EUROPEAN COMMISSION
European Research Area

CArbon-14 Source Term

CAST

CAST

Final overview of CAST (D7.23)
Version 2

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Date of issue of this report: 06/08/2018

The project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 604779, the CAST project'		
Dissemination Level		
PU	Public	**PU**
RE	Restricted to the partners of the CAST project	
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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, Zircaloys), 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 Zircaloys 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		
Work Package: 7	CAST Document no. :	Document type:
Task: 7.7	CAST-2018-D7.23	R = report
Issued by: COVRA		Document status:
Internal no. : -		Final

Document title
Final overview of CAST

Executive Summary

This overview intends to summarize the results and achievements of CAST and their implications for building confidence in the safety of geological disposal. The half-life of carbon-14 is 5730 years. In many disposal concepts for High Level Waste (HLW), there is an engineered containment period up to several hundred thousand 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. Experiments to measure the release of carbon-14 and carbon-14 speciation have therefore been mainly performed at room temperature. The CAST project focused on the release of carbon-14 as dissolved and gaseous species from waste. Carbon-14 can be released as an organic species i.e. carboxylic acids, alcohols, aldehydes, alkenes and alkanes or as an inorganic species i.e. carbonate, bicarbonate and carbon dioxide. All species need to be measured, in order to determine the main released carbon-14 species.

The measurement of released carbon-14 species for the neutron irradiated materials is challenging due to its low chemical amount in waste and low corrosion rates in cementitious materials. Typical carbon-14 activity concentrations in neutron irradiated steel from the core of a nuclear plant are in the order of 10^5 Bq per gram solid matter and for neutron irradiated Zircaloy 10^4 Bq per gram solid matter. The speciation of released carbon-14 species could not be quantified within CAST. These materials contain non-radioactive carbon: for example in steel, the non-radioactive carbon content is three orders in larger magnitude than

the carbon-14 content. In CAST, significant progress has been made to quantify the speciation of released non-radioactive carbon from steel. The major carbon-14 species were dissociated anionic compounds from carboxylic acids in the case when these dissociated anionic compounds and gaseous organic carbon were measured; gaseous organic carbon was negligible compared to dissolved organic compounds. An analytical strategy for the quantification of released alcohols and aldehydes has been developed. For neutron irradiated steel, carbon is released as dissolved non-gaseous non-ionic compounds i.e. alcohols and aldehydes. These compounds cannot be retarded in the cementitious materials by sorption and ion exchange due to lack of electrostatic interactions.

The presence of hydrogen can influence the fate of released carbon species; the carbon-14 released as non-ionic compounds such as alcohols and aldehydes can be further reduced with hydrogen to gaseous organic carbon. Significant confidence has been raised that more than 90% of the hydrogen generated during anaerobic corrosion is picked-up during corrosion of Zircaloy at disposal conditions. No hydrogen is formed during degradation of graphite and ion exchange resins under disposal conditions, the radiolytic hydrogen generation rates are usually insignificant. Consequently, it is only for neutron irradiated steel that the potential reduction to gaseous organic carbon needs to be taken into account. Carboxylic acids are expected only to occur as dissociated anionic compounds at disposal; their presence hinders the reduction to gaseous alkenes and alkanes such as ethene, methane and ethane with hydrogen. Only in acidic media for example in acid digestion tests, this potential reduction of carboxylic acids is expected to be possible.

The OH radicals formed by radiolysis of concrete pore water can also have an influence on the fate of released organic carbon. These radicals can oxidise alcohols and aldehydes into inorganic carbon. This process may have occurred during the experimental investigations in CAST in which neutron irradiated steel and neutron irradiated Zircaloy were exposed to portlandite solutions and perhaps with neutron irradiated graphite, but the gamma-emitting radionuclide content is expected to be smaller for neutron irradiated graphite than for the neutron irradiated metals. Gases released from these solutions were measured to be organic gaseous carbon as well as carbon dioxide. Radiolysis may be the reason why both reduced and oxidised hydrocarbons can exist simultaneously in solutions in contact with corroding metals. If the measured CO_2 is presumed not to be a contaminant, the carbon dioxide may have been formed by oxidation of dissolved organic compounds with OH radicals. $^{14}CO_2$ has also been measured in alkaline solutions with spent ion exchange resins. Any CO_2 released from waste in cementitious materials will form an unstable carbonic acid that is dissociated into bicarbonate and carbonate. The high calcium content in concrete pore water and low solubility will cause precipitation. Another retention mechanism of carbonate is sorption on positively charged cementitious minerals.

Dissolved organic carbon compounds have been measured to be the major carbon-14 species released from neutron irradiated steel and neutron irradiated Zircaloy. For neutron irradiated graphite, the situation is more complicated because irradiated graphites are physically very different from one reactor to another, and hence behave differently. Carbon-14 is released both in the organic and in the inorganic forms. The amount of dissolved organic carbon-14 species depends on the irradiated graphite studied and sometimes on the experimental conditions (anoxic or not). Distinction between carboxylic acids, alcohols and aldehydes is to be made. The release of non-ionic carbon compounds such as alcohols and aldehydes is therefore conservatively assumed to be the main carbon-14 species. The extent to which these species can be assumed to be retarded in engineered and natural barriers is uncertain, and in the case of natural barriers depends on the host rock properties. These neutron irradiated materials are also known to have very small mass loss rates, so the potential carbon-14 fluxes to air from these three waste types as a consequence of their deep geological disposal is expected to be negligible compared to the flux of natural carbon-14 emanating from soil.

The main origin of carbon-14 in neutron irradiated steel and Zircaloy is nitrogen. Measured and calculated carbon-14 contents are of the same order in magnitude. For neutron irradiated graphite, it depends on the chemical and temperature conditions whether nitrogen is the main contributor to carbon-14 in waste. Nitrogen-activated carbon-14 forms a loosely bound carbon-14 gaseous species that may e.g. be released during crushing of neutron irradiated graphite.

Only measured carbon-14 contents in resins that have been prepared for conditioning are representative of behaviour likely in relation to a disposal scenario, due to the high impact of the storage and drying conditions on the contained carbon-14 content. Knowledge of the contained inorganic and organic carbon content is necessary for safety assessments when organic carbon compounds are assumed to be non-retarded species. Conservatively, the speciation of carbon-14 contained by resins is assumed to be released instantaneously. Spent ion exchange resins can only contain anionic carbon-14 compounds. This containment limits the presence of organic carbon in ion exchange resins to dissociated anionic compounds of carboxylic acids such as oxalate and acetate; the only possible contained inorganic compounds are bicarbonate and carbonate. Attempts to measure release of carbon-14 in alkaline media have been made but carbon-14 has not been measured to be released in cementitious pore water. Inorganic carbon is assumed to be retarded in cementitious materials due to the precipitation with calcite i.e. fixation by high calcium amount in the concrete pore water chemistry. This retention mechanism also takes place for oxalate. Sorption of positively-charged cementitious minerals is another retention mechanism and in CAST the literature for sorption of acetate has been found. The last evaluated retention mechanism is ion exchange; formate is exchanged with sulphate in ettringite. Consequently, there is no reason in cementitious materials only to assume retention for inorganic carbon and not for organic carbon during disposal of spent ion exchange resins when processed with cementitious materials. The amount of carbon-14 that is released and not decayed within the waste package may be negligible.

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1 Introduction

All available information of the types of waste investigated in CAST was collected in state of the art reports in the beginning of the CAST project: neutron irradiated steel [Swanton, 2015], neutron irradiated Zircaloy [Gras, 2014], spent ion exchange resins [Rizzato, 2015] and neutron irradiated graphite [Toulhoat, 2015]. The implications for the disposal have been presented as a scientific paper [Williams, 2015]. Achievements of CAST included in this overview have been obtained from the final synthesis reports for neutron irradiated steel WP2 [Mibus, 2018], neutron irradiated Zircaloy WP3 [Necib, 2018], spent ion exchange resins WP4 [Reiller, 2018] and neutron irradiated graphite WP5 [Toulhoat, 2018]. Additional details that are considered relevant for regulators, waste generators, waste producers and waste management organisations - abbreviated to “decision-makers” -are included.

