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# Carbon-14 Source Term

## CAST



### Overview of achievements for regulators for workshop 2 (D7.16)

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## **CAST – Project Overview**

The CAST project (Carbon-14 Source Term) aims to develop understanding of the potential release mechanisms of carbon-14 from radioactive waste materials under conditions relevant to waste packaging and disposal to underground geological disposal facilities. The project focuses on the release of carbon-14 as dissolved and gaseous species from irradiated metals (steels, Zircalloys), irradiated graphite and from ion-exchange materials as dissolved and gaseous species.

The CAST consortium brings together 33 partners with a range of skills and competencies in the management of radioactive wastes containing carbon-14, geological disposal research, safety case development and experimental work on gas generation. The consortium consists of national waste management organisations, research institutes, universities and commercial organisations.

The objectives of the CAST project are to gain new scientific understanding of the rate of re-lease of carbon-14 from the corrosion of irradiated steels and Zircalloys and from the leaching of ion-exchange resins and irradiated graphites under geological disposal conditions, its speciation and how these relate to carbon-14 inventory and aqueous conditions. These results will be evaluated in the context of national safety assessments and disseminated to interested stakeholders. The new understanding should be of relevance to national safety assessment stakeholders and will also provide an opportunity for training for early career researchers.

For more information, please visit the CAST website at:

<http://www.projectcast.eu>



CAST

*Overview of achievements on technical results for regulators for workshop 2 (D7.16)*

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## Executive Summary

The generation of neutron activated radionuclide carbon-14 can be limited by reducing the nitrogen content in water used as moderator and/or coolant and solid materials used in a nuclear reactor such as steel. In this report, the ALARA principle is explored for the types of waste investigated in CAST by suggestions to limit the nitrogen content in order to reduce the potential carbon-14 radiation exposure. Disposal in deep geological facilities and near-surface facilities is the designated end-point management technique for neutron irradiated steel, neutron irradiated Zircaloy, spent ion exchange resins and neutron irradiated graphite for 13 EU countries, Switzerland and Japan as described in the first workshop proceedings. The half-life of carbon-14 is 5730 years and therefore the acceptable carbon-14 concentrations in near surface disposal facilities can be small if the potential release of carbon-14 is large or uncertain.

Carbon-14 in waste is interesting from a radiological characterisation standpoint since its measurement cannot be determined non-invasively due to the emission of weak betas during its decay. The reported carbon-14 activity concentration of the waste may not be measured but calculated. In this report, the parameters necessary to calculate the activity concentration and values that have been updated during progress of the project CAST are included; the thermal reaction to carbon-14 cross section of oxygen-17 was reduced three orders in magnitude in the latest evaluation. This update further increased the importance of knowledge of the nitrogen content in the investigated types of waste if the reported carbon-14 activity concentration in waste is calculated. Information about the nitrogen content of the samples used in CAST, as presented in the first workshop last year and collected by WMOs and REs in CAST and published this year, are therefore shown in this report. For some types of wastes investigated in CAST, carbon-14 can be redistributed during its generation in a nuclear plant and when the waste is processed. A calculated carbon-14 activity concentration that includes this redistribution is not yet available in sufficient detail for the determination of a source term. Measurements to determine the carbon-14 activity and nitrogen content that are performed in CAST are presented in this report. At the first workshop it appeared that many countries multiplied the measured cobalt-60 activity from

waste with a scaling factor to determine the carbon-14 activity in waste. In some countries, this scaling factor is determined with a representative set of samples in which the carbon-14 as well as cobalt-60 activity is measured. In other countries, scaling factors reported in literature are used. The applicability of scaling factors was questioned at the first workshop for spent ion exchange resins.

Carbon-14 is interesting from a disposal standpoint because it is a long-lived radionuclide that can be poorly retarded by engineered and natural barriers. It can be released as a gas and is therefore a key radionuclide with respect to post-closure disposal facilities performance. Hydrogen is generated during anaerobic corrosion of Zircaloy and steel. The potential hydrogen formation may result in enhanced carbon-14 transport provided hydrogen is too slowly dissipated. This potential enhanced carbon-14 transport depends on the disposal concept and host rock. Potential release mechanisms for the waste processed with cementitious materials and expected speciation of carbon-14 are presented in this report, if available.

The carbon-14 source term of neutron irradiated steel, neutron irradiated Zircaloy, spent ion exchange resins and neutron irradiated graphite highly depends on the exposed surface area and degradation rate. Gaseous carbon-14 can be formed during corrosion of neutron irradiated steel and Zircaloy but its generation rates at disposal conditions in cementitious materials are too small to be reliably measured with the present available experimental techniques. Carbon-14 is present as an anion in spent ion exchangers and therefore gaseous carbon-14 formation during chemical degradation of resins is excluded.

Carbon-14 is interesting from a biological standpoint because it is integrated in cellular components, particularly DNA. The aim of CAST is to develop understanding potential release mechanisms of carbon-14 from radioactive waste and not the potential uptake in the biosphere. Relevant information of this uptake is included here in order to accommodate comments from the audience in the first workshop.

## **Acknowledgements**

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## **1 Introduction**

### **1.1 Background**

Carbon-14 in nuclear reactors is generated by neutron activation of impurities present in materials. Its generation is similar to chlorine-36 and cobalt-60. Chlorine-36 has certain characteristics like carbon-14; a long-lived radionuclide from which it is known to be poorly retarded by geological barriers but carbon-14 can be released as a gas during degradation of waste. Gaseous radionuclide can be less retarded by engineered and natural barriers than a radionuclide dissolved in ionic form such as chlorine-36. Carbon-14 may therefore be a key radionuclide with respect to post-closure disposal facilities performance.

The half-life of carbon-14 is 5730 years. In many disposal concepts for High Level Waste (HLW), there is an engineered containment period until several hundred thousands of years. The activity concentration of carbon-14 in waste is significantly reduced in this containment period. Investigation of the Carbon-14 Source Term is therefore of more interest for the Low and Intermediate Level Waste (LILW) than HLW for many countries.

Carbon-14 is a low beta emitter, with a low penetrating power and therefore does not pose an external radiation hazard. Unlike cobalt-60, carbon-14 cannot be measured non-destructively due to absence of gamma emission during its decay. Consequently, carbon-14 is interesting from a characterisation standpoint since its activity in waste cannot easily be measured. Carbon-14 in wastes needs to be isolated from other radionuclides for inventory assay purposes, so that the total carbon-14 content can be determined with measurements. To undertake this isolation, a representative set of samples from the waste is changed into a gaseous form, and the gas containing carbon-14 is separated from the rest of the gas. This analysis is more costly than measuring the activity of cobalt-60 in waste using gamma spectrometry. The carbon-14 content in waste can be determined by calculations instead of, or in conjunction with, a chemical analysis of representative samples. In these calculations, measurements about the neutron irradiation history and impurities present can be used as input. Frequently, assumptions are made for this input.

Neutron irradiated materials investigated in CAST are graphite, steel and Zircaloy. Activated graphite and steel can be dismantling waste. The discrimination in dismantling waste between conventional and radioactive waste is based on the radionuclide-specific exemption or clearance levels. In the latest Council Directive 2013/59/EURATOM laying basic safety standards for protection against the dangers arising from exposure to ionising radiation, the activity concentration for clearance have been set to 1 Bq per gram of solid matter for chlorine-36 as well as carbon-14 [EU, 2013]<sup>1</sup> that is a chemical concentration in e.g. iron of 0.001269 and 0.000024 ppm respectively. The chemical concentrations of precursors of carbon-14 in graphite, steel and Zircaloy can be more than a million times larger. Zircaloy is used as a cladding in fuel elements. Fuel elements are replaced several times during the lifetime of a nuclear plants and consequently neutron irradiated Zircaloy is operational waste. Carbon-14 in spent-ion exchange resins is also operational waste and is also investigated in CAST. Neutron irradiated water – for example coolant water in the primary water circuit of a plant - is filtered using resins. Spent resins from different locations in a plant can become mixed during processing the spent ion exchange resins in a waste product.

Already in the 1980's, European research showed that the dominant source of carbon-14 was characterised as nitrogen impurities in core materials. A management strategy for the carbon-14 was the reduction of nitrogen impurity levels in core materials [Bush, 1984]. It is unknown whether this suggested strategy has been implemented in Europe, there is only literature found for reducing the nitrogen content in the coolant. In this European study, the nitrogen impurity content was assumed to be zero in the coolant [Bush, 1984]. Twenty years later, IAEA made the same management strategy as Bush but also identified that nitrogen can become present in the primary coolant system by air ingress and the use of hydrazine (NH<sub>2</sub>-NH<sub>2</sub>) to control the pH of the coolant. This IAEA document also describes the measures to limit nitrogen in the coolant i.e. use argon instead of nitrogen to control the

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<sup>1</sup> Please note that 1 Bq per gram solid matter for carbon-14 in the latest Council Directive is less than 300 Bq per gram listed in IAEA-TECDOC-855 [IAEA, 1996]. This IAEA report was never finished but the listed clearance level have been used as input in computer codes such as CINDER'90 [Ancius, 2005] to prepare decommissioning of nuclear power plants. The follow-up of TECDOC-855 is the IAEA Safety guide RS-G-1.7 [IAEA, 2004b]. The clearance level for carbon-14 is in the Safety guide also 1 Bq per gram.

nitrogen level in the moderator cover gas and to use LiOH instead of hydrazine to control the pH of the coolant. LiOH is suggested to be depleted in  ${}^6\text{Li}$  to limit the tritium generation [IAEA, 2004b]. At the first workshop, there was one country that provided such metadata as the coolant to control pH to understand carbon-14 inventory. From this metadata, it became clear that hydrazine is used in Europe [Buckau, 2016].

In the latest consolidated version of the Euratom treaty (2016) [EU, 2016], the research on impurities in core materials is limited to zirconium that should be hafnium-free in order to make claddings transparent for neutrons i.e. Hf is a strong neutron absorber. For a safe management of the waste it may be necessary to have knowledge about the nitrogen content in structural materials used in reactors and their neutron irradiation history. The possibility for nitrogen-free structural materials is not yet explored for to-be-built reactors.

## 1.2 Objectives

The workshops are envisaged to ensure that the developed knowledge in CAST is provided in timely manner to target groups. In CAST, waste generators, waste producers, regulators and waste management organisations were invited for the first workshop because these groups have an implementation responsibility in the management of waste. The two aims for the second workshop are:

- 1) Providing tools to bound the inventory of carbon-14 containing waste in order to understand a quantification of the potential volume with hazardous amounts of carbon-14 in this waste. For each type of carbon-14 containing waste investigated in CAST it will be answered preferably by a waste generator what traceable information the generator can share for the waste characterisation to calculate disposal of this waste with a larger certainty for example the nitrogen impurity content and thermal neutron fluence.
- 2) Discuss the understanding of the potential release mechanism of carbon-14 as a function of the disposal conditions to which the waste is exposed.

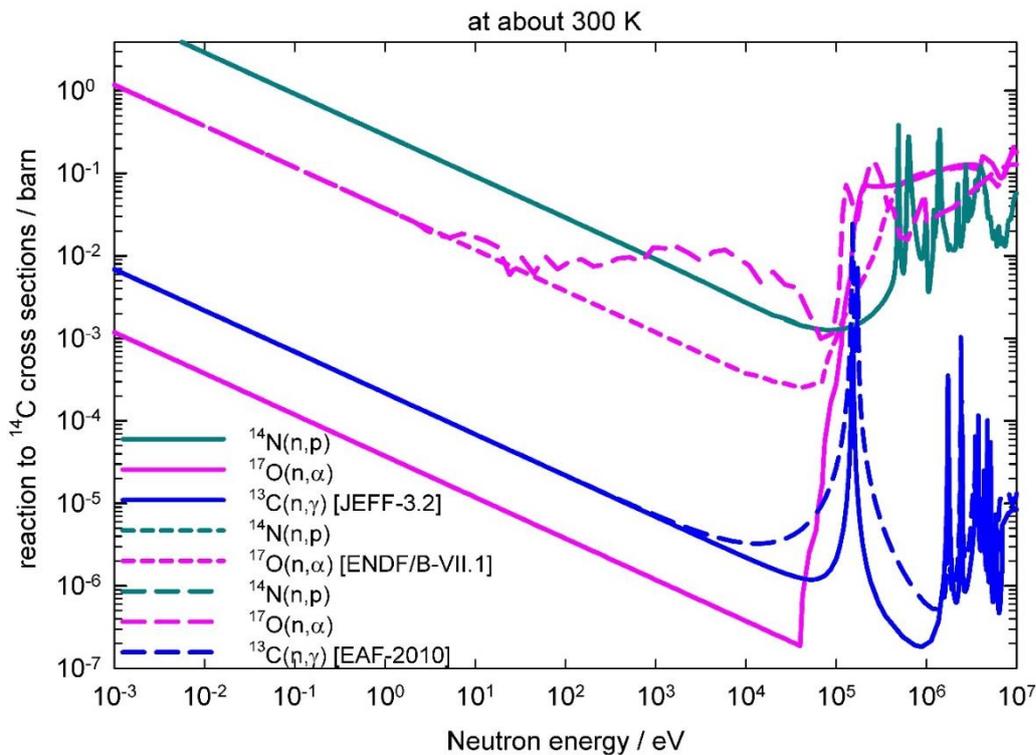
The objective of this document is to let the regulators prepare themselves for the second workshop. In the previous workshop, the regulators expressed the need for the knowledge of the chemical form of carbon-14 entering the biosphere. The biosphere is outside the scope of the CARbon-14 Source Term (CAST) project but some available knowledge about carbon-14 is aggregated in this document.

National examples of safety assessments of the types of waste investigated in CAST have been presented in the first workshop held in 2016. The knowledge supporting safety assessments of carbon-14 has been recently published [Capouet, 2017]. The information contained in this CAST report is also considered of interest to the regulators for their preparation of the second workshop.

## **2 Carbon-14 generation in a nuclear reactor**

The description of the generation of carbon-14 in a nuclear reactor has the purpose to provide arguments in the substantiation to bound the carbon-14 inventory in the waste. Carbon-14 is primarily generated by neutron activation i.e. ternary fission and decay of actinides such as radium and actinium provide negligible contributions to carbon-14 in waste. The reaction to carbon-14 neutron cross sections of nitrogen-15 and oxygen-18 are negligible compared to the precursors nitrogen-14, oxygen-17 and carbon-13 and therefore neglected [IAEA, 2004a]. The chemical concentration and neutron reaction cross sections can be used to investigate which of these precursors would dominate the carbon-14 generation in waste and to what extent it would dominate. The chemical concentrations of the precursors are later described for the types of waste investigated in CAST. Figure 2-1 shows reaction cross sections from the following libraries in the databank from the Nuclear Energy Agency (a specialised agency within the Organisation for Economic Co-operation and Development):

- Joint Evaluated Fission and Fusion File from 2014 [JEFF-3.2];
- the Evaluated Nuclear Data File from 2011 [ENDF/B-VII.1];
- European Activation File from 2010 [EAF-2010].



