C with respect to transport, such as no sorption on engineered barrier materials and host rock, as well as complete conversion to $^{14}CH_4$ in an alternative conceptualisation. Depending on further progress in understanding ^{14}C behaviour, these assumptions may be revisited in future assessment studies.

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Treatment of ^{14}C Release and Transport in the Long-Term Safety Assessment in the Final Repository in Morsleben

Part 1: Chemical Form and Mobilisation

M. Niemeyer, Colenco, Baden, Switzerland

Part 2: Solubility and Transport

U. Noseck, D. Becker and A. Rübel, GRS, Braunschweig, Germany
J. Wollrath, BfS, Salzgitter, Germany

Part 1: Chemical Form and Mobilisation

The Morsleben nuclear waste repository (ERAM) for mainly short-lived low- and intermediate-level radioactive waste is located in an old rock salt and potash mine in Northern Germany. The closure concept currently under investigation is based on extensive backfilling of the salt mine with an inexpensive concrete mixture using state-of-the-art technology. The inflow of brine or water into the remaining openings of the mine is the central scenario for the long-term safety assessment because it provides the transport medium for the radionuclides disposed of to get access to the biosphere.

The chemical heterogeneity of the salts in different parts of the mine and the different materials (mainly salt, the concrete mixture, and the heterogeneous waste) make it difficult to predict the chemical conditions of the solutions around the waste.

The amount of ^{14}C in the waste is substantial ($3.3 \cdot 10^{12}$ Bq, 20g). Thus, it is important for the safety assessment to determine the mobility of ^{14}C and at what ratio it can be released. A high percentage of $^{14}CO_3^{2-}$ relative to organic ^{14}C would be favourable, as the total amount of Ca^{2+} within the repository will be very high due to the concrete backfilling. In such a case, most of the CO_3^{2-} will remain undissolved and thus the solubility limit would also apply to the the $^{14}CO_3^{2-}$. Unfortunately, there is evidence for a high percentage of organic ^{14}C within the waste.

The ^{14}C within the waste from PWR reactors is assumed to be mainly CO_3^{2-}, although organic compounds have been found within the coolant of PWR reactors. But the major portion of the ^{14}C stems from the production and application of radionuclides for research in biology and biochemistry. So, most of these compounds are highly hydrophilic, will dissolve well in water and adsorb only weakly on the backfill materials. Additionally, a radiation experiment had been performed with alumina nitride (AlN) yielding some ^{14}C-carbide that can hydrolyze to $^{14}CH_4$.

Thus, three classes of ^{14}C-containing waste have been disposed of:

- $^{14}CO_3^{2-}$
- organic ^{14}C, readily dissolving in water
- ^{14}C as carbide, yielding $^{14}CH_4$ in contact with water

The situation is complicated by the possibility of microbial reactions. It is possible that – in spite of the extreme conditions (high salinity, high pH and low amount of nutrients) – microbes will survive and degrade the waste. Because of the lack of oxygen, anaerobic degradation will dominate, finally yielding $^{14}CH_4$ and $^{14}CO_2$.

Depending on the degree of degradation and the amount of oxygen available in organic and inorganic compounds, the resulting ratio of carbonate, methane and dissolved organic carbon may vary, as shown in the diagram in figure 1.

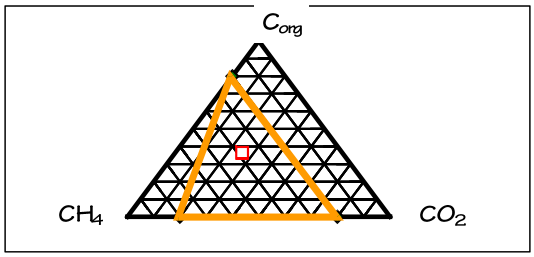

Fig. 1: Ratio of carbonate, methane and organic carbon due to different degree of degradation

Microbial activity decreases the amount of organic carbon, and available oxygen decreases the ratio $^{14}CH_4/^{14}CO_2$ during fermentation. However, there will always be some $^{14}CH_4$ because of the hydrolysis of the irradiated AlN, and some $^{14}CO_3^{2-}$ was introduced with the PWR waste.

Most of the organic ^{14}C is located in parts of the mine close to Carnallitit. The remaining organic ^{14}C is conditioned without much concrete. Thus, the expected pH in these areas will be below 11, allowing microbial activity to degrade the organic carbon. The highest $^{14}CH_4/^{14}CO_2$ ratio of 0.75 would hypothetically be achieved by fermentation of long-chain aliphatic compounds without any oxidizing agents (NO_3^-, SO_4^{2-}) in solution.

Part 2: Solubility and transport

The chemical form of ^{14}C is crucial for its retardation properties. For the inventory of ^{14}C it has to be distinguished between the three different forms: organic, alumina carbide and carbonate. The inventory of the different chemical forms of ^{14}C in different disposal areas of the Morsleben repository is shown in Table 1.

Table 1: Inventory of ^{14}C [Bq] in different disposal areas of Morsleben repository

	organic form	alumina carbide	carbonate
south field	$1.56 \times 10^{+12}$	$6.40 \times 10^{+11}$	$1.56 \times 10^{+11}$
west field	$6.42 \times 10^{+11}$		$1.23 \times 10^{+11}$
east field	$1.60 \times 10^{+09}$		$1.20 \times 10^{+11}$
north field	$5.60 \times 10^{+10}$		$3.10 \times 10^{+09}$
central part	$1.34 \times 10^{+09}$		$2.60 \times 10^{+08}$

As discussed in part 1, the carbon bearing materials will react in contact with the brine. Alumina carbide reacts to methane and carbonate will be (partly) dissolved. Concerning the organic form two different cases are considered in the long-term safety assessment. A microbial degradation is very likely at pH values below 10, which are expected in all disposal areas. Therefore, in the reference case it is assumed that all organic ^{14}C-bearing waste is transformed by microbial degradation into CO_2 and CH_4. In this case ^{14}C occurs only in two chemical forms, i.e. methane and carbonate. A $^{14}CH_4/^{14}CO_2$ ratio of 3 is assumed for the products of the degradation reaction (cf. Part 1). In the second case, a variant, the assumption is made that no microbial degradation takes place. Besides methane and carbonate, transport of ^{14}C in the form of organic compounds has to be considered. The amount of the chemical forms of ^{14}C for the reference case and the variant are summarized in table 2.

Table 2: Inventory of ^{14}C [Bq] for the reference case and a variant

	reference case		variant		
	carbonate	methane	organic form	methane	carbonate
south field	$5.46 \times 10^{+11}$	$1.81 \times 10^{+12}$	$1.56 \times 10^{+12}$	$6.40 \times 10^{+11}$	$1.56 \times 10^{+11}$
west field	$2.83 \times 10^{+11}$	$4.82 \times 10^{+11}$	$6.42 \times 10^{+11}$	-	$1.23 \times 10^{+11}$
east field	$1.20 \times 10^{+11}$	$1.20 \times 10^{+09}$	$1.60 \times 10^{+09}$	-	$1.20 \times 10^{+11}$
north field	$1.71 \times 10^{+10}$	$4.20 \times 10^{+10}$	$5.60 \times 10^{+10}$	-	$3.10 \times 10^{+09}$
central part	$5.95 \times 10^{+08}$	$1.01 \times 10^{+09}$	$1.34 \times 10^{+09}$	-	$2.60 \times 10^{+08}$

2.1 ^{14}C transport in water

2.1.1 Transport as carbonate and organic compound

Since the organic carbon compounds are expected to be easily soluble, it is assumed that they are completely dissolved and not retarded during their transport in the near field and the far field.

For ^{14}C in the form of carbonate/CO_2, the main retardation process in the near field is precipitation due to the reaction with Ca and Mg. The geochemical conditions in the disposal areas of the repository are mainly determined by:

- calcium hydroxide from cemented wastes and from filter ashes,

- carbon dioxide from microbial degradation of organic substances and
- the chemical conditions of the inflowing brine.

The amount of cement, filter ashes, organic material and brine in the different disposal areas varies significantly. Therefore geochemical conditions have to be considered separately for each disposal area. It is very likely that IP-21 brine will occur in the disposal areas.

Based on the amounts of calcium hydroxide, carbon dioxide and IP-21 brine in the distinct disposal areas geochemical calculations have been performed with the code EQ3/6 to quantify the fraction of ^{14}C in the precipitated, dissolved and gaseous phases. The results are shown in table 3. As can be seen there is a large proportion of immobile ^{14}C in the south field and the central part of the repository.