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 which is known to be poorly retarded by geological barriers but carbon-14 can be released as a gas during degradation of waste. Gaseous radionuclides may be less retarded by engineered and natural barriers than radionuclides dissolved in ionic form such as chlorine-36. The potential hazardous exposure is determined by the carbon-14 content in waste, carbon-14 release rate from waste and the speciation of released carbon-14. In Chapter 2, the potential released and formed carbon-14 species and potential retardation mechanisms in engineered barriers made with cementitious materials are described. The potential limits to form gaseous carbon-14 in natural barriers are included.

Carbon-14 is a beta-emitter with low penetrating power and like chlorine-36 a difficult-to-measure radionuclide, and therefore the carbon-14 content is frequently calculated. Confidence in the calculated carbon-14 activity concentration requires knowledge of the main origin of carbon-14 in neutron irradiated materials. In a previous European overview of carbon-14 waste management, the considered neutron irradiated materials were steel, Zircaloy and graphite [Bush, 1984]. In CAST, the same neutron irradiated materials have been investigated but assumptions have been verified with measurements which increases the confidence in the carbon-14 content. Chapter 3, 4 and 5 aspects of the carbon-14 content in waste are described. The released carbon-14 species and carbon-14 release rates and its implications are described in Chapter 6 and 7.

2 Carbon-14 species

As a start, the fate of non-radioactive carbon release is used as an analogue for the fate of radioactive carbon release and as introduced by Wieland in CAST [Wieland, 2015], gaseous inorganic carbon (CO_2) can be reduced into a gaseous organic carbon (CH_4) [McCollum, 2007] see Figure 1.

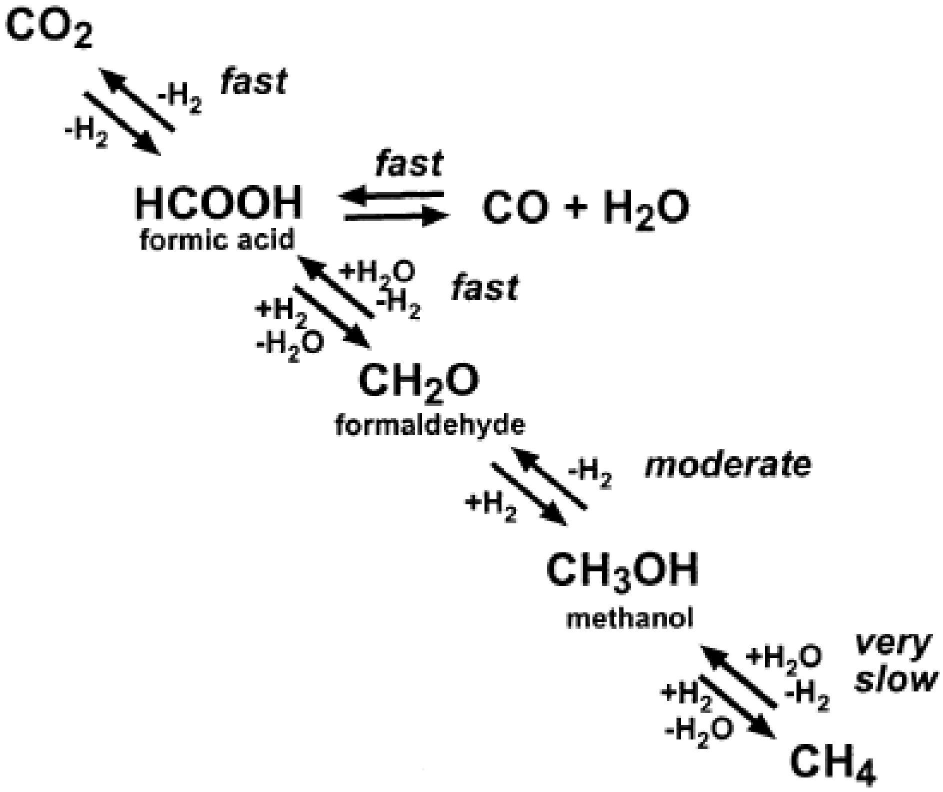

Figure 1: Reaction scheme for sequential reduction of CO_2 to methane, modified from [Wieland, 2015; and [McCollom, 2007]

Such a series of organic compounds consists of carboxylic acids, aldehydes, alcohols and alkanes see Figure 2 with another series of carbon species.

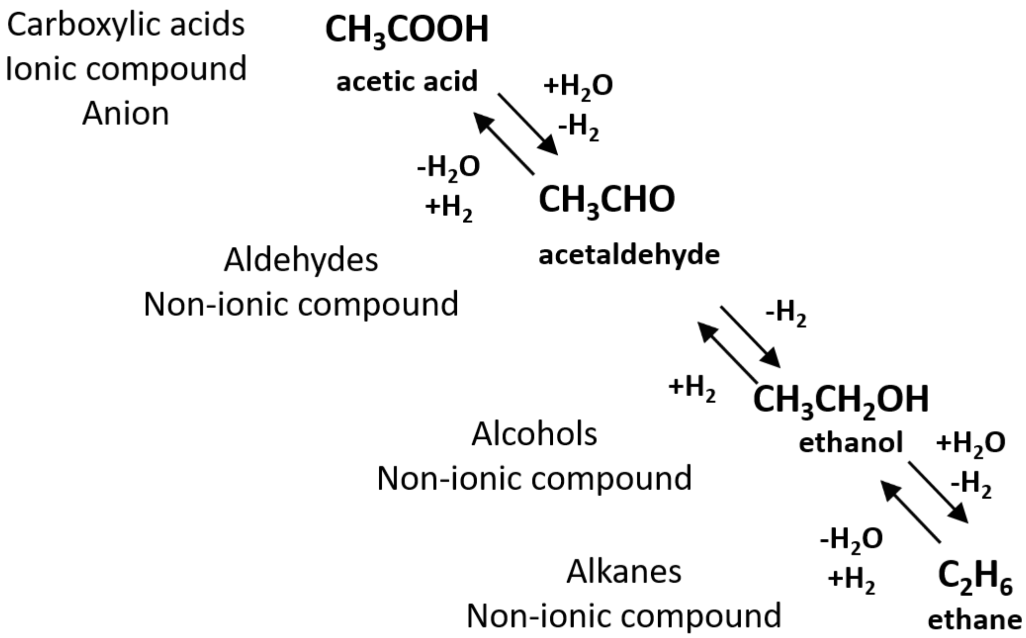

Figure 2: Reaction scheme for sequential reduction of carboxylic acids to alkanes

Non-ionic compounds lack electrostatic interactions and therefore these compounds can access the entire diffusion accessible porosity and sorption as a retention mechanism is excluded in the engineered and natural barriers. Precipitation is another retention mechanism and inorganic carbon is known to be retarded in cementitious materials due to the low solubility of calcium carbonate. Only anionic compounds can form calcium carbon complexes, but the presence of dissociated carbon compounds depends on pH.

Table 1 shows the acidity constants of carbon compounds that are measured in CAST to be released from waste.

