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CAST

Advisory Group Review of CAST Objectives and 1st CAST General Assembly Meeting Minutes (D1.3)

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CAST – Project Overview

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

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

The objectives of the CAST project are to gain new scientific understanding of the rate of 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.

For more information, please visit the CAST website at:
http://www.projectcast.eu

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Advisory Group Review of CAST Objectives and 1st CAST General Assembly Meeting Minutes (D1.3)

Executive Summary

The CAST Project has engaged two independent experts as part of the CAST Advisory Group. The two independent experts help to steer the project by reviewing the minutes from the General Assembly Meetings and the technical work package annual reports. In addition the independent experts will peer review each of the main final deliverables for the CAST projects prior to publication on the CAST website. This report acts as D1.3, where the initial CAST objectives and the minutes from the 1st CAST General Assembly Meeting (D1.1?) are reviewed by the independent experts. The independent experts are:

- Dr. Fraser King, Integrity Corrosion Consulting Limited, and
- Dr. Irka Hajdas, an independent consultant.

The reviews for the CAST objectives and the 1st CAST General Assembly Meeting minutes are given in Section 2 – Review by Dr. Fraser King and Section 3 – Review by Dr. Irka Hajdas. The conclusions from Section 2, the review by Dr. Fraser King, is that the proposed workscopes for WP 2, WP 3, WP 4, and WP 5 are considered to be consistent with the requirements of a programme designed to develop mechanistically based ^{14}C source-term models for the respective waste forms. The conclusions from Section 3, the review by Dr. Irka Hajdas, summarise that the research groups involved have the expertise required to perform the proposed research including the new developments such as low carbon content AMS analysis.

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1 Introduction

The CAST Project has engaged two independent experts as part of the CAST Advisory Group. The two independent experts help to steer the project by reviewing the minutes from the General Assembly Meetings and the technical work package annual reports. In addition the independent experts will peer review each of the main final deliverables for the CAST projects prior to publication on the CAST website. This report acts as D1.3, where the initial CAST objectives and the minutes from the 1st CAST General Assembly Meeting (D1.1) are reviewed by the independent experts. The independent experts are:

- Dr. Fraser King is an independent consultant with over 30 years corrosion-related experience in the nuclear, pipeline, and petrochemical industries. He has B.Sc. and Ph.D. degrees in chemistry and electrochemistry from Imperial College, London, UK, and is a Fellow of the National Association of Corrosion Engineers (NACE International). Following careers at Atomic Energy of Canada Limited and in the oil and gas industry in Calgary, Fraser established Integrity Corrosion Consulting Limited. He is a consultant for nuclear waste management programs in Canada, Sweden, Switzerland, Finland, Japan, the UK, the United States, and the IAEA in the areas of waste container performance, used fuel alteration, and gas generation. His research interests include: corrosion, applied electrochemistry, lifetime prediction, safety and risk assessments, reactive-transport modelling, environmental impact analysis, the design, fabrication, and performance of nuclear waste containers, the performance of used nuclear fuel under disposal conditions, and the corrosion of reactor and steam generator components.

- Dr Irka Hajdas is a physicist by training, applying her expertise in radiocarbon analysis to problems of geochronology, archaeology, and environmental studies. She earned her Master degree in physics at Jagiellonian University Cracow, Poland. From 1986-1989 she worked as a researcher at the Institute of Nuclear Physics in Cracow, where she was involved in measurements of natural radioactivity. This was followed by a PhD at the ETH Zurich, Switzerland where she now conducts research

at the Accelerator Mass Spectrometry facility and lectures in the Earth Science Department. Her main research interest is radiocarbon dating methods using the AMS (Accelerator Mass Spectrometry) technique. This includes the development of new preparative methods, as well as improvements to numerous applications (archaeology, climate research, environmental studies, art and forensic). She is a member of International Radiocarbon Calibration Group INTCAL dedicated to calibration issues, is a member of editorial boards of journals Radiocarbon, Geochronometria and Quaternary Geochronology, and chairs the board of Swiss Quaternary Society.

The reviews for the CAST objectives and the 1st CAST General Assembly Meeting minutes are given in Section 2 – Review by Dr. Fraser King and Section 3 – Review by Dr. Irka Hajdas.

2 Review by Dr. Fraser King

The CAST objectives and the minutes of the General Assembly Meeting 1 have been reviewed by Dr. Fraser King, Integrity Corrosion Consulting Ltd, a member of the project Advisory Group.