Table 3: Distribution of ^{14}C (carbonate/CO_2) in Bq among the precipitated, dissolved and gaseous phases in the near field

	south-field	west field	east field	north field	central part
precipitated	8.75×10^{-6}	1.06×10^{-8}	1.05×10^{-7}	3.41×10^{-6}	9.63×10^{-4}
dissolved	6.10×10^{-2}	1.39×10^{-6}	5.41×10^{-5}	8.31×10^{-4}	1.89×10^{-2}
gas phase	0	8.77×10^{-7}	2.12×10^{-7}	1.33×10^{-7}	0
mobile fraction	7×10^{-5}	0.46	0.67	0.8	2×10^{-3}

Besides immobilisation in the near field, carbonate will be retarded by sorption during its transport through the far field. A distribution coefficient of 0.01 m^3/kg is used in the calculations.

Taking into account these parameters, long-term safety calculations have been performed with the computer code EMOS. The calculated annual radiation exposures with respect to ^{14}C for the reference case and the variant are shown in figure 2. Without going into detail on other aspects of the safety assessment, the main factors influencing the behaviour of ^{14}C are as follows: In the reference case ^{14}C as carbonate plays only a minor role. Due to its limited solubility in parts of the repository and its retardation by sorption in the far field it occurs in the biosphere at about 60 000 years. At that time a significant fraction of ^{14}C is already decayed. ^{14}C in the organic form (variant) is not solubility limited and not retarded in the far field. This leads to radiation exposures by orders of magnitude higher compared to the reference case.

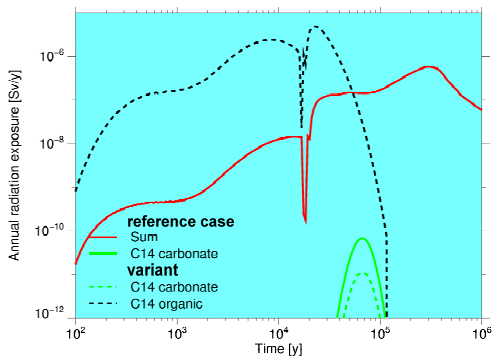

Fig. 2 Radiation exposure due to ^{14}C for the reference case and the variant, compared to the sum over the contributions of all radionuclides

2.1.2 Transport as methane

Methane will be distributed in the gas phase and in the liquid phase. The methane transport in the gas phase is discussed in chapter 2.2. The transport in brine is described in a different way for organic carbon as compared to carbonate because in the current near-field code pressure-dependent solubility of gases in the disposal chambers and further dissolution of gases in other parts of the repository is not implemented.

The simple model described here considers the distinct parts of the repository separately and yields a time-independent radiation exposure for each part. An integral time-dependent model is currently being worked out and will be presented in a future paper.

Within the repository, a gas mixture of methane, residual air and H_2 (the latter due to corrosion of metals) will be built up. The amount of methane dissolved in the brine is proportional to its partial pressure in the gas phase in the specific part of the repository. Therefore the partial pressure of methane is calculated in each part of the repository and from that the respective dissolved concentration at a pressure of 4.9 MPa is derived.

Furthermore, it is assumed that the brine squeezed out of the repository is immediately transported into a near-surface aquifer. Degassing of the brine due to pressure decrease is neglected. The conceptual model is shown in figure 3.

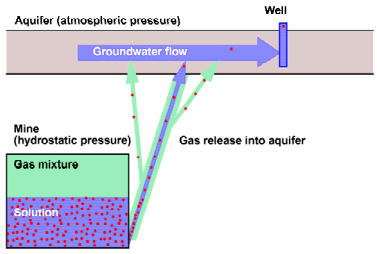

Fig. 3: conceptual model for methane transport in water

In order to calculate the radiation exposure, the concentration of ^{14}C in the brine has to be known. This concentration is proportional to the partial pressure of ^{14}C and the ratio of $^{14}C/C$ in methane $q_{C\text{-}14}$ at the time when brine is released from the disposal area in question. For calculation of the $^{14}C/C$-ratio, the whole amount of active and inactive methane in each disposal area has to be determined. $^{14}CH_4$ is generated fast. The resulting inventories of ^{14}C have been shown in table 2 in the columns for the reference case.

Inactive methane is generated by microbial degradation of cellulose and polyethylene. For calculation of the $^{14}C/C$-ratio in methane in the non-sealed disposal areas, north field and central part (called "residual part" further on) with very early brine release, only the degradation of cellulose is considered, since the reaction of polyethylene is slow. For all other disposal areas, where the time of brine release occurs after more than 10 000 years, methane from polyethylene degradation is also considered.

It is assumed that the $^{14}C/C$-ratio of each disposal area does not change during transport through the repository. Based on all assumptions the radiation exposure D is calculated by

$$D = \frac{c_M \beta_M q_{C\text{-}14}}{f} a_{C\text{-}14} D_{C\text{-}14},$$

where β_m denotes the molar fraction of methane in the gas mixture. All parameters used for calculation of the radiation exposure are listed in table 4. It is assumed that CH_4 is transformed into CO_2 under aerobic conditions in the near surface aquifer. Therefore the dose conversion factor for CO_2 is used.

Table 4: Parameter for calculation of radiation exposure by dissolved $^{14}CH_4$

parameter		sign	value
maximum methane solubility at 4.9 Mpa	[mol/m^3]	c_M	17.64
dilution in aquifer (25 000 m^3/a / 10 m^3/a)		f	2 500
dose conversion factor for ^{14}C	[(Sv/y)/(Bq/m^3)]	$D_{C\text{-}14}$	1.1×10^{-7}
specific activity of ^{14}C	[Bq/mol]	$a_{C\text{-}14}$	2.3×10^{12}

The results of this calculation are shown in table 5. It can be seen that the methane fraction in the gas phase varies in a range from 4.6 to 13.2. The highest $^{14}C/C$-ratio in methane occurs in the south field and the residual part of the repository, leading to the highest radiation exposures of $3.0 \cdot 10^{-6}$ Sv/y, and $1.4 \cdot 10^{-6}$ Sv/y, respectively.

Table 5: Radiation exposure by $^{14}CH_4$ released via transport in water

	south field	west field	east field	residual part
methane fraction in gas β_M [%]	9.4	13.2	9.6	4.6
^{14}C fraction in methane $q_{C\text{-}14}$	1.8×10^{-8}	2.2×10^{-10}	7.6×10^{-14}	1.7×10^{-8}
annual radiation exposure [Sv/y]	3.0×10^{-6}	5.1×10^{-8}	1.3×10^{-11}	1.4×10^{-6}

2.2 ^{14}C transport in the gas phase

The ^{14}C transport in the gas phase and the release to the biosphere were modelled as a transport pathway parallel to the transport in the liquid phase resulting in an additional dose rate. In the following the results for the west-south field (WSF) will be presented as an example. The WSF contains the largest inventory of ^{14}C and has been calculated to result in the highest release rate from the repository among all disposal areas.

The ^{14}C inventory in the WSF is $3.1 \cdot 10^{12}$ Bq. The fraction of 14C in the gas phase is made up of $^{14}CO_2$ and $^{14}CH_4$. For the calculation of the transport in the gas phase, the retention of $^{14}CO_2$ by precipitation was taken into account while dissolution in the brine was conservatively neglected. According to the calculation in section (2.1.1) the resulting gaseous ^{14}C inventory of the WSF is $2.4 \cdot 10^{12}$ Bq.

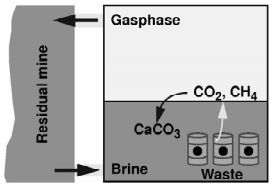

Fig. 4: Model for brine inflow into and gas release from WSF

The following model - shown in figure 4 - roughly describes the scenario for movement of brine into and release of gas out of the WSF: Driven by the hydrostatic pressure at the lowest sealing (4.9 MPa), the brine enters the WSF. The gas production as well as the convergence of the void spaces leads to a rise of the gas pressure. The rising gas pressure hinders the inflow of brine and reduces the inflow rate. As soon as the gas pressure exceeds the sum of the hydrostatic pressure plus gas entry pressure of 3.9 MPa at the top seal, the gas starts to be released from the WSF to the residual mine. Modelling this scenario with EMOS shows that the gas release starts at 17 700 years after beginning of the post-operational phase. At this point in time the gas production has already finished. The gas is completely displaced out of the WSF within 1 200 years at a constant rate by inflow of the brine. Due to radioactive decay the ^{14}C inventory of the WSF is reduced to $3 \cdot 10^{11}$ Bq at the start of the gas release which is 11.5 % of its initial inventory. This results in a constant release rate from the WSF of about $2.5 \cdot 10^{8}$ Bq·y^{-1}. The release rates from the north field and central part were found to be smaller and there is nearly no gas release from the east field.