Table 1: Acidity constants of some carbon compounds [CRC, 2015 & McMurry, 1992]

	Name	**Carbon group**	**pK_{1a}**	**Anionic compound**	**pK_{2a}**	**Anionic compound**
H_2CO_3	Carbonic acid*	Inorganic	6.35	Bicarbonate HCO_3^-	10.33	Carbonate CO_3^{2-}
HOOCCOOH	Oxalic acid	Organic	1.25		3.81	Oxalate: OA $C_2O_4^{2-}$
$HOOCCH_2COOH$	Malonic acid	Organic	2.85		5.05	Malonate: MA $C_3H_2O_4^{2-}$
			pK_a			
HCOOH	Formic acid*	Organic	3.75	Formate: FA $HCOO^-$		
CH_3COOH	Acetic Acid	Organic	4.31	Acetate: AA CH_3COO^-		
CH_3OCH_2COOH	Lactic acid	Organic	3.86	Lactate: LA $CH_3OCH_2COO^-$		
$HOCH_2COOH$	Glycolic acid	Organic	3.83	Glycolate: GA $HOCH_2COO^-$		
CH_3OH	Methanol	Organic	15.5	Methanoxide* CH_3O^-		
CH_3CH_2OH	Ethanol	Organic	16	Ethanoxide* $CH_3CH_2O^-$		

Conservatively, organic carbon-14 species are assumed to be non-retarded species in safety assessments [Capouet, 2017]. In CAST, it is investigated whether there is a hindrance to the formation of organic gaseous carbon i.e. is there evidence that not all carbon-14 is released as an organic gas? The anionic compounds are predominant at a pH larger than the $pK_{a/1a/2a}$. Since dissociated carboxylic acids are predominant at pH values common in cementitious materials, clay and granite, the potential reduction to gaseous carbon-14 is hindered. Furthermore, only the anion accessible porosity is available for diffusion thus these dissociated compounds migrate with a smaller diffusion values in barriers than non-ionic compounds.

Carbonic acid and formic acid are unstable compounds and dissociated into H_2O and CO_2 and CO and H_2O respectively. The equilibrium concentration of carbon dioxide is 1.35×10^{-9} mmol/l at natural atmosphere pressure and 25˚C i.e. highly insoluble. On a thermodynamic point of view, CO_2 is the predominant compound at a pH below 6.35. Such low pH values have been measured during air bubbling at storage; the pH of fluids with spent ion exchange resins was measured to vary between 5 and 8 and $^{14}CO_2$ was released [Aronsson, 2016]. Consequently, at these storage conditions, the inorganic carbon-14 content can be significantly reduced, as a result of which only a fraction may be left for disposal. Unstable anionic compounds are alkoxide ions such as ethanoxide and methanoxide i.e. alcohols will be present as non-ionic compounds.

For the irradiated metals investigated in CAST, steel and Zircaloy, hydrogen can be released during anaerobic corrosion. Another source of hydrogen formation is radiolysis of water [Dzaugis, 2015]. During dissociation of water, hydrogen ions and hydroxyl radicals are generated. A variety of other compounds can be generated with these two compounds and water molecules, as well as more hydrogen gas. In case of insufficient dispersion of hydrogen, gaseous organic carbon can be expected to be the predominant species but only when released directly or indirectly by a reaction of alcohols and aldehydes with hydrogen. The predominance of carbon as shown in Figure 3 has been calculated in CAST [Wieland, 2015; Rizzato, 2015]. The kinetic hindrance to form gaseous organic compounds is simulated by leaving out CH_4 as a carbon species see figure on the right.

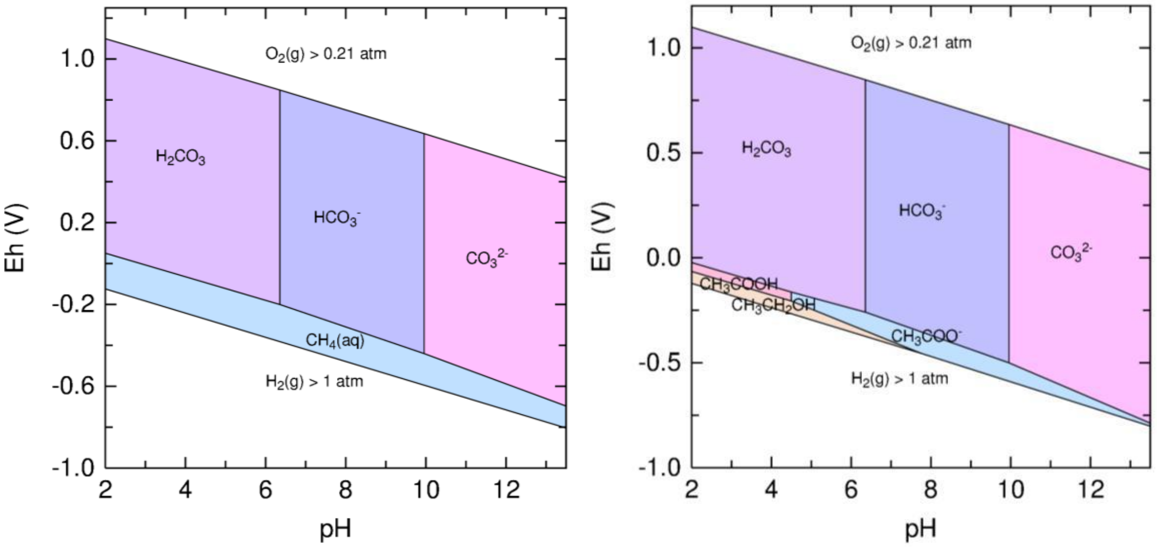

Figure 3: Predominance diagrams of carbon [Wieland, 2015; Rizzato, 2015].

At disposal with cementitious materials as an engineered barrier, the pH can be between 9 and 12.5 and therefore no gaseous carbon dioxide is expected to be present. Also carboxylic acids are dissociated and carbon-14 is present as an anionic compound; in Figure 3, acetate is shown to be the predominant species at pH larger than 4.31, see also Table 1.

Anions such as chlorine are assumed to be poorly retarded due to their high solubility in groundwater that could be present in engineered and natural barriers. Some anionic compounds from carboxylic groups can be retarded by precipitation in cementitious materials. The dissolved calcium content in cementitious pore water at a pH of 12.5 is 20 mmol/l and at a pH of 10 about 0.5 mmol/l [Vehmas, 2017]. The solubility products of some calcium complexes (solid) are shown in Table 2.

Table 2: Stability constants with calcium [CRC, 2015] & [Morel, 1993]

Chemical formula	Name	Stability constants
$Ca(OH)_2$	Calcium hydroxide	5.02×10^{-6} (solid)
$CaCO_3$	Calcium carbonate	3.36×10^{-9} (solid)
$CaC_2O_4\bullet H_2O$	Calcium oxalate hydrate	2.32×10^{-9} (solid)
$CaC_2H_3O_3^-$	Calcium Glycolate	2.51×10^{-2} (aqueous)
$CaC_2H_3O_2^-$	Calcium Acetate	6.31×10^{-2} (aqueous)
$CaC_3H_4O_4^-$	Calcium Malonate	3.98×10^{-3} (aqueous)

Evidence of precipitation in cementitious materials of oxalate is available [Loon Van, 1995] and suggested as a precipitation product [Mibus, 2018]; the solubility product is even smaller than calcium carbonate. Glutamate and acetate are not expected to be retarded based on their high solubility i.e. values for solubility products have not been found. Calcium formate is also known to be highly soluble but in CAST precipitation has been measured in experiments performed in a stainless steel vessel. The mechanism is not yet clear; influence of iron corrosion products is suggested [Wieland, 2018a]. The characterisation of dissociated anionic compounds from carboxylic acids is important to judge whether these dissolved carbon species are not retarded by precipitation such as chlorine. Retardation by sorption on cementitious minerals is familiar for anions such as chlorine and carbonate [Pointeau, 2008]. In CAST, the literature on the sorption of acetate on positively charged cementitious minerals and selective binding of formate by replacement with sulphate in ettringite was collected by Wieland [Capouet, 2017].

Radiolysis of water can have an impact on the carbon-14 speciation since the OH radicals (OH•) can decompose organic compounds. This decomposition is an oxidation by which CO_2 and CO can be formed. In experimental analysis of carbon-14 samples, OH radicals are produced by chemicals such as potassium persulphate ($K_2S_2O_8$) in the determination of organic carbon-14 content in leachate solutions of irradiated Zircaloy corrosion as proposed by Magnusson [e.g. Bucur, 2017a & Sakuragi, 2017], organic carbon-14 content in leachate solutions of irradiated graphite [e.g. Toulhoat, 2018], the amount of organic carbon contained by spent ion exchange resins [e.g. Rizzato, 2015] and carbon-14 activity concentration in irradiated steel and irradiated Zircaloy [Mibus, 2018 & Herm, 2014].