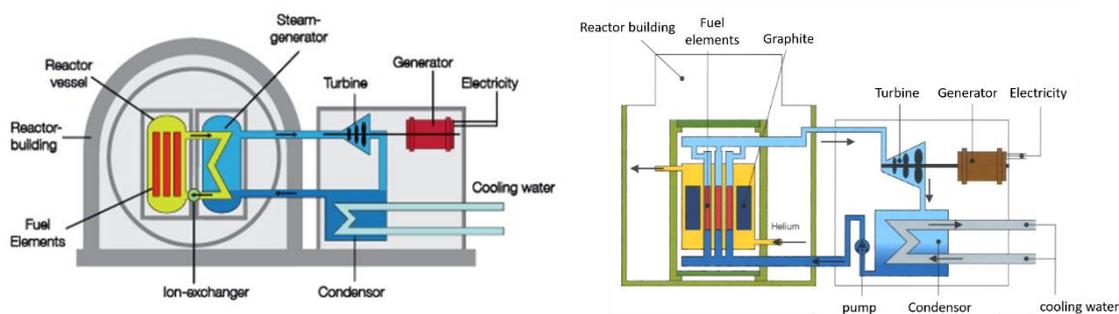
**Figure 2-1: Neutron reaction cross sections at 293.59 K from NEA data bank.**

Neutrons resulting from the fission of actinides have an energy of about  $10^6$  eV. The neutrons lose their energy by collisions with atoms present in a moderator until the thermal energy of neutrons is achieved. The thermal energy of neutrons is about  $10^{-1}$  eV. The neutron reaction cross sections for fission and thermal neutrons can both be viewed in the same graph by using a logarithmic neutron energy scale; x-axis in Figure 2-1. The thermal neutron flux, neutron irradiation period and chemical concentration of the precursors of carbon-14 are used to determine the generation of carbon-14 [IAEA, 2004a]. In these libraries, the reaction cross section for nitrogen-14 for thermal neutrons is the largest one. The cross section relevant for generation of carbon-14 by the reaction oxygen-17(n, alpha) by thermal neutrons has reduced by a factor of a thousand in the latest evaluation of data<sup>2</sup>. The recent evaluation of carbon-13 reaction cross sections (only available in libraries EAF-2010 and JEFF-3.2) has resulted in a negligible change for thermal neutrons.

<sup>2</sup> The reduction in reaction cross section of the oxygen-17 is especially important for Heavy Water Reactors (HWR) that have a larger  $^{17}\text{O}$  content than Light Water Reactors (LWR) [IAEA, 2004a].

Fission neutrons are present in the core of reactors where the fuel elements are located. In the core of a Light Water Reactor (a H<sub>2</sub>O moderated reactor), the neutron flux of fission neutrons is about the same as thermal neutrons. Please note that the y-axis in Figure 2-1 is on a logarithmic scale; for example for thermal neutrons: the reaction cross section for nitrogen-14 is more than three orders magnitude larger than carbon-13 and four orders magnitude larger than oxygen-17 using the JEFF 3.2 database. Consequently, the chemical content of carbon-13 needs to be more than three orders magnitude larger in order to contribute to the same carbon-14 generation as nitrogen-14. The natural abundances of nitrogen-14, carbon-13 and oxygen-17 are 99.64%, 1.07% and 0.038% respectively. A combination of the natural abundance and neutron reaction cross sections yields that the chemical contents of carbon and oxygen need to be respectively five and seven orders in magnitude larger than nitrogen in order to contribute to the same carbon-14 content.

The amount of waste with carbon-14 can be bounded since neutron activation can only take place at those locations in a reactor where neutrons are present. The spatial distribution of neutrons and the energy of neutrons depend on the moderator properties. The range of neutrons surrounding the core with fuel elements can be bounded by these properties. The figures left and right show a Light Water moderated Reactor (LWR, Pressurised Water Reactor) and a graphite moderated reactor (RBMK-type).



**Figure 2-2: Light Water (H<sub>2</sub>O) moderated Reactor and graphite moderated reactor.**

### 3 Carbon-14 release from a nuclear plant

Not all carbon-14 that is generated in a nuclear plant will be contained in the waste for disposal. Nuclear plants have licenses to discharge carbon-14 to the surrounding environment. The Commission of European Communities has recommended to report the radioactive airborne and liquid discharges into the environment by nuclear power reactors and reprocessing plants in normal operation in a template, a compilation sheet. The standardised information for carbon-14 includes the activity discharged each year. In the template, it needs to be indicated whether the discharged activity is based on calculations or on samples. The sampling method needs to be indicated including the detection limit. Reporting the chemical / physical form of the discharged carbon-14 is recommended to be indicated, if available [EU, 2004]. Carbon-14 can be discharged in the form of airborne (gases and aerosols) or liquid (to surface water bodies only) effluents. This carbon-14 release is continuously monitored and attempts have been made to reduce the carbon-14 discharge to the surrounding environment from nuclear plants. For a disposal facility, carbon-14 is released from solid waste without monitoring and therefore the carbon-14 source term is treated differently. A description of the potential carbon-14 release in which the carbon-14 content become less than generated in a nuclear plant will be given for each type of waste investigated in CAST. For the carbon-14 inventory performed in Europe in the 1980's, the fraction of carbon-14 contained in solid waste can be two-third till a half of the amount of carbon-14 generated in LWR (Light Water Reactors, PWR and BWR). The other known part of generated carbon-14 was assumed to be discharged to the atmosphere [Bush, 1984]. In the IAEA study performed, twenty years later, the measures to minimize the carbon-14 discharge to the atmosphere with nuclear power and processing plants are described [IAEA, 2004].

It is interesting to note that the old style CANDU reactors, released large quantities of  $^{14}\text{C}$  in gaseous effluents, owing to the extensive use of nitrogen blanketing inside the reactor. The current CANDU reactors, using  $\text{CO}_2$  as the annular gas, have shown a significant reduction in  $^{14}\text{C}$  production in the annular gas system. Avoiding the use of chemicals that could

produce  $^{14}\text{C}$  during reactor operations is a viable approach to reducing  $^{14}\text{C}$  production [IAEA, 2004: p.38].

Except for PWR's, carbon-14 is mainly released as  $^{14}\text{CO}_2$ . PWR emit carbon-14 as hydrocarbons e.g. methane [IAEA, 2004a]. The French technical support organisation IRSN has further quantified the chemical speciation for boiling water reactors (BWR). In the gaseous effluents of BWRs,  $^{14}\text{C}$  is 95% carbon dioxide ( $^{14}\text{CO}_2$ ), 2.5% carbon monoxide ( $^{14}\text{CO}$ ) and 2.5% hydrocarbon. In the gaseous effluents of pressurised water reactors (PWRs), it is assumed that 80% of  $^{14}\text{C}$  is in organic form ( $^{14}\text{CH}_4$ ) whereas 20% is in the form of  $^{14}\text{CO}_2$ . In the liquid releases, the carbon chemical species are carbonates and various organic compounds, their relative quantities being currently unknown [IRSN, 2010: p.3]. Similar airborne releases have been published earlier by IAEA [IAEA, 2004: p.15]. VVER is a Russian type PWR with a similar speciation in gaseous effluents as Western PWRs [Rajec, 2011].

## **4 Carbon-14 inventory discussed at the first CAST workshop**

Waste management organisations are in many countries responsible for the inventory of waste intended to be disposed. In the first CAST workshop held in October 2016, waste management organisations were therefore asked to present the carbon-14 inventory of the types of waste investigated in CAST. A predefined template was used for the presentation of the carbon-14 inventory in order to facilitate the similarities between the national programmes and to learn from each other's practices. These organisations were asked to answer to following questions for each type of waste:

- What are the amounts you expect to have / will be generated?
- What is the origin of waste?
  - if possible an image of the (processed) waste package
- How is the carbon-14 content determined / specified?
- What is the activity of carbon-14 per waste package / kilogram?
- What is the designated end-point of this waste?

Since the carbon-14 activity concentration cannot be determined using gammaspectrometry and waste dimensions, scaling factors appeared to be frequently used to determine the activity concentration for carbon-14 with an Easy To Measure (ETM) radionuclide [Buckau, 2016]. For radionuclides that are generated by neutron activation, cobalt-60 is used as an ETM. The carbon-14 activity concentration is then determined by the scaling factor times the measured cobalt-60 content. In Chapters 6, 7, 8 and 9, an aggregation of the answers will be presented for each type of waste investigated in CAST. The template to be completed by the waste generators for the second workshop is shown in the Appendix. Figure 4-1 shows the participation of WMOs at the first workshop.



**Figure 4-1. Participation of waste management organisations in the first workshop; orange: attended workshop and contributed to the proceedings, yellow: contributed to the proceedings.**

## 5 Evolving exposure conditions to carbon-14 containing waste

The chemical environmental conditions are usually neutral, and oxidising in case of near surface disposal and reducing in case of deep geological disposal conditions. The waste investigated in CAST project appears to be frequently processed with cementitious materials. The chemical conditions at which potential carbon-14 release takes place are therefore initially alkaline conditions. Concrete pore water can have a pH larger than 11 for a long-term for example several half-lives of carbon-14. Cementitious materials are therefore used for the description of the chemical and microbial conditions.

### 5.1 Evolving chemical conditions

A workshop on the knowledge available on the evolved chemical conditions of cementitious materials and waste has been held in 2009 [NEA, 2012]. The period in time for a pH larger than 7-8 i.e. the pH condition in the environment surrounding concrete, depends on the cement content, type of cement, ionic strength of (aqueous) exposing environmental conditions, the water flow in the environment and varies as a function of the distance between a point in a waste package and exposing environment. The dissolution of portlandite in Portland-based concrete ensures a pH of 12.5 in concrete pore water. After the disappearance of portlandite, a pH around 12.5 to 10.5 controlled by C-S-H mineral phases is expected. In blended cements, for example portlandite with blast-furnace slag or portlandite with fly ash, all portlandite can be reacted with slag to form a dense pore network; the permeability in blast-furnace and fly ash based concrete is therefore smaller than Portland based concrete [Gascoyne, 2002]. The initial pH in these low pH concretes is expected to be around 12.5 to 10.5. The water flow is expected to be very small in concrete i.e. diffusion may be the dominant transport mechanism. For example the diffusion values for intact concrete (Portland-based) for a non-retarded contaminant  $\text{Cl}^-$  is  $4 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  with a porosity of 9.7% and for degraded concrete  $2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  with a porosity of 31% [Kurstén, 2015]. The values for diffusion of  $\text{Cl}^-$  for intact concrete are similar also measured in

(compacted) bentonite [Loon Van, 2007]. A diffusion-controlled slow degradation of concrete is expected.

Surface disposal or near-surface disposal conditions are expected to be aerobic (oxidising) conditions for the degradation of carbon-14 containing waste e.g. Wang [Wang, 2013]. There can be disposal requirements such as a low groundwater table in which the waste does not become wetted. The predominant carbon-14 aqueous species at a pH of 12 at aerobic conditions can be calculated to be  $\text{CO}_3^{2-}$  i.e. a fraction carbon is present as  $\text{HCO}_3^-$  and  $\text{CO}_2$ . These fractions can be determined with equilibrium constants. Till a pH of less than 7, the predominant species is  $\text{HCO}_3^-$ . The retardation values of inorganic carbon for concrete are in the order of  $10^3$  l/kg until cement degradation state III i.e. the state in which the pH of concrete pore water is controlled by CSH phases [Wang et al in NEA, 2012]. Consequently, the major fraction of inorganic carbon is not expected to be released as long as CSH phases are present. For metallic waste such as Zircaloy and steels, localised corrosion can occur at aerobic saline conditions. This localised corrosion (pitting) results in localised acidic environments. As long as alkaline conditions are present, this pitting is not expected to develop due to sufficient neutralising capacity [Smart et al. in NEA, 2012].

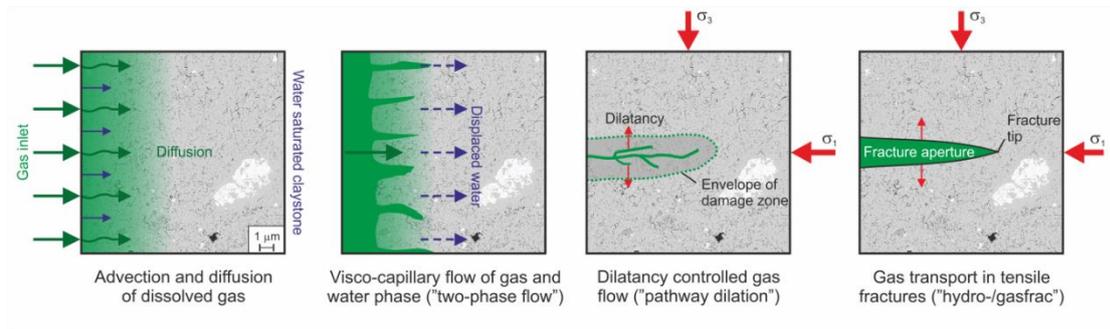
Hydrogen is generated by anaerobic corrosion of metallic compounds and hydrogen may have an impact on the thermodynamic stability of reduced carbon. In CAST, Wieland has performed a preliminary assessment of the formation and thermodynamic stability of carbon-14 containing organic compounds [Wieland, 2015]. The predominant carbon species depends on the pH and hydrogen atmosphere. Generated carbon species can be alkane/alkenes, alcohols/aldehydes, carboxylic acids but alcohols/aldehydes and carboxylic acids can form with hydrogen alkane/alkenes. Usually the smaller carbon species are formed during corrosion i.e. methane and not ethane. Methane is not retarded in cementitious minerals but evidence of precipitation in cementitious materials of carboxylic acid such as oxalate is available [Loon Van, 1995]. In case of a hydrogen pressure build-up due to insufficient dispersion of hydrogen generated by anaerobic corrosion of metals, methane can be expected to be the predominant species either generated directly or indirectly by a reaction with hydrogen and methanol/formaldehyde or formate based on available thermodynamic considerations. In CAST, it is investigated whether there is a kinetic

hindrance to the formation of methane i.e. is there evidence that not all carbon-14 is released as a gas i.e. CH<sub>4</sub>?

For geological (deep) disposal, the waste is expected to be exposed to anaerobic (reducing) conditions [Wang, 2013]. The pores in processed waste are expected to be fully saturated with water due to capillary suction of the small concrete pores and entrapped oxygen will be consumed by degradation processes of the waste such as corrosion. At a pH larger than 7, metallic waste forms such as Zircaloy and steel have usually far smaller corrosion rates under anaerobic conditions than under aerobic conditions. Localised corrosion (pitting, crevice) under anaerobic conditions is not expected due to lack of oxygen; the oxygen content is smaller than the soluble oxygen content in water.