No detailed assumptions can be made about the transport of the released gases in the residual mine and the geosphere. Thus it is conservatively assumed that once released, the gases are instantaneously transported from the disposal area to the surface and released from a point source into the biosphere with the same release rate of $2.5 \cdot 10^{8}$ Bq·a^{-1}. It is further assumed that methane is completely transformed to CO_2 by microbes in the unsaturated zone, thus the release from the geosphere into the biosphere consists only of $^{14}CO_2$.

The distribution of the ^{14}C in the biosphere was calculated according to the "Allgemeine Verwaltungsvorschrift" [1]. This implies a release from a point source and spreading by a Gaussian Plume. A 2D cross-section of the concentration profile at 1,7 m height above ground is shown in figure 5.

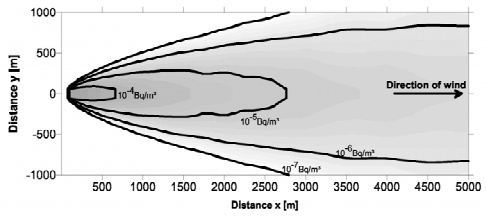

Fig. 5: Distribution of ^{14}C in the biosphere

The calculation of the dose rate was done using the concept of a critical group. The definition of the critical group was chosen according to the reference biosphere 2B from the Biomass project [2]. The group is a community of 300 up to 1 000 people living in an area of 22,4 km^2. 17 % of this area are arable land. The people are living all year in this area and all their food is produced within this area, too. The area of the arable land is indicated by the grey area in fig. 5.

The following scenario was used to calculate the dose rate by inhalation: a person lives all year within the considered area and breathes air which is contaminated according to the mean concentration in 1.7 m height above ground which is $1.8 \cdot 10^{-5}$ Bq·m^{-3}. This results in an annual dose rate of $9.0 \cdot 10^{-13}$ Sv·y^{-1}.

For ingestion it was assumed that the plants assimilate CO_2 from the air in their mean height of 0.5 m, which has a mean ^{14}C concentration of $2.1 \cdot 10^{-5}$ Bq·m^{-3}. The resulting specific activities of the food and the annual dose rate are given in table 6. The annual sum dose rate is calculated to be $1.1 \cdot 10^{-8}$ Sv·a^{-1}, which is more than four orders of magnitude below the regulatory limit.

Table 6: Specific activities, consumption and annual dose rates by ingestion

	activity [Bq/kg]	consumption [kg/y]	dose rate [Sv/y]
plants	1.1×10^{-2}	610	3.9×10^{-9}
vegetables	2.2×10^{-2}	39	5.0×10^{-10}
milk	1.4×10^{-2}	390	3.2×10^{-9}
meat	2.9×10^{-2}	180	3.0×10^{-9}
sum			1.1×10^{-8}

^{14}C is also formed naturally in the atmosphere. The resulting natural ^{14}C concentration in the air is $4.1 \cdot 10^{-4}$ Bq/m^3. The mean ^{14}C concentration in 1,7 m height which was calculated to be resulting from the release from ERAM is more than one magnitude below the natural concentration. So no significant contribution to the ^{14}C concentration in the atmosphere can be expected from the gaseous release out of the repository.

3. Conclusions

In the long-term safety assessment for the final repository in Morsleben, transport and release of ^{14}C in three different chemical forms have been evaluated. The results show that ^{14}C in form of CO_2/carbonate will be efficiently retarded by precipitation with calcium and magnesium in some disposal areas of the repository as well as by sorption during its transport through the overburden. In this case ^{14}C do not play an important role with regard to the sum dose.

In a case where no microbial degradation of organic material occur, transport of ^{14}C in organic form has to be regarded. Assuming high solubility and no sorption of the organic substances during their transport, high radiation exposures by ^{14}C are yielded which dominate the sum dose. Radiation exposures are in a similar order of magnitude if transport of $^{14}CH_4$ dissolved in solution is considered.

Parallel to the transport of ^{14}C in the water, transport in the gas phase has also been considered. In particular, the release of gaseous $^{14}CH_4$ and $^{14}CO_2$ from the disposal area with the highest ^{14}C-inventory was investigated. Assuming that $^{14}CH_4$ will be converted into $^{14}CO_2$ by microbial degradation in the unsaturated zone and released from a point source, radiation exposures are two orders of magnitude lower compared to radiation exposures from ^{14}C in organic form and $^{14}CH_4$ transported in solution.

It has been shown that in spite of the uncertainties concerning the chemical conditions in the near-field and the resulting chemical form of the ^{14}C, the repository ensures long-term safety.

4. References

[1] Allgemeine Verwaltungsvorschrift zu § 45 Strahlenschutzverordnung: Ermittlung der Strahlenexposition durch die Abteilung radioaktiver Stoffe aus kerntechnischen Anlagen oder Einrichtungen. Bundesanzeiger, 42. Jg, Nummer 64a, 1990.

[2] IAEA: BIOMASS Theme 1, Draft Working Document No. 9, Version 2.0, Example Biosphere 2A: Natural Groundwater Release into Agricultural and Semi-Natural Environments. Constant Biosphere, IAEA, Wien 2001.

The Study for The Chemical Forms of C-14 Released from Activated Metals

M. Sasoh, Toshiba

Introduction

In the performance assessment of transuranic (TRU) waste disposal, from the Nuclear Fuel Reprocessing Facility, carbon-14 (C-14) in the hull (activated zirconium alloy cladding waste) and end pieces has been so far estimated to considerably contribute to the radiation exposure to the public. In this performance assessment, however, the estimation is based on the fairly conservatively selected parameters for C-14, since the chemical forms of C-14 leaching from the hull are unknown.

Objective

The leaching experiments of some metals, including the activated metal, were carried out for Identification of the chemical forms of carbon in the solution. From these experiments, we investigated the chemical forms of C-14 from the activated metals, for example hulls, in the radioactive waste disposal facility.

Experimental

In the leaching experiments, zirconium powder (carbon content: 0.02wt.%) and carbon steel cutting powder (carbon content: 0.12wt.%) were used to simulate hull and end pieces[4]. These kinds of metallic powder were immersed in solutions of the pH adjusted to 8 or 12.5 using the several hydroxide compounds. The liquid-to-solid ratio of experimental samples is around 1ml/g. These samples were kept in a glove box under reducing atmosphere. Sampling of the solutions was conducted at regular intervals, and the concentrations of total carbon, organic carbon and inorganic carbon were measured using a continuous total organic carbon analyzer. For the solution of activated stainless samples, the some chemical methods for recovering of the carbon compounds including C-14 were carried out for measuring with liquid scintillation analysis. High performance liquid chromatography (HPLC) was also carried out for the solution samples to identify the organic carbon compounds. The gas chromatographic analysis was carried out for the organic compounds detection in gas phase of the bottles for some of the leaching experiments samples.

Results

Table 1 shows the ratio of the concentrations for organic carbon compounds inorganic carbon in the solution. Only the case for experiments using carbon steel and zirconium metallic powder as the solid phase, the gas chromatographic analysis was carried out for the gas phase. The ratio for the organic carbon compounds versus total carbon in liquid phase is from 55 % to 90 %, there is inorganic carbon in the liquid phase for all experiments. The alkanes and alkenes, these molecular weight are very low, were slightly detected in the gas phase.

Tab. 1: The ratio Organics/Inorganic Carbon in Liquid and Gas Phase

Carbon in Each Phase \ Solid		Carbon Steel	Zr	Fe_3C	ZrC
Organics in Gas Phase (Organics)		~ 0.01%	~ 0.01%	Not Measured	Not Measured
Carbon in Liquid Phase	Organics	70 ~ 85%	55 ~ 85%	55 ~ 65%	88 ~ 90%
	Inorganic	15 ~ 30%	15 ~ 45%	35 ~ 45%	10 ~ 12%

Tab. 2 shows the ratio of the each organic carbon compounds in the liquid phase. In the liquid phase from the metallic samples, including the activated stainless steel, there were low molecule carboxylic compounds or alcohols. The main compounds were formic acid and acetic acid. From the carbides, carboxylic acids were detected in liquid phase without alcohols.