The last feature that is important in the fate of released carbon-14 and justification of assumed corrosion rates is the redox potential of concrete. The initial potential highly depends on the cement used for the production of engineered barriers. The potential environment to which the waste is exposed can be deduced from how the cement is made. For Ordinary Portland Cement (OPC), CaO is made by baking carbonate from limestone without specific precautions to the heating environment. Blast Furnace Slag (BFS) Cement is made in reducing environments as a by-product of steel. OPC concrete lacks electroactive species, is therefore largely unbuffered and is after fabrication slightly oxidising. Potential ingress of oxygen can be consumed by corrosion of metals and ingress of oxygen can be too slow to prevent a local reduction at the interface between metal and concrete [Wang, 2013]. Above all, the amount of oxygen trapped during fabrication of cementitious materials can oxidise only a negligible fraction of metals. BFS concrete contains small amounts of FeS_2 and therefore after fabrication it has a reducing environment. In above-ground civil infrastructures made with this concrete, the oxygen penetration front into the concrete is observed as a loss of the blueish colour. The oxygen exposing levels in underground facilities may be too small to reach the concrete-waste interface i.e. reducing environments may be assumed at start of disposal. In Finland and the Netherlands, BFS is used for waste processing [Buckau, 2016].

3 Main origin of carbon-14

Carbon-14 is primarily generated by neutron activation i.e. ternary fission and decay of actinides such as radium and actinium both 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, 2004]. 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. Figure 4 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].

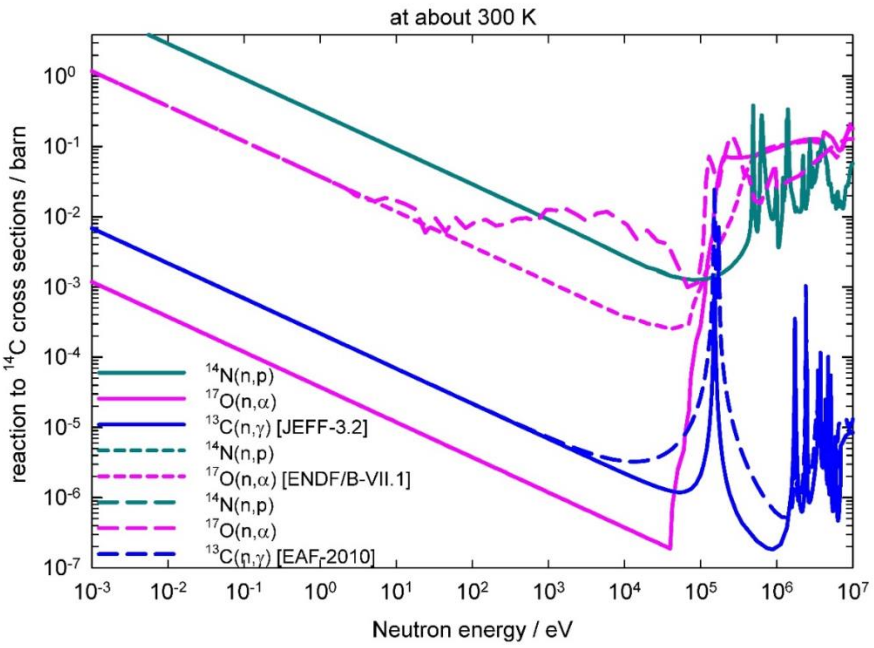

Figure 4: Neutron cross sections at 293.59 K from NEA data bank.

Neutrons resulting from the fission of actinides have energy of about 10^6 eV. The neutron activation cross sections for nitrogen-14 and oxygen-17 have similar values. Assumed nitrogen content in fuels in the previous European study were 10, 25 and 100 ppm [Bush, 1984]. 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 Figure 4. 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, 2004]. 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 using the latest evaluation of data [JEFF-3.2]. Thus, for Light Water Reactors, 0.1 ppm nitrogen in the moderator and coolant is sufficient to have carbon-14 mainly be generation by nitrogen and not by oxygen in H_2O. At typical Boiling Water reactors temperature and pressure conditions of about 290˚C and 70 bar, the nitrogen solubility is about 30 mmol/l [Sun, 2001]. Provided the moderator is prepared at room temperature, the equilibrium concentration of nitrogen at natural atmospheric pressure is 0.48 mmol/l i.e. larger than 0.1 ppm. Air ingress, especially in the moderator and primary coolant systems, has been found to be one of the sources of ^{14}C production during reactor operation. Improving the system design to minimize the potential for air ingress will therefore reduce ^{14}C production and release. Another nitrogen source is the addition of nitrogen containing chemicals to control the pH of the coolant. According to the IAEA, the pH control of the primary coolant in Western PWRs is carried out by lithium hydroxide instead of hydrazine (NH_2-NH_2), to prevent the formation of ^{14}C [IAEA, 2004]. At the second workshop of CAST, it became clear that nitrogen limiting measures have not always been taken in Europe for example NH_4OH is used to control the pH in VVERs [Buckau, 2018].

In heavy water reactors, D_2O is used as a moderator and the process to make heavy water causes oxygen-17 to be enriched with 55% compared to natural levels [IAEA, 2004]. Thus, the abundance of oxygen-17 is 0.059% in heavy water instead of 0.038% in light water i.e. still 10^7 times more oxygen is necessary to have the same contribution as nitrogen. The earlier data with a thousand times larger reaction cross section for oxygen-17 have been used to calculate the carbon-14 generation in CAST. In that case, the chemical content of oxygen needs to be 10^4 times larger than nitrogen i.e. a chemical content of 100 ppm nitrogen is sufficient to be the main carbon-14 contributor. In gas-cooled reactors, an impurity content of 100 ppmv is used to determine the carbon-14 arisings from the Magnox and AGRs [IAEA, 2004].

4 Presence of carbon-14 in waste

The presence of carbon-14 within materials, potential catalytic processes, the environmental conditions to which materials are exposed and radiolysis can have an impact of the carbon-14 speciation released at disposal. The presence of carbon-14 for each type of waste investigated in CAST is described in the following paragraphs.

4.1 *Irradiated steel*

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 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, 2017], [Mibus, 2015]. 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%. With these nitrogen contents, the main contributor to carbon-14 neutron irradiated steel is nitrogen. The nitrogen contents in steel are small enough to assume that nitrogen is dissolved within an iron lattice. 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. It is therefore expected that neutron activation of nitrogen dissolved in iron results in carbon-14 dissolved in iron.

4.2 *Irradiated Zircaloy*

As reducing conditions are necessary to make Zircaloy, the oxygen content of this metal is therefore limited. In the state of the art report made at start of the Carbon-14 Source Term project, maxima of 80 ppm, 270 ppm and 1600 ppm for nitrogen, carbon and oxygen in Zircaloy are described. These maxima are based on vendor (contractual) specifications. 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 ± 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±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.

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 α-Zr (to 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 α-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].

4.3 Spent ion exchange resins

Ion exchange resins are used for example to clean up the primary circuit in nuclear reactors, as well as for other reasons. The most common form of synthetic ion exchange resins is polystyrene divinylbenzene in powdered form with diameters from 5-150 µm or in beads from 0.5-2 mm. The resins have functional groups that are to be exchanged with a radionuclide in cationic form such as $^{60}CoOH^+$ or in anionic form such as $H^{14}CO_3^-$. Carbon species in aqueous fluids can be present as dissolved gas, non-ionic compounds and as an anion but only as an anion, carbon-14 can be concentrated by ion exchange resins. The common functional groups in anion exchangers bear nitrogen for example as a 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]:

F- < CH_3COO^- (acetate) < Cl^- < Br^- < CrO_4^{2-} < NO_3^- < I^- < $C_2O_4^{2-}$ (oxalate) < SO_4^{2-}

Carbon-14 as acetate has a weak affinity and as oxalate a strong affinity. Examples of other anionic compounds i.e. dissociated carboxyl acids that can be expected are $HCOO^-$ (formate), $CH_3OCH_2COO^-$ (lactate), $HOCH_2COO^-$ (glycolate) and malonate ($C_3O_4^{2-}$). Please note that inorganic carbon is not reported in this series but CO_3^{2-} is expected to have a stronger affinity due to the larger negative charge.

