Carbon-14 Source Term

CAST

CAST Final Symposium Report

General Assembly meeting and minutes (D1.15)

Final Symposium

16th-18th January 2018

Lyon, France

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RE	Restricted to the partners of the CAST project	
CO	Confidential, only for specific distribution list defined on this document	

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

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Executive Summary

The CAST Project has been running since October 2013, with five technical work packages focussing on potential release mechanisms of Carbon-14 from irradiated steels, irradiated Zircaloys, ion-exchange resins and irradiated graphite, and assessing how the knowledge gained from the related experimental programmes can inform safety assessments undertaken by waste management organisation, as end-users.

Significant progress has been made on Carbon-14 release mechanisms, speciation and release rates during the CAST project, both in terms of novel experimental development and set-up, and in terms of new results that can be used by waste management organisations.

The CAST Project Final Symposium was held on 16th to 18th January 2018 in Lyon, France. This event aimed to disseminate the outcomes of the CAST project, and to act as a forum for related discussion. In addition, there was the opportunity for relevant research not undertaken in CAST to be presented.

This symposium report records the main points discussed at the event and is deliverable D1.15 for the CAST project.

List of Contents

1 Introduction

1.1 *Welcome*

The meeting was opened by Simon Norris (RWM) who welcomed participants to the symposium.

1.2 *Attendees*

Name	Organisation
Erika Neeft	COVRA
Benjamin Cvetković	PSI
Erich Wieland	PSI
Klas Källström	SKB
Ernestas Narkunas	LEI
Jaap Hart	NRG
Mathieu Charmoillaux	EdF
Dalia Grigaliuniene	LEI
Jens Mibus	NAGRA
Soenke Szidat	University of Bern
Gérard Laurent	Integrated Nuclear Engineering Solutions
Frank Druyts	SCK.CEN
Sebastien Caes	SCK.CEN
Daniela Diaconu	Institute for Nuclear Research (RATEN ICN)
Crina Bucur	Institute for Nuclear Research (RATEN ICN)
Solène Legand	CEA
Diane Lebeau	CEA
Riccardo Levizzari	ENEA
Nikitas Diomidis	NAGRA
Antonietta Rizzo	ENEA
Laetitia Kasprzak	CEA
Sophia Necib	ANDRA
Pascal Reiller	CEA
Manuel Capouet	Ondraf/Niras
Fraser King	Integrity Corrosion Consulting Ltd
Irka Hajdas	ETH Zurich

Name	**Organisation**
Miguel Cunado	ENRESA
Rita Plukiene	Center of Physical Sciences & Technology
Tomo Suzuki-Muresan	University of Nantes
Steve Swanton	Wood
Helen Leung	NWMO
Simon Norris	RWM
Tomofumi Sakuragi	RWMC
Ally Clark	MCM
Michel Herm	Karlsrhe Institute for Nuclear Waste Disposal
Christophe Davies	European Commission
Elena Lagzdina	Center of Physical Sciences & Technology
Stephan Schumacher	ANDRA
Joe Somers	European Commission
Nelly Toulhoat	IPNL
Nathalie Moncoffre	IPNL
Yves Pipon	IPNL
Nicolas Bererd	IPNL
Clotilde Gaillard	IPNL
Marina Rodríguez	CIEMAT
Enrique Magro Lozano	CIEMAT
Petr Večerník	ÚJV Řež, a. s.
Jani Huttunen	Posiva Oy
Kastriot Spahiu	SKB
Liam Payne	RWM
Olli Nummi	Fortum
Eva de Visser-Tynova	NRG
Jean-Charles Robinet	ANDRA
Borys Zlobenko	IEG NASU
Dino Demoli	Ministry of Construction and Physical Planning
Ryo Nakabayashi	Central Research Institute of Electric Power Industry
Peter Molnar	Public Limited Company for Radioactive Waste Management
Andrzej Chwas	Department of Nuclear Energy
Jose Luis Leganés Nieto	ENRESA
Antonín Vokál	Súrao

Name	Organisation
Antoine Ambard	EdF
André Rübel	GRS
Eduard Feldbaumer	ENSI
Ueda Hiroyoshi	Radioactive Waste Management Funding and Research Center (RWMC)
Jérôme Comte	CEA
Andrey Bukaemskiy	Forschungszentrum Juelich GmbH (FZJ)
Irina Gaus	NAGRA
Laurent Charlet	University of Grenoble
Penka Avramova	State Enterprise Radioactive Waste
Eef Weetjens	SCK.CEN
Pierre de Canniere	FANC
Luarent Petit	EdF
Tiina Heikola	VTT
José Vicente Muňoz Serrano	ENRESA
Mayia Mateeva	BNRA
Cyril Plaisir	Ariane Group
Manuela Fulger	Institute for Nuclear Research (RATEN ICN)
Viorel Fugaru	IFNN-HH
Christian Postolache	IFNN-HH
Gunnar Buckau	EC

2 Summary of Work Package 2 (Steels)

The session on steels began with an introduction to the work package by Jens Mibus (Nagra), and was complemented by a wrap-up session by Fraser King (Integrity Corrosion Consulting Ltd.). The key points are highlighted below. Also presented were detailed talks which described: Formation and status of Carbon-14 in activated steel (Michel Herm, KIT); Analytical Techniques and their application (Benjamin Cvetkovic, PSI); and Leaching tests and speciation measurements (Eva de Visser-Tynova, NRG). This session also included a number of invited presentations: Carbon-14 release from steels - State of the Art from Pre- to Post-CAST (Steve Swanton, Wood); and Possible Fate of Inorganic Carbon-14 Released from Activated Steels under Conditions of a Geological Repository (Laurent Charlet, University of Grenoble). Presentation Abstracts for the overview, detailed and invited talks are provided in Appendix 2.

WP2 Aims:

- Understanding of the speciation of Carbon-14 released during corrosion of irradiated steels under conditions relevant to cement-based repositories;
- Techniques for analysing Carbon-14 species in aqueous and gaseous compartments at extremely low concentrations;
- Measuring the release rate and speciation of Carbon-14 in corrosion experiments under various conditions; and
- Validating activation models by measuring Carbon-14 inventories in irradiated steel.

WP2 Challenges:

- Obtaining and working with irradiated samples – This requires specialised equipment and handling procedures, including sample preparation selected in order to keep the metallic surface as representative of real waste as possible.
- Extremely low Carbon-14 release rates in test environments - The low Carbon-14 inventory of activated steel and the very low corrosion rate of stainless steel in alkaline solution make an identification and quantification of Carbon-14 bearing organic compounds formed during anoxic corrosion very challenging.
- Measuring corrosion rates of irradiated materials under alkaline conditions - Special effort was taken to develop a highly sensitive analytical approach allowing compound specific detection of 14C bearing low-molecular weight organic compounds at the expected ultra-trace level.
- Demonstrating congruent release of Carbon-14 - In many countries, the majority of Carbon-14 in a repository for low and intermediate level waste is contained in activated steel. The radionuclide is assumed to be congruently released during corrosion, but with unknown speciation.

- Distinguishing surface contamination from IRF from long-term release - Sample preparation was selected in order to keep the metallic surface as representative of real waste as possible.
- Uncertainty in inventory, in part because of lack of archive material (actual N content) - The inventory can be calculated from activation models but detailed information on the N content in the steel and its irradiation history are required.
- Effect of dose rate on release and speciation of Carbon-14 - A range of samples with differing irradiation histories were used.
- Duration of experiments - Leaching experiments were performed under aerobic and anaerobic conditions at ambient temperature for durations of about one year; in some cases an extension over several years is planned; and
- Characterisation of inventory, i.e. how much, in what form, and distribution within samples – A wide range of analytical techniques were utilised and a suitable technique applied to successfully measure the Carbon-14 release from representative activated steel samples to the gas and aqueous phase.

Fraser King presented the following summary for Carbon-12 and Carbon-14 release, based on the results of experiments conducted during WP2 presented during the symposium:

Organisation	**Conditions**	**Material**	**Liquid phase**		**Gas phase**	
			Spec.	%	Spec.	%
PSI inactive	alkaline anoxic	SS	**AA, FA, OA**	**95**	**Met, Eth**	**5**
PSI active	alkaline anoxic	SS	***FA, AA, LA***	***n.d.***	***n.d.***	***n.d.***
NRJ/ Wood	alkaline anoxic	SS	***CO_3***	***90***	***Met, (CO)***	***10***
KIT	acidic digestion	SS	***organic***	***70***	***organic***	***30***
SCK	alkaline anoxic	CS	**AA, FA**	**n.d.**	**Met**	**n.d.**
Ciemat	alkaline oxic	SS	**n.d.**	**n.d.**	**CO**	**n.d.**
	acidic oxic	SS	**OA**	**n.d.**	**CO**	**n.d.**

WP2 Achievements/highlights:

- Obtaining samples and making Carbon-14 measurements on activated materials – Tested materials include different types of irradiated and unirradiated stainless and carbon steels, as well as carbides.
- Improved understanding of the release of Carbon-14 from irradiated steels – Experimental results point to the existence of a readily available amount of carbon compounds on the surface or within the oxidation layer. Some of them, featuring oxygen containing functional groups, are soluble in aqueous solution, while only a minor amount of hydrocarbons is released to the gas phase.
- Microstructural characterisation of irradiated material – This included the surface of steel coupons, characterised metallographically using optical and electron microscopy techniques.
- Improved understanding of where C-14 is located and in what form (i.e. speciation) - Carbon speciation was successfully characterised by GC, IC and high-performance liquid chromatography (HPLC) combined with MS, liquid scintillation counting

(LSC) or AMS. In some cases simplified analyses of total C and total organic and inorganic analyses (TIC/TOC) were performed.

- Improved understanding of Carbon-14 inventory - The Carbon-14 inventory of the test coupons was usually modelled by activation calculations either using the nominal N content of the alloy or measured values.
- Good understanding of the rate of corrosion under disposal conditions (for inactive samples) - A review of the literature indicated rates for carbon steel in anaerobic alkaline environments generally lower than 100 nm/yr, while corrosion rates of less than 10 nm/yr are reported for stainless steels in similar environments; and
- Issue of congruent release – In the corrosion experiments with activated steel samples a fast release of Carbon-14 mainly to the solution phase (carboxylic acids and indications for carbonate) and a minor amount to the gas phase (CH4, CO) was observed in the first measurement after one week. After that, the Carbon-14 activity concentration in solution remained constant or increased only very slowly. The fast initial release rate was clearly beyond what could be expected from the Carbon-14 inventory and a uniform steel corrosion rate.

3 Summary of Work Package 3 (Zircaloys)

The session on zircaloys began with an introduction to the work package by Sophia Necib (Andra), and was complemented by a wrap-up session by Fraser King (Integrity Corrosion Consulting Ltd.). The key points are highlighted below. Also presented were detailed talks which described: Leaching test and corrosion measurements for irradiated Zr (Crina Bucur, RATEN ICN); Analytical strategy to measure 14C released from irradiated Zr (Tomo Suzuki, University of Nantes); and Corrosion rate measurements on Zircaloy-4 in alkaline media (Sébastien Caes, SCK.CEN). This session also included a number of invited presentations: 14C inventory in irradiated Zircaloys (Michel Herm, Karlsruhe Institute for Nuclear Waste Disposal) and Corrosion of zirconium alloys and 14C release from compacted waste (Antoine Ambard, EdF). Presentation Abstracts for the overview, detailed and invited talks are provided in Appendix 2.

WP3 aims

- State-of-the-art review of Carbon-14 in zircaloy and zirconium alloys - focused on Zircaloys for which Carbon-14 is found either in the alloying part of Zircaloy cladding due to the neutron activation of 14N impurities by 14N(n,p)14C reaction, or in the oxide layer (ZrO2) formed at the metal surface by the neutron activation of 17O from UO2 or (U-Pu)O2 fuel and water from the primary circuit in the reactor by 17O(n,α)14C reaction.
- Advance understanding of Carbon-14 speciation under simulated disposal conditions - Some significant uncertainties remain with respect to speciation of Carbon-14 (inorganic vs. organic), as well as the nature of the organic Carbon-14.
- Develop analytical techniques – Including an analytical procedure for gaseous and dissolved Carbon-14 species quantification.
- Measure release rates – Includes characterising Carbon-14 release from Zr corrosion and Zr oxide dissolution.
- Confirm/measure inventory - There is a lack of reliable data on the chemical state of Carbon-14 in the metal and in the zirconium.
- Oxide layer - Distribution of Carbon-14 between the metal cladding and the zirconia oxide layer depends on the thickness of the oxide. There is a lack of reliable data on the chemical state of 14C in the metal and in the zirconium oxide layer.

WP3 challenges:

- Obtaining and working with irradiated samples – This requires specialised equipment and handling procedures, including sample preparation selected in order to keep the metallic surface as representative of real waste as possible.

- Extremely low Carbon-14 release rates in test environments - Considerable effort was put to develop analytical techniques able to measure Carbon-14 in low concentrations, such as those expected in deep geological repository conditions. The liquid scintillation counting (LSC) was widely used to determine the total Carbon-14 released in alkaline environment as well as the inorganic / organic partition.
- Measuring corrosion rates of irradiated materials under alkaline conditions - Various irradiated and unirradiated Zircaloys (Zr, Zr-2, Zr-4, CANDU and M5TM) have been studied within the project.
- Demonstrating congruent release of C-14 - Leaching experiments in alkaline solutions at pH 12.5 at room temperature suggest that Carbon-14 release would be congruent with the oxide layer dissolution and metal corrosion.
- Uncertainty in inventory, in part because of lack of archive material (actual N content).
- Effect of dose rate on release and speciation of Carbon-14.
- Duration of experiments - Leaching experiments were conducted in alkaline media (NaOH and $Ca(OH)_2$) under anoxic conditions at room temperature for several time durations ranging from 14 days to 6 years.
- Characterisation of inventory – how much, in what form, and distribution within samples.
- Influence of hydride layer.
- Possibility of change in corrosion/release rate as oxide thickens.

WP3 achievements/highlights:

- Obtaining samples and making Carbon-14 measurements on activated materials.
- Good agreement between measured and calculated inventories - Experimentally measured radionuclide contents are compared to theoretically predicted inventories of the irradiated Zircaloy-4 and stainless steel, obtained by means of Monte Carlo

N-Particle (MCNP 2.7)/CINDER calculations as well as SCALE/TRITON/ORIGEN-S calculations.

- Good database of long-term corrosion rates - Various studies have shown that the uniform corrosion rates of zirconium alloys are very low in anaerobic neutral or alkaline waters at low temperature with an envelope value of 20 nm.y^{-1}.
- Unclear whether Carbon-14 released congruently - The results highlight an instant release fraction of Carbon-14 as various experiments showed a relatively constant concentration of Carbon-14 released in static alkaline solution.
- Less Carbon-14 in oxide (7.5%) than currently assumed as IRF in PA - From a safety assessment point of view, the instant release fraction (IRF) was determined on irradiated Zircaloy-2 based on inventory measurements. The results showed that the Carbon-14 inventory in the oxide was around 7.5%, which is below the 20% commonly used in safety case assessments. All in all longer time experiments should be conducted in order to obtain steady state conditions and confirm the current results.

4 Summary of Work Package 4 (Spent Ion-exchange Resins)

The session on spent ion-exchange resins (SIERs) began with an introduction to the work package by Pascal Reiller (CEA), and was complemented by a wrap-up session by Fraser King (Integrity Corrosion Consulting Ltd.). The key points are highlighted below. Also presented were detailed talks which described: Carbon-14 Content and Speciation of SIERs from BWR (Andrey Bukaemskiy, FZJ); Evolution of IERs (Antonietta Rizzo, ENEA); Cementation of SIERs and Consequences on Carbon-14 mobility (Petr Vecernik, UJV); and Particular view of a WMO (Klas Källstrom, SKB). This session also included a number of invited presentations: Carbon-14 Content and Speciation of SIERs from PWR (Jerome Comte, CEA-EdF); and Carbon-14 Content and Speciation of SIERs from CANDU (Crina Bucur, RATEN-ICR). Presentation Abstracts for the overview, detailed and invited talks are provided in Appendix 2.

WP4 Aims

- State-of-the-art review.
- Understanding inventory and speciation - speciation of Carbon-14 associated to the SIERs from the repartition between organic and organic form, up to the more detailed speciation and content of organic acids, and carbonate.
- Determining release rate and mechanism - The initial objective is to obtain further information on the repartition of molecules potentially fixed and/or released from SIERs during their storage in subsurface.

WP4 Challenges

- Wide range of SIER characteristics due to different types of operating plants and different IX locations within a given plant - Using real SIERs samples from pressurized water reactors (PWRs), CANDU reactors, and BWRs it has been made possible to show that retained Carbon-14 in SIERs consisted mainly of inorganic carbonate form, as *e.g.* observed in CANDU SIERs, whereas a small fraction of organic Carbon-14-bearing compounds bound to SIERs was detected.
- Relating release to geological disposal conditions for cemented and immobilised SIERs - The immobilization of resins in cement is a possible solution. These matrices have the advantages to retain CO2 under the form of carbonate ions, and also have the possibility to adsorb organic acids.
- Effects of porosity, groundwater flow, etc.
- Uncertainty over long-term (radiation) stability of resins.

WP4 Achievements/highlights

- Because of the wide variability of SIERS, country-specific inventories and speciation are required - Using real SIERs samples from pressurized water reactors (PWRs), CANDU reactors, and BWRs it has been made possible to show that retained Carbon-14 in SIERs consisted mainly of inorganic carbonate form, as e.g. observed in CANDU SIERs, whereas a small fraction of organic Carbon-14-bearing compounds bound to SIERs was detected. Their ratio was demonstrated to be influenced by the pre-treatment, cleaning circuit and storage conditions of the SIERs.

- Good understanding of speciation - The total Carbon-14 content and its partition between inorganic and organic species as well as inventories of 3H and main gamma emitters (137Cs, 134Cs, 60Co, and 54Mn) were determined on SIERs.
- In general, majority present as inorganic 14C but fraction depends on reactor type:
    - PWR: 1-70% organic
    - BWR: 1-5% organic
    - CANDU: 7% organic (single sample)
- Gas-phase inorganic Carbon-14 is released under conditions that simulate storage and long-term disposal (alkaline pH).
- Effect of immobilization in cement, epoxy, bitumen matrix investigated - If the release of Carbon-14 seems favoured in high concentrated alkaline aqueous media, it seems that cement matrices are not releasing Carbon-14, certainly due to calcium carbonate precipitation and organic acid adsorption.

5 Summary of Work Package 5 (Graphite)

The session on graphite began with an introduction to the work package by Simon Norris (RWM), and was complemented by a wrap-up session by Fraser King (Integrity Corrosion Consulting Ltd.). The key points are highlighted below. Also presented were detailed talks which described: Ion irradiation used as surrogate for neutron irradiation to understand nuclear graphite evolution during reactor operation: consequences for long lived radionuclide behaviour (Nelly Toulhoat, IPNL); Carbon-14 in TRIGA Irradiated Graphite and its Release under Alkaline Conditions (Crina Bucur, RATEN ICN); Oldbury graphite study for RWM (Steve Swanton, Wood); Presentation Abstracts for the overview and detailed talks are provided in Appendix 2.

WP5 Aims:

- Build on earlier EC Carbowaste project outcomes which addressed the "Treatment and Disposal of Irradiated Graphite and other Carbonaceous Waste”;
- Determine the Carbon-14 inventory and concentration distribution in i-graphites and factors that may control these;
- Measure the rate and speciation of Carbon-14 release to solution and gas from i-graphites in contact with aqueous solutions; and
- Assess impacts of selected waste treatment options on Carbon-14 release and relating this to the nature of Carbon-14 in i-graphite.

WP5 Challenges:

- Diversity of national interests with respect to how to manage and safely dispose of graphite, covering treatment, processing and packaging concepts.
- Amount of i-graphite waste in each national inventory varies widely.
- Surface vs. deep geological disposal as a method for dealing with i-graphite wastes and therefore consideration of differing environmental conditions, post-closure timeframes and performance assessment risk criteria.

WP5 Achievements/highlights:

- Detailed understanding of distribution of Carbon-14 within the waste
- Improved mechanistic understanding
- Small releasable fraction –Less than 2% from the total Carbon-14 inventory in the specimens subject to the leaching tests was released as dissolved species. Both inorganic and organic Carbon-14 species are released during leaching test, with

more inorganic Carbon-14 release under aerobic conditions (around 68% from the total Carbon-14 released as dissolved species), and more organic Carbon-14 species in anaerobic conditions (around 65% from the total Carbon-14 released as dissolved species).

- Initial fast release, slow long-term – For example in the leach tests, both for anaerobic and aerobic conditions, the leaching rates are high in the first days of immersing and it decrease after that, indicating a two stage process: an initial quick release (less than 9 10^{-02} % of inventory/day for the first 48 days) followed by a slower release rate (around 4 10^{-03} % of inventory/day).
- Speciation - Carbon-14 can be released to both the gas and aqueous phases. Carbon-14 released to the gas phase may exist as a number of different species with potentially different consequences, including organic species (e.g. CH_4), CO_2 and CO.
- Inventory and especially distribution – the long-term leaching tests on Oldbury graphite for the UK programme have shown the Carbon-14 released was predominantly held in solution, with <1% of the Carbon-14 released entering the gas phase. Gaseous Carbon-14 was predominantly in the form of hydrocarbons and 14CO (or possibly volatile oxygen-containing organic compounds), with $14CO_2$ being retained in the alkaline solution. A fraction of the Carbon-14 in solution comprised organic species.
- Consequences of in-reactor behaviour on the Carbon-14 source term.

6 Summary of Work Package 6 (Safety Assessment)

The session on safety assessment began with an introduction to the work package by Manuel Capouet (Ondraf/Niras), and was complemented by a wrap-up session by Fraser King (Integrity Corrosion Consulting Ltd.). The key points are highlighted below. Also presented were detailed talks which described: Implications of the CAST results for the disposal systems crystalline host rocks (Olli Nummi, Fortum); The role of Carbon-14 for repositories in salt: Integration of the CAST results (Andre Rübel, GRS); Assessment of aqueous 14C transfer in an Intermediate-Level Waste (ILW) disposal cell (Jean-Charles Robinet, Andra); Current position on Carbon-14 in the RWM Environmental Safety Case (Simon Norris, RWM); and An Overview of Carbon-14 Treatment in Post-closure Safety Assessment in a Canadian Deep Geologic Repository (Helen Leung, NWMO). Presentation Abstracts for the overview and detailed talks are provided in Appendix 2.

WP6 Aims:

- Improve treatment of Carbon-14 in safety analysis/ assessment and the safety case - Because of its rapid decay compared to timeframes considered in safety assessment, Carbon-14 radiological flux released in the biosphere is particularly sensitive to its transport characteristic time in geological disposal.
- Speciation, IRF, release rate – how to incorporate this understanding into the safety assessment and safety case.
- Scientific understanding - developing detailed underpinning knowledge of the Carbon-14 inventory and release scenarios for the range of disposal options (e.g. deep/near-surface disposal and different host rock media, i.e. clay and hard rocks) and waste types (cemented versus other media).
- How to influence experimental groups to study processes that are safety-relevant.
- Diversity of national disposal programmes – different waste treatment routes and end-points for Carbon-14 containing wastes.
- Abstraction of data (and uncertainties) from experimental programmes to inform Carbon-14 treatment in the safety case.

WP6 Achievements/highlights:

- Understanding of the relative importance of Carbon-14 for different host rock types - Sensitivity studies for diffusive and saturated scenarios in clay systems reported in the CAST project show that the radiological impact remains well below regulatory limits even considering a transport of unretarded Carbon-14 (organic) compounds. This good performance is due the slow diffusive transport in the geological host rock. The robustness of the system might be challenged in scenarios where a diffusive barrier is either absent or does not afford its intended functionality; in such a scenarios, the residence time of Carbon-14C in the host rock (or in part of the surrounding geology) would be shorter, and the release of Carbon-14 to the biosphere might be e.g. more localised, or at a higher-than-desired rate.

- Understanding of the relative importance of Carbon-14 for different waste types – results that can support understanding for the safety assessment have been reported for steels, zircaloy, graphite and spent ion exchange resins, and safety assessment studies have also been extended to other wastes, e.g., for spent fuel, Carbon-14 will decay significantly in a long-lived canister.
- Understanding of relative importance of Carbon-14 depending on repository location and the expected environmental conditions and their evolution over post-closure timeframes, including saturated conditions and extent of diffusive transport pathways to surface.
- Surface vs. deep disposal - It must be remembered that some national programmes participating in CAST Work Package 5 do not envisage a deep geological disposal approach for the long-term management of irradiated graphite; for example, some consider long term storage in a surface facility or disposal to a near surface / shallow geological facility disposal.

Further to the above general conclusions, the final wrap-up presentation by Fraser King (Integrity Corrosion Consulting Ltd.) indicated the following conclusions relative to each host rock.

Clay host rock

In a typical diffusive and saturated post-closure evolution scenario, results indicate excellent performance of the clay host rock to confine Carbon-14. The performance of a disposal system in clay for Carbon-14 is dominated by the clay barrier: Retention processes might have a strong impact but results indicate different behaviour between non-(weakly) retarded organic Carbon-14 and retarded inorganic Carbon-14. With regards to the performances of the EBS in a clay host rock system: (i) the instant release fraction has limited impact; (ii) the influence of the corrosion rate (release rate) is relevant only over large ranges; and (iii) the diffusion process is limited to short distances if low diffusion coefficient and/or high sorption/retention coefficient is assumed. In terms of post-closure containment of Carbon-14 contributions, the influence of the sorption coefficient (K_d) values of Carbon-14 in clay increases the further away from the Carbon-14 source. The safety assessment simulations performed in CAST are in line with the results of national clay-host rock programme safety assessment results, indicating that the contribution of Carbon-14 to various safety indicators (dose rate to biosphere, radiotoxicity fluxes / concentrations), is small compared to other radionuclides. The uncertainty analysis and safety assessment analyses indicate that assessing the safety consequences of Carbon-14 disposed in a deep geological repository in clay-host rock would benefit from enhancing the understanding of parameters and processes that determine the migration rate of Carbon-14 in the Clay host rock, and to a lesser extent in concrete.

Crystalline host rock

The crystalline host rock safety assessment assumptions consider the possible transport of aqueous and gaseous Carbon-14 species through diffusive transport, therefore the geosphere contributions are predominantly to the isolation safety function, and less so to containment. It is generally assumed that for safety assessment dose rates to be significant Carbon-14 gases must migrate through the engineered barriers in significant quantities and these gases must migrate through the overlying geological environment (either as a distinct gas phase or as dissolved gas). For crystalline host rock post-closure scenarios considered in CAST, Spent Ion Exchange Resins are a key consideration owing to their wide variability (and country-specific) inventories and speciation assumptions, which applies also to other host rocks, but highlights the need to ensure safety assessment approaches, for use in relation to Spent Ion Exchange Resins, are appropriately. For hard rock crystalline systems, the conditioning matrix (e.g. cementitious grout and disposal area backfills, or other robust conditioning media, e.g. epoxy) limits the water flow. Source term release is governed by the cement evolution through time dependent diffusion coefficients and hydraulic conductivities. For systems considering an epoxy matrix for conditioning and immobilisation, a near-field retardation capacity can also be assumed. Sensitivity analysis on sorption coefficients (ranging from K_d [1E-5 to 1E-3] m3/Kg), for both the host formation and cement backfill, shows an impact (one order of magnitude) on assessment results.

Salt host rock

In the salt host rock safety assessment, no release of Carbon-14 is reported, mostly because water-borne radionuclide transport is reduced and retarded by unsaturated or even dry conditions over long timescales for the reference case evolution scenario. Carbon-14 is the only volatile radionuclide with significant inventory and long half-life considered in the salt host-rock system, with assumptions that gas induced transport cannot be prevented due to the following processes: (i) Flow of air displaced by convergence of the host rock; (ii) Gas generation by corrosion and degradation of the waste containers/waste; (iii) Depending on availability of water the gas generation may end at early times; and (iv) Limited gas dissolution due to unsaturated conditions. Assessment outputs indicate that the percentage of IRF has the major influence on the radiotoxicity flux. For Zircaloy, experimental results from CAST suggest values for the IRF which are significantly lower than used until now (by GRS). If results are integrated into future assessment work, a reduction of consequences can be expected. For steels, a congruent release of Carbon-14 with corrosion of the material is suggested in CAST. The instant release fraction is assumed to be very low. If the availability of water is limited in the repository in salt host rock, this also could substantially limit the release of Carbon-14.