## **5.2 Microbial conditions**

Space restriction limits microbial activity. The connecting pore throat of undisturbed Boom Clay is between 10 to 50 nm. The viable microbial size is 0.2 µm. This size is larger than the connecting pore throat by which microbes in undisturbed Boom Clay are in a dormant phase [Wouters, 2016]. In other materials, also space restriction is the key factor to inhibit the microbial activity. In well hydrated Portland based cement also a pore size between 10 to 50 nm has been found [Smart et al in NEA, 2012]. For concrete made with blended cements, for example with Portlandite and blast furnace slag, the permeability is smaller than Portland based concrete. With superplasticisers, concrete with a smaller water-cement ratio can be made resulting in a smaller permeability of concrete [Gascoyne, 2002] caused by a smaller pore throat. In intact concrete and rock salt, the pore throat can even be smaller than in Boom Clay. The microbial activity in undisturbed clay, salt and intact concrete is expected to be limited due to the space restriction i.e. microbes may stay in a dormant phase. Hydrogen gas, for example generated by anaerobic corrosion of metals, can be dispersed by 1) advection and diffusion of dissolved gas, 2) visco-capillary flow of gas and water phase (two-phase flow), 3) dilatancy controlled gas flow (pathway dilation) and 4) gas transport in tensile fractures (hydro-/gasfrac). The following figure shows the gas flow processes investigated in argillaceous materials by BGS [Wiseall, 2015].



**Figure 5-1 Possible gas flow processes in argillaceous material [Wisell, 2015]**

A free gas phase is not formed in the first gas flow process i.e. hydrogen and methane are dissolved in pore water. In the second gas flow process, a free gas phase has formed but the clay fabric has stayed intact i.e. the gas pressure built-up may have an impact on the thermodynamic stability of carbon but the space restriction for the microbes has not changed. An enhanced transport of radionuclides takes place when the second, third or fourth gas flow process occurs. The space restriction is eliminated when the third and fourth gas flow process occurs and therefore the microbial activity cannot be assumed to be negligible when the third and fourth gas flow process occurs. The first, second and fourth gas flow processes are also identified in concrete and rock salt.

Apart from space restriction, the ionic strength of the fluid is important to determine the microbial activity, this strength can be too high for microbial life. The potential generated brines from rock salt have a too large salt concentration for microbial activity, most bacteria thrive at water activities greater than 0.90 [Swanson, 2016] and also the high pH in concrete was judged to inhibit microbial activity [NEA, 2012].

## 6 Biosphere

The paths for potential radiological exposure are external radiation, inhalation and ingestion [IAEA, 2003]. Carbon-14 is a low beta emitter and therefore external radiation by carbon-14 can be considered negligible. For disposal, inhalation is the main exposure path for radionuclides that are not concentrated by living matter such as noble gases. The investigations on the exposure pathways of natural i.e. cosmic generated carbon-14 has resulted in the outcome that the main carbon-14 exposure path to humans is ingestion. During photosynthesis,  $^{14}\text{CO}_2$  is incorporated in the organic material, forming its carbon skeleton. The carbon-14 content in food depends on the carbon content e.g. cereals have a larger carbon-14 content than fruits [IRSN, 2010].

The main exposure path for artificial carbon-14 to humans is also ingestion i.e. accumulation of carbon-14 in the human body by ingestion of contaminated food [IAEA, 2004a]. Carbon-14 is interesting from a radiobiological standpoint because it is integrated in cellular components (proteins, nucleic acids), particularly cellular DNA. The internal radiation causes radiation stress if carbon-14 is incorporated. The resulting DNA damage, involving molecular breaks, may lead to cell death or induce potentially inheritable mutations [IRSN, 2010].

### 6.1 Carbon-14 speciation into biosphere

In CAST, degradation of waste in cementitious materials is investigated since these materials are frequently used for waste packaging of the types of waste investigated in CAST. The conditions to which the waste is exposed determine the carbon-14 speciation to the biosphere.

At the start of near surface disposal, a pH larger than 7 and aerobic conditions are expected. At these conditions, carbon-14 is predominantly expected to be released in ionic form in an

aqueous phase. The fraction of CO<sub>2</sub> can be calculated using equilibrium constants. Carbonation of concrete act as a sink for CO<sub>2</sub> i.e. calcium from cementitious minerals react with CO<sub>2</sub> to form CaCO<sub>3</sub> [Rochelle, 2013]. As long as cementitious minerals are present, the majority of CO<sub>2</sub> is not expected to be released from the waste package. On the long-term, the concrete pore water progressively alters from a high pH to more neutral conditions. The alteration rate depends on the exposure conditions and time-dependent permeability of concrete in the waste packages. These exposure conditions are site-specific for example acidic conditions are present within the root zone of the soil layer above the disposal facility because of the high partial pressure of carbon dioxide as a result of biochemical interactions.

The potential ingress of oxygen can be consumed during degradation of waste, for example by corrosion of metals. But the ingress of oxygen can be too slow by which consumption of oxygen may result in a local reduction of the redox potential at the interface between metal and concrete. This potential can decrease to -800 mV considering pure iron in equilibrium with pore water [Wang, 2013]. In strongly reducing environments, the reduced form of carbon is thermodynamically stable [e.g. Wieland, 2015 & Rizzato, 2015].

The gaseous reduced form of carbon is CH<sub>4</sub>. CH<sub>4</sub> is not incorporated in organic material but microbes in the soil zone can convert CH<sub>4</sub> into CO<sub>2</sub>, which is taken up by organic matter by photosynthesis. The University of Nottingham has investigated the extent of this conversion: most radioactive methane migrating from a repository is likely to be converted to <sup>14</sup>CO<sub>2</sub> in the soil [Lever, 2015]. Long-term Dose Assessment for Carbon-14 is further detailed in BIOPROTA, a collaborative biosphere project for discussing the representation of <sup>14</sup>C in the biosphere and supporting model-model and model-data intercomparisons [Capouet, 2017 and Smith, 2012]. The estimation of the release rate of <sup>14</sup>CO<sub>2</sub> from carbon-14 containing waste to the biosphere is expected to provide the input to determine the potential health related impact. The potential artificial <sup>14</sup>CO<sub>2</sub> release rate can be compared with the natural generation rate of <sup>14</sup>CO<sub>2</sub> with a cosmic origin in order to put the carbon-14 hazard potential from disposal of the waste in perspective with the carbon-14 natural exposure. Cosmogenic carbon-14 release rate is about 2 atoms cm<sup>-2</sup>s<sup>-1</sup> [Kovaltsov, 2012].

For a disposal facility, carbon-14 is released from solid waste without monitoring and therefore the carbon-14 source term should result in an insignificant contribution to the cosmogenic activity concentration and contribution to the carbon-14 dose rate of cosmogenic origin. This natural dose rate is 12  $\mu\text{Sv}$  per year. The carbon-14 activity from nuclear power plants is continuously monitored and globally estimated to result in a maximum in dose rate of 1  $\mu\text{Sv}$  per year assuming a continuing practice of 250 GW energy production per year. The average annual dose rate from globally dispersed  $^{14}\text{C}$  released from nuclear installations is about 0.1  $\mu\text{Sv}$  per year [UNSCEAR, 2000].

## 7 Neutron irradiated steel

### 7.1 Bounding carbon-14 inventory

Carbon steel and stainless steel are investigated in CAST. In many nuclear plants stainless steel is used due to its corrosion resistance by addition of chromium and nickel. Carbon steel does not have a minimum in chemical content of these elements. Stainless steel can be used at the inside of the reactor vessel, as a grid support, ducts et cetera. Not all carbon-14 generated in stainless steel is contained in the waste. Corrosion products of the stainless steel may spall off in the coolant. The outside of stainless steel compartments is expected to have more elements being neutron activated than the inside due to shielding of intermediated and thermalized neutrons<sup>3</sup>.

Reducing conditions are necessary to make steel and therefore oxygen is hardly present within steel. Before neutron irradiation during construction of the nuclear plant, an oxide layer on the surface of steel is formed. Such an oxide layer of a few nm is still present on the metallic surface after neutron irradiation [Mibus, 2015]. Carbon and nitrogen are soluble in iron to some extent [Swanton, 2015]. In Chapter 2, it was explained that the combination of the neutron reaction cross sections and natural abundance require the chemical contents of carbon and oxygen to be respectively five and seven orders in magnitude larger than the nitrogen content in order to contribute to the same carbon-14 content in waste. The carbon-14 content in stainless steel can therefore be calculated from the distribution in thermal neutron fluence in the nuclear plant and nitrogen-14 reaction cross section and natural abundance i.e. neglecting the carbon content and evolved oxygen content in steel for their lower efficiency.

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<sup>3</sup> For carbon-14, a profile of neutron activation is not available. But for other radionuclides that are generated by neutron activation, a variation as a function of depth in stainless steel was measured at several tenths of nanometres [Fisal, 2013]. It is possible that only the stainless steel part on inside of the reactor vessel contains carbon-14 till hazardous amounts. The carbon steel part on the outside of the reactor vessel may be sufficiently shielded. Grinding of the surface of big stainless steel pieces and only designating the grounded-off matter as radioactive waste can therefore be a methodology to reduce the amount of radioactive waste [Ionescu, 2016].

## **7.2 Presence of nitrogen in steel**

In the fabrication process of steel, nitrogen is incorporated. Sources of nitrogen can be charge materials for steel such as cokes, pig iron, and the (partial) pressure used for the stirring gas. An addition of (N) in the specifications of the alloy indicates a larger nitrogen content from 0.1-0.16 wt% [Swanton, 2015] but in CAST samples of 316L(N) (UK programme) has been specified with a nitrogen content of 0.08 wt% [Visser, 2017a], [Mibus, 2015].

In a previous EU research project, a maximum in nitrogen content of 1600 ppm was set for 304 and 302 stainless steel [Bush, 1984]. In the IAEA study performed 20 years later, it was concluded that the materials of core structures contain certain amounts of nitrogen (e.g. the nitrogen contents in stainless steel range from 0.04% to 0.08%). However, nitrogen levels in many reactor materials are not known with certainty, and it is therefore difficult to estimate what reduction might be possible. For to build reactors, it may be sensible to be aware of the nitrogen impurities before neutron irradiation in order to decide whether replacement of the intended material can limit carbon-14 containing waste. For operational reactors or closed ones, the nitrogen impurities are necessary to calculate the potential carbon-14 activity concentration after the operational period.

Stainless steel can also be used for pins to test fuel in nuclear research reactors. These so-called 15/15 Ti claddings are also stainless steel except that the main alloying elements, chromium and nickel, are both around 15 wt% and a little bit of titanium of 0.5 wt% is added [Wegst, 1995]. Titanium is a nitride-forming element and therefore during steel production, separate titanium nitride phases may be present [Swanton, 2015].

In water-cooled nuclear power plants, zirconium based (hafnium-free) cladding is preferred due to its transparency for neutrons. In gas-cooled reactors, the temperature can be too high for zirconium based alloys and stainless steel claddings are used; the fuel is enriched in fissile uranium in order to account for the higher neutron capture. In a previous EU research project, the nitrogen content in these Advanced Gas Reactors claddings appeared to be 100

ppm and 50 ppm [Bush, 1984]. These stainless steel claddings become intermediated level waste if the spent fuel is reprocessed.

### 7.2.1 Samples in CAST

At 10 research institutions, experiments are performed with steel in CAST. The sample descriptions with which experiments are performed have been described in the first, second and third Annual Progress Reports [Mibus, 2015, 2016 and 2017]. The nitrogen content in the steel samples was frequently not known. Belgian (SCK CEN) and Finnish (VTT) research institutes used combustion equipment and LECO analyser to measure the nitrogen content in steel. The nitrogen contents of the steel samples used in the Finnish, English, German and Belgian programme are known:

- For stainless steel, a nitrogen content of 0.008% N<sub>2</sub> was measured (Finnish result). Another Finnish neutron irradiated stainless steel sample was a surveillance capsule. Surveillance capsules are used to monitor irradiation embrittlement of the reactor pressure vessel. The stainless steel capsule was positioned at the inside of the reactor vessel for four years. The nitrogen content was measured to be 0.04%.
- For JRQ carbon steel in the Belgium programme, a nitrogen content of 19 ppm was measured consistent with literature values and technical specifications, usually between 20-30 ppm.
- Nitrogen content in stainless steel claddings were specified by the vendor in the German programme: 41 +/-21 ppm and measured. The measurements showed similar values namely 43 ± 23 ppm but in a retest the measured nitrogen content was 75 ± 6 ppm.
- As described previously for the UK programme, 316L(N) has been specified with a nitrogen content of 0.08wt%.

One of the objectives of the CAST project are to gain new scientific understanding of the rate of release of carbon-14 from the corrosion of irradiated steels but irradiated steel samples were scarcely available for CAST. From a Spanish reactor, planned to be

dismantled, a sample was available. The other two neutron irradiated steel samples for the programmes in Belgium and United Kingdom have been neutron irradiated in research reactors. The carbon-14 activity concentrations are in Bq per gram solid matter:

- 18 (Spain, stainless steel) [Mibus, 2015 and 2016];
- 2000 (Finland, stainless steel from surveillance capsule) [Mibus, 2017];
- 851000 (UK programme, stainless steel 316L(N)) [Mibus, 2016];
- 60 (Belgium, JRC carbon steel) [Mibus, 2016].

### 7.2.2 WMO in CAST

The nitrogen impurities of steel used in Light Water Reactors have been collected in CAST. The maximum content was 1400 ppm N [Capouet, 2017] i.e. 0.035 wt%. The Belgian, Czech, Swiss, Finnish and Swedish waste management organisations had the nitrogen content measured. The reported carbon-14 activity concentration in core internals was in the order of  $10^5$  Bq per gram and in the pressure vessel  $10^3$  Bq per gram solid matter.

### 7.2.3 First workshop

There was a preference at the first workshop to present the national inventory of the types of waste investigated in CAST by waste management organisations since these organisations in many countries are responsible for the inventory of waste intended to be disposed. In the first workshop it appeared that the carbon-14 content was determined by neutron activation calculations in most countries i.e. the distribution in neutron fluence and energy of neutrons was used as input. Some of these presentations also included the nitrogen content used for the calculations: 0.05 wt% Hungary and Switzerland. Hungary and Slovenia presented both a carbon-14 activity concentration of  $10^5$  Bq per gram which is the same order in magnitude as found by WMO in CAST for core internals. The Hungarian value was determined by calculations and the Slovenian value was determined using scaling factors reported by SKB. Some countries could not report the carbon-14 activity concentration in steel [Buckau,

2016]. The diffusion of carbon in steel during neutron irradiated temperatures is so small that apart from spalling off corrosion products, it can be assumed that there is no redistribution of carbon-14 of neutron irradiated steel. The cobalt activity can thus be related to the carbon activity. Consequently, with a representative set of samples, a scaling factor can be made. For the majority of the waste, only the cobalt activity needs to be measured to determine the carbon-14 activity. A substantiation for the use of scaling factors reported in literature may require knowledge of the nitrogen content in stainless steel, neutron irradiation history and decay period since the half-life of  $^{60}\text{Co}$  is 5.3 years i.e. three orders in magnitude smaller than carbon-14 from which the scaling factor is derived and stainless steel for which the carbon-14 activity concentration is to be determined.