Tab. 2: The Ratio of the Each Organic Carbon Compounds in the Liquid Phase

Solid	pH for the solution*	The Ratio of Organic Carbon compounds on Liquid Phase (%)							
		Formic Acid	Acetic Acid	Acet-aldehyde	Form-aldehyde	Methanol	Ethanol	Propanol	Un-known
Fe_3C	8	51	49	N.D	N.D	N.D	N.D	N.D	-
	12.5	52	48	N.D	N.D	N.D	N.D	N.D	-
Parlite	10	23	77	D	D	D	D	N.D	-
Carbon Steel	8	36	45	N.D	12	N.D	7	N.D	-
	12.5	20	71	N.D	6	N.D	3	N.D	-
Activated Stainless Steel	10	10	43	N.D	9	10	6	N.D	22
Martainsite	10	14	26	9	N.D	12	33	6	-
ZrC	8	3	97	N.D	N.D	N.D	N.D	N.D	-
	12.5	6	94	N.D	N.D	N.D	N.D	N.D	-
Zr	8	17	33	N.D	20	N.D	30	N.D	-
	12.5	9	56	N.D	16	3	16	N.D	-

Discussion

The ratio for gas phase carbon is very low from these experiments. The kinds for organic carbon compounds, for example Methane, Ethane, Ethene, Propene, and so on, were similar to the experiments of Baolin Deng's. The solution from these experiments for metals includes not only organic compounds(55.90 %) but also carbonate(10.45 %). We guess that generated organic carbons compounds might be carboxylic acids from carbides in metallic phase. Increasing the ratio of solute carbon in metallic phase would cause the generation of not only carboxylic acid

but also alcohols. The pH of the solution influences the ratio of the concentration for total organic carbon compounds. There are not obvious differences in the kinds of organic compounds and ratio of total organic carbon's concentration among the each material. We think that the generated organic carbon compounds depends on the forms in the metallic phase.

Conclusion

The ratio for organic C-14 released from activated metal in liquid phase is 66~75 % form the experiments with cold samples. (The ratio for inorganic C-14 is 23~34 %.) There is slight concentration of organic carbon in gas phase from the experiments with cold samples. Another experiments are necessary to investigate for generation of C-14 organic forms from activated metals would need, for example leaching for activated Zry or non-activated stainless steel.

References

Baolin Deng, et.al.,Environ.Sci.Technol.,31,1185 (1997).

Methods for measuring ^{14}C on spent ion exchange resins – a review

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Abstract

A literature survey of methods used for measuring ^{14}C on ion exchange resins is presented. Two types of methods are mainly employed: acid stripping and combustion. Some of the methods aim to measure only the inorganic fraction of ^{14}C in the waste, others the total amount of ^{14}C, and some separates the inorganic CO_2 fraction from CO and organic hydrocarbons. The review will be used as a base for setting up methods to measure organic and inorganic ^{14}C in spent ion exchange resins from Swedish nuclear power plants.

Introduction

Ion exchange resins are used in nuclear facilities for the removal of radioactive contaminants in a number of liquid processes and waste streams. For suitable final treatment and/or disposal of spent ion exchange resins, the content of radionuclides needs to be known. ^{14}C is one of the radionuclides ($T_{1/2}$=5730 years) that is of special interest to quantify, because of its long half-life, potential concentration, and environmental mobility. The environmental behaviour of ^{14}C in disposed radioactive waste is greatly dependant upon its chemical form. Therefore not only the total ^{14}C activity is of interest, but also the chemical speciation.

In light-water reactors (LWRs) ^{14}C is produced *e.g.* in the fuel, structures and in the primary coolant. Part of the ^{14}C produced in the primary coolant escapes through the off-gas system, and part is retained in the resins in the water clean-up system.

The aim of this article is to present a literature survey of the methods used to measure ^{14}C on spent ion exchange resins used for clean-up of various water streams in nuclear power plants. Special attention is paid to methods which concern the chemical speciation of ^{14}C in terms of organically (*e.g.* hydrocarbons) and inorganically bound ^{14}C (*e.g.* carbonates). Several of the reviewed documents contain results from measurements on spent ion exchange resins from nuclear power plants. In this paper, however, only the techniques are presented. First, a brief survey about the chemical forms of ^{14}C in the primary coolant and on ion exchange resins is given.

Chemical speciation

Chemical forms of ^{14}C in the primary coolant

There are considerable differences in the chemical form of ^{14}C present in the primary coolant depending on reactor type and mode of operation. In BWRs (boiling water reactors) the major part of ^{14}C is in the form of CO_2. As the conditions at PWRs (pressurized water reactors) are highly reducing, a major portion of ^{14}C appears as hydrocarbons or CO, and a minor portion as CO_2 or carbonates. Several reports on direct measurements of the airborne ^{14}C releases (mainly originating from ^{14}C production in the coolant) exist, by *e.g.* Bleier (1983), Hertelendi *et al* (1989), Kunz (1985), Salonen and Snellman (1985), Uchrin *et al* (1992) and Stenström *et al* (1995). In several of these, the chemical speciation of ^{14}C in the airborne releases has been determined, mainly by determining the fraction of $^{14}CO_2$ compared to the total ^{14}C releases. Reports of ^{14}C measurements on reactor water can also be found (*e.g.* Bleier, 1983; Kunz, 1985; Knowles, 1979; Soman, 1984).

Some authors describe the chemical speciation of ^{14}C in the coolant more in detail. Rosset *et al* (1994) describe the possible forms of ^{14}C in the reactor water at high temperature and reducing conditions (methane and methanol at 300 °C and pH 7.1). When the reactor cools, Rosset *et al* state that methane escapes in the atmosphere, and ^{14}C can be found in methanol, hydrogencarbonate, carbonate and formiate. Matsumoto *et al* (1995) estimate that the organic ^{14}C in the coolant in Japanese PWRs mainly consists of acetaldehyde, methanol, ethanol, acetone and acetic acid. Lundgren *et al* (2002) discuss the chemical forms of ^{14}C in BWRs, and conclude that "lack of accurate data on carbonic chemistry at higher temperature and lack of reports on accurate radiolytic measurements in high temperature water with high intensity radiation makes a quantitative assessment of the C-14 chemistry impossible". Lundgren *et al* however conclude that under reducing conditions the formation of methane, and possibly also formaldehyde and formic acid is expected. Under oxidising conditions Lundgren *et al* anticipate oxidised carbon forms, possibly mainly carbon dioxide and bicarbonate forms.

Chemical forms of ^{14}C on primary coolant ion exchange resins

Different opinions can be found in the literature about the retention of various carbon species on ion exchange resins. Kunz (1985) measured ^{14}C before and after the passage of the primary coolant through the clean-up demineralizers in two PWRs (containing mainly organic ^{14}C) and no removal of ^{14}C was detected. For a BWR (containing mainly $^{14}CO_2$) Kunz (1985) reports two sets of primary coolant samples taken before and after the clean-up and condensate demineralizers. No detectable removal of ^{14}C was found for the condensate demineralizers. For the clean-up demineralizers the first set of samples showed a decontamination factor of about 7, whereas for the second set of samples no decontamination factor could be determined. To Martin (1986), it appears highly unlikely that hydrocarbons are present in mixed ion exchange resins used for water cleanup in PWRs or BWRs; instead Martin believes that the collection of ^{14}C on the mixed resins most likely is in a carbonate form. According to Hesböl *et al* (1990) organic carbon is not retained in the ion exchange system.

However, according to Vance *et al* (1995) it is known, that most of the ^{14}C in PWR and some BWR spent primary coolant demineralizer resins is predominantly organic. Vance *et al* also claim that the attachment mode of these organic species of ^{14}C on the resin is unknown, but probably occurs by some type of sorption process rather than by a classical ion exchange mechanism. Vance *et al* further state that the organic ^{14}C species also can become attached to particulates in the reactor coolant water as witnessed by the relatively high concentrations of ^{14}C measured on some primary coolant filter cartridges. According to Torstenfelt (1996) it has been

shown that very little or no ^{14}C is taken up in BWR demineralizers (as non-condensable gases are removed from the reactor coolant together with the steam and released via the off-gas system), but a substantial amount is taken up in PWR demineralizers. Torstenfelt summarizes that in PWRs, both organic and inorganic carbon is taken up by the demineralizers, with the organic fraction dominating, and with the inorganic fraction dominating only in a few cases. The variation depends mainly on the partial pressure in the hydrogen gas in the reactor coolant. Nott (1982) states that ^{14}C in both organic and inorganic forms may be present on the resins. In Ruokola (1981) it is stated that fresh resins from PWRs have been found to contain mainly ^{14}CO and hydrocarbons, whereas spent resins from PWRs have a completely dominating $^{14}CO_2$ fraction. From this, Ruokola concludes that hydrocarbons and CO are released from resins much more easily than CO_2.