4.4 Irradiated graphite

A colleague from the Lithuanian Energy Institute, Dr Dahlia Grigaliuniene, measured the presence of carbon-14 in neutron irradiated graphite for the second workshop for regulators, waste generators and waste management organisations [Neeft, 2017]. Generally, three different forms of carbon-14 are present in irradiated graphite [AMEC, 2016], [Toulhoat, 2015] and [Takahashi, 1999]:

- Carbon-14 bound up in the graphite matrix generated by carbon-13 activation;
- Carbon-14 in interstitial positions also generated by carbon-13 activation;

- Carbon-14 associated with pore surfaces, edge sites and less ordered regions of the graphite generated by nitrogen-14 activation.

The possible positions of carbon-14 are illustrated in Figure 5.

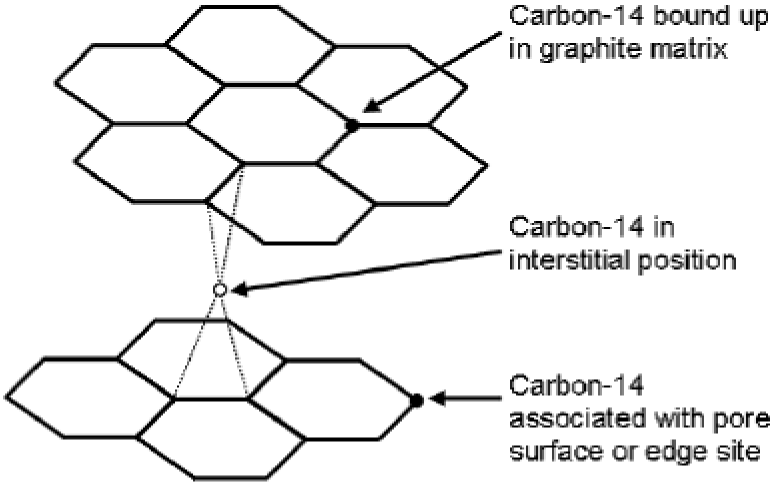

Figure 5: Carbon-14 potential locations in irradiated graphite [AMEC, 2016].

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. The carbon-14 generated by neutron activation of nitrogen is loosely bound. Depending on the reactors operating conditions, this type of generated carbon-14 may be released during reactor operations and may not be present in irradiated graphite for disposal, as explained by the Spanish WMO for the Vandellós I, a Graphite Gas Cooled Reactor. Only carbon-14 generated from carbon-13 with a natural abundance of 1.07% needs to be assumed [Buckau, 2018].

5 Determination of carbon-14 concentration

Two types of waste investigated in CAST can be dismantling waste. In the latest Council Directive 2013/59/EURATOM presenting 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 carbon-14 [EU, 2013], that is, an atomic concentration in e.g. iron of 2.42 ppm. Unlike cobalt-60, carbon-14 cannot be measured non-destructively due to absence of gamma emission during its decay. 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. In practice, the carbon-14 content in waste is determined with a scaling factor in which the carbon-14 content is scaled to the cobal-60 content [Buckau, 2016].

The diffusion of carbon in steel and Zircaloy at neutron irradiation 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}Co is 5.3 years i.e. three orders in magnitude smaller than carbon-14 from which the scaling factor is derived. In CAST, calculations of the carbon-14 content in neutron irradiated metals are made based on the nitrogen content and neutron irradiation history. For neutron irradiated graphite, also the chemical operating history needs to be known in order determine whether nitrogen is the main contributor to the carbon-14 content. For spent-ion exchange resins, the scaling factor method is not applicable, as shown by the Hungarian WMO. A reason could be that cobalt-60 cannot be a chemical analogue for carbon-14 because cobalt-60 is present in a cation exchanger and not in an anion exchanger as carbon-14 [Buckau, 2016]. The determination of the carbon-14 concentration for each type of waste investigated in CAST is described in the following paragraphs.

5.1 *Irradiated steel*

The reported carbon-14 activity concentration in core internals by WMOs in CAST was in the order of 10^5 Bq per gram and in the pressure vessel 10^3 Bq per gram solid matter

[Capouet, 2017]. The carbon-14 activity concentrations of the samples investigated in CAST are in Bq per gram solid matter:

- 18: Spain, stainless steel dismantling waste core internal (guide tube) determined with ^{60}Co scaled activity [Mibus, 2015/2016];
- 2000: Finland, stainless steel from surveillance capsule, calculated from nitrogen measured content 0.04% and neutron irradiation history [Mibus, 2017];
- 15500-28700: research samples from UK programme, stainless steel 316L(N)), calculated from nitrogen content 0.08 wt% and neutron irradiation history [Visser, 2018];
- 60: research sample from Belgium programme, JRC carbon steel) and 19 ppm measured nitrogen content (vendor specifications 20-30 ppm) and neutron irradiation history [Mibus, 2016];
- 4500: Swiss, stainless steel, steel nut core internal determined with 0.011 wt% N nitrogen content and neutron irradiation history [Mibus, 2018]
- 8500/9500: German, Inconel from a plenum spring of an irradiated UO_2 fuel rod segment with 0.008wt% N nitrogen content and neutron irradiation history and two codes SINDER/ORIGEN-S [Herm, 2017 & Mibus, 2018].

The wide range is due to differences in thermal neutron fluence and nitrogen contents. In the Belgium and Finnish programme, combustion equipment and LECO analyser have been used to measure the nitrogen content in steel.

The carbon-14 activity concentration in the Swiss and German programme has also been measured and was found to be 3 to 4 times larger than calculated: $17.8(\pm 2)\times 10^3$ Bq/gram and $2.7(\pm 0.3)\times 10^5$ Bq/gram [Herm, 2017; Mibus, 2018]. In this measurement, a steel sample is dissolved in acid and gaseous carbon is collected for analysis. A part of carbon-14 contained stainless steel remains in the acid solution as dissolved organic carbon. These organic compounds are oxidised using $K_2S_2O_8$ to make radicals as proposed by Magnusson [Herm, 2014] to determine the total carbon-14 content.

All neutron irradiated steel samples investigated in CAST have a carbon-14 content representative for waste.

5.2 *Irradiated Zircaloy*

The activity concentration of carbon-14 was in the order of 10^4 Bq per gram solid matter as reported by WMO [Capouet, 2017]. This activity concentration is an order in magnitude smaller than the activity concentration in steel core internals. 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 to impurity levels to reduce the hydrogen uptake during its oxidation in PWR primary water [Gras, 2014]. The carbon-14 activity concentrations of the samples investigated in CAST are in Bq per gram solid matter:

- 17800: processed by AREVA Zircaloy-4 hull from Switzerland (Gösgen) and have undergone industrial treatment in La Hague reprocessing plant, content determined by nitrogen content 34 ppm and neutron irradiation history (54.5 GWd/tHM) [Caron, 2014] and [Necib, 2018];
- 32000: PWR Gösgen Zircaloy-4 irradiated plenum without industrial reprocessing treatment (50.4 GWd/tHM) calculated with a nitrogen content 65 ppm and neutron irradiation history; average measured value 37000 [Herm, 2014] and [Necib, 2018];
- 13000 and 19500: PWR Zircaloy-4 specimens from two Belgian nuclear reactors (Tihange and Doel) using measured nitrogen content of 17 and 25 ppm and neutron irradiation history [Caron, 2014] and [Necib, 2018];
- 17800: CANDU Zircaloy-4 specimen from Cernavoda NPP calculated with a nitrogen N_2 content of 30 ppm; oxide layers removed by acid treatment; measured value 20000 [Bucur, 2017a];
- Measured carbon-14 content for BWR Zircaloy-2 [Sakuragi, 2017] see Table 3.

Interestingly, a calculated carbon-14 content with a nitrogen content of 65 ppm seems to result in a better resemblance of the carbon-14 activity concentration of a cladding in PWR Gösgen than 34 ppm.