7 Summary of Work Package 7 (Dissemination)

The final session on dissemination began with an introduction to the work package by Erika Neeft (Covra), and followed with a presentation on the CAST – Expert Review Group Findings by Irka Hajdas (ETHZ) and Fraser King (Integrity Corrosion Consulting Ltd.). The key points are highlighted below. Following this, a Panel Session was also held to disseminate the – Implications of CAST Project outcomes on waste management organisations safety assessments. The Panel Members were: Miguel Cuñado (ENRESA); Klas Källström (SKB); Irina Gaus (NAGRA); Antonín Vokál (Súrao); Peter Molnar (PURAM); and Olli Nummi (Fortum). Presentation Abstracts for the overview is provided in Appendix 2.

Key highlights from the overview presentation by Erika Neeft (Covra) on how dissemination of the CAST project has been undertaken included:

- Key performance indicators have been used throughout the project to monitor dissemination activities, these included:
  1. Monitoring hits on the CAST public website (>16,000 to Jan 2018);
  2. Number of peer reviewed papers originating from work of CAST; and
  3. Contributions and involvement with other EU countries towards CAST activities.
- Newsletters have been published to present project outputs on one page.
- The CAST website has made available lecture notes from training courses.

Conclusions made by Irka Hajdas (ETHZ) and Fraser King (Integrity Corrosion Consulting Ltd) included:

- New scientific understanding on Carbon-14 inventory, release, speciation and treatment in the safety assessment have been gained and were clearly achieved within the CAST project;
- With regards to the safety assessment, useful data has been generated for safety analysis and especially underlying information to support the safety case;
- Dissemination to stakeholders of the CAST project events and results has included workshops, an impressive number of reports/ deliverables, the final symposium, and the special edition journal publication.
- CAST has provided a good forum for learning and development for early career researchers. Participants in the final CAST symposium represented a broad range of experts ranging across early, mid, and late-career.

Appendix 1 CAST Symposium Final Agenda and Abstracts

EUROPEAN
COMMISSION

European
Research Area

Final Symposium Agenda

EC CAST (CArbon-14 Source Term) Project

Ibis Style Lyon Villeurbanne,
Lyon, France,
16th – 18th January 2018.

Symposium Venue Address: Ibis Styles Lyon Villeurbanne, 130 boulevard du - 11 Novembre 1918 - 69100, Villeurbanne, Lyon, France.

The research leading to these results has received funding from the European Union's European Atomic Energy Community's (Euratom) Seventh Framework Programme FP7/2007-2013 under grant agreement no 604779, the CAST project.

BACKGROUND

The EC 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.

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 release 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.

SYMPOSIUM OBJECTIVE

The CAST Project has been running since October 2013, with five technical work packages focussing on potential release mechanisms of carbon-14 from irradiated steels, irradiated Zircaloys, ion-exchange resins and irradiated graphite, and assessing how the knowledge gained from the related experimental programmes can inform safety assessments undertaken by waste management organisation, as end-users.

Significant progress has been made on carbon-14 release mechanisms, speciation and release rates during the CAST project, both in terms of novel experimental development and set-up, and in terms of new results that can be used by waste management organisations.

This event aims to disseminate the outcomes of the CAST project, and to act as a forum for related discussion. In addition, there will be the opportunity for relevant research not undertaken in CAST to be presented. The overall intention is to bring together scientists working in this field, both to learn more about the CAST project output, and to discuss the implications of carbon-14 release mechanisms in safety assessments of geological disposal facilities.

FINAL AGENDA

Ibis Styles Lyon Villeurbanne, 130 boulevard du - 11 Novembre 1918 - 69100, Villeurbanne, Lyon, France.

Day 1 Tuesday 16th January 2018

Time	Activity
08.45 - 09.00	Registration & Coffee
09.00 - 09.10	Welcome Speech *Guy Chanfray (IPNL)*
09.10 - 09.25	CAST Project Overview *Simon Norris (RWM)*
09.25 - 09.30	Information on Guided tour of the Traboules of Lyon. *Nelly Toulhoat (IPNL)*
09.30 - 10.15	**Keynote Speaker** Why studying ^{14}C is important: the context of ^{14}C with respect to safety assessment development. *Virginie Wasselin Trupin (IRSN)*
Work Package 2 – Steels **Session Chair – Jens Mibus (Nagra)**	
10.15 - 10.25	Overview of Main WP2 Outcomes. *Jens Mibus (Nagra)*
10.25 - 10.40	Formation and status of ^{14}C in activated steel. *Michel Herm (KIT)*
10.40 - 10.55	Analytical Techniques and their application. *Benjamin Cvetkovic (PSI)*
10.55 - 11.10	Leaching tests and speciation measurements. *Eva de Visser-Tynova (NRG)*
11.10 - 11.40	**CAST Invited presentation** 14C release from steels: State of the Art from Pre- to Post-CAST. *Steve Swanton (Wood)*
11.40 - 11.55	Coffee
11.55 - 12.40	**External Invited presentation** Possible Fate of Inorganic 14C Released from Activated Steels under Conditions of a Geological Repository. *Laurent Charlet (University of Grenoble)*
12.40 - 13.00	WP2 Summary and Conclusions. *Jens Mibus (Nagra)*
13.00 - 14.00	Lunch
Work Package 3 – Zircaloy **Session Chair – Sophia Necib (Andra)**	
14.00 - 14.10	Overview of Main WP3 Outcomes. *Sophia Necib (Andra)*

14.10 - 14.25	**CAST Invited presentation** ^{14}C inventory in irradiated Zircaloys. *Michel Herm (Karlsrhe Institute for Nuclear Waste Disposal)*
14.25 - 14.45	Leaching test and corrosion measurements for irradiated Zr. *Crina Bucur (RATEN ICN)*
14.45 - 15.05	Analytical strategy to measure ^{14}C released from irradiated Zr. *Tomo Suzuki (University of Nantes)*
15.05 - 15.25	Corrosion rate measurements on Zircaloy-4 in alkaline media. *Sébastien Caes (SCK.CEN)*
15.25 - 15.45	WP3 Summary and Conclusions. *Sophia Necib (Andra)*
15.45 - 16.00	Coffee
16.00 - 16.45	**External Invited presentation** Corrosion of zirconium alloys and ^{14}C release from compacted waste. *Antoine Ambard (EdF)*
16.45 - 17.00	Discussion
17.00 - 20.00	**POSTER SESSION** (with buffet/drinks)

Day 2 Wednesday 17th January 2018

Time	Activity
08.30	Welcome & Coffee
Work Package 4 – Ion Exchange Resins **Session Chair – Pascal Reiller (CEA)**	
08.45 - 08.55	Overview of Main WP4 Outcomes. *Pascal Reiller (CEA)*
08.55 - 09.10	**CAST Invited presentation** ^{14}C Content and Speciation of SIERs from PWR. *(Jerome Comte, CEA-EdF)*
09.10 - 09.25	**External Invited presentation** ^{14}C Content and Speciation of SIERs from CANDU. *(Crina Bucur, RATEN-ICR)*
09.25 - 09.40	^{14}C Content and Speciation of SIERs from BWR. *Andrey Bukaemskiy (FZJ)*
09.40 - 09.55	Evolution of IERs. *Antonietta Rizzo (ENEA)*
09.55 - 10.10	Cementation of SIERs and Consequences on ^{14}C mobility. *Petr Vecernik (UJV)*
10.10 - 10.25	Particular view of a WMA. *Klas Källstrom (SKB)*
10.25 - 10.35	WP4 Summary and Conclusions *Pascal Reiller (CEA)*
10.35 - 11.00	Coffee

Work Package 5 – Graphite **Session Chair – Simon Norris (RWM)**	
11.00 - 11.10	WP5 - Overview of Main Outcomes. *Simon Norris (RWM)*
11.10 - 11.35	Ion irradiation used as surrogate for neutron irradiation to understand nuclear graphite evolution during reactor operation: consequences for long lived radionuclide behaviour. *Nelly Toulhoat (IPNL)*
11.35 - 11.55	^{14}C in TRIGA Irradiated Graphite and its Release under Alkaline Conditions. *Crina Bucur (RATEN ICN)*
11.55 - 12.20	Oldbury graphite study for RWM. *Steve Swanton (Wood)*
12.20 - 12.30	WP5 Summary and Conclusions *Simon Norris (RWM)*
12.30 - 13.15	Lunch & Poster Session
13.15 - 13.40	New concept and instruments for ^{14}C measurements in i-graphite. *Gérard Laurent (Integrated Nuclear Engineering Solutions)*
Work Package 6 – Safety Case Relevance **Session Chair – Manuel Capouet (Ondraf/Niras)**	
13.40 - 14.05	Implication of CAST results on safety assessment and safety case: Introduction and focus on disposals in clay formations. *Manuel Capouet (Ondraf/Niras)*
14.05 - 14.30	Implications of the CAST results for the disposal systems crystalline host rocks. *Olli Nummi (Fortum)*
14.30 - 14.55	The role of ^{14}C for repositories in salt: Integration of the CAST results. *Andre Rübel (GRS)*
14.55 - 15.05	Coffee
15.05 – 15.30	Assessment of aqueous ^{14}C transfer in an Intermediate-Level Waste (ILW) disposal cell. *Jean-Charles Robinet (Andra)*
15.30 – 15.40	Current position on ^{14}C in the RWM Environmental Safety Case. *Simon Norris (RWM)*
15.40 – 16.05	An Overview of ^{14}C Treatment in Post-closure Safety Assessment in a Canadian Deep Geologic Repository. *Helen Leung (NWMO)*
16.15 – 18.30	Guided tour of the Traboules of Lyon.
19.30	Conference Dinner (Ibis Style Lyon Villeurbanne)

Day 3 Thursday 18th January 2018

Time	Activity
9.00	Welcome & Coffee
9.15 - 10.00	WP7 Dissemination Overview. *Erika Neeft (Covra)*
10.00 - 10.45	CAST - Expert Review Group Findings.

	Irka Hajdas (ETHZ)& Fraser King (Integrity Corrosion Consulting Ltd)
10.45 - 11.00	Coffee
11.00 - 12.00	Panel Session – Implications of CAST Project outcomes on waste management organisations safety assessments. - Miguel Cuñado (ENRESA) - Klas Källström (SKB) - Irina Gaus (NAGRA) - Antonín Vokál (Súrao) - Peter Molnar (PURAM) - Olli Nummi (Fortum) • *How could the outputs of CAST be used to inform national programmes?* • *Feedback on CAST project approach to dissemination: present and longer-term;* • *Are there any remaining gaps or uncertainties of safety case significance?* • *Are there opportunities for future collaboration?*
12.00 - 13.00	Lunch
13.00 – 16.00 - 2nd CAST Workshop - (*Please note this is not part of CAST Symposium)*	

RADIOCARBON SPECIAL EDITION

There will be a special edition of the Radiocarbon journal containing papers from this symposium. Please advise simon.norris@nda.gov.uk and alastair.clark@mcmenvironmental.co.uk by **31ST JANUARY 2018** if you intend to submit a paper. Note that the target date for submission of papers to the journal itself is **28TH FEBRUARY 2018**. Further details to follow.

OFFICIAL LANGUAGE

English will be the working language for the oral and written communications of the symposium.

CONFERENCE FEE

There will be no conference fee. Advance registration is required.

PRACTICAL INFORMATION AND REGISTRATION

All T&S and accommodation costs will be covered by the attendees. The poster buffet is free to registered participants.

SYMPOSIUM DINNER

Attendance at the symposium dinner can be registered by emailing the hotel directly - h9012-sl@accor.com. The cost of the dinner (exclusive of drinks) is €35 and this charge will be transferred directly to the room bill of those staying at the hotel. For those not staying at the hotel this charge will be payable at the end of the meal.

CONTACTS

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PROGRAMME COMMITTEE

Simon Norris (RWM – CAST Coordinator and WP5 Leader)
Jens Mibus (Nagra – CAST WP2 Leader)
Sophia Necib (Andra – CAST WP3 Leader)
Pascal Reiller (CEA – CAST WP4 Leader)

Manuel Capouet (Ondraf/Niras – CAST WP6 Leader)
Erika Neeft (Covra – CAST WP7 Leader)
Fraser King (Integrity Corrosion Consulting, CAST Expert Review Group)
Irka Hajdas (ETH, Switzerland, CAST Expert Review Group)
Ally Clark (MCM Environmental Services Ltd, CAST Coordinator)
Nelly Toulhoat (CNRS)
Nathalie Moncoffre (IPNL)

WEBSITE

Information on the symposium is available through the CAST website - http://www.projectcast.eu/.

LIST OF SYMPOSIUM PARTICIPANTS

Name	Organisation	Country
Erika Neeft	COVRA	Netherlands
Benjamin Cvetković	PSI	Switzerland
Erich Wieland	PSI	Switzerland
Klas Källström	SKB	Sweden
Ernestas Narkunas	LEI	Lithuania
Jaap Hart	NRG	Netherlands
Mathieu Charmoillaux	EdF	France
Dalia Grigaliuniene	LEI	Lithuania
Jens Mibus	NAGRA	Switzerland
Soenke Szidat	University of Bern	Switzerland
Gérard Laurent	Integrated Nuclear Engineering Solutions	France
Frank Druyts	SCK.CEN	Belgium
Sebastien Caes	SCK.CEN	Belgium
Daniela Diaconu	Institute for Nuclear Research (RATEN ICN)	Romania
Crina Bucur	Institute for Nuclear Research (RATEN ICN)	Romania
Solène Legand	CEA	France
Diane Lebeau	CEA	France
Riccardo Levizzari	ENEA	Italy
Nikitas Diomidis	NAGRA	Switzerland
Antonietta Rizzo	ENEA	Italy
Laetitia Kasprzak	CEA	France
Sophia Necib	ANDRA	France
Pascal Reiller	CEA	France
Manuel Capouet	Ondraf/Niras	Belgium
Fraser King	Integrity Corrosion Consulting Ltd	Canada
Irka Hajdas	ETH Zurich	Switzerland
Miguel Cunado	ENRESA	Spain
Rita Plukiene	Center of Physical Sciences & Technology	Lithuania
Tomo Suzuki-Muresan	University of Nantes	France
Steve Swanton	Wood	UK
Helen Leung	NWMO	Canada
Simon Norris	RWM	UK
Tomofumi Sakuragi	RWMC	Japan
Ally Clark	MCM	UK
Michel Herm	Karlsrhe Institute for Nuclear Waste Disposal	Germany
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Elena Lagzdina	Center of Physical Sciences & Technology	Lithuania
Stephan Schumacher	ANDRA	France

Name	Organisation	Country
Joe Somers	European Commission	EC
Gunnar Buckau	European Commission	EC
Nelly Toulhoat	IPNL	France
Nathalie Moncoffre	IPNL	France
Nicolas Bererd	IPNL	France
Marina Rodríguez	CIEMAT	Spain
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Petr Večerník	ÚJV Řež, a. s.	Czech Republic
Jani Huttunen	Posiva Oy	Finland
Kastriot Spahiu	SKB	Sweden
Liam Payne	RWM	UK
Olli Nummi	Fortum	Finland
Eva de Visser-Tynova	NRG	Netherlands
Jean-Charles Robinet	ANDRA	France
Borys Zlobenko	IEG NASU	Ukraine
Dino Demoli	Ministry of Construction and Physical Planning	Croatia
Ryo Nakabayashi	Central Research Institute of Electric Power Industry	Japan
Peter Molnar	Public Limited Company for Radioactive Waste Management	Hungary
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Antonín Vokál	Súrao	Czech Republic
Antoine Ambard	EdF	France
André Rübel	GRS	Germany
Ueda Hiroyoshi	Radioactive Waste Management Funding and Research Center (RWMC)	Japan
Jérôme Comte	CEA	France
Andrey Bukaemskiy	Forschungszentrum Juelich GmbH (FZJ)	Germany
Irina Gaus	NAGRA	Switzerland
Laurent Charlet	University of Grenoble	France
Nassia Tzelepi	National Nuclear Laboratory (NNL)	UK
Penka Avramova	State Enterprise Radioactive Waste	Bulgaria
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Pierre de Canniere	FANC	Belgium
Luarent Petit	EdF	France
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Manuela Fulger	Institute for Nuclear Research (RATEN ICN)	Romania

Name	Organisation	Country
Viorel Fugaru	IFNN-HH	Romania
Christian Postolache	IFNN-HH	Romania
Gunnar Buckau	European Commission	EC

SYMPOSIUM ABSTRACTS

DAY 1

CAST Project Overview

Dr Simon Norris

Radioactive Waste Management Limited, B587, Curie Avenue, Harwell Campus, Didcot, Oxon, OX11 0RH, United Kingdom.

The EC 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 has focused on the release of carbon-14 as dissolved and gaseous species from irradiated metals (steels, Zircaloys), from irradiated graphite and from ion-exchange materials.

The CAST consortium has brought 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 release 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.

Symposium Objective

The CAST project has been running since October 2013, and concludes in March 2018. Over its duration, significant progress has been made on carbon-14 release mechanisms, speciation and release rates during the CAST project, both in terms of novel experimental development and set-up, and in terms of new results that can be used by waste management organisations.

This symposium aims to disseminate the outcomes of the CAST project, and to act as a forum for related discussion. In addition, there will be the opportunity for relevant research not undertaken in CAST to be presented. The overall intention is to bring together scientists working in this field, both to learn more about the CAST project output, and to discuss the implications of carbon-14 release mechanisms in safety assessments of geological disposal facilities.

Keynote speaker

Why studying ^{14}C is important: the context of ^{14}C with respect to safety assessment development

Dr. Virginie Wasselin-Trupin

Institut de Radioprotection et de sûreté nucléaire (F)

European member states have to define their national radioactive waste management programs in compliance with the European Council Directive 2011/71. In this directive, are given the general requirements for establishing a national program to manage all types of spent fuel and radioactive waste, from generation to disposal. The safety of the disposal relies upon a series of components and design provisions with the objectives of confining and limiting the migration of the radionuclides and chemical toxics toward the biosphere. The concept of the disposal must be designed in order to keep the impact as low as reasonable. The dedicated tool used for assessing the impact of a disposal concept is the safety assessment presented in IAEA safety standard (SSR-5). The aim of this talk is to present the development of such safety assessment. ^{14}C, as activation product, is present in different categories of waste like metallic waste, graphite waste, vitrified waste, spent fuel… The knowledge of its inventory, speciation, release rate and migration in the different components of the disposal is a prerequisite for the development of the safety assessment.

Work Package 2 – Steels

Overview of Main WP2 Outcomes

Speciation of Carbon-14 Released from Activated Steels Under Conditions of a Geological Repository

J. Mibus (1), N. Diomidis (1), S. Swanton (2), T. Suzuki - Muresan (3), M. Rodríguez Alcalá (4), J.L. Leganés Nieto (5), D. Bottomley (6), M. Herm (7), E. de Visser - Týnová (8), B.Z. Cvetković (9), T. Sakuragi (10), F. Druyts (11) and T. Heikola (12)

1. *Nagra, Hardstrasse 73, 5430 Wettingen, Switzerland*
2. *Wood, B150 Thomson Avenue, Harwell Campus, Didcot, Oxfordshire, OX11 0QB, UK*
3. *Armines, 60 Boulevard Saint-Michel, Paris, 75272, France*
4. *Ciemat, 40 Avenida Complutense, Madrid, 28040, Spain*
5. *Enresa, 7 Calle Emillio Vargas, Madrid, 28043, Spain*
6. *JRC Karlsruhe, Hermann-von-Helmholtz-Platz. 1, 76344, Eggenstein-Leopoldshafen, Germany*
7. *KIT, Hermann-von-Helmholtz-Platz 1, 76344, Eggenstein-Leopoldshafen, Germany*
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In many radioactive waste disposal programmes ^{14}C is an important radionuclide with a potential for significant dose contributions in safety assessment for a geologic repository. In nuclear reactors ^{14}C is mainly formed by neutron capture from ^{14}N, ^{17}O or ^{13}C. Little is known, however, on the chemical form of ^{14}C after release from the waste and the migration of the potential carrier compounds. This gives rise to a considerable uncertainty regarding the fate of ^{14}C and a conservative treatment in safety assessment. The EU project CArbon-14 Source Term (CAST) aims to improve our understanding of the ^{14}C release from different radioactive waste materials like irradiated metals from reactor internals (steels and Zircaloy), spent ion exchange resins and irradiated graphite under conditions relevant to geological disposal. The results are evaluated in the context of national safety assessment of the countries involved and disseminated to stakeholders.

In many countries, the majority of ^{14}C in a repository for low and intermediate level waste is contained in activated steel. The radionuclide is assumed to be congruently released during corrosion, but with unknown speciation. Work package 2 of the CAST project studies the release and speciation of ^{14}C from activated steel in a cementitious environment. The objectives of this work are the development of suitable analytical techniques and their application to measure the ^{14}C release from representative activated steel samples to the gas and aqueous phase and the ^{14}C speciation.

Upon initiation of the project, a review of the literature on the rate of corrosion and of ^{14}C release from irradiated carbon and stainless steels in relevant environments was undertaken. The review indicated that corrosion rates of steel under disposal conditions are well documented, with rates for carbon steel in anaerobic alkaline environments generally lower than 100 nm/yr, while corrosion rates of less than 10 nm/yr are reported for stainless steels in similar environments. However, it should be borne in mind that these corrosion rates were obtained on unirradiated steels. On the other hand, the review has highlighted the current lack of well-documented active and inactive studies of the release of carbon from low-carbon and stainless steels that include measurements of carbon releases to both the gas and aqueous phase under aerobic and anaerobic conditions. Additional uncertainties arise from the fact that the ^{14}C inventory for many wastes is unknown. The inventory can be calculated from activation models but detailed information on the N content in the steel and its irradiation history are required.

The low ^{14}C inventory of activated steel and the very low corrosion rate of stainless steel in alkaline solution make an identification and quantification of ^{14}C bearing organic compounds formed during anoxic corrosion very challenging. Special effort was taken to develop a highly sensitive analytical approach allowing compound specific detection of ^{14}C bearing low-molecular weight organic compounds at the expected ultra-trace level. The combination of ion chromatographic (IC) separation with accelerator mass spectrometry (AMS) was successfully applied to separate and quantify carboxylates as dissolved steel corrosion products. A thorough validation process including blank tests and tests with ^{14}C-tracer was performed to demonstrate the feasibility of the method before a final compound-specific analysis of corrosion samples could be performed. For the analysis of gaseous corrosion products, like hydrocarbons, the development of a gas chromatographic (GC) separation coupled with an online oxidation and fractionation with a subsequent AMS analysis for quantification was developed. Further, a method for the extraction of activation products other than ^{14}C in the leaching solution, such as ^{137}Cs, ^{60}Co, ^{59}Ni, ^{125}Sb and others, was developed. The method is based on the use of ion exchange resins characterised by their selectivity for the major radionuclides and their weak interaction with target ^{14}C compounds.

Experiments under a wide range of conditions were conducted. They involved exposing coupons and powders to relevant environments and measuring the release rate and speciation of ^{12}C and ^{14}C species. The tested materials are different types of irradiated and unirradiated stainless and carbon steels, as well as carbides. Sample preparation was selected in order to keep the metallic surface as representative of real waste as possible. The surface of the coupons is characterised metallographically using optical and electron microscopy techniques. The ^{14}C inventory of the test coupons was usually modelled by activation calculations either using the nominal N content of the alloy or measured values. In some cases the ^{14}C inventory was itself measured. Leaching experiments were performed under aerobic and anaerobic conditions at ambient temperature for durations of about one year; in some cases an extension over several years is planned. The test environments were NaOH, simulated groundwaters and simulated cement porewaters. Measurements of the corrosion rate using unirradiated steel were taken as reference rate. Gas and liquid samples were taken at specific intervals and the carbon speciation was characterised by GC, IC and high-performance liquid chromatography (HPLC) combined with MS, liquid scintillation counting (LSC) or AMS. In some cases simplified analyses of total C and total organic and inorganic analyses (TIC/TOC) were performed.

Batch experiments with unirradiated iron powders showed an instantaneous release of ^{12}C in form of carboxylic acids (mainly acetate, formate) and a smaller amount of hydrocarbons (mainly methane, ethane) within one day. Interestingly, after exchanging the solution, the release rate dropped very quickly. In inactive experiments using $Fe^{12}C_3$, a fast release of alcohols was observed in the first stage of the leaching phase. Also in the corrosion experiments with activated steel samples a fast release of ^{14}C mainly to the solution phase (carboxylic acids and indications for carbonate) and a minor amount to the gas phase (CH_4, CO) was observed in the first measurement after one week. After that, the ^{14}C activity concentration in solution remained constant or increased only very slowly. The fast initial release rate was clearly beyond what could be expected from the ^{14}C inventory and a uniform steel corrosion rate.

All these experiments point to the existence of a readily available amount of carbon compounds on the surface or within the oxidation layer. Some of them, featuring oxygen containing functional groups, are soluble in aqueous solution, while only a minor amount of hydrocarbons is released to the gas phase. In the present state of the experimental series, the long term corrosion and release rate and the associated ^{14}C speciation is not yet clear. That would require long term experiments with a duration of several years until steady state conditions have established. The further migration of the observed species in the cementitious near-field and the host rock and the implementation to safety assessment are addressed in separate studies.

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.

Summary of Work Performed by KIT-INE Within WP2 and WP3 of the CAST Project (Formation and status of ^{14}C in activated steel)

M. Herm[1], E. González-Robles[1], M. Böttle[1], N. Müller[1], E. Bohnert[1], R. Dagan[2], S. Caruso[3], B. Kienzler[1], V. Metz[1], and H. Geckeis[1]

1. *KIT-INE, Hermann-von-Helmholtz-Platz 1, 76344, Eggenstein-Leopoldshafen, Germany*
2. *KIT-INR, Hermann-von-Helmholtz-Platz 1, 76344, Eggenstein-Leopoldshafen, Germany*
3. *Nagra, Hardstrasse 73, 5430 Wettingen, Switzerland*

During operation of a nuclear reactor, the long-lived activation product 14C is produced by neutron capture reactions mainly from 14N impurities present in Zircaloy cladding and other metallic components of fuel elements.

For the waste management of irradiated Zircaloy or stainless steel, 14C is a key radionuclide, which must be considered in safety assessments of deep geological repositories for nuclear waste. Corrosion of the emplaced waste possibly releases 14C-bearing volatile and/or dissolved compounds. Organic 14C-bearing compounds reveal a high mobility either in the aqueous or in the gaseous phase and, once released, are potentially transported into the biosphere. On the contrary, volatile/dissolved inorganic 14C-bearing compounds are affected by various retention processes in the near field of a repository and the geosphere.

In this study, the inventory of 14C and other radionuclides present in irradiated Zircaloy-4 cladding and a stainless steel plenum spring is determined. Furthermore, the chemical form of 14C released from these materials is analysed.
Experimentally measured radionuclide contents are compared to theoretically predicted inventories of the irradiated Zircaloy-4 and stainless steel, obtained by means of Monte Carlo N-Particle (MCNP 2.7)/CINDER calculations as well as SCALE/TRITON/ORIGEN-S calculations.

The studied materials were sampled from the plenum of a fuel rod segment, which achieved an average burn-up of 50.4 GWd/tHM in the Swiss Gösgen pressurized water reactor.
The Zircaloy-4 cladding (dose rate (DR) ≤ 20 mSv/h) and the stainless steel spring (X7 CrNiAl 17.7, 10.4 g, DR ≤ 1600 mSv/h) were dry cut and small subsamples (120–300 mg, DR ≤ 120 mSv/h) were digested at room temperature and anoxic conditions in dilute acid solutions using an autoclave equipped with a gas collecting cylinder.

14C is separated from other radionuclides in aqueous and gaseous aliquots by stepwise extraction of the inorganic and organic carbon fractions by conversion into CO2, which is then trapped in various alkaline washing bottles. Finally, the content of 14C is analysed by liquid scintillation counting.
The measured 14C inventory in Zircaloy-4, (3.7 ± 0.4)×104 Bq/g, is in good agreement with the calculated values, (MCNP: 3.5×104 Bq/g, ORIGEN-S: 3.6×104 Bq/g). The vast majority of 14C (88 ± 10)% is released as gaseous organic compounds during dissolution of Zircaloy into the gas phase. Moreover, about

(11 ± 10)% remains as dissolved organic 14C-bearing compounds in the acidic digestion liquor. Almost no inorganic 14C-bearing compounds (< 1%) are found in all experiments performed with Zircaloy, neither in the gaseous nor in the aqueous phase.

Experimental results obtained for the 14C inventory present in stainless steel, (2.7 ± 0.3)×105 Bq/g, agree within a factor of ~3 with the activation calculations performed for the material, (MCNP: 8.5×104 Bq/g, ORIGEN-S: 9.5×105 Bq/g). The majority of 14C (70 ± 10)% is released as dissolved organic compounds during dissolution of stainless steel into the acidic digestion liquor. About (29 ± 10)% is released as gaseous organic compounds during dissolution of stainless steel into the gas phase. Almost no inorganic 14C-bearing compounds (< 1%) are found in all experiments performed with stainless steel, neither in the gaseous nor in the aqueous phase.