In Gruhlke *et al* (1986) it is suggested that compounds such as formaldehyde, formic acid, and acetic acid may be produced in small amounts in PWR wastes. As mentioned in the previous section, Matsumoto *et al* (1995) estimates that in Japanese PWRs ^{14}C in the coolant composed to 40 % of acetaldehyde, 20 % of methanol, 30 % of ethanol and acetone, and 2 % of acetic acid. Matsumoto *et al* further state that it is generally assumed that most of ^{14}C discharged as alcohol or acetone would be released via off-gas during the waste packaging process because of their high volatility. Therefore Matsumoto *et al* consider that the ^{14}C contained in low-level waste packages are mainly carbonate, acetaldehyde, and acetic acid. Lundgren *et al* (2002) believe that under reducing conditions some formate could end up on the reactor water clean-up ion exchange resin, while the formic acid form is expected to mainly form formate salts with the corroding steel, and probably be retained in the condensate cleanup. Under oxidizing conditions Lundgren *et al* anticipate that bicarbonate may be caught in the reactor water clean-up.

In conclusion, there are still uncertainties regarding the size of the fraction of ^{14}C that is retained in ion exchangers and its chemical composition. As an example, Smith *et al* (2002) states that the technical measurements, which can provide good data, are limited to relatively few examples, and the results cannot be readily extrapolated to other circumstances.

Reviewed methods of measurements of ^{14}C in ion-exchange resins

In the following sections some methods to measure ^{14}C in ion exchange resins from nuclear power plants are presented. Special attention is paid to if the performance of the methods has been evaluated. Methods for measuring the chemical speciation of ^{14}C are reviewed as well as methods for measuring the total ^{14}C activity or only the inorganic fraction. Methods found in the literature for measuring ^{14}C on resins have been applied on light-water reactors as well as for heavy-water reactors (HWRs). Two main types of methods are employed: acid stripping and combustion.

Acid stripping methods

Aittola and Olsson (1980)

Aittola and Olsson (1980) used an acid stripping technique for measuring only the inorganic fraction. The experimental setup is outlined in Figure 1. Apart from the resin sample, that flask contained 4 ml 0.05 M Na_2CO_3 with 1 mg formaldehyde/ml and 20 ml of water. 30 ml of concentrated HCl was added to the resin sample in order to evolve carbon dioxide, which was carried by streaming air to the NaOH flasks, where it was absorbed as soluble Na_2CO_3. The purpose of the flask containing $Ca(OH)_2$ in Figure 1 was to visually control that all CO_2 had been absorbed in the NaOH, as the precipitate $CaCO_3$ would be formed by any unabsorbed CO_2. After terminating the flow of air, $BaCl_2$ was added to the NaOH flasks with the absorbed CO_2 and solid $BaCO_3$ was precipitated. The precipitate was cleaned and solved in a suitable medium for LSC analysis.

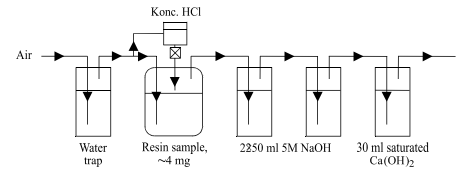

Fig. 1: Schematic layout of the experimental setup in Aittola and Olsson (1980)

To determine the recovery of the process, two tests were done where a ^{14}C standard (not specified) was added to a non-radioactive resin sample. The recovery was 49 % and 33 % respectively. Aittola and Olsson also tried to change the NaOH to Ethanolamine-Methanol, however with an even lower recovery, 34 % and 35 %, in two tests with a ^{14}C standard. To increase the recovery some modifications were done. About 4 g of resin sample was mixed with 1 ml of 10 % NaOH, possible ^{14}C standard and 0.100 g $NaHCO_3$. 250 ml 5 M NaOH was used to absorb the CO_2. The sample was heated to ca 50 °C when adding the HCl. To precipitate $BaCO_3$ the NaOH was heated to 50 °C and 100 ml NH_4Cl and 40 ml 1 M $BaCl_2$ were added. The solution was heated to 70 °C and filtered while still warm. The precipitate was washed with water and acetone, followed by drying at 105 °C for 2 hours. The resulting recovery of this procedure was 85 % (determined by one test). No information is given about reproducibility and memory effect of the method.

Nott (1982)

In Nott (1982) a method for removing inorganic ^{14}C from spent ion exchange resins (from CANDU reactors) is described. The apparatus (Figure 2) - almost entirely constructed of glass - consisted of a resin stripping column with an ultrasonic probe (to enhance the release of $^{14}CO_2$), an acid circulation pump and container, and NaOH absorption traps for CO_2. The bulk of the apparatus was kept under slight vacuum to prevent escape of $^{14}CO_2$ from the system. For the LSC analysis the NaOH concentration of all samples was adjusted to the same level of 0.1 mmol NaOH/ml of sample (in order to avoid variability of the LSC counting efficiency depending on NaOH concentration). At the end of each run, a sample of the acid was also counted for ^{14}C after neutralization with NaOH.

The method was tested on synthetic spent ion exchange resins (Amberlite IRN-150, 30 ml) prepared in the laboratory by addition of known amounts of bicarbonate ^{14}C to the resins (56 MBq of $NaH^{14}CO_3$ solution). The experimental variables (with their ranges within parentheses) were:

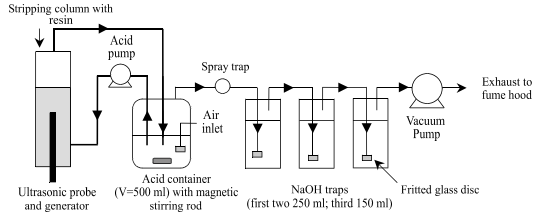

Fig. 2: Acid stripping apparatus for ^{14}C determination (Nott, 1982)

Acid concentration (HCl, 2.0-3.0 mol/l), acid volume (360-480 ml), acid circulation rate (50-90 ml/min), run time (45-90 min), peak ultrasonic power (20-40 W), on/off cycle times of ultrasonic power application (5/55-10/50 s) and NaOH concentration (0.5-2.0 mol/l). The ^{14}C found in the absorption traps and in the acid container after stripping (usually a very small amount) was compared with the ^{14}C in the resin batch prior to stripping.

The resulting recovery varied between 91.8 % and 102.1 %. The mean recovery was 97.4 % with a standard deviation of 3.6 %. In the ranges tested, none of the experimental variables showed an effect on the recovery that was significantly greater than the standard deviation. Hence, the author states that further experiments are required to determine the effect of the individual parameters. Nott also recognises the potential problem of interfering radionuclides to be absorbed in the NaOH traps. Information is lacking about the memory effect of the method.

Salonen/Snellman (1981, 1982, 1985)

Salonen/Snellman (1981, 1982, 1985) have analyzed spent ion exchange resins for ^{14}C by using a technique for simultaneous determination of ^{14}C either in the form of CO_2 or in the form of hydrocarbons and CO. A schematic diagram of the system is shown in Figure 3. The resins samples were first made alkaline in order to avoid the escape of ^{14}C as CO_2. A known amount of the ion exchange resin was then transferred to the sample vial in Figure 3, already containing 200 ml of 2 M NaOH solution, ca 100 mg $NaHCO_3$ carrier, some drops of methyl orange as indicator and a magnetic stirrer. The sample vial was closed and connected to the separation system. Both absorbers were filled with 100 ml 2 M NaOH.

The pressure in the separation system was first lowered by a vacuum pump using a flow rate of 0.8-1 l/min. After a few minutes 6 M HCl was let into the sample vial (to release $^{14}CO_2$) until the colour of the indicator changed from orange-yellow to red. After another few minutes an air flow (purified from CO_2 by a molecular sieve) of 0.2-0.3 l/min was applied, which carried the evolved gases into the absorbing NaOH solution during 1.5 hours. The flow rate of the air was less than that of the vacuum pump to prevent over-pressure in the system.