Zircaloy claddings contain an internal oxide layer due to excess of oxygen in spent fuel and an external oxide layer to oxidation by the coolant. The oxide layer has an important contribution to the calculated hazardous exposure since the carbon-14 contained in the oxide layer is assumed to be instantaneously released. The percentage can be 20% of the carbon-14 inventory [Capouet, 2017] and in CAST the interpretation of the results has advised to assume an amount of 7.5% of carbon-14 in the oxide layer [Necib, 2018]. In the Japanese programme, special care has been taken to measure the carbon activity concentration with and without these oxide layers. Table 3 shows 6 measurements from the Japanese programme [Sakuragi, 2017].

Table 3: Specific activity of 14C for irradiated BWR Zircaloy-2 in Bq/g Zircaloy [Sakuragi, 2017]

Cladding with internal and external oxide	Cladding base metal
15400	14900
14900	15000
14300	14700

From these data, it can also be interpreted that overall, the variation in activity concentration is too high in Table 3 to assign a specific contribution to the oxide layers. A three times higher carbon-14 content is measured from the scraped external metal-oxide but since the thickness of the oxide layer is less than 4% in thickness of the base metal, the contribution to the total carbon-14 inventory is very small. In the final synthesis, it is suggested that carbon-14 during corrosion of the cladding at operating conditions is not released but incorporated into the oxide film [Necib, 2018] instead of neutron activation of oxygen-17 as suggested at the beginning of the CAST project [Gras, 2014].

All neutron irradiated Zircaloy samples investigated in CAST are representative for waste. The variation in carbon-14 content is small due to the similar neutron flux of $(3\text{-}8)\times10^{13}\,\text{cm}^{-2}\text{s}^{-1}$ in the core of the reactor [Buckau, 2018] and similar neutron irradiation periods.

5.3 *Spent ion exchange resins*

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 [Capouet, 2017]. The resins investigated in CAST are mainly beads and the order of magnitude carbon-activity is similar. In the Swedish programme, the inorganic and organic carbon content is measured using acid stripping and wet oxidation as proposed by Magnusson [Aronsson, 2016]. In the acid stripping method, inorganic carbon compounds are decomposed by weak acids to carbon dioxide. Further on, the adsorbed organic carbon is oxidised to CO_2 using potassium persulphate [Rizzato, 2015]. Using this method, drying in air was measured to reduce the carbon-14 content by three orders in magnitude in spent ion exchange resins [Aronsson, 2016]. In all methodologies used, the inorganic carbon-14 content was measured to be reduced after drying but not the organic fraction [Aronsson, 2016 & Comte, 2017]. In the CAST reports, the carbon-14 content in mainly wet unconditioned samples has been measured. More than 90% was measured to be inorganic carbon for spent resins used to clean aqueous fluids from a BWR, and ca. 70-80% inorganic carbon for PWRs [Reiller, 2018].

5.4 *Irradiated graphite*

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. Calculated carbon-14 content below the clearance level i.e. is conventional waste, is possible.

Excluding the potential release of nitrogen activated carbon-14 during reactor operations may overestimate the carbon-14 content when the carbon-14 activity is based on the neutron activation of the nitrogen impurities. During powdering of the samples to measure the carbon-14 activity concentration, nitrogen activated carbon-14 contained in intergranular pores may be released, resulting in underestimated carbon-14 content. Samples from research reactor in Romania TRIGA and Vandellós Graphite Gas Cooled reactor in Spain have both been powdered and measured by destruction of the samples under combustion. The powdered irradiated graphite released gas during heating the irradiated graphite in an oxygen stream is collected and several separation steps are made to have a pure carbon-14 containing compound for further analysis using Liquid Scintillation Counting [Toulhoat, 2018]. The carbon activity concentration presented is likely to be associated only with the carbon-14 generated by carbon-13 activation. For the research reactor in Romania, the average activity was 451 Bq per gram for the thermal column. For the reactor in Spain, the carbon-14 activity was between 10800-13500 Bq per gram.

6 Carbon-14 species released at disposal conditions

The neutron irradiated metals investigated in CAST have undergone a special chemical treatment in the nuclear plant. Reducing conditions are preferred to limit the corrosion of metals during operations, the oxygen content can be below 1 ppb in a PWR [Buckau, 2018]. The photo below is taken during periodic maintenance of a PWR in which fuel assemblies are relocated. New fuel assemblies have a shiny look; spent fuel assemblies have lost this look due to the formation of a very thin iron-oxide (magnetite) layer on the iron surfaces. This layer prevents iron working as a catalyst, for example, to reduce, with available hydrogen, inorganic and organic carbon compounds into gaseous organic molecules. Catalytic reactions can have an impact on the measured carbon speciation i.e. if this iron-oxide layer is not present [McCollum, 2007]. The high pH of cement pore water preserves this iron-oxide layer and therefore catalytic processes at disposal conditions are not foreseen.

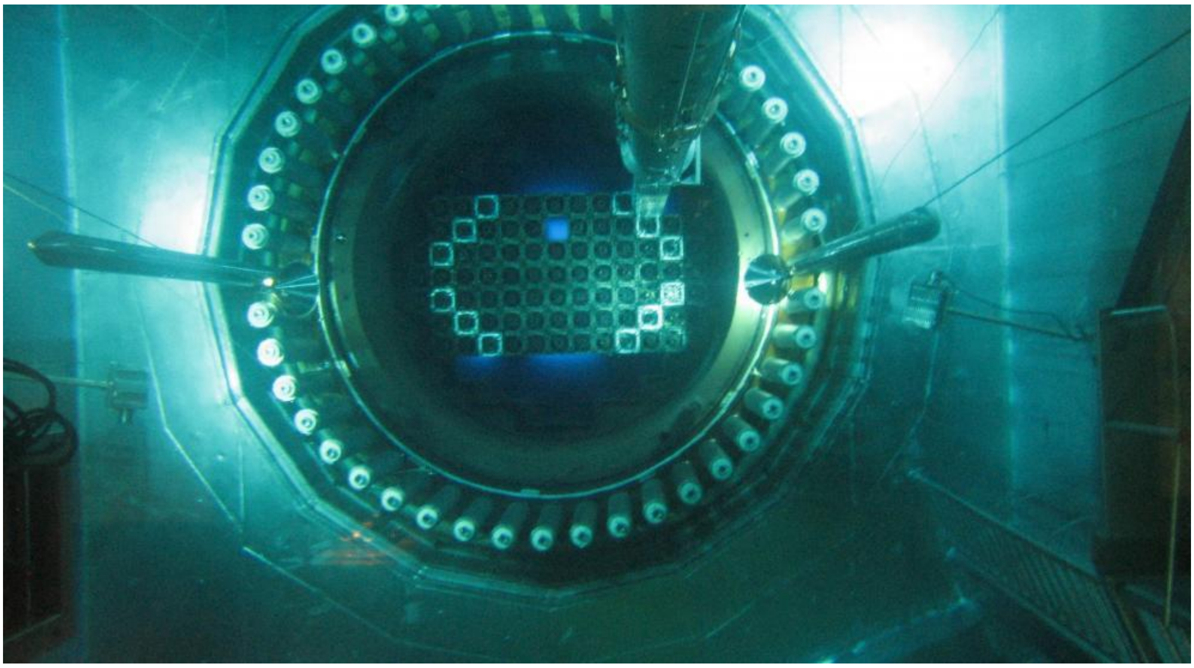

Figure 6: Photo during periodic maintenance of the Dutch PWR Borsele; source EPZ

At a higher pH representative for cementitious conditions but also in nuclear chemical conditions, zirconia and iron-oxide such as magnetite are thermodynamically stable. These oxide layers are removed during acid digestion to determine the carbon-14 content. Consequently, there is no kinetic hindrance to form gaseous organic carbon. Also, carboxylic acids exist as non-ionic compounds in these media by which there is no hindrance to reduce them to alcohols, aldehydes and gaseous organic carbon with the generated hydrogen. Such conditions are not representative for disposal and therefore any carbon-14 speciation measured at these conditions is not included in this overview, its use is limited to the determination of the carbon-14 activity concentration.