Corrosion study with irradiated steel: Analytical developments and first results (Analytical Techniques and their application)

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Safety assessment calculations show that carbon-14 is one of the main contributors to the annual dose from a cement-based deep geological repository for low- and intermediate-level radioactive waste (L/ILW) in Switzerland. For current safety assessment it is assumed that carbon-14 mainly contributes to the dose in its organic form, e.g. as carbon-14 bearing organic compounds, which are only weakly retarded in the cementitious near field. A compilation of activity inventories reveals that carbon-14 in L/ILW in Switzerland is mainly associated with irradiated steel (~85 %) which is produced due to the activation of nitrogen impurities in stainless steel exposed to thermal neutron flux, for example in nuclear reactors, according to the reaction $^{14}N(n,p)^{14}C$. Slow corrosion of irradiated steel will give rise to the release of carbon-14 in the deep geological repository. Although the inventory of carbon-14 in the various waste forms is well known, the chemical speciation of carbon-14 in the cementitious environment upon release from irradiated steel is still poorly understood. The present study is aimed to fill this knowledge gap.

To this end a corrosion experiment with irradiated steel has been carried out in the framework of the EU project “CAST”. The experimental design is based on a reactor system to perform the corrosion experiment and analytical methods capable of detecting and quantifying the carbon-14 bearing compounds in liquid and gas phases. Identification and quantification of these compounds is a particularly challenging task because the inventory of carbon-14 in irradiated steel is low and the corrosion rate of steel in the alkaline conditions of a cement-based repository is very slow (few nm/year). Therefore, the concentrations of the carbon-14 bearing compounds in solution and the gas phase are expected to be very low. The only analytical technique suitable to determine these compounds at the given concentration level is compound- specific carbon-14 accelerator mass spectrometry (C-14 AMS).

The compound-specific C-14 AMS method for carbon-14 bearing compounds will be presented including first results from the corrosion experiment with irradiated steel. The analytical method for the dissolved compounds is based on a combination of chromato- graphic separation of individual carbon-14 containing carboxylic acids using high performance ion exchange chromatography (HPIEC) and carbon-14 detection by AMS. A similar method is currently being developed for gaseous compounds. Latest results from the corrosion study show that the analytical method can successfully be employed to determine the total organic carbon-14 content as well as the individual carbon-14 bearing compounds in solution. The chemical form of compounds formed during corrosion of the irradiated steel is consistent with that determined previously in corrosion studies with unirradiated iron powders. Furthermore, the concentration of the compounds increases very slowly with time in line with the low corrosion of stainless steel in alkaline conditions.

Carbon-14 release from irradiated stainless steel (Leaching tests and speciation measurements)

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The objective of this work is to measure the rate and speciation of carbon-14 release from irradiated stainless steel on leaching under high-pH anaerobic conditions, representative of a cement based near field for intermediate- and some low-level wastes (ILW/LLW). In particular, this includes measurements of releases to the gas phase as well as to solution. The gas phase carbon-14 collection method allows for the discrimination of carbon-14 released as 14CO2, 14CO (and volatile oxidized species) or 14C-hydrocarbons. The carbon-14 solution analysis method used to date has measured the inorganic carbon-14 release only. Work is in progress to measure the total carbon-14 release to solution that includes any dissolved organic carbon-14 species. Three experiments have been in progress in NRG's Hot Cell Laboratory at Petten for a period of 17 months: two contain irradiated stainless steel (Containers 2 and 3) with similar total inventories of carbon-14 (and also cobalt-60); the third is a control experiment with unirradiated stainless steel from the same batch. The steel samples are being leached in 0.1 mol dm 3 NaOH solution. The three experiments have been sampled six times to date and analytical data are now available for the carbon-14 releases to the gas phase, inorganic carbon-14 to solution and cobalt-60 releases to solution up to 13 months leaching. The experiments are still running and further sampling is planned after 2 years.

In both Containers 2 and 3, there is an initial release of accessible carbon-14 species from the surface of the steel during the first week of leaching, followed by a drop in the rate of release at longer times. Most of the carbon-14 is released into the solution, but about 1% of the release occurs to the gas phase in Container 2 and 12% in Container 3. The predominant gas-phase species are hydrocarbons with about 4-12% of the gas phase release collected as 14CO. No 14CO2 is detected in the gas phase from either Containers 2 or 3.

Beyond 3 weeks, the rate of carbon-14 release from the steels in Container 2 drops significantly, but remains measurable to both the gas and solution phases. The ratio of gas phase hydrocarbon species to CO collected from Container 2 is about 13:1 in the first week then remains constant at about 6:1 from one week through to five months, and increases to about 12:1 between five and thirteen months.

The total measured carbon-14 release from Container 3 is higher than from Container 2 over 13 months, with a higher proportion of the release being to the gas phase (10-12%). However, the measured solution phase activity appears to reach a plateau; there is no measurable difference between the 6 week, 5 month and 13 months solution phase results. Releases to the gas phase are still detectable from three weeks to thirteen months. Beyond 3 months the rates of hydrocarbon release are lower than in Container 2, although the release of 14CO remains higher in Container 3 with a cumulative hydrocarbon to CO release ratio of 1.6:1 between 3 weeks and 13 months.

In Container 2, the total carbon-14 releases decrease after the first week and the measured rate of release was approximately constant at 0.16 ±0.02 Bq day 1 between three weeks and 13 months leaching. If it is assumed that the release of carbon-14 over this period was congruent with the corrosion of the steel surface, this would be equivalent to a corrosion rate of about 3 nm yr 1. It should be noted, however, that the amount of carbon-14 released to the solution phase may be underdetermined due to a lack of measurement of organic cabon-14 in solution.

The reasons for the difference in speciation and rates of carbon-14 release measured in Containers 2 and 3 are not yet understood.

Measurement of the release of cobalt-60 into solution has been undertaken as a possible analogue for the corrosion of the stainless steel, on the assumption that cobalt-60 release would be congruent with respect to the corrosion of the steel surface. However, after a fast initial release of cobalt-60 during the first week of leaching, a drop has been observed in the cobalt-60 activity in solution at longer times. It is thought this is due to a combination of solubility limitation and sorption effects. Therefore, it is concluded that cobalt-60 release is not a suitable analogue for measuring the corrosion rate of the irradiated steel in these experiments.

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Carbon-14 release from irradiated steels. State of the Art from Pre- to Post-CAST

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Carbon-14 is a key radionuclide in the assessment of the safety of a geological disposal facility (GDF) for radioactive waste. A significant proportion of the carbon-14 inventory of radioactive wastes worldwide is contained in irradiated steel wastes. These wastes comprise the irradiated ferrous metal components of nuclear reactor structures and nuclear fuel assemblies composed of carbon (mild) steels, stainless steels and/or nickel alloys. Carbon-14 is formed in reactor steels primarily by the thermal neutron activation of nitrogen-14 that is present in all steels as a trace component. Carbon-14 is located throughout the matrix volume of irradiated steels and its rate of release from the steel will be dependent both on its distribution through the matrix and the rate at which the steel corrodes. Work Package 2 (WP2) of the CAST Project is dedicated to the release of carbon-14 from activated steels.

A State of the Art Review (SoAR) of rates of steel corrosion and carbon-14 release from irradiated steels was conducted in the first year of the CAST project. The objective of the review was to incorporate information available from outside the CAST project, relevant to the storage and long-term disposal of waste steels, into WP2. In the SoAR, corrosion rates for carbon steels and stainless steels under different environmental conditions relevant to the storage and disposal of waste steels were collated and reviewed critically. Then, the results of a limited number of studies concerning the release of carbon-12 from cast irons and steels were reviewed to understand the likely speciation of carbon-14 releases from irradiated steels. In some cases, however, the results appeared to be contradictory. Prior to CAST, only three experimental studies on carbon-14 release from irradiated steels had been reported (all in Japan). However, a lack of reports available in English providing sufficient details of the materials and the experimental methods used hindered a proper evaluation of these studies.

The information gathered in the review has been used in two ways:

- to support the design of the experimental programme planned under CAST; and
- to support the assessment of the potential radiological impact of carbon-14 released from steel wastes during storage, disposal operations and after closure of a disposal facility.

In this presentation, the way in which the information gathered was used to help design the experiments undertaken by NRG on carbon-14 releases from irradiated steel samples under anaerobic high-pH conditions will be described and the results obtained will be compared with predictions made.

The way in which the information gathered was used to inform the treatment of carbon-14 release from irradiated steel wastes by the gas pathway in the UK programme will also be described.

The further improvements in the State of the Art made during the CAST project will be highlighted. This includes improvements in measurement techniques used for discriminating carbon-14 speciation and in measuring very low corrosion rates of steels under anaerobic, alkaline conditions.

Some of the key questions raised by the SoAR concerning the likely speciation and rates of release of carbon-14 from irradiated steels will be revisited in the light of the findings of WP2.

Finally, the implications of the improved understanding gained from the WP2 results for the future treatment of carbon-14 release from waste steels in the safety case will be considered.

Possible fate of inorganic Carbon-14 released from activated steels under conditions of a geological repository

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In many radioactive waste disposal programmes ^{14}C is an important radionuclide with a potential for significant dose contributions in safety assessment for a geologic repository. In nuclear reactors ^{14}C is mainly formed by neutron capture from ^{14}N, ^{17}O or ^{13}C. Little is known, however, on the chemical form of ^{14}C after release from the waste and the migration of the potential carrier compounds. Most of ^{14}C is released by steel in a cementitious environment is present as organics, but some will be released as carbonates. The presentation will focus on carbonate and other oxyanions in presence of steel corrosion products, cement and calcite.

We compared first the reactivity of carbonate with that of selenite (Se(IV), a long-lived RN) in two steps. We first reacted $^{13}CO_3^{2-}$ with high-purity 100-200 nm ^{12}C- nano-sized calcite particles, and performed isotopic characterization of the reaction product time evolution with Cavity Ring Down Spectroscopy (CRDS). We show that, based on current kinetic trajectories (run for > 1 year) the equilibration is predicted to occur, at 25°C and 50°C in 19 years and 4 years, respectively. The rate determining process for calcite isotopic equilibration is thought to be the diffusion of ^{13}C through a surface layer of increasing thickness, giving rise to parabolic kinetics. Interestingly, despite an apparent super-saturation relative to bulk calcite, re- precipitation is much slower than expected, with the result that the particle size does not change significantly. We then reacted standard calcite with aqueous selenite ions (IV)), and using Neutron diffraction experiments, EXAFS spectroscopy and a theoretical ab-initio simulations of the crystallographic structure using Vienna Ab initio simulation package (VASP), we found that the calcite unit cell volume increases linearly with Se content in the structure. EXAFS spectroscopy, in combination with our theoretical model of the local structure surrounding the Se atom, confirms the possibility of selenite ion substituting for carbonate anion in the calcite structure (Aurelio et al Chem Geol, 2010). We further have shown that at the steel-concrete interface, carbonate ions will be strongly adsorbed on steel corrosion product (Appelo et al., EST, 2002).

The concrete structures in nuclear waste repositories are supposed to act as barriers to limit the mobilization of ^{14}C and other radionuclides (RNs). However although the redox potential (Eh) in reinforced concrete is controlled by the corrosion of steel and largely affects the speciation and sorption behaviors of ^{14}C and redox-sensitive RNs, it is to date poorly known. We propose a method to determine an experimental “in-situ” Eh value, using redox-sensitive RNs (e.g., Se^{IV}, Mo^{VI}, Sb^{V} and U^{VI}) as species probes. In order to measure the in-situ Eh values imposed by corrosion products couple of steel (i.e., magnetite/hematite, magnetite/goethite, and Fe^0) in N_2 or H_2 atmosphere, RNs present in CEM V (cured by CEA for Andra) cement pore water (CPW) were equilibrated with the above redox couples. The equilibrium RN concentration in CPW was taken equal to the total concentration of the oxidized species. RNs reduced species and their concentrations were identified by X-ray absorption near-edge structure (XANES) spectra, and the specific species were identified by liner combination fitting (LCF) analysis of the XANES spectra. The independently experimentally determined Eh values were remarkably close to each other for all RNs and on each Fe-couple. The experimental "in-situ" Eh values for each RN with nano zero-valent iron (NZVI) are centered between -368 and -434 mV, suggesting the Eh value controlling RN redox reactions is originating from the $Fe(OH)_3/Fe(OH)_2$, rather than $Fe^0/Fe(OH)_2$ couple. The existence of Sb° indicated that the Eh was only temperately controlled by $Fe^0/Fe(OH)_2$ at the beginning. For magnetite/hematite couple, Eh values for each RN are centered between -346 and -427 mV, which are not around the theoretical Eh values (-604.3 mV) imposed by the Fe-couple but also closed to that of $Fe(OH)_3/Fe(OH)_2$. In comparison, the experimental "in-situ" Eh values obtained for magnetite/goethite are a little higher than that for magnetite/hematite, which may be due to its slightly higher theoretical Eh value (-568.9 mV). This work implies that the non correlation between experimental Eh values and the theoretical ones results from the newly formed iron-hydroxides phases on the reactive interface.

Finally immobilization of the redox-sensitive RNs (e.g., Se^{IV}, Mo^{VI}) in cement layered double hydroxides (LDHs), was investigated by a combination of batch isotherm experiments and X-ray techniques was used to examine selenite (SeO_3^{2-}) and molybdate (MoO_4^{2-}) sorption mechanisms on CaAl LDHs with increasing loadings of RN oxyanions. Advanced modeling of aqueous data shows that the sorption isotherm can be interpreted by three retention mechanisms, including two types of edge sites complexes, interlayer anion exchange, and CaRN precipitation. Mo geometry evolves from tetrahedral to octahedral on the edge, and back to tetrahedral coordination at higher Mo loadings, indicated by Mo Kedge X-ray absorption spectra. Moreover, the anion exchange process on chloride- and sulphate- CaAl LDHs was followed by in situ time-resolved synchrotron-based X-ray diffraction, remarkably agreeing with the sorption isotherm. This detailed molecular view shows that different uptake mechanisms (edge sorption, interfacial dissolution- reprecipitation) are at play and control anion uptake under environmentally relevant conditions, which is in contrast to the classical view of anion exchange as the primary retention mechanism. This work puts all these mechanisms in perspective, offering a new insight into the complex interplay of anion uptake mechanisms by concrete LDH phases, by using changes in Mo geometry as powerful molecular- scale probe (Ma et al., EST, 2017).

In conclusion, and based on carbonate-selenite structural analogy, ^{14}C carbonate could be adsorbed on steel corrosion products or concrete LDH edges, undergo anion exchange in these lamellar phases or coprecipitate as ^{14}C enriched calcite.

These projects have received funding from ANDRA, the French Agency for Nuclear Waste Geological Repository.

Work Package 3 – Zircaloy

Overview of Main WP3 Outcomes

Carbon-14 release from irradiated zircaloys in geological disposal conditions

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Carbon-14 is a long-lived radionuclide (5,730 y) of interest regarding the safety for the management of intermediate level wastes (ILW). The current knowledge is relatively limited on the release mechanisms of C-14 from activated materials in repository conditions.

The CAST (Carbon-14 Source Term) project has aimed to gain new scientific understanding on the release rate of carbon-14 from the corrosion of irradiated steels and Zircaloys, as well as from the leaching of ion-exchange resins and irradiated graphites under geological disposal conditions. Particular attention has been brought to determine the C-14 inventory as well as its speciation with regards to dissolved and gaseous species released in alkaline media.

The presented study focuses on Zircaloys for which C-14 is found either in the alloying part of Zircaloy cladding due to the neutron activation of ^{14}N impurities by ^{14}N(n,p)14C reaction, or in the oxide layer (ZrO_2) formed at the metal surface by the neutron activation of ^{17}O from UO_2 or $(U\text{-}Pu)O_2$ fuel and water from the primary circuit in the reactor by $^{17}O(n,\alpha)^{14}C$ reaction.

A literature review was initially carried out to establish the State of the Art [1]. The corrosion behaviour of zirconium alloys was reported in the review highlighting the high resistance to uniform corrosion at low or moderate temperatures. Various studies have shown that the uniform corrosion rates of zirconium alloys are very low in anaerobic neutral or alkaline waters at low temperature with an envelope value of 20 $nm.y^{-1}$. The zirconia solubility remains very low for carbonate concentrations lower than 10^{-2} M. The susceptibility to localised corrosion (pitting, crevice corrosion and stress corrosion cracking) is negligible in anaerobic groundwaters. During the corrosion of Zircaloy, there is a possibility of a mechanism in which ^{14}C is not released immediately by corrosion but is incorporated into the oxide film and then released by diffusion or during the zirconia dissolution. It is supported by the fact that measured ^{14}C specific concentrations in zirconia oxide layers are about twice of that of Zircaloy metal after irradiation in a reactor.

In the CAST project, various irradiated and unirradiated Zircaloys (Zr, Zr-2, Zr-4, CANDU and M5^{TM}) have been studied. Particular attention was brought to characterise the materials in terms of microstructure, composition and oxide layer by means of optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The characterisations were carried out before and after running the experiments. The total C-14 inventory has been determined both experimentally and by calculations. The results seem to be in good agreement. The vast majority of C-14 (90%) is released as gaseous organic compounds during dissolution of Zircaloy into the gas phase.

Leaching experiments were conducted in alkaline media (NaOH and $Ca(OH)_2$) under anoxic conditions at room temperature for several time durations ranging from 14 days to 6 years. Considerable effort was put to develop analytical techniques able to measure C-14 in low concentrations, such as those expected in deep geological repository conditions. The liquid scintillation counting (LSC) was widely used to determine the total C-14 released in alkaline environment as well as the inorganic / organic partition. The measurements of C-14 in leaching solution were performed after decontamination from other high activity level radionuclides (Cs-137, Co-60, Sb-125, Ru-106/Rh-106) by ion exchange resin. Speciation and quantification of dissolved carbon-14 were performed by using separation technique (collection of fractions by ion chromatography) and analysis by liquid scintillation counting method. In addition, accelerator mass spectroscopy (AMS) was used to quantify organic molecules in very low concentrations. Carboxylic acids such as oxalate, formate and propionate could be determined.

The gas samples were analysed by a gas chromatograph (GC). The results revealed the production of methane, ethene and CO_2.

The results highlight an instant release fraction of C-14 as various experiments showed a relatively constant concentration of C-14 released in static alkaline solution. Further, corrosion measurements were performed on unirradiated and irradiated Zircaloys by using hydrogen measurements and electrochemical measurements such as linear polarisation resistance (LPR). Overall, the results showed that the corrosion rates decreased with time. Higher corrosion rates were obtained for irradiated Zircaloys than unirradiated Zircaloys. Electrochemical measurements enhanced discrepancies of the results while hydrogen measurements seem to be the more reliable technique to measure the corrosion rate.

From a safety assessment point of view, the instant release fraction (IRF) was determined on irradiated Zircaloy-2 based on inventory measurements. The results showed that the C-14 inventory in the oxide was around 7.5%, which is below the 20% commonly used in safety case assessments. All in all longer time experiments should be conducted in order to obtain steady state conditions and confirm the current results.

[1] J.M.Gras (2014). State of the art of 14c in Zircaloy and Zr alloys - C-14 release from zirconium alloy hulls. Task 3.1, D3.1 deliverable. CAST. Project.

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^{14}C inventory in irradiated Zircaloys – Summary of work performed by KIT-INE within WP2 and WP3 of the CAST Project

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During operation of a nuclear reactor, the long-lived activation product ^{14}C is produced by neutron capture reactions mainly from ^{14}N impurities present in Zircaloy cladding and other metallic components of fuel elements.

For the waste management of irradiated Zircaloy or stainless steel, ^{14}C is a key radionuclide, which must be considered in safety assessments of deep geological repositories for nuclear waste. Corrosion of the emplaced waste possibly releases ^{14}C-bearing volatile and/or dissolved compounds. Organic ^{14}C-bearing compounds reveal a high mobility either in the aqueous or in the gaseous phase and, once released, are potentially transported into the biosphere. On the contrary, volatile/dissolved inorganic ^{14}C-bearing compounds are affected by various retention processes in the near field of a repository and the geosphere.

In this study, the inventory of ^{14}C and other radionuclides present in irradiated Zircaloy-4 cladding and a stainless steel plenum spring is determined. Furthermore, the chemical form of ^{14}C released from these materials is analysed.
Experimentally measured radionuclide contents are compared to theoretically predicted inventories of the irradiated Zircaloy-4 and stainless steel, obtained by means of Monte Carlo N-Particle (MCNP 2.7)/CINDER calculations as well as SCALE/TRITON/ORIGEN-S calculations.

The studied materials were sampled from the plenum of a fuel rod segment, which achieved an average burn-up of 50.4 GWd/t_{HM} in the Swiss Gösgen pressurized water reactor.
The Zircaloy-4 cladding (dose rate (DR) ≤ 20 mSv/h) and the stainless steel spring (X7 CrNiAl 17.7, 10.4 g, DR ≤ 1600 mSv/h) were dry cut and small subsamples (120–300 mg, DR ≤ 120 mSv/h) were digested at room temperature and anoxic conditions in dilute acid solutions using an autoclave equipped with a gas collecting cylinder.

^{14}C is separated from other radionuclides in aqueous and gaseous aliquots by stepwise extraction of the inorganic and organic carbon fractions by conversion into CO_2, which is then trapped in various alkaline washing bottles. Finally, the content of ^{14}C is analysed by liquid scintillation counting.

The measured ^{14}C inventory in Zircaloy-4, $(3.7 \pm 0.4)\times10^4$ Bq/g, is in good agreement with the calculated values, (MCNP: 3.5×10^4 Bq/g, ORIGEN-S:

3.6×10^4 Bq/g). The vast majority of ^{14}C (88 ± 10)% is released as gaseous organic compounds during dissolution of Zircaloy into the gas phase. Moreover, about (11 ± 10)% remains as dissolved organic ^{14}C-bearing compounds in the acidic digestion liquor. Almost no inorganic ^{14}C-bearing compounds (< 1%) are found in all experiments performed with Zircaloy, neither in the gaseous nor in the aqueous phase.

Experimental results obtained for the ^{14}C inventory present in stainless steel, $(2.7 \pm 0.3) \times 10^5$ Bq/g, agree within a factor of ~3 with the activation calculations performed for the material, (MCNP: 8.5×10^4 Bq/g, ORIGEN-S: 9.5×10^5 Bq/g). The majority of ^{14}C (70 ± 10)% is released as dissolved organic compounds during dissolution of stainless steel into the acidic digestion liquor. About (29 ± 10)% is released as gaseous organic compounds during dissolution of stainless steel into the gas phase. Almost no inorganic ^{14}C-bearing compounds (< 1%) are found in all experiments performed with stainless steel, neither in the gaseous nor in the aqueous phase.

Carbon-14 in CANDU Irradiated Zy-4 and its Release under Alkaline Conditions

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The total ^{14}C content and its partition between inorganic and organic species as well as inventories of main gamma emitters (^{60}Co, ^{137}Cs, ^{134}Cs and ^{125}Sb) were determined in irradiated Zy-4 samples cut from a CANDU spent fuel rod transferred from Cernavoda NPP to RATEN ICN for different investigation inside the hot cells. The analytical method used for ^{14}C measurement on irradiated Zy-4 samples consists in a sequential extraction of inorganic and organic ^{14}C using acid dissolution and wet oxidation, adapted after the method developed by Magnusson for ^{14}C measurement in spent ion exchange resins and process waters. Experimentally measured ^{14}C content was compared to the theoretically one predicted based on the irradiation history and impurity content of Zy-4 by means of Origen computations.

Long term leaching tests (static corrosion tests) and accelerated corrosion tests (electrochemical measurements) were carried out on irradiated Zy-4 to measure the ^{14}C release in chemical conditions relevant to cementitious environment and the corrosion rate, respectively. Electrochemical measurements were also performed on non-irradiated Zy-4 to bring evidences on the potential effect of irradiation on the oxide layer and consequently on the corrosion rate. The non-irradiated Zy-4 samples were oxidized in simulated conditions representative for Cernavoda NPP primary circuit to achieve similar thickness of the oxide layer as the irradiated ones.

The irradiated Zy-4 samples have a ^{14}C content of around 2 10^4 Bq/g of Zy-4, mainly as organic compounds (more than 99%). This content is of the same order of magnitude with the value estimated by ORIGEN simulation for an average burn-up of 7 MWd/kgU (1.78 10^4 Bq/g of Zy-4).

The static leaching tests were carried out in alkaline solution (0.01 M NaOH solution with pH of 12, Total Dissolved Salts of 1100 mg/l, and conductivity of 2.20 mS/cm), in glass tubes adapted to allow N_2 purging before the experiments, in order to ensure anaerobe conditions for leaching and before sampling the leachate solution for ^{14}C measurements, in order to assess the ^{14}C released in gas phase during leaching.

The experimental results obtained for the total ^{14}C released as dissolved species after 18 days, 6, 8, 12 and 18 months of Zy-4 immersing in alkaline solution are almost the same, indicating that a small amount of ^{14}C was available as instant release fraction. Both inorganic and organic ^{14}C were release as dissolved species, but more than 60% from the total ^{14}C released in solution was found to be as organic species.

Since the irradiated Zy-4 samples were washed three times in 4M nitric acid before their use in leaching test (to decrease the dose rate as low as allowed to work with irradiated samples outside of the hot cells), the ^{14}C absorbed from the moderator on the oxide layer of the CANDU fuel during its irradiation was likely released during the rinsing step. In this situation, the amount of ^{14}C released during the leaching tests could come from the fresh Zy-4 metal from the edges of the samples created by sample cutting that were exposed to the leaching solution.

The SEM investigations carried out on the irradiated Zy-4 sample after its immersion for 6 months in 0.01 M NaOH solution, showed that the oxide surface presents large cracks which could have occurred after the mechanical cutting of the irradiated samples inside the hot cells since before cutting such cracks have not been observed on oxide layer of the irradiated Zy-4 tube. By these cracks, also fresh Zy-4 metal was exposed to the leaching solution, allowing the release of some ^{14}C.

The electrochemical tests were performed with a four-electrode setup, using an Ag/AgCl electrode as reference electrode, two platinum rods as counter electrodes, and a Zircaloy-4 sample as working electrode. These measurements were carried out under inert atmosphere in a miniaturized borosilicate glass cells, and their results indicated that the irradiated Zy-4 samples have higher corrosion rates than the non-irradiated samples.

Generally, corrosion rates values ranging between from 46 to 130 nm /y. These results could be affected both by the cracks likely induced by the sample cutting but also by the non-standard experimental conditions.

Acknowledgement

This results were obtained from the work carried out by RATEN ICN in CAST project, that has received funding from the European Union’s European Atomic Energy Community’s (Euratom) Seventh Framework Programme FP7/2007-2013 under grant agreement no. 604779, the CAST project.

Analytical strategy for the Measurement of carbon 14 in alkaline solution

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Carbon-14 is a long-lived radionuclide (5,730 y) and a radionuclide of interest regarding the safety for the management of intermediate level wastes (ILW) in deep geological formation. ^{14}C is found in steel (eg. stainless steel springs) due to the neutron activation reactions: ^{14}N(n,p)^{14}C, ^{17}O(n,α)^{14}C, and ^{13}C(n,γ)^{14}C. Therefore, the release of carbon-14 in aqueous media and its diffusion within the storage site in deep geological disposal is an important issue for safety assessment. Organic carbon is targeted in this work, with a focus on the analysis of ion carboxylic acids having a short carbon chain ≤ 5. Besides ^{14}C target molecules, the leaching solution may contain activation products (e.g. ^{60}Co, ^{63}Ni, ^{55}Fe…), fission products (e.g. ^{137}Cs, ^{99}Tc, ^{90}Sr, ^{125}Sb…), and actinides (e.g. ^{235}U, ^{239}Pu), which are present at a significant activity level compared to ^{14}C [Yamaguchi et al., 1999].

The poster will present a simple and adapted method for the extraction of the main water soluble radionuclides in the leaching solution using ion exchange resins: inorganic ion exchanger for cesium extraction, chelex-Na resin for transition metal extraction, chelex-Fe(III) resin to extract antimony. The resin treatment stage has several aims: i) the reduction of total activity in leachates to avoid further dilution of the leaching solutions due to activity acceptance limits of the laboratories; ii) get clean and non-contaminated leachates in terms of absence of radionuclides which would limit analytical devices contamination, especially for AMS analyses of ultra- low ^{14}C concentrations; iii) the removal of beta emitter radionuclides which cannot be distinguished from ^{14}C activity by LSC. Indeed, soluble radionuclides like as Sb- 125 are negatively charged in the hydroxides or oxo-anions forms and thus may appear in the collected fractions, preventing an accurate quantification of ^{14}C using LSC. This is why a selective extraction of interfering beta emitter radionuclides before the chromatographic separation is required.