### ***7.3 Potential presence of carbon-14 in irradiated steel***

The nitrogen contents in steel are usually so small that it can be assumed that nitrogen is dissolved within an iron lattice. During neutron irradiation, atoms are displaced from the lattice structure resulting in two types of extrinsic defects: vacancies and self-interstitials. These extrinsic defects can cluster into dislocation loops (1-D), platelets and stacking faults (2-D) and voids and bubbles (3-D). 1-D and 2-D defects are always present in steel and can even contribute to the mechanical strength of steel [Callister, 2000]. The neutron irradiation temperatures are expected to be at least in the second stage for indicating the thermal impact on defects in materials [Neeft, 2003] since no amorphisation of steel takes place in a nuclear reactor. At the second stage, self-interstitials are mobile and they can recombine with a vacancy. Bubbles can become present during neutron irradiation but require a high temperature until iron melts, unrealistic high rates of displacing atoms and harsh gas exposing conditions. High temperatures and harsh gas conditions are abundant at fabrication of steel e.g. van Veen [Veen van, 1997]. Such conditions are not expected to be present in an operating nuclear reactor. It is therefore expected that neutron activation of nitrogen dissolved in iron results in carbon-14 dissolved in iron.

## 7.4 Potential release mechanism of carbon-14

In the operational period of a nuclear plant, the steel is irradiated by neutrons, gamma's and beta. The radionuclides present in steel after neutron irradiation, emit of gamma's and beta's during their decay. The energy of these emitted beta's and gamma's is sufficient to cause ionisation of atoms and bonds between atoms [Bourgoin, 1978]. The impact of radiolysis for metals is negligible compared to ionic compounds due to the conductance of electrons i.e. recombination of electron interstitials with an electron vacancy immediately takes place. The exposing medium, the aqueous phase, is expected to be more vulnerable to radiolysis i.e. hydrogen and hydrogen peroxide radicals, as well as hydrogen peroxide, hydrogen and oxygen are formed. Hydrogen (radicals) can chemically change many metals by forming hydrides. The possibility of hydride formation in any type of metal has been known for many decades [Lacher, 1937]. For iron, hydride formation is not expected. It has been found that tritium diffuses through stainless steel in a reactor environment at a high rate, the rate being significantly higher than tritium diffusion through zirconium alloys [IAEA, 2004a]. High diffusion rates can be attributed to an insignificant hydride formation. Literature in which the corrosion rates of unirradiated and irradiated steel are compared, are yet not available but in CAST experiments with unirradiated steel from the same sheet are performed [Visser, 2017]. In addition, the lifetime of stainless steel appears to be frequently larger than earlier anticipated in large radiation fields. For example many reactor vessels (made of steel) do not show sufficient damage to close the reactor after the anticipated lifetime. Many nuclear plants in Europe, Mexico, Korea and United states have an extended lifetime [NEA, 2006]. Consequently, the release mechanism of carbon-14 is corrosion of steel and the corrosion rates obtained for unirradiated steels are expected to be representative for neutron irradiated steel until research performed in CAST or other literature becomes available in which experimental results as well as a substantiation for a difference between irradiated and unirradiated steel, are presented. The combination of the presence of carbon-14 dissolved in the lattice and absence of hydride formation in steel can be used to argument that carbon-14 is congruently released with iron.

The corrosion rates of stainless steel and carbon steel available in literature have been collected and judged at the beginning of the CAST project [Swanton, 2015]. The corrosion

rate of carbon steel is about an order in magnitude larger than stainless steel at the same exposure conditions [Yu, 2012]. In CAST, the measurement of the release of cobalt-60 to the solution phase was included as a potential marker for the overall corrosion rate of the steel. This approach assumed that the release of cobalt-60 in solution is congruent with the rate of steel corrosion. But loss of cobalt-60 from the solution occurs. Some initial scoping calculations suggested that the loss of cobalt-60 could result from the precipitation of cobalt associated with the formation of steel corrosion products. The loss can also be possible by sorption of cobalt-60 onto the steel specimens themselves [Visser, 2017a]

Freshly polished surfaces are used to start a corrosion experiment. After some time, the corrosion rates diminishes several orders in magnitude due to the formation of an oxide layer on steel. The corrosion process is then bounded to an equilibrium between diffusion of water through the oxide layer and dissolution at the solid-liquid interface. Neutron irradiated steel from a nuclear power plant has an oxide layer [Mibus, 2015]. The smaller corrosion rates measured after some time are therefore expected to be more representative than the initial corrosion rates measured at start of a corrosion experiment.

### **7.5 Potential speciation**

The carbon-14 speciation at a pH larger than 10 and aerobic conditions is in the chemical form of carbonate. In cementitious materials, a local reduction in redox potential surrounding steel cannot be excluded. For anaerobic corrosion, preliminary results of experiments performed in the framework of the UK [Visser, 2017b] and Swiss programme indicate that carbon-14 is mainly released in alkaline solutions and that a smaller part e.g. 10-30% is released from this solution as a gas in which CH<sub>4</sub> dominates the composition of the released gas.

There are also experiments performed within CAST in which the hydrogen gas formation rates are larger than representative for disposal conditions that is with iron powders. Hydrogen gas pressure has an impact on the thermodynamic stability on the carbon species [Wieland, 2015] and powders have a larger reactive surface area than neutron irradiated

steel. Cementitious pore water was used and the hydrogen dissipation in pure liquid media is faster than in low-permeable media such as concrete, salt or clay. In this so-called ‘anoxic corrosion’ of iron powder mainly carbon in ionic form is released and not as a gas. But further understanding of the obtained measurements indicated that the observed ionic form was attributed to the production of carboxylic acids in a preceding oxidation process for example exposure of iron particles to air or acid (oxidising) pre-treatment of iron powders. It is not merely the result of the corrosion experiment [Mibus, 2017]. The work to measure carbon-14 speciation is still in progress. The measured chemical forms of carbon during anaerobic corrosion are presented at the CAST Final Symposium.

## **7.6 Source Term**

The magnitude of corrosion rates has been described together with the temperature, chemical exposing conditions and period of exposure. The source term is determined by the justifications for the chosen magnitude in rate or rates. This rate may change as a function of time due to the evolved chemical conditions in concrete. Lab experiments usually start with fresh polished surfaces onto which an oxide layer will be formed after some time. The magnitude in corrosion rate can be several times larger at start of the experiment than after a few years due to the formation of an oxide layer. The corrosion rate with an oxide layer can be representative for disposal at start for neutron irradiated steel.

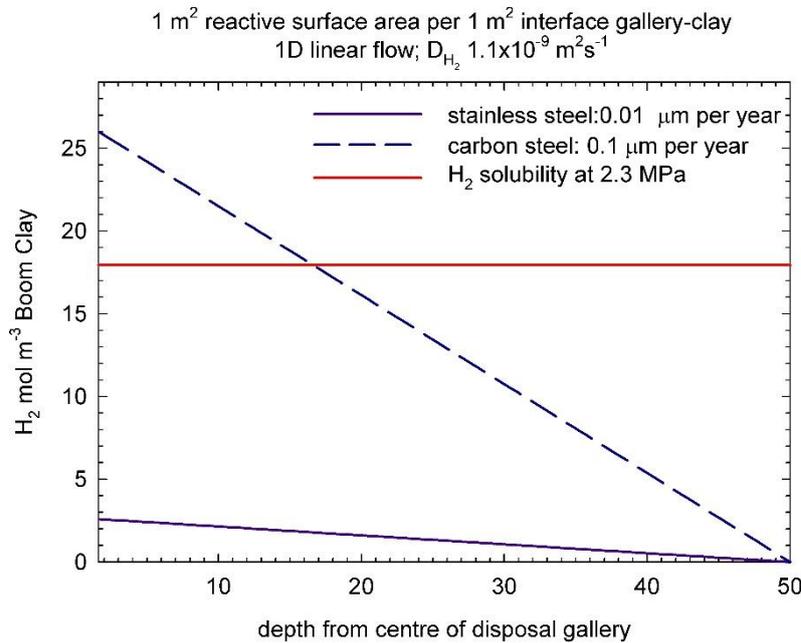
For surface or near-surface disposal, aerobic alkaline conditions at room temperature and 0.1 M NaOH and in equilibrium with  $\text{Ca}(\text{OH})_2$  solutions are considered to be representative for the initial conditions. For the long-term, reducing conditions may also be assumed if entrapped oxygen is consumed and the ingress of oxygen is too slow to accommodate the local reduction in redox potential at the interface between steel and concrete. If it is assumed that these reducing conditions at this interface is not achieved, then the corrosion rates at aerobic conditions are expected to be used. For aerobic conditions, a corrosion rate larger than 1  $\mu\text{m}$  per year has not been found for stainless steel at alkaline conditions [Swanton, 2016: Table 16]. As described previously, the WMO in CAST reported an activity concentration in the core internals in the order of  $10^5$  Bq per gram solid matter. Initially, the

carbonate release rate then becomes in the order of  $10^{13}$  ions  $^{14}\text{CO}_3^{2-}$  per  $\text{cm}^2$  per year in which  $\text{cm}^2$  represents the reactive surface area of irradiated steel. This carbon-14 source term in aqueous media is  $10^{13}$  times larger than carbon-14 of cosmogenic origin in the atmosphere but is not released to the atmosphere but precipitates as  $\text{CaCO}_3$  in cementitious materials. After a period in time, the cementitious minerals can become leached out of the cementitious barrier. This period depends on the disposal concept i.e. thickness of the concrete buffer surrounding steel, (time-dependent) permeability of concrete et cetera. If steel is still left after this period, the neutral aerobic conditions are expected to result in larger corrosion rates of steel perhaps even pitting may take place. The period in time to achieve neutral aerobic conditions may take several half-lives of carbon-14 i.e. a fraction of the initial carbon-14 may be left. Instantaneous release of the fraction of carbon-14 that has not decayed yet may take place but predominantly in ionic form  $\text{HCO}_3^-$  (bicarbonate). Gaseous enhanced carbon-14 transport cannot be assumed since no additional gas is formed during corrosion at aerobic conditions.

For deep geological disposal, anaerobic alkaline conditions at room temperature and 0.1 M NaOH and in equilibrium with  $\text{Ca}(\text{OH})_2$  solutions are considered to be representative after entrapped oxygen in concrete has been consumed. Preliminary results indicate that carbon-14 is released predominantly in solution and a fraction is measured to be released as a gas. For anaerobic corrosion, usually far smaller corrosion rates are found than for aerobic corrosion [Swanton, 2015: Table 17]. The more representative long-term corrosion rates, occurring after an oxide passivating layer is present, are so small that it has yet not been possible to measure reliably the speciation of carbon-14. Therefore, the gaseous form methane is conservatively assumed. Initially, the  $^{14}\text{CH}_4$  release rate then becomes in the order of  $10^{12}$  molecules per  $\text{cm}^2$  per year in which  $\text{cm}^2$  represents the reactive surface area of irradiated steel for the same activity concentration i.e.  $10^5$  Bq per gram solid matter. A corrosion rate of 0.1  $\mu\text{m}$  per years is assumed for this release rate. For stainless steel, an order in magnitude smaller corrosion rate is more representative. Even for stainless steel claddings with a thickness of 0.45 mm as used in a research reactor [Neeft, 2003], it may take more than 7 half-lives of carbon-14 to have the disposed stainless steel completely to be corroded. There is no specific interaction between  $\text{CH}_4$  and cementitious materials as there is for  $\text{CO}_2$ . Methane is therefore assumed to be released from the cementitious barriers

without retardation into the host rock in case of geological disposal or biosphere in case of near surface disposal.

Methane can be further dispersed in the host rock but the containment period of radioactive methane in the host rock highly depends on the possibility of a free gas by the hydrogen formed during anaerobic corrosion of metals. The corrosion rates are in some experiments determined by the hydrogen released from the exposing liquid. At standard conditions, 1 atmosphere and 298.15 K, the mole fraction of hydrogen in water is  $1.411 \times 10^{-5}$  [CRC, 2016] i.e.  $0.8 \text{ mol H}_2 \text{ m}^{-3}$ . The hydrogen solubility at geological disposal conditions is larger mainly due to the higher pressure at larger depth. It needs to be determined at which hydrogen formation rate, hydrogen dissipation at repository scale is too slow to prevent the formation of a free gas in order to be able to assume whether  $\text{CH}_4$  is dissolved in pore water or transported in a bulk gas phase. 3D calculations to prospect the potential evolution of gas-related processes that can influence the long-term behaviour and safety are available [NAGRA, 2016]. In this report, a simplification is used in order to get a grasp when gas enhanced transport of methane is expected i.e. when the formation of a discrete gas will occur. The following figure shows the hydrogen ingress in Boom Clay with corrosion rates of stainless and carbon steel at alkaline and anaerobic conditions and a reactive surface area of  $1 \text{ m}^2$  per  $1 \text{ m}^2$  interface between a disposal gallery and Boom Clay. The parameter values for hydrogen in Boom Clay have been obtained from the Belgian programme [Yu, 2012].



**Figure 7-1: Steady state hydrogen profile for two steel corrosion rates**

Usually, cylindrical symmetries are used to calculate the radionuclide release in scoping studies. For hydrogen, we need to know the possibility of a free gas. On a repository scale, the distance between disposal galleries may be less than 50 metres. The dissipated hydrogen from a single disposal gallery is expected to meet the dissipated hydrogen from a neighbouring disposal gallery i.e. the hydrogen concentration profiles may overlap. Therefore a 1-D result is used here for scoping the potential hydrogen concentration during corrosion of steel. With the above figure, it can be assumed that CH<sub>4</sub> will be dissolved in pore clay water during corrosion of stainless steel in cementitious materials. With this evidence, the diffusion value for methane dissolved in clay pore water can be used to determine the containment period of carbon-14 in the host rock for a radionuclide release scoping study. Gas driven transport in low permeable host rocks such as clay and salt would result in a shorter period in time for decay of carbon-14 than diffusion of carbon-14 species. Transport of hydrogen in crystalline rocks, such as granite and gneiss, takes place through existing cracks. Due to these existing cracks, the periods for time to decay may be shorter in crystalline rocks than clay or salt but enhanced carbon-14 gas transport is less likely especially not with the hydrogen generation rates used for Figure 7-1.