6.1 *Irradiated steel*

In CAST, irradiated stainless steel specimens are exposed to cementitious pore water conditions to investigate the potential release at disposal. The measurement of carbon-14 containing species is challenging due to small chemical carbon-14 content and the small corrosion rates at these chemical conditions. The carbon-14 content in neutron irradiated steel and Zircaloy is a fraction of the non-radioactive carbon content. As a start, the speciation of released non-radioactive carbon has therefore been measured. Table 4 shows six measurements from the Swiss programme [Wieland, 2018b].

Table 4: Analysis of liquid phase and gas phase of stable carbon [Wieland, 2018b]

Time [days]	NOPC [µmol C/L]	HPIEC analysis of carboxylic acids [µM]						GC analysis of hydrocarbons [µM]	
		FA	AA	OA	MA	GA	LA	CH_4	C_2H_4
blank	n.d.	< 5	<5	<0.1	<0.15	<0.5	<0.5	<0.06	<0.03
1	n.d.	7	<5	0.3	<0.15	<0.5	<0.5	<0.06	<0.03
15	204	8	<5	0.5	<0.15	1.3	1.6	<0.06	<0.03
29	216	7	<5	0.5	<0.15	1.4	1.2	0.07	<0.03
93	390	13	<5	0.7	<0.15	1.7	2.8	0.42	<0.03
286	515	49	21	0.3	<0.15	1.6	2.5	0.55	0.08
412	546	20	10	1.0	<0.2	1.3	4.1	0.99	0.06

NOPC: Non Purgeable Organic Carbon i.e. dissolved organic carbon compounds; HPIEC = High Performance Ion Exchange Chromatography, GC = Gas Chromatogram and n.d. not determined.

NOPC contains the dissolved non-ionic compounds. The analytical strategy for the quantification of released alcohols and aldehydes has been made. Please note that these are preliminary results in which the contribution of the used materials in the equipment such as PEEK liner need to be investigated [Wieland, 2018b]. These preliminary results show that the release of gaseous organic carbon is negligible compared to dissolved ionic organic compounds i.e. carboxylic acids and non-gaseous non-ionic organic compounds i.e. alcohols and aldehydes. The released organic carbon is non-retarded organic species in cementitious materials if all NOPC that is measured is released from steel.

6.2 *Irradiated Zircaloy*

Determination of the speciation of released carbon-14 for neutron irradiated Zircaloy is even more challenging than for neutron irradiated steel, due to the small carbon-14 content and smaller corrosion rates. The chemical carbon content is between 0.008-0.027 wt% for Zircaloy-2 and Zircaloy 4 i.e. three orders in magnitude larger than the carbon-14 content. Also, for neutron irradiated Zircaloy, the speciation of non-radioactive carbon can be measured as a start to determine the potential carbon-14 species. A quantification of released carbon species such as performed for steel is a study that could be made in future work.

In the Belgian programme, neutron irradiated Zircaloy and neutron irradiated steel were exposed in portlandite solutions. Gases released from these solutions were measured to be organic gaseous carbon as well as carbon dioxide [Druyts, 2018]. The carbon dioxide may have been formed by oxidation of dissolved organic compounds with OH radicals. Radiolysis may be the reason why both reduced and oxidised hydrocarbons can exist simultaneously in solutions in contact with corroding metals. In the final synthesis report, the measured CO_2 is presumed to be a contaminant produced during leaching [Mibus, 2018].

6.3 *Spent ion exchange resins*

In the above investigated types of waste, carbon-14 has been observed to be released from waste in cementitious pore water. This is not the case for spent ion exchange resins apart from some $^{14}CO_2$ [Bucur, 2017b] that may also be a contaminant as suggested for the leachates in neutron irradiated steel or oxidised by OH radicals. Carbon species as contained by resins are therefore presumed to be released: the anionic compound of dissociated carboxylic acids, bicarbonates and carbonates.

6.4 *Neutron irradiated graphite*

The carbon-14 release rate is affected by the sample preparation process. As the degradation of graphite takes place at such a low rate, neutron irradiated graphite has frequently been crushed into a powder in experiments, to increase the surface reactive area. During this crushing, gaseous carbon-14 contained in pores may be released. It may depend on the operating temperature and chemical conditions as to whether this gaseous carbon-14 is mainly CO_2 or CH_4. In disposal conditions, the release of gaseous carbon species ^{14}CO, CO_2 and ^{14}C-organics and dissolved organic and inorganic species have been identified [Toulhoat, 2015]. For neutron irradiated graphite, the speciation of non-radioactive carbon can be measured as a start to determine the potential carbon-14 species. A quantification of released carbon species in a gaseous and dissolved fraction has been made and summarised by the CAST Advisory Group [Hajdas, 2018]. A gaseous fraction of 5% of the released carbon-14 species or smaller has been found at room temperature under alkaline and anaerobic conditions. A distinction between dissolved inorganic and organic carbon has been noted for Romanian and French irradiated graphite, possibly an artefact of differing graphites and differing irradiation histories. The leaching experiments with the Romanian irradiated graphite show a difference between aerobic and anaerobic conditions. It is unknown whether the dissolved organic carbon is released as carboxylic acids, alcohols or aldehydes.

7 Carbon-14 source term

In a safety assessment, 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, $^{14}CO_2$ 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 larger carbon-14 contents than fruits [IRSN, 2010]. The potential artificial $^{14}CO_2$ release rate into air can be compared with the natural $^{14}CO_2$ emanation rate from soil in order to put the carbon-14 hazard potential from disposal of the waste in perspective with the carbon-14 natural exposure. The daily flux of CO_2 released by the soil appears to be 2 to

13 gram per m^2 [IRSN, 2010]. Cosmogenic generated carbon-14 is present as an impurity with a concentration of about 1 to 1.5 out of 10^{12} non-radioactive carbon atoms. The natural $^{14}CO_2$ flux from soil into air is in the order of 10^9 atoms per cm^2 per year using a daily flux of 2 gram per m^2. Figure 7 shows the potential processes that have an impact on the carbon-14 release rate from waste into air.

Figure 7: Processes resulting into potential carbon-14 exposure

The microbial activity is limited by space restriction in engineered barriers, such as cementitious materials and bentonite, and natural barriers such as rock salt and clay [Neeft, 2017]. This limitation is absent in the biosphere. Carboxylic acids, alcohols, aldehydes and gaseous methane are food sources for microbes; in the root zone and below, organic carbon is converted to inorganic carbon by microbes. The University of Nottingham has investigated the extent of this conversion for the most fast expected migrating organic carbon species methane: most radioactive methane migrating from a repository is likely to be converted to $^{14}CO_2$ in the soil [Lever, 2015]. Dilution would reduce the carbon-14 release rate into the biosphere and common values for dilution in safety assessment are 10^4 for deep geological disposal [IAEA, 2003].

7.1 *Neutron irradiated steel*

The oxide layer on steel found after neutron irradiation has a large impact on the corrosion rate, since the corrosion process is bounded to equilibrium between diffusion of water through the oxide layer and dissolution at the solid-liquid interface. Carbon-14 can be incorporated in the iron-oxide layer and be released when iron-oxide dissolves. Carbon-14 release rate is then equal to the iron release rate. The iron release rate has not been measured but an activation product of iron - ^{60}Co - has been measured. Precipitation of Co as a hydroxide in alkaline environments may result in an underestimation of the corrosion rate. Water hydrolysis is expected at the used potentials to determine the corrosion rate with accelerated tests. An overestimation of the corrosion rate occurs if it is assumed that all current is attributed to corrosion [Mibus, 2018]. A realistic carbon-14 release rate is linearly related to the hydrogen release rate. During anaerobic corrosion at alkaline conditions, a common value for corrosion of stainless steel is 0.01 μm per year. The surface areas of all steel materials are the largest for claddings when it is assumed that both sides of the cladding are exposed to pore water. Even for stainless steel claddings with a thickness of 0.45 mm as used in a research reactor [Neeft, 2003], it may take 70 half-lives of carbon-14 to have the disposed stainless steel completely corroded. Consequently, the main carbon-14 content may decay and is not released. At start of disposal, a reasonable carbon-14 release rate is in the order of 10^{11} carbon-14 molecules per cm^2 per year i.e. two orders of magnitude larger than the carbon-14 emanation rate from soil. After three half-lives of carbon-14, the carbon-14 release rate has reduced by an order in magnitude.