I. Yamaguchi, S. Tanuma, I. Yasutomi, T. Nakayama, H. Tanabe, K. Katsurai, W. Kawamura, K. Maeda, H. Katao and M. Saigusa (1999). A study on chemical forms and migration behaviour of radionuclides in hull wastes, 7th International Conference on Radioactive Waste Management and Environmental Remediation ICEM '99, Nagoya, Japan.

Carbon release speciation from Zircaloy-4 corrosion in highly alkaline solutions

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The release and the speciation of carbon species from both irradiated and unirradiated Zircaloy-4 samples, representative of the fuel cell claddings of Belgian nuclear power plants, were studied at SCK•CEN in a saturated portlandite aqueous solution, relevant for the Belgian Supercontainer design, as perceived for the geological disposal of high level nuclear waste.

Metallographic analysis was performed on both irradiated and unirradiated samples to analyse the influence of radiation on the metallic microstructure. Dislocation lines defects and two types of precipitates were present for both samples. The main precipitates, with a circle-like structure, were identified as Laves phases and were composed of $Zr(Fe,Cr)_2$. A second type, with a needle- or platelet-like structure, was found with a possible ZrC phase. The main effect of the neutron irradiation was the emergence of small dislocation loops and a low amorphisation of precipitates due to neutron activation.

Two different corrosion tests were performed: (i) static corrosion tests (or leaching tests) to obtain information on the Zircaloy-4 behaviour in real geological conditions; these tests were only realised on irradiated samples, and (ii) accelerated corrosion tests (also called polarised corrosion tests) to obtain in a shorter reaction time some indication of the corrosion mechanism and the speciation of light carbon molecules formation.

Before starting the accelerated corrosion tests, polarisation curves were recorded to obtain information on the electrochemical behaviour of the Zircaloy-4 samples. Irradiation seemed to induce some difference in the sample behaviour such as the stabilisation of the passivation layer or the shift of the corrosion potential to a more reductive potential.

Due to the very low expected concentration of carbon-based compounds coming from corrosion processes and due to the presence of some contamination, which was very difficult to avoid, no reliable information on the total inorganic and organic compounds in solution could be obtained. However, the analysis of the gas phase by GC, obtained with a Pulse Discharge Helium Ionization Detector (PDHID) detector, revealed the production of methane, ethene and maybe CO_2 after the 195 days duration of the static tests. Based on the measured concentrations, an approximation of the corrosion rate was calculated and led to 57 to 84 nm per year, which looks very high compared to the conservative corrosion rate of 20 nm per year for Zircaloy. Even if no carbon-based products could be measured after the accelerated corrosion tests, the analysis of the electrical current produced during this test suggested a corrosion rate of 46 nm per year for the unirradiated sample, which is quite close to the estimated value calculated from GC information after the static test.

Corrosion of Zirconium Alloys and ^{14}C Release from Compacted Waste

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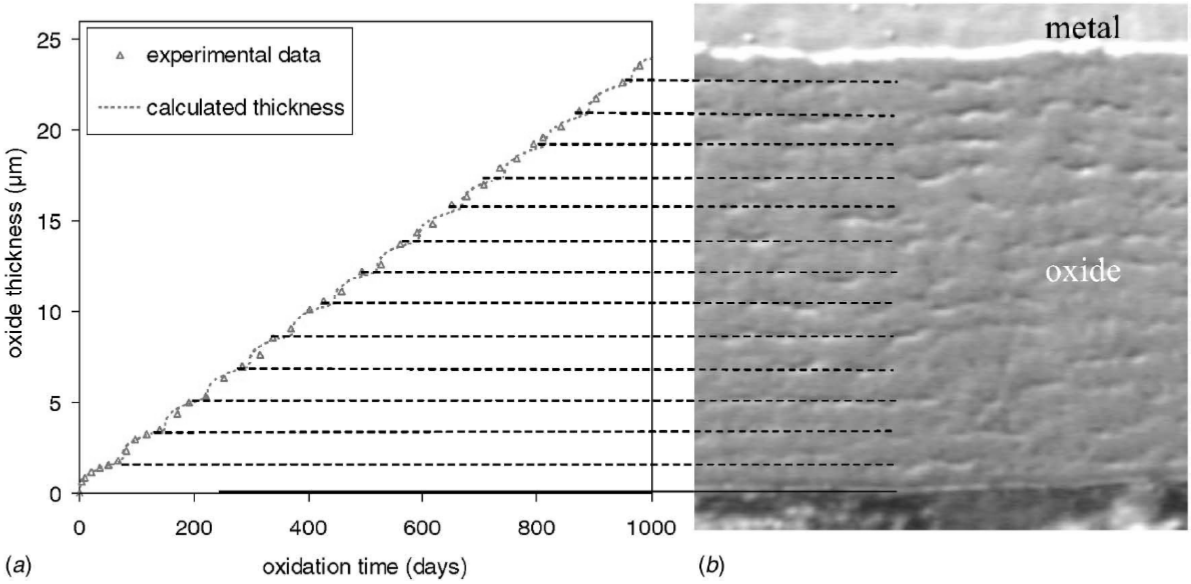
Zirconium alloys are used as cladding and structural materials of fuel assemblies. They corrode in primary water. Under irradiation, residual nitrogen is transformed into ^{14}C by a (n,p) reaction which contributes to the source term of the deep geological repository. After irradiation, fuel rods are defueled and all the zirconium parts will be compacted in pancake forms which will be piled up in a steel container which will be disposed of in a deep geological layer. At ambient temperature oxide growth is negligible. Oxide dissolution is very weak and hardly measurable.

^{14}C originates mainly from the oxide layer where most of the oxygen is stored. Its release is limited by diffusion in the oxide layer towards the surface and by desorption.

Lots of works have been done and are still ongoing to understand zirconium alloys corrosion in primary water under heavy neutron irradiation. It is generally accepted that the corrosion kinetics depends on the alloy composition and microstructure; modern alloys tend to corrode less than their glorious ancestors. Corrosion is thermally activated and therefore the oxide thickness is larger at the top of the fissile column than at the bottom of the rod. With such a knowledge it is possible to evaluate the amount of ^{14}C formed in the zirconia layer. Numerous fuel rods examination have shown that the oxide is very dense. Layers of cracks parallel to the metal-oxide interface are commonly observed. They are related to the oxide growth kinetics which is widely believed to be periodic. The oxide grains are mainly monoclinic zirconia phase with a tubular shape. Therefore ^{14}C release should thus results from the diffusion of carbon in bulk monoclinic zirconia.



Correspondence between cracks and periodicity in the oxide growth kinetics [1]

At ambient temperature, the very low diffusivity of carbon is difficult to measure. Therefore we have estimated it using ab-initio calculations. These are extremely powerful but require to model the system in a simple way. As a result we have shown and confirmed that carbon diffusion is very slow either in bulk zirconium or in bulk monoclinic zirconia.

Corrosion of zirconia is highly textured probably because of the stress generated by the oxidation swelling. The grains organize themselves so that the stress is minimised. Therefore, the surfaces are mainly the (-111) crystallographic planes, which is the most stable surface index and allows to define the system of interest. It is thus possible to try to estimate how carbon atoms leave the surface of monoclinic zirconia and carbon speciation in presence of water using ab-initio techniques. It is an on-going work.

[1] Bouineau et al., A New Model to Predict the Oxidation Kinetics of Zirconium Alloys in a Pressurized Water Reactor, Journal of ASTM International, Vol. 5, No. 5 Paper ID JAI101312

DAY 2
Work Package 4 – Ion Exchange Resins

Overview of main WP4 Outcomes

Carbon-14 source term and release in the case of spent ion exchange resins from nuclear reactors

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In several Reference Cases of disposal systems envisaged by Waste Management Organizations, ^{14}C is one of the most important contributor to the dose. Ion exchange resins (IERs) are widely used in nuclear facilities for the purification of liquid processes or wastes streams. Particularly, significant amount of IERs are used in water clean-up systems in the reactor coolant. The chemical form under which ^{14}C is fixed within or adsorbed to the IERs will be highly linked with the chemical condition of the reactor, including all its operations.

Typically, in boiling water reactors (BWRs) oxidizing conditions should lead mainly to the formation of more oxidized species, i.e., end-product CO_2 and carbonate, whereas in pressurized water reactors (PWRs) less oxidized species should be obtained, *i.e.*, end-product CH_4. Particular situation can lead to intermediate cases, *e.g.*, hydrogen injection in BWRs. Depending on local redox conditions, alcohols, aldehydes, and acids can also be formed. As alcohols and aldehydes are not ionized in water at 25°C, only acids were thought to be retained in spent ion exchange resins (SIERs). The information on the repartition of species, *i.e.*, speciation, under which ^{14}C is fixed to SIERs is scarce. The main information exists under the form of repartition between inorganic and organic fractions.

Within the EU project CAST, seven partners (CEA, EDF, ENEA, FZJ, RATEN-ICR, SKB, ÚJV) from six countries (Czech Republic, France, Germany, Italy, Romania, Sweden) have been involved in the fourth work package (WP4), dedicated to the study of speciation, source term, leaching, and gaseous release of ^{14}C from spent ion exchange resins.

Even if SIERs are not planned to be disposed in deep underground systems but in subsurface storage, the release of ^{14}C from SIERs is a major concern. This work package has been dedicated to the study of the speciation of ^{14}C associated to the SIERs: from the repartition between organic and organic form, up to the more detailed speciation and content of organic acids, carbonate… The initial objective is to obtain further information on the repartition of molecules potentially fixed and/or released from SIERs during their storage in subsurface.

Using real SIERs samples from pressurized water reactors (PWRs), CANDU reactors, and BWRs it has been made possible to show that retained ^{14}C in SIERs consisted mainly of inorganic carbonate form, as *e.g.* observed in CANDU SIERs, whereas a small fraction of organic ^{14}C-bearing compounds bound to SIERs was detected. Their ratio was demonstrated to be influenced by the pre-treatment, cleaning circuit and storage conditions of the SIERs. In general, PWR SIERs are characterised by consistent amounts of retained ^{14}C-organics. The proportion of ^{14}C-organic seems to be descending in the following order PWR > CANDU > BWR. A more detailed speciation of the organic fraction revealed the presence of formic acid, which represents most of the retained organic ^{14}C.

The immobilization of resins in cement is a possible solution. These matrices have the advantages to retain CO_2 under the form of carbonates ions, and also have the possibility to adsorb organic acids. Hence, the interaction of SIERs in particular cementitious system is of interest and alkaline media has been addressed within this work package. If the release of ^{14}C seems favoured in high concentrated alkaline aqueous media (LiOH 1M), it seems also that cement matrices are not releasing ^{14}C, certainly due to calcium carbonate precipitation and organic acid adsorption.

Determination of carbon 14 term source in French SIERs

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CEA/DEN/DPC/SECR/LRMO

This presentation summarises the methodologies and results of experiments carried out on the spent ion exchange resins (SIERS) from EDF PWR (pressurized water reactor) at the Commissariat à l'Énergie Atomique et aux Énergies Alternatives (CEA beneficiary N°4) within the framework of the European program CArbon Source Term (CAST). The studies concern both carbon-14 measurements and its speciation (inventory) and the measurement of organic molecules issued from extraction experiments on SIERS.

- For the measurement of total ^{14}C and/or its speciation, two different methods were developed during this project. These methods were applied on two samples from EDF PWR reactors. The results obtained show that these samples contain a total carbon-14 activity of the order of 2.1 $kBq.g^{-1}$ to 5.6 $kBq.g^{-1}$ of wet resin. Within the time scale of the CAST project consistent and reliable results on speciation were obtained for only one sample with an organic carbon 14 to mineral carbon 14 ratio of 30/70.

- For desorption studies, experiments were conducted on two sub-samples of one SIERS associated to a blank of reagent and two experiments on virgin resin. These experiments confirm that SIERS contain ^{14}C in organic form (38 % of the total ^{14}C). The observed carbon mass balance is around 50 $mg_C.L^{-1}$. Around 12 % of carbon mass balance is identified. The only organic identified compound in resin desorption solutions, glycolate, is identified in very low concentration of around 1 % of Total Organic carbon.

Carbon-14 in CANDU Spent Ion Exchange Resins and its Release under Alkaline Conditions

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Due to large 14C inventory, the spent ion exchange resins (SIERs) generated from moderator and primary heat transport purification systems of Cernavoda NPP have to be geological disposed of. These resins are currently stored under water in reinforced concrete vault lined with epoxy resin, segregated by the SIERs originating from other purification circuits. No SIERs sampling from the Cernavoda storage tanks were perform up to now.

The total 14C content and its partition between inorganic and organic species as well as inventories of 3H and main gamma emitters (137Cs, 134Cs, 60Co, and 54Mn) were determined on SIERs received from Cernavoda NPP that were collected during maintenance operation from the strainers of the purification systems of moderator (MOD) and of Primary Heat Transport System (PHTS) from Cernavoda NPP Unit 1.

Also, desorption tests were carried out on CANDU SIER samples in 0.1 M NaOH (pH 12.5) to assess the release of 14C under alkaline conditions relevant to cementitious environment in a geological disposal facility. Inorganic and organic 14C released both as dissolved species and as gaseous ones were measured. Desorption tests were performed at room temperature (23D3DC), for solid to liquid ratio of 0.01 g/ml (0.4 g of SIER + 40 ml of NaOH solution), in semi-dynamic conditions: 5 ml of leachant solution were sampled at each time step and 5 ml of fresh 0.1 M NaOH were added. At the end of the desorption tests not only 14C activity released as dissolved and gaseous species was measured but also the residual 14C activity in the SIERs samples subject to desorption test.

For total 14C measurement in CANDU SIERs, non-catalytic combustion by flame oxidation method was used. By this method, the SIERs samples are combusted in an oxygen-enriched atmosphere with a continuous flow of oxygen, and all carbon is oxidized to CO2. The CO2 is subsequently trapped in a column filled with a carbon dioxide absorbent (Carbo-Sorb® E) and forms a carbamate that is flushed into the 14C counting vial using the Permafluor® E+ scintillator as a rinsing media.

For inorganic and organic 14C measurement an analytical method adapted after the method developed by Magnusson for 14C measurement in spent ion exchange resins and process waters was used. This method distinguishes between 14CO2 released during acid stripping and 14CO2 released by wet oxidation of hydrocarbons allowing determination of the inorganic and organic fractions of 14C in SIERs as well as in solution sampled from desorption tests. The 14C radioactivity was measured by liquid scintillation counting (LSC) using a Tri-Carb® analyser Model 3110 TR.

The experiments performed show that the SIERs transferred from Cernavoda NPP contains around 3.37 104 Bq/g of 14C predominantly as inorganic species and less than 7% as organic species. Since the main source of the analysed SIERs is moderator purification system and in the CANDU moderator the 14C is mainly present as bicarbonate, the chemical form of 14C absorbed on the resin is also mostly bicarbonate (H14CO3-).

From the total 14C present in the SIERs sample used for desorption test, around 7% was released as inorganic 14C in gas phase and around 79% as dissolved species. Around 94% of 14C content in the SIER sample was recovered at the end of desorption test.

The most part of 14C released as dissolved species was released in the first 2 days, while the amount of inorganic 14C released in gas phase is almost constant during the test.

Acknowledgement

This results were obtained from the work carried out by RATEN ICN in CAST project, that has received funding from the European Union’s European Atomic Energy Community’s (Euratom) Seventh Framework Programme FP7/2007-2013 under grant agreement no. 604779, the CAST project.

Radiocarbon on spent ion-exchange resins arising from boiling water reactors: inventory, speciation and release behaviour

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Organic divinylbenzene-based ion-exchange resins (IERs) are widely used in several cleaning systems of Boiling Water Reactors (BWR) to provide for an adequate purity of the cooling water. The water circuits experience the generation of activation products (APs) that are retained by IERs. Among typical APs, ^{14}C ($t^{1/2}$ of 5730 y) is of high concern, due to the risks of radiation hazard in case of incorporation in the human body. Therefore, the behaviour of ^{14}C retained on spent ion-exchange resins (SIERs) after discharge from the reactor needs to be understood in order to provide for a safe management solution for SIERs, i.e. (pre-)conditioning, intermediate storage and final disposal. SIERs typically fall within the Intermediate Level Waste (ILW) classification due to the presence of long-lived radionuclides (e.g. ^{14}C) and are considered to be disposed of in the german repository Schacht Konrad.

^{14}C retained in SIERs and its release behaviour was investigated in the frame of the EU-project CAST (WP4). The objective of the work was to account for the ^{14}C inventory in BWR SIERs arising from condensate clean-up systems (CCU), together with the speciation of the retained ^{14}C-containing compounds and their release behaviour under conditions relevant to the interim storage and final disposal. This information is supposed to contribute to a theoretical model for ^{14}C release and its fate in the long-term, ensuring the safety of the final repository.

Modern microscopic and spectroscopic techniques were used along with radio analytical methods to understand the speciation and release behaviour of ^{14}C. Some conventional analytical approaches (e.g. LSC, LC) are often not sufficient to detect low amounts of ^{14}C and to perform a speciation; therefore, an optimization of the available analytical tools constituted a considerable part of the work.

Morphological investigations on BWR SIERs pointed out the multi-component (inhomogeneous) nature of this type of waste. The speciation of ^{14}C originated from SIERs demonstrates that most ^{14}C (up to 99.6%) is in inorganic form. The organic fraction ranges from 0.4 % to 1.1 % of the total ^{14}C. High performance liquid chromatographic analyses on the solution obtained from a full regeneration of the SIERs highlighted the presence of formic acid, possibly originating from the reactor coolant or from the degradation of the resins. The presence of ^{14}C in non-ionic form, bound to the resins' backbone or in eventual particulate matter, was also investigated.

The kinetics of ^{14}C release from SIERs during storage was shown to be relatively fast. The equilibrium was reached within few days, demonstrating a saturation-like trend, driven by ion-exchange and/or isotope exchange processes. Radiation-induced degradation of SIERs, caused by the retained APs, as well as age-related effects, seem to be very slow and irrelevant for the fast ^{14}C release, in the present case. Elevated temperatures during storage favour a higher release of ^{14}C due to an enhanced thermal degradation of the SIERs (i.e. detachment/degradation of quaternary ammonium groups). These main factors influencing the release of ^{14}C from SIERs are presented and discussed in detail.

Evolution of IERS

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Ion exchange resins (IERs) are commonly used in PWR nuclear reactors as filters for ^{14} C impurities. Their efficiency, both as filters and as waste containers, is strictly connected with their morphology. The preservation of the spherical shape of both cationic and anionic resins in time, in use or just stocked, is one of the key parameters for their quality assessment and for the evaluation of the potential release of radioisotopes during the storage condition. In the present work we investigated the change in the morphology of the IERs during storage periods. The IERs three-dimensional and symmetric shape has been studied by means of SEM microscopy, on new and aged specimens, in order to assess the quality of the resins after 10 years of disposal and contribute to the understanding of the mechanism of radiocarbon release. The SEM images analysis clearly showed that the two resins (anionic and cationic) behaved differently, as far as the sphericity preservation upon ageing is concerned. The sphericity analysis by means of SEM could become a fast and unexpansive method for the preliminary evaluation of the degradation of SIER, before conditioning, providing valuable input for the performance assessment of the radioactive waste repository.

Behaviour of ^{14}C released from spent ion exchange resins and resins fixed in A cement matrix (Cementation of SIERs and Consequences on ^{14}C mobility)

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The experimental work formed part of the research carried out in the context of the CAST (Carbon-14 Source Term) project. The project is focused on determining the processes of the formation and release of ^{14}C species in radioactive waste and the safety evaluation of the disposal of waste containing^{14}C in radioactive waste repositories. The Czech partners involved in the CAST project consist of ÚJV Řež, a. s. and SÚRAO.

Experimentation involved the use of real spent ion exchange resins (SIERs) samples from nuclear power plants (NPP) and research reactors as well as laboratory prepared samples. Two types of tracer were used in the preparation of the artificially contaminated ion exchange resins, i.e. organic and inorganic carbon compounds (acetate and bicarbonate). The first part of research consisted of the performance of sorption and desorption experiments, and the second part involved the study of the release of ^{14}C following the fixing of the ion exchange resins in a cement matrix. The testing process focused on the kinetics of ^{14}C species leaching into three different liquid phases - distilled water, synthetic granitic water and sodium hydroxide solution.

The ion SIERs samples from NPP operation contained fewer ^{14}C species than the samples extracted from the research reactors and the major carbon species consisted of inorganic forms, either carbonate or bicarbonate. The desorption experiments indicated that the ion exchangers did not demonstrate a significant release of ^{14}C species into any of the liquid phases.

Subsequently, cement (CEM II class) was successfully tested as a fixation matrix for the ion exchange resin samples. Artificially contaminated ion exchange resins were used for fixation into the cement matrix and leaching experiments based on standard leaching method were performed. In this case, no carbon species release into the liquid phases was determined during the course of the leaching experiments.

Acknowledgement:
The project has received funding from the European Union's European Atomic Energy Community's (Euratom) Seventh Framework Programme FP7/2007-2013 under grant agreement no. 604779, the CAST project.

C-14 uptake in ion exchange resins from Swedish Nuclear Power Plants

K. Källstrom (SKB)

For almost 12 years samples of spend ion exchange resins (SIERs) have been collected from the Swedish Nuclear Power plants (NPPs) and analysed for the C-14 content. C-14 is one of the major dose contributing nuclides in the post closure safety assessment of the Swedish repository for short lived low- and intermediate level waste (SFR).

The C-14 content of the SIERs have been analysed for inorganic and organic C-14 content where the organic fraction is the major dose contributor in the post closure safety. With over 300 samples taken we have been able to get an understanding of the amount of c-14 in the SIERs and a model for historical and future uptake has been derived. The C-14 content in the SIERS depends on the downstream processing and can vary a lot depending on the process.

Nevertheless the C-14 content in the SIERs from the Swedish boiling water reactors varies between 1-4 % of the total C-14 production in the coolant. For the pressurised water reactors the C-14 content in the SIERs is in the same range as for the boiling water reactors but the organic content is higher i.e. about 30% of the total C-14 in the SIERs compared to about 1-10 % for the boiling water reactors.

Work Package 5 – Graphite

WP5 Graphite – Overview of Main Outcomes

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Work Package 5 of the EC CAST project considers irradiated graphite and related carbon-14 behaviour and is led by Radioactive Waste Management (RWM) from the UK. The objective of this Work Package is to understand the factors determining release of carbon-14 from irradiated graphite under disposal conditions (to include surface disposal facilities and geological disposal facilities). This has been achieved by:

- Determining the carbon-14 inventory and concentration distribution in i-graphites, and factors that may control these;
- Measuring the rate and speciation of carbon-14 release to solution and gas from i-graphites in contact with aqueous solutions; and
- Determining the impact of selected waste treatment options on carbon-14 releases and relating this to the nature of carbon-14 in i-graphite.

To achieve these objectives, five tasks have been undertaken:

- Task 5.1 – Review of CARBOWASTE and other relevant R&D activities to establish the current understanding of inventory and release of carbon-14 from i-graphites;
- Task 5.2 – Characterisation of the carbon-14 inventory in i-graphites;
- Task 5.3 – Measurement of release of carbon-14 inventory from i-graphites;
- Task 5.4 – New wasteforms and carbon-14 decontamination techniques for i-graphites;
- Task 5.5 – Data interpretation and synthesis – final report.

This presentation covers the main outcomes of CAST Work Package 5, including key learning points.

Reports produced by Work Package 5 participants are published on the EC CAST website, and are publically available – along with other CAST Work Package reports – at https://www.projectcast.eu/publications.

Ion irradiation used as surrogate for neutron irradiation to understand nuclear graphite evolution during reactor operation: consequences for the long lived radionuclide's behaviour

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IPNL

Graphite has been widely used in different types of reactors such as gas or water cooled reactors. Disposal of the irradiated graphite waste is a current management strategy for the resulting graphite waste for which two main radionuclides, 14C and 36Cl, might be dose determining at the outlet. In order to simulate both ballistic and electronic effects induced by irradiation, model and nuclear graphite samples implanted with 37Cl or 14C (to simulate the radionuclides) have been irradiated using ions by varying the Sn(nuclear)/Se(electronic) stopping power ratio. Extrapolating to reactor irradiation, we show that depending on the initial graphite ordering level and texture (binder/grain) and according to the subsequent neutron flux and temperature, graphite irradiation results into a structural "zoning" impacting the radionuclide behavior: except when located close to open pores, 14C is stabilized into graphite whereas 36Cl's release is strongly correlated to the counteracting effects of irradiation and temperature.

Carbon-14 in TRIGA Irradiated Graphite and its Release under Alkaline Conditions

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Irradiated graphite from TRIGA 14MW reactor was investigated in CARBOWASTE project and showed significant 14C and 36Cl activities that impose its deep geological disposal.

Combining experimental data on C-14 activity with numerical calculations, a preliminary inventory of the 14C was estimated to be 3 1010 Bq. Experimental work demonstrated the 14C activity decreases along the thermal column due to the thermal neutron flux attenuation from 105 Bq/g in the first row next to the reactor core to 2 102 Bq/g in the middle of the column, but it is quite uniformly distributed inside a brick, with values ranging between 0.9 103 to 1.9 103 Bq/g (measured on different samples from a graphite block in CARBOWASTE project).

Under CAST WP5, leaching tests were carried out in aerobe and anaerobe conditions to assess the 14C released as dissolved species in alkaline solution simulating the cementitious environment. Both total 14C and inorganic and organic fractions in the leachant solutions were measured.

The irradiated graphite samples used in leaching tests were cut from two cylindrical bars originating from a brick extracted and dismantled in 2000 from the thermal column of TRIGA reactor. Since the extraction from the thermal column the irradiated graphite bars were stored in air at room temperature and no information regarding their position in the thermal column was found.

The total 14C measurement in the powder graphite samples taken during mechanical cutting of the specimens used in the leaching tests was achieved by non-catalytic combustion by flame oxidation method. By this method, the graphite samples are combusted in an oxygen-enriched atmosphere with a continuous flow of oxygen, and all carbon is oxidized to CO2. The CO2 is subsequently trapped in a column filled with a carbon dioxide absorbent (Carbo-Sorb® E) and forms a carbamate that is flushed into the 14C counting vial using the Permafluor® E+ scintillator as a rinsing media. The 14C radioactivity was measured by liquid scintillation counting.

For the measurement of inorganic and organic fractions of the 14C released in leachate solutions an analytical method based on acid stripping and wet oxidation adapted after the method developed by Magnusson for 14C measurement in spent ion exchange resins and process waters was applied.

The experimental results obtained from the leaching tests both in aerobe and anaerobe conditions confirm the low 14C release in alkaline environment. Less than 2% from the total 14C inventory in the specimens subject to the leaching tests was released as dissolved species. Both inorganic and organic 14C species are released during leaching test, with more inorganic 14C release under aerobe conditions (around 68% from the total 14C released as dissolved species), and more organic 14C species in anaerobe conditions (around 65% from the total 14C released as dissolved species).

Both for anaerobe and aerobe conditions, the leaching rates are high in the first days of immersing and it decrease after that, indicating a two stage process: an initial quick release (less than 9 10-02 % of inventory/day for the first 48 days) followed by a slower release rate (around 4 10-03 % of inventory/day).

Acknowledgement

This results were obtained friom the work carried out by RATEN ICN in CAST project, that has received funding from the European Union’s European Atomic Energy Community’s (Euratom) Seventh Framework Programme FP7/2007-2013 under grant agreement no. 604779, the CAST project.

Carbon-14 release from Oldbury graphite. Use of experimental results to inform the safety case

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Carbon-14 is a key radionuclide in the assessment of the safety of a geological disposal facility (GDF) for radioactive waste. The UK's 2013 Derived Inventory contains 17,700 TBq of carbon 14 of which about 7,000 TBq is associated with irradiated graphite. This graphite has the potential to be a source of gases containing carbon 14, if it undergoes degradation or reaction in a GDF environment.

An early assessment model of the release of carbon-14 from irradiated graphite assumed that releases of carbon-14 would be in the form of 14CO2 in solution, with a small fraction as gaseous 14CH4. In a cementitious GDF the CO2 fraction was expected to react with cement minerals and largely be fixed in the solid phase, so migration of carbon-14 in solution was not expected to be an issue. However, methane could migrate with bulk gas (generated from container corrosion or from other wastes) to the biosphere and so presented a more significant risk in the safety assessment, to the extent that it could have affected the viability of graphite disposal. Therefore, to develop a more detailed understanding of the fraction and speciation of releases of carbon-14 from irradiated graphite under disposal conditions, leaching studies have been undertaken on graphite samples from the Magnox Reactor at Oldbury.