A brief overview is provided of the various components that could form part of the development of a source-term model for ^{14}C. Because of Fraser's area of expertise, emphasis is placed here on the development of source terms for irradiated metals, such as carbon and stainless steels and Zircaloy.

The project objectives, scope of work, and progress to date (as reported in the minutes of the General Assembly Meeting 1 [SCOURSE and WILLIAMS, 2014]) are then compared against the overall conceptual model described above.

The proposed workscopes for WP 2, WP 3, WP 4, and WP 5 are considered to be consistent with the requirements of a programme designed to develop mechanistically based ^{14}C source-term models for the respective waste forms.

2.1 Introduction

The review is focussed on the different components required for the development of an overall source-term model for ^{14}C (or, in general, for any contaminant in a host matrix). Because of the current authors area of expertise, greatest emphasis is placed here on the release of ^{14}C from steels (WP 2) and Zircaloy (WP 3), although mention is also made of the Work Packages on ion-exchange resins (WP 4) and graphite (WP 5).

The following discussion is based on a review of the CAST objectives [CAST, 2013], the minutes from the CAST General Assembly Meeting 1 [SCOURSE and WILLIAMS, 2014], and additional reading of relevant project and non-project documents. Section 2.2 presents a framework for the development of a ^{14}C source-term model developed by the current author, against which the detailed workscopes of the different WPs are compared (Section 2.3).

2.2 Framework for a ^{14}C Source Term Model

The development of a ^{14}C source term model requires the understanding of a large number of physical and chemical processes. Figure 1 illustrates a number of these processes, with an emphasis on the behaviour of irradiated metals. The overall approach is conveniently divided into three aspects:

1. Inventory (designated here by I)
2. Release (designated here by R)
3. Transport/Reaction (designated here by T)

2.2.1 Inventory (I)

Clearly, it is important to understand the inventory of ^{14}C present in the irradiated metal at the time of disposal. A complete understanding of the ^{14}C inventory requires knowledge of:

1. The quantity of ^{14}C (I1)

2. The physical location of the ^{14}C (e.g., within the oxide or the metal, at grain boundaries or within the grains) (I2)

3. The chemical state (e.g., as interstitial C atoms in solid solution in the metal or oxide, as carbide phases at grain boundaries or elsewhere in the metal or oxide, or as some other C-containing phase in the metal or oxide) (I3)

Information about the quantity of ^{14}C could be obtained from direct measurement. Information about the location of ^{14}C in the metal and/or oxide may be obtained from direct measurements or by inference based on knowledge of the location of the precursor ^{14}N species [e.g., OLEFJORD and WEGRELIUS, 1996; PETROV et al., 1999]. Information about the chemical nature of the C is more difficult to obtain, but it is important to understand whether the ^{14}C is present in an alloy phase (e.g., as a carbide), as a compound, or trapped in the metal/oxide matrix in some other form.

2.2.2 Release (R)

Two aspects of the release of ^{14}C are important:

1. Release rate (R1)

2. Release mechanism (R2)

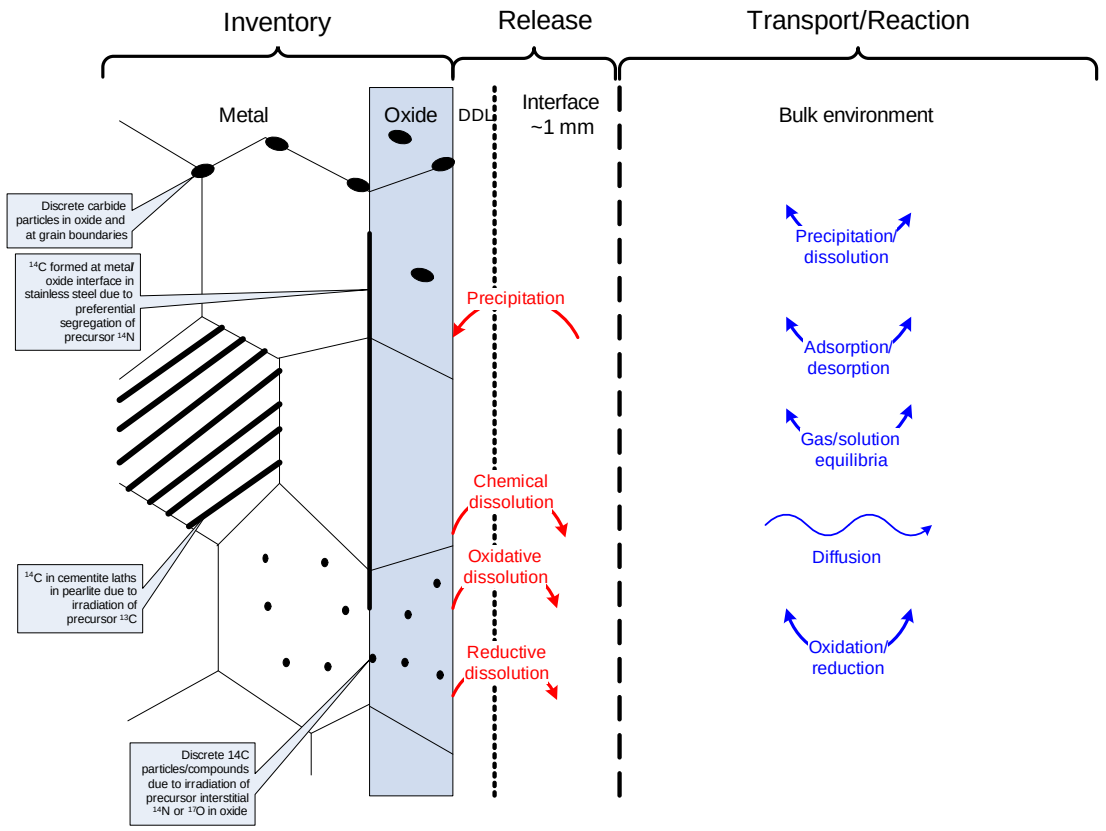

Figure 1: Overview of Processes and Features of Possible Importance in the Development of a Source-term Model for the Release of ^{14}C from Irradiated Metals.

Information about the release rate of ^{14}C is clearly important for the development of a ^{14}C source-term model. Comparison with the ^{14}C inventory and rate of corrosion (or oxide dissolution) provides information on whether ^{14}C is congruently released, as is typically currently assumed.

In addition, knowledge about the mechanism of ^{14}C release is important for the development of a mechanistically-based source-term model. For example, does ^{14}C release involve chemical dissolution of the C-containing entity in the metal (or oxide), in which case the release rate might be expected to be independent of redox conditions? Alternatively, ^{14}C release may involve an oxidative dissolution process or reductive dissolution of an oxide matrix, both of which would be expected to depend on the corrosion potential (E_{CORR}) of the metal (and, hence, on the E_h of the environment).

These release processes are illustrated in Figure 1 as occurring in a near-surface region, arbitrarily defined as within 1 mm of the surface. Electrochemical oxidative or reductive dissolution processes would be controlled by the potential drop across the diffuse double layer (DDL) at the metal/oxide surface. Immediately following release form the surface, the dissolved (or gaseous) ^{14}C species may further interact with the surface (e.g., by precipitation on or within the surface oxide), and such processes are also considered within this step.

2.2.3 Transport/Reaction (T)

Once released from the near-surface environment (arbitrarily defined as distances >1 mm from the surface), the dissolved or gaseous ^{14}C species may undergo various mass transport and reaction processes. Transport will occur by diffusion and/or advection (in systems with relatively high hydraulic conductivity), and will be impacted by whether the ^{14}C is present as a dissolved or gaseous species (T1). Depending upon the nature of the ^{14}C species, possible reactions may involve (T2):

1. Precipitation/dissolution of solid phases, possibly on the surfaces of other materials in the near-field

2. Adsorption/desorption of charged species on oxides, silicates, or other adsorbates (e.g., clay minerals)

3. Gas/solution partitioning (e.g., if the ^{14}C is present as CH_4)

4. Redox processes of electrochemically active ^{14}C species.

It is clear that knowledge of the speciation of ^{14}C is important in understanding the reactive-transport behaviour of the released species.

2.3 *Review of CAST Objectives and Minutes from GAM 1*

In this section, the objectives and scope of work for WP 2, 3, 4, and 5 (as defined in [CAST, 2013] and [SCOURSE and WILLIAMS, 2014]) are compared with the source-term model framework described in Section 2.2.

2.3.1 WP 2 Steels

Much of the planned effort within WP 2 is focussed on the development of analytical techniques for the identification and quantification of ^{14}C species in leach tests. These efforts will clearly contribute to greater understanding of the speciation (and possible reactions) of ^{14}C once released into the near field (T2). The ^{14}C speciation will also provide information about the most likely form of mass transport (T1).