Non-gaseous and non-ionic compounds are measured to be the main carbon-14 released species in a quantification of the carbon-14 released species [Wieland, 2018b]. Due to the lack of electrostatic interactions, the total diffusion porosity in barriers is accessible for these species and no retention is expected in engineered and natural barriers. In case of deep geological disposal of this waste, including dilution would result in a carbon-14 release rate that is negligible is comparison with carbon-14 emanation from the soil. Diffusion and dispersion in the waste package, engineered and natural barriers would further reduce the carbon-14 flux to air.

7.2 Neutron irradiated Zircaloy

The oxide layer on Zircaloy found after neutron irradiation has a large impact on the corrosion rate since the corrosion process is bounded to equilibrium between diffusion of water through the oxide layer and dissolution at the solid-liquid interface. The release fractions of metallic components present in zirconium have been measured in the Japanese programme [Yamashita, 2014] and for CAST converted into corrosion rates [Necib, 2018], see Figure 8.

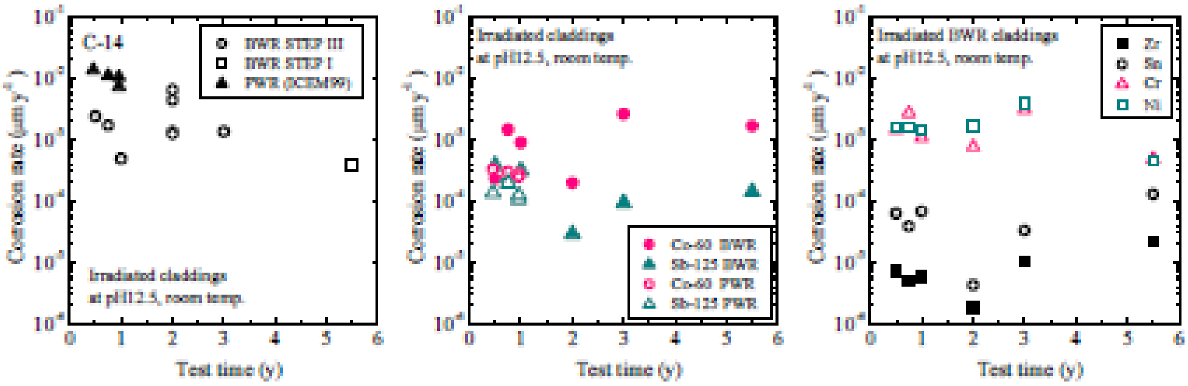

Figure 8: Equivalent corrosion rate or irradiated claddings with regards to carbon-14 release rate (left), release of neutron activated radionuclides (middle) and release of non-radioactive elements [Necib, 2018].

Figure 8 shows a carbon-14 release rate below 10^{-3} μm per year after 5 years. Such values are also obtained for released nickel and chromium compounds, the lower zirconium rate is attributed to the small solubility of zirconia.

The hydrogen generated by anaerobic corrosion of Zircaloy is picked up by Zircaloy. Consequently, the hydrogen released from cementitious pore water would result in an underestimation of the Zircaloy corrosion rate [Gras, 2014]. In the Japanese programme, the hydrogen released and hydrogen absorbed is measured [Sakuragi, 2017]. Figure 9 shows the hydrogen pick-up ratio.

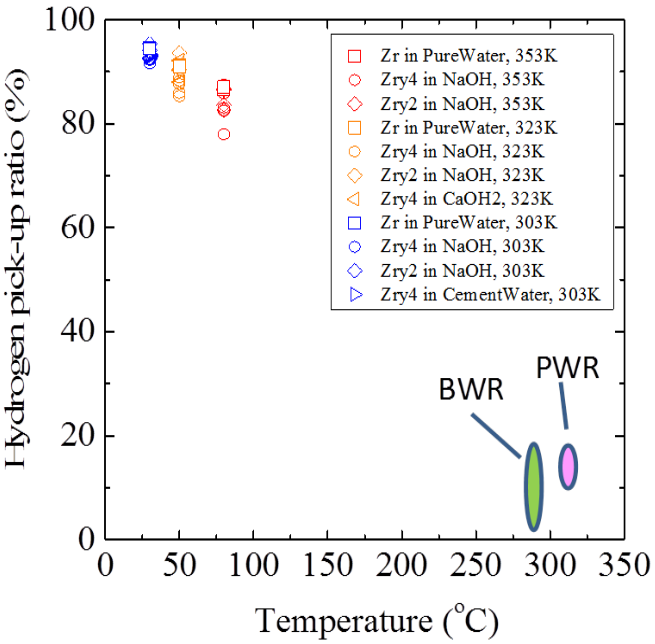

Figure 9: Hydrogen pick-up ratio for the unirradiated Zr alloys by the glass ampoule corrosion tests as a function of temperature [Sakuragi, 2017]

Consequently, at disposal conditions there is less hydrogen available during anaerobic corrosion for the reduction of dissolved organic species than in case of neutron irradiated steel. The corrosion rate of neutron irradiated zircaloy claddings as determined with absorbed hydrogen are also below 1 nm per year [Necib, 2018]. Assuming a value of 1 nm per year and a carbon-14 content of 10^4 Bq per gram, a reasonable carbon-14 release rate is in the order of 10^9 carbon-14 molecules per cm^2 per year i.e. comparable to the carbon-14 emanation flux from soil at start of disposal.

7.3 *Spent ion exchange resins*

Carbon-14 release in cementitious pore water has not observed; carbon-14 species as contained by resins are presumed to be instantaneously released in assessments: the anionic compound of dissociated carboxylic acids, bicarbonates and carbonates. The dissociated carboxylic acids formate and acetate are suggested to be contained by these resins [Reiller, 2018]. Formate is retarded in cementitious materials by exchange with sulphate in ettringite and acetate by sorption on positively charged cementitious minerals [Capouet, 2017].

Released inorganic carbon can only be present as carbonate at a pH above 10. The high calcium content in cementitious pore water and low solubility product will cause retention by precipitation as calcium carbonate. Another retention mechanism of carbonate is sorption on cementitious minerals [Pointeau, 2008]. Processed spent ion exchange resins are already disposed in European countries in near-surface facilities in Sweden, Finland, Hungary, Slovenia, Spain and France [Buckau, 2016]. CAST has provided increase in the confidence that this practice is safe when spent ion exchange resins have been processed with cementitious materials.

7.4 Neutron irradiated graphite

As explained in the previous paragraphs, a chemical corrosion process is assumed to be the main process for the carbon-14 release rate for neutron irradiated metals steels and Zircaloys. Graphite is chemically inert and therefore the main mass loss from neutron irradiated graphite is radiolytic corrosion. In the state of the art collected at the beginning of CAST, common values for neutron irradiated graphite were 10^{-5} to 10^{-7} gram per m^2 per day [Toulhoat, 2015] i.e. 4×10^{-12} to 4×10^{-14} metre day using a density of 2250 kg per m^3 for graphite (the extent of neutron irradiation clearly affects the degree of any radiolytic corrosion). Consequently, the radiolytic corrosion rate ranges between 1.6 nm per year to 0.016 nm per year i.e. similar to or smaller than the corrosion rate of neutron irradiated Zircaloy. The carbon-14 content can be similar to carbon-14 content in neutron irradiated Zircaloy, resulting in similar or smaller carbon-14 fluxes than natural carbon-14 fluxes into air. But, depending on chemical and temperature operating conditions, during this corrosion, some ‘hot spots’ [Toulhoat, 2018] i.e. intergranular pores with carbon-14 containing gas may results in some high carbon-14 peaks.

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