The work on Oldbury graphite has focussed on measuring the rate and speciation of carbon 14 releases to the gas phase, although solution concentrations have also been measured. The baseline conditions were anoxic, with intact graphite pieces immersed in pH 13 NaOH solution, at ambient temperature, to simulate the post-closure conditions in a cement based GDF. Variant experiments were conducted to examine the effects of oxygen availability, crushing to increase surface area, increased temperature and lower pH.

The baseline experiments on Oldbury graphite were started in 2012. In the first year of leaching ~0.07% of the carbon-14 inventory was leached into solution. The carbon-14 released was predominantly held in solution, with <1% of the carbon-14 released entering the gas phase. Gaseous carbon-14 was predominantly in the form of hydrocarbons and 14CO (or possibly volatile oxygen-containing organic compounds), with 14CO2 being retained in the alkaline solution. A fraction of the carbon-14 in solution comprised organic species.

Based on the improved understanding from this and other studies, a revised assessment model of carbon 14 release from irradiated graphite was developed and parameterised. The main characteristics of this model were:

- A large proportion of the carbon-14 remains unreactive and is not released;
- A small proportion of the carbon-14 is released rapidly before closure of the GDF;

- The remaining proportion is released at a slower rate that continues into the GDF post-closure period;
- The release is mainly into solution, with a small proportion released as gas;
- The gas phase speciation depends on the conditions.

The baseline experiments are continuing and appear to show continued decreases in the rates of carbon 14 release under anoxic, high-pH conditions. Between 12 months and 30 months no changes in the solution activity of carbon-14 were detectable within the uncertainties of the measurements and only very small further releases, close to detection limits, were measured to the gas phase. These findings suggest that the current model may be cautious with regards to longer-term releases of carbon-14 from graphite and that there may be scope for further improvements to the model based on improved scientific understanding.

WP5 Summary and Conclusions

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A suggested output from CAST Work Package 5 to Work Package 6 Safety Case is presented. It relates to and outlines the behaviour of irradiated graphite **in the context of deep geological disposal in a cementitious repository**.

It must be remembered that some national programmes participating in CAST Work Package 5 do not envisage this approach for the long-term management of irradiated graphite; for example, some consider long term storage in a surface facility or disposal to a near surface / shallow geological facility disposal.

A regulatory ‘cap’ on the total amount of carbon-14 permitted in a storage / disposal facility may also be in place. Treatment of irradiated graphite, e.g. to reduce the associated carbon-14 inventory, could be being considered as part of the overall management strategy for this waste, also encompassing management of any resulting secondary waste.

As national programme requirements drive research activities related to irradiated graphite (and other inventory components), these activities themselves may involve considerations of varying end points to the management of irradiated graphite. Furthermore, the relative importance in the safety case of irradiated graphite- derived carbon-14 (in the aqueous phase) versus carbon-14 (in the gaseous phase) also can vary by waste management concept; this can affect the prioritisation of research activities.

It is suggested that the following is considered as an output of CAST Work Package 5 learning, for utilisation in CAST Work Package 6 Safety Case **in the context of deep geological disposal in a cementitious repository**:

- A substantial fraction of the carbon-14 in irradiated graphite is not releasable;
- Some carbon-14 would initially be released rapidly, and some would be released more slowly at a rate reducing over time (i.e. the release cannot be defined by a single rate constant);
- Carbon-14 can be released to both the gas and aqueous phases. Carbon-14 released to the gas phase may exist as a number of different species with potentially different consequences, including organic species (e.g. CH_4), CO_2 and CO;
- Release rates and speciation of the released carbon-14 may change depending on the conditions (e.g. pH, presence of oxygen).

New concept and instruments for carbon-14 measurements in i-graphite

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Keywords: 14C, measurement, i-graphite, characterization.

The radioactive graphite coming from nuclear installations is a very special waste form due to its radiological properties. As a result of a long period of irradiation, the graphite waste contains significant amounts of long-lived radioisotopes such as Carbon 14 and Chlorine 36, and short-lived isotopes such as Cobalt 60.

Carbon 14 is a key nuclide in relation to decisions to be taken on irradiated graphite waste management. This paper will focus on new technical devices and concepts that could be used for the analysis of the Carbon 14 inventory.

The main improvements related to these innovations consist of:

- Non-destructive and in situ measurements conducted at the industrial batch scale, without a need of sample collection and radiochemical analysis;
- Direct characterization and inventory provision by these techniques, negating any requirement to derive inventory data through the use of radionuclide ratios to gamma emitters and also avoiding inhomogeneity effects;

The approach is based on reliable and improved techniques used in ore analyses and sensitive material detection, as well as well-known calorimetry measurements.

At this time, fundamental knowledge of Carbon 14 activity is given by sampling and measurements by radiochemical techniques, correlated to calculations and knowledge of reactor history. However, gaining this knowledge is time-consuming, costly and needs a very high level of competence to acquire.

There is therefore an industrial need of good measurements, undertaken in the field with a high level of credibility and in «real time» (understood to be as a complement of reference measures and not as an alternative).

The main difficulty is to get the right D&D design and to give guidance for storage solutions matching the right need, and avoiding precautions that result in the creation of «virtual Becquerels».

A further step will be to develop a view of possible i-graphite decommissioning and characterization processes that could benefit from these innovative measurements, taking into account proven precision and related uncertainties with regard to national Waste Acceptance Criteria and in consideration of possible waste treatment scenarios.

Work Package 6 – Safety Case Relevance

Implication of CAST results on safety assessment and safety case: Introduction and focus on disposals in clay formations

Manuel Capouet

Ondraf/Niras

Because of its rapid decay compared to timeframes considered in safety assessment, C14 radiological flux released in the biosphere is particularly sensitive to its transport characteristic time in geological disposal. Extending the C14 residence time in a geological system from a few thousands to a few tens of thousands years reduces its flux by more than one order of magnitude. Long term safety assessments show that speciation of C14 is crucial for the determination of its radiological impact. As inorganic, C14 provides good retention capabilities in cement (that usually makes the EBS of ILW/LLW repository) and in clay. As organic, C14 is considered not retarded or very weakly giving rise to a more pronounced radiological impact. However, sensitivity studies for diffusive and saturated scenarios in clay systems reported in the CAST project show that the radiological impact remains well below regulatory limits even considering a transport of unretarded C14 (organic) compounds. This good performance is due the slow diffusive transport in the geological host rock. Further, in these conditions, the near field features like the C14 release rate from the waste form or its diffusion rate through the cementitious environment has a minor effect on the output flux of the host formation. The robustness of the system might be challenged in scenarios where the diffusive barrier is shortcut. In these “advective” scenarios, the residence time is shorter and the release in the biosphere might be more localised. The “gas” scenario (volatile C14 transported by a carrier gas) and the “poor- sealing” scenario fall in this category. Their impact is function of design and host rock specific features : the availability of the radionuclide carrier, the amplitude of the driving force and the hydrogeological and geometric characteristics of the preferential path. In order to mitigate these scenarios, or to demonstrate the defence in depth of the geological system, the performance of additional barriers can be reinforced on basis of CAST results. Indeed, next to the uncertainty reduction of the C14 speciation, CAST provided the opportunity to increase the knowledge in different areas touching to C14 long-term impact. This knowledge can be used as qualitative lines of argumentation supporting conservatism or can be directly parameterised in scenario modelling. These areas cover the uncertainty reduction of the inventory (in particular Zy and IERs), the C14 release rate of the Zy and steel metals, the possible retention of small C14 oxygenated organic compounds in clay and cementitious environment, and the biosphere stylisation.

Implications of the CAST results for the disposal systems crystalline host rocks

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The safety assessments for repositories in crystalline host rocks manifest 14C being among the key nuclides contributing to total dose. The speciation of 14C released has typically been assumed organic leading to very low retardation in the engineered barriers and in the geosphere. In addition, the fractured nature of the crystalline host rocks result in relatively fast transport times through the geosphere. The combination of low retardation and fast transport times lead to migration of C- 14 into biosphere without a considerable decay, unless the physical containment mainly provided by the engineered barriers sufficiently delays or limits the release.

The source term - the release rates from the waste and the speciation of 14C - together with the engineered barrier system dictate the release. In general, the results from the CAST project confirm the earlier conservative assumptions of the 14C speciation. For instance, 14C released from the activated metals is mainly in organic form. Thus, the added information does not always lead to a lesser degree of conservatism and reduction in the dose rates, but to reduction of uncertainties and increased confidence. In other waste types (zirconium alloys, spent ion- exchange resins, irradiated graphite), the distribution between 14C released in organic and inorganic forms vary and generally involve larger uncertainties, partly due to different operating conditions at nuclear power plants, heterogeneity of waste materials, their treatment and storage prior to the disposal.

The CAST project has also provided support for the very low steel corrosion rate under anaerobic and alkaline conditions which directly impacts the release rates of all nuclides, including 14C, from activated metals. In addition, experiments outside CAST project indicate weak sorption of 14C into cementitious materials. The overall impacts of these findings depend on their incorporation into national programs, on the disposal concept and to the overall impact of 14C assessment and the handling of 14C in the biosphere assessment.

Key words:
Crystalline rock, 14C, speciation, release rate.

The role of Carbon-14 for repositories in salt : Integration of the CAST results

A Rubel

GRS

In rock salt, the long-time separation of the radioactive waste from the biosphere is done by the salt. This is on the one hand the undisturbed part of the salt host rock formation and on the other hand the crushed salt, which is used to backfill the mine openings in the emplacement areas and galleries. The crushed salt backfill is compacted over time and achieves a sufficiently high hydraulic resistance to avoid entries of brines into the emplacement areas of the repository. Plugs and seals must provide their sealing function during the early post closure phase, until the compaction of the backfill is adequate and the permeability of the backfill is sufficiently low. At a certain stage, backfill and host rock both have a permeability in the same order of magnitude.

In the CAST project, two groups performed simulations to assess the contribution of C-14 to the dose, the influence of source term parameters on the dose and the implications of the CAST results. These are ENEA from Italy and GRS from Germany.

Simulations by GRS

TOUGH2 was used to model the gas and radionuclide transport in a repository for high-level waste, i.e. spent fuel, compacted metal wastes and vitrified wastes. A flow of non-radioactive gases in the mine is caused from the beginning of the post- closure phase by the displacement of air from the mine. This is due to the convergence of the salt host rock and the decreasing porosity in the salt grit. Additionally, a gas flow also results from hydrogen production caused by iron corrosion by the small amount of water initially emplaced with the containers and the salt grit backfill. External waters that might reach the emplacement fields closest to the shaft can potentially lead to a more significant corrosion and gas production, however to late times which are not relevant for the C-14 release. The C-14 instantaneously mobilised from the instant release fraction (IRF) of the Zircaloy is released from the four initially defect spent fuel containers directly at the beginning of the post-closure phase and further on is transported along with the non- radioactive gases through the unsaturated drifts to be released through the drift seal.

Parameter variations were performed to vary the main influencing factors of the source term, i.e. IRF, the release rate and the release start time. As a summarizing conclusion it can be stated that the consequences of the C-14 release from the waste in the early phase of the repository are to a large part controlled by the quantity of the C 14 released. The temporal behaviour of the C-14 release only shows a minor impact if not delayed significantly. The conservatism in the assumption used before regarding the amount of C-14 released during the early phase of the repository can be significantly reduced thanks to the results obtained in the First Nuclides and the CAST projects.

The highest priority to further reduce the uncertainty on the release behaviour of C-14 is mainly related to the question whether water is necessary to transfer C-14 into volatile form or if this does occur also without the presence of humidity.

Simulations by ENEA

The conceptual model of the system “waste-repository-salt rock” has been developed using data of Italian past studies about salt formation, information from literature and analogies with other GDF project (e.g. WIPP). The hypothetical repository should be realized in a deep salt formation, about 800 m depth, with geometry features similar to the US WIPP repository. Results of these simulation of the whole repository have highlighted the low radiological impact of C-14 gaseous emissions in underground facility and in the shaft toward the surface, using appropriate sealing materials. These simulations highlighted the possibility to correlate the Kd values, the volume and the location of sealing materials to the amount of C-14 emitted toward the surface facility. The description of this modelling work is the object of a separate presentation in this symposium.

Assessment of aqueous 14C transfer in an Intermediate-Level Waste (ILW) disposal cell

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The aim of this study was to assess the transfer of aqueous 14C in an Intermediate-Level Waste (ILW) disposal cell taking into account the state-of-the art of the phenomenological behavior of 14C in cements and clay-rocks. The fundamental processes ruling the migration of aqueous 14C were first evaluated for clay-rocks and cement based materials. Inorganic 14C is (i) weakly sorbed in clayrock and (ii) strongly sorbed by cement-based materials. For both materials, solid carbonate minerals contribute to the retention of inorganic 14C. The retention of 14C onto calcite is a time controlled processes related to the isotopic exchange between 14C and 12C constituting calcite. Kinetic exchange experiments of 12C by 13C performed on nanoparticles of calcite by Charlet and Gehin al. (2013) reveal that solid diffusion phenomena can explain the behavior of 14C as regard to calcite. From the work of Charlet and Gehin, a diffusion model was applied to estimate 14C retention kinetics and associated Kd for the Callovo-Oxfordian clay-rock. This model takes into account carbonate content and the mean size of calcite grains. In concrete, the presence of calcareous aggregates will mainly contribute to fix inorganic 14C. Experimental 14C retention experiments on cement-based materials were also successfully interpreted by considering such a solid diffusion mechanism. For hydrated cement pastes, the calcite content is low, and then, a surface adsorption by C-S-H has to be considered likely combined with the carbonation of portlandite. The results of this study provide reliable Kd of inorganic 14C in various materials considered for the 14C bearing waste disposal with the objective of reducing the uncertainties of PA calculations. The retention of organic 14C molecules was evaluated based on a literature review, notably Rasamimanana et al., (2017) for clay-rocks and Wieland et al., (2016) for cements.

The second part of this work was to address the performance assessment of aqueous 14C transfer (no gas phase represented here), released from a disposal cell of intermediate level waste within the Callovo-Oxfordian (COx) clay host rock of the Cigéo project (deep geological repository project in France). These numerical evaluations have considered:

- A 2D vertical cross-section of the disposal cell, involving the inventory of primary packages, and also including several materials, cement-based ones and clay-based ones, such as (i) disposal packages, (ii) disposal chamber (filling concrete surrounding the packages), (iii) concrete liner, (iv) damaged zones of the clay-rock, and (v) pristine clay-rock;
- Inorganic 14C as anionic species (HCO3-/CO32-) and 14CH4 as the sole organic form;
- Transfer parameters for cements and the Callovo-Oxfordian clay-rock (K, De, Kd) including the dedicated work described above. Two sets of parameters “phenomenological” and “envelope” were successively investigated for each of the two forms of carbon.

The time evolutions of 14C molar fluxes were quantified at different surfaces defined at interfaces between materials or within the clay-rock, and then discussed as regard as the different sets of parameters and retention of 14C in particular.

Charlet and Gehin (2013) Interactions 13CO32- calcite et Kd pour 14C. Andra report n° CGRPFSTR150005

Rasamimanana, S., Lefèvre, G., & Dagnelie, R. V. H. (2017). Adsorption of polar organic molecules on sediments: Case-study on Callovian-Oxfordian claystone. Chemosphere, 181, 296-303.

Wieland, E., Jakob, A., Tits, J., Lothenbach, B., & Kunz, D. (2016). Sorption and diffusion studies with low molecular weight organic compounds in cementitious systems. Applied Geochemistry, 67, 101-117.

Current position on carbon-14 in the RWM Environmental Safety Case

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Carbon-14 is a key radionuclide in the assessment of the safety of a geological disposal facility for radioactive waste because of the potential radiological impact of gaseous carbon-14 bearing species during the operational and post-closure periods.

In 2012, RWM established an Integrated Project Team (IPT) to develop an holistic approach to carbon-14 management in a geological disposal system. The overall aim of the project was "*To support geological disposal of UK wastes containing C- 14, by integrating our evolving understanding from current and pre-existing projects, in order to develop an holistic approach to C-14 management in the disposal system*".

In 2017, RWM published an updated Disposal System Safety Case. The

- Derived Inventory (DI) (https://rwm.nda.gov.uk/publication/geological-disposal-2013-derived-inventory/);
- Environmental Safety Case (ESC) (https://rwm.nda.gov.uk/publication/geological-disposal-generic-environmental-safety-case-main-report/);
- Post-closure Safety Assessment (PCSA) (https://rwm.nda.gov.uk/publication/geological-disposal-generic-post-closure-safety-assessment/); and
- Operational Environmental Safety Assessment (OESA) (https://rwm.nda.gov.uk/publication/geological-disposal-generic-operational-environmental-safety-assessment/),

in particular, were informed by learning from the carbon-14 IPT.

Understanding from the Carbon-14 Integrated Project has led to:

- An improved understanding of carbon-14 distribution in the UK inventory and behaviour in the geosphere and biosphere as described in the Gas Status Report (https://rwm.nda.gov.uk/publication/geological-disposal-gas-status-report/); and
- An improved off-site gas release rates for carbon-14-bearing gases in RWM's ESC, including the OESA and PCSA.

Scope for further work on carbon-14 has been identified in:

- Updating the assumed effective release ventilation stack height for carbon-14 bearing gases during the operational period (from 15 to 30 m) in the OESA; and
- Carrying out further research to better understand the effect of gas pressurisation within the facility and its potential implications for carbon-14 release.

An Overview of C-14 Treatment in Post-closure Safety Assessment in a Canadian Deep Geologic Repository

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NWMO

C-14 is one of the key radionuclides in the post-closure safety assessment of a Canadian Deep Geologic Repository (DGR). For Ontario Power Generation (OPG)'s proposed DGR for Low and Intermediate Level Waste (L&ILW), most of the C-14 inventory resides in the Intermediate Level Waste (ILW) resins as carbonate and bicarbonate; for Nuclear Waste Management Organization's Adaptive Phase Management (APM) project, C-14 present in the used fuel bundles originates from activation of nitrogen which is present as an impurity.

An overview is presented of the treatment of C-14 in the post-closure safety assessment for OPG's proposed DGR and APM's illustrative case study and their key dose results.

For post-closure safety assessment of OPG's proposed DGR, C-14 release from L&ILW in the repository is modelled using the AMBER system model and T2GGM gas generation and transport model. For surface contaminated waste and ILW resins, C-14 is released as gas (14CO2 and 14CH4) from degradation of unsaturated wastes and resins, and immediately to the water on contact with water. For activated metallic waste, C-14 is released as 14CO2 and 14CH4 as the metals corrode. C-14 is then partitioned between the model repository water and gas compartments in proportion to the amounts of bulk carbon in water and gas in the repository. The C-14 is transported with gas and water from the repository through the shafts and surrounding host rock to the biosphere for dose calculations.

For post-closure safety assessment of APM's illustrative crystalline rock case study, release of C-14 from used fuel bundles is modelled in the SYVAC3-CC4 system model and FRAC3DVS groundwater flow and transport model. Corrosion of UO2 and zircaloy tubes when in contact with water in failed containers releases C-14 into repository water, where it can be transported through the engineered barriers and host rock, and into the biosphere for dose calculations. C 14 gas release is treated separately and calculated simply based on the minimum of the gas generation rate and the gas transport rate through the geosphere as the vertical flow rate within the bulk gas to the biosphere for crystalline rock.

Day 3

Dissemination

E.A.C. Neeft(1), D. Grigaliuniene(2), V. Montoya(3), G. Buckau(4)

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The objectives of the Work Package *Dissemination* are to disseminate information about the activities as widely as possible to various groups having an interest in the Carbon-14 Source Term (CAST) project and its results. The expected date of deliverables intended for public dissemination was published at the start of the project to allow groups to engage with the CAST project. The transmission of the new understanding of potential release mechanisms of carbon-14 to waste producers and generators, regulators, waste management organisations, experienced researchers, early career researchers and the public was described in the CAST dissemination plan.

The public CAST website www.projectcast.eu has been divided in sections for an efficient dissemination of results to an audience with different interests. At the homepage, a description of natural carbon-14 has been given for an audience with no knowledge in radiation protection and unfamiliar with carbon-14 containing waste. There is a special section for the broad scientific community for the published reports. Links to articles accepted in scientific journals, presentations given at scientific fora and submitted abstracts for other conferences and symposiums have been provided in a designated section (''Other'').

Two workshops were envisaged in CAST. The first workshop was held in 2016 in the Netherlands. The second workshop will be held in conjunction with the CAST Final Symposium in Lyon. The workshops were for participants with an interest in the research executed in CAST but who can also contribute to the confidence in national safety assessments. The research is evaluated from different perspectives in order to specify this contribution. The scientific progress has already been evaluated by the CAST Advisory Group and results obtained in CAST have been and will be presented at several scientific fora. For an implementation of the new understanding developed in CAST, stakeholders with a responsibility in the management of radioactive waste were envisaged. The institutional arrangement of these responsibilities can be viewed in a triangle in which regulators, waste management organisations (WMOs) and waste generators have clearly defined roles.

Carbon-14 is a weak beta-emitter (156 keV) and therefore a Difficult-To-Measure radionuclide. For CAST, the waste generator or waste producer was expected to contribute to the reliability of the characterization of the waste for disposal; the contribution by the regulator was expected to depend on the national progression in disposal of carbon-14 containing waste. Technical overviews have been written for them to prepare themselves for the workshops. Performance indicators of the involvement of type of actors have been set in the CAST dissemination plan. The involvement of regulators in the first workshop was a success: more than 50% of the countries with an organisation participating in CAST participated with professionals from their national regulatory body to the workshop. The involvement of waste generators was less successful: 9 waste management organisations participate in CAST and it was considered achievable to have at least 9 waste generators participating at the workshop. Three waste generators attended the first workshop of which 2 are also waste management organisations for the types of waste investigated in CAST. According to the European Nuclear Safety Regulators Group, there are 16 EU countries with operating nuclear power plants. A total of 15 WMOs in the EU have been involved in CAST either through their participation in CAST or the first workshop. A performance indicator for the dissemination to these organisations has not been made in the CAST dissemination plan. Thus, it cannot be judged whether dissemination to this group has been successful.

The WMO is responsible for the management and eventual disposal of radioactive (including carbon-14 containing) waste. In the first workshop, these organisations presented their radiological characterisation for the types of waste investigated in CAST namely neutron irradiated steel, Zircaloy, graphite and spent ion exchange resins. The methodologies to determine the carbon-14 concentration in the waste varies considerably within the EU. In some EU countries carbon-14 has not yet been identified to be present in the types of waste investigated in CAST. The sharing of the methodologies and discussing them with the regulators present in the workshop is expected to upgrade the radiological characterisation. This can increase the confidence of quantifying the carbon-14 concentration as input for the safety assessment. It can also increase the confidence in clearance of the neutron irradiated graphite and steel.

Two training courses have been envisaged for Master and PhD students with a background in (nuclear) engineering, physics, geology, chemistry and mathematics. The specific interest of this group is to learn, gain knowledge and develop skills to address waste management issues associated with carbon-14 containing waste. Professionals were allowed to attend the training course as well when there were vacancies The first training course has been held in July 2016 in Germany at Karlsruhe Institute of Technology- Institute of Nuclear Waste Disposal (KIT-INE). German, French and Croatian students and professionals from Czech Republic, Finland and Sweden attended the training course. A group of 11 nuclear interested persons were taught in how carbon-14 is generated in a nuclear reactor, what types of waste contain carbon-14, how the carbon-14 in waste can be measured and the disposal concepts for carbon-14 containing waste. The group visited the controlled area and hot cell laboratories of KIT-INE and the low and intermediate level waste treatment, decontamination, conditioning and interim storage facility in Nuclear Waste Disposal of Karlsruhe. On the last day, they experienced wearing protective equipment like face masks and working in a glove box. The content of the second training course has been announced at the Third PETRUS-ANNETTE PhD and Early-Stage Researchers Conference in June 2017 and is scheduled in February 2018 in the Netherlands.

For an audience with no knowledge in radiation protection and unfamiliar with carbon-14 containing waste, newsletters have been issued to disseminate the knowledge developed in CAST. The topics were based on the scheduled publications in the Work Packages on Steels (WP2), Zircaloy (WP3), Ion exchange resins (WP4), Graphite (WP5) and Relevance of results in national contexts and safety assessments (WP6):

(1) Origin of carbon-14 waste;
(2) Radiological characterisation of waste;
(3) Experimental approach to determination of release of carbon-14;
(4) Analysis and chemical forms of carbon-14;
(5) Quantification of source term for safety assessment.

CAST Advisory Group Review Findings

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During the course of the CAST project, an advisory group has monitored the overall progress towards the stated goals of the programme. This presentation will provide a summary of the findings of the two external members of the advisory group; Irka Hajdas, who focussed on the development and application of techniques for the measurement of C-14, and Fraser King, who focussed on the characterization of the different sources and the associated mechanisms and rates of C-14 release and their use in performance assessment modelling.

The study of the inventory, chemical nature, and physical distribution of C-14 in the various waste forms and of their release under repository conditions was a key component of the CAST programme. During the course of the project, progress was made in each of these areas for the four different waste forms, steels, Zircaloy, spent ion exchange resins, and irradiated graphite. Two standard techniques LSC and AMS were applied to measure the C-14 activity realised by corrosion or leaching of these products. We will review the applicability of the techniques as well as the new technical developments achieved in the frame of the CAST project.

Specific areas of progress will be highlighted, as well as some of the challenges. One of the other highlights of the project was the interaction between the experimentalists and those responsible for the performance assessment modelling that helped to achieve progress in the treatment of C-14 in safety assessments.

Poster Abstracts

Use of NA in communications: 2 EU-research project Carbon-14 Source Term

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I. Introduction

Carbon-14 is a radionuclide present in some wastes destined for geological disposal that can be released in a gaseous form during waste degradation. If migration of carbon 14 bearing gas from a disposal facility to the biosphere were subsequently to occur, waste-derived carbon 14 is therefore one of the radionuclides that can reach the biosphere first. Only weak betas are emitted during carbon 14 decay, and therefore it is a so-called 'Difficult To Measure' radionuclide. Its measurement in radioactive wastes cannot be determined non-invasively by gamma spectrometry.

The EU Research project CArbon-14 Source Terms (CAST) aims to develop further the understanding of the potential release of carbon-14 from radioactive waste materials under conditions relevant to waste packaging and disposal to underground geological disposal facilities. The project focusses on the release of carbon-14 as dissolved and gaseous species from irradiated metals (steels, Zircaloys), irradiated graphite and spent ion exchange resins [1].

II. Dissemination for different groups

In the management of radioactive waste, several groups of individuals can be identified. It is essential to consider the knowledge and interest of stakeholders (which could be one person, or a group of people, with a specification of their interest, connection, etc.) when planning for the implementation of research results to be incorporated in safety case studies related to a geological disposal facility. Workshops are organised for regulators, waste generators, waste producers and waste management organisations since these stakeholders have at least one responsibility in the management of radioactive waste [2] for example decision to grant a licence for disposal of waste, pay for the costs for disposal, quality control of the processed waste product and defining waste acceptance criteria. Training courses are made for early stage career researchers.

For groups whose interests cannot be specified, mass media communication tools can be used to disseminate the findings of CAST [2]. These tools are newsletters, scientific articles and a website: www.projectcast.eu. At the homepage, a description of natural carbon-14 is given, in order to familiarise the visitor with carbon-14. The CAST interactive website contains components aimed at encouraging visitors to participate. Figure 1 shows an example available on the CAST website: the production and incorporation of natural carbon-14 is visualised when the cursor is held over the main photo.