The assumption for the reactive surface area depends on how the waste is disposed but in orders of magnitude  $1 \text{ m}^2$  per  $1 \text{ m}^2$  in the two calculated cases is a reasonable assumption but there is also literature in which other assumptions are made. For example, compacting claddings will increase the amount of steel per volume. If it is assumed that both sides of the cladding are being exposed to concrete pore water i.e. taking no credit for the potential closing off access to surfaces by the high compaction force, then the assumed reactive surface area can increase one order in magnitude. The hydrogen solubility at depth can be exceeded as calculated for carbon steel in the above figure for the host rock in the vicinity of 20 meters near the disposal gallery. Gas enhanced carbon-14 transport is then expected.

## 8 Neutron irradiated Zircaloy

### 8.1 Bounding carbon-14 inventory

In water-cooled nuclear power plants, zirconium based (hafnium-free) cladding is preferred over stainless steel claddings due to its transparency for neutrons. In addition, Zircaloy has also a better corrosion resistance than stainless steel and therefore preferred to limit cladding failure [IAEA, 2004a]. Zircaloy-2 is used in fuel claddings for Boiling Water Reactors (BWR). Zircaloy-4 is frequently used in claddings for Pressurised Water Reactors (PWR). The typical thickness of a BWR cladding is 0.81 to 0.86 mm and for PWR cladding 0.57 to 0.64 mm [Gras, 2014]. An oxide layer is formed at the interface between the fuel and internal side of the cladding and on the outside of the cladding interfacing the moderator water. The corrosion thickness of these claddings is limited, lenticular nodules at the outside of the cladding with a maximum size of about 100  $\mu\text{m}$  can be formed. These nodules are parts of  $\text{ZrO}_2$  (zirconia) that spall off and are released in coolant water. Preliminary Japanese measurements indicate that the presence of carbon-14 is higher in the remaining oxide layers but the majority of carbon-14 is present in the bulk of non-oxidised Zircaloy. The higher oxygen content has been attributed to this localisation. The thermal cross section used for the calculations was 0.235 barn [Gras, 2014] i.e. a thousand times larger than the recently updated oxygen-17 ( $n,\alpha$ ) cross section shown in Figure 2-1.

Another use of Zircaloy in a nuclear reactor is the pressure tube. CANDU reactors and reactors developed in the USSR have the fuel bundle in a pressure tube made of Zr-2.5%Nb. Pressure tubes have distinct different dimensions to claddings and are used for a longer period than fuel elements in Light Water Reactors. Zircaloy-2 is also used for a pressure tube. In CAST, there is a focus on various Zircaloy claddings (Zr-2, Zr-4, M5<sup>TM</sup>).

## 8.2 Presence of nitrogen and carbon-14 in processed Zircaloy

In Chapter 2, it was explained that the neutron reaction cross sections and natural abundance are responsible for carbon-14 production i.e. the chemical contents of carbon and oxygen need to be respectively five and seven orders in magnitude larger than nitrogen in order to contribute to the same carbon-14 content in waste. Reducing conditions are necessary to make Zircaloy and therefore oxygen content is limited. Nitrogen is incorporated in the fabrication process of Zircaloy, it is present in zirconium sponge ingot and melt [Akhtar, 2005]. In the state of the art report made at start of the Carbon-14 Source Term project a maximum in 80 ppm, 270 ppm and 1600 ppm for nitrogen, carbon and oxygen in Zircaloy is described based on vendor (contractual) specifications. Nitrogen is soluble in Zr up to 4%, which is much higher than the level at which it is controlled to as an impurity, so all nitrogen should be in solid solution. Carbon has a low solubility in  $\alpha$ -Zr (till 100 ppm) and so it is generally present in the form of small precipitates of carbide fcc-ZrC [Gras, 2014]. Consequently, nitrogen will be the main precursor for the carbon-14 and carbon-14 will (become) present as a small precipitate (fcc-ZrC) due to the low solubility of carbon in  $\alpha$ -Zr. In CAST, attempts have been made to measure the presence of carbon in Zircaloy. The interpreted measurements suggest that ZrC is present as a precipitate [Druyts, 2016].

The maximum in nitrogen content was also used more than 30 years ago. In a previous EU research project, 80 ppm was set for Zircaloy-2 [Bush, 1984]. Zircaloy-2 is used in Boiling Water Reactors (BWR) and Zircaloy-4 in Pressurised Water Reactors (PWR). Both types of Zircaloy contain more than 97.5 weight percent Zr but in Zircaloy-4, nickel is reduced till impurity levels to reduce the hydrogen uptake during its oxidation in PWR primary water [Gras, 2014].

In France, to reduce conservatism, a more realistically average grade of activated elements was sought, already in 2004. For Zircaloy-4, an analysis of 100,000 fuel assemblies manufactured (in France) over 21 years was made. The nitrogen content was  $34 \pm 10$  ppm [Gras, 2014]. Later on, also in other countries, the nitrogen content in French Zircaloy-4 was analysed and compared with certified values. A certified value of  $N_2$  of 56.00 ppm (i.e. 112 ppm N) was given and a value of  $51 \pm 2$  ppm was measured using a carrier gas melt

technique based on standard ASTM specification published in 1973 for quantitative determination of gaseous impurities in metal and alloy solid samples [Akhtar, 2005]. Consequently, the nitrogen content remains at impurity level but its content can also exceed 100 ppm. Nevertheless, Zircaloy claddings contain about a 10 fold smaller nitrogen content than stainless steel. The calculated carbon-14 activity concentration is in the order of  $10^4$  Bq per gram solid matter using 80 ppm nitrogen [Gras, 2014].

From an IAEA study performed more than a decade ago, in a LWR, the zircaloy cladding is the dominant source of carbon-14 and contains approximately 50–60% of its total amount of carbon-14 generated in a nuclear plant [IAEA, 2004a]. Elimination of the nitrogen impurities in the cladding is therefore expected to contribute to the largest reduction on the carbon-14 generation in a nuclear plant. Research to eliminate nitrogen impurities in order to obtain so-called nitrogen and hafnium free zirconium claddings may be more successfully realised by incorporating an operation issue. Nitrogen has been found to be detrimental to the corrosion resistance [Akhtar, 2005]. For waste generators it can therefore be beneficial to have a (further) minimization in nitrogen content in order to (further) reduce the possibility of defective fuel claddings during operation. Zirconium material containing as little as 50 ppm nitrogen is noticeably less corrosion resistance in water at 316°C (i.e. temperature in core of PWR ) than material containing 10 to 20 ppm nitrogen [Akhtar, 2005].

In some countries, spent nuclear power fuel is reprocessed. From a study performed in 1998, the reprocessing plants are estimated to dominate the airborne carbon-14 release in the absence of control from reactors and reprocessing plants [IAEA, 2004a]. In a reprocessing plant, the fuel is almost dissolved completely in hot nitric acid, less than 1% of the fuel inventory is present in processed waste containing Zircaloy [Capouet, 2017]. Under the oxidizing conditions in the dissolution step, carbon-14 is almost completely oxidised to CO<sub>2</sub> which is liberated into the dissolver off-gases. Carbonate precipitation and other separation methods will result in a discharge of carbon-14 to the atmosphere of less than 2% of the generated carbon-14 [IAEA, 2004a].

### 8.2.1 Samples in CAST

At 8 research institutions, experiments are performed with Zircaloy in CAST. The sample descriptions with which experiments are performed in CAST have been described in the first, second and third Annual Progress Reports [Necib, 2014, 2015 and 2016] and CAST report 3.2 [Caron, 2014]. Processed hulls have been provided by AREVA for research performed in CAST by CEA and Subatech. These hulls have been neutron irradiated in PWRs in France and Switzerland and have undergone industrial treatment in AREVA-La Hague reprocessing plant. For other Zircaloy samples, the specified nitrogen content was reported. The nitrogen content was specified as smaller than 50 ppm for Zircaloy-4 in Belgium and smaller than 80 ppm in Germany [Caron, 2014].

### 8.2.2 WMO in CAST

The nitrogen impurities in Zircaloy are based on literature values by the Swiss, Japanese, Belgian, Spanish and French waste management organisations. The range in nitrogen impurities is 30-100 ppm [Capouet, 2017]. The activity concentration of carbon-14 was in the order of  $10^4$  Bq per gram solid matter. This activity concentration is an order in magnitude smaller than the activity concentration in steel core internals.

### 8.2.3 First Workshop

In countries where only spent fuel is disposed, such as Finland, the waste package is engineered to contain the waste for several half-lives of carbon-14. Detailed knowledge of carbon-14 in Zircaloy may not be generated. It can be a more cost-effective measure to gain knowledge about the details of the carbon-activity concentration in Zircaloy for countries that have to or want to dispose processed waste if a less costly engineered containment for processed waste than spent fuel can be used.

The nitrogen content of Zircaloy claddings were supplied by Belgian WMO with a conservative value of 80 ppm and the Hungarian WMO with a value of 25 ppm as specified by the supplier.

For processed waste, the French reported a carbon activity of 20 GBq for each CSD-c and the Dutch and German reported both an activity of 14 GBq for each CSD-c. CSD-c is the French abbreviation for Colis Standard Déchets-compactés (Compacted-Waste Standard Residue). A value of 14 GBq for each CSD-c is a so-called typical value for a PWR with 900 MW. The French reactors can also have a higher power i.e. 1300 MW [Caron, 2014] which might be an explanation for the higher carbon-14 activity concentration. Zircaloy is the main material by weight in a CSD-c. The Inconel end pieces and grid spacers are also parts of the fuel elements and contained in CSD-c. Technological waste arises due to the reprocessing process such as pumps and filters. It is unknown whether the solid precipitated carbon-14, similarly as the iodine immobilization products, contributes to the technological waste.

### **8.3 Potential release mechanism of carbon-14**

The chemical changes during neutron irradiation for Zircaloy are important for the identification of the potential release mechanism of neutron irradiated Zircaloy and are therefore first described. During neutron irradiation of the fuel elements, hydrogen (tritium) and oxygen are released from the fuel. The oxygen causes internal oxidation of the cladding, the dense oxide layer at the inside stabilizes with a thickness of around  $9 \pm 2 \mu\text{m}$  [Gras, 2014]. Tritium, a ternary fission product, reacts with the zirconium alloy cladding to form a hydride, lessening the release of tritium to the reactor coolant [IAEA, 2004a]. The amount of tritium generated at e.g. 45 GWd/tU is  $1.3 \times 10^{17} \text{ } ^3\text{H}$  per  $\text{cm}^3 \text{ UO}_2$ . The hydrogen concentration would not be larger than 1 ppm if this amount was all released and retained in the cladding using the following typical values for fuel assemblies 521.36 kg  $\text{UO}_2$  and 106 kg Zircaloy [Gras, 2014]. The hydrogen content measured in the neutron irradiated cladding can be several hundred times larger to 1000 ppm. Consequently, ternary fission products are not the prime source of hydrogen in the cladding. In the state of the art report made at the start of CAST [Gras, 2014], a fraction of the hydrogen generated by corrosion of Zircaloy on the outside of the cladding is assumed to be picked-up by the cladding in order to understand the measured hydrogen contents.

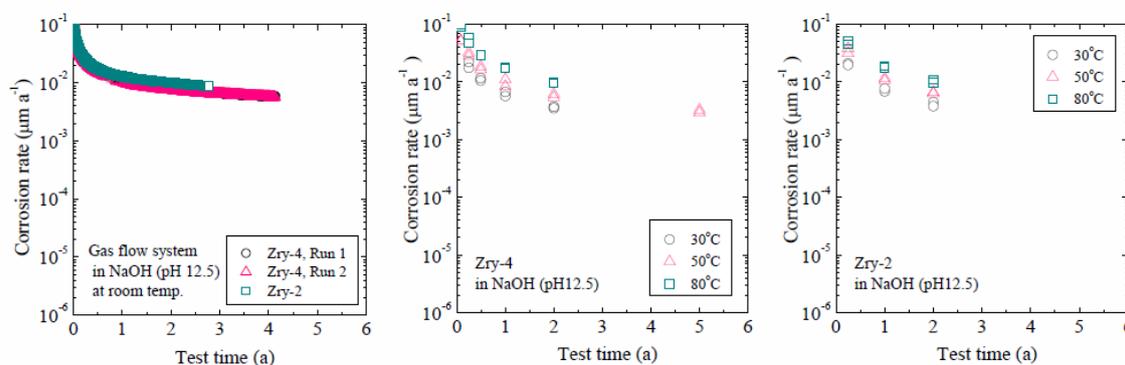
This hydride formation can be understood from thermodynamic considerations. Hydride formation with Zr has been known for decades [Lacher, 1937]. The solubility of hydrogen in Zircaloy increases exponentially with increasing temperature. Consequently, during unloading or after a reactor cycle, the amount of dissolved hydrogen may exceed the solubility limit by which zirconium-hydrides are formed. The collected micrographs from French reports show the presence of hydrides circumferentially oriented and concentrated in the cold periphery of the cladding of fuel rods unloaded from reactors [Gras, 2014]. The oxide layer on the cladding made during corrosion of Zircaloy at nuclear plant conditions has a maximum in thickness to 100  $\mu\text{m}$  [Gras, 2014]. The oxide layer can provide delay to the release of radionuclides [Necib, 2014]. This delay may be used for spent fuel for which there is no argument why the layer can be damaged. For processed waste, the oxide layers can be expected to be damaged due to the cutting, shearing and high compaction. The main reactive surface area may be Zircaloy. The hydrogen pick-up ratio for Zircaloy reaches values of about 90% in alkaline and pure water between 30°C and 50°C. The non-corroded metal of hulls may be partially transformed into brittle zirconium hydrides as it corrodes [Necib, 2015]. This will generate on the surfaces of hulls a high density region of hydrides acting as a brittle layer, and presumably having a corrosion behaviour different from that of zirconium metal. For Zircaloy, estimating the corrosion rate by the hydrogen released from the solution needs to be corrected for this hydrogen uptake. Unlike steel, corrosion rates can be underestimated by measuring the released hydrogen [Gras, 2014]

#### **8.4 Potential speciation**

Release of carbon-14 from Zircaloy at disposal conditions has not yet been measured in CAST [Necib, 2016]. The work to measure carbon-14 speciation is still in progress. It is expected that the chemical forms of carbon-14 during anaerobic corrosion are presented at the CAST Final Symposium. The potential speciation of carbon-14 from Zircaloy is therefore assumed to be the same as described for steel in paragraph 7.5.