The separation of the different chemical forms was accomplished by using two absorbers with a catalyst - copper oxide at 800 °C - in between. With this arrangement CO_2 was absorbed in the first absorber, whereas hydrocarbons and CO passed it, were oxidized in the catalyst and absorbed in the second absorber. After completing the collection, the absorbed CO_2 was precipitated as $BaCO_3$, which was filtered, washed, dried, weighed and measured in a rigid gel by LSC.

Three tests with a known amount of $NaH^{14}CO_3$ showed that only 0.2 % of the ^{14}C was found in the second absorber. The mean recovery was 93 % with minor variations. No recovery determinations were done with ^{14}C-labelled hydrocarbons or CO. However, neither hydrocarbons nor CO were trapped in the first absorber, shown by using a sample from a spent ion exchange column, which first was made alkaline to fix CO_2. It was not possible to make the recovery determinations on the basis of the barium carbonate precipitate, as the weight of the precipitate was always higher than the value calculated from the amount of $NaHCO_3$ carrier added. The origin of the excess precipitate was not localised.

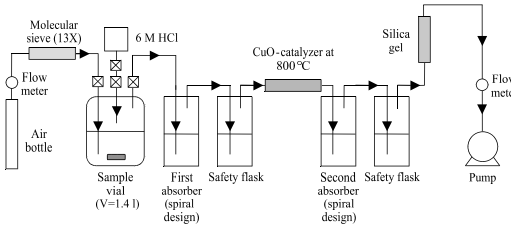

Fig. 3: Schematic diagram of the system used for separation and speciation of ^{14}C from ion exchange resins according to Snellman and Salonen (1981)

The system showed no memory effect. The radiochemical purity of the $BaCO_3$ was controlled by gamma spectrometry for all samples and LSC beta spectrum analysis for some samples. No contamination was observed. There are no reports about the efficiency of the catalyst.

Tests were made to see whether some additional activity would be released during a longer contact of the resin with HCO_3^- or CO_3^{2-} ions. A second separation of ^{14}C was carried out. The resin samples were made alkaline again, $NaHCO_3$ carrier was added and the samples were left for some days. Salonen and Snellman reason that during that time the ^{14}C which originally must have been retained into the resins through ion exchange reactions, would now have a possibility of being exchanged back into the solution. As only minor amounts were released during the second separation (between 0.3 % and 9.0 % of that in the first separation), Snellman and Salonen conclude that combustion of the samples was unnecessary.

In Salonen and Snellman (1985) further tests are reported. After absorption of ^{14}C-labelled carbonate in resin samples, these were left to stand for a month or longer. The average ^{14}C content of the resins was 15 % lower than that adsorbed into the resins. Salonen and Snellman conclude that this amount of ^{14}C may still be adsorbed into the resins or it may have been lost during the adsorption process or when transferring the sample from one vial to another.

For actual samples of spent resins duplicate samples were measured. Duplicate samples showed larger variety in the results for the CO/hydrocarbons than for the CO_2. Salonen and Snellman believe that this originates from that CO/hydrocarbons were more easily lost during the sampling and when handling the sample than CO_2, as this was fixed when the sample was made alkaline. The error introduced due to sample preparation and counting statistics was estimated to be 5-10 %. The differences between ^{14}C bound to CO_2 were however bigger for the duplicate samples, probably due to the difficulty of taking sub-samples with identical ratios of resin to NaOH solution. It was also seen that the second separation gave lower results than the first, which indicates some losses during opening the vial in which the resin was sent to the laboratory. The retention of hydrocarbons or CO in the resin was shown to be poor, and these fractions will be easily lost not only during storage and final management of the resins, but also during sampling and sample preparation.

In Salonen and Snellman (1985) it was shown that drying the resin evaporates ^{14}C from the resin mass. One test using "simulated spent" resins showed that as much as 97 % of the ^{14}C activity of the samples was lost during drying at 150 °C. Other experiments indicated losses of 96-99 % when drying.

Chang et al (1989)

Chang *et al* (1989) have done extensive laboratory tests on simulated spent resins using acid stripping for determining the amount of inorganic ^{14}C. The experimental set-up is outlined in Figure 4. 30 ml of resin containing ^{14}C (1.8 TBq/m^3) was mixed with a stripping solution (HCl, NaCl, Na_2CO_3 or NaOH) in a glass flask containing a magnetic stirrer. Air was bubbled through the solution (135-150 ml/min) to purge the CO_2 evolved, and to carry the off-gas through the system. A vacuum pump was used for drawing the gas though the system and at the same time maintaining a slight negative pressure within the system to avoid leakage of ^{14}C. The water trap was acidified with 5 % HCl and the CO_2 was absorbed in 2 M NaOH.

Experiments were also performed using acid fluidized columns, where acid and air was introduced from the bottom of the column to fluidize the resin. In those experiments magnetic stirring was not applied.

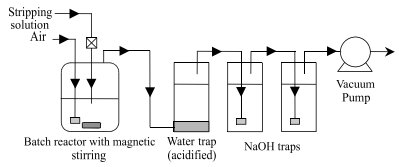

Fig. 4: Apparatus for ^{14}C removal by acid agitation (Chang *et al*, 1989)

Laboratory simulated resins with a known amount of ^{14}C-labelled $NaHCO_3$ or Na_2CO_3 in water solution were used to test the method. The most promising results were obtained with agitating the resins in aerated HCl solution, which gave recoveries of 92-99 %. The high efficiency was attributed to the combined effect of air bubbling and mechanical agitation.

In the acid fluidization without aeration, removal of the CO_2 produced was by diffusion alone, which according to the authors explains a slightly lower recovery by this procedure. When aeration was introduced, the efficiency was further reduced, as the gas bubbles tended to adhere to the resin beads and resulted in their floating together. This isolated the resin beads from reacting with the acid. Ten further tests were performed with aerated agitation in HCl giving recoveries of 98.5-100 (each run used 30 ml of IRN 150 resin with 1.8 TBq/m^3 ^{14}C). Five runs with resins preloaded with 7.4 TBq/m^3 gave similarly results (30 ml resin per run, acid concentrations 0.5-6 M, acid volumes 58-125 ml, aeration rates 100-135 ml/min and reaction times 45-225 min). Almost all the activity was found in the first absorber (<0.1 % in the second absorber, and even lower levels in the spent acid and stripped resin).

The acid stripping technique was also evaluated using 15 samples of spent resins from various sources. In four of the samples $Na_2{}^{14}CO_3$ was added to raise the activity to about 7.4 TBq/m^3 (to approximate the maximum ^{14}C level measured on CANDU moderator spent resins). All the runs demonstrated a ^{14}C removal of over 99 %. It must however be noted that the initial activity of the resins were of course not known. Instead the total activity was calculated by summing up the amounts remaining in the various solutions (spent acid, water trap and absorber traps) and on the treated resin after each experiment. The activity balance was thus assumed to be maintained.

Small amounts of residual ^{14}C (<0.5 % of the total ^{14}C) were detected on the treated spent resins. Chang *et al* believe that the residual ^{14}C was probably present in some organic forms that did not react with HCl. By adding the strong oxidizing agent potassium persulfate ($K_2S_2O_8$), the residual ^{14}C was found to be completely eliminated.

Other radionuclides were also removed from the resins by the acid stripping. Gamma spectrometry of the resins and the various solutions showed that a significant fraction of gamma emitters were found in the acid, and a much smaller amount in the water trap. No detectable quantities were found in the alkaline absorbers.

Acid stripping and combustion methods

Martin (1986)

Martin (1986) presents one combustion method and one acid stripping technique, used for various types of samples. The combustion method used by Martin (1986) is outlined in Figure 5. A tube furnace at 600-700 °C was used to oxidise the samples (liquid or solid) to CO_2. Solid samples were placed in a foil-lined sample boat and combusted for 1 hour at 700 °C. After combustion a few drops of HCl were added to assure release of any residual carbonate. No attempts were made to specify the chemical form of ^{14}C. The volatized carbon from the sample was passed through a ceramic tube packed with copper oxide to convert all carbon species to CO_2. After drying the gas in Drierite, the stream passed through two bubblers filled with Oxyfluor-CO_2 (for trapping CO_2).