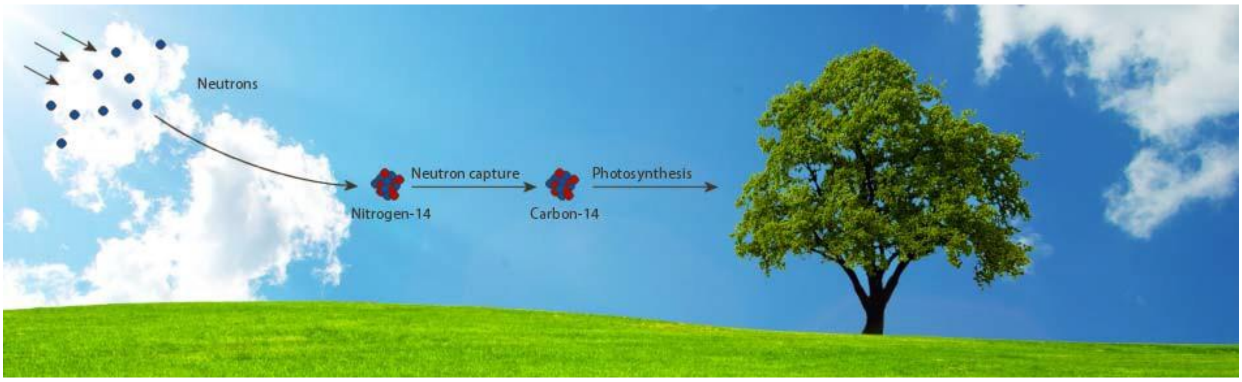

Figure 1: . Visualisation of natural carbon-14

III. Newsletters

For the public, newsletters are written to disseminate the knowledge developed in CAST. Each newsletter focuses on a specific topic using A3 size infographics to illustrate the information. Five newsletters are intended to be produced. The topics are based on the scheduled publications in the Work Packages on Steels (WP2), Zircaloy (WP3), Ion exchange resins (WP4), Graphite (WP5) and Relevance of results in national contexts and safety assessments (WP6):

1) ***Origin of carbon-14 waste;***
2) ***Radiological characterisation of waste;***
3) ***Experimental approach to determination of release of carbon-14;***
4) ***Analysis and chemical forms of carbon-14;***
5) ***Quantification of source term for safety assessment.***

Each Newsletter is intended to contain an example of an analogue associated with carbon-14, in order to familiarise the reader with these topics. An analogue is understood here as a description of the same processes taking place in natural systems and in pure or partly artificial systems such as geological disposal of radioactive waste with engineered and natural barriers. The only differences between both systems are the potential different values in parameters to calculate the processes. In this abstract, the information used to connect carbon-14 in natural systems to carbon-14 in pure artificial systems, in this case nuclear power plants, is described.

IV. Origin of carbon-14

Carbon-14 can be generated by neutron activation of carbon-13, oxygen-17 and nitrogen-14. In the first Newsletter [3], the cosmogenic origin of natural carbon-14 is introduced i.e. the presence of neutrons and nitrogen in our atmosphere. Already in 1970’s, only nitrogen-14 was assumed as a contributor to cosmogenic carbon-14 [4]. This origin is not different from carbon-14 in waste, i.e. it is a (mainly) neutron-activated radionuclide formed due to the presence of nitrogen impurities contained in materials used in nuclear power plants and interaction with neutrons available [5].

V. Radiological characterisation

Measurements are difficult for the radiological characterisation of carbon 14 in waste. Frequently, calculations are used to determine the distribution of the carbon 14 content in waste materials. The neutron irradiation history, neutron to carbon 14 reaction cross sections and the concentration of neutron activation precursors are necessary for this determination. The same parameters are necessary to determine the generation of carbon 14 in natural and artificial systems.

The origin of neutrons in natural and artificial systems is different. Neutrons are generated by fission of actinides in a nuclear power plant. Outside the Earth's atmosphere, high energetic particles, e.g. protons, are generated. A cascade of secondary cosmic rays is made by collisions with these high energetic protons (primary cosmic rays). The Earth's magnetic field and atmosphere provide protection against cosmic radiation. A part of these secondary rays are neutrons [6].

In the second Newsletter [7], it is explained why nitrogen 14 is responsible for the main contribution to the generation of natural as well as artificial carbon 14, rather than the other precursors of carbon-14 i.e. oxygen 17 and carbon 13. The natural abundances of the three precursors are 99.636% for nitrogen 14, 0.038% for oxygen 17 and 1.07% for carbon-13. Figure 2 shows the neutron activation cross sections of the three precursors of carbon-14 as a function of the neutron energy. The graphs show the cross sections from the library Joint Evaluated Fission and Fusion File from 2014, in which the latest results were evaluated. The data available in the free on-line libraries from Nuclear Energy Agency (a specialised agency within the Organisation for Economic Co-operation and Development) have been used to compile the graphs for the three precursors of carbon 14.

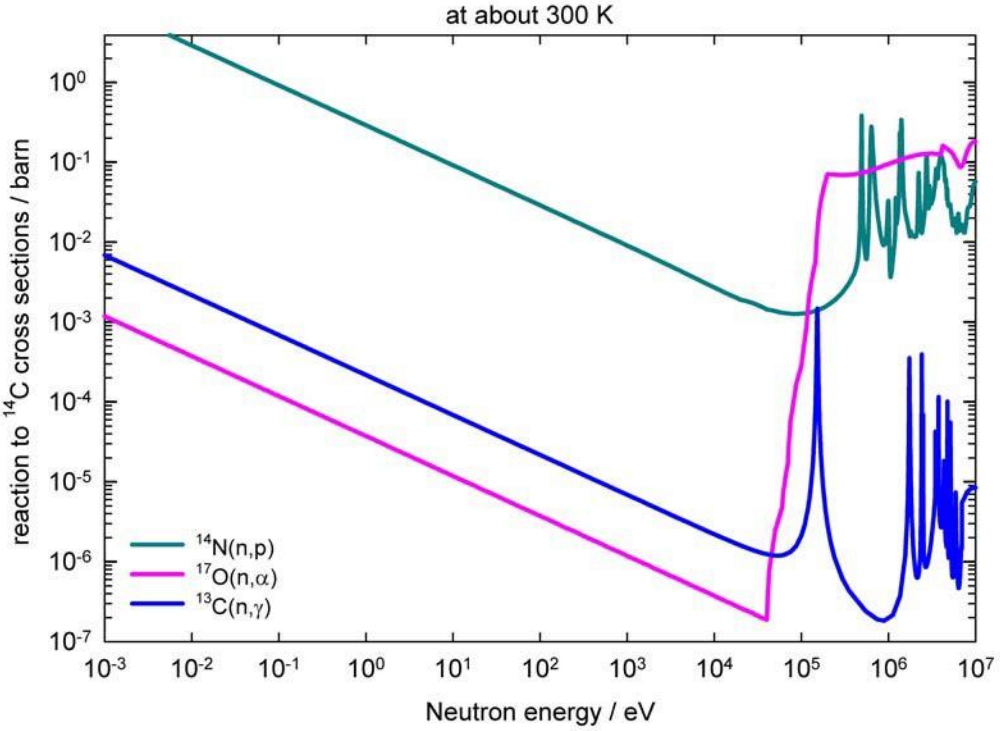

Figure 2: Neutron reaction to carbon-14 cross sections

The energy of neutrons that are generated by fission of actinides is about 1 MeV. The energy of neutrons resulting from collisions with high energetic protons can be several orders in magnitude larger i.e. GeV. The high energetic neutrons lose their energy by collisions with other atoms. Hydrogen atoms are most effective in reducing the energy of neutrons. The operation of a nuclear power plant is focussed of achieving a large thermal neutron flux, as the cross sections for fission of fissionable isotopes such as uranium-235 are largest for thermal neutrons. Water has a high concentration of hydrogen atoms and has therefore a large reducing power. Thermalized neutrons have an energy of about 0.0253 eV at room temperature. Water is therefore frequently used as a moderator in nuclear power plants. The effect of thermalizing neutrons by water is also observed in nature, for example, just a few centimetres below the interface between air and freshwater or seawater, a slight increase of the environmental thermal neutron flux can be measured [8].

The longest-lived lifetime of a neutron in a nuclear power plant is associated with a thermalized neutron. The cross sections for thermal neutrons are therefore used to estimate the carbon 14 content in waste. The reaction relationships relevant to carbon 14 cross sections and the natural abundances of these precursors require the chemical contents of carbon and oxygen to be five and seven orders in magnitude larger than nitrogen in order to contribute to the same carbon-14 content.

About 80% of the Earth's atmosphere is composed of nitrogen. It is easy to understand why only nitrogen is considered as a contributor to carbon 14 from the natural abundances and cross sections of the precursors. During photosynthesis, 14CO2 is incorporated in organic material, forming its carbon skeleton. In living matter, the carbon 14 content can be about 0.25 Bq per gram [9]. 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 solid matter for carbon-14 [10]. Based on the carbon 14 content, the amount of material that can be characterised as radioactive waste depends on the nitrogen impurities, thermal neutron flux and irradiation period.

Neutron irradiated steel and neutron irradiated graphite are types of waste frequently resulting from the dismantling of nuclear power plants. The nitrogen content of these waste materials is frequently unknown. For steel, combustion equipment has been used in CAST to determine the nitrogen content for the radiological characterisation of the investigated samples [11,12]. In a nuclear power plant, stainless steel is frequently used for its corrosion resistance, with carbon steel being used where necessary for its mechanical strength. For example, stainless steel is used for the inner part of the reactor vessel and the outer part is made with carbon steel. Steel scatters neutrons. Consequently, neutron activation takes only place just below the interface of steel and water [13]. It is therefore expected that stainless steel used in a nuclear power plant will only contain carbon 14 generated in the plant. The nitrogen impurities in commercial stainless steel can be 0.10 wt% [14]. Grinding off the surface of stainless steel pieces [15] is therefore a method to reduce the amount of radioactive waste.

Assuming a chemical content of 15 ppm nitrogen in graphite will result in a contribution to carbon 14 by nitrogen of 60%. The contribution to carbon 14 by neutron activation of carbon 13 is then 40%. Frequently, a larger nitrogen content is assumed, for example 40 ppm and 70 ppm in the Romanian and Lithuanian calculations that have been undertaken as part of the CAST project work on irradiated graphite [16]. The contribution by neutron activation of carbon 13 then becomes not a significant issue.

Shielding determines the distribution in magnitude of neutron flux, both for the environmental (natural) system as well as the artificial system of a nuclear reactor. The neutron flux that occurs in nature at altitudes typical for intercontinental flights, related to cosmic radiation, is about 10 neutrons cm 2s 1 [17], whereas, as a consequence of shielding by the Earth's atmosphere, neutron flux at the Earth's surface is consequently smaller, i.e. about 10 3 neutrons cm 2s 1 [8]. The neutron flux in a nuclear power plant reactor is several orders in magnitude larger, for example 1014 neutrons cm 2s 1 [18]. This difference in orders of magnitude in thermal neutron flux causes carbon 14 to be present in waste at hazardous concentrations, even though nitrogen may only be present at impurity levels in materials used in such a reactor.

The nitrogen concentration in materials appears frequently to be unknown, especially before it was decided to use such materials in nuclear power plants. Understanding of the generation of carbon 14 in a nuclear power plant may prevent the potential for hazardous carbon 14 concentrations to be insufficiently considered during dismantling and subsequent waste disposal operations related to nuclear power plant decommissioning, noting carbon 14 activity is not detected by inventory assay techniques such as gamma spectrometry.

References

[1] E Scourse, S Williams, Project presentation, CAST Report D7.2 (2014) available at www.projectast.eu.

[2] EAC Neeft, A Narkuniene, V Montoya, G Buckau, Dissemination plan, CAST report D7.3 (2015) available at www.projectast.eu.

[3] CAST Newsletter 1 (2015) available at www.projectast.eu.

[4] SA Kordd, RB Mendell, M Merker, ES Light, HJ Verschell, WS Sandie, Atmospheric neutrons, NASA Contractor report 3126 (1979).

[5] RP Bush, GM Smith, IF White, Carbon-14 waste management, EUR 8749 (1984).

[6] ICRP, Radiological protection from cosmic radiation in aviation, ICRP publication 132 (2016).

[7] CAST Newsletter 2 D7.4 (2017) available at www.projectast.eu

[8] K Komura, NK Ahmed, EH El-Kamel, AMM Yousef, Variation of environmental neutron flux with the depth of water and soil, Journal of Nuclear and Radiochemical Sciences, 9[2] (2008).

[9] Institut de Radioprotection et de Sûreté Nucléaire (ISRN) Carbon-14 and the environment, Radionuclide fact sheet (2010).

[10] Council Directive 2013/59/EURATOM of 5 December 2013 laying down basic safety standards for protection against the dangers arising from exposure to ionising radiation, and repealing Directives 89/618/Euratom, 90/641/Euratom, 96/29/Euratom, 97/43/Euratom and 2003/122/Euratom, Official Journal of the European Union, L13, 17.1.2014

[11] J Mibus, A Swanton, T Suzuki-Muresan, M Rodríguez Alcalá, JL Leganés Nieto, D Bottomley, M Herm, E De Visser-Tynova, BZ Cvetković BZ, Sakuragi T, Jobbágy V, Lavonen T, WP2 Annual Progress Report - Year 1, CAST project report D2.2 (2015) available at www.projectast.eu

[12] J Mibus, A Swanton, T Suzuki-Muresan, M Rodríguez Alcalá, JL Leganés Nieto, D Bottomley, M Herm, E De Visser-Tynova, BZ Cvetković BZ, Sakuragi T, Jobbágy V, Heikola T, WP2 Annual Progress Report - Year 1, CAST project report D2.5 (2016) available at www.projectast.eu

[13] R Fisal, HE Hassan A Emad-Eldien Elsaadony, A Nada, ZA Saleh, Neutron Activation Analysis of Stainless Steel Samples and its Application for Monitoring Thin Layer Wear and Corrosion, Arab Journal of Nuclear Science and Applications, 46[5] (2013)

[14] SW Swanton, GMN Baston, NR Smart, Rates of steel corrosion and carbon-14 release from irradiated steels – state of the art review, D2.1 CAST project report (2015) available at www.projectast.eu

[15] E Ionescu, C Tuca, D Stanga, R Deju, M Dragusin, Good practices in free release of materials resulting from the decommissioning of the VVR-S reactor, 2nd Petrus-OPERA Conference on Radioactive Waste Management and Geological Disposal (2016)

[16] N Toulhout, E Narkunas, B Zlobenko, D Diaconu, L Petit, S Schumacher, S Catherin, M Capone, W von Lensa, G Piña, S Williams, J Fachinger, S Norris, WP5 Review of Current Understanding of Inventory and Release of C14 from Irradiated Graphite D5.1 CAST project report (2015) available at www.projectast.eu

[17] A Zanini, C Ongaro, E Durisi, L Visca, S DeAgostini, F Fasolo, M Pelliccioni, O Saavedra, Differential neutron flux in atmosphere at various geophysical conditions, 28th International Cosmic Ray conference (2003).

[18] D Ancius D, D Ridikas, V Remeikas, V Plukis, R Plukienè, M Cometto, Evaluation of the activity of irradiated graphite in the Ignalia Nuclear Power Plant RBMK-1500 reactor, Nukleonika Vol 50[3] (2005).

Chemical stability of low molecular weight organic compounds in the cementitious near field of a repository for radioactive waste

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Carbon-14 containing low molecular weight (LMW) organic molecules released during the corrosion of irradiated steel could be chemically unstable under the hyper-alkaline, reducing conditions of a cement-based repository for low- and intermediate-level radioactive waste (L/ILW). In case of complete thermodynamic equilibrium, decomposition of LMW organics is predicted and the predominant products are CO2 (and its bases) and CH4 [1]. Nevertheless, complete thermodynamic equilibrium is rarely achieved in the C-H-O system at moderate temperatures due to kinetic constraints. At present, it is unclear whether or not complete thermodynamic equilibrium will be attained and what kind of organic compounds will pre- dominate in the repository in case partial thermodynamic equilibrium (metastability) prevails.

In this study the chemical stability of small carboxylic acids has been explored, such as formic and acetic acids. Previous studies showed that, in anoxic conditions, the decom- position of carboxylic acids is mainly governed by decarboxylation reactions involving C-C bond cleavage, which requires high activation energies (e.g. [2]). This explains the high resistance of most aliphatic carboxylic acids to decomposition at temperatures below 300°C. Only formic acid is decomposed at lower temperatures due to the absence of a C-C bond. The literature further suggests that the chemical stability of small aliphatic carboxylic acids increases significantly with increasing pH (e.g. [3]). In contrast, the presence of catalyst surfaces such as stainless steel, montmorillonite etc. appears to drastically accelerate decomposition (e.g. [3]).

Formate was used for the present study because it is one of the most important organic compounds produced in the course of the corrosion of irradiated steel in anoxic alkaline conditions. The stability of 13C-labelled Na-formate was investigated up to a temperature of 150°C and at 4 bar overpressure in oxygen-free atmosphere (N2 and H2/N2 5%/95%) and hyper-alkaline solution. The solution was in contact with the stainless steel inner surface of the pressure reactor (Fe catalyst). 13C-labelled Na-formate was used to allow differentiation between organic compounds originating from the decomposition reaction and organic contaminants present in the reactor. Both the liquid phase and the gas phase were sampled at regular time intervals and analyzed for formate and possible degradation products. The chemical stability of 13C-labelled Na-formate was further tested in a batch-type set-up in the presence of varying amounts of Fe powder (catalyst) at 200°C in near neutral and hyper-alkaline solution. In this batch system the pressure in the reactor originated mainly from H2 production due to Fe corrosion during the degradation experiment.

Results from the experimental study will be presented and consequences for the safety case will be discussed.

[1] Wieland, E. and Hummel, W., Mineral. Mag. 79, 1275-1286 (2015).

[2] Bell, J. L. S. et al., Geochim. Cosmochim. Acta 58 (19), 4155 – 4177 (1994).

[3] McCollom, T. M. and Seewald, J. S., Geochim. Cosmochim. Acta 67 (19), 3625 – 3644 (2003).

Integration of CAST results to safety assessment - probabilistic uncertainty/sensitivity analysis of C-14 release and transport

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Based on the Dutch OPERA reference concept for the final disposal of radioactive waste in Boom Clay, a conceptual model has been implemented in the computer code ORCHESTRA to assess the influence of system parameters on the C-14 flux, released from Zircaloy contained in a CSD-C canister, through the surrounding concrete and Boom Clay.

A full probabilistic uncertainty/sensitivity analysis (UA/SA) has been applied to assess how the C-14 flux through the disposal system depends on (1) the Instant Release Fraction (IRF) of C-14 from Zircaloy, (2) the long-term congruent release resulting from the corrosion of Zircaloy, (3) the adsorption coefficient $K_{\mathrm{d,c}}$ of C-14 in concrete surrounding the CSD-C canister, and (4) the adsorption coefficient $K_{\mathrm{d,BC}}$ of C-14 in Boom Clay as the host rock.
The UA/SA has been performed for two different cases, (1) a "*Reference Case*", assuming expert values of the failure time of the CSD-C container and the C-14 diffusion coefficient in Boom Clay, and (2) an "*Enhanced C-14 Migration Case*", assuming an immediate failure of the CSD-C container after disposal, and a significantly increased value of the C-14 diffusion coefficient in Boom Clay.

The sensitivity of the calculated C-14 fluxes at different locations for the four system parameters was analysed by using scatter plots, the Pearson Correlation Coefficient (*PCC*), the Rank Correlation Coefficient (*RCC*), and conditional Cobweb plots.

The results of the UA/SA show that the calculated C-14 fluxes close to and further away from the CSD-C canister hardly depend on the prescribed values of the IRF and the Zircaloy corrosion rate. On the other hand, C-14 fluxes throughout the disposal system are influenced by the adsorption coefficients of C-14 in concrete and Boom Clay, but not to an equal extent.

For the OPERA disposal concept in Boom Clay the flux of C-14 out of the 50 m thick Boom Clay is limited if not negligible. This is caused by the long transport time of C-14 from the waste containers through the concrete engineered structures and the Boom Clay host rock compared to its half-life. Only in case of an assumed early release and a significantly enhanced migration rate a noticeable amount of C-14 may ultimately leave the Boom Clay host rock.

The paper/poster will elucidate on the OPERA disposal concept, the assumptions and modelling efforts of the UA/SA, and present highlights of the results of the simulations.

Modelling of ^{14}C Migration from RBMK-1500 Reactor Graphite Disposed of in a Potential Geological Repository in Crystalline Rocks in Lithuania

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There are two RBMK-1500 type reactors at the Ignalina NPP in Lithuania where graphite was used as a neutron moderator and reflector. These reactors are under decommissioning now and Lithuania has to find a solution for safe disposal of the irradiated graphite. The graphite cannot be disposed of in a near surface repository due to great amounts of ^{14}C; thus a deep geological repository (DGR) is analysed as an option. This study had the following aims: to perform evaluation of ^{14}C migration from the RBMK-1500 irradiated graphite disposed of in a potential DGR in crystalline rocks; to evaluate the impact on humans based on the research performed under the CAST Project; and to identify the potential for conservatism reduction. The gathered information was used to model ^{14}C transport in the near- field and far-field environment by the groundwater pathway, to perform uncertainty and sensitivity analysis and to illustrate the impact on humans by evaluating the radiological impact occurred due to consumption of well water contaminated with ^{14}C. It was demonstrated that substantiated more realistic assumptions could reduce ^{14}C flux to the far-field environment by approximately one order of magnitude in comparison with the previous estimation based on very conservative assumptions. The evaluated dose to humans would make approx. 5.5% from the dose constraint of 0.2 mSv.

The challenge of compound-specific radiocarbon analysis of activated steel

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Little attention has been paid to the behavior of radiocarbon (14C, half-life 5730 yr) in nuclear waste repositories for a long time due to its comparably low activity and the complex carbon chemistry. The potential formation of highly volatile or water- soluble compounds may cause problems to current barrier strategies, however, so that the chemical speciation of 14C under these conditions has recently gained more attention. According to the current Swiss processing, activated steel in cement- based repositories for low- and intermediate-level radioactive waste will become the most relevant disposal form of radiocarbon. Therefore, we have developed instrumentation and procedures to perform compound-specific radiocarbon analysis of activated steel altered by corrosion in the presence of water and cementitious materials.

As corrosion products may be in the gaseous phase (such as carbon monoxide or methane and other alkanes) or in the liquid phase (such as carbonate or formate and other carboxylates), we aimed at the simultaneous separation of individual carbon compounds by gas chromatography and ion chromatography and the quantification of 14C in these compounds with accelerator mass spectrometry (AMS). The challenges of this approach are diverse. On the one hand, corrosion rates and carbon amounts of activated steel are low so that AMS remains the only suitable method that is sensitive enough. On the other hand, the intrinsic 14C/12C ratio of the corrosion products are several orders of magnitude higher than typical radiocarbon dating samples so that a severe contamination of the instrument may occur by wrong operation of the isolation and quantification procedure. Furthermore, the high activity of irradiated steel materials (mainly from 60Co) and the omnipresence of carbon and 14C in our environment requires measures of radiation protection and prevention from contamination during this analysis. These challenges will be presented in detail and solutions will be discussed.

Carbon-14 release and speciation from carbon steel in highly alkaline conditions

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We investigated the release of 14C from carbon steels representative for the reactor pressure vessel (RPV) steel of Belgian nuclear power plants and the 14C speciation in a cementitious environment relevant for the Belgian geological disposal concept, which involves placing the RPV steel in a concrete monolith. To achieve this, we designed static and accelerated corrosion tests, and we obtained irradiated reference material representative for the RPV steel at end-of-life in the Belgian power plants. The static tests consisted of exposing the sample to a representative environment (anaerobic, high pH) for several months without imposing a potential, while in the shorter accelerated tests an electrochemical setup was used to fix the potential of the sample at a more anodic value than the corrosion potential, to accelerate the corrosion. To determine the speciation of carbonaceous compounds, we used gas chromatography. In addition, we applied liquid scintillation counting, total (in)organic carbon analysis, and ion chromatography.

Metallographic analysis was performed on both unirradiated and irradiated material to investigate the influence of irradiation on the metallic structure. The grain structure is that of a ferritic-bainitic steel, which is the expected grain structure for a RPV steel. The main defects present in both the unirradiated and irradiated material are line dislocations, with the dislocation density diminishing through irradiation. Another effect of irradiation is the formation of a small amount of dislocation loops. Two types of carbides were found in both materials: Fe3C and Mo2C. The concentration of Fe3C is increased by irradiation.

Measurements of the 60Co release of JRQ carbon steel in pure portlandite water showed that the corrosion rate seems to obey a parabolic law, as reported in literature. The obtained corrosion rates however are very low, below 10 nm/year. This can be explained by experimental artefacts such as 60Co precipitation in the portlandite solution.

To obtain information on the behaviour of JRQ carbon steel in simulated geological disposal conditions, long-running corrosion tests were performed. Accelerated (polarised) corrosion tests were performed to obtain some indication of the corrosion mechanism and the formation of lower carbon molecules in a shorter reaction time. The electrolyte used was a saturated portlandite Ca(OH)2 aqueous solution of pH 12.5, representative of the geological disposal conditions. In addition, for a second batch of accelerated tests, 0.5 M of CaCl2 was added to the portlandite solution, stimulating pitting corrosion in order to obtain a higher yield of corrosion products.

The accelerated tests were performed in glass test cells equipped with a standard three-electrode setup, using a house-made Ag/AgCl electrode as reference electrode, a platinum mesh as counter electrode, and an embedded and polished

JRQ carbon steel sample as working electrode. Gas chromatography after the tests in saturated portlandite water showed no carbon-containing corrosion products.

The static (leaching) tests were performed in PEEK-lined steel vials with an internal volume of 50 cm^3 filled with 35 cm^3 of electrolyte under a nitrogen atmosphere. After closing the cell gastight with a lid, the whole setup was left behind a lead wall for 231 days. Gas chromatography revealed that during the static tests, hydrogen, methane, ethene, and ethane were produced. Assuming that all carbon released from the metal is transformed into gaseous carbon compounds, this yields a corrosion rate of 68 to 117 nm/year.

Preliminary analysis of gaseous 14C radiological impact in a geological repository hosted in salt rock

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In the context of the European CAST project, a preliminary evaluation of the radiological impact of gaseous 14C under geological disposal conditions in salt rock has been performed. Although in Italy there is still no defined project about GDF, current work may support future Safety Assessment studies for a geological repository. In the framework of Italian radioactive waste, the percentage of 14C bearing waste to be disposed in a possible geological repository is low. Data about radioactive HLW-LL and ILW inventory has been collected to simulate production and migration of gaseous 14C in a hypothetical repository; irradiated graphite is the most important radiological source. Two simulations with TOUGH 2.0 code has been performed: the first one has preliminary evaluated the radiological impact of gaseous 14C referred to the whole inventory; the second simulation has evaluated the impact of the graphite alone. In order to work round the limitations due to the lack of data, some conservative assumptions have been used. A preliminary sensitivity analysis has been carried out, highlighting the importance of the geometry and the distribution coefficients in materials used to seal the disposal areas within salt formation. Results of simulations have showed the possibility to correlate the K_d values, the volume and the location of sealing materials to the amount of 14C emitted toward the surface. More realistic results would be obtained reducing the grid discretization and using more accurate details about repository and host rock.

Analytical strategy for measurement of ^{14}C in leachate of irradiated zirconium alloy hulls

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With a half-life of 5,730 years, Carbon-14 (14C) is a key radionuclide in safety assessments for geological disposal of long-lived waste. In zirconium alloy claddings, neutron activation of 14N, impurity element of these alloys, is the main source of 14C (14N(n,p)14C). 17O coming from the UO2 (or (U-Pu)O2) oxide fuel and from water coolant is also a significant precursor of 14C in the zirconia oxide layers formed in reactor on the internal and external sides of cladding respectively (17O(n,α)14C).

The CAST (CArbon-14 Source Term) project aims to better understand origin and release mechanisms of 14C from radioactive wastes intended to be placed in geological disposal. Among these wastes, those arising from the spent fuel rod claddings of pressurized water reactors (PWR) after reprocessing, which constitute packages of hulls, form a significant part of the radiotoxic inventory of long-lived intermediate level waste (ILW) in France but not only.

Work Package 3 (WP3) is related to Zircaloy in the CAST project. It aims to better understand C-14 behaviour in waste Zr fuel claddings under disposal conditions with regard to C-14 inventory (and origins), release from waste packages and speciation of released C-14.

Zircaloy-based alloy hulls, M5-type (UOX) and Zy-4-type (MOX), supplied by AREVA-La-Hague, have been leached in a basic solution simulating the pH of cementitious water (NaOH solution, pH 12, anoxic conditions) in the hot cells of ATALANTE facility (CEA Marcoule). These samples come from the reprocessing of irradiated spent fuel in PWR reactors. Leachates have been analyzed to allow detection and quantification of organic and inorganic compounds in solution.

Determination of total 14C in the leachate sample has been realized by pyrolysis followed by Liquid Scintillation Counting (LSC). An analytical method has been developed by the LASE laboratory to study the organic and inorganic 14C partition. The sample is acidified with a solution of 25 % H3PO4 under N2 bubbling. The CO2 released (inorganic) was retained in a NaOH trap solution. The remaining solution in the reaction vessel was pyrolysed to measure the organic 14C by LSC.

For the Zy-4-type hulls, total 14C was below the detection limit of LSC (0.5 Bq/mL). Consequently, a method has been developed to have a quantification of 14C by accelerated mass spectroscopy (AMS). For this, the method has been validated by samples which have been measured by LSC and AMS.