## 8.5 Source Term

As described in 8.1, Zircaloy is preferred in a nuclear power plant instead of stainless steel due to its corrosion resistance. Also at disposal conditions, the corrosion rates are smaller than stainless steel [Yu, 2012]. At start of CAST, the corrosion rates for Zircaloy claddings was deduced from a literature review to be 1 to 2 nm per year after a few years of corrosion testing [Gras, 2014]. The experimental research performed in CAST provides further confidence in these low corrosion rates. These experiments are performed at a pH of 12.5 with a saturated calcium-hydroxide solution or sodium-hydroxide solutions [Druyts, 2016]. Figure 8-1 shows the decrease of an order in magnitude in the corrosion rate of unirradiated Zircaloy in NaOH solutions at different temperatures ranging from 30°C to 80°C. The result highlights the influence of temperature on the corrosion rate; higher temperatures tend to increase slightly the corrosion rate.



**Figure 8-1. Corrosion rate measured in alkaline conditions from the Japanese programme [Druyts, 2016] representative for cementitious materials containing  $\text{Ca}(\text{OH})_2$ .**

The corrosion rate of Zircaloy can suddenly increase in  $\text{CaCl}_2$  solutions with a concentration higher than 0.05 M caused by the formation of a ternary complex  $\text{Ca}_3[\text{Zr}(\text{OH})_6]^{4+}$  [Gras, 2014]. For disposal facilities built or intended to be built in saline environments with a chlorine concentration larger than 0.1 M and Zircaloy waste processed with cementitious materials, the corrosion rate in  $\text{CaCl}_2$  solutions can be of importance. For example if the

salinity is equal to the chlorine concentration in seawater of about 0.53 M then the calcium concentration in cementitious materials needs to limit the  $\text{CaCl}_2$  concentration. The pore water in cementitious materials is saturated with calcium ions is 0.0405 M in Portland based cement due to the presence of  $\text{Ca}(\text{OH})_2$  [Kurstien, 2015]. In low pH cements, for example blended cements, the calcium concentrations are determined by equilibrium with CSH phases. The equilibrium concentration of calcium ions is smaller [Gascoyne, 2002]. A smaller calcium equilibrium concentration is also expected in degraded Portland cement based concrete when exhausted in  $\text{Ca}(\text{OH})_2$ . The Finnish contribution in the present running EU research project Cebama shows calcium concentrations in equilibrium with CSH phases with a maximum of 0.02 M. A sudden increase of Zircaloy corrosion rates can be excluded by the choosing the waste packaging material on the chemical understanding of the disposal environment.

The technical work on Zircaloy in CAST is solely devoted to this metal. Zircaloy is however never solely disposed but always in combination with other metals. It is uncertain whether the carbon-14 source term is mainly determined by Zircaloy for spent fuel and processed waste. The nitrogen content in Zircaloy claddings is expected to be at least one order in magnitude smaller than the Inconel / Stainless steel ends and grid spacers. The ten-fold smaller corrosion rate of Zircaloy and ten-fold smaller nitrogen content in Zircaloy may result in a smaller carbon-14 release rate from Zircaloy than the stainless steel in a fuel assembly.

The metallic density for processed waste is larger than this density for spent fuel. Consequently, the need for the knowledge concerning potential hydrogen formation becomes more important to assess the potential of the enhanced carbon-14 transport. If it is assumed that both sides of the cladding are exposed to (evolved) concrete pore water, i.e. taking no credit for the potential closing off the access to surfaces by the high compaction force, then the reactive surface area for a CSD-c with a typical weight of 393 kg would be about 200 m<sup>2</sup>. With these assumptions, the combination of the reactive surface and low corrosion rate, the hydrogen profile would be between stainless steel and carbon steel as calculated in Figure 8-1. In many disposal concepts, several CSD-c are to be disposed in a larger waste package. The calculated hydrogen generation rates by taking no credit for the

potential closing off, is not expected to be sufficiently dissipated by diffusion. In addition, the hydrogen-pick by formation of zirconium hydrides that would reduce to amount of hydrogen released from Zircaloy is neglected.

For the carbon-14 source term of processed waste for example CSD-c, there is an additional uncertainty whether carbon-14 in Zircaloy is the main contributor to the carbon-14 activity; the Inconel ends and, if included in the waste product, the Ba/Ca carbonate precipitated from  $^{14}\text{CO}_2$  dissolver off-gas in the reprocessing plant [IAEA, 2004] may also contribute to this activity. Assuming stainless steel having similar corrosion rates as Inconel, the corrosion rate is an order in magnitude larger. In addition, the nitrogen content of stainless steel appears to be larger than Zircaloy, but the reactive surface area of Inconel may be smaller than Zircaloy. If the main contributor to the carbon-14 activity is the Ba/Ca carbonate precipitate, then the carbon-14 source term is determined by the dissolution rate of the precipitate i.e. another release mechanism in which no hydrogen is formed and only inorganic carbon-14 release is possible. Such inorganic carbon can also be retarded in cementitious materials [Wang et al in NEA, 2012].

## 9 Spent ion exchange resins

### 9.1 Bounding carbon-14 inventory

Ion exchange resins are used to reduce the volume of waste by concentrating the radionuclides from fluids, for example, the moderator water. The most common form of synthetic ion exchange resins is polystyrene divinylbenzene in powdered form with diameters from 5-150  $\mu\text{m}$  or in beads from 0.5-2 mm. The resins have functional groups that are to be exchanged with a radionuclide. When the functional groups are negatively charged, the exchange will involve cations and when they are positively charged, they involve anions. Carbon-14 will be present in water as an anion. The airborne releases for BWR are mainly inorganic [IAEA, 2002; ISRN, 2010] and therefore the speciation in the liquid is expected to be mainly inorganic since carbon is in equilibrium between the gas and liquid phase. During waste processing, the drying of resins causes inorganic carbon-14 to be released and the organic fraction to be left on spent resins. Also bubbling with air enhances the release of inorganic carbon-14 in the form of  $\text{CO}_2$  [Aronsson, 2016]. For PWRs, mainly organic airborne releases are measured and mainly organic carbon-14 is assumed to be present in the liquid. But in the spent ion exchange resins in the French programme, inorganic carbon-14 can be a major compound in spent ion exchange resins before conditioning of the final waste in epoxy resins [Comte, 2017]. Due to the potential speciation of carbon-14 in the coolant and other fluids, carbon-14 is expected to be exchanged with a functional group in anion exchangers under the form of carbonate/bicarbonate (inorganic) or carboxylic acids. The common functional groups in anion exchangers bear nitrogen for example as an tertiary amino group. The affinity typically increases with increasing charge on the exchanging anion and increasing atomic number (decreasing hydrated ionic radii). For anions, a typical series for affinity is [IAEA, 2002:p.6]:



Carbon-14 as acetate has a weak affinity and as oxalate a strong affinity. Please note that inorganic carbon is not reported in this series but since  $\text{CO}_3^{2-}$  has a larger negative charge than acetate,  $\text{CO}_3^{2-}$  is expected to have a stronger affinity than acetate. In CAST, it was measured that most carbon-14 is present in inorganic form by cleaning reactor fluids [Rizzato, 2017].

In practice, the treatment of the fluid with spent ion exchange resins appears to have a huge impact on the carbon-14 content, for example drying can reduce the carbon-14 content by three orders of magnitude [Aronsson, 2016]. The inorganic carbon is shown to reduce after drying but not the organic fraction [Aronsson, 2016 & Comte, 2017]. Also during storage,  $\text{CO}_2$  can be measured to be released [Bucur, 2017].

Carbon-14 is assumed to come from neutron activation of isotopes present in the coolant. Oxygen-17 is considered to be the only source [Aronsson, 2016] and Heavy Water Reactors – moderated with  $\text{D}_2\text{O}$  – are assumed to produce more carbon-14 than Light Water Reactors – moderated with  $\text{H}_2\text{O}$  – since the deuterium enrichment causes oxygen to be chemically enriched about 55% above the natural level [IAEA, 2004a]. During CAST, the NEA OECD has re-evaluated neutron cross sections including that of oxygen-17. As described in Chapter 2, for neutrons with an energy smaller than 1 MeV, thus including thermalized neutrons, the neutron reaction to carbon-14 cross section of oxygen-17 has reduced three orders in magnitude. A chemical concentration of more than 0.1 ppm nitrogen in the coolant is sufficient to supersede the carbon-14 generation by neutron activation of oxygen-17. In the previous chapters, it was described that corrosion products spall off in the coolant. Consequently, neutron activated radionuclides like carbon-14 but also cobalt-60 and zirconium-93 become present in the coolant. The contribution of carbon-14 in the coolant by corrosion of Zircaloy cladding and stainless steel inside the reactor vessel may become more predominant if adequate measures are taken to prevent air ingress and if  $\text{LiOH}$  is used to control the pH. The high impact of waste processing on the carbon-14 content in the waste product make it too difficult to bound the carbon-14 inventory in spent ion exchange resins.

## 9.2 Potential presence of nitrogen in coolant

During reactor operations, the pH of the coolant is controlled by adding chemicals. These chemicals can or could contain nitrogen. The pH control of the primary coolant in Western PWRs is carried out by lithium hydroxide instead of hydrazine ( $\text{NH}_2\text{-NH}_2$ ), to prevent the formation of  $^{14}\text{C}$ . LiOH can also be depleted in  $^6\text{Li}$  to limit the formation of tritium since neutron activation reaction in LWRs is  $^6\text{Li}(n,\alpha)^3\text{H}$ , with a (thermal) cross-section of 942 barn. Air ingress, especially in the moderator and primary coolant systems, has been found to be one of the sources of  $^{14}\text{C}$  production during reactor operation. Improving the system design to minimize the potential for air ingress will therefore reduce  $^{14}\text{C}$  production and release [IAEA, 2004: p.38]. Cleaned coolant water is expected to be discharged from the plant and not to be used again as a coolant, the functional groups in anion exchangers containing nitrogen can become the main nitrogen source if the cleaned coolant is re-used again.

### 9.2.1 Samples in CAST

In 7 organisations, spent ion exchange resins are investigated. The sample descriptions with which experiments are performed have been described in the state of the art [Rizzato, 2015] and the first, second and third Annual reports, [Reiller, 2014], [Bucur, 2015], [Comte, 2017] and in the compilation of the data in WP4 [Rizzato, 2017]. The resins investigated in CAST are mainly beads. The carbon activity concentration expressed per gram of spent ion exchange resins (dry and wet) have become available from the French programme but more work is needed to understand the analytical problems evidenced in wet and dried samples. The order of magnitude in activity concentration was  $10^3$  Bq per gram of wet and dry resin [Rizzato, 2017]. Combustion with oxygen yielded a higher measured carbon-14 activity concentration than acidic dissolution [Comte, 2017] but the order of magnitude of the measured carbon activity concentration is the same. The benefit of the determination of carbon-14 activity concentration using the acidic dissolution methodology is that the

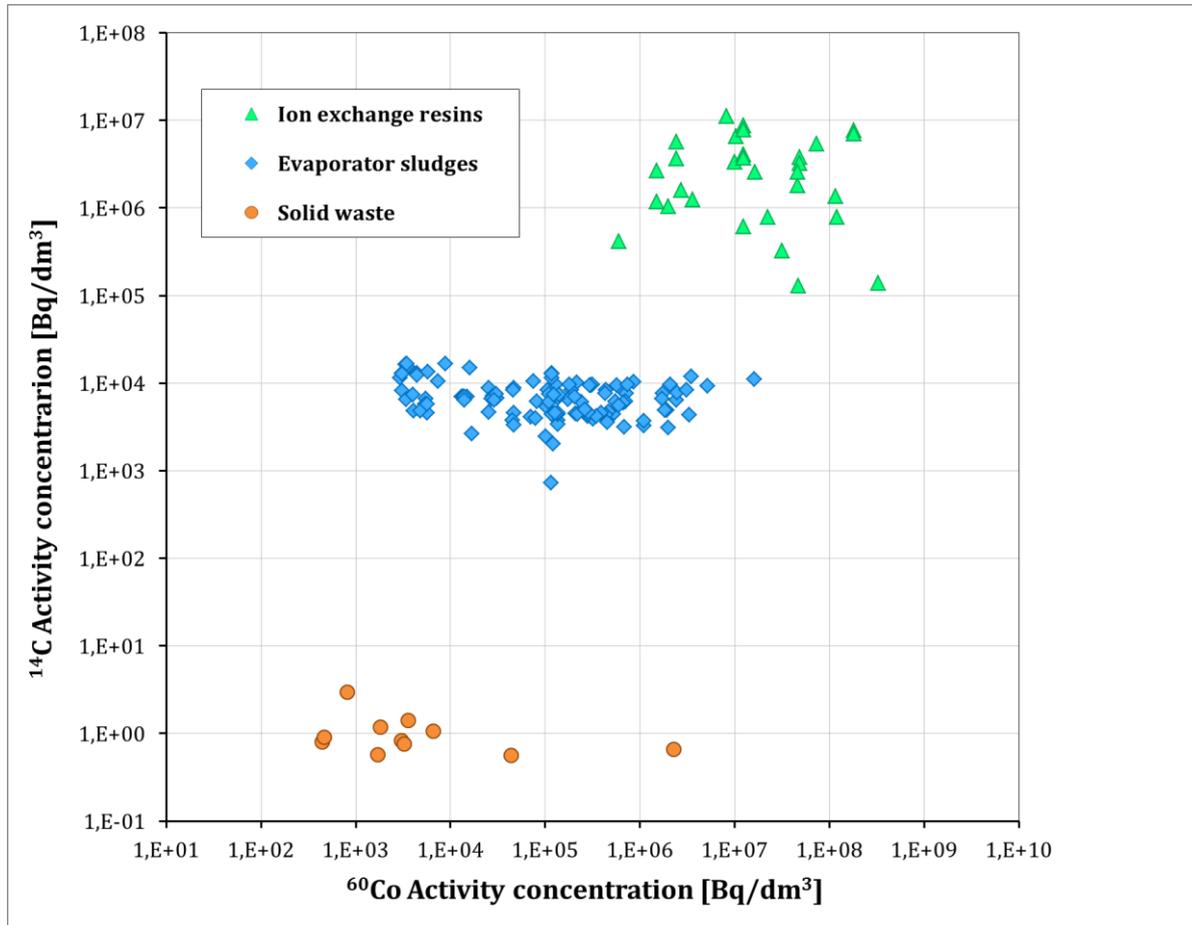
carbon-14 activity can be discriminated between inorganic and organic carbon. Another explored technique in CAST was desorption of carbon-14 using LiOH 1M solutions. A smaller carbon-14 activity than with combustion with oxygen is then obtained [Comte, 2017].

### 9.2.2 WMO in CAST

Measurements of the resins used to clean the PWR coolant have been contributed by the Swedish and French waste management organisations with the same order of magnitude as measured in CAST:  $10^3$  Bq per gram resin.