The acid stripping method shown in Figure 6 is based on resin regeneration procedures. First 3 ml KOH (25 %) was added to a flask containing the resin sample followed by 4 ml of HCl (37 %). The gases produced were drawn through a gas drying tube containing Drierite and through two midget bubblers filled with Oxyfluor-CO_2.

The system for liquid or solid samples was checked for memory effects after each run. No significant residual deposition was found in the apparatus. The recovery of the same system was 93 % based on processing of standard solutions (chemical form not given). The efficiency of the stripping of the resin samples was not tested, nor was the absorption in the bubblers or any possible memory effect.

Martin et al (1993)

Here Martin *et al* (1993) have again tested two techniques for the recovery and analysis of ^{14}C in carbonate form: combustion/oxidation and resin regeneration. A mixed anion/cation type resin (Epicor EP-II, Dow Chemical Co.) was used. A solution containing 50 kBq of ^{14}C in carbonate form was added to a 50 g sample of resin for a period of 4 h. The sample was vacuum filtered to remove the spent solution. LSC measurement of the solution before and after resin treatment showed that 99.8 % of the ^{14}C was transferred to the resin beads, and no gaseous release of $^{14}CO_2$ was observed. Weighed aliquots of the treated resin were processed to compare the techniques of combustion/oxidation and resin regeneration.

In the combustion/oxidation technique (outlined in Figure 7) the sample (0.5 g) was placed in a nickel boat, and was combusted in an electric tube furnace for 30 minutes at 740±6 °C. A 25 mm fused quartz tube was packed at one end with mixed catalysts; CuO wire and platinum on alumina beads. Air of 200 ml/min was drawn through the system by a vacuum pump, carrying the off-gases through an ice bath (two traps) and a system of dryers to remove water, followed by two bubblers filled with an LSC cocktail to trap the oxidized carbon.

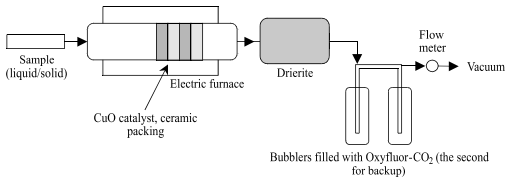

Fig. 5: Layout of the apparatus used for analyzing ^{14}C in liquid and solid samples (Martin, 1986)

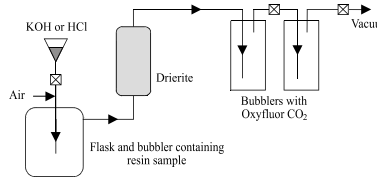

Fig. 6: Layout of the apparatus used for analyzing ^{14}C in resin samples (Martin, 1986)

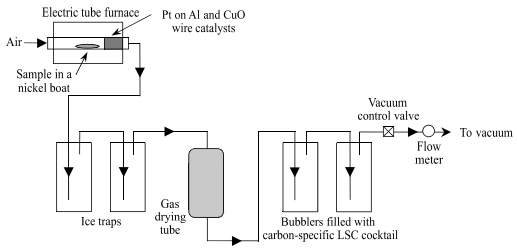

Fig. 7: Apparatus for combustion/oxidation of resin to recover $^{14}CO_2$ (Martin *et al.*, 1993)

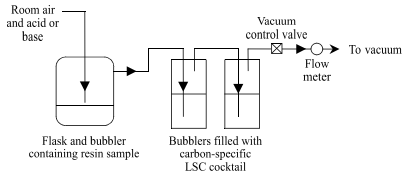

Fig. 8: Apparatus for regeneration of resin to recover $^{14}CO_2$ (Martin *et al.*, 1993)

The resin regeneration technique (schematically drawn in Figure 8) was tested in the following way. About 0.5 mg of the resin samples were regenerated by placing them in a 30 ml reaction vessel (midget bubbler). The off-gas was drawn by vacuum through two bubblers, each containing 15 ml of LSC cocktail. Air was drawn through the system at 200 ml per min. 10 ml of 6 M HCl were pipetted into the reaction vessel and swirled occasionally. The flow rate was applied for 30 minutes.

Dual regeneration by acid/base stripping was also tested by applying KOH prior to HCl. To determine the interference of other possible radionuclides in the LSC measurements one aliquot was dual-loaded with ^{60}Co.

The results showed that the mean recovery of the combustion/oxidation procedure was 63±9 %, while the resin regeneration procedure yielded a mean recovery of 85± 7 %. It is however not stated how well the procedures (*e.g.* combustion temperatures and efficiency of the catalyst) are optimized.

The dual regeneration by acid/base stripping using KOH prior to HCl yielded the same recovery as using HCl only; this is not surprising as the resin tested contained only carbonate. The test using ^{60}Co showed that the regeneration procedure was selective to carbon.

Moir et al (1994)

Moir *et al* (1994) have analyzed two moderator spent-ion exchange resins from the CANDU reactor Bruce Nuclear Generating Station A in Canada. Mixed beds were separated into anion and cation fractions using a sugar solution, and ^{14}C was determined in each fraction. Acid stripping and Parr bomb combustion were used and compared. Also other radionuclides on the resins were studied using γ-spectrometry.

The analysis scheme was designed to provide a detailed characterization of the resin, including not only the distribution of ^{14}C but also other radionuclides on the cation or anion beds. First the liquid in which the resin had been shipped was decanted and filtered, and the filter and filtrate were measured by γ-spectrometry. The filtrates were also analysed with LSC for the study of ^{14}C.

Ten millilitre samples of the two resins were subjected to a two-part ultrasonic washing (water and methanol). The solutions were filtered, and the filter as well as the filtrate was measured by γ-spectrometry. LSC was performed on the filtrates for determination of ^{14}C. The resin was analysed by γ-spectrometry after each washing to ensure that a mass-balance existed.

Ten millilitre samples of the two resins were separated using a sugar solution and the resulting cation and anion fractions were rinsed with 5 to 10 ml of distilled deionised water, and the weight of each fraction was determined. The sugar solution and rinse solutions from the separation procedures were filtered; filters, filtrates and resins were measured by γ-spectrometry, and the filtrates were analysed for ^{14}C by LSC.

As in the case of the separated cation and anion fractions, samples of unseparated samples were subdivided into subsamples of 0.2-0.25 ml. After subdivision, two samples of each of the unseparated resins and subdivided anion and cation fractions of each resin type were selected for combustion in a Parr bomb. The bomb assembly was connected to a gas collection line consisting of an acid trap (100 ml of 2 M HCl), followed by a condensation trap (methanol and dry ice) and two base traps (100 ml of 2 M NaOH in each). Prior to combustion, the samples were dried in the bomb using a heat gun while nitrogen gas flowed through the system. After drying, the Parr bomb was removed from the gas collection line and pressurized to 2.5 MPa using oxygen, then the combustion was carried out (the sample placed in a fused-silica crucible with some special fuel and the bomb fused by platinum wire). After combustion, the Parr bomb was attached to the gas collection line and the gases produced were released into the collection line. The bomb was purged for 10 minutes with nitrogen gas after the release of the gases in the bomb. ^{3}H and ^{14}C was collected as off-gases during the drying and depressurising steps, trapped in the HCl and NaOH solutions, respectively. The inside of the bomb was rinsed with distilled deionised water. 1 ml of the bomb rinse solutions as well as each trap solution was prepared separately with Instagel or Hionic-Flour cocktail prior to ^{14}C determination with LSC.

Two samples (0.2-0.25 ml) of unseparated resin, and cation and anion frations of each resin type, were subjected to acid stripping using HCl. The samples were placed in a reaction vessel connected to a gas collection line consisting of a 50 ml trap of 2 M HCl and two 50 ml traps of 2 M NaOH. 5 ml of 8 M HCl was added to the reaction vessel to release ^{3}H and ^{14}C from the resin sample to be collected in the HCl and NaOH traps, respectively. 1 ml of each trap solution and 100 µl of the acid stripping solution were then prepared separately in either Instagel or Hionic-Flour cocktail prior to ^{14}C determination with LSC. Aliquots of the acid stripping solutions were also measured with γ-spectrometry to determine if any other radionuclides had been removed from the resins in the stripping procedure. Parr bomb combustions were also done on samples of unseparated resins and separated anion and cation fractions following acid stripping.

Control samples (a series of 0.2-0.25 g inactive unseparated resins, spiked with ^{14}C-labelled carbonate solution) were prepared to determine the yields for ^{14}C during the acid stripping and Parr bomb combustions analyses. Recoveries were (93±5) % by the acid stripping and (100±10) % by Parr bomb combustion. The control samples were run after every eight resin samples analysed by either method. All samples (unseparated, anion or cation) were analysed in duplicate using either analysis procedure. Method blanks (inactive unseparated resin) were analysed periodically to ensure that cross-contamination of the samples was not occurring.