Identification of organic compounds has been realized by ionic chromatography at LRMO laboratory. Analysis has shown that organic carbon was mainly in carboxylic acid form ($C \leq 5$).

The measurement of impurity of RBMK-1500 graphite

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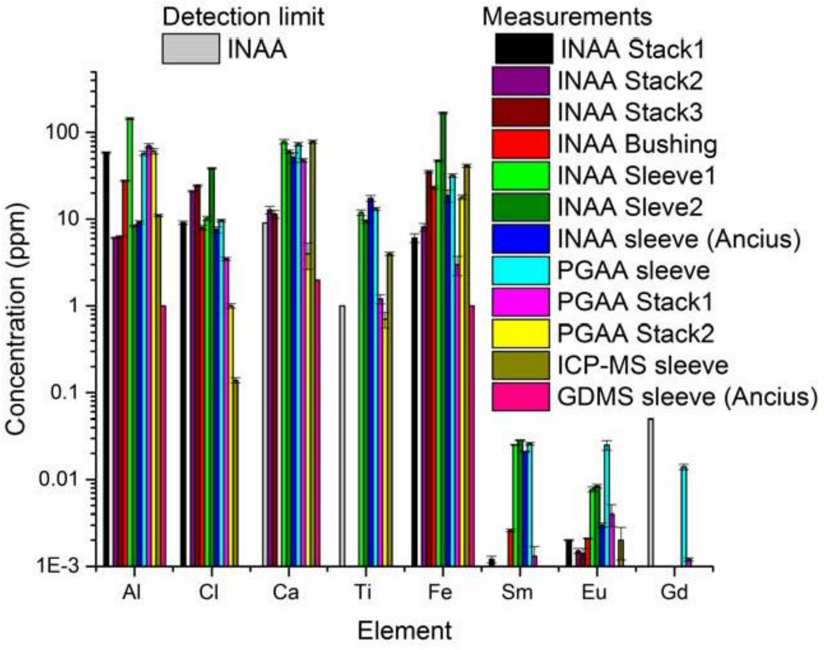
Radiological characteristics of RBMK-1500 graphite are crucial in the choice of irradiated graphite treatment technology. The trace impurities (<0.01% wt) during 20-30 years of irradiation in the neutron flux are transmuted into the long-lived nuclides (e.g. ^{14}C, ^{36}Cl, isotopes of Np, Pu, Am, Cm). Several samples of RBMK- 1500 graphite manufactured for different construction elements (stack column, sleeve, bushing) were analysed with instrumental neutron activation analysis (INAA) method (LVR-15 experimental reactor of the Research Centre Řež, Ltd.) and with prompt gamma activation analysis (PGAA) method (Heinz Maier-Leibnitz Zentrum) in stack and sleeve samples in order to obtain the missing information on impurity distribution in the RBMK-1500 graphite. Also the inter-comparison with previously obtained results with INAA & GDMS (CEA Saclay, France) and ICP-MS (FI, Lithuania) in graphite sleeve have been performed.

Fig. 1 Comparison of 8 impurity elements measured by all methods INAA (2016), INAA & GDMS (2005), PGAA(2016) & ICP-MS (2010) in virgin RBMK-1500 graphite samples.



Graphite samples were analyzed with instrumental neutron activation analysis (INAA) using both short- and long-time irradiations in the LVR-15 experimental reactor (Research Centre Řež, Ltd.), at a thermal neutron flux of 3×10^{13} cm^{-2} s^{-1}. The induced radionuclides were measured with high efficiency, high resolution coaxial HPGe detectors after several decay times to achieve detection limits of elements determined as low as possible. Altogether 45 elements were determined. Other measurements were performed at Heinz Maier-Leibnitz Zentrum by prompt gamma activation analysis. For irradiation thermal neutron flux of 2×10^{10} cm^{-2} s^{-1} was used. For gamma detection Compton-suppressed spectrometer was used. 16 elements were determined by this method. It was also expected to obtain N impurity concentration by PGAA, as it is impossible to get it by other methods, but due to interference it was not measured. Currently the 15 ppm concentration of N is used in the model according to the experimental results of irradiated graphite (Remeikis et al., 2010), but independent evaluation of initial concentration would be of great importance.

In the Fig. 1 results of 8 impurity elements measured by all methods INAA (2016), PGAA(2016), INAA&GDMS (Ancius et. al 2005), ICP-MS (Puzas et al., 2010) were compared. Generally, for all measured impurities, concentrations may vary by order of magnitude comparing stack/sleeve and bushing materials.

We should note, that the impurities of RBMK-1500 graphite stack and bushing samples were analysed for the first time. As it appears from the results - the stack is “cleaner” comparing with graphite sleeve and bushing material.

The obtained information about different impurity concentrations of some clue nuclides as Cl, Mn, Fe, Co, Ni, Cu, Zn, Sr, Cs, Ba, Eu, U, which can be detected by gamma spectrometry in the spent graphite are of great value. The obtained new impurities data will be used for MCNP6 and SCALE6.1 model adapted for RBMK-1500 graphite activation case (Plukiene et al. 2011; Plukiene et al., 2014).

References

Ancius et. al., 2005, Nukleonika 50 (3), 113-120.
Puzas et al., 2010, Lith. J. Phys. 50, 445–449.
Plukiene et al., 2011, Prog. in Nuc. Sc. and Tech. 2, 421-426.
Plukiene et al., 2014 Nuc. Eng. and Design 277, 95-105.

Speciation of Organic Carbon-14 molecules in zircaloy leaching solution

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Carbon-14 is a long-lived radionuclide (5,730 y) and a radionuclide of interest regarding the safety for the management of intermediate level wastes (ILW). ^{14}C is found either in the alloying part of Zircaloy cladding due to the neutron activation of ^{14}N impurities by ^{14}N(n,p)^{14}C reaction, or in the oxide layer (ZrO_2) formed at the metal surface by the neutron activation of ^{17}O from UO_2 or $(U\text{-}Pu)O_2$ fuel and water from the primary circuit in the reactor by ^{17}O(n,α)^{14}C reaction. For deep geological formation, claddings may be found intact and disposed of directly or may be cut into hulls and compacted in steel canister and disposed of in cement container. Therefore, the release of carbon-14 in aqueous media and its diffusion within the repository site is an important issue from a safety assessment point of view. Today, performance assessment of deep geological disposal considers a conservative state with a congruent release of carbon-14 with zirconium during cladding corrosion. A recent theoretical study combining DFT and KMC on the diffusion of carbon 14 within Zr-metal and ZrO_2 showed an extreme weak diffusion of carbon 14, almost inert [Xu, 2015; Xu et al., 2016]. However, a better understanding of the speciation of carbon-14 in leaching solution is required to reduce uncertainties of the model assessment.

The present study will give the experimental results obtained on leaching solution from irradiated Zircaloy claddings (M5 and D4 types), simulating deep geological repository conditions: irradiated claddings leached in NaOH solution at pH 12 in Ar-atmosphere during 2 weeks and 5.5 months. The measurements of carbon-14 in leaching solution were performed after decontamination from other high activity level radionuclides (Cs-137, Co-60, Sb-125, Ru-106/Rh-106) by ion exchange resin. Speciation and quantification of dissolved carbon-14 by using separation technique (collection of fractions by ion chromatography) and analysis by liquid scintillation counting method give results in agreement with modelling: activity level of carbon-14, notably the small organic species of carboxylic acids with a carbon chain below 5-C, in leaching solution is low and close to the detection limit. Fractions of formate, acetate, propionate and oxalate measured by LSC gives mass activity between

180-20 Bq/g$_{hulls}$ after leaching M5 hulls type during 5.5 months, and between 395- 15 Bq/g$_{hulls}$ after leaching D4 hulls type during 14 days. The extreme low activity level in carbon-14 associated to high uncertainties required to analyse the collected fractions by Accelerator Mass Spectrometry (AMS, Vera Facility, Austria). Oxalate fraction from M5 hulls leached during 5.5 months was analysed by AMS which result gives 9 Bq/g$_{hulls}$. AMS measurements confirmed the presence of carbon 14 in the sample, which should correspond to oxalate molecule, and validate the experimental methods to collect fractions. The result also confirmed the sensitivity of the technique which allows more accurate measurements of the activity level for carboxylic acids.

Xu, Y. [2015]. Carbon diffusion behavior in bulk zirconium and zirconia of the used fuel claddings by multi-scale simulations. Paris Saclay University, Thesis, 139 p.

Xu, Y., Roques, J., Domain, C. and Simoni, E. [2016]. Carbon diffusion in bulk hcp zirconium: A multi-scale approach. Journal of Nuclear Materials. Vol. 473 p. 61-67.

Corrosion tests of non-irradiated stainless steel by hydrogen measurement system

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The aqueous corrosion behavior of non-irradiated stainless steel under simulated repository conditions was studied. A sensitive hydrogen measurement was selected to evaluate the very low rate of stainless steel corrosion based on the reaction of $3Fe + 4H2O \rightarrow Fe3O4 + 4H2$. Two experimental systems were applied; the glass ampoule method which is a batch type measurement for a short term at elevated temperatures up to 353 K, and the gas flow system which monitors the hydrogen gas continuously for a long term over 6 years at a constant temperature. Basically a dilute NaOH solution of pH 12.5 was selected as the test solution while pure water for comparison and a fundamental study.

Our long-term observations on the corrosion behavior demonstrated that the corrosion rate decreased with time during the initial first year. This initial corrosion rates showed a tendency to be higher at higher test temperatures. The corrosion behavior in the NaOH solution was comparable to that in pure water. Detailed kinetics on the initial behavior suggested that the stainless steel corrosion follows a parabolic rate law, which implies that the initial corrosion process is under diffusion control. The surface oxide films after each corrosion test were analyzed by TEM together with EDX and electron diffraction. They consisted of Fe, Cr and Ni oxides. However, the passivation was not clear because the oxide film was very thin and amorphous. Silicon contaminants due to the dissolution of the glass test vessel under alkaline conditions made the oxide analysis more difficult. After the first year, the constant corrosion rate, approximately 0.4 nm/y at 303 K, was observed during 6 years and more. This corrosion rate is 1/50 slower than that of the conventional evaluation and can bring a significant impact on the estimation of radionuclide leaching and gas generation in the safety assessment on the disposal of stainless steel waste. This result, however, has not yet been thoroughly explained with respect to the oxide film characteristics, and is expected to be subject for further studies.

This research is a part of the “Research and development of processing and disposal technique for TRU waste” program funded by Agency for Natural Resources and Energy, Ministry of Economy, Trade and Industry of Japan.

Corrosion behaviour of irradiated and non-irradiated zirconium alloys: investigations on corrosion rate, released 14C species and IRF

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The long-term aqueous corrosion of irradiated and non-irradiated zirconium alloys under simulated repository conditions was studied. A sensitive hydrogen measurement, in terms of gas generation and absorption to the alloy, was selected to evaluate the very low rate of the non-irradiated alloy corrosion, based on the reaction of $Zr + 2H2O \rightarrow ZrO2 + 2H2$. Two experimental systems were applied: the glass ampoule method which is a batch type measurement under various types of solution and temperature, and the gas flow system which monitors the hydrogen gas continuously for a long term in a dilute NaOH solution of pH 12.5. The corrosion rates decreased with time and increased at a higher temperature, but the influences of pH and other chemical properties of the solution on the rate were not significant.

With respect to the corrosion tests of irradiated Zircaloy-2 (spent BWR cladding), the leached 14C was measured, identifying its various forms: gas, dissolved organics and dissolved inorganics. The equivalent corrosion rates obtained from the total measurement, i.e., gaseous and dissolved amounts, of the leached 14C by assuming congruence with corrosion were less than that of non-irradiated Zr alloys. Since this could not be sufficiently explained with only the difference in the test conditions, i.e., test temperatures, the congruence of 14C leaching with corrosion is still unclear. The leached 14C from irradiated Zircaloy-2 at pH 12.5 was specified as its amounts in the gas and liquid phases. The fraction in the liquid phase increased with time and reached over 90% after 2 years. The inorganic/organic ratios of the liquid were around 1/3 and seemed to be not depending on time.

Instant release fraction (IRF) for spent claddings was also discussed through the experiment on the 14C leached from irradiated Zircaloy-2 having an oxide film and 14C inventory in it. It was found in the inventory measurement that the abundance of 14C in the oxide was only 7.5%, which is less than 20%, assumed in the past safety assessment in Japan. Further, the leached 14C from the irradiated cladding with oxide was found to be 0.0038% of the total 14C activity after a 6.5 years leaching test. These understandings should be reflected in the future safety assessment so that a lower, or potentially negligible, IRF can be supported.

This research is a part of the “Research and development of processing and disposal technique for TRU waste” program funded by Agency for Natural Resources and Energy, Ministry of Economy, Trade and Industry of Japan.

Characterization of 14C in neutron irradiated RBMK-1500 graphite

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Nuclear graphite waste management strategy during decommissioning of Ignalina NPP is the pending decision in Lithuania. In the RBMK type reactor graphite is a neutron moderator and reflector. The total mass of radioactive graphite from the both Ignalina NPP units is up to 3,800 t. 14C is the limiting radionuclide for long- term disposal of irradiated graphite due to half-life of 5730 years and relatively high activity as well as mobility in geological media. Characterization of irradiated graphite in terms of both 14C activity and chemical bonds in the lattice is crucial for the optimization of treatment technology (e.g. geological disposal, landfill storage, recycling, etc.). For this purpose numerical simulations and experimental analysis are performed.

14C measurements usually are carried out by using liquid scintillation counting (LSC) technique after time consuming sample preparation procedure. Recently we proposed an express analysis method for the specific 14C activity determination in small graphite samples in the range of 1-100 µg. This method is based on the graphite sample combustion in the commercial elemental analyzer and determination of 14C specific activity by using the semiconductor detectors. This method is planned to apply for determination of the graphite homogeneity profile in terms of 14C activity.

Experimentally validated numerical 3D model of RBMK-1500 (MCNP6 and SCALE 6.1.) is effective for description of the change of radiological characteristics of different parts of nuclear reactor during operation and decommissioning periods [1]. Both experimental measurements and modeling data are used for scaling factor determination [2], which subsequently could be used for sorting of spent graphite radioactive waste.

For further graphite treatment technology optimization the structural investigations of graphite should be performed. 14C mobility and position in graphite matrix is determined by neutron irradiation in the reactor at certain operation conditions. In order to understand the processes in the irradiated graphite we observe the propagation of defects induced by 12C+ ion implantation at energy of 700 keV at varying fluences. The structural changes after implantation and thermal treatment later on are investigated by Raman spectroscopy. The SRIM-2013 code is also used to estimate the damage profile in the surface of the graphite samples. The evolution of graphitic sp2-related content as well as formation of an amorphous structure serves for understanding of location and stability of 14C in graphite matrix, while the thermal treatment carries information about recrystallization process. Further structural investigations are currently in progress.

[1] Plukiene et al., 2014, Nuc. Eng. Des. 277, 95-105
[2] Remeikis et al., 2009, Nucl. Eng. Des. 239, 813-818

14C Release From Steels Under Aerobic Conditions

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One of the R&D activities planned in the Spanish context for the next years should provide support and coverage for the drawing up and/or revision of management strategies for the different types of radioactive wastes, based on better understanding of such wastes including the physical, chemical, environmental and radiological properties of the isotopes they contain. Within this framework, the understanding of the 14C behaviour in waste packages could lead to a revaluation of the near surface repository for the disposal of wastes containing this radionuclide in high concentrations.

To achieve these objectives leaching experiments have been planned facing two different scenarios. One in which the leaching solution simulates the expected conditions in a cement based repository over long time periods (NaOH solution of pH ca. 12) in aerobic conditions. The other, using an acid solution of 1M H3PO4, which has been proved as a high efficiency chemical removal agent.

The development of both analytical methods and protocols to measure the release of 14C from the activated steel samples and the speciation in the aqueous and gaseous phase has been performed throughout the CAST project. Analytical methods, suited to identify and quantify low molecular weight organic molecules, comprise Ion Exchange Chromatography and Gas Chromatography coupled to Mass Spectrometry, they are described for aqueous and gaseous samples, respectively. The preparation of the leaching experiments to measure the release of 14C is described in this poster.

14c Leaching and Specification Studies on Irradiated Graphite from Vandellos I NPP

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One of the R&D activities planned in the Spanish context for the next years should provide support and coverage for the drawing up and/or revision of the management strategies applied for the different types of radioactive wastes. These strategies should be based on a better understanding of such wastes, including its physical (dissolved or gaseous species), chemical (carboxylic acids, carbonates, hydrocarbons, etc.) and radiological characteristics and their environmental impact. Within this framework, the understanding of the 14C behavior in waste packages could lead to a revaluation of the near surface repository for the disposal of wastes containing this radionuclide in high concentrations.

Since the CAST project (CArbon-14 Source Term) aims to develop the above mentioned understanding, CIEMAT considered of highly importance to participate in it. Throughout the CAST project the CIEMAT contribution to work package 5 focused on the release of 14C as dissolved and gaseous species from irradiated graphite from Vandellós I nuclear power plant.

Two types of samples have been tested; sleeve graphite core samples (11 mm x 12 mm Ø x H) and powder graphite solidified and encapsulated in the form of cylinders (20 mm x 10 mm Ø x H) in a new glass matrix called Impermeable Graphite Matrix (IGM).

To achieve these objectives, together with the structural characterization of the materials, leaching experiments have been planned considering two different scenarios. One, in which the leaching solution simulates the expected conditions in cement based repository where a granite/bentonite mixture has been used as backfill material (granite bentonite water - GBW), and the other, using deionized water for its high efficiency as chemical removal agent or for comparison purposes.

The development of both analytical methods and protocols to measure the release of 14C from irradiated graphite and IGM samples and the speciation in the aqueous and gaseous phase has been performed throughout the CAST project. Analytical methods, suited to identify and quantify low molecular weight organic molecules, comprising Ion Chromatography (IC) and Gas Chromatography coupled to Mass Spectrometry (GC-MS) have been also implemented.

Regarding the results obtained from the different analyses, it is worth to mention that only has been found one value of 14C higher than the detection limit (graphite core sample), and it is more likely that this could be because of bad filtering of the leachate or cross contamination in the equipment than because of the leaching process itself. Using deionized water as leachant, in the IC analyses, acetate, formate and oxalate has been detected after some stages. However, this technique cannot be used to analyze GBW solutions because of the high concentration of anions and cations present in this media. Both alcohols and aldehydes in leachates have not been detected in any step of the leaching process and, regarding gas samples, nor was CO, except for the first and second leaching period of IGM samples using GBW as leachant (this could be related to the carbonate content in the leachate).

Behaviour of 14C Released from Spent ION Exchange Resins and Resins Fixed in a Cement Matrix

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The experimental work formed part of the research carried out in the context of the CAST (Carbon-14 Source Term) project. The project is focused on determining the processes of the formation and release of 14C species in radioactive waste and the safety evaluation of the disposal of waste containing14C in radioactive waste repositories. The Czech partners involved in the CAST project consist of ÚJV Řež, a. s. and SÚRAO.

Experimentation involved the use of real spent ion exchange resins (SIERs) samples from nuclear power plants (NPP) and research reactors as well as laboratory prepared samples. Two types of tracer were used in the preparation of the artificially contaminated ion exchange resins, i.e. organic and inorganic carbon compounds (acetate and bicarbonate). The first part of research consisted of the performance of sorption and desorption experiments, and the second part involved the study of the release of 14C following the fixing of the ion exchange resins in a cement matrix. The testing process focused on the kinetics of 14C species leaching into three different liquid phases - distilled water, synthetic granitic water and sodium hydroxide solution.

The ion SIERs samples from NPP operation contained fewer 14C species than the samples extracted from the research reactors and the major carbon species consisted of inorganic forms, either carbonate or bicarbonate. The desorption experiments indicated that the ion exchangers did not demonstrate a significant release of 14C species into any of the liquid phases.

Subsequently, cement (CEM II class) was successfully tested as a fixation matrix for the ion exchange resin samples. Artificially contaminated ion exchange resins were used for fixation into the cement matrix and leaching experiments based on standard leaching method were performed. In this case, no carbon species release into the liquid phases was determined during the course of the leaching experiments.

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14C enrichment of surface deposits on Oldbury reactor core graphite determined by secondary ion mass spectrometry and thermal oxidation/liquid scintillation counting.

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Research performed at the University of Bristol as part of the C14-BIG [1] consortium has focused on the characterisation of a number of irradiated graphite samples, from a variety of axial and radial positions, from the core of reactor one at Oldbury Magnox nuclear power station to aid in determining the concentration and distribution of 14C. An overview of results obtained using secondary ion mass spectrometry (SIMS) as well as thermal oxidation with liquid scintillation counting (LSC) will be presented that show the relative enrichment of 14C in the surface deposits found on Oldbury graphite. The results from this work are in good agreement with recent research on leaching of 14C from irradiated graphite, which suggested that there is a rapidly releasable fraction of 14C within Oldbury graphite [2]. The more reactive [3] 14C-rich surface deposits found in the present work are consistent with this rapidly releasable fraction. Further examination of the underlying graphite using thermal oxidation/LSC showed two further fractions containing 14C, both correlating with previous leaching studies.

Channel wall face samples lacking this surface deposit did not exhibit 14C enrichment, implying that the enrichment is due to the surface deposit rather than the lifetime proximity to fuel elements and associated neutron dose. The concentration of 14C in the deposit, determined by both SIMS and LSC, appears to be greater in samples originating lower in the channel than higher up, but there is no correlation with accumulated neutron dose suggesting that there is another reason for the variation in concentration.

(1) www.hud.ac.uk/c14-big
(2) *Baston, GMN, Preston, S, Otlet, R, Walker, J, Clacher, A, Kirkham, M and Swift, B Carbon-14 Release from Oldbury Graphite, AMEC/5352/002 Issue 3 2014.*
(3) *Wickham, AJ, Rahmani, L. Graphite dust explosibility in decommissioning: A demonstration of minimal risk. Vienna, IAEA-TECDOC-1647. 2010*

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Effect of thermal pre-treatment on 14C release from irradiated nuclear graphite from the Rossendorf Research Reactor

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According to the current nuclear waste management strategy in Germany, irradiated graphite (i-graphite) discharged from commercial and research reactors is to be disposed of in the deep geological repository for low and intermediate level radioactive waste Schacht Konrad. Final disposal of i-graphite requires reliable information on the radionuclide inventory and information about release behaviour of radionuclides under the conditions relevant to the repository. The former is usually obtained from the routine analyses of i-graphite, whereas the latter is based on an understanding of release mechanisms of radionuclides and the availability of reliable models capable of predicting the radionuclide release on selected storage conditions. 14C is a radionuclide of major concern regarding the disposal of i-graphite, and has relatively long half-life (5,700 years). It is a weak D-emitter (156 keV) and if incorporated in the human body may cause internal radiation hazard. 14C can be present in i-graphite in different chemical forms, like elemental C, absorbed or trapped in the closed pores CO2 or organic C species. These species have different retention in i graphite, which can be affected by a number of factors, e.g. temperature, salinity and pH of infiltrated groundwater, promoting 14C release into gaseous phase. The release of 14C from i-graphite and benefits of thermal treatment for final disposal of i-graphite was investigated in the frame of WP5 of EU- project CAST (Carbon-14 Source Term). The main objective of the present work is to understand the release behaviour of 14C from i-graphite under conditions relevant to the repository Schacht Konrad and to evaluate the benefits of upstream decontamination by thermal treatment for the final disposal. For that the kinetics of 14C release from i-graphite Rossendorf Research Reactor and the effect of various storage conditions, such as temperature and leaching solution composition, were investigated, in order to answer the question, to what extent German i graphite can be disposed of in Schacht Konrad.

The results of the study demonstrated an annual release rate of 14C of <1%/year, which, according to the Waste Acceptance Criteria (WAC) of Schacht Konrad, allows a graphite disposal with a maximum permitted container loading even without preliminary treatment of i-graphite. The main volatile 14C fraction (> 83%) is in form of CO2; the rest 17 % is comprised of 14CO or/and organic 14C species. Model experiments with i-graphite also revealed almost negligible 14C release into the gaseous phase, if i-graphite is stored in cementitious media (i.e. basic media with pH>12.9). In this case a dominant fraction of 14C remains in the solution in form of carbonate. Thermal treatment of i-graphite at 1300°C during ca. 20 hours results in a selective separation of 8% from total 14C inventory. Further storage experiments with treated i-graphite did not show any detectable release of volatile 14C in neutral and basic solution. Given that thermal treatment allows separation of only a minor 14C fraction, and a proper encapsulation of i-graphite in a cementitious material alone provides for WAC to be met, a preliminary thermal treatment of RFR i-graphite is considered to be unnecessary.

Radiocarbon on spent ion-exchange resins arising from boiling water reactors: inventory, speciation and release behaviour

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Organic divinylbenzene-based ion-exchange resins (IERs) are widely used in several cleaning systems of Boiling Water Reactors (BWR) to provide for an adequate purity of the cooling water. The water circuits experience the generation of activation products (APs) that are retained by IERs. Among typical APs, 14C (t1/2 of 5730 y) is of high concern, due to the risks of radiation hazard in case of incorporation in the human body. Therefore, the behaviour of 14C retained on spent ion-exchange resins (SIERs) after discharge from the reactor needs to be understood in order to provide for a safe management solution for SIERs, i.e. (pre-)conditioning, intermediate storage and final disposal. SIERs typically fall within the Intermediate Level Waste (ILW) classification due to the presence of long-lived radionuclides (e.g. 14C) and are considered to be disposed of in the german repository Schacht Konrad.

14C retained in SIERs and its release behaviour was investigated in the frame of the EU-project CAST (WP4). The objective of the work was to account for the 14C inventory in BWR SIERs arising from condensate clean-up systems (CCU), together with the speciation of the retained 14C-containing compounds and their release behaviour under conditions relevant to the interim storage and final disposal. This information is supposed to contribute to a theoretical model for 14C release and its fate in the long-term, ensuring the safety of the final repository.

Modern microscopic and spectroscopic techniques were used along with radio analytical methods to understand the speciation and release behaviour of 14C. Some conventional analytical approaches (e.g. LSC, LC) are often not sufficient to detect low amounts of 14C and to perform a speciation; therefore, an optimization of the available analytical tools constituted a considerable part of the work.

Morphological investigations on BWR SIERs pointed out the multi-component (inhomogeneous) nature of this type of waste. The speciation of 14C originated from SIERs demonstrates that most 14C (up to 99.6%) is in inorganic form. The organic fraction ranges from 0.4 % to 1.1 % of the total 14C. High performance liquid chromatographic analyses on the solution obtained from a full regeneration of the SIERs highlighted the presence of formic acid, possibly originating from the reactor coolant or from the degradation of the resins. The presence of 14C in non- ionic form, bound to the resins' backbone or in eventual particulate matter, was also investigated. The kinetics of 14C release from SIERs during storage was shown to be relatively fast. The equilibrium was reached within few days, demonstrating a saturation-like trend, driven by ion-exchange and/or isotope exchange processes. Radiation-induced degradation of SIERs, caused by the retained APs, as well as age-related effects, seem to be very slow and irrelevant for the fast 14C release, in the present case. Elevated temperatures during storage favour a higher release of 14C due to an enhanced thermal degradation of the SIERs (i.e. detachment/degradation of quaternary ammonium groups). These main factors influencing the release of 14C from SIERs are presented and discussed in detail.

A Study of Graphite From RBMK-Type Reactors

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Institutions of the National Academy of Science of Ukraine are working out the various options for using graphite from uranium-graphite reactors during their decommissioning. Graphite is key component of RBMK-type reactors and the aim of this research is to develop a better understanding of this material, to support future waste management options. Exposure of graphite to neutron radiation at high temperature causes structural changes over many length scales. Since each grade of graphite has unique structure and texture, its irradiation behavior can be expected to be somewhat different.

The research was carried out to investigate the structure and morphology of the surface layer of samples graphite stack (GR-280) and the split graphite rings (GRP-2-125) from technological channels. Studies of graphite microstructure have been made using XRD, Raman spectroscopy, scanning electron microscopy and energy dispersive X-ray analysis to obtain information of the graphite’s polycrystalline features. X-ray powder diffraction data was collected and the line profiles were analysed using the Warren model, estimates were made of the distance between planes and the magnitude of the coherent scattering. The reflex broadening of the diffraction peak (00l) corresponds to the average Lc size D 35 nm. The shape (broadening and asymmetry) of the diffraction peaks indicates the presence of two fractions with different dispersion and crystalline properties in the sample.
Chemical treatments have been investigated in order to decontaminate irradiated graphite. A wide variety of strongly oxidizing agents and chemicals for intercalation has been used for chemical decontamination of graphite. Powder sample graphite was dispersed in solvents with ultrasonic treatment for destruction of a binder phase. Ultrasonic exposure results in dispersions of polycrystalline graphite that are more suitable for an intercalation process, with further disruption under repeated ultrasonic treatment for “exfoliation”. It was shown that interlayer spacing (d00l) increases as result of intercalation of the treated graphite. The results of leaching experiments show that the 14C leached from graphite without treatment is less compared to graphite samples after treatment with an oxidizing agent.