Other planned activities are focussed on leach (corrosion) tests, the full scope of which is not fully defined in the material reviewed. Such studies will clearly contribute to an understanding of the rate of ^{14}C release (R1), and may provide some mechanistic information (R2), as may experiments with inactive steel samples and Fe_3C. Supplementing these tests with some electrochemical studies would indicate whether the ^{14}C release mechanism involved a reduction/oxidation process.

The inventory of ^{14}C will be determined by modelling of the irradiation process and by complete dissolution and analysis (I1). There are apparently no specific tasks aimed at

determining the distribution (I2) or chemical state (I3) of the ^{14}C, although such information may be derived from the state-of-the-art literature review to be performed.

2.3.2 WP 3 Zircaloy

In addition to effort on developing suitable analytical procedures for released ^{14}C (possibly shared with WP 2), the proposed workscope for WP3 on Zircaloys appears to cover most aspects of the conceptual framework required to develop a ^{14}C source term illustrated in Figure 1. Thus, work is proposed on the origin, distribution, and nature of ^{14}C in Zr alloys and the associated oxide (I1, I2, and I3) and the release rate (R1) and speciation (T1) of dissolved/gaseous ^{14}C. Information on the release mechanism (R2) and subsequent reactions in the near-field (T2) may also be forthcoming from these studies.

2.3.3 WP 4 Ion-exchange Resins

The proposed workscope on ion-exchange resins (IER) (WP 4) also appears to comprehensively address the various aspects required for a source-term model. There are studies of the inventory and speciation of ^{14}C (I1 and I3) based on existing literature information and new studies. Knowledge of the physical distribution of these species (I2) may be of less significance for IER than for metallic wastes.

Similarly, leaching studies will provide information on the release rate (R1) and speciation of dissolved/gaseous ^{14}C (T1) and may provide mechanistic insight on the release (R2) and subsequent reaction of these species (T2).

2.3.4 WP 5 Graphite

The workscope on graphite wastes (WP 5) includes a number of tasks on the characterization and distribution of ^{14}C (I1, I2, I3). As for the other wasteforms, leaching studies will provide direct information on the release rate (R1) and speciation of ^{14}C (T1) in the near field and should provide the associated mechanistic insight (R2, T2).

2.4 Conclusions

The proposed workscopes for WP 2, WP 3, WP 4, and WP 5 are considered to be consistent with the requirements of a programme designed to develop mechanistically based ^{14}C source-term models for the respective waste forms.

The proposed tasks are specifically aimed at providing quantitative information for the development of source-term models. For all WP, there is effort defined for quantifying the inventory of ^{14}C and for determining the rate of release and speciation of released ^{14}C.

Some additional consideration of experiments designed to investigate the mechanism of release may be warranted.

Some additional consideration of the distribution and chemical state of ^{14}C in steels may be warranted in WP 2, unless such information is available in the literature.

3 Review by Dr. Irka Hajdas

The need for understanding sources of ^{14}C release from the disposal of nuclear waste gives the basis for the objectives of the CAST (Carbon-14 Source Term) Project. This review focuses on the analytical methods leading to measurements of ^{14}C activities in various irradiated materials (steel, Zircaloys, ion-exchange resins, graphite) as well as in the carbon released from these disposed materials. The levels of activity as well as form (speciation) are of main consideration for the long-term storage. The long half-life (5730 years) of radiocarbon, as well as a wide range of organic and inorganic carbon compounds that are present in the environment, single out this isotope in future safety measurements. Experiments simulating processes of release (corrosion and leaching) will be performed. The anticipated research requires ^{14}C analyses that are mainly performed using counting techniques (LSC). However some fractions have very low carbon content and will require the use of accelerator mass spectrometry (AMS). This will involve new methodological developments in the final steps of sample preparation, therefore will require a coordinated approach of all the technical WPs.

The review of the objectives of technical Work Packages (WP2, 3, 4 &5) is followed by the review of the General Assembly Minutes GAM1.

In summary: the involved research groups have the expertise required to perform the proposed research including the new developments such as low carbon content AMS analysis.