No ^{14}C was detected in the shipping solutions received with the resins, in either the distilled deionised water or methanol filtrates from the ultrasonic cleaning procedure, or in the filtrates from the sugar solutions used to separate the resins. Hence, Moir *et al* conclude that ^{14}C is not easily removed from the resins by simple washing procedures.

For the unseparated resin samples the results of the two methods showed differences between the subsamples, suggesting that some inhomogeneity existed within the bulk resin, possibly in the fraction of cation and anion beads. From the results of the separated fractions of anion and cation beads, it was seen that >99 % of the ^{14}C was associated with the anion component of each resin. Moir *et al* claim that the small amount of ^{14}C on the cation resin fraction may indicate the presence of ^{14}C-containing organic compounds or carbonates directly bound to metal ions, or that the separation of the anion and cation resin resins fractions was incomplete.

The ^{14}C concentrations for the anion and cation fractions, and unseparated resins by Parr bomb combustion after they have been acid-stripped, showed that the acid stripping appeared to remove almost all ^{14}C from the resins. The small fraction left behind was suspected to be in the form of organically bound species.

Some samples of sugar-separated anion resins that were stored for a few months before analysis were found to have little or no ^{14}C associated with them when acid-stripped or Parr bomb combusted. No leaks were found in the sample preparation systems. A test was made to determine the fate of ^{14}C: 10 ml of one of the resin samples was freshly separated into anion and cation fractions, and the anion fractions were subsampled further. These 0.2 to 0.25 ml samples were acid-stripped periodically over 5 months to determine whether the ^{14}C concentration was decreasing with time. The results showed that the concentration did decrease with time, with a total factor of 4.5. Several theories were suggested for the loss: sample inhomogeneity, change of pH of the samples while stored, or microbial activity due to the sugar-solution. Tests indicated that the third theory was the most likely. Unseparated resin samples did not show this loss of ^{14}C activity with time.

Vance et al (1995)

Vance *et al* (1995) evaluate ^{14}C production in light-water reactors and characterization of its chemical speciation and environmental behaviour. The occurrence of inorganic and organic forms of ^{14}C in reactor coolant water and in primary coolant demineralization resins was identified.

Two mixed-bed test resin-sampling devices were designed to simulate a scaled-down version of a nuclear power plant's purification demineralization system. The devices were installed at a number of PWR's and BWR's and operated at scaled-down flow rates and operating durations to simulate the cleanup of the reactor coolant.

For some samples the total ^{14}C content was determined by using a combustion technique followed by purification and liquid scintillation counting. A modified version of the method of Knowles (1979) was used for determining the inorganic fraction of ^{14}C on the resin. The resin samples were placed in sparging flasks and 6 M H_2SO_4 was used to release $^{14}CO_2$. A stream of CO_2-free air carried the $^{14}CO_2$ through acid purification traps to a saturated $Ca(OH)_2$/methanol trap for absorption. The $CaCO_3$ precipitate formed was further purified. The fraction of organic ^{14}C was estimated by subtracting the inorganic fraction from the total ^{14}C.

No tests of the method are reported.

Combustion methods

Speranzini and Buckley (1981)

Speranzini and Buckley (1981) have made a report on various methods for treatment of spent resins from CANDU reactors.

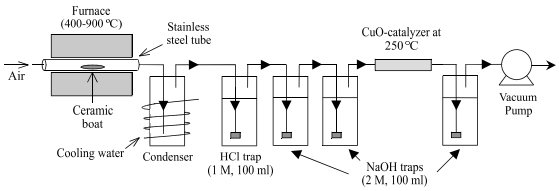

Fig. 9: Schematic drawing of the incinerator with off-gas system presented by Speranzini and Buckley (1981)

For disposal. Among other methods they evaluate the incineration of resins in order to better characterize the gaseous release of ^{14}C when the resins are burnt. In particular, they report a pretreatment procedure which can be used to release ^{14}C at temperatures below 500 °C, which is the combustion temperature of the resin. With the method presented it is also possible to quantify ^{14}C in the resins.

In the experiments reported, IRN-150 resin, traced with ^{14}C, and reactor-contaminated resins were used. For the off-gas studies, the experimental setup outlined in Figure 9 was used. A vacuum pump was used to draw air into the combustion chamber at a rate of 0.4 l/min. The off-gases from the combustion chamber were drawn into a scrubbing system consisting of a condenser, a HCl scrubber (to trap fission products), two NaOH scrubbers, a CuO catalyst (250 °C) to oxidize organic ^{14}C (CH_4, C_2H_6) and a third NaOH flask to trap the oxidized organics.

Samples of Amberlite IRN-150 mixed bed resin (1-2 grams traced with 1200 MBq/l of ^{14}C as carbonate) were heated in excess air at temperatures ranging from 440 °C to 850 °C for 1.5 hours. The results showed that the ion-exchanged carbonate was not thermally stable (the decomposition temperatures of $CaCO_3$ is 900 °C and 1430 °C for $BaCO_3$). 15 % of the ion-exchanged carbonate was combusted at 440 °C; 90 % of the initial ^{14}C was combusted when the temperatures reached higher than 850 °C. Longer combustion times were also tested: At 440 °C the combustion time was increased to 4 hours, and then the amount of ^{14}C recovered in the scrubbers increased from 15 % to 45 %. When the residual ashes of the resin combusted at 440 °C and 580 °C were reheated to 850 °C for 1.5 hours, the total recovery ranged from 93 % to 98 %.

Unsuccessful attempts were made to convert the ion-exchanged carbonate to thermally stable calcium or barium carbonates by adding $CaCl_2$ and $BaCl_2$. The treated resins were heated in excess air at temperatures ranging from 440 ºC to 800 ºC for 1.5 hours. For $CaCl_2$ pretreated resin, ^{14}C releases ranged from 80 % to 99 % for temperatures ranging from 440 ºC to 740 ºC; for $BaCl_2$ pretreated resin, the ^{14}C releases ranged from 45 % to 99 % for temperatures ranging from 440 ºC to 850 ºC. Speranzini and Buckley have an explanation for this. The releases of $^{14}CO_2$ from $CaCO_3$ and $BaCO_3$ at temperatures lower than their decomposition temperatures may be related to the thermal decomposition of the sulfonic acid groups in the ion exchange resin at 300 ºC to produce SO_2, which then reacts with $CaCO_3$:

$$CaCO_3 + SO_2 + ½\ O_2 \rightarrow CaSO_4 + CO_2$$

The rate of this reaction is substantially increased in the presence of $CaCl_2$ (van Houte *et al*, 1981).

Bleier (1983)

Bleier (1983) has analyzed ion exchange resins, with respect to the total amount of ^{14}C, from three German PWRs using a combustion method.

The sample consisting of either cation or anion resin was combusted together with PbO_2 (used as catalyst) at 1200 °C in a flow of oxygen. The off-gases were collected in NaOH and the ^{14}C precipitated as $BaCO_3$. To get rid of interfering radionuclides, the precipitate was acidified and reabsorbed in NaOH. The final precipitate was then analyzed using a proportional counter.

No tests of the system are presented in the article. No error estimations or tests of the method are given in the article.

Other methods

A few other methods that could be used for determining the ^{14}C content - apart from combustion and acid stripping - also exist. Dias and Krasznai (1996) present a method to remove inorganic ^{14}C from ion exchange resins using supercritical carbon dioxide. Another method of removing ^{14}C from dry organic wastes (including resin wastes) has been tested in a pilot-plant at Loviisa nuclear power plant in Finland (Tusa, 1989). A microbial process was capable of decomposing radioactive resin waste completely within about seven days, producing mainly CO_2 and CH_4.

Discussion

Based on the information given in the articles reviewed in this report we plan to design and test a combustion system as as well as an acid stripping system to measure organic and inorganic ^{14}C. The relative merit of the two will be compared. The acid stripping system will be a modified setup of the system of Salonen and Snellman. The combustion system will use the principle of Speranzini and Buckley. Extensive tests using various ^{14}C-labelled species will be made on the systems to ensure the correct function of each and every part.

One (or both) of the optimized systems will then be used to examine spent ion exchange resins from Swedish nuclear power plants.

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