We studied the encapsulation of graphite (pieces and dust) in matrices with different additives (clay-cement, organics-cement) and determined the leaching properties of these different concrete matrices. Leaching experiments were made to detect 14C release from graphite after concrete encapsulation. The results show that the 14C quantity in the leachant from the encapsulation graphite after more than five years is less than lower detectable limit of the analytical technique.

Acknowledgements

We gratefully acknowledge the support of CAST project. The project has received funding from the European Union’s European Atomic Energy Community’s (Euratom) Seventh Framework Programme FP7/2007-2013 under grant agreement no. 604779; http://www.projectcast.eu.

Repository scale two phase flow migration of 14C in the preliminary design phase of French Cigéo project

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Generality

One of the phenomenologies to be studied in the migration of 14C at repository scale is transient 2-phase flow (water and gas, especially hydrogen produced by corrosion and radiolysis) within the repository and the surrounding formations, during the operational and the post-operational phase up to one million years and its impact on radionuclides (gaseous or solute) migration.

The work done for the European Project CAST is based on the preliminary design phase of the Cigéo repository project. Aims of evaluations are to assess operational range of several indicators linked to 14C migration, especially at interface between the bottom of the overlying aquifer and the top of the host rock, with respect to the transient two-phase flow principally linked to H_2 production and migration at repository scale.

Cigeo project

The CIGEO project (Figure 1) provides a repositiry at about 500 m depth at the center of the Callovo-Oxfordian clay layer in the east of France. The project includes separate storage zones for ILLW (Intermediat Long Life waste), which should be stored in large diameter (8-10 m) and long (500 m useful) tunnels and HLW (High Level Waste) stored in small diameter tunnels (approximately 0.9 m) with a length of 80 m or 150 m depending on the type of waste. There will be two surface support zones, one for waste package receipt and dedicated to digging work. The surface-bottom bonds are provided by ramps in the first case and by wells in the second.

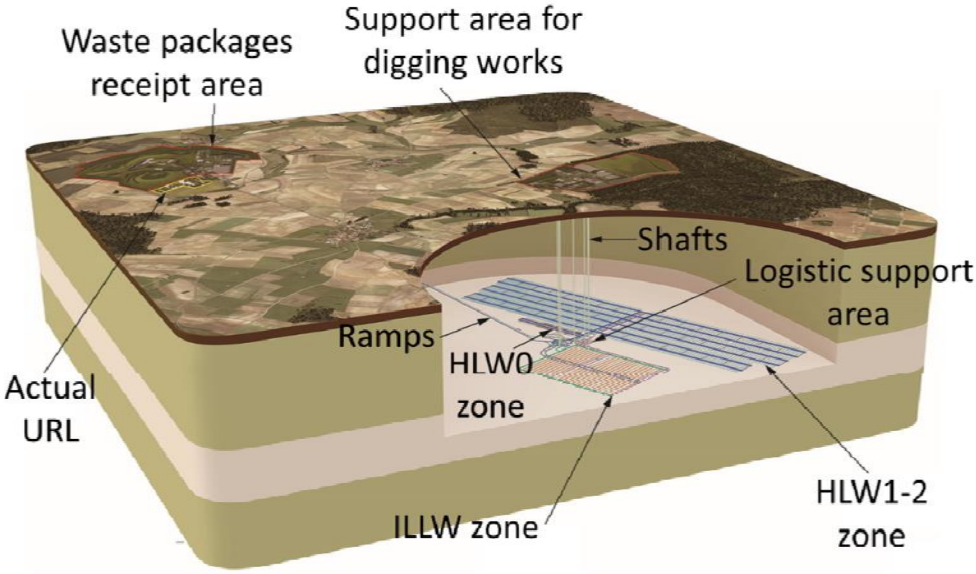

Figure 1 : General scheme of Cigéo project in preliminary design phase (2014)

Carbon 14 source terms

Carbon 14 is mainly stored in the ILLW zone and among the more than 80 waste types, 7 specific waste containers represent more than 98.5% of the total amount of mole present in the repository (one of these families representing around 80% of the total). These containers are distributed in only 14 deposition tunnels among the 50 available.

The 14C source term taken into account in the evaluation represents only these 7 families, all the source terms from other families was supposed to be zero so as not to impact the analysis.

Taking into account the data available for these 7 families, only one, representing less than 3% of the total, can be considered as labile from a phenomenological point of view. For all the other families, sensitivity analysis was performed supposing either à labile form or a source term congruent to corrosion. The total amount of 14C in the repository at closure time is 14 000 moles.

Other gas source terms

Other gases then 14C will be generated in the repository du to different processes and at different levels depending on the zone considered (Figure 2). The vast majority of the gas produced is hydrogen either by corrosion of the metallic part present in the repository or by radiolysis of the water present in or near the wastes. Less than 5% of the total amount of gas produced comes from other processes than corrosion or radiolysis and hydrogen represents more than 95% of the total amount produced.

Taking these facts into account, the only gas present in the evaluation of the TH-Gas transient is hydrogen produced only by corrosion and radiolysis (al other gas and/or production process is neglected).

The total amount of hydrogen produced in Cigéo is of around 2 10^{10} moles (compared to 14 000 moles only for 14C), half of it produced in the HLW cells (metallic liner and waste container), 40% in the ILLW tunnels (waste themselves, concrete container and concrete lining reinforcement) and 10% in the galleries (concrete lining reinforcement and host rock bolding).

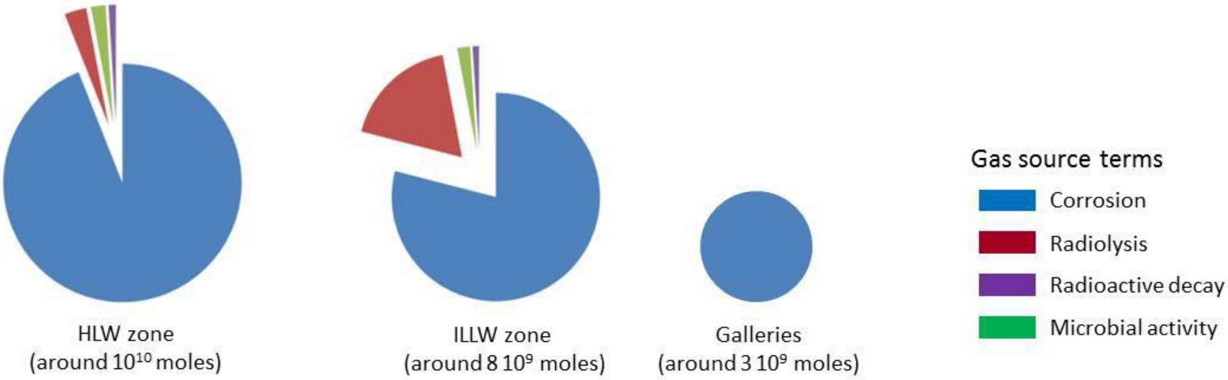

Figure 2 : **Principal type of gas generation processes in each zone**

Assessment of 14C migration at repository scale

As all of the ILLW wastes in the Cigeo project are emplaced in concrete super-container, themselves emplaced in concrete lined deposition tunnels, the chemical conditions around the waste are largely alkaline. Moreover, 14C is present only in stainless steel. Thus, the corrosion rate taken into account is very low. As some uncertainty exists on this value a sensitivity analysis is proposed on a minimum (0,5 nm/y) and maximum value (10 nm/y).

Other sensitivities taken into account are as follows:

- Uncertainty on the thickness if the pieces of metallic wastes containing 14C : minimum value 1 mm, maximum value 10 mm;
- Uncertainty on the inventory of 14C contained in the wastes : minimum value is the reference value (around 14 000 moles), maximum value is reference value multiplied by 10;
- Uncertainty on the form under which 14C will migrate. Analysis assumes a migration under CH_4 or under CO_2, all the inventory being in only one form in a given calculation. For CO_2 an evaluation taking a Kd in concrete elements was realized (no Kd assumed for CH_4).

For sake of simplicity, the corrosion rate for stainless steel in the waste was independent from the hydrogen source term by corrosion (and radiolysis). However, a sensitivity analysis on the hydrogen source term, which is responsible for the development of the gaseous phase at repository scale, was performed: evaluations were made for a high corrosion rate and o low corrosion rate. The difference between these two environmental conditions for gaseous 14C migration is that the former implies a more “rapid” development of the gas phase from the deposition tunnels toward the wells and ramps and a higher gas content in the seals (enhancing the migration of gaseous 14C) at maximum gas pressure.

Figure 3 presents the 14C flux at one of the Cigéo repository shaft (preliminary design phase architecture and inventory of ^{14}C and H_2) at the interface between the host rock and the overlaying aquifer for the different sensitivities produced during the CAST project.

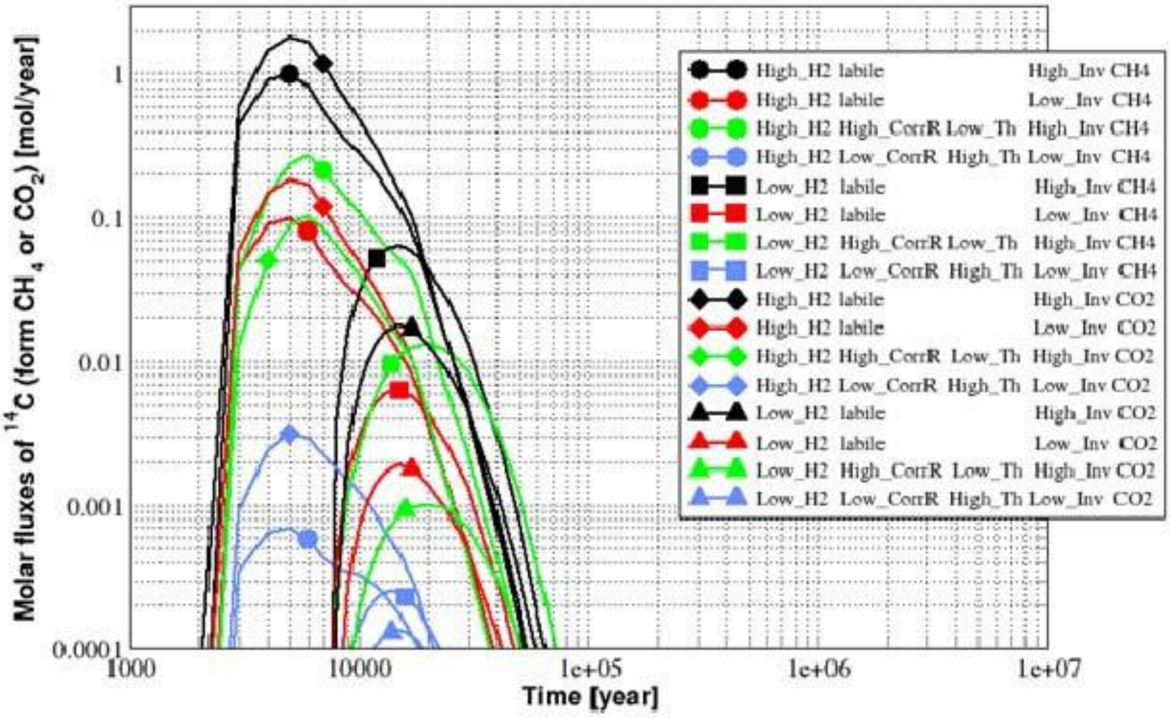

Figure 3 : Instantaneous molar fluxes of 14C in Shaft 2 at the upper limit of the host rock

Identification of chemical form of stable carbon released from type 304L and 316L stainless-steel powders in alkaline and acidic solutions under low-oxygen conditions

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The chemical form of carbon-14 released from irradiated stainless steel is a key parameter in the safety assessment of the sub-surface disposal system in Japan. In this study, unirradiated type 304L and 316L stainless-steel powders were immersed in HCl solutions (at approximately pH 2) and in NaOH solutions (at approximately pH 12) under low-oxygen conditions to identify the chemical form of the released carbon.

Type 304L (particle size under 150 μm) and 316L (particle size under 45 μm) stainless-steel powders, which were produced using water atomization technique, were used in this study. Each of the powders (70 g) was added to a glass ampoule. Then the ampoules were filled with 70 mL of 0.005 M NaOH solution or 0.005 M HCl solution. They were then placed in a thermostatic oven at 25 oC for around 20 days. After the immersion, gas samples were collected and were analyzed. After that, the liquid samples were collected, which were divided into unfiltered and filtered samples to confirm the presence of colloid particles. The filtered samples were filtered using ultrafiltration polyethersulfone membranes (cutoff molecular weight of 10000). The unfiltered and filtered samples were analyzed.

The results showed that the main chemical forms of the carbon were colloidal carbons in the NaOH solution and colloidal carbons, formic acid and acetic acid in the HCl solution. Almost no hydrocarbons were detected. On the basis of results of liquid analysis, it is inferred that the colloidal carbons originated from the C contained in Si oxide layers and that the above carboxylic acids originated from the C contained in the base metals.

^{14}C release from steels under aerobic conditions (D2.14)

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Enresa

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

This work is a part of a series of studies under CAST Work Package 2 concerned to develop analytical techniques for identification and quantification of ^{14}C species formed during corrosion of irradiated steels under conditions relevant to cement-based repositories.

The analysis of the interaction mechanisms of long lived radionuclides with the engineering barriers, of radioactive waste disposal facilities, is a topic of major importance in the safety assessment analysis. One of the main challenges in a repository, for the water intrusion scenarios, is the quantification of the release rate of radionuclides from conditioned waste. As a part of this task, the main activity of Enresa inside CAST project has been the quantification of the release rate of radionuclides from activated stainless steels, highlighting the ^{14}C release rate.

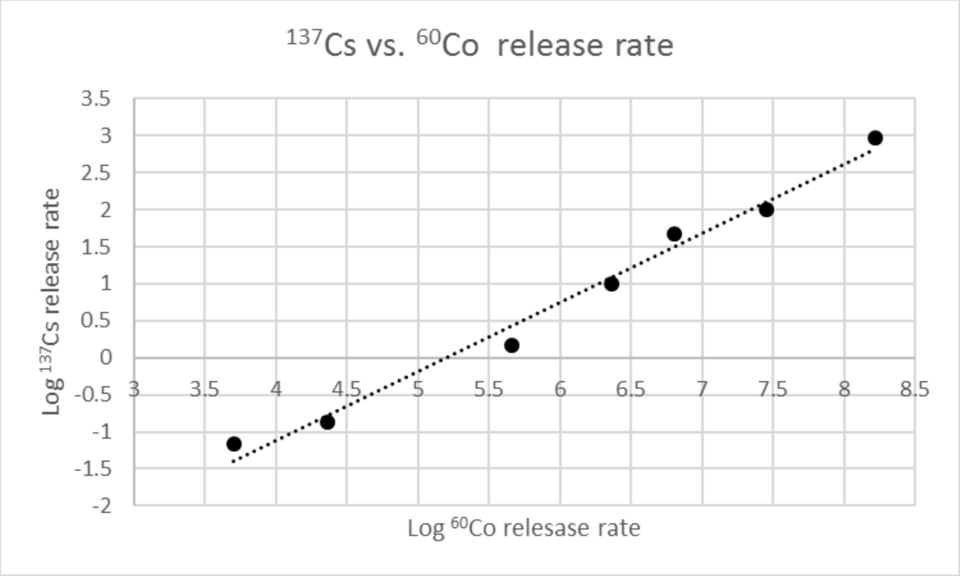
This work describes laboratory tests carried out at El Cabril repository with the aim to measure radionuclides release rates from stainless steel activated pieces. Items from the upper internals of José Cabrera NPP reactor were used, whose removal and cutting were carried out by Enresa in 2012 – 2013. With the goal of the fulfilment of the Waste Acceptance Criteria, analysis of the retention capacities were performed to verify and to assess the required treatment and the eventual additional envelopes to be built for the final disposal of this kind of waste.

To that end, a leaching technique usually performed on waste packages has been adapted to stainless steel SS304-SS316. The activated piece was immersed in deionised water throughout 7 consecutive steps. The activity of Gamma isotopes was determined by means of gamma spectrometry and the activity of C-14 by means of liquid scintillator method.

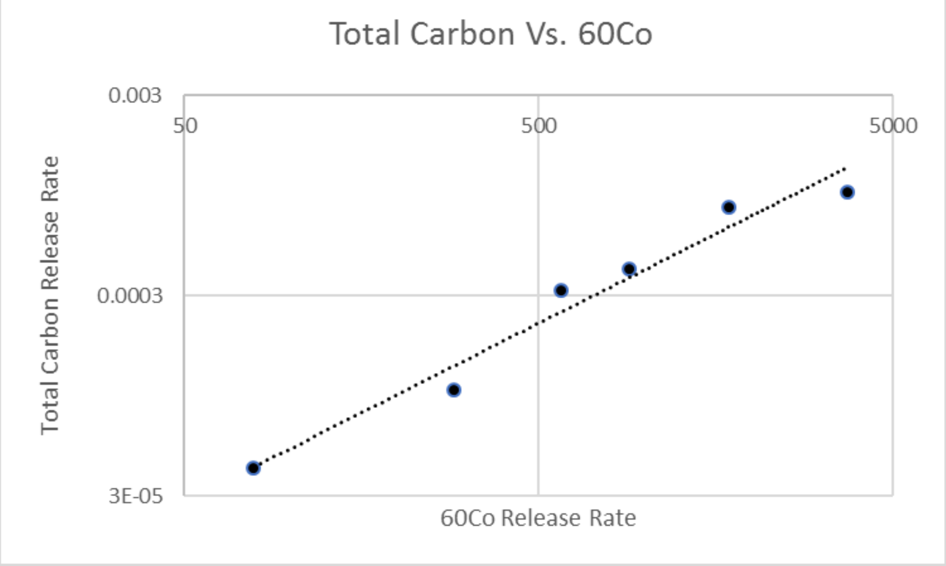
Due to the expected low amount of carbon-14 released in the leaching process, a more sensitive technique is required to quantify it at every step: Accelerator Mass Spectrometry, AMS, currently under development for liquids in the National Centre of Accelerators, in Seville, Spain, is the chosen technique due to its capacity for achieving lower detection limit than the current ones. Two approaches are considered here, on one hand the incorporation of the sample carbon into a carbonate form by precipitation with calcium nitrate $Ca(NO_3)_2$, and on the other hand the direct hydrolysis of the liquid sample.

While waiting AMS results on active samples, a measurement of the total organic plus inorganic carbon content in every steps was determined, and the total carbon release rate was consequently inferred.
A solid and a liquid fraction was observed during the leaching test, the only isotope with values above detection limit, for both fractions, in all the steps measured is ^{60}Co. For ^{137}Cs only the solid fraction shows activities above de detection limit in all the steps, and no detection is obtained in the liquid fraction.

A clear correlation is observed for the release rate of both isotopes, showing that a scaling factor for the release rate of ^{137}Cs could be inferred from the release rate of ^{60}Co.



As in the case of the release rate of ^{137}Cs, a good correlation between ^{60}Co release rate and total Carbon release rate is found (r=0,982), meaning that a Scaling Factor for the total Carbon release rate could be derived from the ^{60}Co release rate.



The sensitivity analysis of the release of carbon-14 from a deep geological repository

Antonín Vokál, Aleš Vetešník

Súrao

The contribution addresses the conducting of the sensitivity analysis of the release of carbon-14 in either its organic or inorganic forms from a deep geological repository for intermediate level waste located in a crystalline host rock environment. The sensitivity analysis methodology employed in the study was based on the pseudo-random selection of values from a range of selected parameter values. The first order and total sensitivity indices, which express the contribution of individual parameters on the calculated output parameters over time were calculated. This contribution briefly summarises the most important results obtained. The analysis revealed that carbon-14 in the organic form only is capable of exerting a non-negligible impact on repository safety, the release of carbon-14 in the free gas phase may exert an important impact, and that the leaching rates of carbon-14 from the waste forms and the equivalent flow rates, which express the transport rates of carbon-14 from the backfill to the surrounding host rock fractures, make up the most important parameters with respect to influencing the release of carbon-14 into the crystalline host rock environment. It was also demonstrated that if the sorption of organic forms of carbon-14 on the host rock is substantiated, then it may exert a significant impact on the release rates of carbon-14 into the environment.

14C Determination in Irradiated Steel and Zircaloy: Progress at JRC Karlsruhe in the realm of the CAST Project

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The JRC examined a number of methods to determine total carbon and 14C in irradiated steels and zircaloy. The samples were taken from irradiated fuel rods exposed to fast reactor conditions (steel) and light water reactor (zircaloy) conditions. For the total Carbon determination a hot extraction technique involving was tested. It is based on the combustion of the sample in air, with the derived CO2 being determined (against calibration standards) using an infra-red detector. The CO2 can be collected on a molecular sieve for 14C preparation in a specially designed glovebox. In addition, two autoclaves were prepared to digest fully steel and zircaloy samples, or to leach carbon from the surface layers, under conditions that would be expected in an underground repository. Using this method inorganic or organic carbon is collected in solution and in a specially devised gas collection vessel. Finally, a glovebox was constructed for the pre-treatment of the samples (gas, liquid, molecular sieve) and to convert the 14C into Na2CO3 for determination using liquid scintillation counting. Progress made as well as the outlook for the future will be presented.

Carbon Release from steel materials in disposal conditions

Tiina Heikola, Kaija Ollila

VTT

Introduction

Radiocarbon, C-14, is a major radiotoxicity contributor in decommissioning waste with half-life of 5,730 years. It arises from the neutron activation of N-14 impurities in steel materials. Because of its chemistry, it may release either in inorganic or organic form. Especially organic species can be highly mobile in geosphere and they can therefore migrate to the biosphere. In the CAST project (Cast-14 Source Term) the aim was to develop understanding of the release mechanisms of C-14 from radioactive waste materials in disposal conditions.

Experimental set-up

The work was started with unirradiated materials. In order to investigate the influence of the initial speciation of carbon, the solid phases chosen for the experiments were AISI316Ti type stainless steel and Fe(III)carbide (Fe_3C) powders, in which carbon is in interstitial atom and carbide form respectively. The experiments were performed inside an anaerobic glove box with two simulated groundwaters of pH 8.5 and 12.5 as leaching solutions. The speciation of released carbon was investigated in both aqueous and gaseous phases. The irradiated sample chosen for the experiment came from the surveillance capsule chains from the Loviisa nuclear reactor. The Co-60 activities for the two specimens were measured to be 227.27 MBq and 619.23 MBq. The initial composition of the material was determined beforehand with optical emission spectrometer (Spectrolab S®). The nitrogen content of the unirradiated capsule steel was 0.04 w-%. The theoretical maximum content of C-14 after exposure was calculated to be 2 x 10^3 Bq C-14/g. The specimens were immersed into the leaching solutions (pH 8.5 simulated groundwater and 0.01M NaOH) and put in a zirconia crucibles inside of a glass bottles. The bottles were placed inside an under pressure glove box behind a lead shield (RT, 1 atm). Only the liquid phase was analysed in the irradiated experiments.

Results

The total amounts of dissolved organic (DOC) and inorganic carbon (DIC) as well as the composition of organic carbon were determined both in liquid and gas phase. The results of DIC/DOC analysis of liquid phase are presented in Figure 1. In all the experiments majority of the carbon was released in organic form.

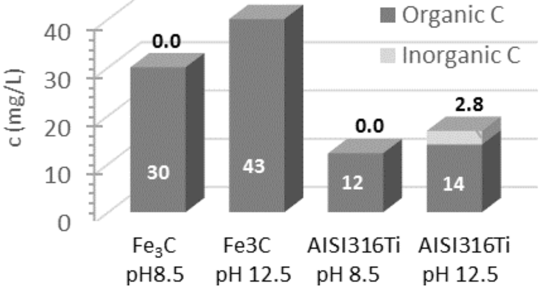

Figure 1. Distribution between organic and inorganic carbon in liquid phase.

The carbon release rates were calculated to be: $7x10^{-4}$–$3.1x10^{-4}$ (fraction/year) for Fe_3C and one order in magnitude less for modified AISI316Ti. In gas phase analysis small hydrocarbons were detected in Fe_3C samples, but not in AISITi samples. Measurable amount of CO and CO_2 were found in the Fe_3C gas phase.
The first samples from the irradiated experiments were taken after 133 days from the start. The measurements were performed without any pre-treatment of the solutions. Without the chemical separation it was impossible to identify present radionuclides with LSC, but it was suspected that they could be ^{55}Fe and ^{63}Ni or ^{14}C. In gamma measurements ^{54}Mn, ^{58}Co, ^{60}Co, ^{125}Sb ^{124}Sb and ^{110}mAg nuclides were identified. Clearly higher activities were detected in lower pH (8.5) leaching solution experiment.

Conclusions

The conditions in the geological disposal facilities will eventually have reducing conditions. In the absence of oxygen the corrosion potential for steel in aqueous solutions is determined by the anodic (oxidation) and cathodic (reduction) reactions involved in the corrosion process. The estimated long-term general corrosion rate of stainless steel in anoxic alkaline conditions is <0.01 μm yr^{-1} but in the initial stage it could be higher than 10 μm yr^{-1} (Smart et al. 2004). The objectives of the CAST project was to gain new scientific understanding of the rate of release of carbon-14 from the corrosion of irradiated materials in these disposal conditions.

Because the uncertainties concerning the form of C-14 in irradiated steel structure, two different materials, Fe(III) carbide powder, in which carbon is in carbide form, and modified AISI316Ti stainless steel powder, in which carbon has been identified being as interstitial atom in the austenitic steel lattice, were selected as solid materials in inactive experiments. The results from the analyses from the liquid phase showed that the content of organic carbon was higher compared to inorganic carbon in all the experiments but especially in the experiments with Fe_3C. According to Vuorinen 2012, this is expected since the presence of carbides in metals seems to increase the formation of organic species at high pH. However, the concentrations of organic carbon were such a low level that the effect of the original form of Con speciation in liquid/gas phase remains uncertain.

The experiments with the irradiated surveillance capsule material were shorter than originally planned. Working inside a glove-box with such active material proved to be more challenging than expected. However, the tentative results suggested stronger corrosion reactions at the lower pH of 8.5. This could be due to the higher chloride concentration in the simulated groundwater solutions but more probable reason was the lower pH. Corrosion of steel materials is increased in lower pH and higher chloride content (Eurajoki, 2010). Due to the removal to the new laboratory facilities there has been a delay in the experiments. The experiments were started in 2016 at our old building. The instruments, including the anaerobic glove-box, were then moved to the new building. However, we were not able to move the experiments to the new building since the licence to work with radioactive material was not in effect and we had to leave the specimens in the old building for storage without possibility to perform any sampling during this time. This work is also part in the Finnish national research programme (KYT2018) and is planned to be continued at least until 2018. The results will be published in at the end of KYT2018 program.

Integration of CAST results in the safety assessment for a generic concept of spent fuel and ILW-LL disposal in Romania

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Romania operates in open fuel cycle two CANDU 600 units. The spent fuel (SF) and the long-lived intermediate level waste (ILW-LL) are foreseen to be disposed off in a geological repository starting with 2055. Since no host rock was yet selected, the in-house safety assessments are aimed to the comparison of different types of rocks from the point of view of their performances as repository host rock. The modelling is based on a generic concept similar to the Canadian one. The previous simulations used as input data assumptions and values from the Canadian studies.

As C-14 plays an important role in the total annual dose, any improvement in C-14 source term can decrease the associated uncertainty. Therefore, as part of the CAST project, RATEN continued to elaborate on the performance assessment of SF disposal in granite, refining and updating the input data related to C-14 inventory and release.

The model considered only the C-14 released from spent fuel and Zy-4 claddings. More realistic values for the C-14 inventory in Zy-4 claddings were used as input based on experimental data obtained by RATEN in the CAST project using Romanian samples from Cernavoda NPP. The new calculations made in CAST included C-14 speciation, considering the experimental values as a reference case, and differentiated for the first time the radiologic impact of CO_2 and CH_4.

Based on the model proposed, the sensitivity analysis followed the influence on the total dose summing the biosphere pathway of: the C-14 instantaneous release fraction from UO_2, the C-14 release rate from Zy-4, the organic/inorganic ratio in the C-14 release from Zy-4 claddings, the diffusivity coefficient in bentonite and granite and the Kd in bentonite and granite.

The sensitivity analysis (addressing only C-14 from spent fuel) pointed out that the most sensitive parameters are the IRF from the UO_2 pellets and the Kd in bentonite.