3.1 Introduction: Radiocarbon ^{14}C and nuclear waste

The discovery of radioactive isotope of carbon ^{14}C that took place in first half of last century was stimulated by the developments of the nuclear physics and radiochemistry. However the early days did not change the natural pool of ^{14}C that is supplied by production that takes place in the atmosphere (LIBBY, 1946). Thermal neutrons, which are secondary particles of cosmic rays interaction in the atmosphere, react with ^{14}N to create ca. 2 atoms of ^{14}C /cm^2 sec. This cosmogenic ^{14}C is fairly quickly oxidized and enters the global carbon cycle. Thanks to the long half-life of ^{14}C (5730±30 years), radiocarbon dating established in 1949 by Libby and co-workers (LIBBY et al., 1949), became a powerful radiometric dating method for the last 50,000 years. The addition of anthropogenic ^{14}C began with its production as a bio-chemical tracer, in nuclear testing (global bomb peak) and as products of irradiation of carbon, nitrogen, and oxygen present in the fuel, cladding, coolant, moderator, and structural materials of reactors. Estimates of the global inventory of ^{14}C show that the anthropogenic pool is dominated by the atmospheric nuclear tests that took mostly place between 1954 and 1964 AD (YIM and CARON, 2006). Monitoring of operating nuclear power plants (NPP) allows the estimates of that the local ^{14}C releases mostly as $^{14}CO_2$ and other gaseous forms (LEVIN et al., 1988). However long term storage of nuclear waste and ^{14}C releases from such remains a subject of investigation that is adequately addressed in the CAST project.

3.2 Objectives of the CAST project

The objectives of the CAST project are centred in technical Work Packages (WP2, 3, 4 &5), which includes analytical development of each specific material group: steels, Zircaloy, ion-exchange resins, and graphite.

3.2.1 Review Objectives of WP2-5

The objectives and tasks of Work Packages 2, 3, 4 and 5 are reviewed with focus on planned ^{14}C activities analyses and analytical approach.

3.2.1.1 WP2 Steels

Understanding and estimation of ^{14}C releases from irradiated steels stored under cement-based conditions will be achieved by:

1. Review of related literature on ^{14}C analysis in irradiated steels
2. Development of ^{14}C separation techniques from different forms of carbon liquid/gas, organic/inorganic,
3. Limitations of ^{14}C analysis—low carbon content, need for AMS analysis
4. Estimate of ^{14}C contents remaining after various corrosion experiments (simulation of alkali and acidic conditions)

3.2.1.2 WP3 Zircaloys

Prediction of ^{14}C behaviour in stored Zr fuel claddings will involve:

1. Review of present state of knowledge on ^{14}C release from Zr waste, corrosion of Zr hulls and dissolution of Zr oxides
2. Estimates of ^{14}C inventory by measurements:
    1. Determination of forms of carbon and separation of ^{14}C as in WP2
    2. Estimation of the limits of carbon separation (carbon content) for LSC or AMS
3. Analytical developments overlapping with WP2 (exchange and collaboration).

3.2.1.3 WP4 Ion-Exchange Resins

Contribution of ^{14}C from stored SIERs will be established in this work package in following steps:

1. Review of current status of knowledge of resins activity and preservation
2. Inventories of ^{14}C and speciation dependent on the origin of SIERs (BWR, PWR, CANDU)
3. Leaching experiments simulating storage conditions (rock type dependent)

4.Forms of carbon inorganic/organic and analytical approach to ^{14}C content estimates (LSC /AMS dependent on amount of carbon and concentrations)
5.Investigation of possible gaseous forms releases – collaboration with WP2&3

3.2.1.4 WP5 Graphites

Building up on knowledge gained in CARBOWASTE the inventory of ^{14}C in i-graphites, their release (long term storage) and possible ways of treatment are the objectives of this work package. Mainly LSC would be applied.

3.3 *Review of the General Assembly Minutes GAM1*

Objectives of the CAST project are centred in technical Work Packages (WP2, 3, 4 &5). Planned analytical development of each specific material group has been presented. Most inventories of ^{14}C will be determined using LSC technique. Separation of ^{14}C at the compound specific level (from gaseous/liquid phase) will require not only application of the AMS technique but also special type of facility that is able to directly analyse CO_2 samples (RUFF et al, 2010).

3.4 *Conclusions and recommendations*

The presented project of CAST is designed to resolve the question of the impact that radioactive waste storage will have on the inventory of long-lived radioisotope of carbon. A major part of the planned research is analytical development. Close collaboration between WPs is important, and already becoming a standard approach (common workshops WP2&3, exchange of samples). This is most important if there is a need for AMS analyses. Considering that most of the AMS facilities are dedicated to geochronology all issues connected to high-level ^{14}C content has to be discussed before beginning of sample preparation.

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