### 9.2.3 First workshop

Resins are processed with sludge with cementitious materials in some countries. It becomes then important whether sludge or resin would dominate the carbon-14 activity. The carbon activity in sludge or evaporator concentrates can be two orders of magnitude larger than in resins for example as measured in Lithuania [Mazeika, 2010]. These resins may be a mixture to clean water in general and not specific for a coolant. In the Hungarian programme, the carbon-14 activity of resins used to clean the coolant is shown together with sludge. At the first workshop, the Hungarian waste management organisation PURAM, shared their experience with the systematic sampling of spent ion exchange resins, sludge and other solid waste. Figure 9-1 clearly shows at least a two orders of magnitude difference of cobalt-60 activity for a similar carbon-14 activity.



**Figure 9-1 Carbon-14 and Cobalt-14 activity in different operational radioactive waste streams from PURAM.**

The scaling factor is not applicable. This inapplicability can also be understood since cobalt is not generally present as anion in mildly acidic to mildly basic aqueous environments, it is present as cationic or neutral dissolved complex. The presence of cobalt-60 is either in the cation exchanger or in the water but not as an anion in spent anion exchangers. Consequently, cobalt-60 cannot be a chemical analogue of the carbon-14 distribution.

### 9.3 *Potential presence of carbon-14 in spent ion exchange resins*

A mineral or inorganic form of carbon-14 is present but is weakly bound and can be released during waste storage (bubbling) and waste processing (drying). The organic fraction is more strongly bound and not expected to be released during waste processing. It depends on the waste processing procedures whether inorganic or organic carbon is the major compound. For example in the Swedish program for resins used to clean PWR coolant 30% organic carbon is deduced from measurements [Aronsson, 2016]. In the first workshop, 15% organic carbon has been assumed for the assessment presented by the Finnish waste management organisation Fortum Power and Oy [Buckau, 2016]. In the French results, there is a high variance in the organic carbon content since the SIER is a mixture of cleaned reactor fluids anywhere in the reactor not just the coolant [Comte, 2017].

### 9.4 *Potential release mechanism of carbon-14*

During waste processing with cementitious materials, inorganic carbon-14 in the form of bicarbonate is thermodynamically expected to be present as carbonate due to the higher pH. The affinity in anions as described by IAEA (2002) can be used for a potential carbon-14 release mechanism. Carbonate ( $\text{CO}_3^{2-}$ ) is assumed to have a stronger affinity than bicarbonate ( $\text{HCO}_3^-$ ) due to higher negative charge. The waste processing with cementitious materials is expected to more strongly bind inorganic carbon-14 to the resins since  $\text{CO}_3^{2-}$  is thermodynamically the predominant carbon species at a pH larger than 10. Ingress of anions from the surrounding environments into the cementitious matrix can be exchanged with carbon-14 provided these anions have a stronger affinity. For fresh environments, the ingress of bicarbonate is not expected to exchange the bound  $\text{CO}_3^{2-}$ . For disposal in saline environments, sulphate resistance cement-based concrete is expected to be used by which delayed ettringite formation is not expected to occur. Ingress of chlorine and sulphate ions takes place but only sulphate ions are expected to be exchanged with  $\text{CO}_3^{2-}$ . Also for carbon-14 bound as a carboxylic acid, the release of carbon-14 is then dependent on the evolving chemical conditions of concrete. The organic carbon-14 speciation is however not

yet established and assuming it all to be acetate i.e. carbon-14 organic carbon with the smallest affinity may be the best approach.

If inorganic carbon is the major component in spent ion exchange resins, than in cementitious materials, carbon-14 is expected to be retarded – mainly through the precipitation of  $\text{CaCO}_3$ , and/or adsorption [Pointeau, 2008], the retardation factors for cementitious materials containing portlandite and CSH phases is in the order of  $10^3$  l/kg [Wang et al in NEA, 2012]. The period in time in which these cementitious minerals are no longer present depends on how fast the chemical evolution takes place i.e. a small period at the edges of the waste packages and a larger period slow in the core of this package.

For organic carbon, retardation factors as a function of the presence of cementitious minerals is not available but earlier work in the previous century investigated the precipitation of carboxylic acids such as oxalate in cementitious environments [Loon, 1995]. In the assessment presented by the Fortum Power and Oy at the first workshop, the carbon-14 release is determined by diffusion in concrete. For the carbon-14 activity concentration, 15% is assumed to be organic carbon. For organic carbon, very small retardation values are used, by which the release rate of carbon-14 to the biosphere is dominated by organic carbon-14. Inclusion of exchange  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  of carbon-14 containing anions such as acetate and oxalate and their potential precipitation with  $\text{Ca}^{2+}$  present in cementitious pore water would make the estimate less conservative but makes the calculation more complicated.

## 9.5 Source Term

Resins are organic matter and are therefore considered as a potential food source for microbes in the EU research project MIND but the usable energy for microorganisms would barely be sufficient to breakdown ion exchange resins [Abrahamsen, 2015]. The microbial degradation in intact cementitious materials is also expected to be limited due to space restriction. The chemical resistance of resins is generally larger than inorganic ion exchangers and resins are therefore preferred [IAEA, 2004]. Chemical degradation of

organic materials can be initiated by a nucleophilic attack of OH<sup>-</sup> ions on a carbon atom with a partial positive charge. Such carbon atoms are generally not present in polystyrene, the basic material for ion exchange resins [Loon, 1995 & Abrahamsen, 2015]. A degradation rate of resins representative for the disposal conditions is therefore not yet available. The potential formation of organic gaseous products during disposal is absent and any CO<sub>2</sub> is expected to be released during the waste processing.

There is a maximum amount in processing resins with cementitious materials to prevent crack formation of the waste matrix due to the swelling pressure of the resins. A maximum in 20 vol% is recommended [Matsuda, 1992]. Due to this processing, the carbon-14 activity in processed waste by resins can be an order of magnitude smaller than the one measured in resins. Resins used to clean BWR coolant are measured to contain mainly inorganic carbon-14: 95-99% [Aronsson, 2016]. CO<sub>2</sub> is in equilibrium with HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. The potential CO<sub>2</sub> release is a bounded fraction of dissolved inorganic carbon and inhibited in concrete. The carbon-14 source term of spent ion exchange resins processed with cementitious materials is expected to be very small compared to neutron irradiated stainless steel due to:

- the smaller carbon-14 activity concentration;
- potential lack of gaseous products such as hydrogen during chemical degradation by which enhanced gas transport can occur;
- carbon-14 release can only be in ionic form since carbon-14 is exchanged present as an ion in ion exchangers i.e. gaseous carbon-14 can be excluded;
- high chemical resistance of resins by which its chemical degradation rate has not been measured yet therefore the best estimate of its potential release may require ingress of anions such as sulphate and chlorine. For low permeability concrete such as low pH blended cements, a sufficient ingress of these anions may require several half-lives of carbon-14.

## 10 Neutron irradiated graphite

### 10.1 Bounding carbon-14 inventory

Graphite was extensively used in the very first generation of nuclear reactors for moderation of fission neutrons in the reactor core. It was mentioned in Chapter 2 that the neutron capture cross section of carbon is extremely low. That allowed the use of natural, non-enriched uranium fuel in the graphite moderated reactors [Lensa, 2011]. Graphite as moderator and reflector was used in gas-cooled reactors (Magnox, AGR, UNGG, HTR), water-cooled reactors (RBMK), High-Temperature Reactors (HTR) and diverse Material Test Reactors (MTR). Many of these facilities are facing decommissioning and large quantities of irradiated graphite have to be managed. Therefore, irradiated graphite is investigated in CAST WP5 to enhance the understanding of the factors determining release of carbon-14 from irradiated graphite.

The irradiation of graphite within a reactor can potentially lead to three types of changes in the material: 1) damage caused by fast neutron irradiation and 2) chemical changes produced by the irradiation chemistry lead to physical, mechanical and thermal property changes; and 3) activation of impurities and transported materials deposited in the graphite pores lead to induced radioactivity.

The activity of carbon-14 in the irradiated graphite depends on the location in the reactor core, operating power history, initial concentration of impurities, amount and composition of surrounding media. Carbon-14 is produced in the irradiated graphite from carbon-13, nitrogen-14 and oxygen-17 mainly. It is known that the reaction  $^{14}\text{N}(n,p)^{14}\text{C}$  is the main contributor to carbon-14 generation due to the high neutron reaction cross section and isotopic abundance of nitrogen-14.

The fraction of carbon-14 produced from the raw carbon activation may be calculated quite precisely as the quantity of carbon in graphite is almost invariant and comprises about 99.9% of mass, while the fraction coming from impurities (nitrogen and oxygen) activation

may differ depending on these impurities initial content and adsorption from surrounding media in graphite pores and can additionally increase the quantity of impurities and consequently increase carbon-14 production [Narkunas, 2010].

The distribution of carbon-14 in the core approximately follows the distribution of thermal neutron flux, i.e. carbon-14 specific activity is higher in the central part of the reactor and decreases in the periphery. Carbon-14 arising from carbon-13 is distributed near-homogeneously throughout the graphite since carbon-13 is intrinsically present within the graphite material. Carbon-14 produced from activation of nitrogen-14 is distributed mainly on the graphite surface layers, which includes not only the outer geometrical surface but surfaces present in the extensive, complex pore structure [Payne, 2015].

The irradiated graphite from thermal column of the Rossendorf Research Reactor (RFR) was analysed by the FZJ (Germany) in CAST. It was known from previous studies that activation products are distributed in irradiated graphite inhomogeneously and usually are present in the form of hot-spots. Investigations of elemental composition in the hot-spot regions demonstrated that the increased activity in these areas was due to carbon-14 bound to the surface of the pore, what is in line with the assumption that the highest fraction of carbon-14 inventory is originated from the activation of nitrogen-14 or oxygen-17 trapped in the pores or absorbed on the pore surface [Shcherbina, 2017].

## **10.2 Presence of nitrogen in graphite**

Though the nuclear graphite is a very pure material, it still contains some impurities and from the generation of carbon-14 point of view the nitrogen-14 impurities are of the greatest concern. Nitrogen-14 is trapped in the pores of graphite at the time of manufacture, component assembly and storage or delivered to the graphite pore surfaces from the coolant.

Investigations on the nitrogen content in an unirradiated nuclear-grade graphite material performed in Japan revealed that the overall nitrogen content of a graphite block was about 44 ppm and the content was unchanged on heating to 400°C, implying that the nitrogen is present as a chemisorbed species. From analysis of nitrogen-14 distribution with depth it was concluded that nitrogen-14 is most concentrated on the surface and at depths greater

than 30 nm the concentration decreases to a background level [AMEC, 2016]. Similar results were obtained from German experiments with irradiated and unirradiated reflector graphite from experimental reactor.

The highest measured nitrogen precursor concentration in unirradiated samples for UK AGR core graphite was 15 ppm and this value was used to estimate the carbon-14 inventory in all stations with AGR [AMEC, 2016].

Determination of nitrogen concentration in irradiated graphite sometimes is back-calculated from measured activities of carbon-14. An example in this case could be estimation of nitrogen impurities in UK Magnox core graphite. The measured activities of carbon-14 in samples taken from six Magnox stations varied from  $4.66 \cdot 10^4$  to  $1.49 \cdot 10^5$  Bq/g. These measurements were used to calculate potential concentration of nitrogen impurities. It was determined that a nitrogen precursor concentration of 25 ppm was sufficient to give rise to the measured carbon-14 activities [AMEC, 2016]. In addition, samples of unirradiated graphite manufactured at the same time and from the same materials as used in the graphite cores were analysed and it was estimated that concentration of nitrogen ranged from 5 to 13 ppm [AMEC, 2016].

Similar approach was used to estimate nitrogen impurities concentration in RBMK reactor graphite in Lithuania. Based on experimental measurements of carbon-14 inventory in the graphite rings/sleeves samples, a back-calculated nitrogen concentration was 13 ppm [Toulhout, 2015].

For the air-cooled reactors the fact that graphite pores are filled with air and this provides a substantial additional source of nitrogen should be taken into account. When estimating carbon-14 inventory in the UK Sellafield core graphite, an equivalent bulk nitrogen impurity in the graphite of 110 ppm was used assuming 10 ppm 'native' impurity plus 100 ppm from air in the pores [AMEC, 2016].

In the absence of manufacturer specification or measurements on nitrogen-14 impurities in the graphite, carbon-14 inventory is calculated based on nitrogen impurity data from literature survey, e.g. nitrogen-14 content for the typical RBMK graphite composition

reported in the literature varies from 0.5 to 70 ppm and the upper value is used conservatively to calculate the carbon-14 inventory [Ancius, 2005].

### 10.2.1 Samples in CAST

At 6 research institutions, experiments are performed with graphite in CAST. The experimental work comprises of investigations of inventory, leaching and speciation of carbon-14 from irradiated graphite and of graphite treatment. In addition, the data on carbon-14 release and speciation in French irradiated graphites is presented by ANDRA, EDF and CEA (France) [Catherin, 2016] as well as information on the release of gaseous carbon-14 during leaching of irradiated graphite samples from Oldbury Magnox power plant under highly alkaline conditions is reviewed by RWM (UK) [Toulhout, 2015]. The sample descriptions with which experiments are performed have been described in the first, second and third Annual Progress Reports of the CAST project [Norris, 2015a, 2015b and 2016] and in the CAST project reports [Fugaru, 2017, Shcherbina, 2017; Magro, 2017].

Irradiated graphite from research reactors for experimental work in CAST was used mostly. Irradiated samples from TRIGA reactor thermal column were investigated by RATEN ICN (Romania). FZJ (Germany) used irradiated graphite sampled from the thermal column of the research reactor RFR (Rossendorfer Forschungsreaktor). CIEMAT (Spain) used irradiated graphite from Vandellós-I NPP (UNGG reactor). The irradiated graphite grades, which were investigated by IFIN-HH, have been taken from the thermal column of the VVR-S research reactor. Unfortunately, the nitrogen content in the samples is not reported. The carbon-14 activity concentrations of the samples in Bq per gram were as follows:

- $451 \pm 16.5$  Bq/g (average activity, RATEN ICN, Romania);
- $(1.21 \pm 0.21) \cdot 10^4$  Bq/g (average activity, FZJ, Germany);
- from  $1.08 \cdot 10^4$  to  $1.35 \cdot 10^4$  Bq/g (CIEMAT, Spain);
- from 213 to  $7.49 \cdot 10^4$  Bq/g (IFIN-HH, Romania).

### 10.2.2 WMO and RE in CAST

Specific activity of carbon-14 in i-graphite as considered by the participants of the CAST project varies in a wide interval: from 1 Bq/g to  $10^6$  Bq/g [Catherin, 2016; Kendall, 2015, Capouet, 2017]. This variation reflects not only the differences in the origin and the irradiation history of the graphite but also the differences in the assumptions when deriving the inventory. Specific activity of the irradiated graphite in France and Romania was estimated combining computation and radiochemical measurements. The upper value of  $10^6$  Bq/g corresponds to Lithuanian RBMK graphite; in the absence of data the specific activity in this case was calculated assuming maximal nitrogen-14 impurity reported in the literature, i.e. 70 ppm. However, during CAST project some results on activity measurements in irradiated graphite in Lithuania were obtained and the inventory was updated combining modelling and measurements results. The reassessed average specific activity of Lithuanian irradiated graphite is  $1.895 \cdot 10^5$  Bq/g [Narkunas, 2017].

### 10.2.3 First Workshop

According to the information presented mainly by the waste management organizations in the first CAST workshop, the carbon-14 content in the irradiated graphite waste is estimated in different ways: by activation calculations (UK, Hungary, Japan), from measurements (Romania, Spain), combining radiochemical measurements and computation (France), using scaling factors for operational waste (for graphite rings, Lithuania) or from comparison with the data from other reactors of the same type (Slovenia). Information about nitrogen-14 impurities in the presentations was not asked and perhaps therefore not provided.

Carbon-14 activity concentration of  $10^4$ - $10^5$  Bq per gram in the graphite waste is typical for the majority of the countries and that is in line with the information provided by WMO and RE in CAST. However, a certain fraction of graphite waste has considerably lower carbon-14 activity concentration – about 10-300 Bq/g. Some countries could not report the carbon-14 activity concentration in graphite or informed that such kind of waste is not present [Buckau, 2016].

### **10.3 Potential presence of carbon-14 in graphite**

Carbon-14 created by activation of carbon-13 will mainly be integrated into the lattice of graphite crystallites or as an interstitial atom between the graphene layers. Therefore chemical form of carbon-14 is primarily elemental and bound covalently in the graphite structure. This part of carbon-14 is mainly homogeneously-distributed throughout the graphite matrix. Carbon-14 generated from nitrogen-14 is, in contrary, heterogeneously distributed on graphite surfaces and enriched in hotspots [Toulhout, 2015]. According to analysis of the graphite from Tokai plant (Japan), nitrogen content from surface to about 30 nm in depth decreases. At a depth of more than 30 nm, the decrease flattens out. The variation of nitrogen concentration in the depth direction suggests that nitrogen molecules cannot penetrate interior of nuclear-grade graphite as it is protected by scale-like graphite plane [Takahashi, 1999].

Oxygen-containing surface species have been observed on irradiated graphites that are chemically similar to the intermediates formed on carbon surfaces during oxidation at elevated temperatures. The association of hydrogen with active carbon sites could provide a mechanism for the formation of hydrocarbons and/or other volatile organic species [AMEC, 2016]. Canadian studies on the CANDU reactors also pointed out that the carbon-14 atoms created in the graphite can be chemically bound with hydrogen, nitrogen or oxygen [Toulhout, 2015].

### **10.4 Potential release mechanism**

When the formed carbon-14 displaces a carbon-12 (or 13) atom in a graphite lattice position or penetrates into a sequence of stacking of layers in the crystal, it is considered that hardly any carbon-14 is released out from graphite crystalline matrices [Takahashi, 1999]. The removal of the bulk of the carbon-14 would only occur by oxidation / corrosion processes (with conversion to either  $^{14}\text{CO}$  or  $^{14}\text{CO}_2$ ) and associated mass loss. Radiolytic and general oxidation of graphite could occur during reactor operation. Oxidation can enhance release of carbon-14 and it also results in an increase of porosity and the opening up of closed pores within the graphite increasing the accessibility of carbon-14. On the other hand, it was observed that at high operating temperatures reordering of the graphite structure and re-

incorporation of displaced carbon-14 into the graphite matrix occurs, which makes carbon-14 less accessible [Toulhout, 2015]. When disposed in a deep geological repository, oxidation of graphite could be hardly expected as the graphite matrix is extremely resistant to oxidation at repository temperatures and is unlikely to undergo oxidation once conditions have become anaerobic after closure [Toulhout, 2015].

The release of loose bound carbon-14 on surfaces as well as from disturbed structures proceeds faster than the matrix bound carbon-14. The surface species are readily mobilised in contact with water. But it has to be mentioned that a fraction of carbon-14, which is 'sealed' in the closed porosity, is unlikely to be leached at all, as this area is not accessible to the leaching solution [Shcherbina, 2017].

Therefore, based on the available results of the chemical treatment studies it is suggested to distinguish three different forms of carbon-14 that may be present in irradiated graphite and differ in their accessibility and releasability on leaching [AMEC, 2016]:

- Carbon-14 bound up in the graphite matrix would be least accessible for release and would only be released via oxidation (or similar chemical process) processes of the bulk graphite;
- Carbon-14 in interstitial positions between graphene layers would potentially be accessible if degradation of the graphite structure occurs, e.g. by intercalation of anions between graphene sheets;
- Carbon-14 associated with pore surfaces, edge sites and less ordered regions of the graphite would be the most accessible for potential release.

The possible positions of carbon-14 are illustrated in Figure 10-1.

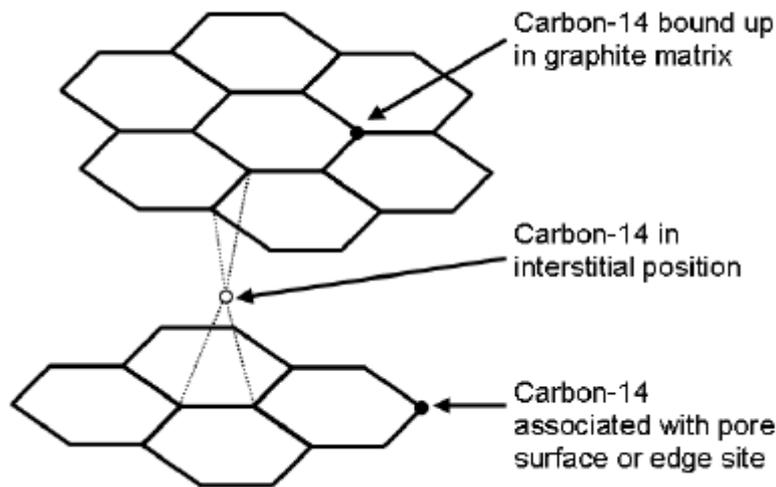


Figure 10-1 Carbon-14 potential locations in irradiated graphite [AMEC, 2016].

### 10.5 Potential speciation

Carbon-14 can be released from irradiated graphite as organic or inorganic species. The need to distinguish between these species is their different behaviour (e.g. sorption, solubility) in the environment (engineered and natural barriers).

The leaching experiments suggest that majority of carbon-14 release from irradiated graphite occurs to the solution phase and only small amounts of gaseous phase releases (about 1-5% of the released carbon-14) have been measured [Toulhout, 2015; Catherin, 2016].

There is evidence from separate studies that carbon-14 is released into the solution in organic as well as inorganic forms under alkaline conditions that prevail in a deep geological repository. According to information presented in [Toulhout, 2015], the inorganic form includes carbon dioxide, carbonate or bicarbonate. The organic forms that could be found are methane and other organic molecules, which are supposed to react in the long term and form methane or carbon dioxide. In case of slow degradation of irradiated graphite it is expected that mainly  $^{14}\text{CO}_2$  and  $^{14}\text{CH}_4$  will be formed [Toulhout, 2015]. In a deep geological repository with cementitious engineered barriers  $^{14}\text{CO}_2$  can be well retarded (e.g. precipitate as calcium carbonate) while  $^{14}\text{CH}_4$  passes the cementitious barriers without retention.

Partition between organic and inorganic forms depends on the environmental conditions (e.g. pH, presence of oxygen) and is not clearly defined. Some sources reported in [Toulhout, 2015] indicated the amount of inorganic compounds to be 65–75%. The leaching studies of moderator and reflector graphites from the Tokai (Magnox) reactors in Japan indicated that about 80% of the released  $^{14}\text{C}$  was in organic form with only 20% as carbonate. The attempt to identify the organic species revealed that they elute at similar times to small organic molecules, but are more strongly sorbed in cement than small organic species (methanol, formate, acetate, etc). As a result, the identities of the leached organic carbon-14 species were not confirmed [AMEC, 2016].

Gas phase releases at high pH include both volatile  $^{14}\text{C}$ -hydrocarbon/organics (probably  $^{14}\text{CH}_4$ ) and  $^{14}\text{CO}$ . At near-neutral pH  $^{14}\text{CO}_2$  is also purged from solution due to lower solubility of  $\text{CO}_2$  as carbonate. The form of gaseous carbon-14 release is affected by redox conditions with a lower redox seeming to favour  $^{14}\text{C}$ -hydrocarbon/organic compounds [Toulhout, 2015].

There are also experiments performed within CAST in which it was obtained that the dominant fraction of carbon-14 is released in form of  $^{14}\text{CO}_2$ , which mostly remains in solution, but some carbon-14 was also released as organic species. The released carbon-14 in the gas phase samples was as a mixture of organic species and/or CO [Shcherbina, 2017]. In the experiments performed by CIEMAT (Spain) with irradiated graphite from nuclear grade graphite rods used in thermal column of the VVR-S reactor using pure water as a leachant acetate, formate and oxalate were detected in certain steps of the sampling while alcohols and aldehydes were not identified [Magro, 2017].

## 10.6 Source Term

Experimental results indicate that carbon-14 is released initially at higher rate, which is followed by a decreasing release rate in the long-term. A significant fraction of carbon-14 in irradiated graphite appears to be bound up as part of the graphite matrix and is inaccessible to leaching [Toulhout, 2015; AMEC, 2016]. This correlates with the carbon-14 position in the irradiated graphite as described in Chapter 10.4. The rapidly releasable carbon-14 is associated with carbon-14 absorbed onto the graphite surfaces and pores while slowly

releasable fraction of inventory is attributed to carbon-14 incorporated in the crystal lattice or at an interstitial position. The leaching experiments performed with UK graphite revealed that even under harsh acidic conditions, not more than 30% of the  $^{14}\text{C}$  could be released over experimental timescales of up to 4 years [AMEC, 2016].

Total fractional releases (i.e. the total release as a fraction of the sample's total carbon-14 inventory) may vary by several orders of magnitude reflecting the different sources, irradiation histories and irradiation conditions of the graphites, as well as differences in the geometries of leached samples. In general carbon-14 leaching rate is very slow and in order to obtain a measurable amount of released carbon-14 and to reliably estimate the annual release rates graphite powder is used. It is observed that carbon-14 release increases with reduction of particle size and increase in overall surface area [AMEC, 2016]. Therefore, the results obtained with powdered or crushed graphite samples may overestimate carbon-14 release rate, compared with the graphite blocks.

According to information presented in [Toulhout, 2015], under various conditions studied, a quasi-steady state in the total carbon-14 release rate to solution is reached over a period of 10 to 200 days. In case of long-term modelling this is such a short time that it may be considered as an initial instant release. However, it should be noted that the greater part of the labile fraction might be released during encapsulation / storage directly as gas. Some studies point out that the initial rapid release of gaseous carbon-14 under alkaline conditions identified from intact graphite was not seen for crushed graphite what suggest that volatile carbon-14 may be lost during treatment [Toulhout, 2015].

Slower long-term release rates obtained in the laboratory experiments reported in different references vary by two to three orders of magnitude. This reflects the different sources, irradiation histories and irradiation conditions of the graphite as well as shape of the samples used in the experiments. Studies of leaching of moderator and reflector graphite from the Tokai (Magnox) reactors (Japan) in alkaline solution revealed that about 0.1% of the total carbon-14 inventory of the graphite samples was released to solution over three years (with the majority of the release occurring in the first month) [Toulhout, 2015]. Experiments with Oldbury graphite samples (UK) under the baseline conditions (anoxic, at

pH = 13 solution, ambient temperature) indicated that about 0.07% of the carbon-14 inventory is released to solution in one year [AMEC, 2016].

In the frame of the CAST project investigations of elevated pH and temperature effect on the release kinetics of carbon-14 from irradiated graphite were performed in leaching experiments with monolithic graphite samples from RFR (Rossendorfer Forschungsreaktor) by FZJ (Germany). For this purpose deionized water (DIW) and 1 M NaOH (to simulate cementitious environment expected in the repository) as a leaching media were used. Experiments were carried out at room temperature and at 50°C. It was demonstrated that the dominant fraction of carbon-14 (>83%) is released in the form of  $^{14}\text{CO}_2$ , which mostly remains in the leaching solution (DIW or NaOH). The highest fraction of volatile  $^{14}\text{CO}_2$  is released in i-graphite/DIW systems at 50°C. Besides that, application of NaOH as a leaching solution results in the higher fraction of carbon-14 being absorbed in the aqueous phase. The evaluated annual release rate from the irradiated graphite samples in NaOH system was estimated to be  $7.3 \cdot 10^{-3}$  %/year [Shcherbina, 2017].

Initial higher release rate followed by the slower release rate also was confirmed in the leaching experiments performed by IFIN-HH (Romania) with the monolithic samples taken from nuclear grade graphite rods used in thermal column of the VVR-S reactor. It was also obtained that carbon-14 release to the gas phase was considerably lower than that to the solution [Fugaru, 2017].

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## Appendix 1

# CARbon-14 Source Term CAST-workshop

Country: XXXXXXX

Organisation: XXXXX

Name: XXXX

This presentation **can/cannot** be used for the Proceedings of the workshop that will be published at CAST website



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## What type of reactor



- PWR/BWR/VVER/RBMK
  - $MW_e$
  - Neutron flux (fast, thermal) [ $\text{neutrons cm}^{-2}\text{s}^{-1}$ ] distribution from core to reflector



## Irradiated Steels



- Expected neutron irradiation period
- Origin
  - Cladding/other (grid support, ducts et cetera)
- Is the nitrogen content of (stainless) steel in the reactor core specified? **Yes/No**
- If yes
  - Nitrogen content in N ppm or N wt %
    - Vendor specifications or own measurements?



## Irradiated Zircaloy



- Limited to claddings
- Zircaloy-4 (PWR) / Zircaloy-2 (BWR) / (VVER)
  - Nitrogen content in ppm
    - Vendor specifications?
  - Neutron irradiation period



## Spent Ion-exchange resins



- Coolant
  - Is there control of air ingress?
  - Discharged from the plant after cleaning?
- pH coolant controller
  - LiOH /  $\text{NH}_2\text{-NH}_2$
  - Other please specify
- Waste treatment
  - Fluid with resins **bubbled and/or dried** ?
    - Further details available for drying i.e. temperature, volume, period of heating
- Carbon-14 activity concentration measured? **Yes/No**
- Carbon-14 speciation measured? **Yes/No**
- If yes, how?
  - **For example combustion with oxygen/acidic dissolution**



## Irradiated Graphite



- Expected neutron irradiation period
  - Moderator / sleeves
- Is the nitrogen content of graphite in the reactor core specified? **Yes/No**
- If yes
  - Nitrogen content in N ppm or N wt %
    - Vendor specifications or own measurements